Top 20 innovative bio-based products

Task 3 of “Study on Support to R&I Policy in the Area of Bio-based Products and Services”

Written by University of Bologna and Fraunhofer ISI
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Research and Innovation

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EUROPEAN COMMISSION

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edited by University of Bologna and Fraunhofer ISI

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Table of Contents

ABSTRACT

This study was carried out for the EC-DG RTD in the framework of the BIOSPRI tender "Study on support to R&I policy in the area of bio-based products (BBPs) and services", and was implemented by the University of Bologna (Italy) and Fraunhofer ISI (Germany) as part of a Consortium led by COWI A/S (Denmark). The study mapped the most relevant value chains currently under development that derive from main biomass components (natural rubber, plant fibres, lignin, renewable oils and fats) and low-volume high-value (LVHV) biomass components (terpenes, natural polyelectrolytes), in addition to urban wastes. The sugar platform was not included in the present study because its potential exploitation for the development of biofuels and biochemicals was covered in a previous study commissioned by the European Commission, and concluded in 2015 [1]. While more than 100 innovative BBPs were monitored, lignin was found to be generating the highest number of innovative products, together with terpenes and urban wastes. More than 30 innovative BBPs are approaching full availability on the market, and more than 20 products are now at the pilot plant level. Through an assessment based on the active marketplace, EU-based development, degree of innovation and market potential, the TOP20 most innovative BBPs holding the greatest promise for commercial deployment within the next 5-10 years were identified. This selection includes engineering materials, new bioplastics, high added-value products for demanding applications in the pharmaceutical and biomedical fields, as well as sustainable substitutes for critical raw materials. Detailed case studies were developed on the TOP20 innovative BBPs.

RÉSUMÉ SCIENTIFIQUE

Cette étude a été réalisée pour le compte de la CE-DG RTD, dans le cadre du projet BIOSPRI «Study on support to R&I policy in the area of bio-based products (BBPs) and services». Elle a été menée par l'Université de Bologne (Italie) et Fraunhofer ISI (Allemagne), parties prenantes du consortium dirigé par COWI A/S (Danemark). L'étude a permis de dresser une liste des chaînes de valeur les plus pertinentes en cours de développement, provenant des principaux composants de la biomasse (caoutchouc naturel, fibres végétales, lignine, huiles et graisses recyclables), des composants de la biomasse à faible volume et à forte valeur (terpènes, polyélectrolytes naturels), ainsi que des déchets urbains. Le sucre en tant que matière première n'a pas été abordé dans cette étude car son exploitation potentielle pour le développement de biocarburants et de produits biochimiques a déjà été traitée dans une étude commandée par la Communauté Européenne et présentée en 2015 [1]. Sur plus de 100 BBPs analysés, il a été constaté que la lignine, le terpène et les déchets urbains généraient le plus grand nombre de produits innovants. Plus de 30 BBPs innovants sont sur le point d'être commercialisés à grande échelle, et plus de 20 produits en sont à l'étape de l'usine pilote. Grâce à une évaluation basée sur le marché actif, le degré de développement au niveau de l'Union Européenne, le degré d'innovation et le potentiel commercial, le TOP20 des BBPs les plus innovants offrant les meilleures perspectives de déploiement commercial dans les 5 à 10 prochaines années a été déterminé. Cette sélection comprend des matériaux d'ingénierie, de nouveaux bioplastiques, des produits à haute valeur ajoutée pour des applications exigeantes dans les domaines pharmaceutique et biomédical, ainsi que des substituts durables aux matières premières critiques. Des études de cas détaillées ont été réalisées sur chacun de ces 20 BBPs innovants.

REFERENCES

E4tech, RE-CORD and WUR (2015) "From the Sugar Platform to biofuels and biochemicals".Final report for the European Commission, contract No.ENER/C2/423-2012/SI2.673791

EXECUTIVE SUMMARY

Building new value chains through the valorization of main and low-volume high-value (LVHV) biomass components for the development of innovative bio-based products (BBPs) aimed at specific market sectors, will accelerate the transition from traditional production technologies to the concept of biorefineries.

New technologies and traditional methods coupled with biotechnologies applied to biomass feedstocks and waste streams from various sources, such as urban wastes or agricultural residues or wastes from food and feed streams, will convert renewable resources into high added-value sustainable BBPs.

This study was aimed at mapping innovative BBPs currently under development, at any stage of advancement, and deriving from the main biomass components listed in Table 1. The number of innovative products under development that were identified for each biomass component is also reported in Table 1. The biomass components included in the study are briefly described in Section 3 of this report.

Table 1: Biomass components included in the study, and respective number of innovative BBPs that were mapped

	Main biomass components	Number of innovative BBPs mapped
Major biomass components	Natural rubber	5
	Plant fibres	17
	Renewable oils and fats	19
	Lignin	23
Low volume high value (LVHV) biomass components	Terpenes	18
	Polyelectrolytes	6
Urban biowaste	Urban biowaste	19

One-hundred and seven (107) innovative BBPs were identified and mapped through this study.

A database was developed to collect the following information for each of the BBPs identified under current development from the above-mentioned biomass components:

- Biomass feedstock
- Maximum TRL achieved
- Number of active firms
- Production facilities (EU / rest of the world)
- Leading actors
- Estimated market size

- Non bio-based or traditional alternatives
- Innovation highlights
- Applications
- Selected sources of information.

Figure 1 shows the global TRL distribution of the innovative BBPs mapped in the study. The figure shows how many products are next close to commercialization, and how many are actually reaching the highest levels of technical development. Almost one-third of the products are approaching full availability on the market (currently at TRL 9). More than 20 products are now at the pilot plant stage (TRL 5), but there are very few products at TRLs 7 and 8.

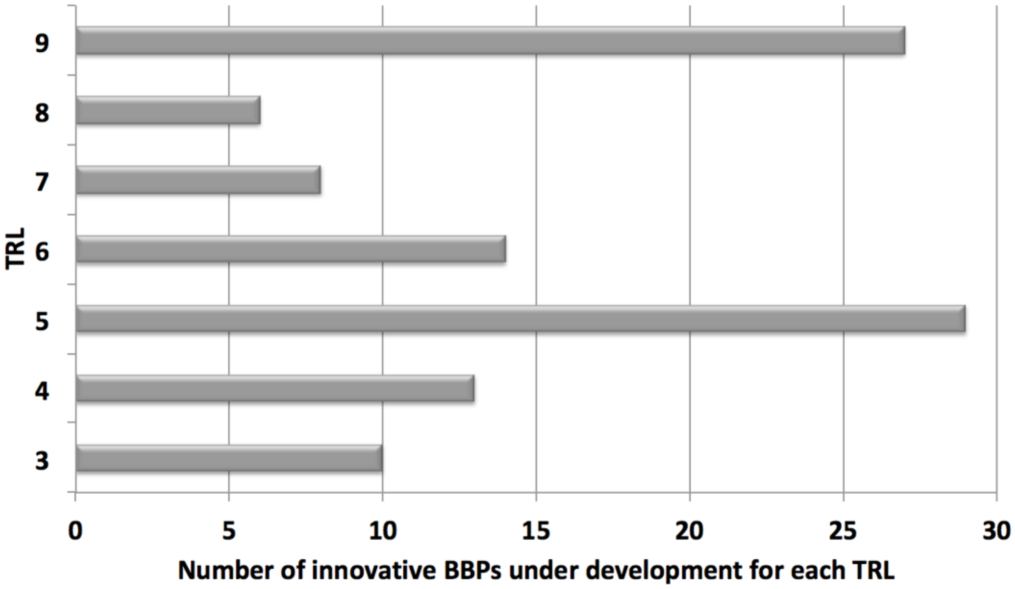

Figure 1: Global TRL distribution for the products included in the innovative BBPs database

Figure 2 shows TRL distributions for the products belonging to each of the seven biomass components included in the study. While lignin is the most intensively investigated biomass component at present, the most innovative products that are close to commercialization actually derive from plant fibres. Urban wastes are also intensively investigated, and there are products under development at all stages of technical advancement. Therefore, an almost continuous release of new products from the valorization of urban wastes should be expected in the coming years.

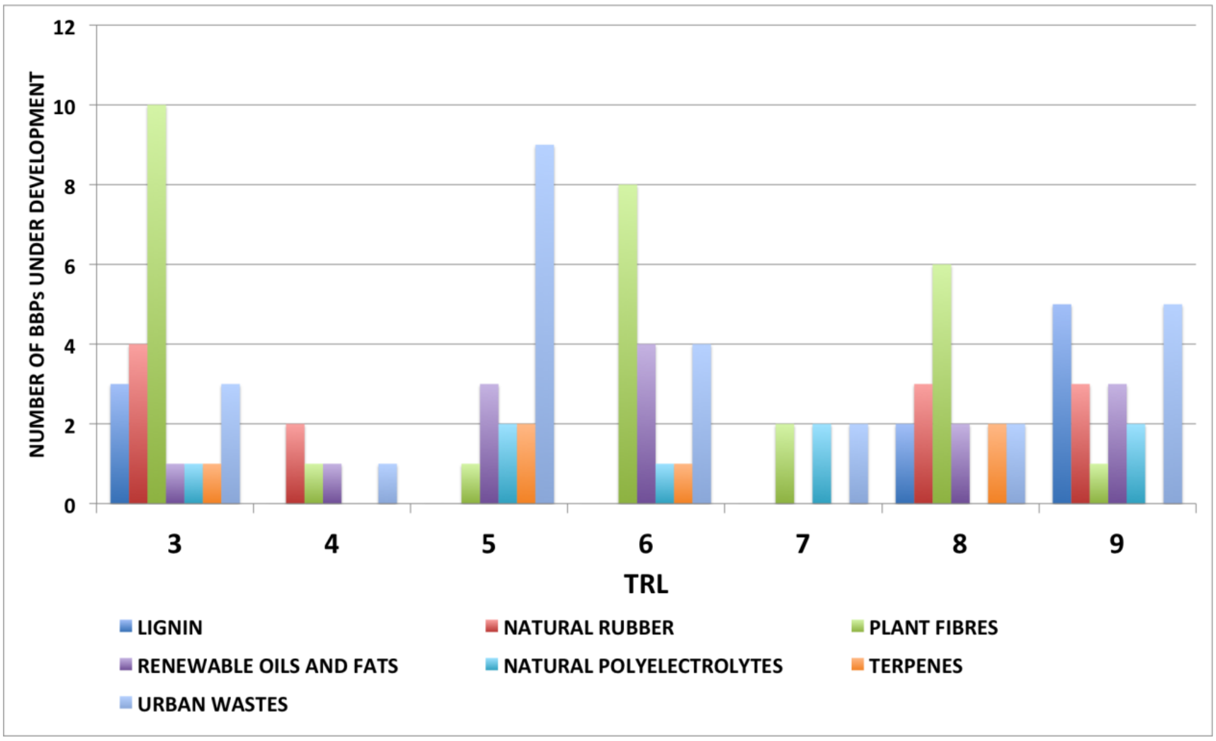

Figure 2: Number of innovative BBPs mapped at the different TRLs for the investigated biomass components

Through an assessment based on active the marketplace, EU-based development, degree of innovation and market potential, the twenty most innovative BBPs (TOP20) holding the greatest promise for commercial deployment within the next 5-10 years were identified.

This selection includes the BBPs listed in Table 2, organised on the basis of the biomass component from which they were derived. In the third column (key markets and applications), Table 2 reports the most relevant applications connected to the BBPs, identifying the industrial sectors for which these products are most relevant.

Table 2: Selected top 20 BBPs under development, holding greatest promise for commercial deployment in the next 5-10 years, and their key applications

Biomass category	TOP BBPs under development	Key markets and applications
Natural rubber	• Guayule rubber	• Substitute for natural rubber from Hevea Br. in all rubbery goods. Automotive. Biomedical items.
Plant fibres	• Lignin biocomposites reinforced with plant fibres • Microfibrillated cellulose • Thermoplastic biopolymers reinforced with plant fibres • Plant fibres reinforced bioresin pre-pregs • Self-binding composite non-woven plant fibres	• Injection molding of plastic items • Rheology modifier, reinforcing filler, emulsions stabilizer, filtering media, biomedical field. • Alternative to glass or

		carbon-fibres reinforced plastics • Alternative to glass or carbon-fibres reinforced pre-pregs • Plastic paper
Renewable oils and fats	• Biolubricants • PHAs • Biobased polyamide 12	• Automotive and industrial field • Biodegradable plastics • Technical plastics
Lignin	• Lignin-based carbon nanofibres • Bio-BTX aromatics • Lignin bio-oil • Lignin-based phenolic resins • High-purity lignin • Biobased phenol and alkylphenols	• Alternative to PAN-based carbon fibers. Composites • Bio-based raw chemicals • green chemicals and biofuels • alternative to phenolic resins. Constructions. • thermosets. Composites. Additive for plastics. • Aromatic chemicals and monomers
Terpenes	• Limonene-based engineering polymers	• Bio-based polyurethanes, polyamides, polycarbonate
Polyelectrolytes	• Bacterial biosurfactants (sophorolipids and rhamnolipids) • Biotechnological chitosan	• Medical and pharmaceutical formulations, cosmetics, personal care, food industry
Urban biowastes	• PHAs from urban wastes • Volatile fatty acids (VFAs) mixtures	• Biodegradable plastics • Raw chemicals to produce esters, solvents, polymers.

The outcome of the selection of the top 20 BBPs reveals important information on the general trends in the bio-based industry.

- The greatest attention is focused on the industrial development of new bio-based materials targeted as advanced technical applications. **Engineering materials** with elevated thermomechanical properties suitable for the automotive and construction fields, such as biopolyesters, biopolyamides, matrices and fillers for reinforced biocomposites, as well as biolubricants, represent the vast majority of the top 20 innovative bio-based products: more than 13 can actually be attributed to this category.

- Bio-based innovative solutions related to the **plastics** sector most certainly occupy the most relevant position. Plastics are versatile materials widely employed in almost all industrial and commercial sectors, but their elevated durability in the open environment results in the global problem of plastic litter in the soil and sea. Even when properly collected at their end-of-life, plastics are not always easily recycled due to the impossibility of obtaining elevated mechanical properties from the mechanical processing of mixed plastic waste streams. Therefore, sustainable solutions, either bio-based or bio-based and biodegradable, are intensely investigated. More than 10 of the top 20 selected products are related to the plastics world. Both thermosets and thermoplastic innovative plastic materials are currently under development, and innovation is found either in the synthesis of completely new polymeric structures (an example is the case of limonene-based engineering polymers - polyurethanes, polycarbonates, polyamides), or the development of drop-in substitutes derived from renewable resources (i.e. biophenolic resins). Poly(hydroxyalkanoate)s PHAs are currently the subject of intensive research regarding promising biodegradable substitutes for a number of commodity polymers, such ad HDPE, PP and others. The fact that PHAs can be obtained by purely biotechnological routes starting from a variety of carbon-rich biomass feedstocks, including agricultural wastes, organic fractions of solid municipal wastes and urban wastewater, hence making them particularly attractive. At present, the development of PHAs based on renewable oils and fats and urban biowastes (OFMSW and UWW) is at TRL 6-7. These production routes nevertheless compete with the one based on sugars, which is more advanced, having reached level TRL 9.

- Innovative bio-based products for commercial solutions with **high added value** due to their technical specificity are also of particular importance in the top 20. For example, the anti-bacterial, anti-fungal and anti-cancer activity of 3rd generation chitosan attract noteworthy attention for highly demanding applications in the pharmaceutical and biomedical field.

- The chemical platform related to **lignin** is the one giving rise to the highest number of innovative products at present. Lignin's natural abundance and global availability are the main reasons for the current efforts toward exploitation beyond its current relevant role as a bioenergy source. This is undoubtedly associated to its chemical versatility and uniqueness as a source of aromatic building blocks. Aromatics, in general, are only available from fossil oil, and their essential role in numerous industrial sectors, including fuels, solvents, lubricants, and plastic materials among others, makes them very attractive if derived from renewable resources. Innovative products derived from lignin range from fundamental chemical building blocks, such as BTX aromatics, to materials for advanced applications in technical fields such as construction engineering, where, for instance, both carbon fibres and thermoset resins play major roles. Seven (7) of the top 20 selected BBPs derive from lignin.

- The complete dependency of Europe on imports of natural rubber sourced from the rubber tree, Hevea Brasiliensis, from Southeast Asia, has motivated the recent inclusion of this elastomer in the list of **critical raw materials** for the EU. The need to develop solid alternative provision routes for natural rubber, based on regional biomass feedstock availability, supports the current research on natural rubber from guayule, Russian dandelion and rubber derived from the polymerization of the bio-based isoprene monomer.

- The **TRL distribution** of the top 20 selected innovative BBPs shows that half of them currently have had their technology validated in the relevant environment (TRL 5), while only approximately 10% have a fully developed and qualified system (TRL 8). Figure 3 shows the TRL distribution for the selected top 20 products. The detailed commercialization status of the selected top 20 products is reported in Figure 4.

The 20 detailed case studies exist as standalone documents and are included in this report in Section 6. Infographics were also derived by the respective extended case studies, and were collected in a booklet printed by Ecologic Institute (DE) in June 2018. The booklet is available for free download at the following link: https://www.ecologic.eu/sites/files/event/2018/ts3_booklet_final.pdf

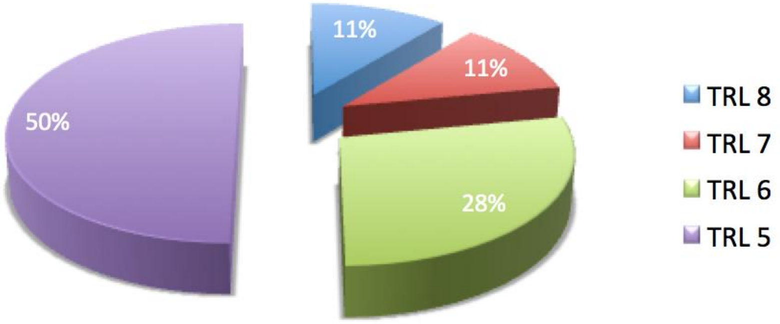

Figure 3: TRL distribution for the selected top 20 BBPs

The study concludes by elaborating on the key research and development gap themes and outlook perspectives that are discussed in depth in Section 7. Most of the products show difficulties to enter the market due to high production costs; hence implying significant research needs to improve various aspects of the process. Some products also have challenges with stability or performance of the final product. In these cases, this is of higher priority in order to meet consumer needs at the level or better of potential substitutes. Finally, in many cases, raw material provision in the EU is not straightforward and adequate solutions may be needed for the required feedstock. Most of the products considered can, in fact, use different sources of biomass and end up in a variety of final products, so the consideration of the most suitable portfolio of market opportunities can indeed be key for future development of bio-based products.

TRL	5	6	7	8	9
	Pilot	Demonstration		Commercial	
Key for categories		Guayule rubber			
				Nanocellulose	
		Composite non woven plant fibres			
Natural rubber		Lignin biocomposites reinforced with plant fibres			
Plant fibres		Plant fibers bioresin prepregs			
Lignin	Plant fibres reinforced biopolymers				
Renewable oils and fats				Bio-phenolic resins	

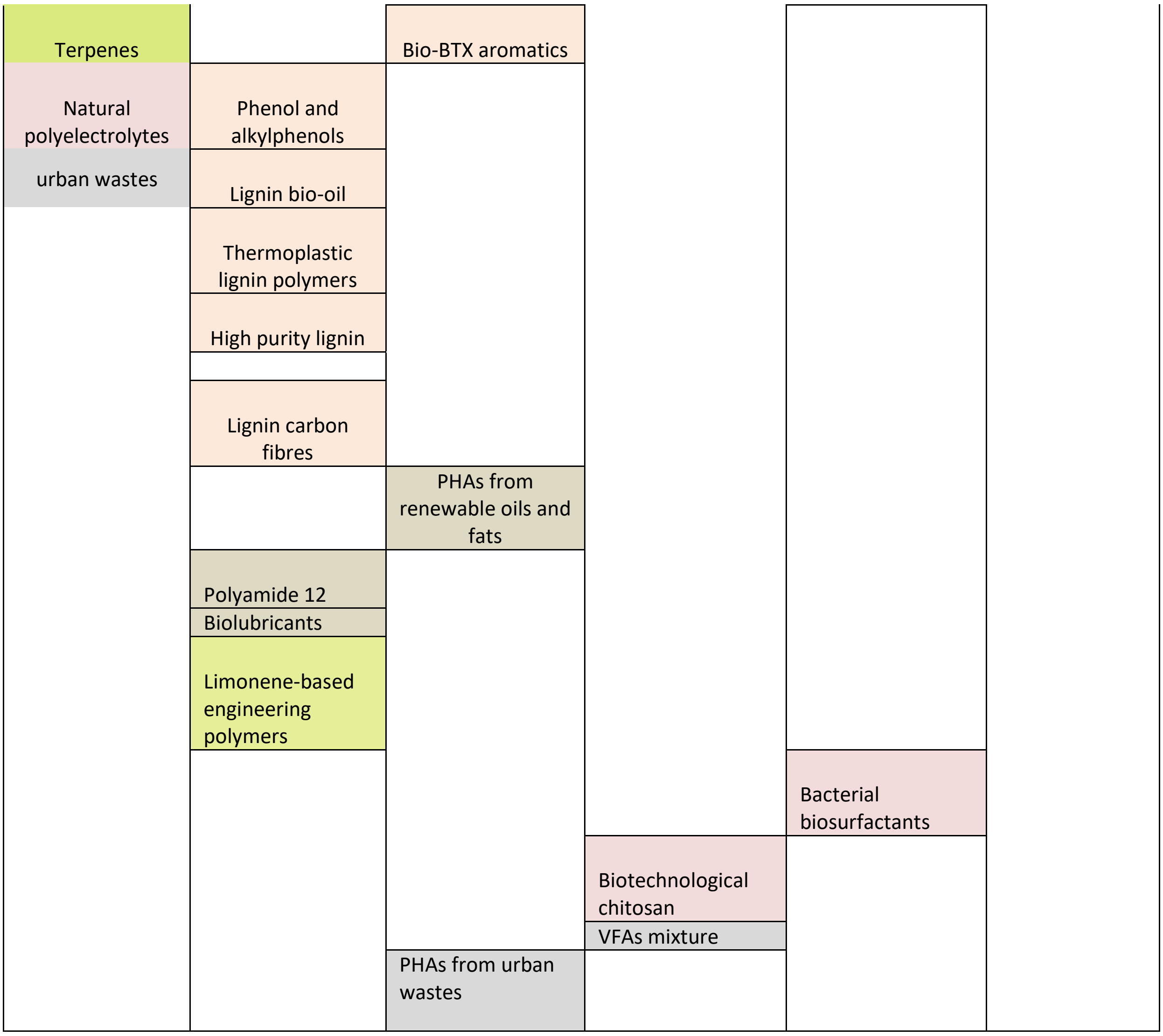

Figure 4: Commercialization status of the selected top 20 products

RÉSUMÉ

La construction de nouvelles chaînes de valeur, à travers la valorisation des principaux composants de biomasse à faible volume et à haute valeur (LVHV: low volume-high value biomass) pour le développement de bio-produits innovants (BBPs: Bio-Based Products), destinés à des secteurs spécifiques du marché, accélérera la transition des technologies de production traditionnelles au concept des bioraffineries.

Les nouvelles technologies et les méthodes traditionnelles couplées aux biotechnologies appliquées aux matières premières de biomasse et aux flux de déchets provenant de diverses sources (tels que les déchets urbains, les résidus agricoles ou les déchets provenant des flux d'aliments et d'aliments pour animaux) convertiront les ressources renouvelables en BBPs durables à haute valeur ajoutée.

Cette étude vise à dresser une liste des BBPs innovants actuellement en développement (à n'importe quel stade d'avancement) et dérivant des principaux composants de la biomasse énumérés dans le tableau 1 ci-dessous (qui rapporte également le nombre des produits innovants en développement qui ont été identifiés pour chaque composant de la biomasse). Les composants de la biomasse inclus dans l'étude sont décrits brièvement à la section 3.

Table 1: Composants de la biomasse inclus dans l'étude et nombre respectif de BBPs innovants identifiés

	Principaux composants de la biomasse	Nombre des BBPs innovants identifiés
Principaux composants de la biomasse	Caoutchouc naturel	5
	Fibres végétales	17
	Huiles et graisses renouvelables	19
	Lignine	23
Composants de biomasse à faible volume et à haute valeur (LVHV)	Terpènes	18
	Polyelectrolytes	6
Biodéchets urbains	Biodéchets urbains	19

Dans le cadre de cette étude, 107 BBPs innovants été identifiés et cartographiés.

Une base de données a été développée pour recueillir les informations suivantes pour chacun des BBPs identifiés actuellement en développement, à partir des composants de biomasse susmentionnés :

- matières premières de biomasse
- TRL *(Technology readiness level)* maximum atteint
- nombre d'entreprises actives
- installations de production (UE/reste du monde)
- principaux acteurs
- taille du marché estimée
- alternatives non biologiques ou traditionnelles
- faits marquants de l'innovation
- applications
- sources d'information sélectionnées

La figure 1 montre la distribution des valeurs de TRL des BBPs innovants listés dans cette étude. La figure indique combien de produits sont sur le point d’être commercialisés et combien atteignent les plus hauts niveaux de développement technique. Près du tiers des produits approchent une disponibilité totale sur le marché (actuellement à TRL 9). Plus de 20 produits en sont au stade de l’usine pilote (TRL 5), mais très peu de produits sont aux TRL 7 ou 8.

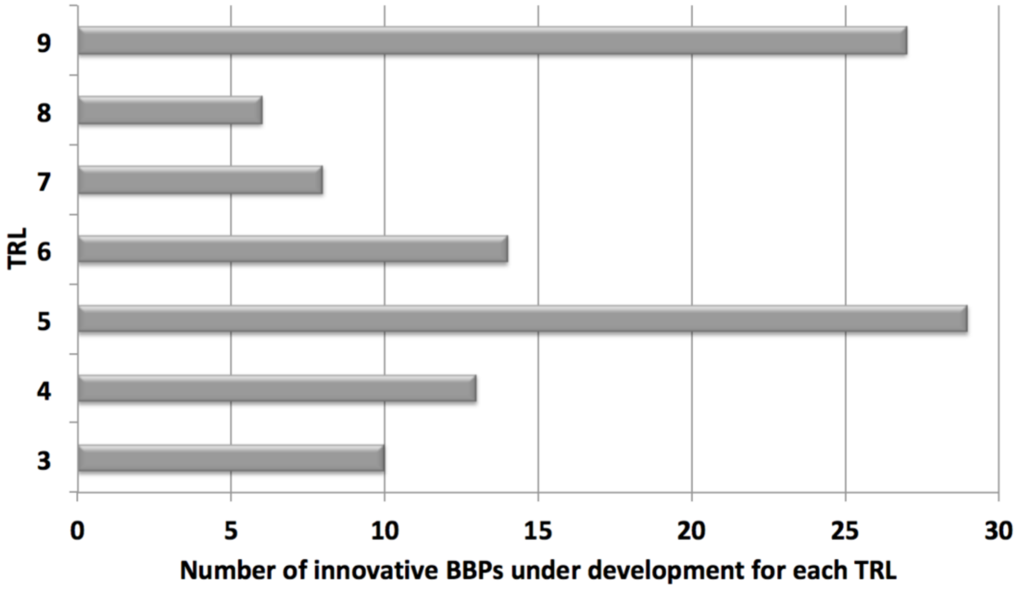

Figure 1 : Distribution des TRL pour les produits inclus dans la base de données des BBPs innovants

La figure 2 montre la distribution des TRL pour les produits appartenant à chacun des sept composants de la biomasse inclus dans l'étude. Alors que la lignine est le composant de la biomasse le plus étudié à ce jour, le plus grand nombre de produits innovants prêts à être commercialisés dérive des fibres végétales. Les déchets urbains sont également très étudiés et on trouve des produits en développement à tout stade d'avancement technique. Par conséquent, il faut s'attendre à une sortie quasi-continue de nouveaux produits issus de la valorisation des déchets urbains au cours des prochaines années.

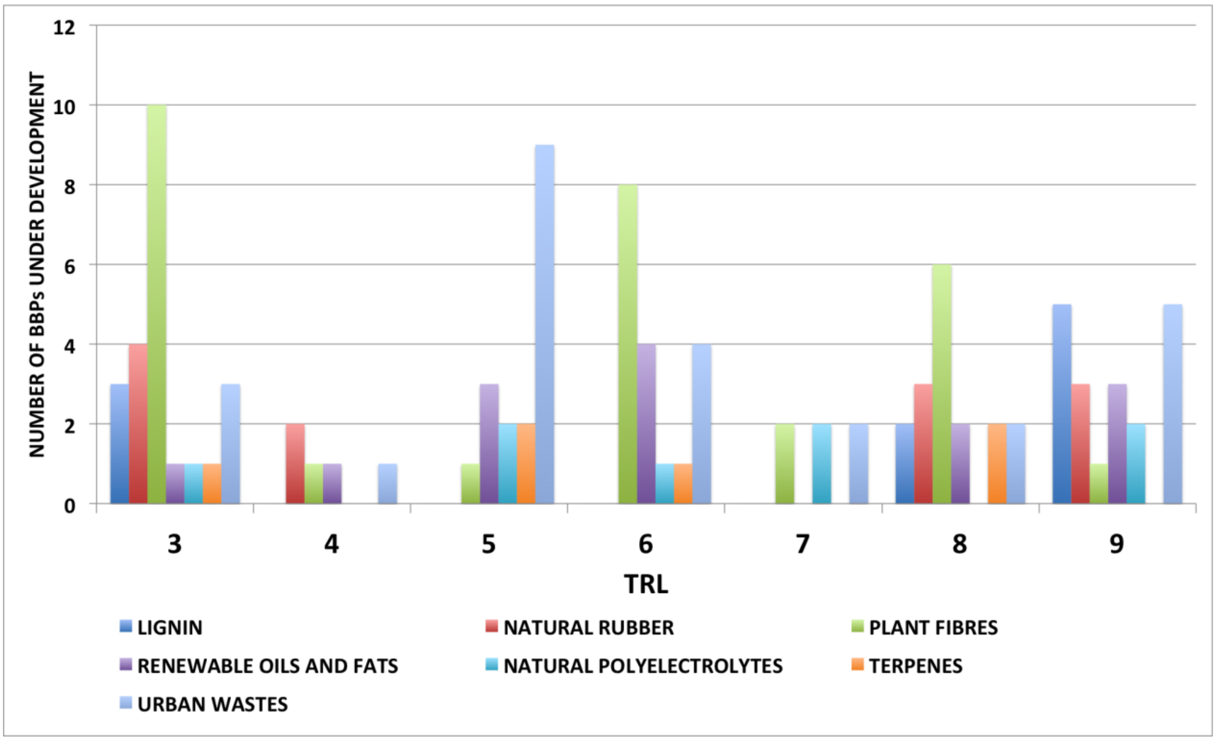

Figure 2 : Nombre de BBPs innovants identifiés à différents TRL pour les composants de la biomasse étudiés

Grâce à une évaluation basée sur le marché actif, le degré de développement au niveau de l'Union Européenne, le degré d'innovation et le potentiel commercial, les vingt BBPs (Top 20) les plus innovants et prometteurs pour un déploiement commercial durant les 5-10 prochaines années ont été identifiés .

Cette sélection comprend les BPPs énumérés dans le tableau 2 suivant, organisés sur la base du composant de la biomasse dont ils dérivent. Dans la troisième colonne (principaux marchés et applications), le tableau 2 répertorie les applications les plus pertinentes connectées aux BPPs, identifiant les secteurs industriels pour lesquels ces produits sont les plus pertinents.

Tableau 2 : Top 20 des BBPs en cours de développement, ayant le plus grand potentiel de commercialisation au cours des 5-10 prochaines années, et leurs applications clés.

Catégorie de biomasse	Les BBPs les plus prometteurs en cours de développement	Principaux marchés et applications
Caoutchouc naturel	• Caoutchouc à base de guayule	• Substitut de caoutchouc naturel de Hevea br. dans tous les produits caoutchouteux. Automobile. Articles biomédicaux.
Fibres végétales	• Biocomposites de lignine renforcés par des fibres végétales • Cellulose microfibrillée • Biopolymères thermoplastiques renforcés par des fibres végétales • Biorésine pré-imprégnées renforcées par des fibres végétales • Fibres végétales composites non tissées auto-liantes	• Moulage par injection d'articles en plastique • Modificateur rhéologique, remplisseur de renfort, stabilisateur d'émulsions, milieu filtrant, domaine biomédical. • Alternative aux « pre-pregs » renforcés par des fibres de verre ou de carbone • Alternative aux plastiques renforcés par des fibres de verre ou de carbone • Papier plastique
Huiles et graisses renouvelables	• Biolubrifiants • PHAs • Bio-polyamide 12	• Secteur automobile et industriel • Plastiques biodégradables • Plastiques techniques
Lignine	• Nanofibres de carbone à base de lignine • Aromates Bio-BTX	• Alternative aux fibres de carbone à base de PAN. Composites • Bio-produits chimiques

	• Bio-huile de lignine • Résines phénoliques à base de lignine • Lignine de haute pureté • Bio-phénols et bio-alkylphénols	bruts • Produits chimiques verts et biocarburants • Alternative aux résines phénoliques. Constructions. • Thermodurcissables. Composites. Additif pour les plastiques. • Produits chimiques aromatiques et monomères
Terpènes	• Polymères d'ingénierie à base de limonene	• Bio-polyuréthanes, bio-polyamides, bio-polycarbonates
Polyélectrolytes	• Biosurfactant bactérien (sophorolipids et rhamnolipides) • Chitosan biotechnologique	• Formulations médicales et pharmaceutiques, cosmétiques, soins personnels, industrie agroalimentaire
Biodéchets urbains	• PHAs des déchets urbains • Mélanges d'acides gras volatils (VFAs)	• Plastiques biodégradables • Produits chimiques bruts pour la production d'esters, solvants, et polymères.

Les résultats de la sélection des 20 meilleurs BPPs révèlent des informations importantes sur les tendances générales de la bio-industrie.

- Comme première preuve, la plus grande attention est portée sur le développement industriel de nouveaux bio-matériaux destinés à des applications techniques avancées. Les matériaux d'ingénierie ayant des propriétés thermomécaniques élevées, adaptées aux domaines de l'automobile et de la construction, tels que les bio-polyesters, les bio-polyamides, les matrices et les charges pour les biocomposites renforcés, mais aussi les biolubrifiants, représentent la vaste majorité des 20 premiers bio-produits innovants: plus de 13 peuvent être attribués à cette catégorie.

- Des bio-solutions innovantes relatives au secteur des plastiques occupent une position de premier plan. Les plastiques sont des matériaux polyvalents utilisés dans presque tous les secteurs industriels et commerciaux, mais leur longétivité dans l'environnement pose le problème mondial des déchets plastiques retrouvés dans le sol et la mer. Même quand ils sont correctement collectés en fin de vie, les plastiques ne sont pas toujours facilement recyclés en raison de l'impossibilité d'obtenir des propriétés mécaniques élevées du traitement mécanique des flux de déchets plastiques mélangés. Par conséquent, des solutions durables, soit biologiques, soit biologiques et biodégradables, font l'objet de nombreuses études. Plus de 10 des premiers 20 produits sélectionnés sont liés au monde des plastiques. Les matériaux plastiques thermodurcissables et thermoplastiques innovants sont actuellement en cours de développement, et l'innovation repose soit sur la synthèse de structures polymères complètement nouvelles (un exemple étant le cas des polymères d'ingénierie à base de limonene - polyuréthanes, polycarbonates et polyamides), soit sur le développement de substituts dérivés de ressources renouvelables (par exemple, les résines biophénoliques). Les polyhydroxyalcanoates, ou PHAs, sont aujourd’hui intensément étudiés comme substituts biodégradables prometteurs pour un certain nombre de produits polymères, tels que HDPE, PP et autres. Le fait que les PHAs puissent être obtenus par voie purement biotechnologique à partir d'une variété de matières premières de biomasse riches en carbone, y compris les déchets agricoles, les fractions organiques des déchets municipaux solides et les eaux usées urbaines, les rend particulièrement attrayant. À l'heure actuelle, le développement de PHAs basés sur des huiles et des graisses renouvelables et sur des déchets urbains (OFMSW et GSM) se trouve au TRL 6-7. Ces itinéraires de production rivalisent néanmoins avec celui des sucres qui est plus avancé, étant actuellement au TRL 9.

- Des bio-produits innovants destinés aux solutions commerciales à **forte valeur ajoutée** en raison de leur spécificité particulière occupent également une place importante. Par exemple, l'activité antibactérienne, antifongique et anti-cancéreuse du chitosan de 3ème génération attire beaucoup d'attention pour ses applications dans les domaines pharmaceutique et biomédical.

- La plate-forme chimique relative à la lignine est celle qui génère aujourd’hui le plus grand nombre de produits innovants. Son abondance naturelle et sa disponibilité mondiale constituent les principales raisons des efforts déployés actuellement pour son exploitation au-delà de son rôle actuel de source de bioénergie. C’est sans aucun doute associé à sa polyvalence et à son unicité chimiques comme source d’éléments aromatiques. Les éléments aromatiques, en général, ne sont disponibles qu'à partir d'huile fossile, et leur rôle essentiel dans de nombreux secteurs industriels, comme les carburants, les solvants, les lubrifiants et les matériaux plastiques parmi tant d’autres, les rendent très attrayants s’ils sont dérivés de ressources renouvelables. Les produits innovants dérivés de la lignine vont des blocs de construction chimique fondamentaux, tels que les BTX aromatiques, aux matériaux destinés à des applications avancées dans des domaines techniques comme le génie civil, où, par exemple, les fibres de carbone et les résines thermodurcissables jouent un rôle majeur. Sept des 20 BBPs sélectionnés proviennent de la lignine.

- La totale dépendance de l'Europe à l'importation du caoutchouc naturel, provenant de l'hévéa Brasiliensis du sud-est de l'Asie, a motivé la récente inclusion de cet élastomère dans la liste **des matières premières critiques** pour l'UE. La nécessité de développer des filières d'approvisionnement alternatives solides pour le caoutchouc naturel , basées sur la disponibilité régionale des matières premières de biomasse, soutient la recherche actuelle sur le caoutchouc naturel de guayule de pissenlit russe et le caoutchouc dérivé de la polymérisation du monomère de bio-isoprène.

- **La distribution des TRL** pour les 20 BBPs innovants sélectionnés montre que la moitié d'entre eux disposent actuellement de la technologie correspondante validée dans l'environnement concerné (TRL 5), tandis qu'environ 10% seulement ont un système entièrement développé et qualifié (TRL 8). La figure 3 montre la distribution des TRL pour les 20 produits. La Figure 4 schématise le statut détaillé de commercialisation de ces produits.

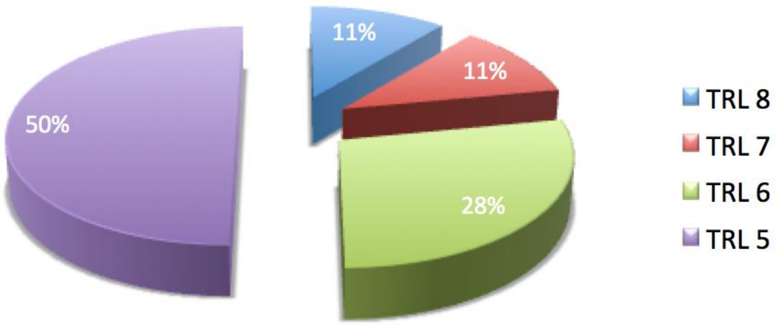

Figure 3 : Distribution des **TRL des 20 meilleurs BBPs sélectionnés**

TRL	5	6	7	8	9
	Pilote	**Démonstration**		**Commercial**	
Les catégories clés		Caoutchouc de guayule			
				Nano cellulose	
		Fibres végétales composites non tissées			
Caoutchouc naturel		Biocomposites de lignine renforcées par des fibres végétales			
Fibres végétales		Biorésines de fibres végétales « pre-pregs »			
Lignine	Fibres végétales renforcées de biopolymères				
Huiles et graisses renouvelables				Résines bio-phénoliques	
Terpènes		Produits aromatiques bio-BTX			
Polyélectrolytes naturels	Phénol et alkylphénols Bio-huile de lignine Polymères de lignine thermoplastiques Lignine de haute pureté				
Déchets urbains					
	Fibres de carbone de la lignine				
		PHAs obtenus à partir d'huiles et de graisses renouvelables			
	Polyamide 12 Biolubrifiants				
	Polymères techniques à base de limonène				
				Bio-surfactants bactériens	
			Chitosane		

		PHAs obtenus à partir de déchets urbains	biotechnologique Mélange de VFAs		

Figure 4 : Statut de commercialisation des 20 meilleurs produits sélectionnés

Les 20 études de cas détaillées existent en tant que documents autonomes et sont incluses dans le présent rapport à la section 6. Les infographies ont également été établies à partir des études de cas étendues correspondantes et ont été rassemblées dans une brochure imprimée par Ecologic Institute (DE) en juin 2018. La brochure est disponible en téléchargement gratuit au lien suivant :

https://www.ecologic.eu/sites/files/event/2018/ts3_booklet_final.pdf

L’étude se termine en mentionnant les principales lacunes en matière de recherche et développement et les perspectives, qui sont examinées de manière approfondie à la section 7. La plupart des produits présentent des difficultés dues à des coûts de production élevés, qui impliquent des besoins de recherche importants pour améliorer différents aspects du processus de développement. Certains produits présentent également des problèmes de stabilité ou de performance du produit final. Dans ce cas, la priorité est plus élevée afin de répondre aux besoins des consommateurs, avec des substituts potentiels au même niveau, voire à un niveau supérieur. Enfin, dans de nombreux cas, l'approvisionnement en matières premières dans l'UE n'est pas simple et des solutions adéquates peuvent être nécessaires pour la matière première requise. La plupart des produits considérés peuvent utiliser différentes sources de biomasse et, finalement, aboutir à une variété de produits finis. Dès lors, la prise en compte des opportunités de marché les plus appropriées peut être la clé du développement futur de nouveaux bio-produits.

SECTION 1 BACKGROUND, POLICY CONTEXT AND AIM OF THE STUDY

1 Background

The bio-based industries in Europe and all over the world are evolving rapidly, driven by business and consumer demand, as well as society's demands for more sustainable products that avoid depletion of natural resources and reduce environmental impact. The total turnover of the bio-based industries increased from 647 billion in 2008 to 698 billion Euro in 2015, and according to forecasts the bio-based share of all chemical sales will rise to 22% by 2020, with a compounded annual growth rate close to 20% [1]. Moreover, the European bioeconomy provides jobs for 18.3 million Europeans, over half of them in primary biomass production (agriculture, forestry and fisheries). Bio-based industries employ 3.2 million people [2].

The development of innovative technologies for the valorization of biomass components, and their up-scaling to commercial levels, will enable a further boost to the transition from fossil to renewable sources. Dynamic and sustainable bio-based industries have the potential to deliver many environmental, economic and social benefits. They can help to meet objectives in areas ranging from economic growth, job creation, the circular economy and resource efficiency to climate change mitigation, security, agriculture modernisation and regional development.

Bio-based industries are important players in building the European circular economy. They are pioneering processes to produce added-value products from feedstocks such as agricultural residues, urban biowaste (the organic fraction of municipal solid wastes and sludge from waste water treatment), side streams from food processing, and reducing industrial emissions of greenhouse gases (GHG), including CO_2.

Building new value chains through the valorization of the main components of biomass feedstock for the development of innovative bio-based products aimed at specific market sectors will accelerate the transition from traditional production to the concept of biorefineries. New technologies and traditional methods coupled with biotechnologies applied to biomass feedstock and waste streams from various sources, such as urban wastes or agricultural residues or wastes from food and feed streams, will convert renewable resources into high added-value sustainable bio-based products. Beyond technological barriers, market acceptance and commercialization will then need to be supported by public policy and the economic context.

Some specific value chains originating from lignocellulosic, agricultural and organic waste into chemicals and materials, experienced a rapid growth in the last few years, some others are still currently un- or underexploited for bio-based operations.

A clear example of an already technologically advanced value chain is that of sugars; many platform chemicals and important building blocks for the development of sustainable materials, such as 1,4-butanediol (BDO), 2,5-furandicarboxylic acid (FDA) or poly(lactic acid) already occupy a relevant commercial position. Pioneers of bio-based technologies have paved the way for sustainable BDO production from renewable feedstock, which has positively influenced consumption patterns in recent years, because companies are increasingly adopting good manufacturing practices and integrating advanced production technologies to comply with transitioning regulatory frameworks and consumer specifications. Producers have shifted their focus towards sustainable production and boosted reliance on renewable resources to reduce resource demand, waste and pollution.

Therefore, the development of new specific bio-based value chains, making the best possible use of cascading and circular approaches, represents the most effective tool to positively influence consumption goods at the industrial level, which in turn supports economic growth, job creation, resource efficiency to climate change mitigation, security, agriculture modernisation and regional development.

To guarantee a secure and sustainable supply of biomass feedstock for biorefineries, the development of integrated and sustainable value chains using agricultural-based, forestry-based, aquatic feedstock and their residues and side streams, and bio-waste, should be rapidly implemented. The exploitation and valorization of all the main components of biomass pursuing solutions that fulfil such sustainability and circular economy principles, will result in new, larger and more diversified business proposals for sustainable chemicals and products.

The European Commission has already commissioned a study to map out all of the potential value chains for the production of biofuels and biochemicals originating from the sugar platform [3]; therefore, sugar is out of the main scope of this study.

The present study simultaneously depicts the panorama of innovative bio-based products recently developed or currently under development, originating from a wide set of main biomass components, assessing them on a common basis to determine what will be technically achieved in the next 5 to 10 years and which are, at present, the most promising fields for market growth and industrial investment. The biomass components included in this study are: natural rubber, plant fibres, renewable oils and fats of vegetable and animal sources, lignins, terpenes, natural polyelectrolytes and urban waste.

2 Policy context

At the European level, policies linked to bio-based products include the following:

- The Renewed *industrial policy strategy for Europe* [4], which aims to raise industry’s contribution to EU GDP to 20% by 2020. The bio-based products sector, is one of the priority areas with a high potential for future growth and for addressing societal challenges.

- *The Europe 2010 Flagship Initiative - Innovation Union* [5] under the Europe 2020 strategy supports the shift towards a resource-efficient, low-carbon, economy to achieve sustainable growth. The flagship initiative placed innovation at the heart of the Europe 2020 strategy in order to maintain Europe's competiveness in a demographically changing and increasing competitive world.

- The 2018 update *Bioeconomy strategy* [6] aims to accelerate the deployment of a sustainable European bioeconomy so as to maximise its contribution towards the 2030 Agenda and its Sustainable Development Goals (SDGs), as well as the Paris Agreement. The update proposes an action plan with 14 concrete measures to be launched in 2019, based on three key priorities: (1) Strengthen and scale up the bio-based sectors, unlock investments and markets; (2) Deploy local bioeconomies rapidly across the whole of Europe and (3) Understand the ecological boundaries of the bioeconomy.

- The 2015 *Circular Economy Package* [7] was created to help European businesses and consumers make the transition to a stronger and more circular economy where resources are used in a more sustainable way. The proposed actions contribute to 'closing the loop' of product lifecycles through greater recycling and re-use, and bring benefits for both the environment and the economy. Biomass and bio-based products are one of the five priority areas. It indicates that bio-based materials can also present advantages linked to their renewability, biodegradability or compostability. The transition towards a circular economy will be supported financially by ESIF funding, €650 million from Horizon 2020 (the EU funding programme for research and innovation), €5.5 billion from structural funds for waste management, and investments in the circular economy at the national level.

- In January 2018, as part of the implementation of the Circular Economy Package, the EC adopted the *EU Strategy for Plastics in the Circular Economy* [8] and annex to transform the way plastics and plastics products are designed, produced, used and recycled. By 2030, all plastic packaging should be recyclable. The Strategy also highlights the need for specific measures, possibly a legislative instrument, to reduce the impact of single-use plastics, particularly in our seas and oceans.

- The *European Innovation Partnerships* (EIP) were launched in 2012-2013 under the Innovation Union flagship programme to accelerate the market uptake of innovations that address key challenges for Europe. Specifically:

    - The EIP for Agricultural Productivity and Sustainability (EIP-AGRI) aims to promote competitive and sustainable agriculture and forestry that "achieves more from less". It contributes to ensuring a steady supply of food, feed, and biomaterials.

    - The EIP on Raw Materials seeks to achieve the transition to a circular economy by providing valuable lessons on how to boost recycling and the re-use of materials. A list of critical raw materials was also released as implementation of the Circular Economy Package.

- The *Lead Market Initiative* between 2008 and 2011 fostered the development of the bio-based products sector by exploring demand-side innovation policy tools such as standardisation, labelling, and public procurement. The main outcomes of this initiative were an interim report, "Taking Bio-based from Promise to Market"; policy papers on financing and communications; and a list of priority recommendations (22 kB) to enable the market uptake of bio-based products. In the framework of the Lead Market Initiative, the European Commission issued several standardisation mandates to the European Committee for Standardisation (CEN).

At the State level, since 2015, six new dedicated bioeconomy national policy strategies have been adopted in France, Italy, Latvia, Norway and Spain. The most recent addition is Ireland, which passed its national bioeconomy policy strategy in March 2018. In addition, Austria, Estonia, Iceland and the UK have announced their intention to introduce bioeconomy policies. Most of the recently published strategy documents, however, focus on the production and utilisation of bio-resources. High-tech approaches are found to a greater extent in Germany and the UK, where the focus is more on biosciences and the "biologization of the economy" [9].

3 Aim of the study

Scope

This study was carried out in the framework of the BIOSPRI tender "STUDY ON SUPPORT TO R&I POLICY IN THE AREA OF BIO-BASED PRODUCTS AND SERVICES", implemented by a Consortium led by COWI A/S for the European Commission (COM), Directorate General for Research & Innovation (DG RTD), under contract 2016/RTD/F2/OP/PP-04541-2016.

The overall objective of this tender is to provide new information and analyses that will enable policy-makers, the scientific community, primary producers, business enterprises and other stakeholders to make more informed decisions about innovative bio-based products. The study is composed of three pillars: LCA of bio-based products, EU success stories of bio-based products on the market, and top emerging bio-based products.

The part of the tender study reported in this document, implemented by the University of Bologna (Italy) in collaboration with Fraunhofer ISI (Germany), is related to the selection and description of the twenty most innovative emerging bio-based products. It was designed to provide a comprehensive overview of undergoing innovation, at any level of technology readiness, in the production of bio-based products derived from a number of main biomass components and urban biowastes. It was conceived by DG RTD as an instrument to assist policy makers and industry stakeholders, and was developed by experts in sustainable chemistry and materials from renewable resources.

The focus of this study is on innovative bio-based products as defined by the Lead Market Initiative [6]:

> *"Bio-based products refer to non-food products derived from biomass (plants, algae, crops, trees, marine organisms and biological waste from households, animals and food production). Bio-based products may range from high-value added fine chemicals such as pharmaceuticals, cosmetics, food additives, etc., to high volume materials such as general bio-polymers or chemical feedstocks [i.e. building blocks]. The concept excludes traditional bio-based products, such as pulp and paper, and wood products, and biomass as an energy source."*

Products identified through this study are either business-to-business or business to consumer, and belong to relevant product groups and end applications. They include products combining bio-based and non-biobased components.

The study was conducted in parallel on eight categories of **main biomass components** (i.e. renewable oils and fats of vegetable and animal origin, plant fibres, lignin, natural rubber, terpenes, alkaloids, proteins, polyelectrolytes) and two categories of **urban biowaste** (i.e. the organic fraction of municipal solid waste and sludge from urban wastewater treatment).

Three main activities were developed:

1. Selection of the most promising main biomass components to bio-based products*, aimed at selecting the biomass components holding the greatest potential to* result in a large number of innovative bio-based products.

For the purposes of this selection, the main biomass components included in this study have been divided into two categories, as follows (Figure 5):

(1) Major biomass components:

- renewable oils and fats (vegetable and animal origin)
- plant fibres
- lignin
- natural rubber

(2) Low volume high value (LVHV) biomass components:

- terpenes
- alkaloids
- proteins
- polyelectrolytes

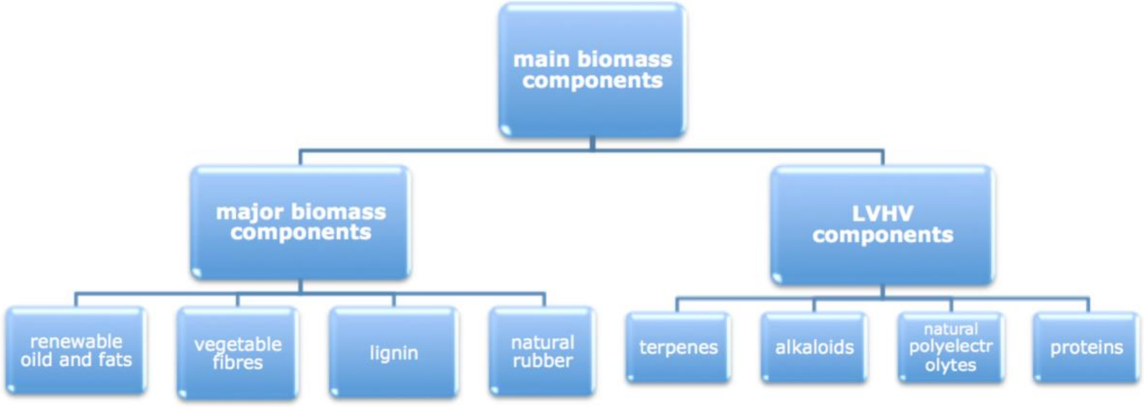

Figure 5 : Biomass components included in the study

After collecting preliminary information on the biomass components listed above, alkaloids and proteins were dropped and not included in the subsequent steps of the study. This was mainly related to the limited expertise available on these components in the group of experts on the consultants team, and their highly specialised use in sectors such as food and medicine.

2. Implementation of a database of innovative bio-based products currently under development, aimed at creating a comprehensive collection of information on the upcoming bio-based products derived from the above-mentioned selected biomass components, as well as the category of urban wastes. For each product, the database collects information on biomass feedstocks, maximum TRL achieved at present, number of active firms, presence of dedicated production facilities in Europe and in the rest of the world, leading actors, market size indicators, existence of non-bio-based alternatives, innovation highlights, main applications and selected references for information harvesting.

3. Development of detailed case studies on the twenty most innovative emerging bio-based products (top 20) holding the greatest promise for market development in the next 5 to 10 years. The top 20 innovative bio-based products with the greatest promise for commercial deployment in the coming 5 to 10 years, were identified through assessment, and detailed case studies were developed on each of them. An assessment of the innovative bio-based products on a common basis for a number of important aspects, such as: active marketplace, Europe-based development, degree of innovativeness and potential for market development - was carried out in order to select the top 20 BBPs.

The detailed case studies include: (i) general information; (ii) product description (chemical-physical characteristics, main uses, production process); (iii) markets (current volume, market value, prices); (iv) actors (general setting, Europe, rest of the world); (v) value proposition and sustainability (co-products, environmental impacts, benefits, sustainability, socio-economic advantages, health impacts, bio versus non-bio alternatives); (vi) overview of the state of future development (projected trends, competitiveness and role of Europe in global production.

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SECTION 2 APPROACH AND METHODOLOGY

The focus of this study was the development of detailed case studies on the twenty most promising BBPs, derived from a number of biomass components and urban biowastes, that are currently under development and that may be commercially deployed in the next 5 to 10 years. Identification of R&D gaps and outlook perspectives were also a main target.

Building a comprehensive database of all of the BBPs that are currently investigated worldwide, starting from the biomass components included in this study, was the first action to be implemented. Three levels of biobased products were taken into consideration, as detailed in the following:

- basic chemicals/building blocks (i.e. acids, alcohols, monomers, oleochemicals, etc.)

- secondary chemicals/ polymers (i.e. fine chemicals, polymers and other materials)

- final products and applications (i.e. products for the industrial sectors of food, packaging, agriculture, automotive, buildings, etc.)

The mapping of the innovative biobased products under current development was carried out by collecting updated information from several sources: scientific literature [1], industrial sources of information and patents [2-5], community research and development information service (CORDIS) [6], Task42 IEA bioenergy reports [7], market reports, Nova Institute Reports [8], JRC reports [9], and others. The full list of References which have been consulted to implement this Section is reported in Appendix B.

The database was developed in the form of an Excel file, containing 7 Excel sheets, each dedicated to products derived from one of the selected key biomass intermediates and LVHV products, and from the Urban Biowastes. There is a separate row for each product.

Based on the available literature and accessible data, the following information is provided for each product included in the Database:

- *Product*

  The description of products and materials based on their chemical structure was favoured, when possible/applicable, in order to group products with structural and compositional similarities.

- *Biomass Feedstock*

  The initial biomass feedstocks taken into consideration include any kind of agricultural residues, forestry, algae, crops, animal fats, the organic fraction of municipal solid wastes and the sludge of urban waste water.

- *max TRL achieved*

  The key metric used to assess the maturity of the evolving technologies related to each bio-based product is the TRL (Technology Readiness Level).

  All kinds of conversion technologies have been accounted for: mechanical, thermo-chemical, chemical and biotechnological options have been considered, and cited when possible. Attention has been focused on innovations related to the use of biotechnologies for the development of new bio-based products.

- *number of Active Firms*

number of companies working on each product, involved at any level (from patent filing to commercial launch), have been included in this field.

- *number of Production Facilities (EU/rest of the world)*

Due to data constraints, the Database is not a fully comprehensive record of every production facility worldwide. In several cases, companies claim that their existing plants have been "partially" converted to the production of innovative products, without giving further details. Information included in this field nevertheless gives an idea of the geographical distribution of production plants between Europe and the rest of the world.

- *Leading Actors*

The most advanced global developers have been classified as leading actors. They commonly also share more information and data because confidentiality is less pressing when higher TRLs have been reached.

- *Market size (estimated price €/kg; estimated sales kt per year)*

Information related to estimated price and global sales volumes for innovative products under development is usually not freely accessible, due to the extreme confidentiality of the matter. For this reason, it was not possible to fill in this field for several products included in the database. When possible, this information was taken from press releases, technical presentations and company web sites.

- *non bio-based alternatives (price €/kg; sales kt per year)*

Information related to commercial alternatives originating from non-renewables have been included, when possible. For some products there is no alternative possible, as in the case of nanocellulose for instance, but in other cases the market offers several alternatives. Efforts were made to select the most relevant non-biobased competitors for specific applications, but it was not always possible to do so in a comprehensive manner.

- *Innovation Highlights*

A broad meaning has been associated with the term "Innovation" for the purposes of the implementation of this Database. Innovation can be related to: i) the development of a completely new product, not previously available on the market; ii) the development of the new bio-based version of a previously available product derived from non-renewable resources (drop-in products); iii) the conversion of biomass feedstocks with a new/different technology for the development of new products and/or processes. In the vast majority of the cases, innovation was found to originate from a combination of the above-mentioned factors; therefore, short explanations of the most relevant aspects of innovation were briefly included in the database, to allow for an easy positioning of the product in the framework of the industry-targeted innovation.

- *Applications*

Several products included in the Database are intended for more than one application, or could be used in different sectors. A comprehensive description of all of the possible application fields was not possible; therefore, a selection of the most relevant or most economically attractive applications has been reported.

- *Selected References*

Extended use of literature survey, patent search, records from research and development projects at the national and international level, web-sites, have been carried out to collect information about every single product included in the database. Only the most relevant sources of information have been included directly in the database. Further information can be found in the documents listed in APPENDIX B DATA SOURCES AND LITERATURE SURVEY.

As a general remark about comprehensiveness of information included in the Database, one could take into consideration that information and data sharing about innovative products is not always in the interest of Actors. Therefore, for a number of cases that can be assumed quite elevated, the lack of freely accessible information could have generated a number of records that is lower than the real situation.

In order to develop a quantitative and objective tool for the assessment and ranking of the innovative bio-based products under development included in the Database, four selection criteria were applied, relative to:

1. Active marketplace
2. EU-based development
3. Degree of innovativeness
4. Market potential

For ranking purposes, these assessment criteria have been applied to each of the products included in the Database.

Assessment led to the selection of the twenty most promising BBPs, on which detailed case studies were developed through intensive industry reviews.

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SECTION 3 BRIEF INTRODUCTION TO THE BIOMASS COMPONENTS INCLUDED IN THE STUDY

This section examines in brief the following specific aspects for each of the biomass components included in this study:

- sources and structure
- feedstock and feedstock availability
- main innovation trends in related products and technologies
- brief market insights
- selected references and additional sources of information

Due to the heterogeneity of the biomass components considered in this study, it is rather difficult to describe them in a joined way. All have peculiar aspects that must be taken into account when discussing on their future potential exploitation for the development of new commercial products.

NATURAL RUBBER

Natural rubber (NR) plays a fundamental role in the development of bio-based products and innovation within the bio-based economy because it's the exclusive source of elastomeric polymers coming from renewables which is suitable for large-scale technical applications, such as tires. Beyond being the unique natural elastomer, it holds an outstanding combination of mechanical and physical properties, that make it rather irreplaceable by synthetic elastomers.

From 2014, both indicators for economic importance and supply risk of NR have been assessed as above the criticality threshold for Europe, mainly due to an import dependency of 100% and the lack of readily available substitutes for all identified end-use applications. From 2017 NR has entered the list of the critical raw materials for Europe [1] .

NR is commonly produced from the rubber tree *Hevea brasiliensis*, which is mainly harvested in South East Asia (Malaysia, Indonesia, Vietnam and Thailand account for nearly 70-75% of the world’s global production), representing the unique relevant commercial source of NR at present. The danger that the South American native fungal pathogen *Microcyclus ulei* might spread to Southeast Asia, which would severely affect the NR production and its world-wide commercial availability, and the general trend towards the replacement of oil-based products with renewables, represent the main driving force to play close attention to potential alternative sources of rubber production.

Other crops that produce natural rubber include guayule, Russian dandelion, rubber rabbitbrush, figtree, goldenrod, and sunflower. In between these, guayule and Russian dandelion have been investigated as feasible alternative sources for the production of NR on the large scale. Guayule is considered the most promising crop for cultivation in Mediterranean areas, whereas dandelion should be developed in northern and eastern European countries. Both types of rubber may be suitable in applications such as tyres and car parts, whereas guayule rubber may also find specific applications in the area of medicine, due to absence of proteins that may induce allergic response. Diversifying sources of natural rubber from the current feedstock, which is solely *Hevea Brasiliensis* (cultivated in tropical regions) by including guayule rubber (arid climates) and Russian dandelion rubber (temperate climates), mitigates the overconcentration of natural rubber production in a certain region and from a certain crop. This prevents deforestation and alleviates dependencies.

Although guayule processing yields high quality rubber, the cost of cultivation, harvesting, and processing is significant. A competitive advantage of guayule rubber against *Hevea Brasiliensis* rubber would require achieving higher crop yields, which are currently significantly below those of optimised cultivars of Hevea rubber, as well as development of economic processing methods. Guayule processing also gives rise to valuable side-products, which could find good positioning on the market. Low-molecular weight rubber could serve as a feedstock for liquid natural rubber, which has wide applications in adhesives and moulded products manufacture. Bagasse remaining after rubber and resin extraction can be used as a fuel for processing plants, soil amendment, and others.

Beyond NR extracted from Guayule and Russian Dandelion, high molecular weight polyisoprene chains can also be obtained by polymerization of isoprene monomers having bio-based, renewable origin. This is the case of polyisoprene derived from plant oils or natural turpentine [2] or algae [3] which is currently under investigation mainly in US (Texas-based GlycosBio announced in May 2010 a collaboration with Malaysia's Bio-XCell Sdn Bhd to build a biorefinery with a planned 20,000 tonne/year capacity to produce isoprene using glycerine (derived from oil palm) as a feedstock) [4] and Japan (Ajinomoto Co. has successfully manufactured bio-based isoprene at the laboratory scale using a fermentation process from biomass raw material, and Bridgestone has also succeeded to produce synthetic rubber (polyisoprene) from Ajinomoto Co.'s bio-based isoprene.) [5]

Biologically produced synthetic isoprene monomer technology provides high-yields of isoprene from low-cost feedstocks, such as crude glycerol that are globally available and can be sustainably used on a large scale.

While the collection of isoprene from plants different from Hevea Br. is technically and economically unfeasible at present, as its production rate is simply not sufficient enough to match the demand, microbial production of isoprene is attractive, as the large-scale fermentation together with downstream processing units can meet the industrial requirements of bioisoprene.

PLANT FIBRES

The industrial interest in plant fibres is primarily focused on using them as renewable reinforcing fillers for plastic-based composites, mainly for the automotive and packaging applications, or for the production of sustainable textiles and fabrics exploiting fibres from waste residues, in an optic of valorization of side/waste streams.

In the framework of the bioeconomy, plant fibres therefore represent the renewable substitutes for artificial fibres such as carbon fibres, currently obtained starting from polymeric fossil-based poly(acrylonitrile) fibres, mainly used for the fabrication of light-weight advanced composite materials, or glass fibres.

The use of plant fibres in innovative areas of materials science gained considerable attention because of three potential advantages, namely: (i) their biorenewable character, (ii) their ubiquitous availability in a variety of forms, and (iii) their low cost.

At present, the main innovation trend for plant fibres is related to their use in combination with bio-based and/or biodegradable polymer matrices, both thermoplastic and thermoset. This allows the fabrication of advanced composite materials for industrially relevant goods (mainly devoted to construction engineering), that are fully derived from renewable resources, and which in some cases additionally possess complete biodegradability. On the other hand, certain disadvantages limit their application on an industrial level. This include variable quality of the products depending on several factors, such as moisture absorption, limited maximum processing temperature, incompatibility with the hydrophobic polymer matrix and the tendency to form aggregates during processing, lower durability, poor fire resistance, and fluctuations in price according to harvest results or agricultural politics, as well as unpredictable influences, such as weather.

Inorganic matrices reinforced with plant fibres also represent a main innovation field for construction engineering. Fibre-reinforced cement (FC) can be made with a range of plant fibres including wood waste, industrial hemp, and flax.

A major trend of innovation is related to microfibrillated cellulose (also named nanocellulose), obtained by almost every kind of cellulose fibres that are fibrillated, meaning that the mother fibre is split into a higher number of thinner fibres/fibrils. Nanocellulose possesses many special properties compared to traditional pulp fibres; a much higher surface area, great bonding potential, and a high water binding capacity. This product holds great potential as highly efficient biodegradable reinforcement for bioplastics, suggesting itself as the potential bio-based substitute for carbon fibres in advanced technical composites. Beyond the composites sector, highly separated microfibrils of cellulose dispersed in a polar liquid give creamy products, which find wide industrial use as nonwoven binders, as well as in foods, paints, cosmetics, and medicine. They are also useful as advanced rheology modifier, have very interesting spraying characteristics, and an unusually high viscosity at rest. They find also application as stabilizer, especially for water-in-oil or oil-in-water emulsions, and as water absorbing, retaining and releasing materials, also suitable for medical applications and hygiene products.

RENEWABLE OILS AND FATS

Fats and oils are, beside carbohydrates and lignin, the most important renewable feedstock available from biomass. Fats and oils are the most versatile renewable raw materials for the chemical industry. Their multifunctional chemical composition allows their exploitation through a number of different synthetic methods, giving rise to an almost infinite range of bio-based chemicals that can be produced starting thereof, going far beyond biodiesel. Biosurfactants, biolubricants, bio-based monomers for advanced polymers are just a few of the most relevant examples of high added value chemicals for the bio-based industry, derived from renewable oils and fats.

There are three main categories of renewable oils and fats (O&F): plant oils, animal fats, and marine oils. From a chemical and technical viewpoint, most O&F are interchangeable; however, costs for processing and specific end-use requirements may differ considerably. This also leads to marked differences of prices in function of the source, the latter being for example either a true renewable source, e.g. obtained from a dedicated crop, or a by-product from another production, as in the case of animal fats.

The basic oleochemicals are:

- fatty acid methyl esters (obtained by transesterification of O&F)
- fatty acids, obtained by hydrolytic splitting
- glycerol, which is the co-product of transesterification or hydrolysis of O&F.
- fatty alcohols, produced by hydrogenation of fatty acids.

Major technical efforts are currently devoted to the development of new biobased lubricants for many industrial sectors. Biolubricants possess advantageous characteristics such as renewability, non-toxicity, economic and environmental friendliness, among others. They can also offer superior performance compared to mineral based lubricants, in terms of stability and performance (for example, suitable for heavy truck engines).

Cosmetics, medicine and nutraceutics are also relevant application fields for green chemicals coming from renewable oils. Plant oils, used as a cosmetic base, prevent water loss through the skin, by making a protective layer on the epidermis. Because of their oiling, softening, smoothing, and protective properties they are classified to the group of emollients. Medicine recognizes the beneficial effects of plant oils in dietary, e.g., in the biological synthesis of components of cell membranes. Omega-3 Fatty Acids have gained considerable importance due to their association with the prevention and treatment of several diseases [6] like atherosclerosis, thrombosis, arthritis, cancers, etc.

Finally, the plastics sector shows great interest in monomers and polymer building blocks derived from plant oils. Several oils-based biopolyamides already gained a relevant commercial positioning, and new biopolymers such as poly(hydroxyalkanoate)s PHAs are currently under development.

LIGNINS

Lignin is one of the most abundant organic polymers on Earth, and the only compound with aromatic properties extractable from biomass. It is currently almost exclusively used for generating energy, but more is possible and lignin is destined to help the forest industry expand into the emerging bio-economy. Lignin, which represents up to 30 percent of the lignocellulose biomass, is an unexploited treasure – at least from a chemical point of view. The resinous substance consists of different aromatic basic building blocks, so-called phenylpropanoids, which are extremely useful. Aromatic compounds are normally extracted from petroleum and used to produce plastics, drugs and paints. The potential of lignin is therefore quite high: besides cellulose and chitin, lignin is the most abundant polymer in nature - and the only one that contains such a large number of aromatic compounds.

Lignin conversion for bio-based products therefore holds a very promising potential. The unique structure and chemical properties of lignin allow the production a wide variety of chemicals, particularly aromatic compounds. Hence, lignin can be considered as the major aromatic resource of the bio-based economy.

In terms of polymer industry, the enormous quantity of lignin renders excellent opportunities for production of aromatic monomers and polymers. However, the full potential of lignin for commodity polymers is still underutilized mainly due to the difficulty in obtaining pure aromatic chemicals from lignin. Hence, new technological developments are required to breakdown the chemical structure of lignin into commodity chemicals such as benzene, toluene, xylene, phenols, hydroxybenzoic acids as well as coniferyl, sinapyl, and p-coumaryl compounds, including vanillin. Once lignin is isolated and degraded into aromatic compounds, the subsequent processes do not require too much improvement. There is already a mature technology for conversion of these compounds into commodity monomers and polymers [7]. The combination of the new and current technologies would provide novel opportunities for conversion of lignin to commodity polymers like polyethylene terephthalate (PET), polystyrene, Kevlar, unsaturated polyesters, polyaniline and many more aromatic polymers, such as phenolic resins.

Beyond chemical building blocks, lignin is a valuable source of a number of other technical products that may find relevant positioning in the market. As an example, carbon fibers obtained from lignin can efficiently substitute traditional PAN-derived carbon fibres, with a much lower environmental impact.

TERPENES

Terpenes comprise one of the largest classes of industrially relevant bioactive natural products and have found wide use as flavours, fragrances, vitamins, and pharmaceuticals. Nowadays terpenes are being considered as well as building blocks to produce commodity chemicals and polymers with a very high added value. Terpenes (also known as terpenoids or isoprenoids) are a group of molecules whose structure is based on a various but definite number of isoprene units. They are metabolites synthesized mainly by plants, but also by a limited number of insects, marine micro-organisms, and fungi. In plants, terpenes constitute a naturally occurring, chemically diverse set of metabolites associated with developmental physiology. They often have a strong odour and may protect the plants from herbivores. Terpenes, together with aromatic compounds, constitute the essential oils of plants, with the highest concentration usually being found in the specialized storage cavities of leaves. Algae are prolific sources of secondary metabolites (i.e. organic compounds that are not directly involved in the normal growth, development, or reproduction of an organism, widely used in drugs, medicines, flavorings) that might represent useful leads in the development of new high value bio-based products. Besides the natural character of algae, other important aspects are their rapid cultivation on a large scale, their fast growth and the possibility to control the production of their bioactive compounds such as proteins, polyphenols and pigments by manipulating the culture conditions.

The bioplastics sector is widely interested in terpenes. Abundant terpenes constitute the logical precursors to polyterpenic materials destined for bulk applications. In this context, pinenes, readily isolated on an industrial scale from turpentine, are obvious candidates. β-pinene is by far the most studied. Lately, limonene has been the object of an increased interest to produce monomers for bio-plastics, in particular polycarbonates since in this case the terpene could replace the bisphenol-A (also known as BPA) which is fossil fuel derived molecule that has been pointed out as a potential endocrine-disruptor, neurotoxic, and carcinogen.

Terpene-based green propellants, pesticides and antioxidants also intended for food and cosmetics applications, are currently attracting a lot of interest. Their chemical properties combined with innovative technologies such as microencapsulation is rapidly releasing new solutions for several commercial field.

NATURAL POLYELECTROLYTES

Polyelectrolytes are polymers bearing ionic groups on their macromolecular chains. Among those derived from the biomass and based on polysaccharides from plant and algae, alginates (carboxylic polyelectrolytes), carrageenans and agars (sulphated polyelectrolytes with the exception of agarose that is a neutral polysaccharide) are located in the cell walls of seaweeds whereas pectins are contained in fruits. These polymers have a characteristic molecular architecture but their exact composition depends on the species, habitat, harvesting season and on the extraction conditions.

The corresponding animal-derived polyelectrolytes are chitin and its derivative chitosan. Chitin, the second most abundant polysaccharide in nature after cellulose, is a linear polysaccharide and it is widely distributed in the animal and vegetal kingdom. Chitosan, obtained by partial deacetylation of chitin, is also present in significant quantities in some fungi.

Polyelectrolytes are usually extracted from their natural biomass, however, there is a great interest in the development of new biotechnological processes to extract them from unconventional biomasses (for example soil sludge or lignocellulose biorefinery recalcitrant by-products). These studies are in their early stages of development and data are not yet available.

The most important properties of polyelectrolytes are their thickening and stabilizing character and their gel-forming ability in presence of counterions. They are widely and industrially used as food additive and many companies are producers and suppliers of the raw material. They are used as wastewaters treatment chemicals thanks to their flocculation and precipitation properties, for medical and biomedical applications, and in formulations for cosmetic and personal care industry.

Thanks to their charge, they may react with any other opposite ionically charged polymers giving a polyelectrolyte complexes; these supramolecular structures display physical properties different from those of the individual constituent macromolecules and they are extremely promising materials in many fields as gene therapy in order to deliver modified nucleic acids and other biomolecules into a patient’s cell as a drug to treat diseases.

Sophorolipids and rhamnolipids are surface-active molecules produced by microorganisms and they belong to the family of biosurfactants, which are surfactants that are produced extracellularly or as part of the cell membrane by bacteria, yeasts and fungi [8].

URBAN WASTES

Urban biowastes include all the organic fractions of municipal solid wastes (OFMSW), which represent up to 50% of the whole MSW. The main features of such fractions are correlated strictly to the waste sorting strategy: OFMSW can be very diverse and inhomogeneous, when mechanically-sorted from non-separated collections, while source-sorted matrices may be mainly composed by specific fractions [9]. Among the latter, biodegradable garden and park waste, food and kitchen waste from households, restaurants, caterers and retail premises, and comparable waste from food processing plants are included [10]. Still, landfilling is the main approach used for biowaste disposal leading to the release of uncontrolled greenhouse gases (mainly CH_4) from landfills.

Beside urban biowastes, also the sludge resulting from the biological treatment of urban wastewaters (UWWS) in dedicated plants can be considered as a potential source of organic fermentiscible matter (to be bioconverted into carboxylic acids or biomethane under conventional anaerobic digestion processes) and nutrients. Thus, the development of urban biorefinery schemes may take such wastewaters into consideration. The four main products, which can be obtained from wastewater are biomass, biosolids, char/ash, and nutrient chemical products. Wastewater treatment plants are the main facilities for the development of commercially viable technologies dedicated to the recovery of nutrients.

Phosphorus (P)- and nitrogen (N)-minerals represent the most prominent nutrients that can be recovered from sludge resulting from the biological treatment of urban wastewater. Nevertheless, some lack of policies and regulations about the recovery of resources from wastewaters needs to be faced up [11]. The circulation of fertilizers in the EU is regulated by the EU Regulation 2003/2003 [12], which contains a list of approved fertilizers, depending on the method of preparation, the minimum contents of nutrients and the absence of adverse environmental effect. There is still a certain degree of uncertainty about the possible inclusion of nutrients collected from UWWS in the list of approved fertilizers. However, some companies are active in the market jet, waiting for the expected update of the regulation. The present work does not cover the recovery of nutrients from the effluents of anaerobic digestion processes fed with OFMSW and UWWS, because these processes are dedicated to energy recovery, thus out of the scope of this study.

Magnesium ammonium phosphate (MAP), calcium phosphate and iron phosphate are among the main phosphate compounds, which can be recovered from the UWWS; MAP is more commonly referred to as struvite, and it is a slow releasing granular P-fertiliser. At present, struvite from UWWS is not included in the list of approved fertilizers in the EU.

Volatile fatty acids (VFAs) actually represent one of the urban wastes-derived products holding highest potential for future valorization in the frame of the carboxylate platform [13], and in particular for the production of polyhydroxyalkanoates (PHAs). VFAs can represent suitable precursors for PHAs production, reduced chemicals and derivatives, and biofuels, provided that they can be recovered economically. In this respect, longer chains VFAs are potentially easier to be recovered, supporting further their production.

PHAs production from urban biowastes can be obtained by the employment of open bioreactor operating with selected and acclimated mixed cultures fed with VFAs-rich effluents. This approach, combined with NaOH digestion for the downstream (if required), could potentially represent an economically sustainable process for the obtainment of fully bio-based and biodegradable polymers, most likely poly(hydroxybutyrate-co-hydroxyvalerate) (PHB/HV), suitable for industrial use as fully bio-based substitutes of commodity plastics such as polypropylene.

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SECTION 4 THE DATABASE OF BIO-BASED PRODUCTS UNDER DEVELOPMENT: RELEVANT OUTCOMES

Based on the scientific and technical information available, and through intensive interaction with stakeholders and experts, we have developed a database of innovative BBPs currently under development originating from the selected biomass components (i.e. natural rubber, plant fibres, lignins, renewable oils and fats, terpenes, natural polyelectrolytes and urban wastes).

The database gives:

- name(s) of the product
- max TRL achieved
- number of active firms worldwide
- number of production facilities in EU and rest of the world
- leading actors
- estimated market size
- non bio-based or traditional alternatives
- innovation highlights
- main applications
- list of selected references

The consolidated version of this database includes 107 products, divided into the seven respective biomass components as shown in Table 4. As previously mentioned, several products included in the database actually represent a group of products with homologous chemical structure (as an example the "*short-chain esters of an acid*" jointly represent methyl, ethyl, propyl and butyl esters of the same acid). This was done to simplify the understanding and the classification of the products, but this action was limited to the cases in which assembling products into a single line was not hindering the diverse potential of each of the single units of the group. In general, classification of products on the basis of their use or application was avoided. Classification related to chemical or materials composition has been favoured, because this allows for a more comprehensive understanding of the potential of the products for different applications. Efforts were made to generate a homogenous way of depicting the current developments for the different categories. The database has been implemented with information available from the mentioned data sources, plus information obtained by direct contact with relevant stakeholders.

Table 4 : Number of innovative products included in the Database for each category

Main biomass components		Number of related innovative products included in the database
Major biomass components	Natural rubber	5
	Plant fibres	17
	Renewable oils and fats	19
	Lignin	23
Low volume high value (LVHV) biomass components	Terpenes	18
	Polyelectrolytes	6
Urban biowastes	Organic fraction of municipal solid waste Sludge from waste water treatment	19

An extract of the database is reported in the following table 5.

Table 5 : Extract from the database of innovative BBPs under development, separated per biomass components ordered by TRL

PRODUCT	MAX TRL	# ACTIVE FIRMS	PRODUCTION FACILITIES		LEADING ACTORS
			EUROPE	REST OF THE WORLD	
LIGNIN					
vanillin	9	>10	10	3	Borregaard; Rhodia; Takasago International Corporation; Jiaxing Zhonghua Chemical Co., Ltd.; IFF Inc. New York; Advanced Biotech. Inc.; Comax Flavors; BASF; De Monchy Aromatics
lignin-based thermoplastic biocomposites	9	1	1	0	Tecnaro GmbH
lignosulfonates	9	>10	6	>5	Sappi Europe Domtar; Green Agrochem-Lignin Unit; Borregaard LignoTech and LignoTech Ibérica; Changzhou Shanfeng Chemical Industry; CIMV; Asian Lignin Manufacturing India Private Limited (India). Tembec (Canada). MeadWestvaco (USA), Georgia Pacific (USA). Northway Lignin Chemical. KMT Lignin Chemicals. BIOTECH Lignosulfonate Handels GmbH (Czech Rep.)

bio-phenolic resins	8	>20	16	1	Collanti Concorde Srl; Foresa Industrias Quimicas Del Noroeste Sa; Rampf Eco Solutions Gmbh & Co. Kg;; Novamont Spa; Biochemtex Spa; Biosyncaucho SL; Avantium. Akzo Nobel Coatings International B.V. Chimar Hellas S. A.; AVALON Industries AG. Biophenolix
organosolv lignins	7	>5	2	2	Borregaard, Chempolis, American Sc Techn, Lignol Innovation Corp.
BTX aromatics (benzene toluene xylene)	6	>10	2	5	Biochemtex; Anellotech Inc.; FPInnovations; Lignol; Weyerhaeuser; Alberta Pacific Forest Industries Inc..
phenol and alkylphenols (coniferyl, sinapyl, p-coumaryl compounds)	5	13	9	4	Avantium. Chemelot InSciT. Bio Base Europe Pilot Plant. DSM ChemTech Center. FPInnovations; Lignol; Weyerhaeuser; Alberta Pacific Forest Industries Inc
lignin bio-oil	5	>20	14	>5	Lantmännen, SP Processum AB, Cooperativas Agro-alimentarias de España, Nutria S.A.; Shell Oil Company; Honeywell UOP. Total Raffinage Chimie SA; Italian Bio Products SRL; Metgen; Metgen. Foresa (Spain). Vertoro BV
dispersants, concrete and mortar plasticizers	5	10	10	0	Vertech Group (france); Exergy Ltd (UK); Metsä Fibre; Andritz Group (Finland); ST1 Biofuels Oy (Finland); Cimv (France); Biochemtex (Italy); Dow (Germany) Deutschland Anlagengesellschaft Mbh. RTO.
thermoplastic lignin polymer	5	>5	1	1	Toyota (Japan); Metso Power Oy (Finland), Oy Metsä-Botnia Ab (Finland), Stora Enso Oyj (Finland), Myllykoski Oyj, UPM
high purity lignin	5	5	5	0	Avantium, AkzoNobel, Chemport Europe, RWE and Staatsbosbeheer, Covestro
lignin pyrolysis char	5	3	1	0	Apollo Global R&D. Dura Vermeer Infrastructure. Progression Industry
lignin carbon fibers	5	17	9	3	Innventia. Zoltek. Aksa Power Generation (Turkey); SABIC (Saudi Arabia); Holding Company Composite-HCC (Russia); SGL Automotive Carbon Fibers - BMW (Germany), Cytec Engineered Materials, Hexcel, TohoTenax,Toray and Mitsubishi Rayon Co.Ltd
muconic / adipic acid	5	1	1	0	none industrial
acrylonitrile-butadiene-lignin (ABL)	5	1	0	1	Advanced Lignin Biocomposites LLC (ALB-LLC).
syringaldehyde	5	0	0	0	none

methylated lignin	4	4	4	0	Chemtex Italia SpA (CTXI); Avantium Chemicals (AVT); Solaronix SA; Repsol SA
BTX from bacterial degradation of lignin	4	2	2	0	Biome Bioplastics (UK)
reactive lignin "CatLignin®"	4	1	1	0	none industrial
lignin hybrid copolymers	4	2	0	2	UT-Battelle, LLC (USA)
lignin nanoparticles, nanolignin, colloidal lignin	3	6	4	3	Solenis Technologies L. P.; BENANOVA INC.
lignin based terephthalic acid	3	1	1	1	Anellotech.
anthraquinones	3	0	0	0	none industrial
NATURAL RUBBER					
butyl rubber	9	2	0	2	Arlanxeo (joint venture of LANXESS and Saudi Aramco). ExxonMobil
guayule rubber	6	3	0	2	ENI Versalis (Italy); Bridgestone (UK); Yulex Corp (USA); PanAridus LLC (USA); Cooper Tyres (USA)
polyisoprene from plant oils	5	7	0	3	GlycosBio (USA, production in Malaysia). DuPont Industrial Biosciences (USA), Goodyear, Ajinomoto (Japan), Bridgestone, Zeon, Yokohama Rubber (Japan), Amyris. Braskem.
polyisoprene from natural turpentine	4	0	0	0	none industrial
Russian dandelion rubber	4	2	0	0	Apollo Vredestein (made test during EU project, no further production). NEIKER-Tecnalia (genotyping of plants). Continental Tyres (Germany)
PLANT FIBRES					
geotextiles	9	>10	2	>10	Tetex Ltd (UK and Poland). Several in China, East Asia, Africa.
plant fibres reinforced concrete	9	>10	>5	>10	Ecotech Aliance (Australia). Kafus Bio-Composites Inc. (Canada). TTS BIOCOMPOSITE (TEKLE TECHNICAL SERVICES INC.) (Canada). Basf (Germany). BASF Construction Chemicals (Italy). Elmo (Italy). Azichem (Italy). Buckeye Technologies Inc. (USA). CMF GREENTECH (Italy)

plant fibers reinforced prepregs	9	>10	8	>5	Meshlin Composites Zrt. (Hungary). Procotex Corporation SA (Belgium; production in Lituania). Stemergy (Canada). NetComposites (UK), in collaboration with Tilsatec and FORMAX (UK), LINEO, Bcomp Ltd. (Switzerland), Ecotechnilin (France), Group Depestele and Solvay
wood plastic composites	9	>50	>10	>50	AERT Inc (USA). Dura Composites (UK). FIBERON LLC (UK). Kafus Bio-Composites Inc. (Canada). Polymera Inc. (USA). Trex Company, Inc. (USA). UPM Biocomposites (Finland). WEYERHAEUSER COMPANY (USA). Tecnodeck (Portugal). Numerous players in China, Japan, India. Beologic (Belgium. Fkur Kunststoff Gmbh (Germany). Josef Ehrler Gmbh & Co. Kg. (Germany). Polyplank Ab (SE).
plant fibres reinforced thermoset composites	9	>10	5	>10	Bcomp Ltd. (Switzerland). Ecotech Aliance (Australia). TTS BIOCOMPOSITE (TEKLE TECHNICAL SERVICES INC.) (Canada), NetComposites (UK), Tilsatec (UK), Formax (UK). Aimas (Spain). Composites Technology Park, Bangalore (India)
plant fibres reinforced thermoplastic granulates and composites. Thermoplastic matrix of major interest: PP.	9	>50	>5	>50	Bcomp Ltd. (Switzerland). FiberGran GmbH & Co.Greencore Composites Inc (Canada). Greengran B.V (The Netherland; production plant in Hong Kong). TTS BIOCOMPOSITE (TEKLE TECHNICAL SERVICES INC.) (Canada). UPM Biocomposites (Finland). Aimas (Spain). BIOS (Spain). Ford.
non-woven mats and fabrics for plastic composites	9	>10	2	>10	Ecotech Aliance (Australia). FlexForm Technologies (USA with prod. in South Korea). POLYVLIES FRANZ BEYER GMBH & CO (Germany). Sunstrand LLC. USA). TTS BIOCOMPOSITE (TEKLE TECHNICAL SERVICES INC.) (Canada). Ecotechnilin (France)
woven mats and fabrics for plastic composites	9	> 10	>5	>10	Meshlin Composites Zrt. (Hungary). Procotex Corporation SA (Belgium; production in Lituania). Composites Evolution (UK). Flaxcomposites (France).
primary fibres for industrial (no textile) use	9	>50	>10	>50	Limagrain (France). Bast Fiber LLC (USA). Stemergy (Canada). Ecotechnilin (France). Friedrich Platt GmbH (Germany), Lenzing AG (Austria), Polyfibre Industries Pvt Ltd.(India), Grasim Industries Ltd. (India), Wellman Advanced Materials (USA), Shanghai Tenbro Bamboo Textile Co., Ltd. (China), China Bambro Textile (Group) Co., Ltd. (China), Pilipinas Ecofiber Corporation (Philipines), Teijin Limited (China), David C. Poole Company, Inc. (USA), Foss Manufacturing Company, LLC (USA). Several in China, India, Japan, South

					America, Middle East and Africa.
micro- and nano fibrillated cellulose (also named nanocellulose)	8	>10	4	>10	ITT Rayonnier (USA), Borregaard (UK and Norway), INNVENTIA AB (Sweden). Suzano (Brazil). WEIDMANN Fiber Technology (Switzerland). FiberLean Technologies. Aditya Birla Group (India), Lenzing (Austria), Fulida (China), Daicel FineChem Ltd. (China). CelluloseLab (Canada). CelluComp (UK). Celluforce (Canada)
micronized superabsorbent fibres	8	2	0	2	Hemp Inc. (USA). Stemergy (Canada)
lignocellulosic microfibres	7	2	1	1	Greencore Composites Inc (Canada). Orineo (Belgium)
Crailar® flax and hemp fibres	7	1	0	1	CRAiLAR Fiber Technologies International Inc. (Canada). Start-up, a development stage company
composite non woven fibres (self-binding; no need of plastic matrix; polymer surface impregnated)	6	6	5	4	Basf (Germany). Sunstrand LLC. (USA). TTS BIOCOMPOSITE (TEKLE TECHNICAL SERVICES INC.) (Canada). YFY JUPITER Ltd (USA). Organoclick (SE). BIOS (Spain). Paptic (Fi).
lignin biocomposites reinforced with plant fibres	6	2	2	0	Tecnaro GmbH (Germany). Organoclick (SE)
natural fibers reinforced bioresin prepregs	6	3	3	0	Composites Evolution Ltd. (UK). NetComposites UK), in collaboration with Tilsatec and FORMAX (UK)
wood and plant fibres reinforced thermoplastic biopolymers (PLA, PBS, PHAs, others).	5	2	2	0	EconCore's (Leuven, Belgium). Fkur (Germany). Bio on spa (Italy).
RENEWABLE OILS AND FATS					
polyesters of azelaic acid	9	3-5	4	3	Novamont, BASF, DuPont, Matrica, Plantic, National Starch Int Co.
glycerides from oilve oil	9	5	2	-	Liquidflora, ROELMI HPC, Arkema, Cobiosa, Principium
glycerides from lipids	9	>10	>10	>10	Henry Lamotte,Southern Cross Botanicals, Textron, Olvea, Naturex, Oleos, Bionap, Gustavheess, Interfat, Esperis, ITERG, IMCD
OMEGA-3: EPA (eicosapentaneoic acid), DHA (docosahexaenoic	9	>10	4	1	BTSA, Live Fuels, Aurora Algae, Market Biosciences,Blue Biotech International GmBH, Lonza, Photonz, IngrePro BV,

acid)					Henry La Motte, Nordic Naturals
low-calories oils	9	>10	4	>10	Croda, BASF, DSM, UNILEVER. Viachem, Connoils, Green Source Organics, Vivion, Arista, DuPont, Stepan. A few companies in China. KLK Oleo
polyamide 11	8 9	1	1	1	Arkema
dodecanedioic acid	7	1	0	1	Verdezyne
esters of long-chain fatty acids LCFA	6	5	2	4	Shandong HILEAD Biotechnology, Cathay, BASF, Unilever, Cargill
poly(hydroxyalkanoate)s PHAs	6	>5	3	6	Bio on SpA, DSM
glycerol esters	6	>7	3	2	ENI (Italy)Air Liquide, Lyondell, DOW
acrolein	6	1	2	NA	Acrolein from propylene: Akzo Nobel N.V., The Dow Chemicals Company, Shanghai Huachen Energy Company, Ltd. and The Shell Oil, Arkema, Adisseo,
esters of azelaic acid	5	< 5	3	0	Novamont Matrica (new ester of azelaic acid with 2- ethylhexanol). Emery Oleochemicals, BASF
esters of gondoic or erucic acids	5	< 5	1	NA	Arkema
esters of fatty acids	5	0	0	0	none
polyamides C6 from short-chain dicarboxylic acids	5	1	0	1	Verdezyne
polyamide 9	5	1	1	0	Arkema
polyamide 12	5	< 5	3	1	Evonik, Arkema, EMS Chemie, UBE Industries
esters of pelargonic acid with glycerol, diglycerol or other non-biobased polyols (NPG, TMP, PE) (Bio-OILs for COSMETICS)	5	>5	1	>5	Pelargonic acid: Matrica (JV Novamont/Versalis). Tripelargonate for cosmetics: ROELMI HPC
esters of short- and medium-chain fatty acids with polyols	5	>20	>10	>10	Novamont, Oleon, Croda, BASF, SO.Gi.S, Cargill
NATURAL POLYELECTROLYTES					

chitin and chitosan as raw materials (1st generation chitosan)	9	>40	30	>20	Chitosanlab, Geneart AG, Gillet Chitosan Eurl, Cosphatec Gmbh, Greenaltech Sl, Artes Biotechnology Gmbh, Enantia Sl, Apronex S.R.O, Biotech Surindo PT, Novamari, Evonik Industries AG, Clariant, Danisco, Dupont Nutrition Biosciences APS, Sanofi-Aventis, Libragen, GTP Technology SA, Mahtani Chitosan Pvt. Ltd, Norwegian Chitosan AS, G.T.C. Bio Corporation, Biolog Heppe Gmbh, France Chitine, Marshall Marine Products, Biophrame Technologie
enzymatic chitosan (2nd generation chitosan)	9	25	>20	>10	Ardilla Technologies UK Ltd, Arterra Bioscience Srl, Avantium Chemicals, Biome Technologies, Sabic, Ynsecta, Geneart AG, Gillet Chitosan Eurl, Cosphatec Gmbh, Greenaltech SL, Artes Biotechnology Gmbh, Heppe Medical Chitosan Gmbh, Enantia SL, Danisco Dupont, Sanofi-Aventis, Libragen, GTP Technology SA, Pennotech, Apronex, Evonik Industries AG, Clariant
chitosan from fungi, bacteria and algae (3rd generation chitosan, also named biotechnolgical chitosan)	7	>20	>10	15	KytoZyme (Belgium), Qingdao ChiBio Biotech Co., Ltd.(China), Xi'an Geekee Biotech Co., Ltd. (China), Xian Lukee Bio-Tech Co., Ltd. (China), Union Agol Company, Beijing Wisapple Biotech Co., Ltd. Chitosanlab (France, production in China), Neweaver (France), Plater Bio (UK), ERA-IB. Gillet Chitosan EURL(France), Cosphatec GmbH(Germany), Bio Base Europe Pilot Plant (Belgium), Greenaltech SL(Spain), Greendelta GmbH (Germany), ARTES Biotechnology GmbH (Germany), Heppe Medical Chitosan GmbH (Germany), Enantia SL(Spain) ,Geneart Life Technologies AG (Germany)
sophorolipids and rhamnolipids	7	>15	4	>10	Allied Carbon Solutions (ACS) Ltd. (Japan); Kaneka (Japan). TeeGene Biotech (UK), AGAE Technologies (USA), Jeneil Biosurfactant Co LLC (USA), Rhamnolipid Company (USA), Saraya Co Ltd (Japan), Ecover Belgium, Groupe Sliacnce (France), Synthezyme LLC (USA), Henkel (Germany). BioFuture (Ireland), Ecochem Ltd (Canada)
pectin-based (i.e. muconic acid based) bioplastics	5	2	0	0	Amyris. Heiz, Ford. VTT.
bacterial (biotechnological) pectins, agars and carrageenans	4 5	10	2 (?)	NA	Danisco, Dupont Nutrition Biosciences, Sanofi-Aventis Recherche & Developpement, Gillet Chitosan, Geneart, Libragen, Artes Biotechnology Gmbh, GTP Technology, Bayer Bioscience, Bayer Cropscience, CP Kelco

TERPENES					
ß-pinene silane resin	9	8	1	>5	Arizona Chemical, SI group, Pinova solutions, Arakawa Chemical, Yasuhara Chemicals, DRT Chemicals, Songyuan Chemical, Foshan Baolin
limonene-based pesticides	9	10	4	7	Agriphar SA -Arysta LifeScience, Bayer Cropscience AG, Tyra Tech Inc., Syngenta, BASF, Dupont, Dow Agroscience, Monsanto, Sumimoto Chemicals, Nufarm.
algae carotenoid-rich extract	8	13	11	2	Sensient Cosmetic Technologies, A4f Algafuel Sa, Subitec Gmbh, Protéus S.A., Microphyt, Greensea Sas, Algae Health Limited, Deinove, Rothamsted Research Limited, Algatechnologies Ltd, Hafren Investment Limited, Nature Beta Technologies (NBT) Ltd, Monzon Biotech SL (MBT), Dynamic Extractions (DE), and several academic institutions and research centers
lycopene-containing functional food	8	11	9	2	Lycotec, Licofarma, Association Méditerrannéenne Internationale De La Tomate Transformée, Medizinische Klink Für Kardiologie, Angiologie, Pneumologie Charité – Universitätsmedizin, Conservas Vegetales De Extremadura, Juver Alimentacion S.A., LycoRed, Superfruit Nutrition, Pierre, Tomatia, Parry Nutraceuticals and Perennial Lifesciences
polymyrcene-based adhesives	6	7	2	5	Kraton Polymers. DRT, Ernesto Ventos, Yasuhara Chemical, Sky Dragon Fine-Chem, Wansong Forestry Perfume Manufacturing, Xinhua Chemical, EcoGreen Intl
pinene-based medical formulations	6	0	NA	NA	Commissariat Energie Atomique
p-cymene	5	2	NA	NA	CSIRO Petroleum Resources (Australia), UC Davis
terephthalic acid	5	2	1	1	Sabic, Coca-Cola
limonene-based polyurethanes	5	13	2	10	Cargill, BASF, Reverdia, Rennovia, Lubrizol, Elevance,Verdezyne, Genomatica, Amyris, DSM, Myriant, Wanhua Chemicals
poly(limonene carbonate)s	5	15	5	5	Arkema, Nature works -JV Cargill, Novamont, Metabolix, Reverdia, Solvay, Corbion/Purac -JV BASF, Dupont, Genomatica, Toray, Novozymes, Versalis, Lanzatech, Kuraray , Plantic Technologies
squalene-based nanoassemblies	5	4	NA	NA	Universite Paris-Sud, Commissariat A L Energie Atomique Et Aux Energies Alternatives, Bertin Pharma, Universite

					Catholique De Louvain.
cyanobacteria-derived terpenoids	5	2	2	1	Photanol B.V, Cyano Biotech, Novacta
farnesene	4	1	NA	1	Intrexon
limonene-based polyamides	4	13	2	9	Bio-Polyamides, DSM, DuPont, BASF, Toray, EMS-Grivory, Evonik, Arkema, Revedia, DSM, Amyris, Wanhua Chemicals
biosynthetic taxadiene	4	NA	NA	NA	none industrial
limonene-based propellant	3	12	NA	NA	Arkema, Deltacat limited, USafran Aircraft engines, German Aerospace center DRL, Evonik industries ag, Snecma sas
limonene-based antioxidants	3	7	5	5	Eden Research, Ainia Centro Tecnológico, Citresa, AIJN, Aimplas, TNO, Logoplaste, Omniform. Aimplas, Emco Packaging,Sivel Ltd
URBAN WASTE					
N K P Fertilizers, struvite	9	12	>10	>20	Ostara Nutrient Recovery Technologies Inc (Canada); NuReSys (BE); Royal HaskoningDHV (NL, Crystalactor® water technology); Unitika CSR (JP, Phosnix process); Veolia (Phostrip and Struvia systems); Paques (NL, Phospaq process); Colsen (NL, Anphos); CNP Technology Water and Biosolids Corporation (US, Airprex technology); Remondis Aqua (D, Rephos); Suez (FR, Phosphogreen technology); Clearas (US, Advanced Biological Nutrient Recovery - ABNR™); Lystek (US); BCR solid solutions (US)
bioethanol	9	4	2	2	Emerken (Canada); Fiberight (US), IMECAL (Spain) (5-9 ML/year); Abengoa (Spain) (2 ML/year)
verming compost	9	2	1	1	Vermico (India), VERMICULTURE FARM MOUTTA (France)
lubricants	9	4	4	0	Avista (Germany); LPC SA (formerly Cyclon Hellas SA) (Greece); PURAGLOBE (formerly PURALUBE) (Germany); Viscolube (Italy)
glycerol (as the by-product of biodiesel production)	9	many industries	4	>5	Renewable Energy Group, Buffalo Biodiesel Inc., Pacific Biodiesel, Bently Biofuels and SeQuential Pacific Biodiesel (biodiesel from yellow grease). Kris Biofuels Sdn Bhd (KBSB) (Malaysia). Biocomenergia (Spain); Greenenergy; Olleco (UK); MÜNZER Bioindustrie GmbH (Austria); wasteOilNet (Bulgaria)

cellulose	7	2	2	0	CirTec Bv (NL); wwtp Geestmerambacht (Municipality; NL)
volatile fatty acids (VFAs) mixture	7	4	4	0	InnovEn (IT); Afyren (FR); Twence (NL)
Polyhydroxyalkanoates (PHAs); most likely poly(hydroxybutyrate-co-hydroxyvalerate) (PHB/HV)	6	4	4	0	WW Treatment Plant Treviso (Italy); Bio on (Italy), NOVA ID FCT (Portugal);
Polyhydroxyalkanoates (PHAs); most likely poly(hydroxybutyrate-co-hydroxyvalerate) (PHB/HV)	6	2	3	0	NOVA ID FCT (Portugal), Veolia Env. SA by the Brussels North WWTP (Belgium)
alginates	6	1	1	0	Nereda wastewater treatment system (NL). Dutch National Alginate Research Programme (NAOP) [1]. STOWA and three Dutch waterboards (Rijn & IJssel, Vallei &Veluwe andVecht- stromen)
microalgae hydrolisated	5	0	0	0	none
lactic cid	4	>5	4	5	Corbion purac; Henan Jindan; Chongqing Bofei Biochemical Products; Galactic; Plaxica; Jungbunzlauer. Glycos Biotechnologies. HiSun; Wuhan Sanjiang Space Gude Biotech
succinic acid	4	4	2	2	Reverdia (joint venture of DSM and Roquette), Succinity (joint venture of BASF and Corbion Purac), Myriant
vivianite	4	0	0	0	Wetsus (NL): Green Water Solutions; Kemira, Oosterhoh Holman. FreshAWL (USA)
single cell proteins	3	0	0	0	none
biosurfactants	3	0	0	0	none
nanoparticles	3	0	0	0	none
VFAs ethyl esters	3	0	0	0	none
cyanophycin	3	0	0	0	none

In Figure 6 the spread of TRL values achieved by the products included in the database is shown. In general terms, this graphical representation allows a visible comparison of how many products are next to commercialization, and how many are actually reaching highest levels of technical development. As the figure clearly shows, almost one third of the products are already at a very elevated level of development (TRL 9), approaching full availability on the market. More than 20 products are now at the pilot plant level (TRL 5), but there are just very few products at TRLs 7 and 8. This trend replicates similar findings obtained in the study on the sugar platform.

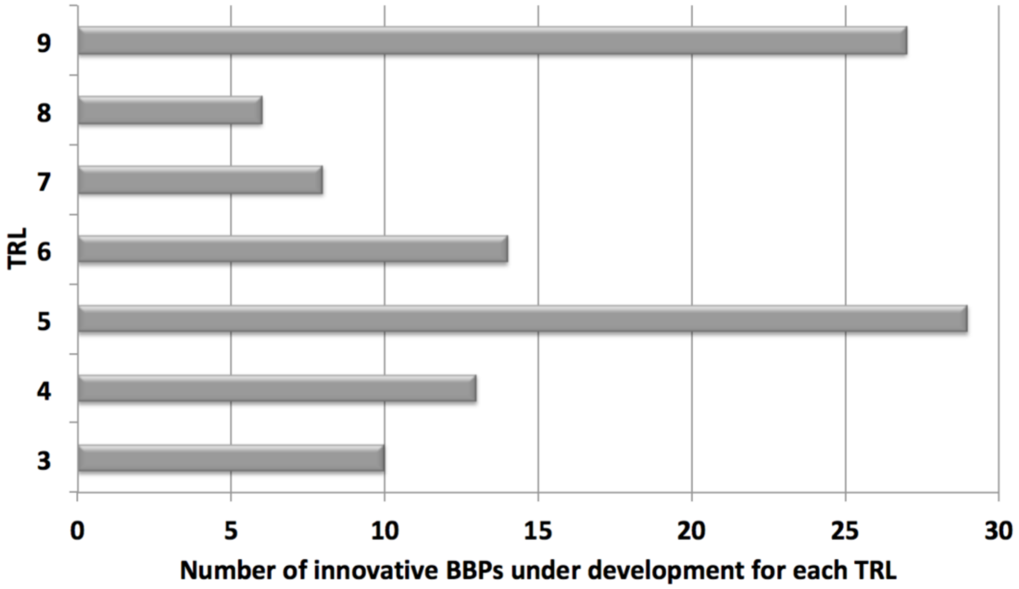

Figure 6 : TRL distribution for the products included in the Database

Figure 7 shows TRL distributions for the products splitted into the respective seven different biomass components considered in this study. Figure shows that while lignin is the most intensively investigated source of innovative BBPs at current, the highest number of new products next to commercialization actually derives from plant fibres. Urban wastes are also intensively investigated, and there are products under development at all stages of technical advancement. Therefore an almost continuous release of new products coming from the valorization of urban wastes has to be expected during the next few years.

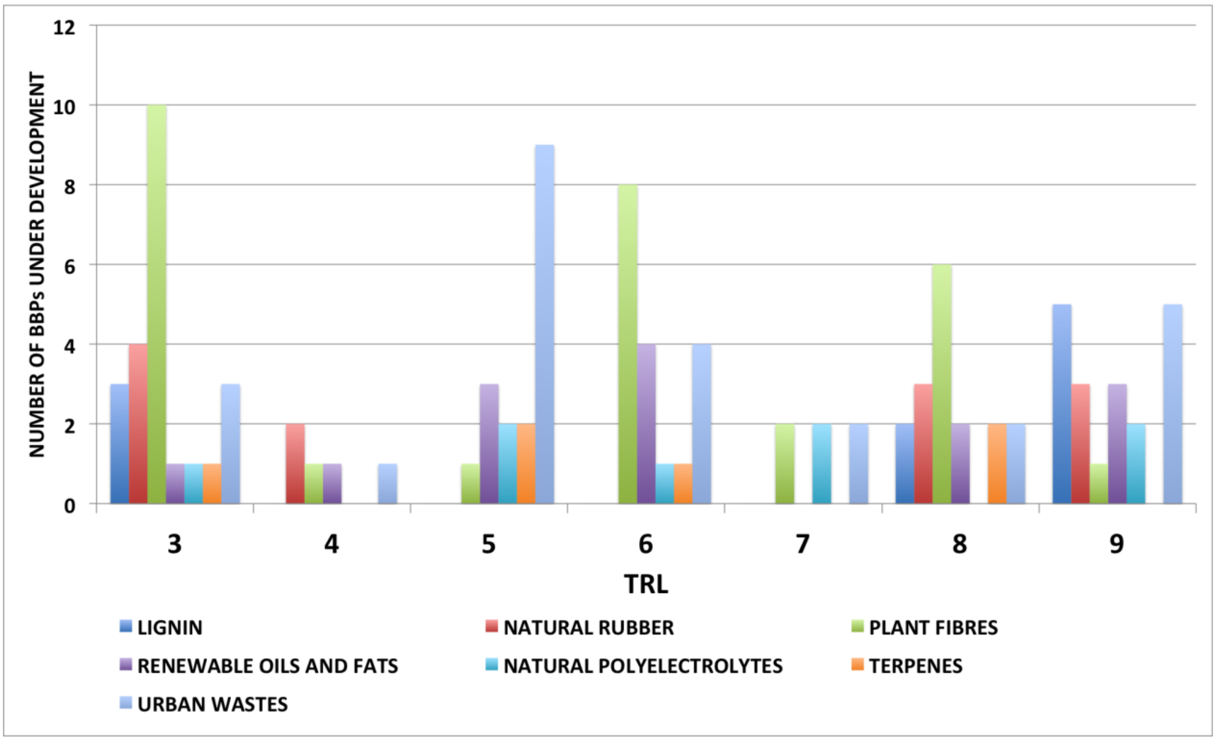

Figure 7 : Number of innovative BBPs mapped per category, and their TRL

For ranking purposes, assessment criteria reported in section 2.3 of this report have been applied to each product included in the database. These criteria take into account:

- presence of an active marketplace
- EU-based development
- degree of innovativeness
- market potential

A number of 28 products (reported in Table 6) received the maximum score.

Table 6 : Products derived from each biomass component included in the study, receiving the maximum ranking score

Biomass components	Top-score products
Natural rubber	1 guayule rubber
Plant fibres	5 microfibrillated cellulose (nanocellulose; composite non woven fibres (self-binding); lignin biocomposites reinforced with plant fibres; plant fibres reinforced bioresin prepregs; wood and plant fibres reinforced thermoplastic biopolymers (PLA, PBS, PHAs, others)
Renewable oils and fats	5 PA9, PA11, PA12, esters of short- and medium-chain fatty acids with polyols (biolubricants), PHAs
Lignin	7 bio-phenolic resins, BTX aromatics (benzene toluene xylene), phenol and alkylphenols, lignin bio-oil, thermoplastic lignin polymer, high purity lignin, carbon fibres
Terpenes	3 limonene-based polyurethanes, poly(limonene carbonate)s, limonene-based polyamides
Polyelectrolytes	4 3rd generation chitosan, also named biotechnolgical chitosan, sophorolipids and rhamnolipids, pectin-based (i.e. muconic acid based) bioplastics, bacterial (biotechnological) pectins, agars and carrageenans
Urban biowastes	3 volatile fatty acids (VFAs) mixture, Polyhydroxyalkanoates (PHAs) from OFMSW, Polyhydroxyalkanoates (PHAs) from UWWS

SECTION 5 THE SELECTED TOP 20 INNOVATIVE BIO-BASED PRODUCTS: RELEVANT OUTCOMES

Finalization of the selection of the group of the twenty most innovative bio-based products for the development of detailed case studies was made after additional experts and stakeholders consultation.

Down-selection from the previous list of highest-performance products (previously reported in Table 6) resulted in the following list of innovative TOP 20 bio-based products, on which detailed case studies were developed:

1. Guayule rubber
2. Microfibrillated cellulose (nanocellulose)
3. Self binding composite non-woven fibres
4. Lignin biocomposites reinforced with plant fibres
5. Plant fibres reinforced bioresin prepregs
6. PA12
7. Wood and plant fibres reinforced thermoplastic biopolymers (PLA, PBS, PHAs, others)
8. Biolubricants from oils&fats
9. PHAs from oils & fats
10. Bio-phenolic resins
11. Bio-BTX aromatics (benzene toluene xylene)
12. Phenol and alkylphenols
13. Lignin bio-oil
14. High purity lignin
15. Lignin carbon fibres
16. Limonene-based technical polymers (polyurethanes, polycarbonates, polyamides)
17. 3rd generation chitosan
18. Bacterial biosurfactants (sophorolipids and rhamnolipids)
19. Volatile fatty acids (VFAs) mixture
20. PHAs from urban wastes: OFMSW and UWWS

The outcome of the selection of the TOP 20 bio-based products, reveals important information on the general trend of the bio-based industry.

- As a first evidence, largest attention is focused on the industrial development of new bio-based materials targeted at advanced technical applications. **Engineering materials** with elevated thermomechanical properties suitable for the automotive and construction fields, such as biopolyesters, biopolyamides, matrices and fillers for reinforced biocomposites, but also biolubricants, represent the vast majority of the TOP 20 innovative bio-based products: more than 13 can actually be attributed to this category.

- Bio-based innovative solutions somehow related to the **plastics** sector, certainly occupy the most relevant position. Plastics are modern, versatile, but polluting materials mainly in relation to their priority eligibility as disposables and long-term durability if released in the enviroment. Therefore sustainable solutions, either just bio-based or bio-based and biodegradable, are intensely investigated. More than 10 over the TOP 20 selected products are related to the plastics world. Both thermosets and thermoplastics innovative plastic materials are currently under development, and innovation lays either on the synthesis of completely new polymeric structures (an example is the case of limonene-based engineering polymers - polyurethanes, polycarbonates, polyamides), or the development of drop-in substitutes derived from renewable resources (an example is biophenolic resins). Poly(hydroxyalkanoate)s PHAs are intensely explored as biodegradable promising substitutes for a number of commodity polymers, such ad HDPE, PP and others. The fact that PHAs can be obtained by purely biotechnological route starting from a variety of carbon-rich biomass feedstocks, including agricultural wastes, organic fractions of solid municipal waste and urban wastewater, makes them particularly attractive. At present, the development of PHAs based on renewable oils and fats and urban biowastes (OFMSW and UWW) is at TRL 6-7. These production routes nevertheless compete with the one based on sugars, which is more advanced, being at present at TRL 9.

- Innovative bio-based products for commercial solutions having a **high added value** due to their peculiar specificity, also hold a relevant position. As an example, the anti-bacterial, anti-fungal and anti-cancer activity of 3rd generation chitosan attract lots of attention for highly demanding applications in the pharmaceutical and biomedical fields.

- The chemical platform related to **lignin** is the one giving rise to the highest number of innovative products at present. Its natural abundance and global availability certainly represent the main reasons for its actual strong attempt of exploitation beyond its actual relevant role as bioenergy source, but this is for sure associated to its chemical versatility and uniqueness as a source of aromatic building blocks. Aromatics, in general, are only available from fossil oil at current.

  Their essential role in numerous industrial sectors, including fuels, solvents and lubricants, plastic materials among others, therefore makes aromatics very attractive if derived from renewable resources.

  Innovative products derived from lignin range from fundamental chemical building blocks, such as BTX aromatics, to materials for advanced applications in technical fields like construction engineering, where for instance both carbon fibres and thermoset resins play a major role and are currently not available from renewable sources. 7 over the TOP 20 selected bio-based products actually derive from lignin.

- The full dependency of Europe on import from south-east Asia of natural rubber sourced by the rubber tree Hevea brasiliensis, mainly motivated the recent inclusion of this elastomer into the list of the **critical raw materials** for EU. The need to develop solid alternative routes of provision for natural rubber, based on regional biomass feedstock availability, supports the current research on natural rubber from guayule, Russian dandelion and rubber derived from the polymerization of the bio-based isoprene monomer.

- The **TRL distribution** for the top 20 selected innovative bio-based products shows that half of them currently have the related technology validated in relevant environment (TRL 5), while just approximately 10% have the system fully developed and qualified (TRL 8). The picture below (Fig 8) shows TRLs distribution for the selected top 20 products. Figure 9 shows the actual development status of the twenty selected most innovative BBPs.

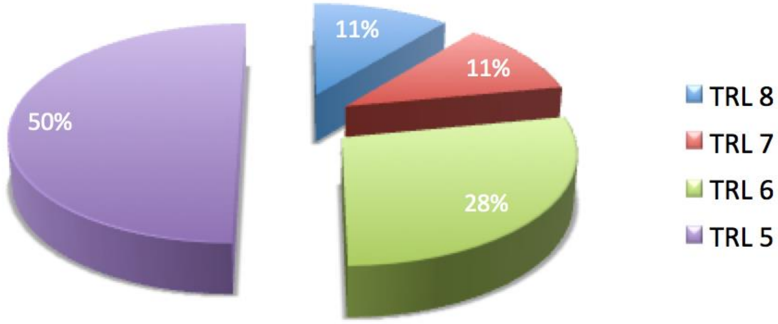

Figure 8 : TRLs distribution for the selected TOP 20 products

TRL	5	6	7	8	9
	Pilot	demonstration		commercial	
		guayule rubber			
Key for categories				nanocellulose	
		composite non woven plant fibres			
natural rubber		lignin biocomposites reinforced with plant fibres			
plant fibres		plant fibers bioresin prepregs			
	veg fibres reinforced biopolymers				
lignin				bio-phenolic resins	
		bio-BTX aromatics			
renewable oils and fats	phenol and alkylphenols				
terpenes	lignin bio-oil				
natural	thermoplastic				

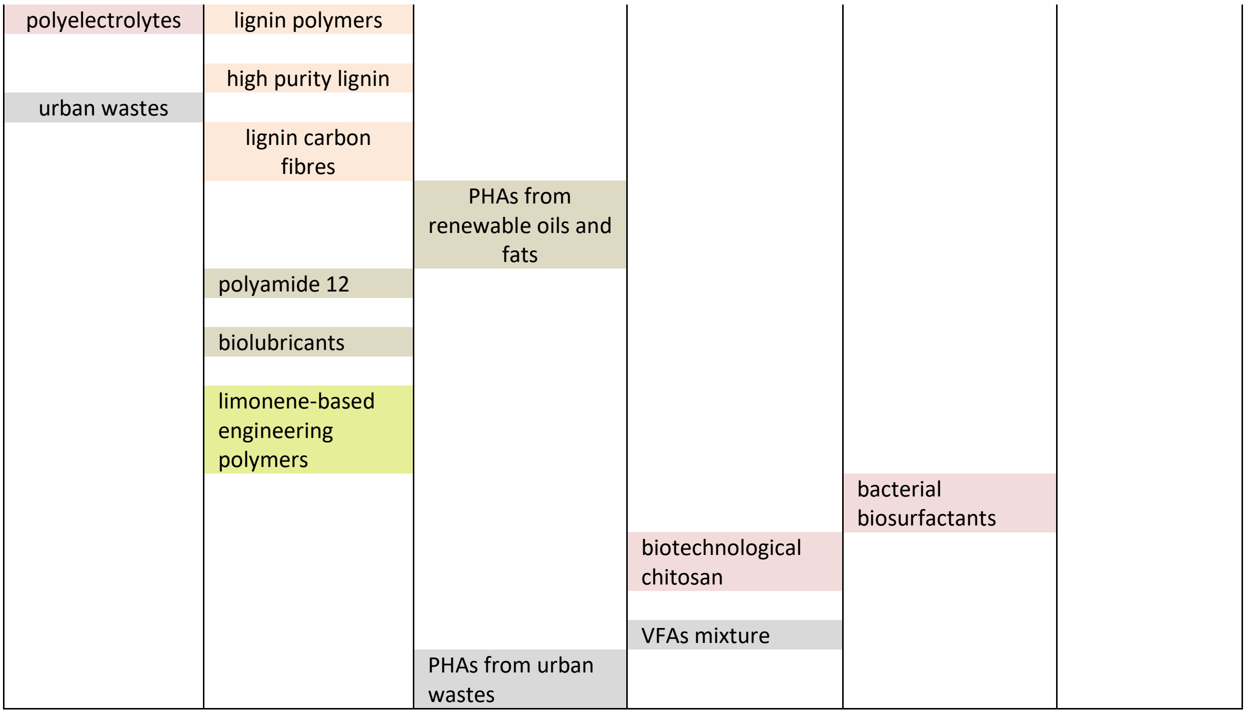

Figure 9 : commercialization status of the selected top 20 products

SECTION 6 DETAILED CASE STUDIES ON THE TOP 20 INNOVATIVE BIO-BASED PRODUCTS

This section reports detailed case studies on the twenty most innovative BBPs identified through this study.

Each detailed case study is a review of the product's properties, technical applications, accessible and reference market, main actors involved, value proposition and sustainability, and the expected market outlook.

Each case study is structured as follows:

- A brief product description, including its applications and competing fossil products. A supply chain overview, which highlights the technologies and pathways involved, plus any competing routes.
- A market analysis which describes the current market volumes and prices. Particular applications or regions of dominance are also examined.
- An activity summary of companies/actors involved in the bio-based product. Each actor is briefly examined to establish manufacturing location, status (pilot/demo/commercial), and application focus. Any partnerships, joint ventures or noteworthy customers are also highlighted.
- The value proposition of the bio-based product, as defined by the production costs (current or expected), the environmental sustainability, and the physical properties of the product, especially in comparison to the fossil-based product(s) it may compete against. Trade-offs, particularly cost versus environmental credentials, are also highlighted.
- The product prospects and outlook over the next few years. This includes the expected market growth rates and prices (especially against fossil competitors), plans in place to expand/commercialise, and also highlights what markets/applications may be expected to develop. Finally, any key drivers or plays necessary to unlock the market potential are briefly discussed together with potential limitations.

1 Guayule rubber

General information

Product Name	Guayule Rubber
Technology readiness Level (TRL)	6 (YULEX, USA)
Biomass Platform	Natural Rubber
Business to Business (BtB) or Business to Consumer (BtC)	BtC & BtB

Natural rubber (NR) produced from the rubber tree Hevea brasiliensis is an elastomeric material consisting of cis-1,4-polyisoprene; it is unique in that for many applications it has no affordable synthetic equivalent. NR is used in over 40,000 consumer products, including more than 400 medical devices. The tyre industry is the largest consumer of NR, accounting for around 75% of annual demand. The annual average consumption of NR in the EU was 1 101 164 tonnes over the 2010-2014 period.

There are many uncertainties in natural rubber production for both end-user and producer given the biotic nature of the raw material. Production is dominated by Thailand, Indonesia, Vietnam, India, China and Malaysia which account for close to 75 % of global production.

From 2014 both indicators for economic importance and supply risk of NR have been assessed as above the criticality threshold for Europe, mainly due on an import dependency of 100 % and the lack of readily available substitutes for all identified end-use applications (European Commission Reports, 2017).

Guayule (Parthenium argentatum) has long been known to produce natural rubber (National Academy of Sciences, 1977) (Van Beilen, 2007) , and it is now considered as the most promising specie for the next-generation of NR sources. Guayule rubber can substitute natural latex from Hevea br. in almost all kinds of applications. Its latex is hypoallergenic because it does not contain the proteins that can cause severe allergic reactions (E.g. for medical rubber gloves and medical items).

It is indigenous to the arid northern Mexico (Chihuahua desert) and southwestern U.S., and has the potential to grow in similar arid and semiarid climates across the world (Thompson and Ray 1989; West et al. 1991), such as regions of European Mediterranean countries. Guayule is 5 to 10 % cis-1,4-polyisoprene by weight and delivers high technical performance, with absence of allergenic latex proteins.

Product description

Chemical-physical characteristics

NR obtained from Guayule has the same molecular weight and general physical mechanical properties as H. brasiliensis rubber. Therefore it allows the same applications and can be considered as an excellent and straightforward substitute for the main production targets of rubbery goods, where high elasticity, outstanding resilience and low hysteretic behavior is desired. Recent results from the EU-funded research project EU-

PEARLS (EU-PEARLS) demonstrated its suitability for the fabrication of car tyres and medicinal gloves. The possibility to apply Guayule NR in medical fields is supported by the special fact that it does not contain the proteins that can induce severe allergic reactions to NR extracted from Hevea brasiliensis.

Guayule shrub extract contains the rubber part composed of 1,4 cis-polyisoprene chains and a residual resin (up to 40% by weight), which is a very complex mixture of sesquiterpene ethers, triterpenoids, and fatty acid triglycerides. This resin may be used as a rubber additive or as a wood preservative. Low molecular weight rubber could serve as a feedstock for depolymerised rubber (liquid natural rubber), which has wide applications in adhesive and moulded product manufacture.

Main uses

Main uses of guayule NR include tyres (car, truck and airplane), rubbery parts for automotive industry, wetsuits and foamed elastomers and other commodity rubbery goods. Applications relate to building and energy industries are also envisaged. Finally, guayule NR is suitable for high-value medical products markets.

Production process

Guayule rubber is produced by extracting rubber from the *Parthenium argentatum* shrub. Rubber can be extracted following a solvent-based or and aqueous-based process. With the first process, organic solvents (e.g., acetone, hexane, or pentane) dissolve the rubber. After solvent removal, a hard rubber is produced that is suitable for transportation tyres. In the second process, the plant material runs in a large vat with an alkali solution (dilute sodium hydroxide). The woody tissue sinks to the bottom while the rubber particles float to the top with resin components. The rubber is then deresinated with acetone. The product is a stable latex emulsion, used for products such as balloons and gloves.

Guayule cultivation has been mechanized, and cultural practices have been enhanced or adapted for a large production scale. Current agronomic selection has made possible for the crop to be harvested on an annual yield (Lane, 2015), despite 6-month harvesting intervals can be also envisaged (Coffelt et al. 2009).

The performance of the mechanical harvest depend on the machine used. According to Bedane (2007) guayule seed harvested ranged from 1.73 to 7.18 kg/ha and harvest efficiency varied from 77 to 91 %. The percentage of immature seeds removed from the crop during mechanical harvesting was as low as 0.1 %.

The amount of water required to produce 1 kg of rubber with existing cultivars (with rubber contents of 40 to 70 g kg^{-1}) ranges from 20 to 30 m^3, and should decrease substantially with the development of cultivars with higher rubber contents (Miyamoto and Bucks, 1985). According to Colleen et al. (2012), at least in the southwestern U.S. a limited water requirement compared to, e.g., alfalfa is needed to grow guayule shrubs. It requires approximately 350-640 mm of rainfall/year according to the EU-NARS-G, 2015, and 2100 mm/year of irrigation water according to Rasutis at al., 2015. Following Bucks et al. (1985) water-use efficiencies for guayule cultivars after 2 years could range from 0.70 to 0.85 kg/m^3 for dry matter, 0.045 to 0.055 kg/m^3 for resin, and 0.03 to 0.04 kg/m^3 for rubber production.

- **Markets**

Current volume, market value, prices

Around 27 million tonne of natural rubber are produced naturally or synthetically on an annual basis. During January to October 2017, the world supply of natural rubber (NR) amounted to 10.429 million tonne, while the world shortfall was 688 000 metric tons by June 2017 (ANRPC, 2017). This is due to an increasing world demand, recorded at 10.730 million tonnes (1.1 % increase on a year-on-year basis) in the same period. The global natural rubber consumption is expected to reach 17 million tonnes by 2025 (EU-NARS-G, 2015), while the global NR shortage may increase to over one million tonnes by 2020, as a result of the rise in demand from tyre makers in emerging markets.

Currently, Europe uses and imports more than 1 million tonne of NR (EU-NARS-G, 2015). However, recently NR rubber supply and prices in both physical and futures markets have been volatile and are continuing to descend. This is due to different factors such as low prices for raw materials (e.g., oil), hurricanes and weather in the growing regions, disease in hevea trees grown in Asia, and speculation in Asian commodity markets, amongst others.

In the light of that, the current commercialization of guayule is mostly driven to create a source of domestic natural rubber in EU, to meet the expected shortage by 2020 (Foster et al., 2011).

The price of guayule rubber or latex is not publically available yet. However, it is estimated to exceed that of Hevea latex (Rasutis et al., 2015), ranging from around 5 USD/kg (in 2011) to ca. 1.92 USD/kg (in 2014), according to Weber and Schaer (2017). Indeed, the commercialization of Guayule depends upon whether it is economically competitive with Hevea rubber: Guayule latex must either perform the same as hevea at a lower cost or perform better at the same cost. However, the big challenge is not that of replacing Hevea production but complementing its supply to cope with the NR shortage, which is increasing worldwide. Clearly, its economics will be more favourable if in addition to latex extraction high value coproducts are developed.

Biomass/yield and feedstock availability

Yields vary depending on area of cultivation, weather, soil conditions, irrigation, type of seed line, amongst other factors. In 2009, IN U.S. shrub biomass ranged from 26 721 kg/ha to 32 951 kg/ha, depending on the type of guayule seed planted. In 2008, rubber yield was between 222 and 639 kg/ha, depending on the cultivar, while in 2009, different cultivar lines yielded between 717 kg/ha and 2006 kg/ha (Foster et al., 2011).

Coffelt et al. (2009), harvesting at 6-month intervals, beginning 1 year after transplanting, showed that the time of harvest (fall vs. spring) affect plant size or latex concentration or yield consistently. The sixth (last harvest) in the fall planting date and the fifth harvest date in the spring planting date were the optimum for plant biomass and latex, rubber, and resin concentrations and yields. A greater plant population (54 000 plants ha^{-1}) had higher biomass, rubber, and resin yields than the lower population (27 000 plants ha^{-1}) at the early harvest dates, but not at the later harvest dates (5 and 6).

According to Estilai et al. (1991) at a young age (21 months), guayule can produce as much resin as rubber. At 45 months, however, annual resin production can become substantially higher than rubber production. Growing guayule beyond the age of two years could not improve the rubber yield on an annual basis, although it can result in an increase in the total rubber.

In time, yield has grown thank to research devoted to increase plat productivity (Blake, 2016). Yulex Company created about 1,200 different varieties of Guayule and spent two years refining its hybrids in Southern California greenhouses. The best guayule hybrid can produce, in Arizona, one metric tonnes per acre catching up the rubber tree yield.

According to the European Innovation Partnership consortium EU-NARS-G, (2015) in Europe, rubber and resins content in the shrub ranges from 5 to 12 %. Potential yield reported is between 500 kg to 1 tonne/ha/year (while the Hevea yield records 1200 kg/ha/year on average). Snoeck et al. (2015) reports that 25 tonnes total dry biomass/ha/year with a good rubber content from the stems (9%), resulting in up to 1600 kg of latex/ha/year.

- **Actors**

General setting

The scene is occupied by huge tyre companies, such as Bridgestone and Cooper Tyre & Rubber Co., as well as by smaller companies such as Yulex. Despite the international context is currently still led by US, European piloting sites are emerging and commercial development of the guayule production is expected in the short-to-medium run. Commercial agreements and scientific/technical collaborations exist already. Three main productive reality exist currently. A few hectares in south Italy for test productions from Eni Versalis, and cultivations in Arizona and California from Yulex and PanAridus.

Europe

Yulex (Arizona) and Eni-Versalis (Milan) reported recently to have signed an agreement to develop guayule in southern Italy. A pilot phase guayule-cultivation is under way in Sicily: in June 2016, 100 000 guayule seedlings were transplanted in two farms belonging to the Sicilian Agricultural Development Authority (ESA) (Yulex, 2013). Simultaneously, the Gela refinery, still in Sicily, is undergoing a process of conversion from a traditional to a bio-refinery, which will be completed in 2018 (Eni website, 2016). The Gela refinery will potentially involve a cultivation of 5 000 hectares of land to produce around 5 000 tonne of product per year (Eni website, 2017).

Versalis strategy is that of selling the bio-rubber to the Italian tyre maker Pirelli in the next future (Yulex, 2013); indeed, in 2013, a partnership between Eni Versalis and Pirelli entered into a Memorandum of Understanding (MoU) and an agreement was signed (Yulex, 2013). In the next five years, Versalis intend to spend over EUR 200 million on the biorubber complex, "including both agro and industrial segments" (ICIS, 2014).

While pilot plants are underway, today, large-scale commercial guayule production does not yet exist in Europe and in Mediterranean area (Snoeck et al., 2015).

Rest of the world

Yulex is a start-up born in 2012 and based in Chandler (Arizona, US), which set a pilot plant in the same site, and detains a molecular breeding facility plus several greenhouses near San Diego. It partnered with Eni Versalis to develop guayule in southern Italy and with Patagonia (in 2008) that is making its Yulex wetsuit from Guayule stems in a 60-40 blend (60 % guayule, 40 % neoprene), reducing dependence on conventional neoprene.

Bridgestone Corporation is the largest tyre manufacturer in the world, with headquarters in Findlay, Ohio. A 281-acre farm was set in Arizon to breed and test guayule. The second facility is an experimental 10-acres farm and bio rubber research-center in Mesa (Arizona), created in 2014 (Snoeck et al., 2015) to improve the rubber extraction process. In October 2015, it announced the creation of the first tyres made entirely of guayule latex.

Cooper Tyre & Rubber Co.: is leading the consortium on Biomass Research and Development Initiative (BRDI) that includes United States Department of Agriculture

(USDA-ARS), the guayule research start-up PanAridus, and the Arizona State University. The team received USD 6.9 million as a federal grant to advance research on guayule on agronomic aspects, to plant, irrigate, and harvest the shrub (Tullo, 2015). In 2016, the corporation completed a number of tyre builds and nearly finished guayule-based tyre components tests with promising results (Coopertyres website, 2016). In 2017, the 100-percent guayule-based concept tyres underwent extensive evaluation and rigorous wheel and road tests (Business Wire, 2017).

PanAridus LLC (Casa Grande, Arizona) holds the largest number of privately owned guayule strains in the world and the guayule seed they own is the only state- and federally-certified seed on the market (American Recycler, 2012). The company aims to commercialize guayule as a domestic source of natural rubber and new industrial crop for Arizona growers. In 2016, they declared their intention to build a pilot plant in Pinal County south of Phoenix to process, annually, about 7,000 tonnes of guayule for latex, bagasse, as well as resin (Blake, 2016). With Cooper Tyre and Rubber, PanAridus has developed a proprietary solvent-based process to extract latex from guayule plants and reached a rubber production quantity never before achieved for use in modern tyres. As a partner of the BRDI Initiative that includes the United States Department of Agriculture (USDA-ARS) and Cooper Tyre & Rubber Co., amongst others, PanAridus has to supplying raw materials (Coopertyres website, 2016).

- **Value proposition and sustainability**

Co-products

The residual plant material (±10% of total dry biomass), after extracting 1,4-cis polyisoprene chains (±12% of total dry biomass), can be transformed into valuable co-products (Rasutis et al., 2015) for the flavor, fragrance, cosmetics, pharmaceuticals, paints and adhesive markets (Nakayama, 2005; Rasutis et al., 2015). Similarly, the bagasse (±80% of total dry biomass) detains a very high-energy value and can be used to produce (jet) fuel, amongst others (Blake, 2016).

Resin is an important guayule by-product that may provide additional revenue for economic commercialization of the crop. The increase in annual resin yield with plant age, according to Estilai et al. (1988) suggests that it is beneficial to grow guayule beyond two years, if increased resin production is the primary objective. The resin content in the shrubs does not change greatly with irrigation or salinity levels, thus the resin yield increases proportionally with shrub yield or irrigation amount (Miyamoto and Bucks, 1985).

- **Environmental impacts, benefits, sustainability**

Guayule is considered as a low input crop and entails the potential to reduce environmental impact and contribute to sustainable development (EU-Pearl Project, 2017). As alternative to Hevea —the world’s main source of natural rubber— is useful in terms of possible reduction of deforestation in the developing world.

For the time being, no pesticides are required (the plant produces terpene resins, which are natural pesticides) and fertilization requirements are low (minimal application of nitrogen are sufficient). Herbicides are mostly necessary for stand establishment. Moreover, compared to the hevea production, which is known to contribute to air and water pollution by spreading dangerous levels of polycyclic aromatic hydrocarbons in the workplace and by treating improperly acidic wastewater (Tekasakul and Tekasakul, 2006; Chaiprapat and Sdoodee, 2007) the guayule processing is more sustainable.

According to the Business Wire (2017) the results of 10 LCA conducted by the consortium within the Biomass Research and Development Initiative (BRDI), highlight that a 100 percent guayule-based tyre production generates between 6 to 30 percent lower emissions, compared with a conventional tyre.

Socio-economic advantages, health impacts (also comparison with alternatives)

Guayule represents a viable crop in southern Europe and Mediterranean, which can enable profitable use of marginal lands and can offer economic opportunity for rural development. Indeed, cultivation in EU can be expected in marginal and unutilized land, while not competing with food production (Cornish et al., 2006). In addition, compared to the Heava rubber which causes (Type-I latex) allergic reactions to the rubber, the guayule latex is much less allergenic and can therefore be highly accepted especially in the medical industry.

Economics: bio vs non-bio based alternative

Non bio-based alternative shows a sale price 1.2-1.6 USD/kg; and shows a production value of 10.5 billion tonnes/year. In contrast, while the current price of guayule rubber or latex is not yet publically available, it is estimated to be higher than Hevea latex (Rasutis et al., 2015). The Hevea latex prices have ranged from around 5 USD/kg (in 2011) to ca. 1.92 USD/kg (in 2014), according to Weber and Schaer (2017).

In Europe (Spain and France case studies), the breakeven price for guayule is approximately 2.76 USD/kg dry rubber.

According to Snoeck et al. (2015), compared to Hevea, guayule is faster producing crop (yet, every 10 years, guayule shrubs have to be replanted), giving an earlier return for the farmer: it shows a payback period of 4 years (Rasutis et al., 2015).

- **Outlook**

Projected trends (baseline)

The synthetic rubber consumption is growing due to the rising demand for automobiles in developing countries such as China and India. Only in 2017, the rubber consumption has been equal to 28.37 million tonnes with China, US, and India being the three major consumers. The synthetic rubber market is estimated to be USD 28.88 billion in 2017 and is projected to reach USD 37.82 billion by 2022, at a CAGR of 5.5 %. The synthetic rubber market is driven by tires, footwear's, and industrial market segments (MarketsandMarkets, 2019). According to the International rubber study groups (2018), the share of synthetic rubber compared to total rubber consumption was 53.76 % in 2017, despite the natural rubber share has great potential and is growing in time. The world synthetic rubber production, in the 2017, has been around 11.2 million tonnes and the total global production of natural rubber in 2000 and 2016 has been respectively 6.8 million metric tons and 12.4 million metric tons (Statista, 2018) with a CAGR of 10.53%..

However, it is complicated to forecast the growth rate of NR considering that the supply may depend on whether conditions and environmental policies. In addition, NR production is affected by seasonality conditions which makes the production unstable. In fact, the Association of Natural Rubber Producing Countries (ANRPC) forecasts 1.3 % supply deficit in 2022, followed by 4.34 % and 7.27% in 2023 and 2024, respectively, due to the reduction in replanting activities in the producing nations (Yai Cian Lim, 2018). Also in the report by ReportLinker, (2018) it is underlined that the global natural rubber market will continue to be in short supply in the period from 2017 to 2027, with the supply and demand gap of about 800,000 tons by 2027.

In any case, in terms of market value it is estimated that the market of NR based products would reach around USD 218 billion by 2020 (Reportlinker, 2018).

Competitiveness and role of Europe in global production

Europe, today, is strongly dependent on the import of strategic raw materials and one of that is natural rubber. Its dependence is (100%) so natural rubber that NR has been listed as a critical raw material by the European Commission.

The main competitor of Guayule is natural rubber, produced outside Europe. The role of Europe in the production of guayule latex will depend on both the ability to grow guayule locally and in areas that are not competing for food, and the ability to improve process yield.

The current commercialization of guayule is mostly driven by the objective of creating a source of domestic natural rubber in EU, to meet the expected shortage by 2020 (Foster et al., 2011).

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2 Microfibrillated cellulose (nanocellulose)

- **General information**

Product Name	Microfibrillated cellulose
Technology readiness Level (TRL)	8
Biomass Platform	Plant fibres
Business to Business (BtB) or Business to Consumer (BtC)	BtB

- **Product description**

Microfibrillated cellulose (MFC), also commonly named nanocellulose, is obtained by delaminating cellulosic fibres in high-pressure, high-temperature, and high-velocity impact homogenization, grinding or microfluidization. Cellulose fibers are fibrillated, i.e. the mother fiber is split into a higher number of thinner fibers/fibrils. This creates an increased surface area giving the novel fibril product new characteristics. Fully delaminated nanocellulose consists of long (1-2 micrometers) microfibrils (typically 5-20 nanometers in diameter) and has the appearance of a highly viscous, shear-thinning transparent gel. It is pseudo-plastic and exhibits thixotropy property.[1]

Chemical-physical characteristics

In the context of this case study, the focus is posed on the cellulose nanofibrils (CNFs) or nano-fibrillated cellulose (NFC).

While CNFs, that are micrometer-long entangled fibrils, contain both amorphous and crystalline cellulose domains, CNCs show almost perfect crystallinity (ca. 90 %). The highly viscous aqueous suspensions is provided by the entanglement of the long particles at relatively low concentrations (below 1 wt %) (Abitbol et al. 2016).

Properties of NFC are strictly dependent on both the starting raw material (source) and the used production process (Abdul Khalil, 2014). In particular, NFC prepared from renewable lignocellulose sources have enhanced mechanical properties such as high strength, flexibility, high surface area/volume ratio and high aspect ratio (in terms of the average length/width ratio of the fibrils) (Sehaqui, 2011). Another example of NCF is nanocellulose obtained from agro-industrial soy wastes that exhibits high elastic modulus, high specific surface area, optical transparency, low thermal expansion coefficient and chemical reactivity (Flauzino Neto, 2013).

Regarding NFC suspensions, they appear as high viscous shear-thinning transparent gels, with high optical transparency and specific barrier properties (Lavoine, 2012). For these reasons, NFC gels represent an interesting biodegradable matrix for the preparation of nanocomposites materials (Qing, 2015). Moreover, in the last decades, NFC have also

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[1] Thixotropic gels or fluids show a shear thinning property: they are thick (viscous) under static and normal conditions and flow (become thin, less viscous) over when shaken, or otherwise stressed. They then take a fixed time to return to a more viscous state.

gained attention as reinforcing filler for polymer-based nanostructured composites (Siqueira, 2010; Lavoine, 2012).

NFC is electrically conductive, highly absorbent, non-toxic, and the crystalline form is transparent and gas impermeable (Belbekhouche,2011; Herrera,c2014). It can work as a stabilizer, especially for water-in-oil or oil-in-water emulsion, it has very interesting spraying characteristics and an unusually high viscosity at rest. Compared to the synthetic fiber Kevlar, used to manufacture high-strength, durable materials, it shows exceptional strength characteristics (Larsson et al. 2012).

According to Roman (Roman 2015), bio-toxicity is not a totally resolved issue for nanoparticles of cellulose. Finally, it is still unknown whether nanocellulose presents a similar explosion hazard than cellulose. Testing activities are need to construct a Safety Data Sheet (Glenn Ostle for Trendspotting Nanotechnology 2018).

Main uses

There are a wide variety of potential applications for nanocellulose. In general, dispersing microfibrils of cellulose in a polar liquid creamy products can be produced that finds use as nonwoven binders, in foods, paints, cosmetics and medicine, and as reinforcement for plastic composites, etc. More specifically, the following uses can be mentioned (Mautner et al. 2018; Conservation 2012): piezoelectric sensors, high barrier packaging also for food; foams with high insulating and fireproof properties for buildings, paper additive (lighter, and stronger sheets), filters or membranes (nanocellulose can purify all kinds of liquids, from saltwater allowing it to be drinkable to blood cells during transfusions); hygiene or pharmaceutical applications, cosmetic applications (composite coating agent for nails, hair, eyelashes and eyebrows), reinforcement for thermoplastics and thermosets; in the medical field, nanocellulose can be used to generate antimicrobial films, to foster bone regeneration and for non-woven products or tissues.

Production process

Despite nanocellulose is generally produced from wood pulp it can also be prepared from any cellulosic source material (AzoNano 2012).

To extract the CNFs from cellulosic fibers three types of processes can be used: the mechanical treatments, the chemical treatments, and a combination of both. Depending on pre-treatment and mechanical treatment applied, energy consumptions for CNF production from wood pulp can range from 500 kWh/t to 70 MWh/t (de Assis et al. 2017).

In the first treatment type the extraction results from homogenization, microfluidization, microgrinding, and milling, while in the second treatment type e.g. the (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl commonly known as TEMPO oxidation can be implemented (Abitbol et al. 2016). In this, delicate phase if the material dries out the nano-fibers stick together forming rough clumps and losing their outstanding mechanical properties. In light of this, researchers and industries have started developing processes that allow drying the nanocellulose without the formation of clumps to conserve their properties. A solution is represented by the nanocellulose transformation into powder which maintains the same properties as undried bio-nanocomposite materials. This makes the product an attractive alternative to the aquatic cellulose suspensions, which, consisting of more than 90 % of water, have shown various problems in addition to higher shipping costs (e.g., if the material dries out the cellulose fibers stick together forming rough clumps and it loses its mechanical properties).

- **Markets**

Current volume, market value, prices:

Since 2014, NFC has been accounting for the largest share (over 50 %) of the global cellulose additives market. This trend will likely continuing in the next future (Transparency Market Research 2015). According to data collected from different sources and presented during a Webinar held by the VTT Technical Research Centre of Finland Ltd, the market size of nanocellulose can grow at different rates depending on the application market. In 2015, greater CAGR rates were registered for the paper and paperboard, the natural fiber composite, the cement segments (Qvintus and Kangas 2015). The application areas from 2011 to 2017 varied with increasing use mainly in eletronics, medicine, and filtration segments.

NCF price varies according to the market place and the specific format and characteristics of the sold bio-material. For example, the type I cellulose nanocrystals in reverse osmosis water product (8.0% w/w suspension) provided by the Blue Goose biorefineries is sold at around 1 000 USD/kg (http://bluegoosebiorefineries.com/purchase/).

CelluloseLab (http://www.celluloselab.com/) applies different prices for different bio-material formats. Cellulose Nanofibrils costs between USD 2.0-6.0 per gram depending on the form (freeze-dried, spray-dried, etc.), while cationic and anionic type cellulose nanofibrils costs between USD 20.0-25.0 per gram.

Biomass/yield and feedstock availability:

The biomass source for CNF is characterized by the cellulose, which is the most abundant organic compound on Earth, and is renewable. Cellulose is the main component of plant stems, leaves and roots. Softwood and hardwood sources can be used, as well as fiber crops. Plants contain on average 33 % cellulose, and cotton is the purest form at 90 % (ACS Chemistry for Life 2018). Increasing or efficient reuse of sludge from the paper industry, can support the stabilization of this market. A major component of pulp and paper sludge, indeed, is tiny cellulose fibers that are usually washed away during paper manufacturing. The extraction of nanocellulose is therefore possible from the pulp and paper process.

A major component of pulp and paper sludge is tiny cellulose fibers that are usually washed away during paper manufacturing. Melodea’s technology recovers these fibers and convert them to nanocellulose.

- **Actors**

General setting

Several actors chacterize the global CNF market both in Europe and abroad. Various players exist in the international area either working in industrial (pilot and commercial) or research entities (e g., JRS, Booregaard, Innventia, VTT, Sodra, UPM, Stora, CTP/FCBA, Nippon Paper). In addition, many European projects have been recently founded on nanocellulose.

A picture presented in 2015 by Qvintus and Kangas (2015) highlight major businesses in the global scene, distinguishing plants according to their commercial advancement in 2015 (Figure 2.1).

Figure 2.1: CNF production status Source: Qvintus and Kangas (2015)

In 2014 Europe accountd for the second-largest share of the global nanocellulose market, after US. Compared to North America and Europe, Latin America, Middle East & Africa, and Asia were lagging behind. In recent years, their market penetration is increasing (Transparency Market Research 2015).

Europe

Europe has several production facilities and boasts of several international leading actors. Examples are the following.

The Exilva project, presented by a Consortium driven by Borregaard (Norway), received grant from BBIJU (EU H2020) as a flagship project EUR 25 million over 3 years (May 2016-April 2019) (Exilva, 2016). Exilva microfibrillated cellulose is the Borregaard commercially available product (Commercial scale brought to 1 000 tonne/year by 3Q16.). Production capacity declared was 300 kg/day (Bras, 2012) https://www.borregaard.com/Products-Solutions

CelluComp (UK) extract cellulose from root vegetables and invented Curran® cellulose nano-fibres that can be fully utilized for paints & coatings, concrete, drilling fluids, cosmetics, personal care and home care products. http://cellucomp.com/

Imerys (France) is a multinational company producing FibreLean MFC combination of kaolin or calcium carbonate with MFCs. In 2015 the production capacity was ~1 000 to > 10 000 tonne/year http://www.imerys.com/scopi/group/imeryscom/imeryscom.nsf/pagesref/SLMM-8RGJYT?opendocument&lang=en

INNVENTIA AB (Sweden) extract cellulose from wood fibres. In 2011, they opened the world's first pilot plant for the production of nanocellulose on a large scale having a capacity of 100 kg/day (Bras 2012; Glenn Ostle for Trendspotting Nanotechnology 2018). In 2013 they started developing a mobile demo plant for paper mill trials that was built in 2017. The plant provides a cost effective solution to evaluate the effect of nanocellulose in various products and processes in the paper mills. http://www.innventia.com/

FiberLean Technologies (Joint Venture between Imerys and Omya, UK), developed FiberLean® MFC, a composite of MCF and mineral useful to replace around 10-15 % of the fiber content in products such as paper. This biotechnology which consents reducing the raw material costs, also allows using the Micro Fibrillated Cellulose in full scale papermaking. http://www.fiberlean.com/

Lenzing Group (Austria) mainly developed two cellulose-based products derived from sustainable wood sources, the VEOCEL™ and the TENCEL™ Lyocell fibers. VEOCEL™ fibers are used for body and health care while TENCEL™ Lyocell fibers for textile applications. https://www.lenzing.com/

WEIDMANN Fiber Technology (Switzerland) has a portfolio of three nano-cellulose based products. These find use in structural re-inforcement, surface protection, gas barriers, rheological modifiers in cosmetics, high capacity absorbents, membranes and various applications in health care. https://weidmannfibertechnology.com/

JRS, J. RETTENMAIER & Söhne Group (Germany) produce a line of cellulose based products called ARBOCEL®

ZelfoTechnology GmbH (UK) produces highly fibrillated macro (MaFC) micro (MFC) and nano (NFC) cellulose fibres, either as separate entities or in controlled mixtures. http://www.zelfo-technology.com/

BASF (World leading company, Germany). Since 2013 a collaboration with Zelfo Technology was favored in order to engineer superior micro-fibrillated cellulose. BASF further improved Zelfo’s fibre technology through a wide range of chemical additives for paper making. https://www.basf.com/de/en/company/career/why-join-basf/basf-in-germany/basf-group-companies.html

InTechFibres (France), is a partnership between the CTP (French Pulp and Paper Research and Technical Institute) and FCBA (French Institute of Technology for Forest-based and furniture sectors). In 2015 production capacity was ~ 0.1 tonne/day, 100 g to 80 kg CMF/CNF http://intechfibres.com/

AkzoNobel (Netherlands), multinational company focused on creation of paints and performance coatings; it produces specialty chemicals for both industry and consumers. https://www.akzonobel.com/about-us/what-we-do/pulp-and-performance-chemicals

Sappi group (Netherlands) has built a pilot-scale plant for CNF production in The Netherlands. The plant will also be capable of producing CMF. Products sold: CNFs dry powder readily redispersed in water. Its production capacity in 2016 was 8 tonne/year target (pilot plant). https://www.sappi.com/nanocellulose

Stora Enso (Finland). They produce in the Enocell mill located in Finland, with annual capacity of 460 million tonne. New board grades containing MFC are entering the packaging market (Glenn Ostle for Trendspotting Nanotechnology 2018). http://www.storaenso.com

UPM-Kymmene OYJ (Finland), recently lauched cellulose-based GrowDex nanocellulose gel for growing human cells. In addition, wound care product that uses UPM’s nanocellulose is also being developed. https://www.upmbiofore.com/

Rest of the world

Prominent producers and vendors outside Europe are mainly located in Canada and Japan although other players are growing around the world. Already in 2015 there was a consortium of 100 companies in Japan built to explore nanocellulose applications (Jack Miller 2015).

In Japan main actors are: Daicel Finechem Ltd., Dai-ichi Kogyo Seiyaku Co., Ltd., Daio Paper (10-tons/year pilot plant facility mainly for application in fiber reinforcement for plastic composites), Nippon Paper Industries (Established Japan’s largest CNF production line with planned annual production of 500 tonne).

In Canada main actors are: FP Innovation (https://fpinnovations.ca/Pages/index.aspx), BioVision (80 kg/day) (https://www.biovision.com/about_us/), CelluForce (200-500 kg/day; 300 tonne of Cellulose NanoCrystals (CNC) per year) (http://www.celluforce.com/), Alberta Innovates (In 2010, was funded to design and construct a new CNC pilot plant. 100 kg/day) (https://albertainnovates.ca/).

In the USA main actors are: Forest prod Lab (50 kg/day, https://www.fpl.fs.fed.us/), American Process Inc. (500 kg/day, http://www.americanprocess.com/), ITT Rayonnier (MFC, http://www.rayonier.com/), UMaine Nanomaterial Pilot Plant (CNF, 1 000 kg/day, https://umaine.edu/pdc/facilities-available-for-use/nanocellulose-facility/), Southworth Company/Paperlogic (CNF, estimated: 2 000 kg/day)

Other active firms are: Indian Council of Agricultural Research - Central Institute for Research on Cotton Technology (ICAR-CIRCOT) (CNFs and CNCs 10 kg/day (data for 2015), http://circot.res.in/circot/), Melodea Ltd. in Israel (CNC, NCC) (http://www.melodea.eu/), Suzano in Brasil (http://www.suzano.com.br/).

- **Value proposition and sustainability**

Environmental impacts, benefits, sustainability

NFC belongs to a group of nanomaterials consisting of the nanosized cellulose fibrils that offer advantages from an environmental point of view since they are obtained from a fully biodegradable sources (Klemm, 2011) and their production process does not require harmful solvents (Paakko, 2007).

The nanocellulose is characterized by being a 100% natural raw material which is not expected to impact environment during the biomass accumulation if this is sustainably sourced from certified and monitored forests. The same result can be ensured if the biomass is represented by rejects, sludge and process waters containing valuable cellulose fibre (e.g., sludge from, e.g., the paper industry). These waste materials, currently severely underused, can be seen as potentially valuable feedstock.

The use of nanocellulose as input for many products, by replacing fossil fuel contents, provides environmentally friendly alternatives able to compete with other cutting edge products; this allows reducing the amount of emissions released into the atmosphere in fossil-based productions.

In addition, compared to synthetic materials, cellulose fibers quickly and fully dissolve into their purely biological components, even in salt water.

Socio-economic advantages, health impacts, bio vs non-bio based alternative

On the economic side, the availability of forest biomass is certainly an advantage. This can lead to foster the security of supply and guarantee a more stable price and market. Innovations related to the production and application of nanocellulose biomaterial are already leading to new business opportunities and job creation.

Additionally, the declining demand for traditional products in traditional markets supports the derivation of greater value from harvested biomass.

Compared with non–bio-based substitute alternatives, nanocellulose-based products are less carbon intensive (greener carbon footprint), are recyclable, reusable, and compostable. For these reasons, their production favours the adoption of manufacturing technologies needed to address the problem of climate change.

On the health impacts, nanocellulose can improve citizens' health through the development of new health care products.

- **Overview of the future development state of the product**

Projected trends (baseline)

It is very likely that the share of the NFC will follow past increasing trend in the future (Transparency Market Research 2015), due to its wide variety of potential applications. The current share of NFC on the global cellulose additives market is about 50%.

It has been estimated that the annualized Compounded Average Growth Rate (CAGR) of 19 % between 2014 and 2019 will project nanocellulose composite market to the value (market size) of USD 250 million by 2019 (Markets and Markets 2015). The market size of nanocellulose can grow at different rates depending on the application market (VTT Technical Research Centre). Averaging the different CAGRs for the different market segments, we can assume an annual increase of 10% and a market size of 333 USD $ -million, in 2030. Amongst factors pushing the growth of the global nanocellulose market we can mention improving living standards, increasing automotive production & sales, and expanding cosmetics market. Additionally, the rapid urbanization combined with rising disposable income in developing economies is projected to fuel NFC demand (MRFR 2018).

According to the market place and the specific format and characteristics of the NCF, its price may greatly vary. CNF-related applications are on a different technology readiness level (TRL), implying different production costs and sale price. The current price value for NCF, depending on different bio-material formats may range between 2 and 25 USD/g. There exist factors influencing both positively and negatively price dynamics. For example, the ehnancement of the production process (e.g., by reducing drying cost and waste management cost or by improving energy efficiency) allows removing the technology-related barriers and favours the stability of sale price. Additionally, the worldwide demand for cellulose each year, corrently overcoming 1.6 million tonnes, is expected to raise.

The feedstock price is another factor which is able to affect the final NFC price. Cellulose is a commodity whose price may depend on currencies fluctuation and arbitrage, but also on climatic factors and the environment. A considerable amount of cellulose is produced in areas subject to natural hazards such as forest fires or hearthquakes (e.g. China and Indonesia) and extreme events, such as droughts (e.g., Brazil, North and South America). These events, which are expected to increase in time, are believed to shock the supply of cellulose, raising the commodity price and creating instability in international markets. On the same line, the increasing demand of cellulose from the paper industry is expected to excert a pressure on its prices. Innovative applications in packaging, paper & board, composites, coatings & films, medical & healthcare, textiles, oil & gas, filtration, rheology modifiers, aerogels, 3D printing and printed & flexible electronics will have the same impact on price. These upwards effects, however, could be partially contained by making use of recylced cellulose and by well managing feedstock stocks.

Competitiveness and role of Europe in global production

According to Market Research Future, U.S. and Canada are among the main contributors to the regional growth of Nanocellulose Market. They are predicted to see a significant demand (MRFR 2018). The same can be said for Europe where demand is estimated to grow in numerous countries (e.g., Poland, Italy, Germany, Spain, the UK, France, and Russia) due to increasing disposable income and purchasing power of consumers. Germany and the UK, emerged as the prominent consumer market due to increasing automotive production and sales coupled with increasing demand for lightweight passenger cars.

In Europe, rising requirement for commercial production is creating need for technological developments in the industry to commercialize the product. As a result, companies are investing heavily in R&D to develop application specific finished products. This is expected to boost market expansion over next years.

At the same time, promotional activities and product positioning can guide consumers toward the adoption of nanocellulose-related products.

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3 Thermoplastic biopolymers reinforced with plant fibres

- **General information**

Product Name	Thermoplastic biopolymers reinforced with plant fibres
Technology readiness Level (TRL)	5
Biomass Platform	Plant fibres
Business to Business (BtB) or Business to Consumer (BtC)	BtB

- **Product description**

With the growing environmental awareness, bio-plastics (e.g. PLA, PHAs, starch blends and others) start to be extensively used as substitutes of traditional fossil-based plastics.

However, some bio-plastics lack thermo-mechanical properties to ensure full responsiveness to the requirements needed for several technical applications. Reinforcement with plant fibres start to represent a valuable solutions to the lack of mechanical properties of bio-plastics and to environmental problems because these reinforced bio-composites are able to keeping the formulation 100% biodegradable and bio compostable. These materials actually represent the fully renewable version of the widely diffused short-fibre reinforced thermoplastics that have been developed to increase the physical and thermos-mechanical properties of standard plastics, such as polypropylene (PP) reinforced with glass or carbon fibres. In the last ten years synthetic fibres were partially replaced by ecofriendly renewable plant fibres, characterized by recyclable and sustainable features (Vilaseca et al. 2018). This transition attracted lots of interest mainly from the automotive sector that fast moved to PP reinforced with plant fibres for car interiors. Nowadays, this transition could get completed by also moving from fossil-based thermoplastic matrices to bioplastics derived from renewable resources, to reach high technical standards with a fully bio-based NF-reinforced thermoplastic solution.

Chemical-physical characteristics

As a general result of using biopolymers blended with plant fibres, full biodegradability is a common physical characteristics (Le Duigou et al. 2016).

Several technical considerations must be addressed in order to evaluate the benefits in terms of mechanical properties of reinforcing bioplastics with plant fibres, with respect to the unreinforced bioplastics or to bioplastics reinforced with artificial fibres.

Fibres distribution and interfacial adhesion with the polymer matrix, as well as the degree of crystallinity of the polymer and environmental moisture play a key role (Mukherjee & Kao 2011). Tensile mechanical properties of plant fibres (e.g., cellulose, abaca and jute) reinforced bio-composites with Polylactic acid (PLA) and poly-hydroxyalkanoate (PHA) matrices, compared to analogous PP-based composites, showed a general improvement of the characteristics (Bledzki and Jaszkiewicz (2010).

Composites based on PHA polymers embedded by *Posidonia oceanica* fibres, have reported a more rapid degradation in marine sediment indicating that the presence of *Posidonia oceanica* fibres facilitated the disintegration of the films in marine environment (Seggiani et al. 2017). When biodegradable plastic is reinforced or mixed also with plant fibres, has been observed a reduction in odour emissions from compost piles (Chauhan & Chauhan 2013).

Advantages of Thermoplastic biopolymers reinforced with plant fibres

Low cost (Mohanty et al. 2002a), low density, acceptable specific strength properties, eases of separation, carbon dioxide sequestration, homogeneous recyclability and biodegradability (Sabinesh et al. 2014) are the main advantages of using plant fibres with respect to carbon or glass fibres.

Disadvantages of Thermoplastic biopolymers reinforced with plant fibres

Minor disadvantages are related to the limited thermal stability of plant fibres with respect to the temperatures needed to process bioplastics in the molten state.

- **Main uses**

The main applications are for a range of technical parts. Plant fibres reinforced with biopolymers represents an alternative to glass reinforced composites to be used especially for the structural parts for cars for showing sufficient mechanical properties and low weight (Khademi 2016; Mohanty et al. 2002a).

In aerospace and automotive industries, plant fibres reinforced with biopolymers are also used in engineering components production such as bearings, gears, fan blades, and chassis structures

Automotive sector is one of the beneficiary of the natural bio composites so much so that Toyota Company is already proposing automotive application parts using natural molded kenaf-PLA bio composites (Rusu et al. 2011).

Also in packaging sector, the green composites have created a consistent commercial markets for value-added products (Singh et al. 2017).

Production process

Thermoplastic biocomposites based on biopolymers reinforced with different plant fibres can be processed by standard techniques, such as injection molding, compression molding, extrusion, thermoforming, pultrusion and resin transfer molding (Birat., 2015; Singh, 2017).

- **Markets**

Current volume, market value, prices.

In general terms, plant fibres usable as reinforcements for thermoplastic matrices are less expensive than synthetic alternatives (glass and carbon) (Pickering,2016). Currently, plant fibres are priced at one third of the cost of glass fiber or less.

In contrast, bio-plastics price still remain quite expensive if compared with the synthetic one being the plastic price correlated with the oil price and volatility.

The market of plant fibres as reinforcements for thermoplastic matrices shows a Compound Annual Growth Rate (CAGR) of 11 % from 2016, which will be confirmed over the next 3 years.

The market is driven by the increasing use of plant fiber composites in automotive applications.

First in Europe and then in North America, the automobile models featured natural fiber reinforced thermosets and thermoplastics in many components. The range of products is no longer restricted to interior and non-structural components such as door panels or rear shelves. The automotive industry's adoption of natural fiber composites is led by price, weight reduction, recycling, and marketing incentives rather than technical demands (Faruk et al., 2012).

Biomass/yield and feedstock availability

Based on company announcements, by 2020 the most important bio-based polymers will be starch with 1.3 million tonnes, PLA with 0.8 million tonnes, PHAs with 0.4 million tonnes and bio-based PE with 0.6 million tonnes. All quantities are annual based (Shen, 2009).

According with Mukherjee and Kao, (2011) PLA thermoplastic polymer which can be produced nowadays with a capacity of over 140 000 tonnes per year.

Plant fibres biomass is very abundant on hearth, with the only limitation connected to the harvests fluctuating across years as a function of weather and other factors.

The annual world production of global plant fibres data suggests that wood, is a major source of bio-based fibres (Singh, 2017)

- **Actors**

General setting

To date, a number of composite manufacturers have introduced in their product range bio plastic composites reinforced with several plant fibres. Many manufactures are situated in Europe.

Europe

EconCore's (Belgium), one of the Company production field is the high-performance composite and bio-based polymers such as the Poly-Lactic Acid (PLA). (http://www.econcore.com/en)

FKuR (Germany). The company is specialized in bio-plastic and its use is enlarge to several different field. The company developed a wood-reinforced PLA compounds called FIBROLON®, which can be injection molded into complex profiles, panels, and hollow profiles and/or into components for automotive interiors. (http://www.fkur.com/en)

Bio-on SpA (Italy). By licensing out the proprietary know-how to produce PHAs (polyhydroxyalkanoates). (http://www.bio-on.it/)

JEC group (France). The JEC Company was created in December 1996 as a subsidiary of The Center for Promotion of Composites (CPC), and a non-profit association. It develops new materials, such as composites using plant fibres or biodegradable polymers. (http://www.jeccomposites.com)

Kareline Oy (Finland). The Kareline Oy company, made Kareline® PLMS natural composite. The material is a biodegradable fiber-reinforced with PLA composite. (http://www.plasthill.fi/en/kareline)

GreenGran BV (Germany). The GreenGran BV company made granules from injection moulded wood or natural fiber-reinforced with PLA. (http://www.greengran.com)

FASAL WOOD KG (Austria). The company FASAL WOOD KG, developed and markets granulates from PLA and wood waste for injection molding under the brand name Fasal®. (http://www.fasal.at)

FuturaMat (France). Products of wood and biodegradable polyesters are also developed by FuturaMat under the tradename BioFibra® in grades suitable for injection, extrusion, or thermoforming. (http://www.futuramat.com)

Rest of the world

Scion (New Zelan). Scion is a Crown Research Institute (CRI), which is a government-owned company that carries out scientific research for the benefit of New Zealand. Plants and polymer chemistry to make wood fibre-rich dice that can be used in typical extrusion operations. The technology is patented. (http://www.scionresearch.com)

- **Value proposition and sustainability**

Environmental impacts, benefits, sustainability

There are several reason that makes bio-composite environmental friendly and sustainable material. First at all, the biodegradability and biological degradation of the whole composite.

Specifically for plant fibres, they are abundant in nature and renewable and if compared with glass fibres, the production has lower environmental impacts (Pamuk 2016). However, the environmental advantages in term of energy and CO_2 balances are partially counterbalanced by the use of fertilizers to grow the crops the production of fibres requires land and water, and may steals resources for agricultural food production (Zini & Scandola 2011).

Socio-economic advantages, health impacts, bio vs non-bio based alternative

According to Miao and Finn (2008), plant fibres gives better vibration damping than glass or carbon fibres. In addition, plant fibres provide a better insulation both for acoustic and thermal.

Natural materials and technologies have been developed to increase issues related with health and safety, emission of volatile organic compounds, energy consumption, and toxicity from manufacturing. For this reason naturally-derived fibres and biopolymers polymers are perceived as being green material compared with their synthetic alternatives, (Netcomposites; 2014).

Has been pointed out by MP Westman et al., (2010) plant fibres composites are not without problems. One of this is water absorption of the plant fibres which limiting a large scale production. Plant fibres absorb water from the air and direct contact from the environment. This absorption deforms the surface of the composites by swelling and creating voids.

- **Outlook**

Projected trends (baseline)

The interest in bio-composite manufacturing made from renewable raw materials are increasing large corporation’s interest. Thermoplastic biopolymers reinforced with plant fibres with a TRL equal to 5 demonstrates that there is an interest in technology development and validation. Raw materials used to manufacture the biopolymers and plant fibres composites are environment-friendly and may replace synthetic plastic and fibres.

In the leading countries such as Italy, Finland, Sweden and Germany, bio-degradable polymers have already been applied in the packaging of supermarket products and also big brand such as Procter & Gamble, Coca-Cola, Danone Puma, Samsung, IKEA, Tetra Pak, or Toyota have already introduced first large scale products in Europe. (Bioplastics.org, 2018)

According to the report published by EuropaBio (2016) also the European job market could take advantages by the bioplastics sector. In Europe, in 2013, 23 000 new jobs were registered. In addition, the labour market is forecasted to offer 300 000 new high-skilled jobs in 2030.

Considering the total bioplastic capacity (degradable and non-degradable), only in 2017, 2 054 million tonnes have been produced globally and the production capacity is set to increase from around 2 189 million tonnes in 2020 with a CAGR of about 2.14%.

In terms of market value, according to the literature and market reports, the global bio-plastics market raised to a value of USD 17.50 billion in 2016 and is expected to reach USD 35.47 billion in 2022, with an estimated CAGR from 2016-2022 up to 12.50% (Zion Market Research 2018).

This expected increasing volumes on the market, may adapt the production cost with a decreasing price for the future. The bioplastic price depends on oil price and biomass availability. The currently low oil prices are making bioplastics price difficult to be competitive if compared to conventional plastics.

In terms of market barriers, the inputs for biomass production should be considered. The land used to grow the renewable feedstock for the production of bioplastics amounted to approximately 0.82 million hectares in 2017 and is expected to reach 1.03 million hectares in 2022. The competition in food could affect the raw material availability (European Bioplastic, 2017) and the future bio-plastic volume.

Competitiveness and role of Europe in global production

Europe have a significant leading role in driving global bioplastic growth and this can be attributed also to proactive regulatory efforts.

Respective regulations in France (BSF, 2018), Italy (BIT, 2017) and Spain (SBS, 2018) have helped build up infrastructure across southern Europe, and EU’s Circular Economy package is supporting market demand Europe-wide (Philp, 2013)

The commitment of the European Commission to the transition to a circular economy may further accelerating the growth of the bioplastics industry in Europe.

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4 Plant fibres reinforced bioresin pre-pregs

General information

Product Name	Plant fibres reinforced bioresin pre-pregs
Technology readiness Level (TRL)	9
Biomass Platform	Plant fibres
Business to Business (BtB) or Business to Consumer (BtC)	BtB

Product description

Fibre-reinforced composites represent the best technical solution for metal replacement with lighweight alternatives. The composite sector has increased almost 25 times from the 1960s to nowadays, according from a recent report from Lucintel (Lucintel, 2018), and it is expected to grow even at a faster rate during the next 5 years. The major drivers for growth in this market are increasing demand for lightweight materials in the aerospace and defence and automotive industry; corrosion and chemical resistance materials demand in construction and pipe and tank industry; electrical resistivity and low flame retardant materials demand in electric and electronic industry. Within the global composites market, pre-pregs layup is within the major processes utilized to manufacture composites part.

Pre-pregs are composed of reinforcing fibres impregnated with reactive resins, not fully cured, that will undergo complete curing just after shaping of the product. Pre-pregs are used because of an easier manipulation during lamination with respect to dry mats. They optimize mechanical properties in the final product because problems related to voids inclusion in the composite material are avoided, which would reduce its technical performance. Therefore composites fabrication results faster and easier by using pre-pregs.

The most common pre-pregs contain glass or carbon fibres impregnated with epoxy resins. The resulting composites cannot be recycled, and thermal valorization is their unique valuable end-of-life option. That's why the environmental sustainability of these materials is considered very poor.

A significant innovation in the field of fibre-reinforced composites is related to the use of renewable plant fibres to replace glass and carbon fibres, in combination with standard thermoset resins. The aim, of course, is to increase material's environmental sustainability through the use or renewables while retaining acceptable technical properties. Epoxy resins reinforced with plant fibers such as wood flour, flax, kenaf, hemp, jute and others, already represent a commercial reality (Lucintel, 2018b).

In order to maximize the environmental sustainability of fibres reinforced composites, the step forward is represented by the combination of renewable reinforcing plant fibres with bio-based thermoset resins. Bio-resins can be used as natural, sustainable alternatives to traditional petro-chemical derived thermosets in the manufacture of composite products (Jones 2007).

Bio-epoxy resins can be prepared from plant oils (soybean or linseed oil) and from polysaccharides (sorbitol or cardanol) as well (Niedermann 2015). Typically, these resins are modified with chemical functionalities to promote crosslinking (Fowler, Hughes, and Elias 2006). These bioresins reinforced with high-strength plant fibres hold great promise for replacing many of the glass or carbon reinforced composites currently in use.

Plant fibres reinforced bioresin pre-pregs will open up a very interesting 100 % bio-based world for renewable composites. These completely bio-based and partially biodegradable materials would be useful for highly technical applications such as construction and mechanical engineering.

Chemical-physical characteristics

Plant fibres reinforced bioresin pre-pregs are composed of two phases: the matrix is a bio-resin and the plant fibres are the reinforcements. The specific composition and structure of the different plant fibres (e.g., cotton, flax, hemp etc.) leads to different mechanical properties (Bledzki, Reihmane, and Gassan 1996) which in turn influences their potential use as reinforcing fillers in composites, affecting their value and market price (Pickering, Efendy, and Le (2016).

As for thermoset bio-resins, they can be derived by a wide range of plants and plant oils. The latter are triglycerides (esters of different fatty acids) which can be functionalized with reactive groups (e.g., with hydroxyl, carboxyl, amine and epoxy). This allow to cross-link them to form rigid polymers.

Epoxy components require curing agents to form the three dimensional cross-linked structure of the matrix material. These curing agents can be synthesized from synthetic or also from natural sources (polysaccharides and carbonic acids) (Niedermann 2015). Synthetic chemical cross-linkers are still used, despite current research is concentrating on finding isocyanates from a biological source (Knowledge Transfer Networks 2014).

In addition, polyfurfuryl alcohol (PFA) resins are a family of thermosetting bio-resins derived from the renewable furfuryl alcohol. PFA resins are particularly attractive to the composites industry as they detain interesting properties such as high levels of thermal stability, chemical resistance and fire resistance (Knowledge Transfer Networks 2014). Along with jute and flax fibres reinforcements, PFA thermosetting bio-resin have recently been used in the market for fire-resistant composite applications. They show performances similar to phenolic pre-pregs, having the advantage of impacting less the environment and performing better in terms of health and safety issues (Campilho, 2015).

Unidirectional flax linen fibre pre-pregs with biobased epoxy resin can reach tensile modulus as high as 33 GPa, specific tensile modulus 25 GPa and specific tensile strength 220 MPa (Lingrove). This is higher stiffness than E-glass traditional composites and higher vibration damping.

Advantages of plant fibres reinforces bioresin pre-pregs

The high levels of composite stiffness and strength achieved by pre-preg technology, combined with the low density of the constituents, make components manufactured suitable for several applications in different industries.

As for bio-resins per se, they have the advantage of being used as natural, sustainable alternatives to traditional petro-chemical derived materials such as phenol-formaldehyde and isocyanate resins in the manufacture of composite products. Therefore, environmental and safety issues of petro-chemical derived materials are in this way overcome.

With respect to glass and carbon fibres reinforcements, the plant fibres reinforced bioresin pre-pregs, could improve vibration damping, reduce the costs for the same performance, and reduce the part weight and having a natural look.

Finally, two main aspects influence the selection of the pre-pregs material; the cost and the performances. Figure 4.1 shows the many advantages of using pre-pregs, that is the reason for their fast increasing industrial use (Lucintel, 2018b).

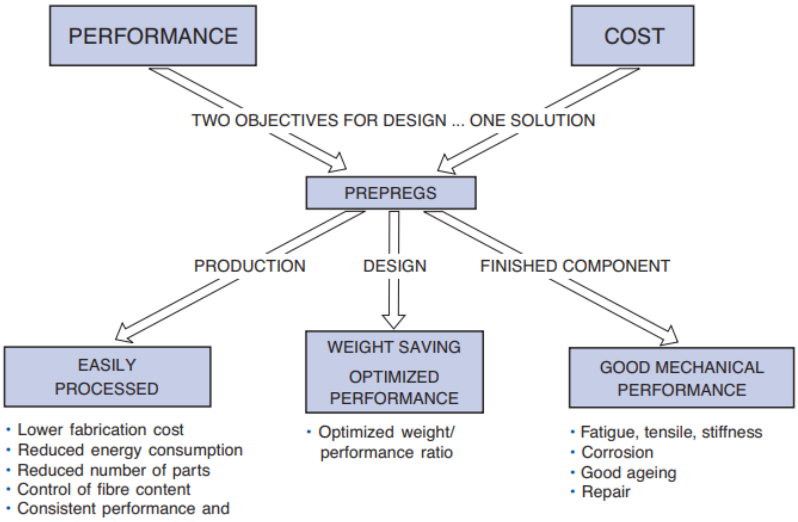

Figure 4.1: Pre-pregs advantages (Source: Hexcel Corporation, 2013)

Disadvantages of plant fibres reinforces bioresin pre-pregs

The quality of plant fibres may be instable due to several influences, such of weather. In addition, their properties are essentially dependent on the locality, on the maturity of the plant and how the fibres are harvested and preconditioned (Balakrishnan et al. 2016). Other disadvantages relate to the limited maximum processing temperature, incompatibility with the hydrophobic polymer matrix and the tendency to form aggregates during processing, poor fire resistance and lower durability than synthetic fibres (Väisänen, Das, and Tomppo 2017).

The fluctuation of the composition of natural sourced plant fibres, and therefore the mechanical properties represents a disadvantage. Consequently, plant fibres application in structural composites is not yet solved (Niedermann 2015).

- **Main uses**

Plant fibres reinforced bioresin pre-pregs can be used for technical applications mainly in the aeronautical sector (civil aircraft, primary structures, interiors, helicopters), in automotive and wind turbine blade manufacturing (Pickering, Efendy, and Le 2016). They can also serve the construction sector. Using pre-pregs in combination with plant fibres also characterizes a good basis for light-weight and high-strength construction parts.

Production process

Pre-pregs are produced using two main processes: hot melt process and solvent dip process.

Hot Melt Process: Both fabric and unidirectional pre-pregs can be produced using the hot melt process. There are two stages in this process. The first stage involves coating a thin film of the heated resin on a paper substrate. The reinforcement material and the resin are allowed to interact in the pre-pregs machine. On application of pressure and heat, the resin is impregnated into the fibres resulting in the final pre-pregs, which is ultimately wound on a core.

Solvent Dip Process: Only fabric pre-pregs can be produced using the solvent dip process, which involves dissolving the resin in a solvent bath and dipping the reinforcing fabric in the resin solution. Using a drying oven, the solvent is then evaporated off the pre-pregs.

Despite the high technical performance of the pre-pregs materials, these are characterized by low production volume (Figure 4.2).

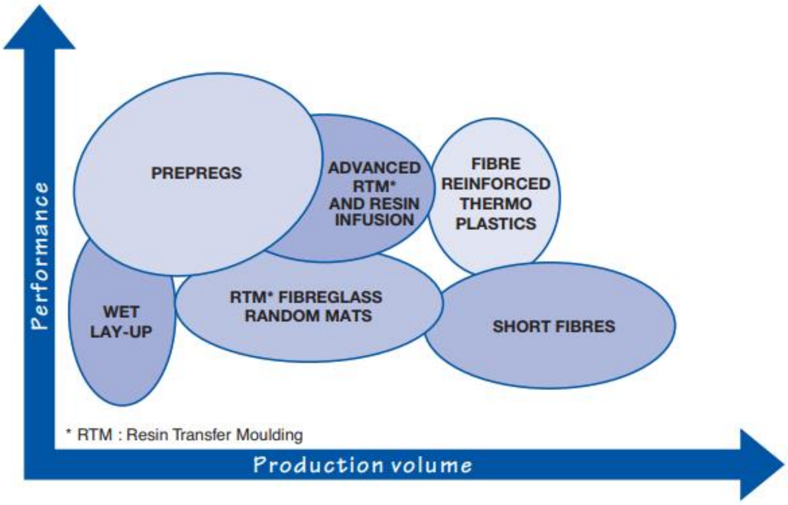

Figure 4.2: Pre-pregs technology in terms of performance and production volumes (Source: Hexcel Corporation, 2013)

- **Markets**

Current volume, market value, prices

The future of the bio-composites market looks promising with opportunities in building and construction, automotive, industrial and consumer goods industries. The global bio-composites market is expected to reach an estimated $7.6 billion by 2023 and is forecast to grow at a CAGR of 7.9% from 2018 to 2023 (Lucintel, 2018b). Some of the products made with bio-composites are decking, railing fencing, cladding, door panels, and dashboard. The market for end-products made with bio-composites is expected to reach an estimated $12.2 billion by 2023. The major growth drivers for this market are increasing demand for Wood Plastic Composites (WPC) in the construction industry due to its wood finish like appearance and durability, and growing use of Natural Fiber Composites (NFC) in automotive interiors due to its aesthetics and growing concern for passenger safety.

Emerging trends, which have a direct impact on the dynamics of the bio-composites industry, include the emergence of new applications, and government support to innovate and commercialize the use of bio-based composites. They could cost between 8-20 EUR/sqm (Väisänen, Das, and Tomppo 2017). In 2012 the European automotive industry used 90 000 tonnes of plant fibres composites.

Market drivers for plant fibres reinforced bio-resin pre-pregs are the rising costs of feedstock's and oil price instability combined with the increased costs of compliance with environmental and safety legislation. Also, the market increase strictly depends on industrial availability and development of bio-based polymer matrices. Additionally, the application of plant fibres remains contained due to a difficult reproducibility in the manufacturing processes (Väisänen, Das, and Tomppo 2017). On the other hand, the low price of plant fibres will support the development of the industry.

As for the bioresins, the generally high production costs characterize a significant barrier to their development. This, however, is not always the case. Large quantities of cashew nuts are produced in Africa, India and Brazil, which means that the price of CNSL is lower than similar synthetic phenolic, although its composition is significantly more variable. However, bio-resins production is becoming viable as technologies evolve. This will bring economies of scale for bio-based chemical feedstock's for the resin formulators (Jones 2007).

Biomass/yield and feedstock availability

Plant fibres biomass is very abundant on earth, with the only limitation connected to the harvests fluctuating across years as a function of weather and other factors.

Instead of the commercial glass or carbon fibres, jute fibres can be used as composite reinforcing material in the case of plant fibres reinforced bio-resin pre-pregs, if it fulfils the requirements for mechanical properties. Worldwide availability and production of jute is much higher than in case of commercial hemp or flax.

- **Actors**

General setting

There are different research activities and business development projects across Europe and the rest of the world. Examples of suppliers are reported below.

Europe

Meshlin Composites Zrt. (Hungary) (http://www.meshlin.hu/products/) has developed thermoplastic laminate pre-pregs with the technologies towards the higher molding temperature for a high performance application. These pre-pregs are made from flax, continuous fibre for UD and woven textiles. The pre-pregs provide transparency and amazing patterns.

The University of Warwick (UK) has developed plant fibre-plant oil composites for the body panels of their Eco One and WorldF3rst sustainable racing cars (https://worldf3rst.wordpress.com/about/). Also, a team of UK companies including the Eden Project, Homeblown, Sustainable Composites and Laminations have developed a surfboard comprising plant fibre-bioresin skins with a biofoam core (http://www.notox.fr/En/).

Other companies are working in this direction including Procotex Corporation SA (Belgium), Composites Evolution (UK), LINEO (FR), Bcomp Ltd. (Switzerland), Ecotechnilin (France), Group Depestele (FR), and Solvay (BE).

NetComposites (UK) has developed a range of biobased pre-pregs based on plant fibres textiles and a polyfurfuryl alcohol (PFA) resin which can then be processed into composite parts by vacuum, autoclave or press consolidation (https://netcomposites.com/media/1211/biocomposites-guide.pdf).

Research is also investing in exploring advancements in plant fibres reinforced bio-resin pre-pregs and different market roads for these composite products. For example, the European BIOCOMP project developed thermosetting biocomposites, including flax fibre polyfurfuryl alcohol (PFA) bioresin and wood fibre linseed oil resin (https://cordis.europa.eu/project/rcn/75744/reporting/en). The URBANREC H2020 Project (http://www.urbanrec-project.eu) is working for the valorization of recovered fibres and textiles coming from post-consumer waste (mattress, carpets, furniture).

Rest of the world

The Affordable Composites from Renewable Sources (ACRES) programme at the University of Delaware (USA), has combined the soybean resin derivatives, with flax, hemp and jute fibres to produce biocomposites for applications including chairs, hurricane-resistant houses and automotive body panels.

Soy bean oil - plant fibres composites have been used commercially by John Deere American Corporation (that manufactures agricultural, construction, and forestry machinery, diesel engines, drivetrains), under the trade name HarvestForm®, to produce body panels and cab roofs for hay balers. The parts are produced by the RIM process and 25 % weight savings are claimed.

- **Value proposition and sustainability**

Environmental impacts, health impacts, benefits, sustainability

Production of plant fibres reinforced bio-resin pre-pregs which shows a non-toxic and benign nature creates incentive to replace current technologies and foster spillover effects.

As for the impacts on health, the use of plant fibres reinforced bio-resin pre-pregs present low emission of toxic fumes when subjected to heat and during incineration at end of life. For the pre and post-harvesting/cultivation facets, the energy consumption related to the plant fibre separation process is lower than that of synthetic fibre production processes. Because of plant fibres non-abrasive behavior, the filler loading within the polymer matrix can be used in larger quantities than non-organic fillers as it is unlikely to cause damage to machinery or health during manufacturing.

The use of thermoset bio resins allows to use less hazardous alternatives to binders such as urea and phenol formaldehyde for wood products (Knowledge Transfer Networks 2014). Additionally, the bioresins recycling is facilitated having a nature-based structure. Throughout the chemical reactions taking place during the cure of thermosetting resins, volatile gases are released and become encapsulated in the cross-linked resin. A critical requirement of any process is that it is able to minimize void formation and ensure uniform distribution of resin as well as fibres throughout the component (Balakrishnan et al. 2016).

In general, products made from composite materials can offer significant environmental benefits because of their characteristically low weight, good mechanical properties, excellent resistance to corrosion and the possibility of being sustainably sourced. Also the energy consumption related to the plant fibres separation process is lower than that of synthetic fibres production process.

While environmental benefits of composites are known, there is far less understanding of the environmental and social implications associated with the manufacture of composite materials and products, and the options at end-of-life.

Socio-economic advantages, bio vs non-bio based alternative

The natural composite material can be produced with lower investment costs making the composite an interesting business opportunity also for low-wage countries.

Some synthetic resin present issues associated to the utilization of particular chemicals, most notably formaldehyde, in their synthesis. Synthetic adhesive resins, such as phenol-formaldehyde and urea-formaldehyde, are largely used for bonding wood in the furniture making industry and also to bond wood based construction products. Human and environmental exposure of formaldehyde is of concern as it is a suspected carcinogen. Additionally, the use of bio-composites reinforced with natural materials ensure no skin irritation for workers.

Bisphenol A is used in the manufacture of epoxy resins, which are widely used in many industries due to their strong bonding properties and are used in flooring, aircraft and car manufacture as well as DIY applications. Bisphenol A has received attention from regulating authorities and health organizations due to its alleged hormone disrupting effects (Jones 2007).

Epoxy resin is used extensively in aircraft composite structures, but cannot be safely used inside cabins because of its poor fire performance. Most epoxy resins easily ignite when exposed to fire, and release copious amounts of heat, smoke and fumes. Bioresin can show better performance in this respect (Wang, 2017).

- **Outlook**

Projected trends (baseline)

Being a composite product, the estimation of future market conditions for the plant fibres reinforced bio-resin pre-preg composite is not trivial and entails several elements of uncertainty. On the one hand, one should understand the potentiality of plant fibres in replacing synthetic ones. On the other hand, bio-resin market should be considered when assessing the future ability to produce 100 % bio-based products.

Raw materials used to manufacture plant fibres composites are environment-friendly and have the potential to replace synthetic fibres over the coming years, being 25.0 % to 30.0 % stronger than glass fibres of the same weight (Bourmaud, 2018). Also, reducing the mass of the component, the use of plant fibres lowers the total energy consumption with respect to working with synthetic fibres, dropping therefore production costs. On the other hand, plant fibres drawbacks, may limit their expansion.

As for bio-resins, high potential is seen in them replacing traditional petro-chemical derived materials also due to regulations. However, the generally high production costs characterize a significant barrier to their development, despite their production is becoming more and more viable as technologies evolve. This will bring economies of scale for bio-based chemical feedstock's for the resin formulators (Jones 2007).

Expectations on the price of plant fibres reinforced bio-resin pre-pregs are strictly linked with trends on feedstock's costs and oil price, as well as their instability combined with the increased costs of compliance with environmental and safety legislation. The low price of plant fibres will also support the development of the industry.

Overall, major market driver of these composites are stable demand for lightweight products from the automotive industry, and the construction and aeronautical sectors. Pre-pregs technologies has a wide margin of growth due to their high performance compared to other fibres-based composite materials and to their current low-volume production.

The global plant fibre composites market size was valued at USD 4.46 billion in 2016 (Grand View Research 2016).

Technology advances and economies of scale will make the bio-prepreg technology more and more competitive with respect the use of synthetic fibres and resins. This trend will be supported by the low price of plant fibres. For this reasons, after a slight increase in price, the bio-composite products is expected to show a decreasing price trend.

The specific composition and structure of the different plant fibres that can be used influence strongly their market value and price. The current price, ranging between 8-20 EUR/sqm (Väisänen, Das, and Tomppo 2017), is expected to grow as a result of an increasing demand.

Competitiveness and role of Europe in global production

Research on plant fibres reinforced pre-pregs is developing more in the EU than rest of the world. The fibre crops are abundant, but mainly outside the EU; sustainability issues may arise in relation to the possible alternative uses of food crops and land, while synergies can come with some crops also usable for biofuel production e.g. for soybean.

Future developments in fully bio-based composites are likely to be dependent, at least in part, by the speed of development in plant fibres and bio-based polymers. Consistent quality plant fibre products are required in appropriate forms for composite moulding and at an affordable price. To achieve this, improvements in crop growing and fibre processing are required.

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5 Self-binding composite non-woven plant fibres

- **General information**

Product Name	Self-binding composite non-woven plant fibres
Technology readiness Level (TRL)	7
Biomass Platform	Plant fibres
Business to Business (BtB) or Business to Consumer (BtC)	BtB

- **Product description**

Non-woven fibre-reinforced plastic composites are commonly manufactured by lamination of non-woven fibres mats and polymer matrices.

Thermoset and thermoplastic matrices are both used, but the former is most common because of the advantages deriving from the possibility to impregnate the fibres with liquid precursors that increase viscosity and solidify upon curing. Bio-based plastic matrices, notwithstanding if they are biodegradable or not, combined to plant fibres reinforcement, give rise to composites 100% from renewable resources.

One of the main drawbacks of non-woven fibres-reinforced plastic composites is represented by the possibility of generating weak bonding interfaces between the polymer matrix and the plant fibres, mainly due to the hydrophobic character of the former, and hydrophilic character of the latest that avoid complete interfacial compatibility. This induces a decrease in the expected mechanical properties and advantages deriving from using a fibres reinforcement significantly drop.

Self binding composite non-woven plant fibres represent an innovation targeted to avoid the aforementioned technological restrictions. In this case, in fact, plant fibres are surface modified through deposition of a layer of polymer or polymer-precursor, that induces thermoplasticity to the fibres themselves. When the polymer-surface-modified plant fibres are heated, the thermoplastic coating melts (or reacts) and generate a matrix that binds the fibres together. An example of the product is reported in Figure 5.1.

One of the most innovative material of self binding composite non-woven plant fibres is the thermoplastic paper, such as PAPTIC® a success case study of bio-base products (https://paptic.com). It is produced by a Finnish start-up (PAPTIC® Ltd) and spin-off from VTT Technical Research Centre of Finland established in April 2015. Thank to its properties, PAPTIC® challenges plastics.

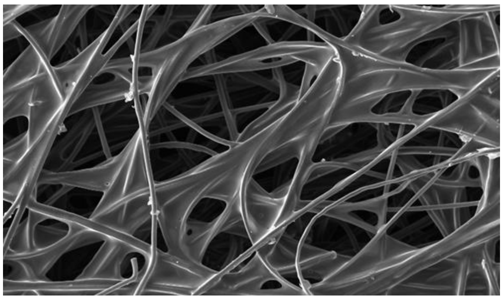

Figure 5.1: Self binding composite non-woven (Source: Edana https://www.edana.org/discover-nonwovens/what-are-nonwovens-)

Chemical-physical characteristics

Plant fibres and thermoplastics could have different combination with different performances as a results (Das and Pourdeyhimi, 2014).

The thermoplastic paper represents the most innovative product in this sector; its chemical-physical characteristics are considered given as an example in the following.

The thermoplastic paper product named PAPTIC® has several advantages and good proprieties. This material can be stretched up to 20 %, compared to 5–7 % in typical packaging papers. The tensile strength is high compared to plastic films and it does not lose its shape as easily when loaded. As with plastic bags, the PAPTIC® bag can be folded to a small volume. In addition it is available in various basis weights from 30gsm to 150gsm. Its thickness is available in a range from 30–200 micrometers (EASME, 2017).

Advantages

Thanks to the chemical modification of the fibres surface, plant fibres are self-binding and there is no need to laminate or combine them with a plastic matrix to generate a fibre-reinforced composite. The risk of generating weak fibres-polymer interfaces is therefore significantly reduced, and mechanical properties of the composite are enhanced.

Composite non-woven can provide an engineered solution by creating multi-functional products as well as an economical solution by eliminating manufacturing processes and replacing two or more products by a single product (www.sunstrand.com).

Thermoplastic paper shares common features with paper but could replace plastic; it is a water-resistant, biodegradable and compostable product. In the specific case of the PAPTIC product this can easily be produced with an existing production line, no matter if the line is designed for paper or plastic.

Disadvantages

No specific disadvantages apply.

- **Main uses**

Composite non-woven are useful in many contexts and sectors such as for hygiene, wiping medical, filtration, insulation, geotechnical, automotive, agriculture and packaging (Das and Pourdeyhimi, 2014).

The thermoplastic paper can be used like a carrier bag, sting bag for food industrial packaging, medical packaging, wrappers (Zamfir, 2010). Additional applications relate to e-commerce mailing box and cosmetic bags (www.paptic.com).

Production process.

At present, the use of plant fibre composites is mainly restricted to non-structural components due to limitations in mechanical properties. The typical performance of a plant fibre composite is inferior in comparison to those of synthetic composites. However, the specific properties of some plant fibres are close to or even better than those of E-glass fibres, which indicates that their composites' performance can be improved.

The primary focus of this innovation is to demonstrate a new manufacturing process to fully realize the potential of plant fibre composites in the form of thermoplastic impregnated non-woven plant fibres.

Producing polymer surface-impregnated non-woven plant fibres as a precursor of reinforced composites, would allow fibres in the final product to be highly connected to each other and to the polymer matrix, enabling the production of a well-designed and efficient part.

Impregnation of the plant fibres with polymer or pre-polymer solution is commonly applied to generate a thin layer of thermoplastic coating onto the single fibres. Upon heating, solvent is removed and the solid coating is generated. For some polymers available in the powder form, also powder coating can be applied to the plant fibres.

Full consolidation of the composite material is based on the self-binding ability of the surface-modified plant fibres when heated, allowed by the thermoplastic behavior of the polymer coating.

Consolidation can be achieved by compression at elevated temperatures (to induce melting or polymerization of the polymer coating) and high pressures (to reduce voids and increase mechanical properties). Another option is to pass the surface-modified plant fibres between heated consolidation rollers, that melt and compact the material during transfer (McGregor *et al.*, 2017).

- **Markets**

Current volume, market value, prices.

Non-wovens production in Europe increased in volume by 3.6 % to reach 2 318 523 tonnes in 2015 (Figure 5.2). This compares with growth rates in the two previous years of 4.8 % in 2014 and 2.2 % in 2013. The estimated total turnover of the European non-woven goods industry is around EUR 7 471 million. The industry employs around 25 000 employees in Europe and is more capital than labour-intensive (Edana, 2015).

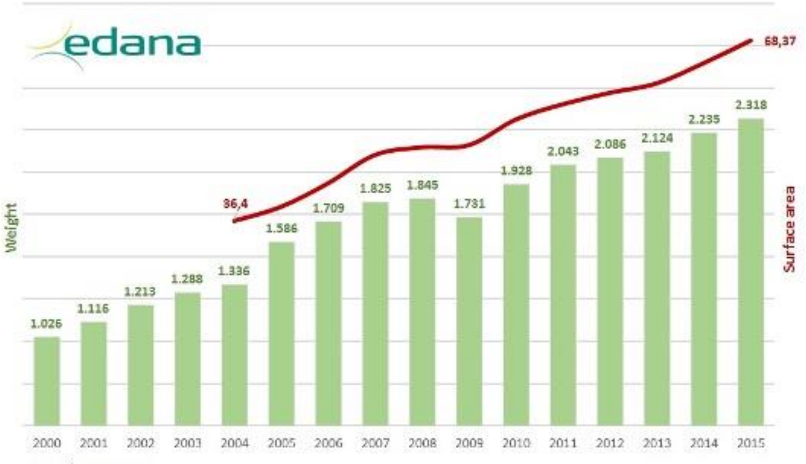

Figure 5.2: Non-woven production in Europe (in thousand tonnes 2015) (Source: Edana, 2015)

Total non-woven exports from the EU 28 to the rest of the world amounted to 371 688 tonne in 2015 (as compared to 341,811 tonnes in 2014) representing a value of almost EUR 1 716 million.

Biomass/yield and feedstock availability

Plant fibres are very abundant on Earth with the only limitation connected to the harvest fluctuating across years as a function of weather and other factors.

- **Actors**

General setting

Currently there are two association of non-woven producers, namely EDANA (the European Disposables and Nonwovens Association) and INDA (North America Association of the Nonwoven Fabric Industry). Organoclick (SE) and Paptic (FI) are the main EU players in this segment.

Europe

Basf (Germany). BASF company realized CONTOURA a biocomposite that combines Acrodur® resins with a variety of natural, recycled or synthetic fibres to produce a pre-preg composite that is ready to be molded for a variety of uses in the automotive, RV, and home & office furnishing industries. (http://www.basf.com)

Paptic Lld (Finland). PAPTIC® Ltd is a Finnish start-up and spin-off established in April 2015 and the PAPTIC® thermoplastic paper project creator. (https://paptic.com)

Organoclick (SE). This business offers bio-based binders under the trade name OC-biobinder™. These are used to strengthen the mechanical properties of woven and nonwowen textiles. (http://www.organoclick.com)

Rest of the world

TTS BIOCOMPOSITE (Canada). The Canadian firm have developed five different value-added products with plant fibres such as fibre panels, fibre-reinforced cement, structural insulated panels, engineered fibre mats, and fibre-plastic composites. (http://www.ttsfpl.com)

Sunstrand LLC (USA). Sunstrand firm works with different feedstocks including bamboo, hemp, kenaf, flax and jute to create composite non-woven materials. (http://www.sunstrands.com)

YFY Jupiter Ltd (USA). (http://www.yfyjupiter.com/)

Andritz (Wuxi) (China). The company provides process technology and service for a variety of non-wovens applications for the Asian markets. (https://www.andritz.com)

- **Value proposition and sustainability**

Co-products

There exist no co-products.

Environmental impacts, benefits, sustainability

Plant fibres reinforced materials offer target environmental advantages such as reduced dependence on non-renewable energy/material sources, lower pollutant and greenhouse emissions. Advantages of plant fibres over traditional ones are: low cost, high toughness, low density, good specific strength properties, reduced tool wear (nonabrasive to processing equipment), enhanced energy recovery, CO_2 neutral when burned, biodegradability and fully recyclable.

Socio-economic advantages, health impacts, bio vs non-bio based alternative

The non-woven industry brings a wealth of advantages to people throughout the world, in diverse walks of life. Diapers, incontinence products and feminine hygiene products support people daily life.

Non-woven surgical gowns and drapes help prevent infection during operations, while state-of-the-art short-use protective suits and masks protect against hazardous dusts and chemicals. Non-woven filtration media improve indoor air quality, while absorbent non-woven oil spillage products and geotextiles we see the enormous environmental benefits of this versatile fabric. Finally, the material is lightweight, soft and breathable.

- **Outlook**

Projected trends (baseline)

Thermoplastic paper shares common features with paper but could replace plastic. As indicated above, currently self-binding composite non-woven production technologies is mostly in TRL 7 development and a few company are producing on a commercial scale.

As a result, realistic estimates for price or cost development are missing. In addition, the composite price is also directly correlated to natural fibers and their property, quality, type, and market of origin.

As general information the European non-wovens production increased in volume by 3.6 % to reach 2 32 million tonnes in 2015.

According to Smithers Pira, in 2017, a total volume of non-woven materials of about 10.1 million tonnes had a value of USD 42.3 billion. The market is projected to grow up to 13.6 million tonnes in 2022 reaching USD 57.4 billion. The annual growth rate for the 2017-2022 period is projected to be around 6.3% (Smithers Pira, 2017).

Competitiveness and role of Europe in global production

Up to now a success bio-base products in Europe is PAPTIC® realized by Paptic Lld in Finland. Other firms in Europe and abroad (USA, China, Canada) are starting the production of self-binding material but the market is still a niche.

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6 Lignin biocomposites reinforced with plant fibres

- **General information**

Product Name	Lignin biocomposites reinforced with plant fibres
Technology readiness Level (TRL)	6
Biomass Platform	Plant fibres
Business to Business (BtB) or Business to Consumer (BtC)	BtB

- **Product description**

Lignin fibres composites are materials, which combine various proportions of lignin together with other plant fibres and additives, and sometimes fossil-based or bio-based plastic compounds, to create specific desired characteristics. Many of these composites are designed specifically as 'green' alternatives to displace petroleum-based plastics. There are 'pure green' versions, which mix lignin with fine plant fibres made of wood, hemp or flax and natural additives such as wax. The role played by lignin mixed in plastics or bioplastics reinforced with plant fibres is mainly that of a stabilizing additive and properties aid, as it improves the physical-mechanical properties and process of the fibres-reinforced material. It is also known as "liquid wood" for its easy process as a standard thermoplastic.

Chemical-physical characteristics

Plastic composites reinforced with plant fibres suffer from a restricted thermal stability during processing, that significantly limit their applications at industrial level and commercial expansion. In addition to these fabrication issues, plant reinforcement in plastic matrices show poorer fire resistance and lower durability than synthetic fibers. The stabilizing effect induced by lignin to biocomposites reinforced with plant fibres, allows the formulation of a material made from 100% renewables, suitable for standard processing such as injection molding. The raw material is lignin, which, mixed with plant fibres (flax, hemp or other fibres plants) and some natural additive produces a fibres composite that can be processed at raised temperatures and, just like a synthetic thermoplastic material, can be made into moldings, plates or slabs on conventional plastics processing machines. Mechanical properties of lignin biocomposites (tensile stress, impact resistance) are comparable to those of some common plastics (PP, PS, SAN) and aesthetics can be tailored through the use of pigments or by the natural look given by the plant fibres.

Advantages of lignin biocomposites reinforced with plant fibres

Plant fibres-reinforced biocomposites make the construction industry more sustainable by reducing the use of non-renewable resources and CO_2 emissions.

The properties of lignin (e.g.: abundance, low weight, CO_2 neutrality, antioxidant, antimicrobial and biodegradable nature) make it suitable for new composite materials development. The global warming potential for producing lignin is much lower compared to a number of common polymers.

Disadvantages of Lignin biocomposites reinforced with plant fibres

No disadvantages apply

- **Main uses**

Lignin biocomposites reinforced with natural fibers find main applications as thermoplastics to be processed in standard injection molding machines. Uses vary a lot in different sectors: in the construction industry and in the automotive sector these materials are very valuable due to their good performance as acoustic and thermal insulators (Väisänen, Das, and Tomppo 2017). Technical parts, furniture and interiors, sport and leisure, packaging and clothing are all application targets for lignin biocomposites reinforced with natural fibers. The "natural" look, for example by using visible plant fibres so that the material's special quality is instantly apparent, is considered a plus for these materials.

Production process

Pure lignin in liquid form is highly viscous. It can be used to produce a wide range of bio-plastics through injection molding technologies (e.g. building panels).

By combining lignin with other natural polymers and plant fibres, however, its range of extruded products potentially is very wide. These other compounds also provide more scope for pure lignin (or '′liquid wood') to be designed and engineered to develop desired characteristics. To improve the thermos-plasticity and mechanical properties of technical lignin, polymers or plasticizers are usually integrated with lignin by blending or chemical modification.

Further addition of plant fibres produces a reinforced fibres composite with improved mechanical properties that can be processed at raised temperatures.

- **Markets**

Current volume, market value, prices

A well-developed supply chain and market exists for lignosulfonates, which are water soluble compounds produced by the sulphite chemical pulping process, a distinct, but allied process to the kraft pulping process. Moreover, many firms are established as suppliers of lignosulfonates and kraft lignin chemicals. Although it is a distinct pulping process, some of the end-use markets for lignin that can be produced as a distinct by-product of the kraft process are the same as those for lignosulfonates. This is important because, as already noted, the oil-based plastics industry is already open to the displacement of some of its oil-based feedstock by bio-chemicals and bio-plastics. The motivation is the rapidly emerging 'green market' for hybrid plastics.

Except for soybeans plastics, most current sources of existing bio-plastics are reported to be 2 times to 5 times more costly than oil-based plastics. At a reported price of around 4,5 cents per kg for lignin feedstock (Alberta Finance and Enterprise 2010), lignin could be price competitive with oil-based commodity plastics.

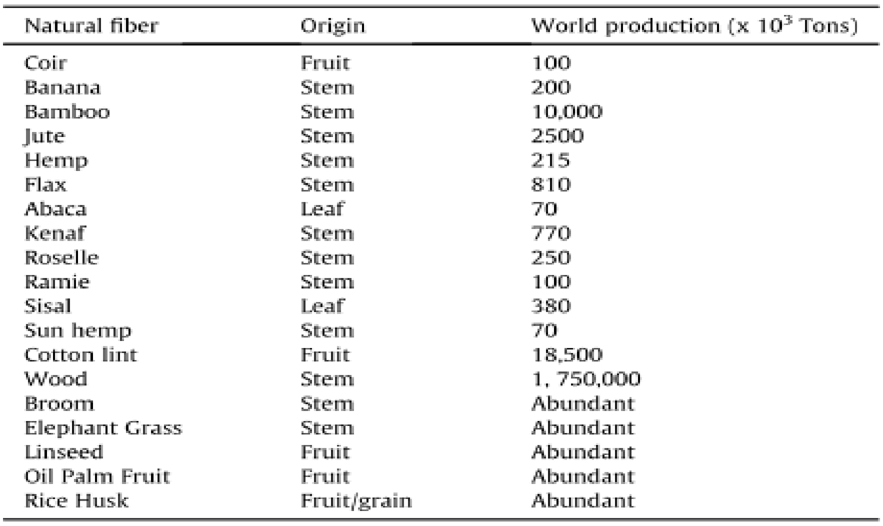
Existing markets for lignin chemicals are well developed. Projections indicate that modest growth is taking place in demand for these products. The global market is between 1 million and 1,1 million tonnes per year (Alberta Finance and Enterprise AFE 2010).

Biomass/yield and feedstock availability

Lignin, on which lignin composites is based, is the second most abundant biopolymer after cellulose and it accounts for 1-45 w.t.% of natural fibers (Dias et al., 2016). Lignin is a by-product of a number of industries involved in retrieving the polysaccharide components of plants for industrial applications, such as in paper making, ethanol production from biomass, etc. (Thakur et al. 2014), and it accumulates around 50 million tons per year worldwide (http://teknaro.de).

Plant fibers biomass is very abundant on earth, with the only limitation connected to the harvests fluctuating across years as a function of weather and other factors. According to Sanjay et al. (2018) the annual production of natural fibers is that reported in Table 6.1.

Table 6.1: Annual production of Plant Fibers



Natural fiber	Origin	World production (x 10^3 Tons)
Coir	Fruit	100
Banana	Stem	200
Bamboo	Stem	10,000
Jute	Stem	2500
Hemp	Stem	215
Flax	Stem	810
Abaca	Leaf	70
Kenaf	Stem	770
Roselle	Stem	250
Ramie	Stem	100
Sisal	Leaf	380
Sun hemp	Stem	70
Cotton lint	Fruit	18,500
Wood	Stem	1, 750,000
Broom	Stem	Abundant
Elephant Grass	Stem	Abundant
Linseed	Fruit	Abundant
Oil Palm Fruit	Fruit	Abundant
Rice Husk	Fruit/grain	Abundant

Source: Sanjay et al. (2018)

- **Actors**

General setting

Almost 90% of the files patented during the last 3 years on fibres are related to the composition and/or technologies for the processing of composite materials reinforced with renewable fibres. The scientific community is mostly focusing the attention on the modification of plant fibres to make them suitable for industrially relevant applications. Some examples of these composites reinforced with natural fibers already exist even at the commercial scale, such as in the case of building panels. In general, two active firms exist in EU. Leading actors are Tecnaro GmbH (Germany) and Organoclick (SE).

Europe

In august 2012 OrganoClick AB (http://organoclick.com/) (Täby, Sweden) started a project called Fiber composite which funded by the EU in its Eco-innovation program. The project aimed at developing and introduce into the market a moulded burial coffin, made of bio-fibers modified with OrganoClick´s technology to comply with the high demands put upon a burial coffin. The coffin needs to have a high degree of strength, it needs to withstand both dry, humid and cold conditions, and it also needs to burn in a controlled speed during cremation. Currently, OrganoClick sells OrganoWood® and OC-aquasil™ to the market. The first product is a wooden material having an excellent resistance to fungal decay and fire while the second mimics the Lotus-flowers water repellent features modification of biofibers developed a range of products that solve these problems. The product has been developed, rendering wood with highly water repellent properties and dimensional stability.

TECNARO, (Ilsfeld, Germany) www.tecnaro.de. The company produces several biodegradable biocomposites combining lignin with natural fibers, such as ARBOBLEND® and ARBOFORM®.

Rest of the world

One relevant reality working on reinforcing lignin bio-composites with natural fibers outside the European context is represented by the Tipco Industries (www.tipco.in/) (Mumbai, India), which launched a commercial production of TIPWOOD®50EX eco-friendly building material, applicable for door panels, trims, office cabinet, marine flooring, furniture, mono-block chairs, and various artificial wood product.

Tipwood® Plant fibre Composites, supersede traditional materials such as wood, steel, aluminium and fiberglass, with its features of high strength, flame retardancy, UV resistance, water resistance, anti-biological and many more.

Other relevant realities are mainly placed in Canada and North America.

- **Value proposition and sustainability**

Environmental impacts, health impacts, sustainability

Plant fibres reinforced biocomposites play a big role in the development of innovative sustainable materials for the built environment. The construction industry is one of the major and most active sectors in Europe and represents 28 % and 7 % of employment respectively, of the industry and of all the European economy (Fangueiro, 2011). Unfortunately, this industry is also responsible for the depletion of large amounts of non renewable resources and for the release of high value of carbon dioxide gas emissions. Building products leave an environmental footprint at every segment of their life cycle.

The use of renewable resources by the construction industry could help, therefore, to achieve a more sustainable consumption pattern of building materials, in line with what established recently the European Union requiring a reduction in raw materials consumption and a cut in waste production in this sector (European Commission 2018). In general, the development of natural composites are being supported by legislative requirements in all sectors (Väisänen, 2017). As for the impacts on health, the use of bio-composites reinforced with natural materials ensure no skin irritation for workers. In addition, plant fibres and composites present low emission of toxic fumes when subjected to heat and during incineration at end of life (Pickering, 2016).

Socio-economic advantages, bio vs non-bio based alternative

Compared to synthetic fibers such as glass, the hollow tubular structure of natural fibers provides better insulation against noise and heat. This can be a very useful property in automotive applications such as door/ceiling panels and panels separating the engine and passenger compartments (Fowler, 2006). The same is for building and construction applications, in doors and windows frames for example. Lignin used in bio-plastics has the potential to displace several oil-based plastics. In vinyl/PVC, which is the dominant plastic used in windows, there are substantial concerns about its health and safety aspects.

- **Outlook**

Projected trends (baseline)

There is considerable interest in developing lower cost supplies of natural feedstock among which lignin has considerable potential. Existing markets for lignin chemicals are well developed. Moreover, projections indicate that modest growth is taking place in demand for these products. The global market is around 1 million tonnes per year. The annual growth rate (CAGR) is around 2% (Alberta Finance and Enterprise AFE 2010).

However, to be competitive with oil-based alternative products, lignin feedstock price should not overcome 5 cents per kg. The Ontario Auto Council reported a price for lignin feedstock of about 22 cents per kg. Lignin could be price competitive with oil-based commodity plastics priced much higher.

Competitiveness and role of Europe in global production

Especially for the case of lignosulfonates there exist several Mediterranean and central-European countries (Italy and France, Spain, and Germany) already operating in this sector despite northern EU (Finland, Sweden, Norway) show a greater annual production capacity.

In Europe, composites as a material and the entire associated industry hold enormous potential. Legislation and an increasing awareness about preserving the planet is expected to play and important role in further boosting the market.

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7 High-purity lignin

General information

Product Name	High-Purity Lignin
Technology readiness Level (TRL)	5
Biomass Platform	Lignins

Business to Business (BtB) or Business to Consumer (BtC)	BtB

- **Product description**

The first major step involved to add value to the unconverted lignin is its separation from other biomass constituents to give high-purity lignin.

High-purity lignin, also named high-grade lignin, is the starting point for the development of further formulations suited for use as raw chemicals such as vanillin, benzene, toluene, and xylene aromatics, food and beverage additives, nutritional supplements advanced materials: such as carbon fibers for reinforced composites, adhesive binders, resins and coatings, PU-based foams, films, paints, and plastics.

Therefore, the future use of lignin (except as fuel) will mainly depend on the possibility of either degrading it into low molecular weight aromatics or to take advantage of lignin as a multi-functional macromolecule. High-purity lignin can be considered as a platform chemical from which a wide variety of high-added-value products can be derived.

Applications of both lignin-derived aromatics and lignin as macromolecule are at lab stage, and seem to work optimally with sulphur-free lignins which have low levels of impurities too. Actually, at present, technical lignins, coming from steam explosion processes and others, present large heterogeneity in terms of purity and chemical structures. Therefore, the first major step involved to add value to the unconverted lignin is its separation from other biomass constituents, such as hemicelluloses, cellulose, ashes to give high purity lignin.

Several processes for recovering lignin from black liquor have been recently developed. Resulting “Kraft lignins” are relatively low (1-3 %) in ash and metals content (e.g., 1 500–7 500 ppm sodium). Such purity is suitable for lower-value applications (e.g., phenolic resins, PU foams, and clean-burning biofuels), while “ultraclean” lignins (with metals contents of <100 ppm Na) are required for higher-value applications. For example, lignin precursors suitable for conversion into carbon fibers for structural automotive applications must be ultraclean, as metal impurities >100–200 ppm create flaws in the fibers upon carbonization, deleteriously affecting their properties (Klett, Chappell and Thies, 2015).

Chemical-physical characteristics

Lignin is composed of p-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) units linked by C–O or C–C bonds, which exhibit a complex three-dimensional amorphous structure. The content and chemical structure of lignin are primarily influenced by its sources and isolation methods. The physical and chemical properties of lignin change depending on the process conditions, adding further structural complexity to this already heterogeneous polymer.

The chemical structure for lignin from different sources is different in terms of proportion of p-coumaryl-alcohol, coniferyl-alcohol, and sinapyl-alcohol (C9 unit). More than 95 % of guaiacyl units (that derived from coniferyl alcohol) are estimated to be in softwood lignin, while the proportions of coniferyl-alcohols and sinapyl-alcohols are approximately equal in hardwood lignin. Herbaceous biomass (e.g., straw) lignin and woody lignin are of different chemical structures because of the extra content of p-hydroxyphenyl units and significant amounts of hydroxycinnamic acid (mainly p-coumaric acid). The proportions of p-coumaryl-, coniferyl- and sinapyl-alcohols in lignin depend on sources of lignin.

Therefore, one of the major problems for lignin is its indistinctly defined structure and quality variation in terms of origin, separation, and fragmentation processes, which mainly limits its utilization.

Main uses

Lignins are now considered as the vital aromatic renewable resource. The unique structure and chemical properties of lignin allow the production a wide variety of chemicals and materials. As a consequence of its polyaromatic nature and large availability, lignin is the obvious candidate to serve as future "green" source for aromatic chemicals, especially phenols. Aromatic building blocks derived from lignin are particularly attractive for use in polymerization, as substituent of oil-derived phenols, e.g. phenol formaldehyde resins or epoxy resins. Moreover various possible value-added applications are under study for use of lignin without conversion to molecules of lower molecular mass, such as, e.g., blending with polyolefins giving UV stabilization, or blending with PLA giving 100 % renewable resins, or implementing uses which take advantage of its antimicrobial and antioxidant action (Cotana *et al.*, 2014). The combination of lignin with bio-based polymers generates reinforced composites fully derived by renewable resources.

Lignin is expected to add value to composites also as an additive, by improving their flame retardancy and UV stability. Lignin-based carbon fibers are actually considered as the most promising substitutes for polymer PAN-based carbon fibers, suitable for the formulation of advanced and structural carbon composites.

Lignin is an abundant phenolic polymer that can be used as a substitute for toxic and expensive raw materials, such as phenolic monomers, to fabricate aerogels. Aerogels are highly porous, lightweight materials with high surface areas and nanometer-scale pore sizes. These characteristics of aerogels result in a combination of extraordinary properties and make them outstanding materials for many applications, such as thermal and acoustic insulators, adsorbents, filters, catalyst supports, and electrodes for hydrogen and electrical storage.

Overall, high-purity lignin can be seen as a product platform and a building block for many industrial uses. Possible future applications can be broken down in different groups: carbon-based materials, macromolecular applications, fine- and specialty chemicals, bulk chemicals (e.g., aromatics and acids), higher value fuel additives, and, finally, as source of energy/heat.

Advantages of high-purity lignin

High-purity lignin serves as the common starting point for the development of an elevated number of valuable chemicals and materials. No pre-treatment is required for pure lignin to be used as reinforcing filler in composites, while fractionating pre-treatments will provide streams for pure aromatics, chemicals, additives and plasticizers. The notable properties of lignin, such as highly abundance, environmental friendly, low weight, CO_2 neutrality, and its antioxidant, antimicrobial, and biodegradable nature and reinforcing capability, make it a perfect candidate for the development of polymer composite materials.

Another major advantage is that the technologies to develop all the above-mentioned chemicals and materials from high-purity lignin, are already fully developed and well consolidated. This will accelerate the technical development and commercial uptake of lignin-derived products, once that high-purity lignin will be largely available at affordable costs.

Disadvantages of high-purity lignin

The high cost of purification of commercial lignins formed as a by-product of the pulp and paper industry represents the main drawback related to high-purity lignin. Unlocking new lignin conversion strategies holds enormous potential to enable a green economy for sustainable consumption.

Production process

Being an integral part of the plant fiber cell wall, lignin cannot be readily separated in a high quantity and high purity without significant alterations of its native structural properties. Isolation methods depend on the plant tissue that is used as the source of the polymers.

Lignin isolation via preceding extraction of pulp is usually applied on wood as a starting material. The procedure preceded by cell wall extraction and combined with lignin complexation with thioglicolic acid is used for plant tissues containing various kinds of cells or low lignin content comparing with protein content. Lignin purification is needed prior to its transformation into value-added products. Mostly used green solvents for biomass are ionic liquids.

The research of novel methods for the efficient and cost effective extraction of lignin is active, and for instance, recent work focusing on bamboo biomass makes use of microwave assisted extraction (Li *et al.*, 2012) or sequential processes with ethanol and soda (Sun *et al.*, 2012), or steam explosion followed by methanol treatment (Sasaki *et al.*, 2013) other methods reported in the literature include use of innovative "green" solvents such as Ionic liquids (Adlie Shamsuri and Kuang Abdullah, 2010).

The recent discovery and application of the deep eutectic solvent (DES) provided new insight. DES is a mixture of two or more chemicals acting as either hydrogen-bond donors (HBD) or hydrogen-bond acceptors (HBA). Studies suggest that DES may have a unique capacity towards dissolving lignin from plant materials, generating a low molecular weight lignin product while maintaining its properties. For this reason, DES has significant potential for industry applications (Alvarez-Vasco *et al.*, 2016).

Fortunately, the dominant lignin source available is commercial lignins formed as a by-product of the pulp and paper industry. Typically, kraft and organosolv lignins are suitable candidates for high-value applications thanks to the lower content of impurities, whereas lingosulphonate lignin most likely is used for lower value products. Additionally, kraft lignin covers several applications, including the high-value ones, and is considered mid-range in terms of price. It is also readily available in sufficient quantity from pulp and paper manufacturers to start meeting the industrial demand and is considered a good intermediate between lignosulphonates, unsuitable for high-value applications due to the low-purity, and organosolv lignin, which is considered as the best starting point for the development of activated carbon, phenolic resins, carbon fibres, vanillin and phenol derivatives.

An estimation of the global amount of high-grade lignin production is currently not available.

- **Markets**

Current volume, market value, prices.

Lignin depolymerization and conversion has a significant potential as a sustainable source for the production of fuels and bulk chemicals, and so as a direct alternative to the petrochemical industry. Those aromatic compounds spread over a wide range of market demand and prices (Figure 7.1).

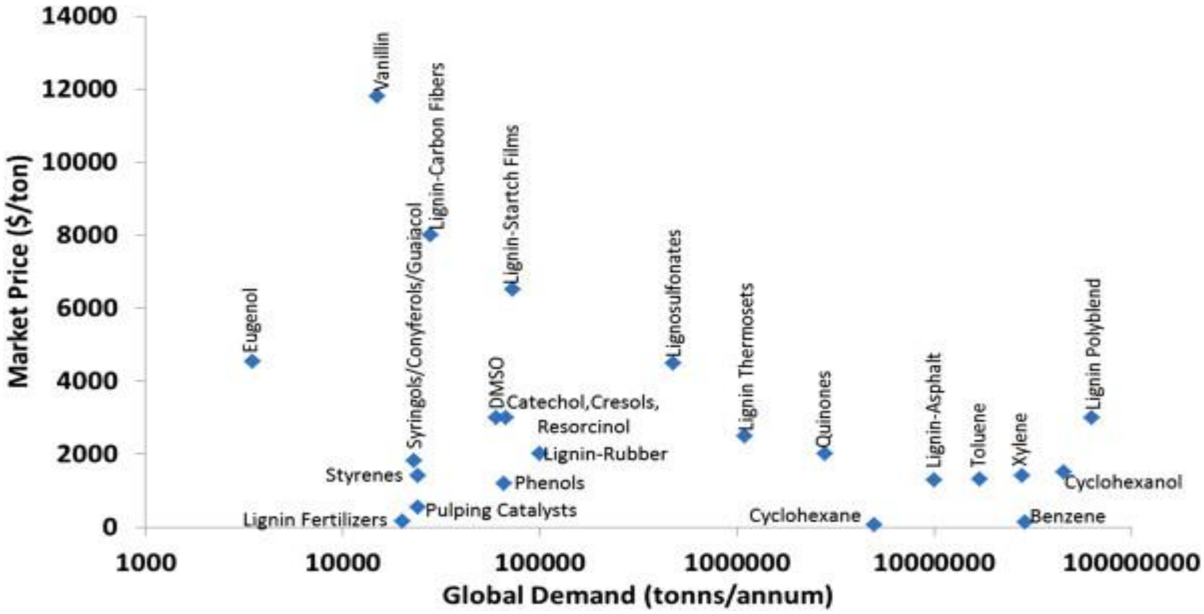


Figure 7.1. Demand and price for lignin-based products (Source: Varanasi et al., 2013)

Currently, despite research is going on, the cost of extracting high-purity lignin from plants is rather high. Identifying methods enabling the extraction of a large quantity of lignin from woody biomass with high purity and limited chemical modifications will provide a breakthrough pathway to realize the high value proposition of lignin. High-purity or high-grade lignin characterizes therefore the highest market value potential (Figure 7.2). There exist a strong correlation between the price of each type of lignin and the added value of the products derived from it. The actual value can range between USD 650-1 000 per tonne while high-purity lignin-based products can reach a value of USD 1 300-6 500 per tonne (Smolarski 2012).

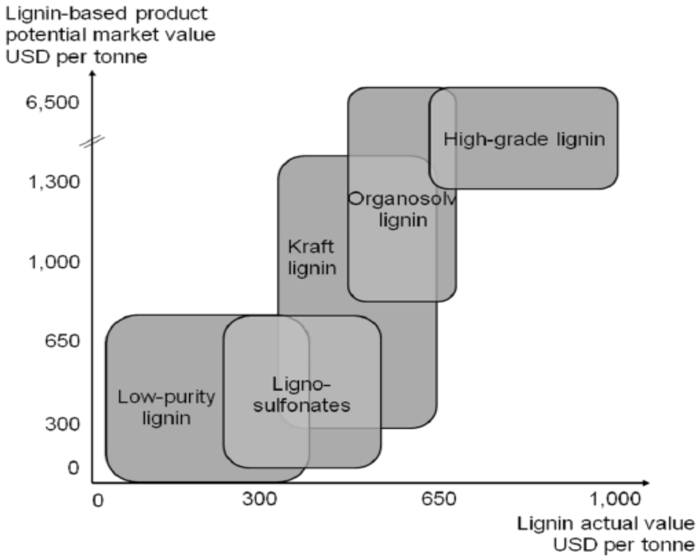


Figure 7.2. Lignin value versus lignin based product value, by lignin type (Source: Smolarski, 2012)

According to Behling et al. (2016), high-grade lignin entails good opportunities for different value added chemicals such as carbon fibers, vanillin, and phenol derivatives. They are valued between 2 500 EUR/tonne and 5 000 EUR/tonne (Figure 7.3).

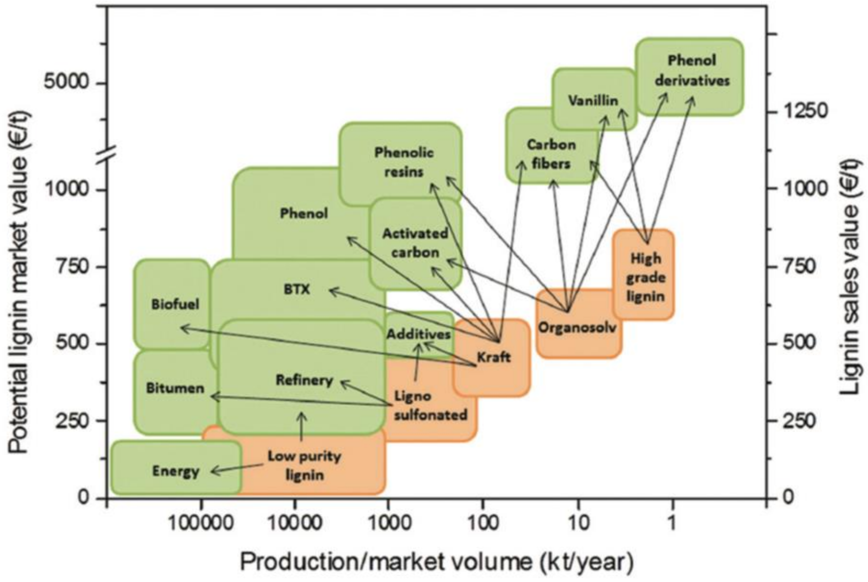


Figure 7.3. Potential market value for lignin-based products (orange) and corresponding value-added chemicals (green). Source: Behling et al. (2016)

Market volume for lignin was about approximately 1 100.0 ktonnes in 2014 representing a market value of about USD 775 million and expected to reach around USD 900 million in 2020 (Market Research Store, 2015). Regional disaggregation of market volume in 2013 places North America as the first region with its 34.9 % of market share, followed by Europe (38.9 %), and Asia Pacific countries (19.5 %) (Global Market Insights, 2017).

Biomass/yield and feedstock availability

Lignocellulosic biomass is mainly composed of cellulose, hemicellulose and lignin. The structure and the quantity of these plant cell wall components vary according to species, tissues and maturity of the plant cell wall. Generally, lignocellulosic biomass consists of 35–50 % cellulose, 20–35 % hemicellulose, and 10–25 % lignin.

Lignin as biomass can derive directly from nature or it can be sourced by industries using forestry residue, pulp or agricultural by-products (wood, corn stover, bagasse, sugar beet residue).

As for natural sources, softwoods have a lignin content of 25-30 % and hardwoods 20-25 %. Numerous annual plants have a lower lignin content, e.g. flax (around 3 wt %). Grasses typically contain up to 10 % of lignin. The total amount of lignin present in the biosphere exceeds 300 billion tonne and annually increases by around 20 billion tonne (Gregorová, Košíková and Moravčík, 2006).

As for industrial sources, lignin at present is a by-product from 2^nd^ generation bioethanol production. The annual world production of Kraft pulp is around 130 million tonne (55 million tonne of Kraft lignin) (McHenry, 2014). In addition, about 1 million tonne of lignosulfonates is produced annually, despite this availability is declining due to the higher versatility of the Kraft process.

Finally, a typical amount of lignin that can be extracted from black liquor is (45–65 $g \cdot L^{-1}$) (Humpert, Ebrahimi and Czermak, 2016).

- **Actors**

General setting

Numerous are the companies that could take advantage of high-purity lignin. The global lignin market is characterized by integration at various levels of the value chain. Numerous participants such as Borregaard, MWV, and Green Value are integrated across the value chain. These companies are engaged in lignin production which is used as captive consumption for manufacturing a range of products including aromatics, binders and dispersing agents. Both in Europe and abroad there exist different realities already using lignin as a raw material. The most relevant are listed below.

Europe

Borregaard, (Norway) (https://www.borregaard.com/)

Staatsbosbeheer, (Netherlands) (https://www.staatsbosbeheer.nl/)

AkzoNobel, (Netherlands) (www.akzonobel.com)

Avantium, (Netherlands) (https://www.avantium.com/)

Chemport Europe, (Netherlands) (https://chemport.eu/)

TNO, (Netherlands) (https://www.tno.nl/en/)

Green Value SA, (Switzerland) (https://www.greenvalue-sa.com/)

Metsa Group, (Finland) (https://www.metsagroup.com/)

Lenzing A.G., (Austria) (https://www.lenzing.com/)

VITO, (Belgium) (https://vito.be/en)

Covestro, (Germany) (https://www.covestro.com/)

Rest of the world

Mead-Westvaco (MWV), (US) (www.mwv.com)

Rayonier Advanced Materials, (US) (http://rayonieram.com/)

Liquid Lignin Company LLC, (US) (n.d.)

Domtar Corporation, (Canada) (https://www.domtar.com/en)

Asian Lignin Manufacturing Pvt. Ltd., (India) (https://www.indiamart.com)

Aditya Birla Group, (India) (www.adityabirla.com/home)

Changzhou Shanfeng Chemical Industry Company, (China) (www.sfhgyx.com/en/index.asp)

Nippon Paper Industries Co. Ltd., (Japan) (www.nipponpapergroup.com/english/)

Fibria, (Brazil) (www.fibria.com.br/)

- **Value proposition and sustainability**

Co-products

Lignin itself it is often seen as a co-product in the production of second generation biofuels. At the same time, its valorization, by transforming lignin into a valuable product, would greatly impact the remunerability of the process, making it economically viable.

The process of producing high-purity lignin entails the recovery and purification of lignin pulp, which generate residues as co-products. When wood is cooked by the alkaline process the lignin present in the wood is dissolved in the alkaline liquor (black liquor). Silica can be a co-product of lignin from black liquor despite it could require additional processing steps.

When lignocellulosic biomass feedstocks are pre-treated, lignin and hemicellulose in black liquor are generated. Mild processes applied to black liquor to separate them give rise to a stream of high-grade lignin ready for market and further transformation in high-value products, and a stream of hemicellulose containing sugars ready for fermenting. Products made from hemicellulose in bio-refinery and standard ethanol production processes, actually represent valuable co-products of the separation of high-purity lignin.

Environmental impacts, benefits, sustainability

Lignin is a renewable wood based, non-toxic alternative to fossil-based materials. Natural materials and technologies have been developed to increase health and safety, reduce emission of volatile organic compounds, energy consumption, and toxicity from manufacturing. In terms of impacts and sustainability, lignin-based products outperform their synthetic alternatives.

Socio-economic advantages, health impacts, bio vs non-bio based alternative

The declining demand for traditional products in traditional markets supports the derivation of great value from harvested biomass. The availability of woody biomass is certainly an advantage and allow securing supply. Once a reasonable production cost and a competing high-purity lignin product price are achieved the wide range of possible applications will lead to numerous business opportunities and will foster job creation.

High-purity lignin applications have the potential to be comparatively more recyclable, reusable, and compostable.

- **Outlook**

Projected trends (baseline)

Global lignin market demand was estimated at USD 4 222.1 million in 2014 and is expected to reach USD 6 190.5 million by 2022, growing at 4.9 % from 2015 to 2022.

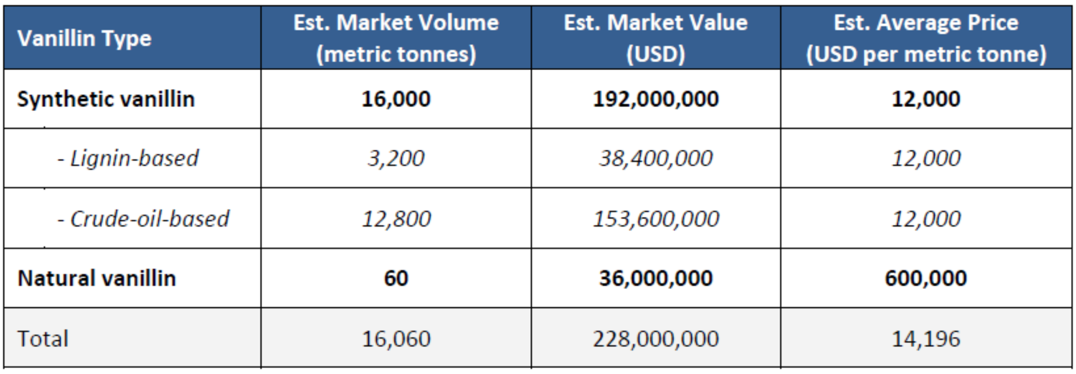
Anyway, the trend of the lignin market will strongly be correlated to that of high added value products (Aromatic monomers, Phenol, Vanillin).

BTX account for around 60 % of all aromatics representing a USD 100 billion in the market, petroleum based (24 % of the global petrochemical market in value). While aromatic applications are relatively at a nascent stage, they account for over 52 % of global revenues, owing to the use of the more expensive high-purity lignin. Volume demand for these applications is expected to grow at a CAGR of 5.7 % from 2015 to 2022.

Current phenol production volumes amount to 8 million tonnes per year, with a market value around USD 1 500 per tonne. The phenol market is expected to grow at a CAGR of 3.9 % over the next 10 years. Lignin can replace phenol in the petrochemical process, or can be used as a feedstock to produce lignin-based phenol. However, currently, neither of these uses is commercially viable, but could become so after 2025.

As for natural vanillin, while it represents around 1 per cent of the total volume it accounts for around 40 % of the total market value. Being very demanded and expensive, synthetic vanillin is still used instead of natural one, making up around 97% of vanillin used. Demand is steadily growing at an annual growth rate of 2 % in both European and American markets, and at 10 % in China.

The increase in demand and uncertainty in supply are positively affecting the natural and synthetic vanillin price (Figure 7.4).



Vanillin Type	Est. Market Volume (metric tonnes)	Est. Market Value (USD)	Est. Average Price (USD per metric tonne)
Synthetic vanillin	**16,000**	**192,000,000**	**12,000**
- Lignin-based	*3,200*	*38,400,000*	*12,000*
- Crude-oil-based	*12,800*	*153,600,000*	*12,000*
Natural vanillin	**60**	**36,000,000**	**600,000**
Total	16,060	228,000,000	14,196

Figure 7.4. Vanillin market in 2011 (Source: Smolarski , 2012)

According to FT.com (FT COM) uncertainty about the 2018 year's crop from the major world's grower (Madagascar) has driven the vanilla price to record levels ($600/kg) after a cyclone hit the tropical island off the south-east coast of Africa. Climate change and environmental conditions will likely exert higher magnitude impacts in the years to come, affecting crop prices. Producers are looking at alternative natural sources of vanilline instead of vanilla beans. This trend could foster the use of high-purity lignin for the production of vanilline, being a natural alternative to vanilla beans.

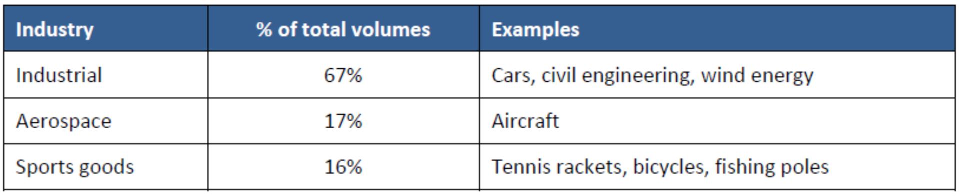
Competitiveness and role of Europe in global production

Europe have good opportunities in this sector, in relation to its strengths in wood-based industries.

The ability to take advantage of lignin’s full potential in an industrial production setting relies on different factors, such as technology maturity, interest from game-changing investors, and potential funding opportunities and options (Smolarski 2012).

In the specific case of natural vanillin production from lignin the current world leader is the Borregaard Company (Norway) which has no big competitors around the world. It achieves an estimated market share of 20 %. The increasing oil price and Asian demand of natural vanillin could make economically viable and interesting to switch to the natural vanillin production.

As for carbon fibres the global demand which was around 46 000 tonnes in 2011, is forecasted to rise to 140 000 tonnes by 2020. Sales are expected increase to USD 4.5 billion in 2020. In terms of applications, global sales of carbon fibre reinforced plastics are forecasted to reach USD 48.7 billion by 2020. On the other hand, carbon fibre price is still very high (USD 18 per kilogramme) compared to other composites and materials. It should decrease to USD 7–11 per kilogramme to become interesting. Hence, the use of lignin as an alternative to polyacrylonitrile (PAN), the precursor to almost 80 per cent of the commercial carbon fibre, could strongly reduce the cost, despite recovering a clean-pure lignin form is, in its turn, costly. In terms of carbon fibres applications, these could span from industrial to sport and goods sectors (Figure 7.5).



Industry	% of total volumes	Examples
Industrial	67%	Cars, civil engineering, wind energy
Aerospace	17%	Aircraft
Sports goods	16%	Tennis rackets, bicycles, fishing poles

Figure 7.5. Carbon fibres applications, 2010 status. (Source: Smolarski , 2012)

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8 Lignin-based carbon nanofibres

- **General information**

Product Name	Lignin-based Carbon Nanofibres (CF)
Technology readiness Level (TRL)	5-6 (Innventia, Sweden)
Biomass Platform	Lignin
Business to Business (BtB) or Business to Consumer (BtC)	BtB

Although the use of carbon fibre reinforced polymers (CRFP) is discussed for many applications, the global production of carbon fibres with approx. 50 000 t per year is low. The advantages of CRFP are their low weight, their high tensile strength and their high elasticity (comparable with steel). Commercial carbon fibres use polyacrylonitrile (PAN) as the starting raw material, but its high costs of USD 7-8/kilogram (kg) limit the application to high performance materials. Lignins, however, should permit the production of low-cost carbon fibres. Furthermore, the development of lignin-based high performance materials will result in real benefits in the contexts of increased energy efficiency, reduced environmental emissions and use of renewable raw materials. By introducing a cost-effective lignin-based carbon fibre, the CRFP market could increase considerably. In Europe, the development of manufacturing carbon fibre-reinforced plastic composites from kraft lignin is driven by RISE (Research Institutes of Sweden) in close cooperation with Swerea SICOMP, KTH and industrial operators (such as Södra Skogsägarna, Scania, Volvo Cars, Fiat, Oxeon, Netcomposites, etc.) in different projects (Innventia, 2019).

- **Product description**

Chemical-physical characteristics

By far the most important starting material for the production of carbon fibres is polyacrylonitrile (PAN) with the chemical formula $[C_3H_3N]_n$. PAN is a hydrocarbon with an attached nitrogen in a triple bond: $[-CH2-CH\ (C\equiv N)\ -]_n$. 90 % of world production of carbon fibres comes from PAN (Ullman, 2011). The polyacrylonitrile fibres are dehydrated for 5 to 10 hours at 250-300 °C and subsequently cooked in partial oxidation (pyrolysis) in an atmosphere of nitrogen at 1 500 °C for 1 to 3 hours. The nitrogen is expelled and a carbon fibre which is 7 µm thin and almost pure remains. Graphitization (structural change) at 2 500 °C further increases the stiffness of the fibre for high-quality applications (Römpp, 2018; Ullmann, 2011). Carbon Fibre Reinforced Plastics (CFRP) is a composite of carbon fibres embedded in a plastic matrix. The matrix used in high-quality applications is epoxy resin, which hardens through the reaction of two components which form a thermosetting plastic. Other thermoplastics and thermosets are used in certain applications. The carbon fibre significantly increases the strength and rigidity of the matrix material in the fibre direction. Transverse to the fibre direction, the inserted fibres cannot absorb forces; the strength of the base material is weakened in this direction. In order to absorb the expected forces of the component, the carbon fibres are used as intersecting fibre layers. To prevent the carbon fibres from being pulled out under load, there must be an intimate adhesive bond between the fibre and the plastic matrix.

Table 8.1. Comparison of carbon fibre with other materials (Ullmann, 2009)

Material	Density g/cm^3	Tensile strength N/mm^2	Elasticity Modulus N/mm^2
Carbon fibre	1,75	3 500	230 000
High-tensile steel	7,87	1 300	210 000
Aluminia	2,7	370	70 000
Glass fibre	2,60	3 400	22 000

The main disadvantage for broad industrial use, in comparison with metals, is the complex and thus expensive forming operation: The carbon fibre parts have to stay in the presses for 10 minutes for hardening, while deep drawing steel parts have cycle times of a few seconds. So typical CFRP products in the past have included high-priced tennis rackets, bicycle frames, fishing rods, ski poles, boat hulls and wind turbine blades. However, the material is also gaining importance in aircraft and vehicle construction. The hull of the Boeing 787 "Dreamliner" is entirely made of CFRP. Airbus also uses CFRP components in its aircrafts. In addition, BMW have built their *i*-Series vehicles with monocoques of CFRP.

A survey among engineers shows the opinion; CFRP could only be used as a material on the broad market if a high-quality recycling process was available. The aim must be to recover the carbon fibres without the loss of quality and it must be possible to reuse them for high-quality components in the manufacturing process (EUWID, 2015).

Advantages of lignin-based carbon fibres

The advantage of lignin-based carbon fibers is cost structure for the raw material source as well as processing, which is commonly derived from wood via Kraft pulping. Lignin is also a by-product of cellulosic ethanol production, so the supply will increase as biorefineries are built. However, the lignin quality from processing of different feedstocks are different: hardwoods, softwoods and annual plants. The development of the bio-based society is an important trend which fits with the development of lignin-based CFs. It is assumed, that lignin fibres would be less expensive than other precursors by ~USD 2-3/kg. The cost for lignin-based CF has a potential to be more stable and largely independent of oil prices (Downing, 2013). It also important to add that the properties for lignin-based CFs are more, but in future not restricted to, focused on opportunities with "a good enough" CF to a lower price compared to todays PAN-based CF.

Disadvantages of lignin-based carbon fibres

For more than 40 years, activity in research and patents have shown a wide interest for lignin-based CFs, which are offered readily available at relatively competitive prices. The first CFs made with lignosulfonate lignin, using poly (vinyl alcohol) as a plasticizer, were developed and manufactured by NipponKayuka Company under the name of Kayacarbon between the years 1967 and 1973 (Laurichesse and Avérous, 2014).

Various types of lignin have been studied for the production of low-cost CFs, however there is not much scientific work on the initial selection of the optimal lignin quality for production of CFs. Kadla et al. (2002) use Kraft lignin without chemical modification. This was the result of a concept study because they reported the first lignin-based CF made with commercially available Kraft lignin, without any selection of an optimal starting material. The use of pyrolysis lignin has also been studied, showing that under precise condition parameters, the mechanical properties of CFs prepared in this way were similar to those obtained using Kraft or Alcell (organo-solv) lignins (Qin, 2012).

But until the present the challenges for lignin-based CFs are the need to purify lignin (i.e. selection of the optimal lignin quality) to make it suitable for melt spinning and carbon fibre production. This increases the cost of lignin-based CFs, even though lignin is a low cost raw material compared to PAN, and can provide mechanical properties suitable for commercial grade CFs (Warren, 2006; Maradur et al., 2012).

Production process

The CF manufacturing process involves melt or wet-spinning, oxidative stabilization at 200-300 °C and carbonization under an inert atmosphere at 1 000-2 000 °C, (in some cases, graphitization at 2 000-3 000 °C), which is then followed by surface treatment and sizing (Norberg et al., 2013). About 50 000 of the wafer-thin carbon fibres are twisted into an endless thread and wound onto spools. With these carbon threads textile scrims (textile mats) are woven, which absorb the forces in the later composite with the plastic matrix (Marscheider-Weidemann et al., 2016).

Figure 8.1. The cost of manufacturing carbon fibre divided into terms of percentages

(Source: Frost&Sullivan, 2016)

As per the percentage split shown above, around 50 % of the total cost of carbon fibre manufacturing is due to the precursor (PAN). This is due to the high cost of acrylonitrile (AN), the low mass throughput of wet spinning, the quality of the PAN and the low conversion yield of the precursor to carbon fibre (~50 %). For this reason, companies and research institutes are looking at other precursors such as textile-grade PAN, rayon, pitch, lignin, and polyolefin.

The next most expensive step is the oxidation process when, usually, big convection ovens are used. Companies are trying, among others, plasma oxidation and microwave-assisted plasma carbonization, and advanced surface treatments and sizings. Plasma oxidation consumes significantly less energy and reduces the processing time by over 65 %. This technology is being developed by RMX Technologies along with Oak Ridge National Laboratory (Frost&Sullivan, 2016).

A complementary area of lignin research which has attracted increased attention in recent years is the use of lignin to produce carbon nanofibre (CNF) materials (Dallmeyer et al., 2014; Hu et al., 2014; Lai et al., 2014; Wang et al., 2013). These CNFs differ from carbon fibre in that the diameter of the fibres is submicron in size (Graichen et al., 2017). The CNFs are produced by electrospinning which results in a CNF web, normally without any orientation of the nano fibres. Carbon nanofibres are a rapidly emerging new class of carbon nanomaterials with a range of potential applications including the use in batteries, supercapacitors, fuel cells, structural composites and filtration devices (Inagaki et al., 2012; Zhang et al., 2014). A lignin solution can be electrospun to form lignin nanofibres, which is a different process to melt-spinning. The lignin nanofibres can then be converted to CNFs through thermal stabilization and carbonization processes which are much faster than for CFs (Baker and Rials, 2013).

Producing CNFs from electrospun lignin offers several advantages over using PAN that include improved nanofibre production rates, a lower carbonisation temperature and no emission of toxic gases, and the benefits of using a low cost, renewable bio-based feedstock.

- **Markets**

Current volume, market value, prices:

The current global production of carbon fibres is approximately 60 000 t (Frost&Sullivan, 2016). Carbon fibre is used in applications where high mechanical performance and low weight are more important than low cost. Carbon fibre is therefore currently used primarily in applications with a demand for high mechanical performance, such as sports equipment, aircraft, satellites, Formula 1 cars, pressure vessels, specialized tools, wind turbine components and for reinforcing concrete in areas with a high risk of earthquakes. However, the automotive industry is seriously evaluating the use of carbon fibres in vehicles. WE and EU regulations to reduce carbon dioxide emissions and improve fuel efficiency primarily drive this. Another need is to reduce the weight of vehicles; the light weighting trend is especially prevalent in these two regions. With a lower price, the market for carbon fibre would be considerably larger than it is today.

The global market size for carbon fibres was estimated to be approximately USD 2.5 billion in 2015. According to Frost&Sullivan (2016), the market is assumed to reach USD 3.8 billion by 2020 at a CAGR of 8.7 %. The market volume for 2015 was estimated at 60 000 t and is expected to reach 102 kilo tonnes (kt) by 2020 at a CAGR of 11.2 %, see figure 3-1.

Presently, the price of PAN is around USD 7 to USD 8/kg and non-aerospace-grade carbon fibre is around USD 20 to USD 30/kg (Frost&Sullivan, 2016).

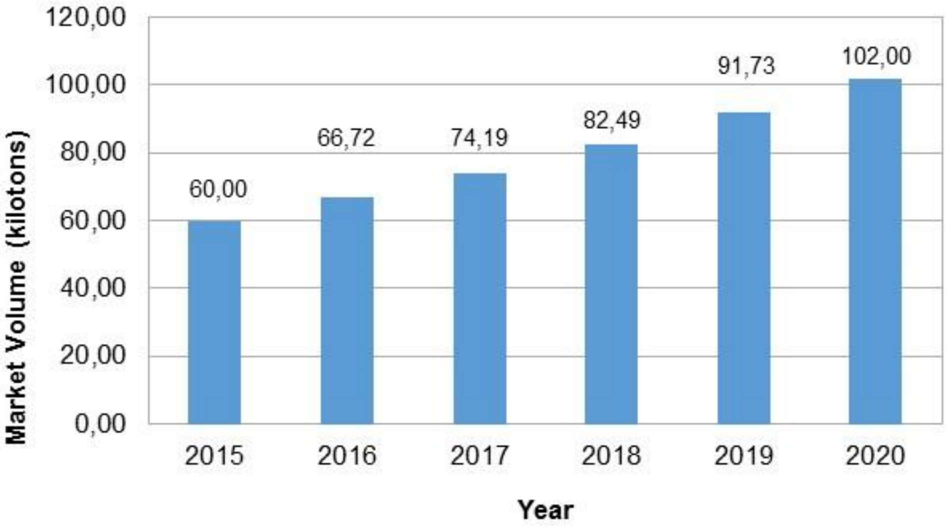

Figure 8.2. Global carbon fibre market volume, forecast 2015-2020 (Source: Frost&Sullivan, 2016)

Biomass/yield and feedstock availability

Using PAN, the yield of the precursor to carbon fibre is approximately ~50 %. This can also be assumed for lignin (Brodin, 2012).

According to Gosselink (2011), the Pulp & Paper industry extracted globally 50 million tonnes of lignin. Only 2 % are commercial lignins, of these 1 million tonnes are lignosulfonates, 0.1 million tonnes kraft lignins and 5 000-10 000 t sulphur-free lignins. Efficient processing and extraction can make 2-4 mt of extra kraft lignin possible in 2020.

- **Actors**

General setting

Key research groups in the field of low-cost carbon fibres manufacturing, including RISE Bioeconomy (former: Innventia AB; Norberg et al., 2013), have developed technologies for melt-spinning lignin fibres and thermally processing these fibres into carbon fibre.

Europe:

RISE Bioeconomy: Baker et al. (2017) have developed a new softening agent for melt spinning softwood Kraft lignin based on ultra-filtrated black liquor. They obtain CFs of very good quality solid carbon fibres. In parallel, they have also developed a method to stabilize lignin-based CFs using special oxidative conditions. These improvements in lignin-based CFs have the potential of reducing time and cost production and of using lignin in larger scale applications (WO, 2012).

Innventia (today RISE Bioeconomy) coordinates and brings key competence (research on optimal lignin quality for CFs) to the GreenLight project where lignin-based CFs are developed (www.greenlight-project.eu/) using 100% lignin from a softwood kraft pulp mill. RISE Bioeconomy also develops lignin-based CNF:s and have used neddleless electrospinning to produce a 0.5 m wide web of lignin nano fibres and converted these lignin nano fibres to CNFs.

The work by Innventia (RISE Bioeconomy) has been shown in demonstrators such as a car roof for a toy car (Volvo) made by waived lignin-based CFs and a battery for this car made with electrodes from lignin-based CFs and a lignin-based resin. The work on lignin-based batteries and super capacitors is done together with KTH in Stockholm and Queen Mary University in London.

Stokes Laboratories at the University of Limerick in Ireland lead the European project LIBRE – Lignin-Based Carbon Fibres for Composites (LIBRE, 2018). The goals of the project are the development of new bio-based composite materials utilising lignin from the pulp and paper industry blended with biopolymers as a precursor and to reduce energy consumption and greenhouse gas emissions during the manufacturing process by using microwave and radio frequency (MW/RF) heating technologies. Other aims are surface functionalisation using non-aqueous processes to enhance the performance of polymer composites and to increase the sustainability of composite materials.

Rest of the world

The US are the biggest market for carbon fibres. The primary research focus area of the region is developing low-cost industrial grade carbon fibres. The major focal areas are: alternative precursors like textile-grade PAN, advanced, energy-efficient processes and scaling of the production processes. Research institutes like Oak Ridge National Laboratory (ORNL) and Michigan State University are focusing on developing disruptive cost reduction processes in the manufacturing of carbon fibres without sacrificing the performance of carbon fibres (Graichen et al., 2017). More actors characterize the United States arena compared to the European scenario.

Researchers at Scion and Revolution Fibres (Auckland, New Zealand) have recently developed a technology for producing non-woven carbon nanofibre mats from an industrial lignin. In the first step, lignin-based solutions have been electrospun on a commercial scale producing continuous metre-wide lignin nanofibre mats. Two different lignin formulations were developed based on laboratory and pilot-scale testing. Lignin nanofibre mats with a range of fibre densities and nanofibre diameters could be produced, depending on the lignin formulation and the production rate used (Graichen et al., 2017). Lignin-derived CNF mats could be produced with a range of thicknesses, weights and fibre diameters, depending on the lignin formulation and processing conditions used. The mats exhibited high surface areas and excellent electrical properties, both of which are important parameters for use as electrodes in batteries or supercapacitors. A key point of the difference of lignin-derived carbon nanofibres is their low production cost relative to other carbon nanomaterials.

- **Value proposition and sustainability**

Co-products

There are no co-products from the production of lignin carbon fibres. Environmental impacts, benefits, sustainability

The use of low cost lignin carbon fibres from lignin enables a broader use of lightweight materials in end-user industries such as automotive and aerospace. Carbon fibre composites can reduce the weight of a vehicle by up to 50 % and improve fuel efficiency.

Up to now, carbon fibre cannot be recycled like other materials; it can be chopped and molten. However, the resultant material loses its strength and cannot be reused.

Socio-economic advantages, health impacts (also comparison with alternatives):

The development of low cost carbon fibres can generate inputs in other sectors like thermal insulation at high temperatures, batteries that use commercial carbon fibres as active electrodes or storage of hydrogen gas with activated carbon fibres made from lignin (Axegård et al., 2018).

Economics: bio vs non-bio-based alternative:

As discussed, the main benefit of lignin-based carbon nanofibres is seen in finding a low-cost precursor other than PAN. PAN is relatively costly (USD 7- 8/kg), Lignin has an average gross price of USD 660 per tonne dry solid (for 2013). Non-aerospace-grade carbon fibre is around USD 20 to USD 30/kg (Frost&Sullivan, 2016).

- **Outlook**

The RISE Research Institutes of Sweden – Innventia, SP, Swerea and Swedish ICT published a roadmap for lignin-based carbon nanofibres for the period 2015-2025 (Axegård et al., 2018). The following information is mainly taken from this publication.

Projected trends (baseline):

As indicated above, currently lignin-based carbon fibres production is mostly in development (TRL 4-6) and the market entry on commercial scale a few years away. A first demonstration plant with 50.000 tonnes is planned in Sweden. Hence, the market volume in 2020 will be minor. According to current announcement, production on commercial scale will be ready well before 2025. Although at present mainly Research institutes are developing lignin-based CF, there are a number of firms in the conventional carbon fibre market, which will be active, when lignin-based carbon nanofibre will reach technological and price targets.

Because of the early stage of developments, estimates for price or cost development for lignin-based carbon fibres are speculative. The developers of lignin-based carbon fibres assume that the total precursor cost in carbon fibres may be USD 2-3/kg for lignin compared to USD 7-8/kg for PAN (Frost & Sullivan, 2016). Thus, one can achieve low-cost carbon fibres (~USD 10-12/kg), which are of interest for the automobile market.

Competitiveness and role of Europe in global production:

Up to now, there is no production of lignin-based carbon fibres or lignin-based carbon nanofibres.

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9 Lignin bio-oil

General information

Product Name	Lignin bio-oil
Technology readiness Level (TRL)	5
Biomass Platform	Lignin
Business to Business (BtB) or Business to Consumer (BtC)	BtB (maybe eventually BtC)

Bio-oil is the fluid product of the chemo-thermal conversion of biomass, preferrably via some sort of fast pyrolysis (Bridgwater, 2012; Kan et al., 2016; Mortensen et al., 2011). Alternative labels are pyrolysis oil, pyrolysis liquid, pyrolysis tar, bio-crude, wood liquid, wood oil or wood distillate (Kan et al., 2016). The liquid constitutes a complex mixture of hundreds of organic compounds like acids, phenols or lignin-derived oligomers (Kan et al., 2016; Zhang et al., 2013; Xiu and Shahbazi, 2012).

As pyrolysis feedstock can comprise different materials (e.g. energy crops or leather waste) (Bridgwater, 2012) *lignin* bio-oil denotes pyrolysis oil derived from any feedstock containing lignin (crop residues, sawdust, wood chips, etc.) Lignin is one of the most abundant natural polymers. It is one of the three plant constituents together with cellulose and hemicellulose. The major source of industrially available lignin today is the pulp and paper industry. Currently most of the potential feedstock is used as fuel, nonetheless: In 2015, 180 mt of pulp was produced (Bogliano, 2016), which translates into between 50 to 70 mt of potential lignin capacity annually (Bogliano, 2016; Gosselink, 2011; Laurichesse and Avérous, 2014), out of which around 95 % are burned to fuel boilers in the pulp plants locally and 2-5 % is used for low value commercial applications (Gosselink et al., 2004; Gosselink, 2011; Laurichesse and Avérous, 2014). Lignin from the pulp and paper industry is usually Kraft lignin (Schutyser et al., 2018), which is not pure lignin but a sulphided/sulphated product and is thus different to pure lignin (Bruijnincx et al., 2016).

Thanks to its chemical structure, lignin is not only suitable for energy production, but also as a platform molecule for bio-based chemical development (Bogliano, 2016; Kan et al., 2016). Possible deployment of bio-oil comprises electricity and heat production in boilers, furnaces, and combustors, diesel engines and gas turbines. Alternatively, one could use it as input to obtain special chemicals like phenols for resin production, additives in pharmaceutical or flavouring agents in food industries (Kan et al., 2016). In consequence, lignin bio-oil might substitute fossil-oil in various applications. Given that in 2016 the global production of such oils (conventional crude oil, tight oil, extra-heavy oil and bitumen) amounted to about 76 million barrels per day (mb/d) with a projected growth up to 2040 (OECD, 2017), bio-oil seems to have a huge market potential.

Product description

Chemical-physical characteristics:

In general, bio-oil is a dark brown, free-flowing liquid with a smoky smell (Kan et al., 2016; Zhang et al. 2013). Its general composition depends on feedstock and process conditions. Over 300 different compounds have been described with principle classes such as water, hydroxyaldehydes, hydroxyketones, sugars, carboxylic acids, esters, furans, guaiacols, and phenolics (Kan et al., 2016; Mortensen et al., 2011).

Since it contains up to 30 weight percent (wt%) of water, bio-oil is immiscible with crude oil, which consists of hydrocarbons (Mortensen et al., 2011). In addition, its oxygen content lies between 10 wt% and 50 wt%, influencing its homogeneity, polarity, viscosity and acidity. In fact, the elevated oxygen content is a major reason for bio-oil's various drawbacks (Bridgwater, 2012; Mortensen et al., 2011). Together, water and oxygen content also affect the oil's heating value, which is only about half that of conventional fuel oil. For example, Zhang et al. (2013) list values of between 19 MJ/kg for wood pyrolysis oil compared to 40 MJ/kg for heavy petroleum fuel oil. Also, bio-oil shows poor ignition and combustion values (Zhang et al. 2013). Its pH value ranges from 2 to 4. This is mainly due to the contained carboxylic acids and makes the substance corrosive. In terms of storage, transport and processing equipment, some construction materials (e.g. carbon steel, aluminium) hence cannot cope with the oil (Mortensen et al., 2011; Zhang et al., 2013). Furthermore, it comprises highly reactive compounds, so that it is rather unstable when stored, which affects viscosity, heating value and density (Mortensen et al., 2011; Kan et al., 2016). From an engineering point of view, one can address such drawbacks by supplemental treatment, i.e. by upgrading the oil (Bridgwater, 2012; Zhang et al., 2013). Yet, besides technical challenges (Bridgewater, 2012), doing so drives production cost (Xiu and Shahbazi, 2012).

As compared to fossil fuels, bio-oil promises potential advantages. To start with, its feedstock is based on renewable resources and might even comprise waste materials. In terms of global warming potential, one can consider the combustion of bio-oil CO_2 neutral, since it only releases as much CO_2 is as was taken up during feedstock growth and as will be taken up again, if additional feedstock is grown. Likewise, combustion generally does not yield any SO_2 emissions due to the insignificant sulphur content of plant feedstock. Lignin taken directly from Kraft processes would produce sulphur emissions depending on technology. Similarly, NO_x emissions are reported to be below those of diesel oil if used in a gas turbine (Xiu and Shahbazi, 2012).

Main uses:

Given corresponding product portfolios, many stakeholders seem focused on possible fuel applications of bio-oil. For example, Finnish Fortum Power and Heat markets its *Otso bio-oil* as an option for heat and steam production (Fortum, 2018). Likewise, Canadian Ensyn promotes its *Renewable Fuel Oil* for heating and cooling purposes (Ensyn, 2018a). In addition, the company also presents its bio-oil as a blend to be processed alongside petroleum to reduce products' carbon footprints (Ensyn, 2018b). Nevertheless, Ensyn (2018c) also highlights the possibility to use its product as an intermediate to create chemicals for food flavours.

Production process:

As initially stated, lignin bio-oil is obtained from the chemo-thermal conversion of biomass containing lignin. A preferential production mechanism is pyrolysis, i.e. the thermal decomposition of biomass in the absence of oxygen and without solvent (e.g. Fan et al., 2017; Kan et al., 2016; Schutyser et al., 2018; Zhang et al., 2013). The process always yields the three products (bio) oil, char and gas to a degree depending on the specific process parameters (Bridgwater, 2012; Schutyser et al., 2018). Fast (heating rate > 10-200 °C/s, hot vapour residence time < 2 s) and flash pyrolysis (heating rate > 10^3 - 10^4 °C/s, hot vapour residence time < 0.5 s) create up to 70 wt% or 80 wt% of bio-oil based on dry biomass feed yield (Kan et al., 2016).

The process scalability seems to be subject to discussions yet (e.g. Kan et al., 2016; Schutyser et al., 2018; Xiu and Shahbazi, 2012).

- **Markets**

Current volume, market value, prices:

Due to its different chemical-physical properties compared to fossil fuels, bio-oil is not yet capable to substitute for its petroleum counterparts.

Nevertheless, one can expect replacement to some extent as concerns industrial power and heat generation (Bauer, 2017; Lehto, 2013) or marine markets (IEA, 2018). Alternatively, one can already use it as a blending component for petroleum fuels today. Canadian company Ensyn, markets its biocrude as a way to reduce fossil refinery streams' carbon intensity. Moreover, co-refining up to 5 % alongside petroleum streams still lead to renewable gasoline and diesel in accordance with ASTM standards (Ensyn, 2018b). Another application of bio-oil could be as a chemical intermediate. Assuming that about 5 % of fossil oil production is used as feedstock for high value chemicals (Bridgwater, 2012) there seems to be untapped market potential.

Bauer (2017) declares that pyrolysis oil production by 2018 was at least 500 000 tonnes and that the price of pyrolysis oil from Canada delivered to Rotterdam was about USD 13 per Giga Joule in 2014 (about USD 228 per tonne). Assuming these values to be representative, a possible volume of the bio-oil market might be around USD 114 million per year. Beyond this claim, there does not seem to be much market data yet.

Anyway, given the liquid's current technology readiness level and the corresponding uncertainties, it seems wise to orient to conservative figures. Moreover, although business analysts claim that bio-oil was above-medium attractiveness and success probability, it still ranks below comparable products like biogas (Frost & Sullivan, 2015).

Biomass/yield and feedstock availability:

For a successful production of lignin bio-oil, a sustainable supply of lignin feedstock proves to be key. The total lignin availability in the biosphere exceeds 300 billion tonnes (bt) annually growing by around 20 bt (Frost & Sullivan, 2012). At industrial level, lignin production especially takes place during the pulping process in paper production (Baskar et al., 2012; Bruijnincx et al., 2016). Kraft pulping probably will remain the predominant method to separate lignin from cellulose and hemicellulose for papermaking (Schutyser et al., 2018).

At the moment, out of 50 to 70 mt of annual global lignin production, only 2 % to 5 % is used for low value commercial applications (Gosselink et al., 2004; Gosselink, 2011; Laurichesse and Avérous, 2014).

- **Actors**

General setting:

According to market research, key players in biomass pyrolysis, the crucial technology for bio-oil production, come from North America and Europe (Frost & Sullivan, 2016). However, despite the liquid's potential to substitute for fossil fuels and for chemical feedstock (Biorizon, 2017; Kan et al., 2016) and although research and commercialization attempts are ongoing (Bauer, 2017; Bridgwater, 2012; Kan et al., 2016), currently only a few actors can be traced who effectively operate bio-oil production facilities on a larger scale (Empyro, 2018d).

Europe:

Two research projects currently dealing with lignin bio-oil as identified by experts from the University of Bologna (UNIBO 2018) are:

AGROinLOG: It includes partners from six EU member states and aims at assessing the technical, environmental and economic feasibility of integrated biomass logistic centres (AGROinLOG, 2018a; AGROinLOG 2019). On one project demonstration site, the potential of bio oil production from the residues of straw-ethanol production shall be evaluated (AGROinLOG, 2018b).

FALCON biorefinery: Partners from seven European states (Falcon, 2018a) research the conversion of lignin waste from bioethanol production into low-sulphur marine fuel, feedstock for aromatic fuel additives or for chemical building blocks. One objective is to replace thermo-chemical transformation by enzymatic treatment (Falcon, 2018b).

As regards commercial development and application of bio-oil technology and products, notable companies are located in the Netherlands as well as in Finland.

BTG-BTL: a Dutch company, subsidiary of BTG, focuses on dissemination of its proprietary fast pyrolysis technology (btg-btl, 2018a). In 2005, it built a semi-commercial pyrolysis plant in Malaysia, which processed 2 tonnes (t) per hour of palm oil mill residues into 28.8 t of bio-oil a day (btg, 2018).

Empyro: a joint venture between BTG-BTL, Tree Power, a private investor and the province of Overijssel, started operating a demonstration pyrolysis plant in the Netherlands in 2015 (btg-btl, 2018b). The facility should process 120 t per day of wood residue, producing 20 million litres of bio-oil, 80 000 t of steam and 4 500 MWh of electricity on a yearly basis which translates into a CO_2 reduction of about 24 000 t (Empyro, 2018a). The project consortium comprises actors from Denmark, Germany and the Netherlands (Empyro, 2018b; Empyro 2018c).

Fortum Power and Heat: a Finnish energy company that operates a commercial pyrolysis facility in Finland since 2013, which is integrated into a combined heat and power plant. Fortum labels the obtained oil *Otso bio-oil* (Fortum, 2018). Valmet Corporation constructed the facility as turnkey delivery. Its output amounts to 50 000 t of bio-oil per year (Valmet, 2013) at a process capacity of 10 t of feed per hour (Empyro, 2018d).

Green Fuel Nordic: a Finnish biorefining company that plans to build biorefineries in Finland and to produce bio ash and bio oil (Green Fuel Nordic, 2018a; Green Fuel Nordic 2018b).

Valmet Corporation: a Finnish technology provider for the pulp, paper and energy industry advertises an integrated pyrolysis concept for boiler plants (Valmet, 2018). Since 2007, Valmet has been cooperating with Fortum, UPM and VTT in a project on integrated pyrolysis technology (Valmet, 2013).

UPM: a Finnish forest-based products company which researched integrated pyrolysis technology in the past together with Valmet Corporation, Fortum and VTT (Valmet, 2013). The company inter alia supplies BioVerno Diesel and Naphtha, which it derives from pulping tall oil (UPM Biofuels, 2018a).

VTT Technical Research Centre of Finland: VTT's fast pyrolysis group was a part of an IEA pyrolysis network for several years. Altogether, VTT has developed fast pyrolysis technology since 1982 (Empyro, 2018d) taking part in projects including the operation of four pyrolysis plants. From 2008 to 2014, it contributed to the commercial development of an integrated pyrolysis plant together with Valmet, Fortum and UPM (VTT, 2018).

As regards key multinational European energy companies, Bologna experts name Royal Dutch Shell and Total (UNIBO, 2018).

In the end of 2017, Royal Dutch Shell opened a new technology centre in India. Onsite, the company plans to build a demonstration plant in order to pioneer efforts in terms of the so-called IH2 technology, a catalytic thermo-chemical process to convert lignocellulose and other biomass types into fuel (CRI Catalyst, 2014; Shell 2017).

Likewise, Total together with five partners collaborates in a project to produce biofuel from lignocellulose feedstock via thermochemical conversion. Total plans to have the technology at demonstration level in 2020 (Total, 2018).

Rest of the world:

Like in Europe, a notable market for bio-oil does not seem to exist and one readily finds cases of businesses, which proved unsuccessful in the end (Empyro, 2018d). Overall, bio-oil seems to be a field largely occupied by Canadian and US actors.

ABRI-Tech: the Canadian company offers products and services for thermochemical biomass transformation like biomass dryers and pyrolysis units (ABRI-Tech, 2018a; ABRI-Tech, 2018b). ABRI-Tech is said to have operated at least 4 units with a maximum capacity of about 2 t per hour in the past (Bridgwater, 2012).

Avello Bioenergy: The US based company commercialises proprietary technology developed at Iowa State University. Via its FRAC process, it converts biomass into several pyrolysis oil fractions and biochar (Avello Bioenergy, 2018a; Avello Bioenergy, 2018b). Projections suggest that products will be fully competitive in the range of USD 50-65 per barrel oil equivalent (assuming USD 60-70 of cost per dry tonne feedstock) (Lane, 2015).

Battelle Memorial Institute: a US research company, which inter alia investigates biofuels (Bloomberg, 2018a). In a past project, it produced up to 60 gallons of upgraded carbon fuel per dry tonne of feedstock. This meant a remarkable efficiency gain. Moreover, Battelle developed a pilot mobile pyrolysis system that yields about 130 gallons of bio-oil per day at an input of 1 t woody residues. The machine's mobility allows for lowering the cost of feedstock transport (Lane, 2015).

CanmetENERGY: a Canadian governmental research and technology organization in the field of energy research, which also cooperates with industry (NRC, 2018a). Within its research focus on renewable energy, CanmetENERGY inter alia investigates second-generation bio fuels like pyrolysis or bio-oil, respectively (NRC, 2018b).

Ensyn: the Canada based company supplies a bio-oil called biocrude, which can be used either directly as fuel oil for heating and cooling or as blending component for fuels, or as intermediate to produce chemical compounds such as fragrances. It is derived from lignocellulose feedstock via Ensyn's proprietary RTP technology, a commercial thermal conversion process (Ensyn, 2018b; Ensyn, 2018d). Besides its Ontario plant that produces about 86 thousand barrels of biocrude per year (kb p.a.), Ensyn has envisaged additional facilities in Canada (300 kb p.a.) (Ensyn, 2018e), Brazil (629 kb p.a.) (Ensyn, 2018f) and the US (571 kb p.a.) (Ensyn, 2018g) as well as expansion beyond. Next to its own plants, Ensyn sold five RTP plants to Red Arrow (now Kerry) with the largest being able to process 30 to 40 dry tons a day. The American food chemicals company manufactures food ingredients and heating fuels from the obtained biocrude (Ensyn, 2018h). To capitalise further on its RTP technology, Ensyn closely cooperates with US company Honeywell UOP in terms of licensing and supply of RTP equipment as well as commercialisation of refinery co-processing (Ensyn, 2018d).

UOP Honeywell: a US company that inter alia supplies and licenses process technology, equipment and consulting to petroleum refining, petrochemical and gas processing industries (Bloomberg, 2018b). Envergent Technologies, a joint venture between UOP Honeywell and Ensyn, offers Ensyn's proprietary RTPTM thermal conversion technology (Envergent, 2018). Within its renewable fuel business line, UOP Honeywell offers diesel and jet fuel made from oily and fatty biomass inputs, which are with fossil fuels

(Honeywell UOP, 2018a; Honeywell UOP, 2018b). According to market research, UOP Honeywell holds two recent key patents for the production of low oxygen bio-oil and for the use of low water biomass for pyrolysis (Frost & Sullivan, 2016).

- **Value proposition and sustainability**

Co-products:

Pyrolysing biomass always produces the three substances char, gas and bio-oil. Nevertheless, one can maximise one of these by specifically varying process parameters (Bridgwater, 2012; Kan et al., 2016). Moreover, if using fast or flash pyrolysis to maximise oil yield, one can use char and gas to provide the heat required for the conversion process. According to Bridgwater (2012), burning char in a conventional system could make the process self-sufficient. In fact, both Ensyn and Empyro burn all char they obtain from the process in order to produce heat for pyrolysis. Moreover, one could utilize excess combustion heat for drying the feedstock or sell as energy.

Environmental impacts, benefits, sustainability:

As compared to fossil-based oil, lignin bio-oil provides more sustainable features. For example, it is able to harness waste streams as a feedstock (Bridgwater, 2011; Xiu and Shahbazi, 2012). Thus, it could contribute to the goal of a circular economy, making it an efficient and environmentally sound chemical and energy option. Moreover, using waste as feedstock would prevent bio-oil from competing with food production. However, if specific feedstock is produced, the oil's LCA probably changes depending on the applied production method. For example, intensive agricultural or silvicultural production systems coud lead to eutrophication, the loss of biodiversity (EEA, 2017; UBA 2017, UBA 2018) or an increase in CO2 emissions due to land use change.

Regarding the use of bio-oil, one may consider it a carbon neutral fuel in terms of combustion, since it does not add overall greenhouse gases when burnt. Moreover, some studies seem to indicate that deploying bio-oil might result in a decrease in greenhouse gas emissions. For instance, citing different publications, Peters et al. (2015) list values from 60 % to 88 % as compared to fossil fuels[2]. In the same vein, bio-oil is said not to produce any SO_x emissions thanks to lignin's commonly low sulphur content. Likewise, NO_x emissions are reported to be below those of diesel oil if used in a gas turbine (Xiu and Shahbazi, 2012).

With respect to product safety, bio-oil shows two appealing traits. First, it seems to be better biodegradable (Blin, et al., 2005; Zhang et al. (2013). Furthermore, apparently it is of low eco-toxicity (Blin et al., 2005).

Socio-economic advantages, health impacts:

In 2005, a comprehensive study on the (eco-) toxicity of bio-oil was completed (Blin et al., 2005; IEA, 2018). The authors analysed 21 bio-oils from most commercial producers worldwide considering factors, which might influence toxicity or mutagenicity. Out of these, one representative oil was chosen and scrutinised in-depth. Given the results of the conducted toxicological experiments (e.g. Bacterial reverse mutation test on *Salmonella Typhimurium*), the researchers concluded that bio-oils do not pose significant health, environmental or safety risk overall (Blin, et al., 2005; Bridgwater, 2012).

Economics: bio vs non-bio-based alternative:

Following Bauer (2017), if oil prices rose above USD 55 per barrel, pyrolysis oil would have a price advantage over fuel oil. In addition, in 2014 Ensyn and Honeywell UOP declared that their RTP technology was able to produce biocrude at USD 45 per barrel of oil equivalent (Lane, 2015). According to the European Biomass Industry Association, studies suggest possible prices of pyrolysis oil between USD 92 and USD 371 per tonne (USD 5-22 per Giga Joule), provided feedstock costs lie between USD 0 and USD 124 per tonne (USD 0-2.3 per Giga Joule) (Eubia, 2017; Oanda, 2018). According to Bauer (2017), the price of pyrolysis oil from Canada delivered to Rotterdam was about USD 228 per tonne in 2014.

- **Outlook**

Projected trends (baseline)

As indicated above, currently the development of lignin bio-oil’s production is underway, yet mostly in development (TRL 5 at maximum according to UniBO, 2018). Nevertheless, there is proof of commercially operating plants (e.g. Ensyn) as well as (semi-) commercial plants (btg, 2018). According to Bauer (2017), pyrolysis oil production exceeded 500 000 t by 2018. Looking at the near future production capacities of the very prominent player in bio-oil business, Ensyn (about 300 000 t p.a.), seems to underpin this opinion.

Due to its different chemical-physical properties in comparison to fossil fuels, presently one cannot consider lignin bio-oil a drop-in. Therefore, it largely is not capable to substitute for petroleum produce from a technical angle. Nevertheless, one can expect replacement to some extent as concerns industrial power and heat generation (Bauer, 2017; Lehto, 2013) or marine markets (IEA, 2018). Taking thusly the market for fuel oil as a reference yields a bio market share of about 0.1 % in terms of quantity. In terms of energy, this translates into a market share of about 0.05 % due to bio-oil's lower heating value.

Regarding market development, there seems to be little data on those markets, though. As a heuristics, it seems thus reasonable to fall back on the compound annual growth rate of the bio liquid heat and power generation market of Bioethanol and Diesel, i.e. 6.54 % (Markets and Markets, 2017). However, the latter constitute higher-value fuels. Therefore, one should treat 6.54 % annual growth rather as maximum possible range. Because of the early stage of development, estimates for price or cost development for lignin bio-oil are speculative. Nonetheless, indicated values range from USD 92-371 per tonne (Eubia, 2017) to USD 1 120 per tonne (Bauer, 2017). In addition, Ensyn and Honeywell UOP declared that their RTP technology was able to produce biocrude at USD 45 per barrel of oil equivalent in 2014 (Lane, 2015).

Competitiveness and role of Europe in global production:

At the moment, the main competitor of lignin bio-oil is fossil-based crude oil, with 10 (non-EU) countries accounting for about 70 % of global crude oil production. An alternative competitor is pyrolytic oil, which is produced abroad, e.g. in the USA or in Canada. Possible future competitors are alternative lignin fuels like e.g. liquids produced by other processes than pyrolysis.

Bio-oil activities are distributed across different world regions. They especially concentrate in countries that can tap into suiting resource pools (e.g. large forests, much lignin biomass from agricultural production). Moreover, it seems reasonable to assume that production will further concentrate in those countries, once bio-oil technology matures.

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10 Lignin-based phenolic resins

General information

Product Name	Lignin-based phenolic (LBP) resins
Technology readiness Level (TRL)	8
Biomass Platform	Lignin
Business to Business (BtB) or Business to Consumer (BtC)	BtB

Phenolic resins, also called phenol-formaldehyde resins are a group of the most versatile polymers ever invented. They are produced in chemical industry by reacting phenol (an aromatic alcohol derived from benzene) with formaldehyde (a reactive gas derived from methane). Phenolic resins are synthetic thermosetting resins, invented by Dr Leo Baekeland in 1907. Back then, the material was trademarked and called Bakelite™. This was the first completely synthetic plastic to be commercialised in the world (Britannica, 2018).

Phenolic resins are known for their excellent physical properties, such as mechanical strength, heat and moisture resistance and very high ablative properties (Siddiqui, 2013). This makes them very important industrial polymers that are mostly used in molded plastic products (e.g. billiard balls, laboratory countertops and also as coatings) (Britannica, 2018) and most notably as plywood adhesives (Siddiqui, 2013), with a global volume of around 6 million tonnes per year (mt p.a.) (Hussin et al., 2017).

In the chemical industry, 95 % of the phenol used in the production of phenolic resins is derived from petroleum products (LigniMATCH, 2010). Due to declining of the global fossil fuel reserves and fluctuations in its price, which in turn also influences phenol price combined with the increasing negative effect of GHG emission in the atmosphere, there is a strong interest in finding a sustainable alternative source and technology for the production of phenolic resins (Siddiqui, 2013). Furthermore, there are serious safety concerns about chronic exposure of workers to phenol during the manufacturing process (Kalami et al., 2017).

Given the wide availability of lignin as well as its low cost and low toxicity in comparison to petroleum-derived phenol, lignin is expected to provide a more sustainable and cheaper alternative raw material to substitute phenols in the production of PF resins (Connor and Piskorz, 1994; Hodasova, 2015; Hu et al., 2011).

Product description

Chemical-physical characteristics:

The phenolic resins are one of the most versatile high-volume resin systems, divided between two different types of polymers, depending on the method of heating and the mixing ratio: novolacs and resoles. Novolacs are made when the molar ratio of formaldehyde to phenol in below one and they comprise less formaldehyde than resoles *(Polymer Properties Database, 2018)*.

Novolacs are solid at room temperature. During heating, it melts and after cooling down, it returns to solid state. Resoles are liquid at room temperature and once heated they turn permanently solid (Plenco, 2018).

They can be both characterized by very high temperature resistance (up to 350 °C) after curing in final products and high water and chemical stability (e.g. corrosion resistance). Furthermore, they have excellent dimensional stability, high resistance to creep at high temperatures, low humidity absorption and high dielectric strength (Polymer Properties Database, 2018). They are lightweight and have a dark colour ranging from yellow to dark red with a molecular weight between 250-900 g/mol for novolacs and between 200-450 g/mol for resoles (Chemical Company, 2018; Plenco, 2018).

Main uses:

Phenolic resins are extensively used in numerous applications including different coatings, composites, adhesives, insulation, lamination, wood bonding, in molded parts and most notably as plywood adhesives (Siddiqui, 2013). Phenolic resins are the second most common after urea formaldehyde resins in wood applications, and are widely used in producing exterior grade wood products like plywood for exterior construction purposes, oriented strand board, engineered laminated composite veneer lumber (Zhao et al., 2011; Kalami et al., 2017).

Phenolic resins are also used for improving the performance of epoxy, acrylic, polyester and alkyd-based adhesive or coating products. This includes e.g. tank, drum, and pipe linings; marine and industrial applications and different electrical devices (i.e. wires, motor and wound coils) (Polymer Properties Database, 2018).

Due to their excellent physical characteristics (i.e. low flammability and low generation of toxic gases, and slow heat release) phenolic resins are widely used in the aerospace and railway industry, such as in interior structures of airplanes and trains (Raquez et al., 2010). Furthermore, phenolic resins-based polymers are also used in products that are used in high-temperature and -pressure environments in industrial oil and gas applications (Polymer Properties Database, 2018).

Production process:

Among different sustainable resources, such as modified pyrolytic oil, bio-crude from hydrothermal liquefaction of biomass, biomass tar, bark, and tannin, lignin is considered to be the best candidate as a phenolic-like material for utilization in phenolic resins production, mostly because of its aromatic structure (Zhao et al., 2011; Cheng et al., 2011; Wang et al., 2009).

In LBP resins, lignin directly substitutes (a fraction of) phenol. It is important to note that there are also technologies, where phenol is produced from lignin and thereafter used in resins production, but this is not in the scope of this study.

Mostly because of low reactivity, complex structure, i.e. robust and amorphous chemical structure, but also its diverse properties depending on temperature, humidity and ultraviolet exposure (Chung and Washburn, 2012), it is challenging to use untreated lignin as a starting material to replace fully phenol for the production of bio-phenolic resins.

Therefore, modifications are necessary for pre-treatment to increase lignin’s reactivity e.g. by breaking its 3D structure into oligomers of smaller molecular weight ranges (Siddiqui, 2017). Other potential modifications include demethylation (Li et al., 2016; Ferhan et al., 2013; Ibrahim et al., 2011), methylolation and phenolation (Hodasova, 2015) to increase the reactivity of lignin. Lignin demethylation is one of the most promising method by converting methoxyl groups into phenolic hydroxyl groups, generating catechol moieties in lignin framework (Hu et al., 2011). Also, hydrogen iodide (Pinheiro et al., 2017), hydrogen chloride (Chung and Washburn, 2012), and other diverse hydrolysis reactions have been employed to remove methoxy groups and cleave ether groups through demethylation route (Li et al., 2017). However, all these different modification technologies of lignin require additional energy and in most cases also chemicals. This requires more time and resources from the manufactures that make it less attractive for the industry to produce lignin-based bio-phenolic resins, even though replacing phenol with lignin in phenolic resins production would increase the share of renewable raw material and biosafety.

- **Markets**

Current volume, market value, prices:

Phenolic resins are produced globally with a volume of around 6 mt annually (Hussin et al., 2017). The global phenolic resins industry was valued at USD 9.3 billion (2015) (Grand View Research, 2017a), and woud therefore reach over USD 15 billion by 2025 accordingly, at an estimated CAGR of 5.4 % by Grand View Research (2017a). Around 95 % of the feedstock phenol is produced using petroleum-based benzene and propylene with the Cumene process production of 10.7 mt p.a. globally. The primary application of phenols is production of phenolic resins (LigniMATCH, 2010).

Currently, North America is the largest market for phenolic resin in wood adhesive applications, accounting for more than 54 % of global consumption (Kalami et al., 2017).

The actual price of lignin isolated from various pulping processes is estimated to be an average USD 660 per tonne on a dry basis (Frost & Sullivan, 2016), while the price of phenol is higher, reaching USD 1 300 per tonne on the European market (S&P Global Platts, 2015).

The market price of phenolic-resins is between USD 1 100 and USD 2 300 per tonne dry solids, depending on the purity, quality and application of final resin (Hodasova, 2015).

The first product currently on the market, where phenol is 100% replaced by lignin, is a WISA BioBond technology, developed by UPM, where fossil based phenol is replaced by lignin in the adhesive used in the production of plywood (WISA BioBond, 2018). Apart from UPM, 100 % lignin-based phenolic resins are not yet commonly produced on a commercial scale.

Biomass/yield and feedstock availability:

Besides technological challenges, for bio-phenolic resins production, the sustainable supply of a sufficient amount of lignin feedstock is a key prerequisite. Using lignin to produce bio-phenolic resins is driven by three main factors, first lignin is the second most abundant renewable resource, available after cellulose (Li et al., 2017). Second, the price of lignin is considerably lower than synthetic phenol. Third, there are strong structural similarities between phenols and lignin (Hu et al., 2011). Especially Kraft pine lignin is considered to be the best phenol substitute in the synthesis of bio-phenolic resins, as it has the highest number of activated free ring positions, highest molecular weight and thermal decomposition temperature compared to other lignin types (Tejado et al., 2007).

The total lignin availability in the biosphere is more than 300 billion tonnes (bt) and annually increases by around 20 bt (Frost & Sullivan, 2012). According to Gosselink (2011) and Laurichesse & Avérous (2014), there are between 50 to 70 mt of lignin produced annually in the world. The pulp and paper industry extracted globally 50 mt of lignin, out of which around 95 % are burned to fuel boilers in the pulp plants locally and only 2-5 % is used for low value commercial applications (mainly lignosulfonates) (Gosselink et al., 2004; Gosselink, 2011; Laurichesse and Avérous, 2014).

Lignin is available all the year around from different pulping processes (e.g. paper and biorefinery industries), however, direct use of unmodified lignin is not considered as an attractive technology for the production bio-based phenolic resins because of low bonding properties of resins produced from unmodified lignin (Hu et al., 2011). Preparing/processing lignin for phenolic resins production adds costs, which increases its price and makes it therefore less attractive material for industry.

- **Actors**

General setting:

In general, there are few companies globally, who have developed commercial solutions based on lignin. Also, the production of phenolic-resins based fully on lignin does not exist yet on commercial scale. However, there are some companies who have developed solutions, where phenolic resins are partially replaced by lignin. An overview is given below of the main players on whom any relevant information is available. The main R&D activities are currently based in Europe. As for the rest of the world, only in North-America two actors were found.

Europe:

UPM-Biofore: this Finnish forestry company has developed a UPM BioPiva™ technology, the solution replaces fossil-based phenol with bio-based lignin in the adhesive, used in the production of plywood (UPM, 2018). In th UPM BioPiva™ technology, 70 % of the fossil-based phenol has been replaced with lignin obtained as a by-product of pulp production, with a goal to increase the amount to close to 100 % in the coming years (UPM, 2018). Furthermore, the company has developed WISA BioBond™ technology, replacing fossil-based phenol with lignin in plywood manufacturing (WISA BioBond, 2018).

Prefere Resins: this German company has developed a technology, where the solution replaces fossil-based phenol with bio-based lignin in the production of phenolic resins. In this new technology 50 % of the fossil-based phenol has been replaced with lignin obtained as a by-product of pulp production. Prefere's Finnish plant at Hamina is currently producing the new lignin-phenol resin already on a regular basis (Prefere Resins, 2017).

StoraEnso: the Finnish company StoraEnso launched in March 2018 its lignin-based product under the name Lineo™, as a renewable replacement for oil-based phenol that is used in combination with formaldehyde in phenolic resins for different applications. The lignin used is separated during the Kraft pulping process of Nordic softwood. The production capacity of lignin is 50 000 tonnes per year (t p.a.), making Stora Enso the largest Kraft lignin producer in the world. The company is selling Lineo™ as a phenol replacement (Bioplastics News, 2018; BiofuelsDigest, 2018).

VTT: The Technical Research Centre of Finland has developed technology known as "CatLignin" to produce reactive lignin from pulp industry side streams to be used as a replacement for phenol. Unlike existing technologies, this method has the possibility to modify the lignin structure already at the pulp mill. The technology development is underway and VTT is currently seeking partners for upscaling and commercialisation of the technology (VTT, 2017; VTT, 2018; BEsustainable, 2018).

Avalon Industries: this company, based in Switzerland, has launched a research project, 'Development of a formaldehyde-free phenol type adhesive system for the manufacturing of plywood', The project aims to investigate the replacement of phenol with lignin in order to develop 100 % bio-based phenolic resins. There is no further information available, regarding results (BiofuelsDigest, 2017).

Furthermore, there is a large-scale research project running, REHAP (www.rehap.eu), financed by the European Commission that is a relevant contributor to R&D in this field: REHAP (2018): the project runs from 2016 until 2020 and aims to develop a new high-performance bio-resins to produce eco-friendly wooden panels. The project partners cover a number of different European countries, including Belgium, Finland, France, Germany, Italy, the United Kingdom (www.rehap.eu).

Rest of the world:

West Fraser Timber Co. Ltd.: this Canadian company aims to develop a technology to use lignin as a natural adhesive in its engineered wood products - as a renewable substitute for the petroleum-based phenol-formaldehyde resin currently used in the engineered wood products it manufactures (Plastics Today, 2016).

Hexion Inc.: this USA based company is a global leader in thermoset resins. At the end of 2017, the company announced completion of expansion of R&D facility to develop LBP resins for wood panels (PaperAdvance, 2017).

- **Value proposition and sustainability**

Co-products:

There are no co-products from the production of phenolic resins where phenol is directly substituted by lignin.

Environmental impacts, benefits, sustainability:

Lignin-based phenolic resins have a number advantages over phenolic resins, such as reduced toxicity and lower energy consumption (Siddiqui, 2013).

Phenolic resins have a significant impact on the CO_2 footprint of engineered wood products. For example in plywood, around half of CO_2 footprint is caused by resin usage (VTT, 2017). The CO_2 footprint of lignin is only approximately 20 % of the footprint of phenol. Replacing lignin with phenol in the production of phenolic resins could therefore strongly improve its environmental profile – i.e. every tonne of lignin substituted in phenolic resins, prevents a tonne of CO_2 emissions to the atmosphere (Plastics Today, 2016). Replacing phenol with lignin also reduces toxic formaldehyde usage (VTT, 2017) and dust in manufacturing facilities on the site (Kalami et al., 2017).

Socio-economic advantages, health impacts (also comparison with alternatives):

Formaldehyde, used in phenolic resins, is a carcinogen. It has adverse effects on human health and is increasingly receiving public and political concerns and criticism (Plasticstoday, 2016). Incorporation of lignin, which is non-toxic/has very low toxicity, into the production processes of phenolic resins enables to significantly improve workers health and safety, furthermore, it enables to produce safer end-use products for consumers (Hall et al., 2012).

Economics: bio vs non-bio-based alternative:

Economically, the production of phenolic resins from lignin is attractive for industry, because phenol prices are depending on oil prices and are therefore very unstable (Hodasova et al., 2015).

Commercialization of LBP resins is still limited due to their key physical and technical properties, as the in adhesive strength of 100 % LBP resins is significantly lower compared to conventional phenolic resins. Latest data indicates a successful substitution up to 50 % of phenol with lignin in phenolic resins, without decreasing bonding properties of resins. Furthermore, LBP resins, compared to phenol-based resins have reduced reactivity and thermal stability, inferior bond strength, and colour and curing issues (Siddiqui, 2013).

There is no source available regarding the possible price of LBP resins produced at a commercial level. According to consulted experts, it could be lower than commercially available phenolic resins.

- **Outlook**

Projected trends (baseline:

The markets for (fossil-based) phenolic resins is likely to increase steadily at a growth rate around 5,4 % in the following years (Grand View Research, 2017a) and would reach therefore over 11 million t p.a. by 2030. As LBP resins are not a complete drop-in, i.e. once produced the lignin based phenolic resins are not completely identical to the fossil derived resins. However, they can still step-in the market, if cost-competiveness achieved or regulation/ environmental advantages lead to a take up.

As indicated above, currently LBP resins production technologies are mostly in TRL 8 development and 100 % LBP resins are commonly not produced on a commercial scale yet, apart from UPM Biochemicals (WISA BioBond, 2018). The wider commercial scale production of 100 % lignin-based resins is still some years away. Currently, there are some other producers in the EU: StoraEnso (BiofuelsDigest, 2018) in Finland and Prefere Resins (2017) in Germany, which have both recently announced commercial scale production of phenolic resins, where 70 % and 50 % of phenol accordingly has been replaced by lignin.

Because of the early stage of developments, realistic estimates for price or cost development for LBP resins are mostly missing. Preliminary price estimate for LBP resins indicate that the average price may be lower compared to phenolic resins, because of the lower price of lignin (Hall et al., 2012), i.e. USD 660 per tonne versus USD 1 300 per tonne for crude-oil-based phenol.

Competitiveness and role of Europe in global production:

LBP resins are in price competition with phenolic resins. Europe is one of the front-runners in the field of LBP resins R&D together with the USA and Canada, driven by Europe's pulp and paper industry – i.e. lignin as feedstock availability. Finland especially stands out in both, R&D and commercial activities. The first 100% lignin based production plant is Europe based. North-America is a close competitor due to the pulp and paper industry. Supportive policies and well-developed global market are crucial for wider uptake of LBP resins globally, especially in APAC countries, which is one of the fastest growing regions for resins, accounting 42% of the global market share and is dominated by India and China (Business Wire, 2017).

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11 Bio-BTX aromatics

- **General information**

Product Name	Bio-BTX Aromatics
Technology readiness Level (TRL)	6
Biomass Platform	Lignin
Business to Business (BtB) or Business to Consumer (BtC)	BtB

Benzene, toluene and xylenes (BTX) are basic aromatics that are produced globally in very large volumes. They are highly important intermediates and used as starting materials for a wide variety of products in chemical industry, for example pharmaceuticals, packaging materials, textiles, car tires etc. (Siemens, 2015). BTX aromatics are currently all commonly produced from fossil oil, i.e. from reformate, pyrolysis gasoline, naphta and liquified petroleum gas (LPG) in petrochemical industry (Siemens, 2015).

The aromatics industry is expecting an increasing deficiency of aromatics from the petrochemical industry as the world aromatic market is under pressure (benzene shortage in the United States due to shale gas, xylene undersupply in China due to xylene production facilities closure (Bio-Cluster, 2018)). Some predictions say that by 2020, the annual benzene demand will be 5 million tonnes (mt) higher compared with supply (Bio-Cluster, 2018). Therefore, the demand for chemicals from renewable sources is rapidly increasing and there is an urgent need for alternative feedstocks and sustainable technologies to produce BTX aromatics in bio-based industry (Reinikainen and Thomas, 2015). They would serve as drop-in (i.e. they are identical to the fossil-based chemicals) and can thus be used as replacement for the existing technology.

Lignin is one of the most abundant natural polymers. Due to its chemical structure, lignin is not only suitable for energy production, but also as a platform molecule for bio-based chemical development, i.e. bio-BTX aromatics. It is one of the three plants constituent together with cellulose and hemicellulose that as part of the biomass, can be derived from many different sources: energy crops, agricultural waste, industrial biomass-based waste or by product from bioethanol production (Bogliano, 2016). However, the major source of lignin is pulp and paper industry. In 2015, 180 mt of pulp was produced (Bogliano, 2016), which translates into between 50 to 70 mt of potential lignin capacity annually (Bogliano, 2016; Gosselink, 2011; Laurichesse and Avérous, 2014), out of which around 95 % are burned to fuel boilers in the pulp plants locally and 2-5 % is used for low value commercial applications (Gosselink et al., 2004; Gosselink, 2011, Laurichesse and Avérous, 2014).

Currently, all lignin-based bio-BTX aromatics are still in the R&D phase and much technological progress needs to be done to improve both, yield and specificity. Experts in this field indicate that commercial scale production could begin the earliest within 10-20 years (UNIBO, 2018).

- **Product description**

Chemical-physical characteristics:

The BTX acronym refers to mixtures of benzene, toluene and three xylene isomers (meta, para and ortho). They are produced in the same process in the petroleum industry, but BTX is not an article of commerce on its own. BTX aromatics are the lowest weight aromatic hydrocarbon analogues, currently produced by reforming naphthalenes (Sweeney and Bryan, 2007). They belong to the six major platform chemicals (together with ethylene, propylene and butadiene).

Benzene (C6H6) is clear, colourless, highly flammable and volatile, toxic liquid aromatic hydrocarbon. It has a gasoline-like odour. Benzene causes central nervous system damage acutely and bone marrow damage chronically and is carcinogenic (PubChem, 2018). Toluene (C7H8) is a clear, water-insoluble liquid with a typical smell of paint thinners. Xylenes (C8H10) are colourless watery liquids with a sweet odour. They are less dense than water and have high octane numbers (Thring et al., 2000). Bio -BTX aromatics from lignin, as drop-in chemicals, have the same physical and chemical properties as the fossil-based products they are replacing (Meuwese et al., 2013).

Main uses:

Benzene has the highest demand among BTX aromatics. It is used as an intermediate for different plastic and electronics production. Ethylbenzene and subsequent (poly) styrene production is the major use of benzene. Other important downstream products are phenolic compounds, acetone and nylon-6. Benzene is not a desired additive to gasoline (unlike toluene and xylene), due to its toxicity (Treobostad, 2016).

Toluene is used as a solvent and a precursor for polyurethane production. It has a high octane number, therefore it is used to increase octane numbers in gasoline (Ozokwelu, 2006). The market for toluene and its products is relatively small. Since toluene is produced in a larger amount than needed, a large part of the produced toluene is hydrodealkylated to form benzene (also works with xylene) or disproportionated to form benzene and xylene (Bender, 2013).

Within the xylenes, meta-xylene is used relatively little. Ortho-xylene has some precursor and additive uses, but para-xylene has the largest market, since it is a precursor for polyethylene terephthalate (PET) and high end polymer applications such as aramid fibres (Kroschwitz and Seidel, 2004, Meuwese et al., 2013).

BTX-based commodity polymers and high value chemicals are used as starting materials for a wide range of products in different industries: 1) in healthcare to manufacture pharmaceuticals, 2) in automotive industry to produce a wide range of car parts, 3) packaging industry, 4) electronics industry (DVDs, keyboards, mobile phones etc.), 5) textile industry to develop innovative fibres, 6) sports equipment manufacturing for a number of different light-weight, high performance materials and 7) construction industry for insulation, piping materials and window frames (Aromatics Online, 2018).

Production process:

The process of making bio-BTX aromatics from lignin is still in its infancy (Meuwese et al., 2013). At the same time, the fossil derived BTX aromatics production process is a decade’s old process and well optimized (Meuwese et al., 2013).

The maximum theoretical obtainable yield of bio-BTX aromatics from lignin is expected to be around 36-42 wt%, as lignin contains 60-65 % carbon of which 60-65 % in C6 aromatic rings. The main difficulty is to deoxygenate and de-alkylate the C6 aromatic structures, without hydrogenating and destroying the C6 aromatic ring (Bruijnincx et al., 2016).

The MOGHI (Biochemtex, 2018) project is one example of technology development, to produce bio-BTX aromatics from lignin. It is based on lignocellulosic biomass sources and currently it is available only on pre-commercial scale. The core of the technology process is a catalytic de-oxygenation and de-polymerization of lignin, followed by a purification step and separation of the desired products (i.e. bio-BTX aromatics). The process itself uses hydrogen, generated *in situ* from the reactions and re-introduced as a reagent during the process itself, together with an off-the-shelf commercial La-Zn-zeolite catalyst. This process is designed to be drop-in replacements for the existing BTX aromatics technology in chemical industry. By using a wood-based lignin feedstock in the gasification process with catalysts, the resulting oil contains over 80 % benzene, toluene and xylene (VTT, 2018).

Another technology, to produce bio-BTX aromatics from lignin, has been recently introduced, called integrated Cascading Catalytic Pyrolysis (ICCP) by a Dutch company BioBTX. Catalytic pyrolysis is a well-known method to produce aromatic compounds from biomass. However, the zeolite catalyst, needed for the process, is sensitive to minerals found in biomass. The ICCP technology uses an integrated two-step pyrolysis, which protects the zeolite catalyst from the minerals. The end product is chemically identical to petrochemical BTX aromatics (Chemport Europe, 2018).

Another potential pathway is to produce bio-BTX aromatics directly from lignin. In this technology, lignin is hydrolysed, followed by isolating the components by nanofiltration or pervaporation. Separation technology is crucial in this step that will produce phenolics, oligomeric phenols and polymers, that can subsequently be processed to fine chemicals, fuels, lubricants and more, with bitumen as a rest product (Biorizon, 2015).

- **Markets**

Current volume, market value, prices:

The annual production of BTX aromatics was around 103 mt in 2012 and is forecasted to grow at a 4.4 % CAGR until 2020, reaching 145 mt (Bruijnincx et al., 2016), most likely the growth will continue also after 2020 at the same rate.

Therefore, there is potentially a very large market for sustainably produced bio-BTX aromatics from lignin (Meuwese et al., 2013). They also have a competitive advantage compared to new biochemicals, as BTX aromatics from biomass can be used as a direct replacement of BTX aromatics from fossil sources (i.e. drop-in) and no further resources have to be allocated for generating a new market (Meuwese et al., 2013).

Today, the market share for chemically produced BTX aromatics is 67:5:28 (for B, T and X accordingly) (Meuwese et al., 2013). For benzene, global consumption was over 40 mt per year (mt p.a.) in 2012 and it is growing steadily around 3.5 % p.a. (VCI, 2012), based on this expected to reach 51 mt by 2018 (MarketsAndMarkets, 2014). Toluene is used as a chemical feedstock in smaller volumes (approximately 19 mt p.a. in 2012) compared to benzene and xylene (Bender, 2013). Out of this total, 11 mt p.a. are used for benzene/xylene production (status 2009). 2.5 mt p.a. go to the solvent market and 1 mt p.a. serve for the manufacture of toluene disocyanate (TDI, a pre-product for polyurethane). The worldwide demand for toluene is forecasted to grow by 5.5 % p.a. in the next decade (VCI, 2012).

Xylenes are consumed by about 43 mt p.a. (VCI, 2012), with Asia accounting for the biggest share. The global demand is expected to grow by 6 % p.a. With a volume share of 90 %, para-xylene has the greatest commercial importance. Its global annual consumption grew by 10 % (i.e. 2 800 000 t) between 2009 and 2010 (Wikipedia, 2018). Ortho-xylene and meta-xylene contribute 9 % and 1 %, respectively (VCI, 2012).

The prices of BTX aromatics range between EUR 0.52 and EUR 0.86 per litre (Sweeney and Bryan, 2007; ICIS, 2012; Meuwese et al., 2013) or around USD 1 200 per tonne (Frost & Sullivan, 2012). The preliminary price for lignin-based bio-BTX is calculated at

EUR 1.4 per litre, which remains currently more expensive than the current crude-oil derived material (Reinikainen and Thomas, 2015).

Biomass/yield and feedstock availability:

For bio-BTX aromatics production, the sustainable supply of a sufficient amount of lignin feedstock is a key prerequisite.

Lignin is considered to be the main renewable resource and alternative feedstock, that can be used to produce aromatic compounds (Fan et al., 2014). The total lignin availability in the biosphere is more than 300 billion tonnes (bt) and annually increases by around 20 bt (Frost & Sullivan, 2012).

There are between 50 mt and 70 mt of lignin produced annually in the world, out of which around 95 % are burned to fuel boilers in the pulp plants locally and only 2-5 % is used for low value commercial applications (Laurichesse and Avérous, 2014; Gosselink et al., 2004; Gosselink, 2011). This total lignin volume co-produced today in the pulp industry would translate into a theoretical benzene volume of 52 mt p.a. (Bender, 2013). Lignin is available all the year around from different pulping processes.

Its extraction from lignocellulosic biomass represents the keypoint to its use for bio-BTX aromatics production on industrial scale (Laurichesse and Avérous, 2014). Production of 150 mt yearly of bio-BTX aromatics can be easily covered with the lignin parts from the forestry and agricultural residues (i.e. non-food feedstock) (Deneyer et al., 2018).

However, processing lignin (i.e. isolation, purification and drying) is very costly that increases its price and sets limits as a starting material. Lignin prices are between EUR 50 and EUR 1 200 per tonne, depending of the grade of lignin (Laurichesse and Avérous, 2014). One of the main potential drawbacks for bio-BTX production from lignin could be that there are other technologies in the pipeline that also require lignin as a feedstock to offer more sustainable alternatives to petrol based chemicals (Meuwese, 2013).

- **Actors**

General setting:

In general, there are very few companies globally, who have developed commercial solutions based on lignin. However, there is a lot of interest from end-users in BTX bio-based products (i.e. IKEA, Coca-Cola and Lego), that are all working on different products based on bio-aromatics (KETS, 2017). The involvement of multinational companies can have a strong positive effect on the transition towards bio-based products. Nevertheless, the supply quantity is currently on pilot and demonstration scale, which is too low for large-scale production (KETS, 2017).

Europe:

In Europe, regions advancing the technology development for bio-BTX aromatics are concentrated in the Northern and Western parts of Europe. Especially Flanders and various Dutch and German regions are leading the way. For example, the cross–regional consortia Biorizon that is a Dutch/Flemish research cluster (TNO, ECN, VITO and Green Chemistry Campus), working with industry on the technological development for the production of aromatics from biomass. Biorizon predicts to have technology and facilities ready to start commercial production of bio aromatics from lignin by 2025 (Biorizon, 2018).

BIG-C Cluster: this Bio Innovation Growth mega Cluster (BIG-Cluster) is a cross-border ‘Smart Specialisation Initiative’ aiming at transforming Europe’s industrial mega cluster in the Flanders region of Belgium, the Netherlands and the German state of North Rhine-Westphalia into the global leader of bio-based innovation growth. The objective of BIG-Cluster is to initiate demonstration plants for the production of chemicals and fuels based on sustainable resources – namely biomass. Among, others, BIG-Cluster aims at establishing novel value chains within the topics "Aromatics and Fine Chemicals from Woody Biomass" (Bio-Cluster, 2018).

Vanguard Initiative (VI): it is an European network of 28 industrial regions. The main aim of the VI is to take demonstration activities, often taking place at regional level, to a higher interregional level. The long term objective is to set up several value chains, starting at lignin, moving via thermochemical lignin de-polymerization lines to drop in aromatic molecules and finally to new applications in the field of materials and products. The short term goals of VI are to produce test samples with existing facilities in Europe for bio-based aromatics, set up of an application lab and further, a pilot productions (annually 5 t) (Vanguard Initiative, 2018).

BioBTX: this Dutch company, is focussed on developing a technology to produce bio-BTX aromatics catalytically from different types of biomass, including lignin, in one step. BioBTX is the first company to successfully convert biomass into BTX in a commercially viable manner. The process is currently still in development, they expect to start a commercial scale production by 2022 (Chemport Europe, 2018; BioBTX, 2018).

Biochemtex: it is an Italian company that has developed a technology within a project MOGHI that enables to convert lignin into bio-BTX aromatics. The goal is to establish a first demo plant worldwide, with a production capacity of 1 000 t p.a. of bio-BTX aromatics, using lignin as a feedstock (Biochemtex, 2018). Recently, the company has entered into an agreement with creditors and the outcome of it, is not yet clear.

At the VTT in Finland, a demonstration plant for bio-aromatics production from lignin exist, in the frame of the iBet project Thermochemical Bioeconomy, where bio-BTX aromatics are currently produced in multi-kilogram scale (Reinikainen and Thomas, 2015).

At Wageningen University, in 2010 a Lignin Platform has been created, with the objective to promote interdisciplinary research and to create a network on the valorisation of lignin for the industrial production of lignin-derived chemicals and compounds, including bio-BTX aromatics (WUR, 2018).

Rest of the world:

Wood is considered to be the main feedstock for bio-BTX aromatics production. Since Canada is the biggest global wood feedstock supplier (KETS, 2017), there are also a number of companies, active in developing technologies to bring bio-BTX aromatics to the market.

Anellotech Inc.: the USA based company has developed a clean technology platform, the Bio-TCat™ process to produce cost-competitive bio-BTX aromatics. After successful completion of TCat-8 pilot plant that is making available kilogram-scale quantities of bio-BTX aromatics to strategic partners for downstream development, on the 4th of January 2018, the company announced that an intensive process development & testing program has begun to confirm process economics and collect data for commercial plant design (Anellotech, 2018).

Virent: founded in 2002, the USA based company is one of the global leaders in catalytic biorefinery research, development and commercialization. Among other, the company has also developed BioForming® Technology to replace crude oil with bio-BTX aromatics (Virent, 2018). There is no information available whether the technology is already commercialized.

FPInnovations: FPInnovations is a not-for-profit organization in Canada (FP Innovations, 2018). On January 22, 2018, FPInnovations announced in collaboration with Resolute Forest Products significant investment in the implementation of a pilot project, that will focus on developing new technological solutions to produce and commercialize innovative bio-chemicals, including aromatics derived from wood (Newschannel 6, 2018).

Alberta Pacific Forest Industries Inc. (Canada): it is a Canada based private company that operates a pulp mill that produces kraft pulp. The company is working closely with research organizations like FPInnovations and Alberta Innovates-Technology Futures to develop new sustainable products and processes (Alpac, 2018). However, no demonstration plant level activities have not been announced yet.

Lignol Innovations Ltd: the company based in Canada, has developed an unique and economical integrated process technology for biorefining abundant and renewable ligno-cellulosic biomass feedstocks into ethanol (fuel alcohol), pure lignin and other valuable co-products. However, there is no info available whether it also includes bio-BTX aromatics (STDC, 2018). In 2015 Fibria acquired Lignol Innovations Ltd, today called Fibria Innovations (Fibria, 2015).

Weyerhaeuser Company: the company is one of the world's largest private owners of timberlands, owning or controlling nearly 13 million acres of timberlands in the U.S. and managing additional timberlands under long-term licenses in Canada (Wyerhaeuser, 2018).

The NSERC Biomaterials and Chemicals Strategic Research Network (or Lignoworks): is one of four networks created In Canada, in 2010, as a part of the NSERC Forest Sector R&D Initiative, with a goal to generate new knowledge to develop innovative, high value-added lignin-based materials and chemicals (Lignoworks, 2018). Based on unconfirmed data, the Network is not active anymore.

- **Value proposition and sustainability**

Co-products:

The lignin left after extraction/isolation of BTX aromatic molecules is more condensed than the starting material, and can be subjected to subsequent harsher cleavage steps, which focus on cleaving more recalcitrant bonds. All the residues left, could then be cracked for use as fuel, used for the applications the asphaltene fraction of crude oil is used for today or burnt for the generation of heat and power, making full use of the complete lignin input for various process streams (Bruijnincx et al., 2016).

Environmental impacts, benefits, sustainability:

The current process for BTX production suffers from some environmental problems such as high energy consumption and by-products (Elfadly et al., 2016). Furthermore, BTX aromatics themselves are hazardous and classified as main pollutants by the US Environmental Protection Agency (EPA), as they are one of the most common organic contaminants in air, water and soil. Due to their toxicity, they are also considered as a threat to human health (Singh et al., 2015). Sustainable production of bio-BTX aromatics would help to reduce footprint of industrial processes, especially when using non-food crops and waste biomass as a feedstock. Since arable land is limited, it should ideally be dedicated growing crops for food production. (Meuwese et al., 2013). Such drop-ins also demonstrate lower greenhouse gas emissions in comparison to the petrochemical building blocks (KETS, 2017). Furthermore, the ability to make high performance materials means that over their lifetime, lignin-based bio-BTX aromatics can make a significant difference by the environmental merit of the products they are used for (e.g. lighter vehicles) (Meuwese et al., 2013).

Socio-economic advantages, health impacts (also comparison with alternatives):

Aromatics production is a billion euro market and the share of Europe is around 25 %. This is an interesting domain for Europe, where in bio-BTX production, Europe could can have a key role at the economic level, as the aromatics production employs 20 000 people directly plus 70 000 extra in the plastics industry and about 1 million in a wider approach to the applications (Vangard Initiative, 2017).

Economics: bio vs non-bio-based alternative:

Non-bio-based alternative shows a sale price below EUR 1 per litre. In contrast, while the current price of lignin-based bio-BTX aromatics is not yet publicly available, it is estimated to be higher, around EUR 1.4 per litre (Reinikainen and Thomas, 2015).

- **Outlook**

Projected trends (baseline):

The markets for (fossil-based) BTX is likely to increase steadily to around 220 mt per annum (mt/a) in 2030. As bio-BTX is a drop-in, it could easily step-in the market, if cost-competiveness achieved or regulation/environmental advantages lead to a take up.

As indicated above, currently bio-BTX aromatics are mostly in TRL 5-6 development and the market entry on commercial scale is a few years away. While a first demonstration plant is planned, construction has not started yet. Hence, the market volume in 2020 will be minor. According to current announcement, production on commercial scale will be ready around 2025 (Biorizon, 2018). Most probably a very few number of firms will be commercially active. The 2SBIOM market study (S2Biom, 2015) assumed production capacities for bio- BTX of 150 kilo tonnes (kt) in 2020. From a current viewpoint, this would be rather a reasonable estimate for 2025 or after, as this a few middle-scale industrial plants. Reducing uncertainty regarding supply, technological improvement and rather increasing fossil energy prices may lead to increase until 2030 in the range of 450 kilo tonnes a 0.2 % bio-share.[3]. Hence, bio-BTX aromatics would remain a niche.

Because of the early stage of developments, reasonable estimates for price or cost development for lignin-based bio-BTX are mostly missing. Preliminary price estimate for lignin-based bio-BTX indicate that the price may be as twice as high than current BTX (Reinikainen and Thomas, 2015), but no information on cost reduction potential is available. As mentioned, since lignin based bio-BTX is a drop-in product, the price gap between fossil-based and bio-based BTX has to be limited, in case of such described market development. For the calculation below, the price of fossil BTX is assumed.

Competitiveness and role of Europe in global production:

Today, all BTX aromatics are produced from fossil oil in petrochemical industry (Siemens, 2015) and lignin based bio-BTX aromatics are not yet produced on a commercial scale. Nevertheless, these bio-aromatics would serve as drop-in (i.e. they are identical to the fossil-based chemicals) and can thus be used as replacement for the existing technology. The development and production of the lignin based BTX-aromatics is closely linked to the chemical industry. Next to North-America, European chemical industry has a very

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strong global position - it is one of the biggest markets and suppliers of the chemicals in the world, although Asia’s chemical industry is emerging as a strong competitor (KETs, 2017).

Like North-America, the EU has the necessary critical R&D resources and capacities, to secure a leading position on the global bio-BTX aromatics market. In Europe, regions advancing the technology development for bio-BTX aromatics are concentrated in the Northern and Western parts of Europe. Especially Flanders and various Dutch and German regions are leading the way. This illustrates that for the bio-BTX aromatics, R&D capacities outweigh cheaper locations and production costs in Asia, as there are no lignin based BTX-aromatics related activities taking place yet (KETs, 2017).

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12 Bio-based phenol and alkylphenols

- **General information**

Product Name	Bio-based Phenol and alkylphenols
Technology readiness Level (TRL)	5
Biomass Platform	Lignins
Business to Business (BtB) or Business to Consumer (BtC)	BtB

- **Product description**

Phenolic compounds are chemically defined as compounds containing hydroxylated aromatic rings, the hydroxy group being attached directly to the phenyl, substituted phenyl, or other aryl group.

There are several sources of bio-based phenols and alkylphenols, and lignin is among them (Vithanage, 2018). In fact lignin has a complex molecular structure composed by three different phenylpropane monomers units (monolignols) namely para-cumarly alcohol, coniferyl alcohol, and sinapyl alcohol (Pandey and Kim, 2011) and the percentage of the monolignols components change from plant to plant (Hodásová *et al.*, 2015).

Advantages of phenol and alkylphenols

One of the lignin advantages is to contain different phenolic monomers which are considered natural antibacterial compounds and used against plants aggression by pathogens and parasites. Phenolic also contribute to plants colors (Dai and Mumper, 2010)

In addition, phenolic, ketone and other chromophores contained in lignin are all considered a UV- absorbing functional groups and used like a defense against ultraviolet radiation (Qian, Qiu and Zhu, 2015).

Apart from being used as a source of fine chemicals, it is equally viable to consider lignin as a raw material for sustainable liquid fuel additives (Zhao, 2010). In this example, phenol can help with determining the physical properties of fuels, since certain alkylphenols are being used as antioxidants in diesel at present.

From an energy point of view, according to Kleinert and Barth, (2008) lignin could be considered as a raw material both from liquid fuel additive and chemicals production. In this context, since phenol and alkylphenols are able to establish the physical characteristics of fuel they are used as antioxidant in diesel production.

Disadvantages of phenol and alkylphenols

LigniMATHC, (2010), a spin-off project from the ScanBalt Campus Knowledge Network Environmental Biotechnology identified some drawbacks in the production process of phenols from lignin. The main problem is in cost to obtain pure phenol which is considered a high quality product in the lignin-based market. LigninMATCH related this disadvantages with an immaturity of the technology and on the high costs for producing pure lignin (LigniMATHC, 2010), a necessary starting point for the production of high purity phenols.

Main uses

Phenols are raw chemicals suitable for several industrial needs; mostly used as solvents and fuel additives for industrial applications, used also as bio-pesticides or insecticides or sold as dietary supplements or as drug components (Bruijnincx, 2016).

Phenols are important in plastics production and other materials, as aromatic functional building blocks. Main applications of phenols are in production of phenol-formaldehyde resins, polyurethane foams or polyurethanes for automotive industry (Hodásová *et al.*, 2015).

Phenols are UV absorbing chemical moieties, and can enter into sunscreen cosmetic formulations (Ugartondo, et al., 2008).

Production process

One of the way for the phenol extraction from the lignin compound is the thermochemical conversion (Amen-Chen, Pakdel and Roy, 2001).

Hydrogenolysis process if compared with pyrolysis process is a favorable method to obtain elevate monomeric phenols from lignin. This because with a non-hydrogen-donating solvent, hydrogenolysis leads to higher net conversion, higher yields of monophenols, and less char formation (Pandey and Kim, 2011).

According with Smolarski, (2012) another way able to produce monomer phenolic compounds its the supercritical depolymerisation (SD). This is an emerging technology still a field of research and very expensive. However, this exctraction method could be considered with great potential for the future for its environmental friendly solution.

Phenolic substances from lignin, once produced and purified, do not differ from the fossil derived ones (LigniMATHC, 2010).

- **Markets**

Current volume, market value, prices.

Phenol price and the general concerns about workers exposure of to chemical phenol during the manufacturing process are the reasons why many researchers have studied how to replaced phenol with biobased phenol from lignin materials (Kalami *et al.*, 2017).

Smolarski, (2012) identified as a current phenol production volumes, an amount of 8 million tonnes per year with a market value around USD 1 500 per tonne. Main advantage of producing phenol from lignin is that nowadays phenol prices are depending on oil prices.

From the costs point of view, based on the energy content of lignin and the current price of biomass for energy, lignin would cost about USD 330 per tonne. Phenols exctracted from lignin wich have a yield of 40 %, would induce a raw material price of the lignin-based phenol about USD 800 per tonne (LigniMATHC, 2010).

Also Hodásová *et al.*, (2015), confirmed that in 2012 annual production of phenol reached 8 million tonnes with a market value of phenol approximately from 1 000 to 2 000. Phenol has many derivatives such as nitrophenols or rather p-nitrophenol and aminophenols, cyclohexanone and bisphenol and their prices are shown in Figure 12.1.

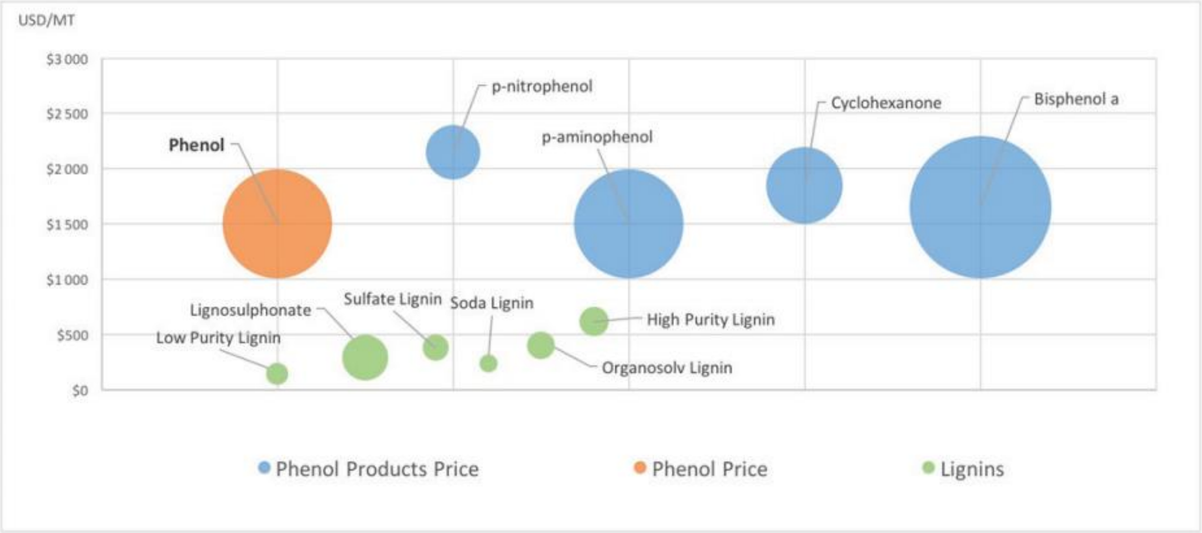

Figure 12.1: Phenol and its derivatives price compared with lignin prices (Source: Hodásová et al., 2015)

Biomass/yield and feedstock availability

LigniMatch, a joint industry-academy-project evaluated the possible upgrading of lignin that can be extracted from pulp and paper industry and trasformed into value-added products able to substitute fossil-based products and cumpounds.

Has been estimated that currently there are $3*10^{11}$ metric tonnes on earth and most of the lignin is generated by the pulp industry (kraft lignin and lignosulfonate) but according with less than 5 % of the averall lignin is used for purpose such as phenolic foam, surfacants, and phenolic resin (Hu *et al.*, 2011).

LigninMatch, has identified as a market required products phenol derivef from lignin. These phenols should be purified. The maximum yield of pure phenol from lignin is between 40 and 60 %.

- **Actors**

General setting

A European organization named Biorizon (www.biorizon.eu/biorizon), is a Shared Research Center with a focus on technology development for the production of biobased bulkaromatics (BTX) and functionalized biobased aromatics for performance materials, chemicals & coatings.

Europe

Chemelot InSciTe, (Netherland). The Chemelot Institute for Science & Technology (InSciTe) is an institute and project coordinator of “SCeLiO-4B project”, which focus on renewable feedstock (sugar, cellulose, and lignin) for the production of chemical building blocks (e.g. bio-aromatics) (http://www.chemelot-inscite.com)

Bio Base Europe Pilot Plant, (Belgium). Europe Pilot Plant is collaborating with Biorizon group to assess a method for lignin extraction. They tested four different lignin extraction method such as:

Soda lignin from CTMP process (coproduct paper industry)

Soaking aqueous ammonia extraction (lignin-first)

Organosolv lignin extraction (lignin-first)

Ammonium lignin from residue of bottom still – 2nd generation ethanol process. (http://www.bbeu.org)

DSM ChemTech Center, (Netherland). It is also collaborating with Biorizon Shared Research Center. (http://www.dsm.com)

Stora Enso, (Finland). The company which is a global major of the Pulp and Paper industry, announced recently the launch of its lignin-based phenol under the trademark Lineo™. (http://www.storaenso.com)

Rest of the world

New Zealand Crown research institute, working with Biorizon is partner in a new project, called LigniOx: Lignin oxidation technology for versatile lignin dispersants. The aim of the LigniOx Innovation Action is to demonstrate the techno-economic viability of alkali-O2 oxidation technology (LigniOx) (http://www.mbie.govt.nz)

Avantium, (Canada), is a corporation which collaborates in several trans-oceanic project to improve and develop green chemistry products. (http://www.avantium.com)

FPInnovations, (Canada), in collaboration with the Centre for Research and Innovation in the BioEconomy (CRIBE), Natural Resources Canada (NRCAN), Abitibi Bowater’s Thunder Bay mill are realizing a pilot scale plant to produce active lignin obtained from kraft black liquor on a scale of 100 kg/day. (http://www.fpinnovations.ca)

- **Value proposition and sustainability**

Co-products

Phenol which is a lignin components is a common by-product of the paper industry and of the second generation bioethanol manufacture. In these processes, the surplus lignin is often burnt off for heat and/or electricity recovery (Verboekend *et al.*, 2016).

Environmental impacts, benefits, sustainability

The potential environmental benefits from finding alternative uses of lignin are extensive, and with a double effect. Lignin can be used to replace fossil based raw materials, as phenols, in a wide range of products, from plastics to individual chemical products.

Phenols can be made from hydrolysis, sulphite and kraft lignin. Theoretically, enough wood is processed worldwide to cover the global phenol market. Lignin is the only natural biological aromatic polymer known. Environmental impacts depends on the energy demand for cracking the lignin, as well as catalysts (especially those containing Pb) and solvents needed in the production process. At present, processes result in a mix of phenols with an uncertain market value. Pure lignin-based phenol is expensive and not expected to be competitive compared to oil-based phenolics at today’s price levels.

Bio-derived methoxylated alkylphenols are promising alternatives to traditional alkylphenols as their toxicity is significantly lower. Furthermore, methoxylated alkylphenols from lignin can possess unsaturated alkyl chain (i.e. eugenol). The unsaturation is also proposed to benefit the biodegradability of the alkylphenol, as unsaturated compounds often degrade faster in various environments than their saturated counterparts.

Socio-economic advantages, health impacts, bio vs non-bio based alternative

If there is a market for such value-added products derived from lignin, such as phenols, fossil resources will be less spoiled and the mills will also have an additional economic incentive to take measures for higher energy efficiency. Economically, lignin can be the basis of new innovation systems. Once produced and purified, the phenolic substances from lignin do not differ from the fossil derived ones.

- **Outlook**

Projected trends (baseline)

The market for fossil-based phenols is forseen to reach USD 31.73 billion by 2025, driven by the rising demand for derivatives such as parmaceuticals, phenolic resin, polycarbonates, etc. with an estimated CAGR of 3.08 % during the period 2017-2020 by Hexa Research (2017).

Despite this new market potential for syntetic phenolic, new opportunities in the production of chemicals and materials can be found also into building blocks contained in lignin and corn-based renewable feedstocks.

From the costs point of view, lignin would cost about USD 330-500 per tonne and phenols exctracted from lignin, wich have a yield of 40 %, would induce a raw material price of the lignin-based phenol of about USD 800 per tonne (LigniMATHC, 2010). Therefore a preliminary price estimate for phenol from lignin indicates that the average price may be lower compared to phenols from Benzene, which is about USD 1 300 per tonne (Bhayani Rajesh, 2014). This is because of the lower lignin price compared to fossil-based sources. In the future, prices could either remain the same, or, eventually, decline, due to an increase in technology efficiency and yields.

Also, Hodásová *et al.*, (2015), confirmed that in 2012, annual production of phenols reached 8 million tonnes with a market value ranging approximately from 1 000 to 2 000 in 2015. Lignin-based phenols market value is about 1000 – 2000 USD per million tonne. The demand for phenols from lignin production is increasing as well as the corresponding market price, which is a function of macroeconomic factors and oil and lignin prices (Hodásová *et al.*, 2015).

Also, if is well know that lignin market has great potential, it is also acknowledged that lignin from different sources can vary in terms of chemical properties (and therefore its appropriateness for different downstream uses) and is mostly utilised in bioenergy production rather than chemicals.

Finally because of the early stage of developments (5 TRL), reasonable estimates for future price/cost and volume development for lignin-based phenols are mostly missing within the literature.

Competitiveness and role of Europe in global production

The current market is leaded by North Europe, Canada, and US. In Europe a great investment has been recently realized by Stora Enso (Finland) that can be considered as the largest Kraft lignin producer in the world. It invested EUR 32m to build a world-class bio-refinery at Sunila Mill in Finland containing lignin extraction plant and drye. Europe is expected to advance rapidly in the production of lignin-based phenols being the major market for lignin-based products.

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13 Bio-based polyamide 12

- **General information**

Product Name	Bio-based Polyamide 12
Technology readiness Level (TRL)	5
Biomass Platform	Renewable oils & fats
Business to Business (BtB) or Business to Consumer (BtC)	BtB

Aliphatic polyamides (PA) are industrially synthesized by ring opening polymerization of cyclic monomers (lactams) or by step-growth polycondensation of diacids/diesters with diamines, or ω-amino acids/esters. PA are engineering polymers, used as high performance materials (Brehmer, 2013) and they include the PAs 6 to 12, and PA 4,6, 6,6 ,PA 6,10, and PA 6,12. (Jiang and Loos, 2016). Arkema produces the bio-based Polyamide 11 (RILSAN), but also bio-based Polyamide 10.10 and partially bio-based variations using the same monomers. Similarly, bio-based Polyamide 10.10 is manufactured by EVONIK and other suppliers.

As an example, PA 6 is synthesized by ring opening polymerization of caprolactam and PA 6 6 is synthesized by polycondensation of adipic acid with hexamethylenediamine.

Aliphatic polyamides are semi-crystalline as they consist of crystalline and amorphous phases. The regular spatial alignment of amide groups allows a high degree of hydrogen bonding to develop when chains are aligned together. The crystalline regions contribute to the hardness, yield strength, chemical resistance, creep resistance and temperature stability, while the amorphous areas contribute to the impact resistance and high elongation.

Aliphatic polyamides are versatile engineering plastic and excellent fiber materials. As per their application aliphatic polyamides are categorized in two divisions: polyamide fibers and polyamide thermoplastics.

PA fibres are mainly used in carpets, apparel, tire reinforcement and in other industrial applications. They are used in racing car tires and airplane tires owing to their excellent strength, adhesion to rubber and fatigue resistance in these demanding applications. Molecular weight, in case of PA 66 fibers, is in the range of 12 000 to 15 000 for apparel fibers and 20 000 for tire yarn is preferred.

PA thermoplastics are important engineering plastics because of their toughness over wide range of temperatures. Also they have good resistance to impact and abrasion, organic solvents and petroleum products. They are used in many automotive applications such as gears, bearings etc. Reinforced PA are used for exterior body compartments such as fender extensions, decorative louvers, filler plates, head lamp housings, cross-over panels and many other applications. In electrical and electronic area, polyamides are used in making plugs, sockets, switches, connectors.

PA 12 has a low concentration of amides moieties compared to other commercially available polyamides. PA 12 absorbs very little moisture, has excellent resistance to chemicals (e.g.: hydraulic fluids, oil, fuels, etc.), dampens noise and vibration and is highly processable.

- **Product description**

Polyamide 12 (PA 12), is a long-chain linear polyamide belonging to the aliphatic polyamides groups (Jiang and Loos, 2016; Ladkau *et al.*, 2016), and is characterized by 12 carbon atoms between two nitrogen atoms of the two amide groups. It presents a melting point of 180 °C and medium to high viscosity grade (Fornes and Paul, 2004).

The PA 12 currently commercialized is based on fossil sources. This is prepared on industrial scale via ring-opening polymerization of lauryl lactam converted after multiple step synthesis starting from butadiene (Kolb *et al.*, 2014). It could also be prepared from the ω-aminododecanoic acid (Wolfgang Griehl; Djavid Ru Estem, 1970). UBE in Japan is using 12-aminododecanoic acid in its process to make PA12.

For PA 12, the bio-based ω-amino-lauric acid (ALA) or 12-amino-dodecanoic acid (saturated amino acid) is an alternative to petroleum-based lauryl lactam (LL), the latter produced from the butadiene. Both PA 12 should present identical properties apart from the input use and production process. As soon as Bio-Butadiene will be available, this PA 12 can be made bio sourced with reduced technology risks.

With the ongoing decrease of fossil fuel and the increasing debate about a more sustainable production, fatty-acids from renewable resources have been proven to be able to synthesize polymers for the bio plastic production, and the PA 12 represents a high performance member of bio plastic family.

With regard to the preparation of renewable polyamides in general, ω-aminoundecanoic acid, which is synthesized from the castor oil derived 10-undecenoic acid, is also used for a large scale production of PA 11, which is already commercially available from Arkema (Kolb *et al.*, 2014).

The German chemical company Evonik is aiming to produce bio-based ω-amino lauric acid; a pilot-scale plant entered into operation in 2013, in Slovakia. The biotechnological manufacturing process starts from palm kernel oil (PKO) that the company was already using like a platform for the production of chemicals. The PKO contains good portion of lauric acid (C12:0) and more of its 50% is saturated (Evonik Industry, 2015). The fruit palm tree containing the PKO is mainly produced in Asia.

Arkema is investigating an alternative process, using the C11 undecenoic acid methyl ester produced from Castor oil, and cross metathesis with acrylonitrile, which however, can be, potentially, a hazardous substance. Bio-based PA 12 was produced during the EU project EUROBIOREF funded under FP7 (Eurobioref, 2014).

Chemical-physical characteristics

PA 12 represents a high performance polymer, featuring extraordinary heat, abrasion, chemical, UV, and scratch resistance.

With its 180 °C, it is characterized by the lowest melting point among all the important polyamides and because of its long hydrocarbon chain has a density of only 1.01 (low densities are an advantage for weight savings) and a relatively low water absorption (Wolfgang Griehl; Djavid Ru Estem, 1970) (Table 13.1).

Table 13.1: PA 12 properties

Properties	**PA 12**	**Properties**	**PA 12**
Melting point range, °C	178-180	Specific resistivity, ohm. cm	1x10 14
Specific gravity, g/cc	1.01	Dielectric loss factor at 106 c/s	0.05
Water absorption, 65% RH at 2O °C, %	0.85	Water vapor permeability (0.05-mm thick films), g/m2 24 h	9
Tensile strength at break, psi	9240	Oxygen permeability (0.05 mm thick films), cc/m2 24 h 1 atm	300
Notched impact strength, cm psi	427-771	Aroma impermeability	Good
Indentation hardness (Ball test), psi	9240	Grease impermeability	Good
Modulus of elasticity, psi	170	Solvent absorption in 1000 h at 20°C	1.4
Linear swelling in water, %	0.2		

Source: (Wolfgang Griehl; Djavid Ru Estem, 1970)

PA 12 is exceptionally strong even when temperatures dip below freezing. It is characterized by high strength, stiffness, strong resistance to cracking under stress, and an excellent long-term constant behavior. Furthermore, with a lower concentration of amides (nitrogen-containing organic compounds) than any other commercially available polyamide, PA 12 absorbs very little moisture, has an excellent resistance to chemicals including hydraulic fluids, oil, fuels, grease, salt water, and solvents, dampens noise and vibration, and is highly processable.

In addition it is resistant to stress cracking even for metal parts encapsulated by injection molding or embedded into the plastic and easy process ability (EVONIK, 2018). It is highly resistant to greases, oils, fuels, hydraulic fluids, and many solvents as well as to salt solutions and other chemicals.

Disadvantages of Bio-Polyamide 12

According to the Regulation (EC) No. 1907/2006 as amended by (EC) No. 1272/2008, the lauryl acid methyl ester is a toxic substance to aquatic life. While, the substance would require requiring therefore caution in its disposal (Cayman Chemical, 2017) we do not expect an uncontrolled release of the methyl ester; this, can be considered as an unlikely event.

From the economic point of view, in general, bio-polymers are still more expensive compared to conventional commodity polymers (Imre and Pukánszky, 2013). As an example, bio-based PE derived from sugar has a price commonly 20-30% higher than fossil-based PE.

Overall, comparing PA 12 with other PA, PA 11 could have a better compromise of properties, despite its comparative advantage depends on the application to be developed.

Main uses:

PA 12 is frequently used as a coating on fuel and braking systems in most passenger carsworldwide due to its extraordinary heat, abrasion, chemical, UV, and sc ratch resistance capabil ities.

The PA 12 is actually used for several applications such as in automotive, construction, and medical industries (Ladkau *et al.*, 2016). Due to its remarkable capability of heat, abrasion, chemical (Goodridge *et al.*, 2011), UV and scratch resistance, is commonly employed as a coating on fuel and braking system in most passenger cars (Ahsan *et al.*, 2018) and like a denture base material (Stafford *et al.*, 1986). PA 12 is used to manufacture trailer brake hoses, fuel lines, etc. for the automotive/transportation market.

PA 12 based on powders is an excellent compound for rapid prototyping of functional part for its rapid manufacturing or direct manufacturing of bespoke of even small batches of plastic parts.

PA 12 is the most widely used powder material for selective laser sintering as it exhibits comparatively good mechanical properties at room temperature, and offers the possibility to produce very complex geometries without any supports (Goodridge *et al.*, 2011; Türk *et al.*, 2017).

Production process

To make bio-based PA 12 different alternatives exist: 1) Fermentation (Evonik route); 2) Metathesis (Arkema's route from C11 unsaturated ester), a C10 unsaturated ester route (Invista and Rhodia patents), and 3) a route from bio-based Butadiene.

In the biobutadiene route, the major issue is that bio-butadiene becomes available. Then there is no risk for the PA 12 producer to switch to bio-butadiene, as there is no need to change its production process.

The Evonik process results in ω-amino lauric acid methyl ester, an alternative to petroleum-based lauryl lactam. The palm kernel oil generates a new alternative PA 12 precursor stage ω-amino lauric acid equivalent (ALA), which could be subsequently polymerized to an identical PA 12 (Evonik, 2013).[4] The C12monomer - 12-aminolauric

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acid methyl ester (ALAME) - used to produce the PA 12, is obtained by fermentation from lauric acid methyl ester via the *Escherichia coli* bacteria fermenter (Ladkau *et al.*, 2016).

Evonik is not the only group which has been working on a fermentation process. For example, one of the product considered by the Commonwealth Scientific and Industrial Research Organization (CSIRO) is also a C12 amino-acid.

A biotechnological catalytic method for the conversion of the bio-based dodecanoic acid methyl ester (DAME) to the C-12 monomer suitable for the synthesis of PA 12, i.e. 12-aminododecanoic acid methyl ester (ADAME), was developed by Schrewe et al using a combined oxygenase and transaminase catalyst (Ladkau et al. 2016). ADAME was produced in *Escherichia coli* via a three-step cascade, in which terminal DAME hydroxylation and alcohol oxidation both catalyzed by the alkane monooxygenase AlkBGT from Pseudomonas putida GPo1 were followed by terminal amination by means of the *Chromobacterium violaceum* ω-transaminase CV2025 (ω-TA). Thereby, dodecanedioic acid monomethyl ester (DDAME) was formed as a major by-product.

In an alternative approach, the C12 amino-ester can be produced through olefin metathesis. Arkema has several patents on such a process mostly targeting PA 11 and PA 12. In particular, Arkema prefers PA 11 which has a better technical property compromise, and would not be made from palm kernel oil. Arkema's current process for PA 11 uses the non-edible castor oil and its metathesis process can use any kind of plant oil provided that it contains sufficient amount of oleic acid.

The successful application of cross metathesis to synthesize PA 12 and PA 13 precursors from oleic acid has been reported by the literature. For example, the method reported by Rupilius & Ahmad (2007) provides a shorter and simpler route for production of both PA 12 and PA 13 from an abundant and inexpensive, and thus preferred starting material. In addition, Abel, Nguyen, Viamajala, Varanasi, & Yamamoto, (2014) results demonstrate that cross metathesis could be applied directly to crude fatty acid methyl ester extracts from algal biomass. However, while metathesis can be regarded as bio-based process since the raw material used is renewable, the underlying chemical reaction could create undesired by-products and hazardous wastes than alternative organic reactions.

- **Markets**

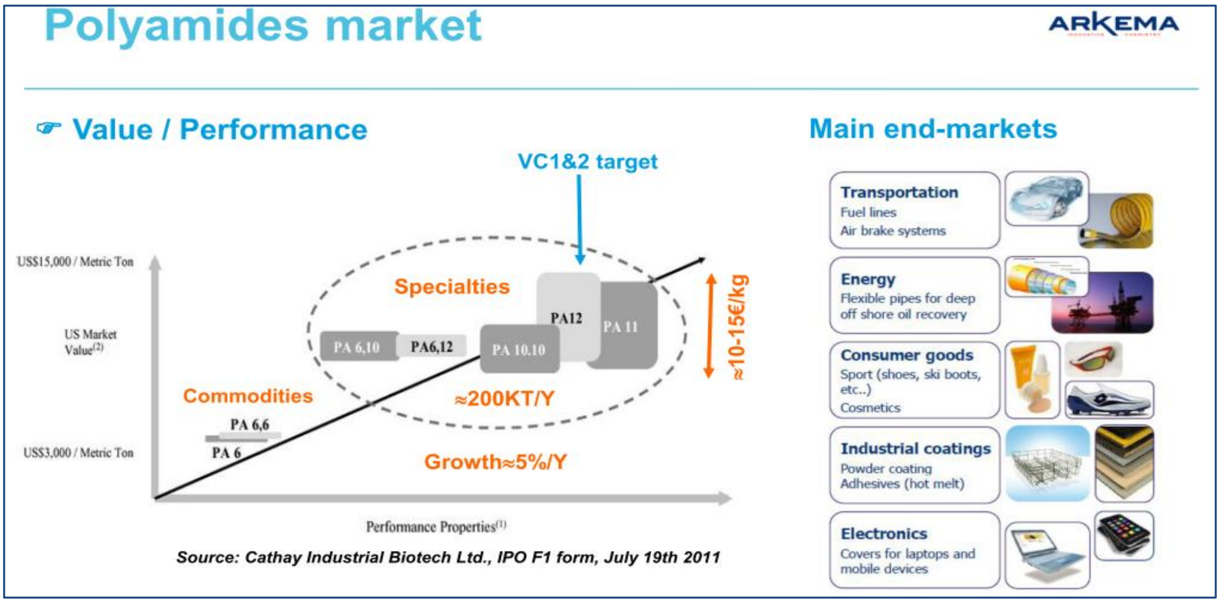
Current volume, market value, prices:

Important drivers, leading current and future trends in PA markets are increasing oil prices, that will make conventional polymers more and more expensive (European Bioplastics, 2014; Markets and Markets, 2018). Finally, more stringent regulatory policies would be needed to reinforce and support the polyamide market growth even further. An increase in auto sales and the rising of housing market in emerging economies will also drive the polyamide market (Grand View Research, 2018).

While the global PA market was valued at USD 25.14 Billion in 2016 (Markets and Markets, 2017) the bio-based PA market was valued at USD 29,454 million in 2012 and USD 110.5 million in 2016 (Grand View Research, 2017a). Amongst the specialty PA expected to achieve a good balance between value/performance we find the PA12 (Figure 13.1).

Polyamide market at global level is projected to reach USD 30.76 Billion by 2021, at a CAGR of 4.1% from 2016 to 2021 (Markets and Markets, 2017) and USD 32.7 billion by 2025 (Grand View Research, 2017b). In general, the demand for the fastest-growing type of segment of the polyamide market by 2021 is projected to be the bio-based and specialty polyamide (Markets and Markets, 2018).

The largest market is represented by the Asia Pacific area and is followed by Europe and then North America where we find the fastest growing segments of automobile, packaging, electronics, and consumer goods including retail.



Polyamides market

ARKEMA

Value / Performance

Main end-markets

Transportation
Fuel lines
Air brake systems

Energy
Flexible pipes for deep off shore oil recovery

Consumer goods
Sport (shoes, ski boots, etc..)
Cosmetics

Industrial coatings
Powder coating
Adhesives (hot melt)

Electronics
Covers for laptops and mobile devices

Source: Cathay Industrial Biotech Ltd., IPO F1 form, July 19th 2011

Figure 13.1. Polyamides market (Source: Aresta, M.; Dibenedetto, A.; Dumeignil, F., et al. (Ed.) (2015). Biorefineries. An Introduction. Berlin, Boston: De Gruyter)

The Chinese, Japanese, Indian, Brazil, and Russian markets are also surging the growth of this market. Growth of transportation industry due to growing disposable income levels, mainly in China and India, is likely to drive the regional markets. This picture is expected to be preserved in the future, which will be still dominated by the Asia Pacific region showing the highest growth rate, despite new market alliance will possibly stabilize the overall business. Korea, Taiwan, and Japan are expected to create important opportunities for specialty PA manufacturers, due to increasing demand in PA 12-based applications. On the other hand, Central and South America will show only moderate growth over the next future (Grand View Research, 2018).

To better meet customers' strong PA 11 demand in Asia, Arkema company will boost its production capacity by 50% with a platform in China that is expected to come on stream in late-2021 (Arkema, 2017). This investment will support the strong demand in growth applications, such as cable protection, lightweighting (metal replacement) in automobiles, improved high performance sports shoes (running, soccer, etc.) and evolving applications in the consumer electronics segment. Indeed, the growth rates in these applications are expected to exceed 7% per year in Asia, in the mid-term (Bioplastics Magazine, 2018).

Biomass/yield and feedstock availability

Palm oil is a plant that produce two different types of oils, the palm oil from mesocarp and palm kernel oil from the seed of kernel with different chemical and physical property. The fatty acid (lauric satured C12) content in palm kernel oil is about 48.2 % (Evyap Oleo, 2018). One of the advantages compared to the other crop oil is that palm oil yields about from 4.09 tonne/ha to 0.5 tonne/ha of palm kernel oil (Basiron, 2001). A competitive yield compared with the 0.37 tonne/ha of soybeans oil, 0.5 tonne/ha of sunflower oil and 0.75 tonne/ha of the rapeseed oil (Rupilius and Ahmad, 2007; World Bank, 2011). In terms of availability nowadays Indonesia and Malaysia account for 85 % of global palm oil production (Evyap Oleo, 2018). Indonesia is expected to continue to be the leading producers with expansion in land for palm oil; differently in Malaysia the expansion is expected to slow in view of limited land availability. Nevertheless, more and smaller producers' country are started with the palm oil market like Cameroon, Colombia, Costa Rica, Cote d'Ivoire, Ghana, Guatemala, Honduras, Nigeria, Papua New Guinea, and Thailand.

- **Actors**

General setting

Nowadays there are very few suppliers worldwide of PA 12.

Europe:

Evonik, (Germany): Evonik began operating a pilot plant for ω-amino lauric acid (ALS) from Palm Kernel Oil in Slovenska Lupca, Slovakia. (https://corporate.evonik.com/en/media/press_releases/Pages/article.aspx?articleId=100566)

Arkema, (France): Arkema is producing bio-based PA 11 and PA 10.10. It has both the monomers and polymer productions. Arkema, expanded its offer with Rilsan® T range, a new biosourced polyamide 10.10 processed from castor oil. Arkema will launch a new plant for PA 12 in China by mid-2020. The project involves the launch of a line for Rilsamid - the PA 12 brand marketed by Arkema (https://www.arkema.com/en/media/news/news-details/Arkema-announces-a-new-project-to-produce-polyamide-12-in-China-mid-2020/).

EMS-Grivory, (Switzerland): The EMS Group offers several polyamide products among wich the Grilamid PA12 from the basic raw material butadiene. Under the general term GreenLine, EMS-GRIVORY markets a wide range of bio-based polyamides from castor oil (www.ems-group.com/en/).

Rest of the world

Ube Industries, (Japan): UBE is the only manufacturer in Japan that produces PA 12 with integrated manufacturing from raw materials. This product is known by the name UBESTA XPA series: https://www.tandfonline.com/doi/pdf/10.1271/bbb.80210. (www.ube-ind.co.jp)

Invista, (US): in 2012 has started working been working on its own route to PA12, and it was also a supplier of cyclododecatriene (CDT), feedstock for laurolactam, the monomer to produce polyamide 12. However, it seems that they have stopped this production few years ago.

- **Value proposition and sustainability**

Co-products

Based on palm oil physical and chemical properties, two main industries have been developed, palm based food and oleo chemical industries (Basiron, 2001).

Several oil palm industry co-products can be utilized as animal feed, notably oil palm fronds (OPF), oil palm trunks (OPT), palm press fiber (PPF), empty fruit bunches (EFB), palm kernel cake (PKC) and palm oil mill effluent (POME). These co-products are obtained either during the harvesting of the fruits, or the extraction and refining of crude palm oil (CPO) or palm kernel oil (PKO). Many of the co-products from the plantation (field residues) and processing mills need further processing before they can be used effectively in livestock (Suzana, M; Rahimah, A R; Maizura, I and Singh, 2015).

Evonik has a pilot plant for the production of amino-lauric-acid (ALA), a precursor of PA 12, from palm kernel oil (Evonik, 2013). Several suppliers added a PA 1010 to their portfolio, which is entirely based on castor oil, and features a property profile that fits in the gap between PA 12 and PA 6 or PA 66, respectively. Nevertheless, enhancing the basis of raw materials suitable for polyamide production and investing in renewable raw materials can be a good idea because, in addition to improving the security of energy supplies, this may yield new polyamides with interesting properties ('Engineering Plastics TREND REPORT', 2014; Engineering Plastics, 2014).

Environmental impacts, benefits, sustainability

It is ambiguous, whether polyamides based on renewable raw materials are in fact more sustainable than other types when considering factors such as landscape consumption (Azhar *et al.*, 2017), land market (Krishna *et al.*, 2017) use of agrochemicals fertilizers, water, transport, working conditions (Elmhirst *et al.*, 2017) and the impacts on food security (Azhar *et al.*, 2017).

In terms of sustainability, there is a demand of the consumers to verify the way palm oil has been produced. The Round Table of Palm Oil (RSPO) Supply Chain Certification systems (SCCS) addresses this issue by reducing the risk of non-sustainable palm oil use by consumers while further driving the mainstream trade of sustainable palm oil, according to the company (Green Chemical Blog, 2015).

Socio-economic advantages, health impacts, bio vs non-bio based alternative

In order to allow a future sustainable development of palm oil industry, it is crucial to consider the increment of palm tree yield per hectare, the value-addition of the oil. At the same time it is important to reduce production costs. In this respect, a special attention should be put on the improvement of oil palm varieties with higher yields, good oil quality, and compact in architecture, better adaptation to climate change and higher tolerance to diseases (Zulkifli, et al. 2018; Masura et al. 2017). Switching from fossil-based to bio-based PA 12, sustainably produced, would support the economics of countries growing palm oil, in addition to reduce the carbon footprint of the wide variety of final products that are produced using PA 12 as input. In general, the production of petrochemical PA has a severe impact on global climate change, expressed as carbon dioxide equivalents released and the production also require high fossil energy (Vink *et al.*, 2003). In the PA 12, the extraction of ω-amino lauric acid, like alternative to petroleum-based lauryl lactam, require less steps (Ladkau *et al.*, 2016). On the other side, the replacement of petrochemical products with bio-based alternatives often requires the whole production chain to be re-optimized" (Scott, Peter and Sanders, 2007).

- **Outlook**

Projected trends (baseline)

PA12 from bio-based sources is basically an alternative to PA12 from fossil sources. Its future will depend on the balance between growing fossil resources prices on the one hand, and availability of suitable bio-based feedstock in the EU. Cost is still higher than competing fossil substitutes.

Polyamide market at global level is projected to reach USD 30.76 billion by 2021, at a CAGR of 4.1 % from 2016 to 2021 (Markets and Markets 2017) and USD 32.7 billion by 2025. Fastest growing PA markets have shown rates above 7 % in the fastest moving market, such as China. Using 7% CAGR as a reference and starting from an estimate of bio-based PA market USD 110.5 million in 2016 would lead to 283 million USD in 2030

Given the wide number of applications and the current regulatory pressures this figures could increase in a relevant way, included the market share of bio-based PA12 which is currently very low.

Competitiveness and role of Europe in global production

Currently most of the few producers are in Europe. However castor and palm oil production are currently mostly outside the EU and are very competitive with oil crops such as soybean that can be produced in Europe. The competitive role of the EU in bio-based PA12 will depend largely on ability to produce locally the needed feedstock (Elevance, 2017).

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14 Biolubricants

- **General information**

Product Name	Biolubricants
Technology readiness Level (TRL)	7-8 for high performance lubricants 9 for loss lubrication
Biomass Platform	Renewable oils and fats
Business to Business (BtB) or Business to Consumer (BtC)	BtC & BtB

Lubricant is a collective term for substances that reduce friction and (mechanical) stress on counteracting or moving machine parts. Lubrication reduces energy consumption and material wear and acts as a coolant (Roempp, 2017). For example, in passenger cars, one-third of the fuel energy is used to overcome friction in the engine, transmission, tires and brakes. The direct frictional loss, without breaking friction, is 28 % of the fuel energy spent (Holmberg et al., 2012). Globally, the consumption of lubricants amounts to 39.4 million tonnes (Frost & Sullivan, 2014)

In regard to environmental impact of lubricants the special sub-group of biolubricants is of growing interest. Based on the European Standard EN 16807 ("Bio-lubricants — Criteria and requirements of bio-lubricants and bio-based lubricants" from 2014), biolubricants are partly derived from vegetable oils and other renewable sources. Basically, these could be triglyceride esters and thereof transesterified synthetic esters. For lubricant base oil use, vegetable derived materials are preferred, such as high oleic canola oil, castor oil, palm oil, sunflower seed oil and rapeseed oil from field plants and Tall oil from tree sources. Other naturally derived lubricants include lanolin (wool grease, a natural water repellent) or historically important whale oil.

A lot of products referred as "biolubricants" are available on the market, but especially in the field of these special lubricants, there has been some confusion of different expressions concerning the prefix “bio”. Initially, the only condition to be met for biolubricants was a high biodegradability (Luther, 2015).

To overcome this confusion, the European Committee for Standardization (CEN) defined specific characteristics for biolubricants:

- bio-based carbon content has to amount to at least 25 % according to ASTM D 6866:2012 (^{14}C analysis),
- biodegradation of oils >60 %, of lubricating greases >50 % respectively, within 28 days according to OECD 301 test methods,
- not hazardous to the environment according to CLP Directive 1272/2008/EC,
- specific technical performance criteria to be met.

Moreover, the European Directorate General Taxation and Customs Union (DG TAXUD) has defined an own Combined Nomenclature (CN) for classifying biolubricants, based on EN 16807:

CN code for biolubricants: 3403 19 20,

Description: Lubricants having a bio-based carbon content of at least 25 % by mass and which are biodegradable at a level of at least 60%.

The EU Ecolabel for Lubricants (EEL), also called "Euro-Marguerite", represents more stringent standards than the CEN. The lubricant's hydrocarbon content (as weight percent) derived from renewable resources, must amount to at least 45 % for biogreases, 50 % for biolubricants and as much as 70 % for bio-based total loss lubricants. Currently the label is under review, it is planned to include the level of hazardous substances to be lower than <0.01% w/w, as well as levels of non-biodegradable and bioaccumulative substances to maximum 0.1% w/w and even very restricted aquatic toxicity limits. Moreover, in the new version, it is proposed to include the origin and traceability of vegetable oils to the label, to prove their origin from sustainably managed plantations (for instance if palm oil or palm kernel oil are used, at least the 25% w/w shall be certified) (JRC, 2018).

- **Product description**

Chemical-physical characteristics:

There are different application areas for lubricants, like hydraulic fluids, engine oils, gear oils, lubricating greases, chain saw oils, moulding oils, engine oils, metalworking fluids etc. Thus, it is necessary to adjust the lubricants for each application separately.

A lubricant can be characterized, among others, by the following specific key figures (Behrain Oil Co, 2018; Singh et al., 2017):

Table 14.1: Common properties of biolubricants

Property	Value	Comments
Specific density	0.89 – 9.7 g/ml	Oils and their derived lubricants have a lower density than water.
Viscosity	For example: 500 mm²/s (40 °C.) 32 mm²/s (100 °C.)	Viscosity as a measure of oil's resistance to flow. An ideal oil film on a bearing, depends on selecting an oil with the right viscosity, to maintain separation of two metal surfaces. The viscosity depends on temperature, pressure and shear strain.
Viscosity index	100 - 200	A high Viscosity index is an expression of a low effect of change of temperature on the viscosity of oils.
Pour point	-22 to +12 °C	Pour point is the temperature at which oil will remain fluid
Flash point	-	Flash point is the temperature at which the oil gives off sufficient vapours, which can be ignited.

Advantages of biolubricants in comparison to oils and fats

Due to their poor degradability under natural conditions and end-of-life issues of mineral-oil-based lubricants, bio-based lubricants were primarily developed for applications whereas the lubricant is directly ejected into the environment, such as in chainsaw bars, two-stroke engines, and other marine applications – so-called total loss lubrication. In practice, lubricants are expelled to the environment through leakages, blown pipes as well as due to human errors. It has been reported that more than 50% of the lubricants used throughout the world are the contributors of environmental pollution due to total-loss lubrication, spillage and evaporation. It has been estimated that 40% (i.e. 400,000 t/a) of lubricants is used annually and a significant amount of lubricants is lost to the environment each year (N.A.Zaina et al, 2018).

Many municipalities merely allow the use of degradable oils in their area, e.g. bio-based hydraulic oils during work at surface waters. Depending on the application, bio-based synthetic ester oils are particularly suited for producing high-performance lubricants that at least equal conventional crude-oil-based lubricants.

In December 2013, the United States Environment Protection Agency (EPA) introduced the "Vessel General Permit" (VGP), requiring any vessel greater than 79 feet to use environmentally acceptable lubricants (EAL) in all oil-to-sea interfaces. This regulation imposes stringent requirements for the control of waste and waste-water from ships in coastal water. EPA estimated that approximately 61,000 domestically flagged commercial vessels and approximately 8,000 foreign flagged vessels will require VGP permit coverage, but only a subset of these vessels will incur incremental costs as a result of the revised permitting requirements However, because many of the nation’s busiest ports are considered to be impaired by a variety of pollutants found in vessel discharges, strengthening the requirements contained in the VGP, is expected to increase the demand for biolubricants in marine area and this should reflect in a reduction of concentrations of nutrients, metals, oil, grease, and toxics in waters with high vessel traffic. (EPA, 2013)

Disadvantages of biolubricants

The main disadvantages are the poor oxidative stability at higher temperatures and the high viscosity at reduced operating temperatures, so in these conditions, biolubricants are not applicable. These limits can be improved gradually by using additives (antioxidants) or by chemical modification (such as hydrogenation) but this has an impact on the final costs.In fact, biolubricants are in general priced approximately 1.5 to 2 times higher than mineral-oil-based lubricants, which cost an average 3,100 USD per tonne (Frost & Sullivan, 2014). There is an end-user reluctance to switch from conventional lubricants and a lack of performance confidence among Original Equipment Manufacturers (OEMs) (Frost & Sullivan, 2014).

Main uses:

Due to their less toxicity and environmental sensitivity, biolubricants are used in a wide range of applications like transmission fluids, gearbox oils, hydraulic fluids turbine and compressor oils, chainsaw oil and special type like oil for track switches. Bio-lubricant can replace mineral oils as gear box oil, hydraulic oils, engine oils, lubricants for 2 stroke engine, tractor transmission oils, insulating oils, aviation oil, grease, metal grinding oils or multipurpose oils (Singh et al., 2017; Mobarak et al., 2014).

Production process:

Liquid lubricants mainly consist of base oils and additives, the latter are added to improve the performance characteristics to the lubricant. For example, lubricating grease consists of base oil and a thickener to achieve the required semi-solid consistency.

Base oil can be produced from plants such as rapeseed. Chemical methods are used to further optimize the plant oils. This is achieved in a reaction called esterification, which involves combining an alcohol and the fatty acid contained in the oils to yield an ester plus water. These synthetic ester oils form the basis for high-performance lubricants. It is also possible to introduce modifications in the fatty acid chains. Modification or chemical conversion offers the possibility of changing the properties of fats and oils within wide limits, thus making them available in sufficient quantities for the widest variety of applications. The following processes are essentially applied: fractionation - separation by melting point by cooling; transesterification - modification of the molecules by transferring the fatty acids to other (synthetic) alcohols; esterification - production of esters from fatty acid and alcohols; hardening - a chemical process, adding hydrogen; mixing - mixing fats and oils.

The base substances used for the production of synthetic esters can be biogenic, i.e. produced from plant oils, animal fats or from algae in the future. However, they can conventionally be derived from crude-oil products.

While lubricants like hydraulic oils can contain 99 % base oil and only 1 % additives, there are some, e.g. metal working fluids, containing up to 30 % additives (Ullmann, 2012). These can be antioxidants, viscosity modifiers, pour point depressants, detergents and dispersants, antifoam agents, demulsifiers, dyes, corrosion inhibitors, friction modifiers or antiwear and extreme pressure additives. Nevertheless, adding a higher quantity of additives does not always means more benefits gained, and at times the performance actually deteriorates. In addition, increasing the percentage of a certain additive may improve one property of an oil while at the same time degrade another, affecting the overall oil quality. For instance, if a high concentration of an anti-wear agent is added to the oil, the corrosion inhibitor may become less effective. The result may be an increase in corrosion-related problems. This is due to the fact that these additives compete with each other for the same space on the metal surface (Noria Corporation, 2018). Moreover, biolubricants formulations should include only additives that are biodegradable and non-toxic for the environment.

Table 14.2: Common additives for lubrificants of different systems.

Machine	Common Additive used	Percent of the Oil Volume
Engines	Antioxidant, corrosion inhibitor, detergent/dispersant, anti-wear, anti-foam, alkalinity improver	13-30%
Steam turbines, compressors	Antioxidant, corrosion inhibitor, demulsifier, anti-foam	0.5-5%
Gears (spiral, bevel or hypoid)	Anti-wear, antioxidant, anti-foam, sometimes corrosion inhibitor, extreme pressure	1-10%
Gears (worm)	Extreme pressure, antioxidant, corrosion inhibitor, fatty acids	3-10%

Hydraulic systems	Antioxidant, anti-wear, anti-foam, corrosion inhibitor, pour-point depressant, viscosity index improver	2-10%

Source (Noria Corporation, 2018)

- **Markets**

Current volume, market value, prices:

According to Frost & Sullivan (2014), the total lubricant market in 2013 comprised around 39.4 million tonnes, see figure 3-1. Due to an increasing world demand, the compound annual growth rate is expected to be 3.2 % in the years 2013-2020. The market revenue (2013) was USD 123,643 million. Thus, the average price of lubricants was USD 3,137 per tonne. The market is dominated by automotive lubricants (58 %, 2013), followed by industrial lubricants (34 %), marine lubricants (5 %) and aviation lubricants (3 %). The automotive share is expected to continue dominating the market due to robust growth in automotive demand.

Bio-based lubricants hold a smaller share of 1.5 % (i.e. 0.6 million tonnes in 2013), as the price is higher and it is assumed, the performance standards could not effectively compete with mineral and synthetic counterparts. The largest market of biolubricants in the world is the United States, closely followed by Germany, Sweden, Denmark, Norway and Finland (Aslanian, 2015).

German biolubricants demand is estimated to grow just above 2 % per year for the next 10 years. The largest product category in Germany are hydraulic fluids, used in construction, forestry and agriculture, as well as smaller industrial applications. Sweden and Finland are mostly focused on the forestry sector for biolubricants; Denmark on the off-shore and marine segments and Norway on transformer oil applications (Aslanian, 2015).

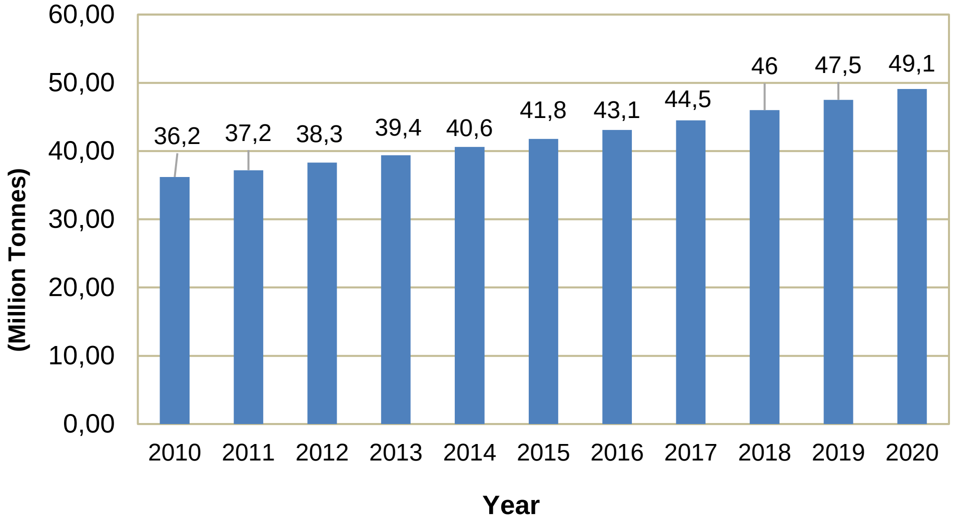

Figure 14.1: Forecast of the total lubricants market, global, 2010-2020 (Source: Frost & Sullivan, 2014)

Biomass/yield and feedstock availability:

Depending on the type of biolubricant, the content of *bio-based feedstock* can vary widely. For calculation, an average content of 90 % is assumed. There are different oils used as feedstocks for lubricants, see Table 14.1.

Table 14.3: Specific applications of various plant oil

Plant oil	Application
Canola oil	Hydraulic oils, tractor transmission fluids, metal working fluids, food grade lubes, penetrating oils, chain bar lubes
Castor oil	Gear lubricants, greases
Coconut oil	Gas engine oils
Olive oil	Automotive lubricants
Palm oil	Rolling lubricant,-steel industry, grease
Rapeseed oil	Chain saw bar lubricants, air compressor-farm equipment, Biodegradable greases.
Safflower oil	Light-coloured paints, diesel fuel, resins, enamels
Linseed oil	Coating, paints, lacquers, varnishes, stains,
Soybean oil	Lubricants, biodiesel fuel, metal casting/working, printing inks, paints, coatings, soaps, shampoos, detergents, pesticides, disinfectants, plasticizers, hydraulic oil
Jojoba oil	Grease, cosmetic industry, lubricant applications
Crambe oil	Grease, intermediate chemicals, surfactants
Sunflower oil	Grease, diesel fuel substitutes
Cuphea oil	Cosmetics and motor oil
Tallow oil	Steam cylinder oils, soaps, cosmetics, lubricants, plastics

Source: Panchal et al., 2017

- **Actors**

General setting:

The lubricants market is highly competitive with approximately 130 major oil companies competing with 590 small and medium-sized specialized independent players. The World-wide top 10 finished lubricants manufacturers hold more than 50 % of global volumes while the remainder of more than 700 manufacturers share less than 50 % (Selent and Steinert, 2015).

Table 14.4: Global top 10 lubricant manufacturers

Manufacturers/product name	Country
Shell	Great Britain/The Netherlands
Exxon Mobil	USA
BP	UK

Chevron	USA
Total	France
Petrochina	China
Lukoil	Russia
Fuchs	Germany
Nippon Oil	Japan
Valvoline	USA

Source: Singh et al., 2017

Europe:

The leading suppliers of finished bio-lubricants are Panolin (Switzerland) and Fuchs (Germany) in Europe and worldwide, driven by their bio-lubricant range and focus, global reach and OEM partnerships. Both companies are directly competing with such global oil majors as BP (UK), Shell (Great Britain/The Netherlands), ExxonMobil (USA) and Total (France) (Luzuriaga, 2017).

In 2015 Fuchs acquired Statoil's Fuel and Retail Lubricants business. Binol (Sweden), a leading player in the Nordic bio-lubricants market, was acquired by Quaker Chemical (Luzuriaga, 2017).

Rest of the world:

The combined Houghton and Quaker Chemical Co.(USA) is the leading metalworking fluids supplier. Quaker Chemical also is active in other bio-lubricant product segments through acquisition activities.

- **Value proposition and sustainability**

Co-products:

If only the fatty acids are used from the bio oils, glycerine is obtained as a co-product. Glycerine also comes in large quantities from the production of biodiesel.

Environmental impacts, benefits, sustainability:

Feedstock production and biolubricant formulation: The results of Life Cycle Assessments comparing biolubricants with fossil-based lubricants depend strongly on the boundary conditions.

In principal, the production of mineral lubricants has higher energy consumption and CO_2 emissions but bio-based lubricants are the major contributor to the acidification and eutrophication potential (Cuevas, 2010; Bart et al., 2013).

More in detail, the contributions to acidification are approximately 50% higher for vegetable oil-based hydraulic fluids than for mineral oil-based hydraulic fluids due to high emissions from rapeseed cultivation (Ekman and Börjesson, 2011). The contributions to eutrophication are at least 20 times higher for vegetable oil-based hydraulic fluids. This is mainly due to nutrient leaching in rapeseed cultivation. As regards CO_2, (Ekman and Börjesson, 2011) found a fourfold higher emission of this gas for fossil-based lubricants

(4.8 kilogram per liter (kg/l) of base fluid for hydraulic fluids) comparing to biolubricants (1.3 kg CO_2 equivalents).

Biolubricants use: Major portion of the lubricants consumed worldwide ends up in polluting the environment. It is claimed that 50 % of all lubricants sold worldwide end up in the environment via total loss, spillage and volatility. Estimates for the loss of hydraulic fluids are as high as 70–80 % (Madanhire and Mbohwa, 2016). Many efforts are made to minimize spillages and evaporation. These high lubricant losses into the environment were the reason of the development of environmentally friendly bio-based lubricants with higher biodegradability and lower toxicity. Biolubricants also have, in part, other performance characteristics that may provide benefits for some applications, such as better lubricating properties. Besides, the idea that oil soon may no longer be available, industries have been searching for a cheap, renewable source of lubricant (Mang and Dresel, 2007).

Socio-economic advantages, health impacts (also comparison with alternatives):

The literature does not report significant health impacts. .

Economics: bio vs non-bio-based alternative:

Biolubricants often have higher prices with respect to the traditional counterparts, being in general priced approximately 1.5 to 2 times higher than mineral-oil-based lubricants (Frost & Sullivan, 2014).

- **Outlook**

Projected trends (baseline):

As indicated above, biolubricants are already part of the market (TRL 7-8 for high performance lubricants and TRL 9 in case of loss lubrication). Although Fuchs Petrolub estimates, from a technical point of view 90 % of the mineral-oil-based lubricants can be replaced by biolubricants (Rübberdt, 2017), they are priced approximately 1.5 to 2 times higher than mineral-based lubricants. According to Frost & Sullivan (2014), the CAGR for the biolubricants market with 3.9 % will be higher than for the lubricant market as a whole (3.2 %) until 2020.

Competitiveness and role of Europe in global production:

Biolubricants are in price competition with fossil based lubricants. The leading suppliers of finished biolubricants are Panolin (Switzerland) and Fuchs (Germany) in Europe and worldwide, driven by their bio-lubricant range and focus, global reach and OEM partnerships. Both companies are directly competing with such global oil majors as BP (UK), Shell (Great Britain/The Netherlands), ExxonMobil (USA) and Total (France) (Luzuriaga, 2017).

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15 PHAs from renewable oils and fats

- **General information**

Product Name	PHAs from renewable oils and fats
Technology readiness Level (TRL)	6
Biomass Platform	Renewable oils and fats
Business to Business (BtB) or Business to Consumer (BtC)	BtB

- **Product description**

Polyhydroxyalkanoates (PHAs) are bio-polyesters synthetized and accumulated like carbon or energy storage supply by various microorganism. The homopolymer poly(3-hydroxybutyrate) (PHB) and its copolymers containing valerate units (PHBV) or hexanoate units (PHBH) represent the most diffused types of PHAs.

PHAs macromolecular chains can be synthesized from numerous carbon-rich substrates by the biosynthetic action of selected prokaryotic microorganisms. Sugar-rich substrates, such as sugar beets molasses or sugar cane bagasse, have been widely studied for the industrial production of PHAs. All the industrially-relevant productions worldwide are actually based on these kinds of feed for the microorganisms (http://www.bio-on.it. http://www.biomer.de. http://www.kaneka.jp). The PHAs granules function inside bacterial cells is that of carbon and energy storage, that can be degraded when necessary by several microorganisms producing depolymerizing enzymes. This makes the PHA degradable to water and carbon dioxide (or methane, under anaerobic conditions) in all biologically active environments such as soil, open waters (i.e. rivers and lakes, seas and oceans), compost and sewage (Somleva, Peoples, and Snell 2013; Castilho, Mitchell, and Freire 2009).

A variety of waste streams different from sugars have been tested in last decades to produce PHAs in economically sound ways. Examples of used carbon sources are different kinds of agro-industrial food waste (Tsuge et al. 2002; Wolf et al., 2005, Chaudhry et al. 2011), organic municipal waste (Pagliano et al. 2017), and activated sludge coming from waste water treatment (Chua et al. 2003).

It is noteworthy that the molecular structure of PHAs chains accumulated inside bactierial cells, and their consequent physical and mechanical properties as plastic materials, does not directly vary upon the kind of biomass feedstock used as carbon source. It is only dependent on the bacterial stream used for the fermentation process, its operative conditions, and the number of carbon atoms available in the chemical moieties of the feedstock, that are used as building blocks by bacteria.

In the process of searching for more affordable carbon sources, the attention has been also focused on fat wastes from animal industry (slaughterhouse), glycerol for microorganisms like yeasts. Finally, to obtain PHA monomers (i.e., the 3-hydroxyvalerate) it is possible to proceed towards the biotechnological transformation of the saturated fraction (fermentation carbon feedstock) of animal-fats, derived from the biodiesel production.

Chemical-physical characteristics

As claimed above, PHAs chemical-physical properties does not vary upon the specific kind of biomass feedstock used for the bacterial fermentation. This means that PHB or PHBV polymers derived from sugars or renewable oils and fats will show exactly the same features, provided that the fermentation processes lead to the same molecular weight and molecular weight distribution of the chains.

According to the literature, chemical and physical properties of PHAs polymers are very similar of those characterizing petroleum-derived commodity polymers, such as polypropylene and polyethylene. This makes PHAs very good substitutes of conventional plastics (Zhu et al. 2013), and their uses and applications can vary accordingly to their specific molecular structure.

Depending on the chain length in the PHA subunit (monomer) the hydrophobicity and a number of other properties including the glass transition temperature, the melting point, and level of crystalline color, can vary. Normally, short-length PHAs are hard crystalline materials (Williams et al. 1999), medium-chain length PHAs are elastomers and have a much lower melting point and glass transition temperature (Wolf et al. ,2005); whereas PHAs with longer pendant groups are elastomeric.

Notwithstanding the bacterial strain and carbon-rich substrates selected for their synthesis, PHAs always show spontaneous and complete biodegradability in several environmental conditions, ranging from composting industrial and home facilities to open waters, i.e. rivers, seas, oceans, wet lands. This makes PHAs particularly attractive because this feature is coupled with their 100% renewable and biotechnological origin.

For the PHB, which represents the most-studied example of biodegradable polyesters belonging to the group of PHAs, its use is mainly as substitute of rigid commodity plastics as HDPE, PP and ABS. It is highly crystalline, therefore it is optically opaque, highly stiff and resistant to tensile stress. PHB suffers from being quite brittle, and its processing on standard industrial equipment can be achieved upon optimization of processing parameters, mainly to accommodate its rheological and thermal properties. Several PHB-based grades, fully or partially biodegradable, can be developed by polymer modification or melt blending with several other commercial plastics and bioplastics. The resulting level of biodegradability depends on the composition of the blend.

At present, PHB still has higher production costs with respect to its fossil-based alternatives (HDPE and PP mainly), but it holds advantages mainly related to the full biodegradability, full renewable origin and possibility to be obtained by the valorization of wastes.

The most important features of PHAs, encompass its biodegradable capacity in aerobic and anaerobic condition. Degradation are often upon exposure to soil, compost o marine sediment. However, the biodegradation rate is depending on factors such as exposed surface area, moisture, temperature, pH and molecular weight (Roland-Holst et al. 2013).

Biocompatibility is perhaps the most important property for applications in the medical field (Chua et al. 2003). In addition, bio-polyesters are inert, water-insoluble, not affected by moisture and indefinitely stable in air.

In pharmaceutical applications, PHA synthase is the key enzyme for PHA biosynthesis and can be a source for a rich chiral pool. Pure chiral compounds are finding increasing applications with their natural effectiveness and are preferred to their chemically synthesized counterparts (Chen 2009). Chiral drugs ensure greater wellbeing and increased effectiveness to patients at low dosages. Blending PHAs with high or low molecular weight help improve their material properties (Philip et al., 2007).

Moreover, food and beverage industry take advantages from PHAs latex. Due to their properties, such as water-resistant surfaces, moisture vapor barrier properties, and UV resistant ones, they can be used in packaging industry (Bugnicourt et al. ,2014).

Advantages of PHAs

Compared with the conventional plastic, one of the PHAs advantages is the biodegradability to CO_2 and water as the final products of mineralization (Yang, Hanna, and Sun 2012). It is well recognized that PHAs is a bio based, biodegradable, and biocompatible material and is perfectly embedded in the natural carbon cycle. Roland-Host et al. (2013) pointed out that, depending on the condition, the PHAs may degrade in 45 days to eight weeks. Because of proprieties resembling those of crystalline thermoplastics functional polymers PHAs could be further processed to produce other vendible items (Yang, Hanna, and Sun 2012).

In addition, bio-derived PHAs, compared to conventional plastic which are usually obtained by starting from expensive substrates of nutritional importance, can circumvent this controversy using agro-waste and surplus material.

An advantage of the PHAs derived from crude glycerol, is the widespread amount of biodiesel production that has been supported, since 2008, by European legislation.

Indeed, crude glycerol represents the main waste material of the biodiesel production (Koller, Marsalek, and Koller 2015). One mole of glycerol is obtained for every three mole of fatty acid methyl esters (biodiesel) produced (Gholami, Abdullah, and Lee 2014).

The price of fossil-based plastics depends on oil prices and fluctuates with them. Conversely, the prices of bio-based plastics depend, amongst others, on biomass prices that are more stable (van den Oever et al. 2017).

Disadvantages of PHAs

One of the disadvantages linked with the PHAs from oils and fats categories is the limited number and microbial strains isolated from soil and slaughterhouse wastewater as promising lipolytic and PHAs producing bacteria. Nevertheless, the final PHAs yields are still far from the values required for industrial applications. Unfortunately, it is very rare that a microorganism found in nature is both excellent producer of PHAs and suitable for an industrial process requiring the ability to utilize fatty waste as carbon source (Romanelli et al. 2014).

Main uses

Four main areas of application can be envisaged for PHAs: rigid and flexible packaging materials, injection molded products, fibers and biodegradable particles.

As far as packaging, moldings and fibers is concerned, PHAs take advantage of being "standard" thermoplastics; their peculiar rheological behavior and weak thermal stability during processing have to be supported by a proper selection of the suitable plastic formulation (i.e. proper additives selection and dosing).

PHAs micro and nanoparticles are now attracting vast interest due to their possible application in cosmetic, and detergent formulations that will not induce any plastic littering to the oceans thanks to the spontaneous biodegradability of the particles. Mattifiying powders for blushes and make-up, as well as skin scrubs or abrasive detergents, are just a few examples of the fully biodegradable formulations that can be developed using PHAs powders.

PHAs are also attracting a lot of interest due to their biocompatibility with biological tissues, and suitability to be implanted for temporary bio-resorbable medical devices.

PHAs are investigated for tissue engineering, wound healing, cardiovascular uses, orthopedics, and drug delivery due to their biocompatibility and biodegradation in human tissues. PHA-based sutures, artificial esophagi and artificial blood vessels are already offered as commercial products (Roland-Holst et al. 2013).

Production process

PHAs derived from animal fat and used cooking oil can be synthetized by different microorganisms as shows Table 15.1.

Table 15.1: Sources and yields of PHAs

Food waste sources	Microorganisms	PHA polymer type	Cultivation	Dry cell weight (g l -1)	Maximum PHA production reported (gPHA g−1 dcw)	References
Tallow	Cupriavidus necatorH16	PHBV	Fermenter, two-stage batch	5.8	80%	(Taniguchi, Kagotani, and Kimura 2003)
Waste frying rapeseed oil	Cupriavidus necatorH16	PHB	Flask, batch	10.8	67.9%	(Obruca et al. 2014)
Waste frying palm oil	Cupriavidus necatorH16	PHB	Flask, batch	11.9	58.0%	(Obruca et al. 2014)
Waste frying sunflower oil	Cupriavidus necatorH16	PHB	Flask, batch	10.812.53	52.4%	(Obruca et al. 2014)

The process optimization could also be made by use of substrates mostly divided into three macro-categories such as monosaccharide’s, triacylglycerol and hydrocarbons as shows in Figure 15.1. For each substrates, different PHAs molecules can be obtained.

The triacylglycerol containing long chain fatty acyl groups tend to be solid like fats, in contrast the triacylglycerol containing short chain fatty acyl group tend to be liquid like oil.

Direct use of triacylglycerols requires triacylglycerol-utilising bacteria, which can secrete lipases. The released lipases in the fermentation media catalyse the release of fatty acids from triacylglycerol molecules. The fatty acids are then transported into the cell through the cell membrane, where they are catabolised via a β-oxidation cycle to produce PHA monomers and then synthesized into PHAs (Jiang et al. 2016).

In the 1996, Cromwick at al. (1996) found that on four different microorganism only *P. resinovorans* could produce PHA polymer on unhydrolyzed tallow, with a PHA content of 15 % of the cell dry weight. However, the ester of the fatty acids from tallow with methanol can be fermented using *P. citronellolis*, with a productivity for medium chain length *mcl*-PHA of 0.036–0.050 g/(L*h) and PHA contents of 20.1%–26.6% (wt)(Muhr, et al. 2013).

Therefore, *mcl*-PHA could be also produced from saturated biodiesel fractions (SFAE) stemming from animal waste lipids. Only in Europe, animal lipids from slaughtering and animal-processing industry amount to more than 500,000 t per year. Using them for biodiesel production by alkaline transesterification, the available crude glycerol is estimated to be 50,000 t. SFAE reduce the biodiesel properties as engine fuel, but, if separated, it can be used as feedstock for the biotechnological production of PHA, whereas the remaining unsaturated biodiesel fraction performs as excellent 2nd generation biofuel (Muhr, Rechberger, Salerno, Reiterer, Malli, et al. 2013).

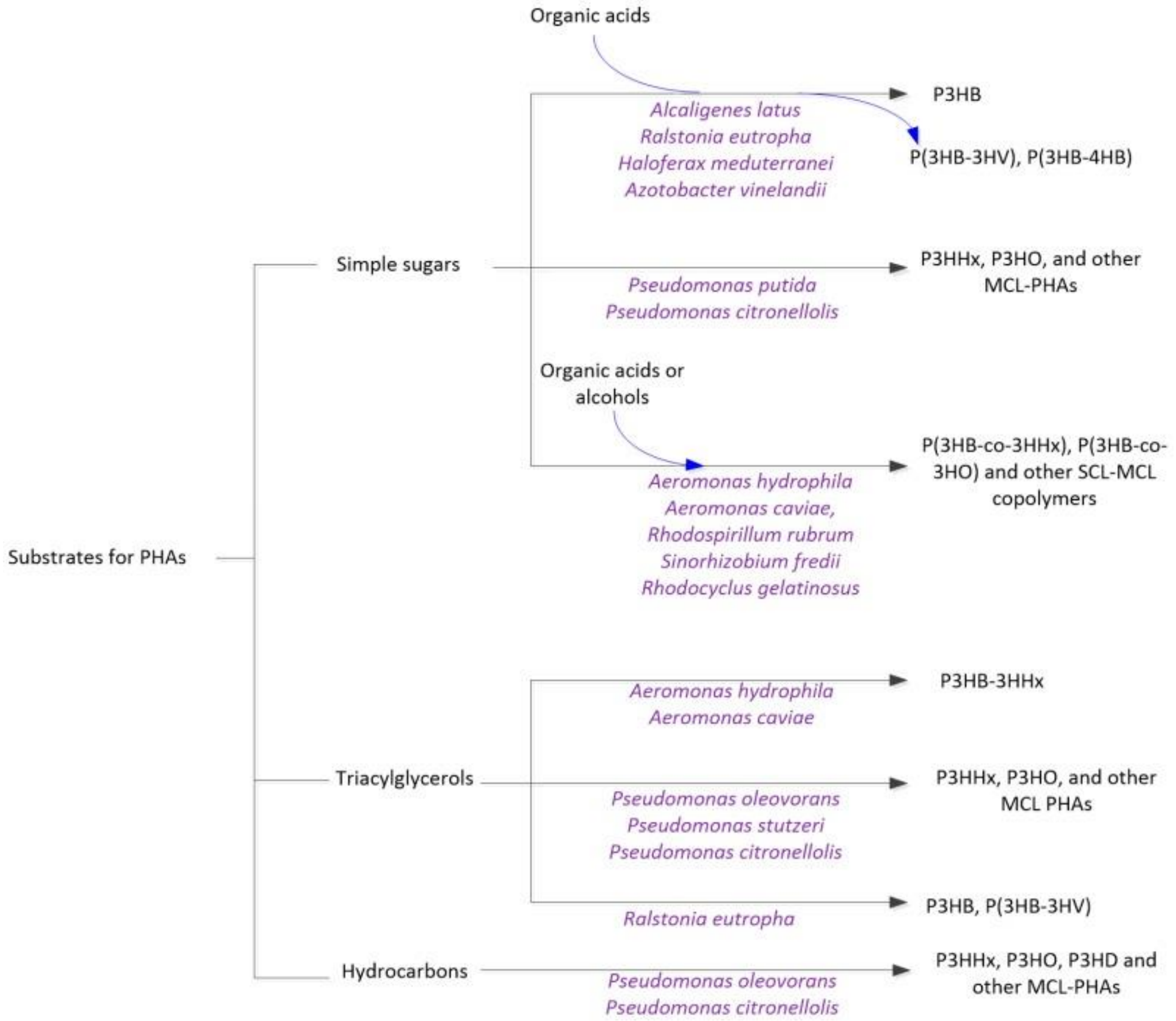

Figure 15.1: Substrates and microorganisms that can synthetized PHAs (Source: Jiang et al. 2016)

The process that leads to the production of PHA from crude glycerol, starts from lipids of different origins. These lipids, which undergo the process via alkaline-catalyzed transesterification, turn into biodiesel, giving glycerol as the main sub-product.

The entire process has been explained by Koller, Marsalek, and Koller (2015) and is represented in Figure 15.2.

In a wide range of carbon substrates, Ashby et al. (2004) reported a PHAs production from crude glycerol and PHB – example of polyesters belonging to the PHAs group - with *Paracoccus denitrificans* and *Cupriavidus necator,* attaining similar polymers to those obtained from glucose. In addition, Koller et al., (2015) recognized the crude glycerol phase (CGP) from biodiesel production or from pitch from petro-chemistry as a promising feedstock for PHA.

Production costs highly vary and depend on: bacterial stream selected, carbon source, production technology applied, recovery technology applied. It should be mentioned that producing PHA from sugars is actually the less expensive option, and technology is at TRL9.

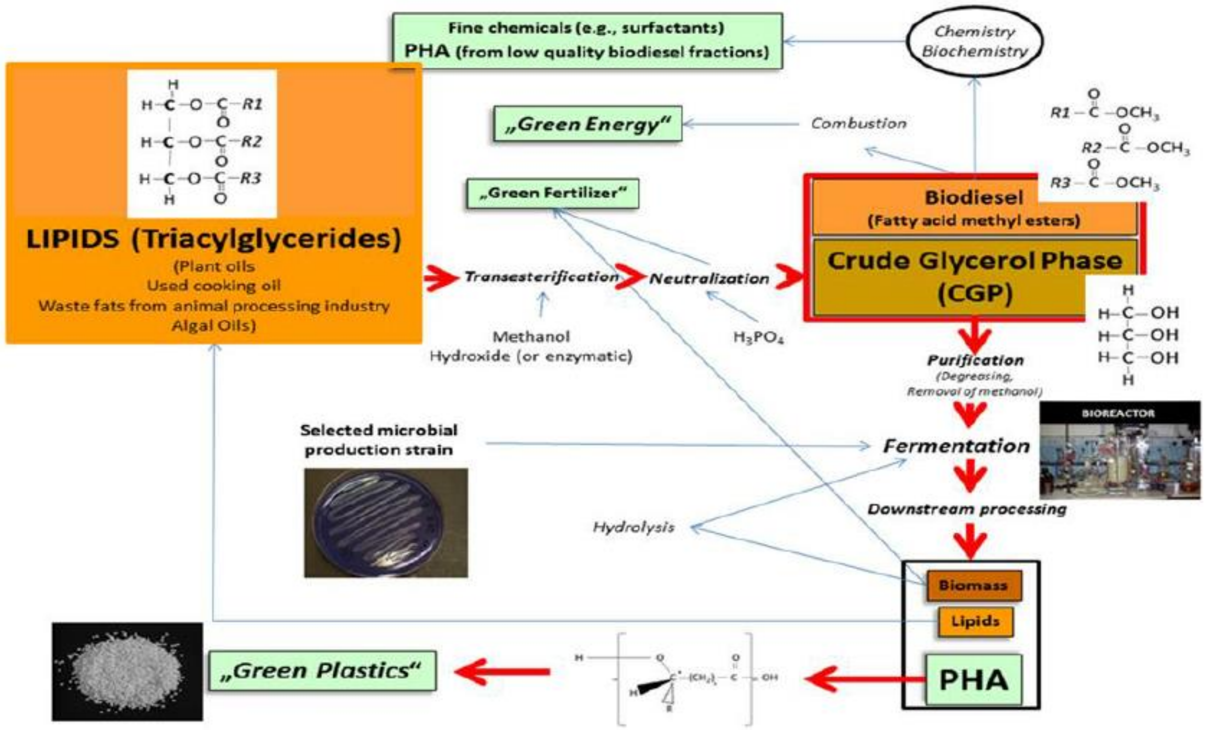

Figure 15.2: PHA production from Crude Glycerol Phase (CPG) in biodiesel industry (red arrows indicate the main path from lipids to the biopolymer as a final product) (Source: Koller, Marsalek, and Koller, 2015)

- **Markets**

Current volume, market value, prices

Worldwide demand of bio plastics has grown over the past several years, even though it still represents a small fraction of global plastics demand.

In 2007 worldwide production of bio plastics amounted to approximately 360,000 metric tons (Mt). This quantity arise to 725,000 Mt in 2010, 890,000 Mt by 2012, and to around 2.02 million Mt in 2016 (European Bioplastic 2017). It is projected to reach up to 4.4 million Mt by 2020 (Roland-Holst et al. 2013), and represent a market of around USD 5.08 Billion by 2021, growing at a CAGR of 12%.

The PHAs price, in 2016, was higher than euros 10/kg. For PHA with density ranging between 1200-1250 (kg/m3), the 2016 price was 5 euro/kg, which is too high for most applications (van den Oever et al. 2017). The commercially viable price should come to US$3–5 per Kg close to other biodegradable plastic material (Reddy et al. 2003). It is expected that when conversion into products becomes more favorable due to economy-of-scale of production the prices of bio-based plastics will decline.

Biomass/yield and feedstock availability

Further, it was estimated that a 10 million gallon per year biodiesel plant would have the potential of producing 20.9 ton PHB. More recent reports showed that *Pseudomonas oleovorans NRRL B-14682* could also be used for PHB production from crude glycerol (Yang, Hanna, and Sun 2012)

For instance, the entire amounts of animal lipids from the slaughtering process have been quantified with more than 500 000 tonnes per year. However, the cost-effective production of PHAs from animal lipids has not been addressed so far because microbes with the combination of substrate-utilization and PHAs production are not currently available (Romanelli et al. 2014).

- **Actors**

General setting

The global PHA market is poised to grow at a CAGR of around 6.3% over the next years to reach approximately $119.15 million by 2025. Some of the prominent trends that the market is witnessing include growing demand from healthcare industry, increasing market for renewable materials, and recent advancements in PHA manufacturing technologies (Research and Markets, 2017). At the global level, there are just few technologies which have been succesfully upscaled to the commercial level, and the overall commercial availability of PHA is still limited (Research and Markets, 2017).

Europe

The European region represents a major hub in the field of research and development for bio plastic production. There exist some projects and research activities related to PHAs from oils and fats. Examples are listed below.

ANIMPOL (Biotechnological conversion of carbon containing wastes for eco-efficient production of high added value products: http://www.animpol.tugraz.at/), elaborated a process used to convert animal residuals into bio plastic (European Bioplastics 2018).

Bio-on, founded in 2007 with the purpose of operating in the sector of modern applied biotechnologies, produces MINERV-PHA, a linear polyester naturally occurring as a result of bacterial fermentation of sugars. Nowadays, Bio-on's technology has been adapted to by-products as: sugar beet, sugar cane, glycerol from biodiesel, potatoes, animal fats, fruits and vegetables, wood, domestic wet waste, wine production waste, and CO2. In 2018 Bio-on started its world's first facility for the production of PHAs bio plastic in Italy (http://www.bio-on.it/production.php), with a capacity of 2 000 tons/y. In 2015 an agreement was signed by Bio-on and S.E.C.I. S.p.A. part of Gruppo Industriale Maccaferri holding, for Italy's and world's first facility for the production of PHAs from biodiesel production co-products, namely glycerol. The two companies, operating in sustainable biochemistry and industrial development of levulinic acid with Eridania Sadam, will work together to build a production site with a 5 thousand tons/year output, expandable to 10 thousand tons/year. (https://omnexus.specialchem.com/news/industry-news/bioon-and-seci-with-worlds-first-plant-for-bioplastic-from-biodiesel-coproduct-glycerol-000179340)

Rest of the world

Many companies exist producing PHAs for bio plastics and using PHAs in their application. Within this wide range of this firms, only a few are using tallow, animal fats and glycerol like a feedstock.

One of these is the CSIR-Central Salt and Marine Chemicals Research Institute (CSIR-CSMCRI: http://www.csir.res.in/networkdata/csir-csmcri) which makes use of crude glycerol as raw material. The crude glycerol is obtained as a by-product from the waste stream during biodiesel production from the Jatropha oil in India. They filed for the patent in 2009. The production has been made at sample scale with the purpose to make the process commercially viable

- **Value proposition and sustainability**

Co-products

Crude Glycerol, one of the PHAs feedstock is a by-product of the palm oil refining process and used as a humectant as well as a plasticizer in certain applications such as oral-care products, tobacco, cosmetics, food and beverages. In addition, it is the most significant co-product generated in biodiesel processing. It already competes with other products in the market but is also available in high quantities (Chee et al. 2018).

Environmental impacts, health impacts, benefits, sustainability

the estimation of cradle-to-cradle life cycles for bio plastics such as PHB ranges from 1 to 10 years, which would be a substantial benefit when compared with conventional plastics obtained by fossil feedstock's (Roland-Holst et al. 2013).

In addition, the substitution of fossil plastics by bioplastics can lead to lower non-renewable energy use and GHG emissions (Bos et al. 2012). In terms of competition in food, feed and land, if compared with primarily food crop such as sugar cane or crop oils, waste stream used for PHAs, do not represent a food-based material. However, the use of land for the production of feedstock for bioplastics may lead to direct and/or indirect land use change. This can result in higher GHG emissions (van den Oever et al. 2017). On the other hand, the environmental impacts of PHA production depend on the carbon substrate used. If the latter is a waste by-product stream, little to no land competition impact is registered.

On eutrophication and acidification, bio-based plastics may have a higher impact than fossil plastics, but this is not always the case (van den Oever et al. 2017).

The main environmental benefit related to PHAs is their complete biodegradability when exposed to different environmental conditions. PHAs are compostable in aerobic and anaerobic conditions, but also spontaneously biodegradable in open waters (i.e. rivers, oceans, wet lands) thanks to the degradation action of natural bacterial enzimes. PHAs therefore represent one of the best opportunities to reduce plastic pollution and plastic littering on lands and seas as they are the only bioplastics that spontaneously degrade in open waters. Additionally, PHA powders and particles as abrasives in detergents formulation do not impact on the environment.

As for the product safety and health issues, PHA is biocompatible and bioresorbable. Its bio-medical applications include bone-marrow scaffolds, cardiovascular patches, nerve repair devices, bone.

Socio-economic advantages, bio vs non-bio based alternative

One of the socio-economic advantages for the PHAs production from inexpensive carbon substrates is the feedstock availability and the abundancy of its resources. According to Koller et al. (2013), using animal lipid and waste stream for biodiesel production through transesterification results in 50,000 t of SFAE fraction, meaning a yield of 0.7 g of PHAs per g of SFAE.

From an evironmental perspective, PHA offer peculiar characteristics, In fact, PHA have been recognized as the only plastics that spontaneously biodegrade in open sea (Calrecycle, 2012). Ordinary plastics break down to tiny unnoticeable fragments that can easily enter into the food chain (van den Oever et al. 2017) while biodegradable plastics like PHA spontaneously biodegrade under the bacterial action in open environment, such as rivers and oceans, thus representing a solid mitigation strategy of the plastic pollution in the environment. PHA are also compostable. This property can be tested and certified according to the European standard for industrial composting EN 13432. The EN 13432 also assured that no heavy metal and harmful substances are left in the soil after the degradation (European Bioplastics 2018).

- **Outlook**

Projected trends (baseline)

Following current trends highlighted above (starting from 2.05 Mt in 2016) and assuming the value of CAGR registered for late years (12 %), production and its value will reach 13,7 Mt and 14 billion USD in 2030.

Costs are still too high for most applications. On the other hand, while conventional plastic are obtained using expensive substrates of nutritional importance, bio-derived plastics using PHAs can circumvent this controversy using agro-waste and surplus material.

Also, costs are of the same magnitude of competing products, implying the possibility to increase sharply production via achieving important economies of scale. The latter are possible as PHA still represents a small proportion of total plastic market (worldwide demand of bio plastics has grown over the past years, even though it still represents a small fraction of global plastics demand).

Additional factors supporting an increase in production and a reduction in costs (hence, in sale price), relate to market trends for PHA-based products as well as legislation, which is more and more keen to recognise efforts in environmental sustainability. For example, supporting the production of bio-diesel, European legislation is indirectly fostering the spreading of PHAs derived from crude glycerol, representing the main waste material of the biodiesel production. Future opportunities will then depend on trends in biodiesel production (highly dependent on legislation) and the capacity to link the two production processes.

In addition, trends such as importance and increase in market size for packaging can be expected to further improve opportunities for the use of bio-derived PHAs. On the other hand, biocompatibility is perhaps the most important property that will support applications in the medical field. Additionally, increasing meat consumption trend at global level can provide further cheap feedstock for the production of PHAs from animal lipids.

PHA-based products show similarity in performance with petroleum-derived commodity polymers (such as polypropylene and polyethylene), which, added to biodegradability and/or compostability, makes PHAs particularly attractive. In addition, PHAs production allows creating high added-value products by using material that would represent just waste otherwise.

As for price, the PHAs price depends on the substrates cost and the bacterial used that influence the PHA yield and efficiency, in addition to be influenced by the technology used to produce it. In 2016 it was between 5 and 10 euro/kg, depending on PHA density, which is too high for most applications.

Competitiveness and role of Europe in global production

Europe is the second continent after Asia for the production of PHA, with a current capacity of 0.45 million tonnes for bio-plastic production (18% of global production). Despite that, the European region represents a major hub in the field of research and development.

The responsiveness of EU markets to the final products interesting characteristics will help boosting the use of PHA-based products in the EU; however, availability of cheap raw material is likely lower in the EU than elsewhere. Competitiveness will depend on future developments of biofuel production, while in general the EU is not very competitive for the production of oil crops that would, in addition, conflict with food and feed production if this has to be carried out using dedicated crops.

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16 Limonene-based engineering polymers

General information

Product Name	Limonene-based engineering polymers
Technology readiness Level (TRL)	5
Biomass Platform	Terpenes
Business to Business (BtB) or Business to Consumer (BtC)	BtB

Product description

Plant-derived chemicals are good candidate for polymer synthesis, as they are renewable and environment friendly.

Limonene (Figure 16.1) belongs to the family of terpenes and is the main element of the citrus fruit peels essential oils. Limonene is mainly derived from the oil and peel of citrus fruits such as lemon, orange, mandarin, lime and grapefruit and is with a clear colorless liquid at room temperature (Lopresto *et al.*, 2014). It can be obtained naturally by more than 300 plants and its worldwide production exceeds 70 000 tonne per year (Firdaus, Montero De Espinosa and Meier, 2011). It is classified as a cyclic monoterpene made up of two isoprene units and it is an optically active compound having one internal and one external double bond. Therefore limonene is very good substrate for range of chemistries involving double bonds, mainly polymerizations.

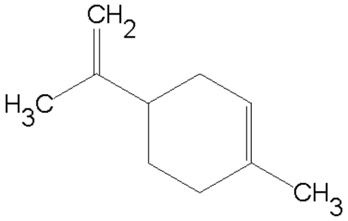

Figure 16.1: Molecular structure of limonene

Since 1960 limonene has been the object of an increased interest to obtain monomers for durable (i.e. not biodegradable) bio-plastics, and polylimonene was developed (Modena, 1965).

At current, technical polymers for engineering use, having elevated thermomechanical properties, are under development starting from limonene. Beyond being an aromatic moiety that induces elevated molecular stiffness to the polymer chains, it results particularly attractive for the substitution of traditional monomers showing relevant environmental and health impacts.

Limonene is particularly attractive for the synthesis of polycarbonates (Fig. 16.2), acting as bio-based substitute of bisphenol-A (BPA), a fossil-derived molecule recognized as toxic (Hauenstein, Agarwal and Greiner, 2016).

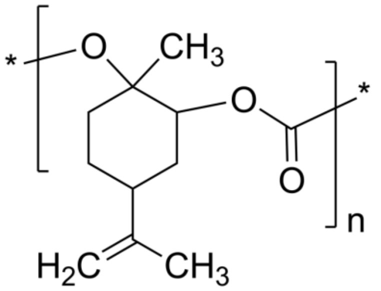

Figure 16.2: Chemical structure of poly(limonene-carbonate)

Polyamides (PAs) and polyurethanes (PUs) are among the most important polymeric materials, and since they display versatile properties, they can be used for many applications, such as tubings, footwear, industrial machinery, coatings and paints, elastic fibers, rigid insulations, soft flexible foam, medical devices, and many others. Both polyamides and polyurethanes can be produced from petroleum resources or renewable feedstocks, and limonene can serve as a building block for PAs and PUs based on renewables.

In the synthesis of polyurethanes, highly versatile in several applications mainly for the possibility to make rigid and flexible foams, limonene-based polyols are a safe bio-based alternatives for traditional Mannich polyols, based on nonyl-phenol considered estrogenic compounds and toxic especially for aquatic life (Gupta *et al.*, 2015).

Limonene carbonates can be used as intermediates to prepare a wide variety of linear, branched and cross-linked hydroxy-functional green polyurethanes which do not require either phosgene or toxic isocyanate monomers (Bähr, Bitto and Mülhaupt, 2012).

Chemical-physical characteristics

Completely bio-based high molecular weight aliphatic poly(limonene carbonate) with excellent transparency, superior hardness compared to BPA-PC and a high Tg of 130 °C is under development (Hauenstein *et al.*, 2016). Its overall properties are similar, but generally higher, that polystyrene. Renewable transparent coating resins based on poly(limonene carbonate) can show highly tunable glass transition temperatures, ranging from approximately 60 up to ca. 120 °C (Chunliang Li *et al.*, 2018) and can be cured with conventional curing agents and catalysts. Also thermoset UV-curable powder coatings can be realized, having pencil hardness 2H to 4H.

Due to its high carbonate content and rigid structure, the cure of limonene carbonate with polyfunctional amines affords rigid and brittle non-isocyanate-polyurethanes (NIPUs). This is reflected by high Young's modulus, high glass transition temperature and low elongation at break. Using diamines linear NIPUs are formed with end groups and molar mass being controlled by the amine/carbonate molar ratio. The resulting amine and carbonate terminated oligo-NIPUs are attractive new additives and curing agents for epoxy resins and the production of segmented polyurethanes. In contrast to all conventional NIPU based upon seed oils, limonene polycarbonates do not contain ester groups which can interfere with the amine curing and amine advancement reactions.

Purified limonene carbonate also enables to increase stiffness and molar mass of linear NIPUs which are of interest regarding the preparation of reactive NIPU prepolymers, NIPU thermoplastics, and thermoplastic NIPU elastomers containing alternating rigid LC-based hard segments and elastomeric segments.

Renewable PAs based on readily available limonene derivatives can be synthesized via interfacial condensation with various diacid chlorides, or also by polycondensation with renewable diesters (Firdaus, 2013). Renewable PAs from amorphous to high-melting semicrystalline polymers with molecular weights up to 12 kDa can be obtained.

Main uses

Engineering polymers, and among them polycarbonates, polyamides and polyurethanes, showing elevated thermomechanical properties, find wide application in technical fields such as construction engineering and automotive industry.

Polycarbonates find several uses as ductile and tough thermoplastic transparent materials; protective coatings as well as optically clear sheets and films can be prepared thereof. Polyamides and polyurethanes are among the most important polymeric materials for technical use, and since they display versatile properties, they can be used for many applications, such as tubings, footwear, industrial machinery, coatings and paints, elastic fibers, rigid insulations, soft flexible foam, medical devices, and many others. Polyurethanes find wide application as foams, both rigid and flexible depending on their molecular structure.

All polycarbonates, polyamides and polyurethanes can be produced from petroleum resources or renewable feedstocks. However, due to the depletion of petroleum resources and their escalating prices as well as environmental impact, innovative research on renewable resources as well as the design of synthetic pathways that are more sustainable and environmentally benign is under development.

Limonene represents a versatile building block for the preparation of all these classes of technical polymers, without any negative impact on their possible application with respect to the well-known non-renewable counterparts.

Production process.

Limonene worldwide production exceeds 70 000 tonnes per year (Firdaus, Montero De Espinosa and Meier, 2011). It is currently extracted from the skin of citrus fruits via mechanical or distillation methods (Rossi *et al.*, 2011; Lopez-Sanchez *et al.*, 2014) but the availability and quality could be insufficient for all its applications. Therefore, complementary microbial production of limonene could be also considered. Since Limonene can be derivatized to high-value compounds, microbial platforms also have a great potential beyond just producing Limonene (Jongedijk *et al.*, 2016).

Limonene could be also produced using biological methods such as fermentation and biosynthesis (Paggiola, Van Stempvoort and Bustamante, 2016). Moreover, in order to optimizing D-limonene extraction from lemon peels after citrus processing, Lopresto *et al.*, (2014) reported a non-conventional solvent extraction method.

The limonene oxidation product LO (Limonene oxide) has been used as a monomer for direct cationic polymerization and catalyzed formation of poly(limonenecarbonate) as reported by Pena Carrodeguas *et al.*, (2015), or as a dioxide for isocyanate-free synthesis of polyurethanes or for copolymerization with CO_2 (Hauenstein *et al.*, 2016).

The addition of cysteamine hydrochloride to (R)-(+)- and (S)-(−)-limonene is described as a versatile and effective way to obtain new amine functionalized renewable monomers for polyamide and polyurethane synthesis. Thus, through different combinations, limonene, fatty acid, as well as Nylon 6,6 copolymers can be prepared. Moreover, limonene-diamines van been transformed into dicarbamates via a phosgene-free route and used in polycondensations to synthesise linear renewable polyurethanes, from amorphous to semi-crystalline, via an isocyanate-free route. (Firdaus, 2013)

- **Markets**

Current volume, market value, prices.

World wide, it has been estimated that the (R)-enantiomer ((+)-limonene), wich constitutes between 90-96 % of citrus peel oil, accounts for around 49 895-74 843 tonne/year (Byrne *et al.*, 2004). Being limonene the main component of orange oil also, it is a quite abundant alicyclic terpene, resulting in a capacity of more than 520 000 tonne/year (estimated from 70 million tonnes per year oranges produced), of which, 70 000 tonne of limonene are extracted each year (Hauenstein *et al.*, 2016).

According to Paggiola, Van Stempvoort, and Bustamante (2016), around 130 million tonne of citrus fruit are growing worldwide every year where 65 million tonne per year are generated as a waste citrus peel. According to Lopez-Sanchez *et al.*, (2014) the worldwide production of d-limonene in 2013 was estimated to exceed 70 000 tonnes.

Lopez-Sanchez *et al.* (2014) have evaluated the D-Limonene price which, in 2011, has firstly reached USD 11 per kg to then fell to USD 3.3 per kg. In 2014, the price in the US has exceeded USD 10 per kg. A decade ago, manufacturers of industrial cleaning products were paying as low as USD 0.4 per kg.

The potential poly(limonene carbonates) market is high and competitive. Poly(limonene carbonates) have high mechanical, thermal, optical and chemical properties and will be produced where conventional oil-based polycarbonates cannot compete in terms of properties (Pagliaro *et al.*, 2018).

Biomass/yield and feedstock availability

The citrus production is affected by seasonality and the availability of citrus waste feedstok for D-Limonene extraction is not certain. The waste citrus peel is abundant if considering that during the processing of citrus fruits account for half of the raw fruit and are discarded as waste. This has been estimated to amount of about 15.6 million tonne of citrus waste every year (Jerome and Luque, 2017).

Annual global production of citrus fruits exceeds 88 million tonne (Varzakas and Tzia, 2016). More than half of this production arond 70 % is usually used in the juice and marmalade industries (Varzakas and Tzia, 2016), where about half of the processed citrus, including peels, segment membranes, and seeds ends up as citrus waste (Wilkins *et al.*, 2007; Pourbafrani *et al.*, 2013).

- **Actors**

General setting

Different actors characterize the scene both in EU and abroad.

Europe

- DSM, (Germany) (http://www.dsm.com/corporate/home)

- Evonik, (Germany) (http://www.corporate.evonik.com)
- EMS-Grivory, (Switzerland) (http://www.emsgrivory.com)
- Novamont, (Italy) (http://www.novamont.com)
- Reverdia, (Netherland) (http://www.reverdia.com)
- Solvay, (Belgium) (http://www.solvay.com)
- Corbion/Purac (Netherland) (http://www.corbion.com)
- Versalis, (Italy) (http://www.versalis.eni.com)
- JV BASF, (Oland) bio-PET (https://www.goinpharma.com/)
- Arkema, (France) (http://www.arkema.com)

Rest of the world

- DuPont, (USA) (http://www.dupont.com)
- BASF, (USA) (http://www.basf.com)
- Toray, (Japan) (http://www.toray.com)
- Amyris, (USA) (http://www.amyris.com)
- Wanhua Chemicals, (China) (http://www.whchem.com)
- Nature works -JV Cargill (USA-Japan) (http://www.natureworksllc.com)
- Metabolix, (USA) (http://www.yield10bio.com)
- Genomatica, (USA) (http://www.genomatica.com)
- Toray, (Japan) (http://www.toray.com)
- Novozymes, (USA) (http://www.novozymes.com)
- Lanzatech, (USA) (http://www.lanzatech.com)
- Kuraray, (Japan) (http://www.kuraray.com)
- Plantic Technologies, (Australia) (http://www.plantic.com.au)

- **Value proposition and sustainability**

Co-products

The citrus manufacturing process, could generate different co-products where limonene is one of that. For example, Limonene could be used for a large variety of products and applications vary. Traditionally, the limonene is used as flavoring compound, cleaning anti-microbial, and insects repellent. In Figure 16.3 the citrus co-products are reported (Jongedijk *et al.*, 2016b).

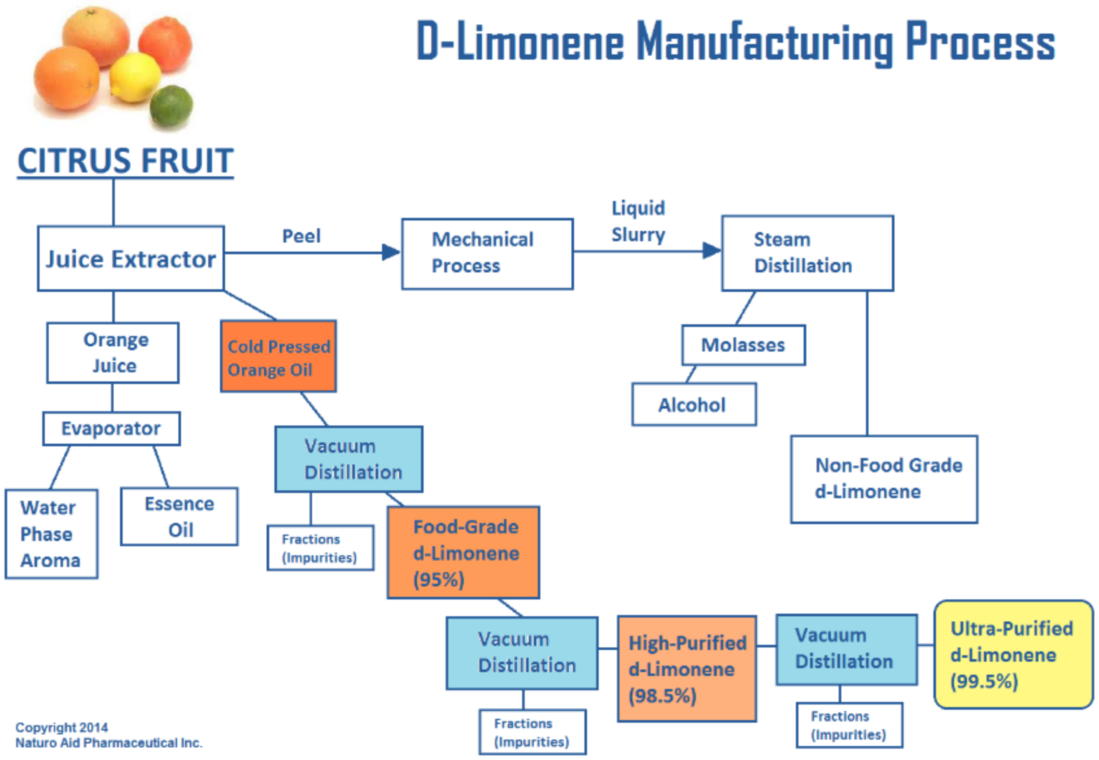

Figure 16.3: D-limonene manufacturing process (Source: Vita Aid, 2014)

Environmental impacts, benefits, sustainability

Limonene is a biodegradable chemical, but due to its low flash point, it must be treated as hazardous waste for disposal. It does not contain any ozone depleting chemicals but is currently regulated as a volatile organic compound. D-Limonene has a zero net global warming potential and is an environmentally preferable product (EPP) used as is or as part of an EPP formulation.

In the synthesis of polyurethanes, highly versatile in several applications mainly for the possibility to make rigid and flexible foams, limonene-based polyols are a safe bio-based alternatives for traditional Mannich polyols, based on nonyl-phenol considered estrogenic compounds and toxic especially for aquatic life.

In general, limonene-based polymers are not biodegradable in environmental conditions, so they represent fully bio-based altermatives to technical durable plastics such as aromatic polyesters and polycarbonates. Their end-of-life options priviledge mechanical recycling due to the high thermomechanical stability.

Socio-economic advantages, health impacts, bio vs non-bio based alternative

D-limonene is listed in the Code of Federal Regulation as generally recognized as safe (GRAS) for a flavoring agent (Sun, 2007). In terms of health impacts D-limonene has been clinically used to dissolve cholesterol-containing gallstones and also to relieve heartburn, (Sun, 2007).

Limonene is particularly attractive for the synthesis of polycarbonates, acting as bio-based substitute of bisphenol-A (BPA), a fossil-derived molecule recognized as toxic (Hauenstein, Agarwal and Greiner, 2016).

Technical properties of limonene-based engineering polymers (PCs, PAs, PUs) resemble those of the analogous fossil-based counterparts, thus generally allowing for the same or similar application.

For Limonene-based materials to compete on price with petroleum-based a Limonene production independent on citrus production should be developed. For example, the fermentation-based production method. However, for this method to be competitive, high efficiency in yield and productivity is needed.

Microbial production could meet the Limonene demand but still needs important engineering efforts (Jongedijk *et al.*, 2016).

- **Outlook**

Projected trends (baseline)

Limonene is produced several crops by-products and is used in the production of technical polymers that are basically substitutes of fossil-derived products, with similar properties. The future trends will hence follow the trends in oil prices and availability of cheap feedstock. The wide range of applications implies a demand that may vary strongly depending on trends in downstream markets (footwear, industrial machinery, coatings and paints, elastic fibres, rigid insulations, soft flexible foam, medical devices, foams).

As for price, D-Limonene confirmed its price volatility in the market just like any other agricultural product (Lopez-Sanchez *et al.*, 2014). In the decade between 2004 and 2014 the price in US has increased by more than 100% and it is reasonable to expect a further increase in time, although less than proportional. Starting from the market volume and assuming a compound, precautional, and increasing price variation.

Competitiveness and role of Europe in global production

Europe is very active in research and market of limonene, as well as other countries. Competitiveness and market shares will depend on local availability of feedstock at stable and low prices.

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17 Bacterial biosurfactants: sophorolipids and rhamnolipids

General information

Product Name	Sophorolipids and rhamnolipids
Technology readiness Level (TRL)	7
Biomass Platform	Natural Polyelectrolytes
Business to Business (BtB) or Business to Consumer (BtC)	BtB

Product description

Biosurfactants, widely known as biological surface-active compounds or microbial surface-active agents, are a structurally diverse group of molecules synthesized by microorganisms. They all have amphiphilic character. In the last five decades, they have reached a market niche as alternatives to chemical surfactants, due to their exclusively environment-friendly properties (Nitschke & Costa 2007).

There are five major categories of biosurfactans: (i) glycolipids, (ii) phospholipids and fatty acids, (iii) lipopeptides and lipoproteins, (iv) polymeric biosurfactants and (v) particulate biosurfactants. All of these have found applications in agricultural, pharmaceutical, food, cosmetics, and detergent industries.

Sophorolipids and rhamnolipids, belong to the class of microbial glycolipids (Randhawa & Rahman 2014) and are now biotechnologically manufactured in the industrial scale (Evonik, Germany, in the production site in Slovakia) from yeasts and bacteria. For this reason, sophorolipids and rhamnolipids have been selected as most promising biosurfactants under current development, and are subject of this case study.

Chemical-physical characteristics

Glycolipids biosurfactants are composed by a hydrophic fatty acid tail combined to a carbohydrate hydrophilic moiety. Depending on their chemical composition, they can be sub-divided into rhamnose lipids, trehalose lipids, sophorose lipids, cellobiose lipids, manno-sylerythritol lipids, lipomannosyl-mannitol, lipomannas and lipoarabinomannanes, diglygosyl diglycerides, monoacylgycerol and galactosyl-diglycedide. Among them, the best know are rhamnose lipids and sophorose lipids (Kitamoto et al. 2002; Mnif & Ghribi 2016).

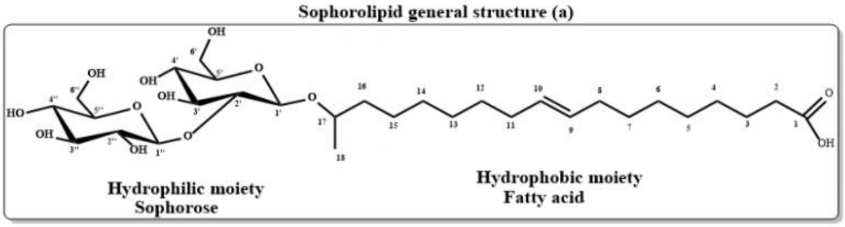

Figure 17.1 : General structure of Sophorolipids (Source: De Oliveira et al., 2015)

Advantages of sophorolipids and rhamnolipids

Sophorolipids have numerous properties that make them superior to synthetic surfactants. These include stability in the wide range of pHs, temperatures, and salinity (De Oliveira et al., 2015).

Several advantages characterize the biosurfactants when compared to their synthetic counterparts:

- biosurfactants are considered environmental friendly chemicals due to their complete biodegradability and full biological origin; they combine green chemistry with lower carbon footprint;
- biosurfactants are considered a low toxic material (Nitschke & Costa 2007) for living organisms and for the environment;
- biosurfactants can be produced from very cheap different raw material (Fakruddin 2012), therefore are easily and widely available.

In addition, they also show low-foaming and excellent detergent properties, water hardness (high concentration of divalent cations) does not affect their interfacial properties, synergism between acidic and lactonic forms of Sophorolipids increase surfactants activities, are readily biodegradable and exhibit good surface activity (De Oliveira et al., 2015). They are excellent emulsifiers making them comparable or superior to their synthetic counterparts. These remarkable physical properties derive from their more complex chemical structures (Abdel-Mawgoud et al. 2010).

Disadvantages of sophorolipids and rhamnolipids

No specific disadvantages apply.

Main uses

Due to their eco-friendly characteristics, biosurfactants are used in several field such as in detergent production, paints, cosmetics, textile, agriculture, food and pharmaceutical industries.

In particular, rhamnolipids have being used mostly as a bioremediation for oil recovery. Specifically, they are characterized by emulsification proprieties that can remove crude oil from contaminated soil. Furthermore for their low toxicity and antimicrobial activities, rhamnolipids are used in pharmaceutical fields and cosmetics (Randhawa & Rahman 2014).

Sophorolipids are not used only as detergents but also in agriculture, such as phytopathogens control and as adjuvant in formulation of herbicides (Mnif & Ghribi 2016). Sophorolipids have excellent promise as natural surfactants/emulsifiers for post emergence herbicides. Post emergence herbicide formulations contain adjuvants to allow greater adherence to the plant surface and for increased penetration of the plant cuticle. Non-ionic surfactants, such as polyethoxylated tallowamines (POEA) currently used in several post emergence herbicides are petroleum-base, ecotoxic and toxic to a wide range of organisms. Sophorolipids can replace synthetic surfactants like POEA. Lactonic Sophorolipids from *Candida bombicola* (LacSLP), acidic SLP from *Candida kuoi* (AcSLP) form emulsions with lipophilic contact herbicide lemongrass oil (LGO). The AcSLP formed longer-lasting and stable emulsions with LGO better than commercial POEAs.

The herbicide damage ratings (HDR) values are greater with the AcSLP/LGO and LacSLP mixtures than with LGO applied alone or together with POEA. Additionally, the low-foaming by the SLP preparations is highly desirable to minimize air entrapment, which can cause pump and sprayer malfunctions.

In food industry, the emulsifying property of Sophorolipids can be used for improve the physical properties (volume, texture, viscosity, stability and general eating characteristics) of products of vegetable fat emulsion-based or starch-based and animal food products. Sophorolipids added to wheat flour or a product containing it, modifies quality of final product. Production of bread from the wheat flour containing the Sophorolipids promotes better volume, appearance and shelf- life of bread. Germicides composition for cleaning fruits, vegetables, food processing equipment, surfaces and utensils, includes a mixture of surfactant (anionic surfactant - sodium lauryl sulfate or biosurfactant like Sophorolipids) and fruit acids (glycolic, lactic, malic, citric and tartaric acid). Besides acting as agent surfactant/emulsify Sophorolipids act as antimicrobial/germicidal agent. Sophorolipids presents antimicrobial properties and the ability to inhibit and disrupt biofilms formation by gram-positive (*Ralstonia eutropha* A TCC 17699) and gram-negative microorganisms (*Bacillus subtilis* BBK006).

Their use is also recognized in biomedicine, particularly as anti-microbial, antitumor, antiviral and immune-modulator (Roberto De Oliveira et al. 2015).

Sophorolipids biosurfactant have been produced and commercially applied as active ingredient in cosmetics products for body and skin applications. They are used as emulsifiers, foaming agentes, solubilizers, wetting agents and detergents. Among of several expected characteristics for cosmetics application, Sophorolipids show low cytotoxicity towards human keratinocytes and fibroblasts. In addition, Sophorolipids promote the metabolism of fibroblasts and collagen neosynthesis in the dermis of the skin, acting as an agent that restructures repairs and tones up skin. Sophorolipids stimulate leptin synthesis through adipocytes, which may reduce subcutaneous fat overload, which make its role in cellulitis treatment.

The increase in elastase activity from dermal fibroblastos leads to aging skin and the appearance of wrinkles. Sophorolipids inhibit free radical formation through inhibition of elastase activity.

Production process

Biosurfactants can be produced biologically, via fermentation process, by using by-products from other industries (e.g., from the bio-diesel production or the agro-industrial value chain) taking advantage of cheap substrate (Table 17.1).

There are different setting and extraction methods for rhamnolipids reported in the literature but the most widely used solvents for this surfactant are solvent ethyl acetate, diethyl ether, and chloroform/methanol (Çakmak et al. 2017).

Table 17.1 : Production methods for biosurfactants and feedstocks

Production Method/Source	100% bio-based Feedstock	Reference
Biological production by yeast or bacteria	sugar, oils, alkanes, waste	Mulligan C N. 2004

Fermentation	From agro-industrial by-products and waste: fats, oils, waste friyng oil, roundnut oil, coconut oil, gingelly oil, castor oil, palm oil, sunflower oil, mahua oil	Elazzazy et al. 2015; Shah et al. 2007; Nalini & Parthasarathi 2014
From the bio-diesel production	Glycerol (bio-diesel by-product)	Randhawa & Rahman 2014

Markets

Current volume, market value, prices.

Surfactants constitute an integral part of chemical feedstock inventory to many industries and are mainly synthesized from petrochemicals (Satpute et al. 2017). The market size of surfactants (both syntetic and natural) is projected to reach USD 39.86 Billion by 2021, registering a CAGR of 5.4% between 2016 and 2021. Instead, the market for biosurfactants was 2.210 million US dollars in 2011 and it has been growing at a rate of 3.5 % per year from 2011 to 2018 (Kaur Sekhon 2012). According to Kosaric and Vardar-Sukan (2015), the biosurfactants market volume is expected to reach around 476 512.2 tonne by the end of 2018. Currently, synthetic surfactants account for major share of the surfactants market. However, the demand for bio-based surfactants is growing owing to the increased inclination of consumers towards products made from natural feedstocks.

There has been an increasing awareness about the use of the biobased products for cleaning purpose which has resulted in propelling the growth of the global market for microbial biosurfactants. Favorable rules and regulatory outlook in the established economies has further strengthened the growth prospects of the global microbial bio surfactants market. However, there is a high cost associated with the microbial biosurfactants when compared to those derived from plants and synthetically manufactured surfactants. This is expected to act as an impeding factor in the development of the global market. On the flip side, the global market for microbial biosurfactants has a big opportunity to expand due the rising demand from the environmental segment for these microbial biosurfactants. The global market for microbial biosurfactants is expected to show a healthy CAGR of 4% by 2020. The overall market valuation of microbial biosurfactants market is estimated to reach a worth of US$17.1 mn by 2020 (Transparency Market Research, 2014).

Surfacants pricing strongly depends on feedstock and production costs. The differences in prices between synthetic and natural surfacants are influenced by the crude oil prices and Europe dependence on crude oil. Demand for oleochemical-based feedstocks is expected to grow at the expense of petrochemical-based surfactants.

The current price of sophorolipids offered by Sophoron™ at “Saraya” (Japan) and “Soliance” (France), are approximately between 0.7 and 2.5 USD/kg (Freitas et al. 2016).

Instead, the current price of the solid/granular rhamnolipids (90 % pure) offered by the AGAE Technologies Company is about 7.5 USD/g and the 95 % pure price is about 10 USD/g (Anon 2018).

Biomass/yield and feedstock availability

Rhamnolipids are predominantly produced by Pseudomonas aeruginosa and classified as: mono and di-rhamnolipids. Other Pseudomonas species that have been reported to produce rhamnolipids are P. chlororaphis, P. plantarii, P. putida, and P. fluorescens. Some bacteria are known to produce only mono-rhamnolipids while some produce both. The ratio of mono and di-rhamnolipid can also be controlled in the production method. There are enzymes available that can convert mono-rhamnolipids into di-rhamnolipids.

- **Actors**

General setting

Several big companies have entered into biosurfactants manufacturing and market.

Europe

TeeGene Biotech, (UK): TeeGene is a spinout venture and supply non-toxic and biodegradable biosurfactants produced via microbial fermentation. The manufacturing process has been developed with Bio Base Europe Pilot Plant (BBEPP). (http://www.teegene.co.uk/)

Ecover, (Belgium): The company manufactures and sells cleaning products produced by biosurfactants. Biosurfactants, especially sophorolipids are made by rapeseed oil and glycerol by a fermentation reaction of yeast *Candida Bombicola*. (https://us.ecover.com/)

BioFuture, (Ireland):This Irish company produces biosurfactants, specifically rhamnolipids for bioremediation of hydrocarbon-contained soil. (http://www.biofuture.ie/)

Rest of the world

Asia-Pacific held the largest market, accounting for almost 40% of the global surfactants market share in 2017 (Mordor Intelligence, 2018). Major players of the surfacants markets are BASF SE, DowDuPont, Evonik Industries AG, Kao Chemicals, Huntsman International LLC, 3M, and Akzo Nobel N.V, amongst others. Producers or bio-surfacants are highilighted below:

Allied Carbon Solution L.t.d., (Japan): The company, in collaboration with the National Institute of Advanced Industrial Science and Technology (AIST, and the University of the Ryukyus), produces biosurfactants from Mahua Oil, a non-edible biomass. The product, named ACS-Sophor, is a 100 % natural made by Stamerella (Candida) bombicola. The strain first utilize Mahua Oil, then biosynthesize sophorolipids. The patent number that the company use is 2013-024713. This product is used especially in agricultural production. (http://www.allied-c-s.co.jp/english.php)

Kaneka Co., (Japan): The company produces biosurfactants for cosmetic sectors. (Http://www.kaneka.co.jp)

Saraya Co Ltd, (Japan): The company is working on the biosurfactants area manufacturing ecofriendly detergents and cleaning agent. Sophorolipids are manufactured also by RSPO (Roundtable on Sustainable Palm Oil). (http://www.worldwide.saraya.com)

Ecochem Ltd, (Canada): The Canadian company is involved in the cleaning up oil spills in sand, gravel and soil. One of the product, EC-1800 is an eco-friendly formulation which contains beneficial microbes and a blend of surfactants effectiveness in deep cleaning surfaces contaminated with petroleum hydrocarbons. (http://www.ecochem.com)

AGAE Technologies, (USA): The American company produces rhamnolipids biosurfactants for several market sectors. The company prices for rhamnolipids change depending on the purity of the product. (http://www.agaetech.com)

Synthezyme LLC, (USA): The company produces sophorolipids for several applications such as cosmetics, agriculture including pesticide, and personal care. (http://www.synthezyme.com)

Jeneil Biosurfactant Co LLC, (USA): Is an American agro-industrial company which produces mainly Rhamnolipids on a large scale. (http://www.omri.org)

Rhamnolipid Company, (USA): Rhamnolipid Companies, Inc. in conjunction with rhamnolipid, Inc. has been researching since 2003 for a cost-efficient method for the production of rhamnolipid. The company produces rhamnolipids with different carbon substrates mainly glycerol and sun flower oil. (http://www.rhamnolipid.com)

- **Value proposition and sustainability**

Environmental impacts, benefits, sustainability

World-wide interest in biosurfactants significantly increased in the recent years due to their ability to mitigate most requirements of chemical surfactants.

In europe the European Surfactant Regulation exists (EC No.: 648/2004). This regulation requires clear and precise description of the biodegradability of the surfactant and test methods to give assurance of its aerobic biodegradability. This regulation establishes rules designed to achieve the free movement of detergents and surfactants for detergents in the internal market while, at the same time, ensuring a high degree of protection of the environment and human health.

In terms of sustainability a large scale production of biosurfactants may be expensive also for the amount of solvents used. However this problem could be overcome by coupling the process with the utilization of waste substrates also if will be difficult to obtain pure substances biosurfactants (Rahman & Gakpe 2008).

Sophorolipids are reported to be fully biodegradable and to have a low toxicity. A recent study demonstrated that they do not affect *Daphnia* reproduction, and that the chronic toxicity is an order of magnitude lower than that of reference industrial surfactants, with a no-observed-effect concentration (NOEC) of 11.3mg/L as compared to approximately 1mg/L. (Develter, 2010).

Socio-economic advantages, health impacts, bio vs non-bio based alternative

Bio Surfactants constitute an important class of industrial chemicals and are widely used in almost every sector of modern industry. These products have the labels “bio-based” or “green” or “eco-friendly” or “sustainable” (Roberto De Oliveira et al. 2015).

As for socio-economic aspects, the diffusion of oleochemical-based biosurfactants is favoring a gradual emergence of new product and market application opportunities for different crop types, such as soy. In addition, biosurfacants production, under a circular economy approach, is able to use by-products from other industries or waste material, rather than using new raw material. This allows valorizing waste and fostering the development of eco-industrial parks. In terms of health and safety, the biosurfactant processing, is able to produce non-pathogenic rhamnolipid and probiotic organisms wich will both play a key role in the future of biosurfactant market. Edible emulsifiers from these processes would be suitable in many fields such as food, cosmetic, environmental clean-up, biomedical and natural therapy (Randhawa & Rahman 2014).

Finally, it has been demostrated that biosurfactants have therapeutic application for their large number of bioactivities. For instance biosurfactants could inhibit bacterial growth, toxic effects, and are tumor growth inhibition (Gudiñ et al. 2013). In addition they have effects on migration of human neutrophils, respiratory action (anti- asthma activity), food digestion, inhibition of cell wall synthesis, fungicidal properties or enzyme stimulation. All properties typical of biosurfacatns (Gharaei-Fa 2011).

- **Outlook**

Projected trends (baseline)

Bacterial biosurfacatnts are already part of the market (TRL 7) and the technology has been demonstrated in an operational environmental. In the last five decades, they have reached a market niche as alternatives to chemical surfactants (Nitschke & Costa 2007).

Price forecast for biosurfacants vary amongst companies and the biosurfactant characteristics (e.g., purity). According to Freitas et al. (2016) the current prices of sophorolipids offered by Sophoron^{TM} at “Saraya” (Japan) and “Soliance” (France), are approximately between USD 0.7 to 2.5 per kg. On the other hand, the solid/granular rhamnolipids offered by the AGAE Technologies Company is about 7.5 USD/g with 90 % purity and 10 USD/g with 95 % purity (Anon 2018).

Competitiveness and role of Europe in global production

The global microbial biosurfactants market has been dominated by Europe in the last few years. Europe has shown high consumption of microbial biosurfactants because of the strict regulations imposed by the local governments on the use of bio-based materials. It is projected that Europe will remain as the fastest growing regional market during the course of forecast period. This progress is followed by North America which is estimated to reach an overall valuation of US$4.3 mn by the end of 2020. The growth of Asia Pacific is projected to be at a considerable rate because of the rising awareness among people about the benefits of using bio-based products. (Transparency Market Research, 2014).

Some of the key players in the market include names such as Ecover, MG Intobio, Saraya, Jeneil Biotech, and AGAE Technologies among others.

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18 Biotechnological chitosan

- **General information**

Product Name	Biotechnological Chitosan (3rd generation)
Technology readiness Level (TRL)	7
Biomass Platform	Natural Polyelectrolytes
Business to Business (BtB) or Business to Consumer (BtC)	BtB

- **Product description**

Chitin is a very abundant biopolymer in nature (Ravi Kumar 2000) being the second most available polysaccharide after cellulose. It can be obtained from many sources such as exoskeletons of crustaceans, mollusks (endo- skeleton of cephalopods) and cell walls of fungi, microalgae and insects shells, yeasts and the spines of diatoms (Hamed et al. 2016; Harish Prashanth & Tharanathan 2007; Y Asadpour et al. 2007). At present, crustacean shells represent the most important source of chitin for industrial productions, due to the availability of marine waste material from the seafood processing industry (Dhillon et al. 2013), and well-established chemical processes of deacetylation.

In fact, chitin use on the large scale is limited due to its water and (most-of) solvent insolubility. Deacetylation to chitosan represent the most relevant modification of chitin to a water-soluble derivative, with much wider potential applications. (Hamed et al. 2016).

Chitosans are effective materials for biomedical applications because of their biocompatibility, biodegradability and non-toxicity, apart from their antimicrobial activity and low immunogenicity, which clearly points to an immense potential for future development. These biopolymers can be easily processed into gels, sponges, membranes, beads and scaffolds forms. Chitin and chitosan based nanomaterials, including the preparation and applications of chitin and chitosan based nanofibers, nanoparticles and nanocomposite scaffolds for tissue engineering, wound dressing, drug delivery and cancer diagnosis represent a huge potential for future development in advanced materials for medical use. They also find relevant uses in other sectors, such as bioremediation.

Chemical-physical characteristics

Chitosan, classified by the European Commission as “basic substance” in 2014, is a renewable polysaccharide. Specifically, it is an aminoglucopyran. It is a linear cationic heteropolymer (Figure 18.1). As a natural cationic biopolymer in its dissolved form (ph<5,7), chitosan possesses a positive charge, giving rise to versatile uses based on its chelating, anti-microbial, gelling and film-forming properties. (Yui et al. 1994; Peter et al. 2005).

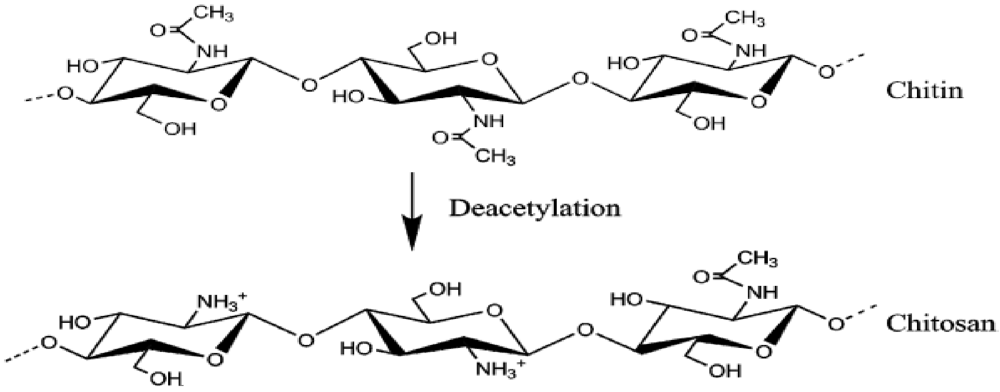

Figure 18.1 : Chemical structure of chitin and chitosan (Source: Nilsen-Nygaard et al. ,2015)

With reference to the origin and the chemical characteristics, there are three kinds of chitosan. Chitosan derived from marine source through chemical (soda) treatment is referred to as the 1st generation chitosan. If chitosans come from the enzymatic processing of animal chitin, then they are called 2nd generation chitosans, which are better defined than 1st generation chitosan in terms of their degrees of polymerization and acetylation, and are therefore more suitable for the development of reliable products with batch-to-batch consistency for industrial applications. A mix of molecules showing a different chain length, different degree of acetylation, and different acetylation pattern characterizes 1st and 2nd generation chitosan.

Finally, biotechnological chitosan (3rd generation chitosan) is a high-purity non-animal sourced compound, derived exclusively from renewable, non-GMO sources such as algae and fungi, without any synthetic manipulations. Source biomass is mainly represented by wastes from agro-alimentary industries. It shows medium-low molecular weight (1-12 x 10^4 Da) with high molecular weight homogeneity (Nwe & Stevens 2002, Ghormade et al. 2017, Kaur & Dhillon 2013) and non-random patterns of acetylation and therefore a well defined chemical structure, known cellular modes of action, and defined biological activities (Nano3Bio Project). It is expected that these chitosans will create important opportunities for the market in the next future for advanced applications, mainly in the medical field, due to its high purity and a well defined chemical composition.

Regarding the chemical characteristics, the molecular weight and degree of de-acetylation of fungal chitosan can be controlled by varying the fermentation conditions, while it's rather randomly obtained with chemical treatment of animal sourced chitin. Specifically, compared with chitosan from crustacean, characterized by a high molecular weight (1.5 x 10^6 Da), fungal chitosan produces a medium-low molecular weight (1-12 x 10^4 Da) with molecular weight homogeneity (Nwe & Stevens 2002, Ghormade et al. 2017, Kaur & Dhillon 2013). Chitosan with a medium-low molecular weight can be used as a powder in cholesterol absorption (Ikeda et al. 1993) and as thread or membrane in many medical-technical applications. Furthermore, as for raw material supply, due to dis-continuous supply and seasonal variations of the marine sources, the use of fungi could be an alternative.

The properties of fungal chitosan compared with those of a commercial chitosan derived from crab shells are shown in table 18.1. The degree of deacetylation is an important parameter affecting the physicochemical properties of chitosan. Chitosan with a high degree of deacetylation has high positive charges and is more suitable for food applications as a coagulating or chelating agent, a clarifying agent or an antimicrobial agent. In addition, chitosan with a low molecular weight was reported to reduce the tensile strength and elongation of the chitosan membrane but to increase its permeability.

Table 18.1: Properties of fungal chitosan (Source Pochanavanich, 2002)

Chitosan from	degree of deacetylation (%)	molecular weight (Da)	viscosity (cP)
crab shell	97.9 ± 0.9	9.4 ×105	372.7
Aspergillus niger	90.0 ± 2.1	1.4 ×105	6.2
Rhizopus oryzae	87.9 ± 2.1	6.9 ×104	3.5
Lentinus edodes	86.5 ± 2.2	1.9 ×105	5.8
Pleurotus sajo-caju	83.8 ± 0.1	1.1 ×105	5.6
Zygosaccharomyces rouxii	85.1 ± 1.1	2.7 ×104	3.3
Candida albicans	83.8 ± 0.8	1.1 ×105	3.1

Advantages of Biotechnological Chitosan

Chitosan belongs to a new class of biomaterial showing low toxicity, excellent biocompatibility, versatile biological activity, complete biodegradability, and adsorption properties (Mourya & Inamdar 2008; Malette et al. 1986; Nampally et al. 2015; Rinaudo 2006; Bellich et al. 2016). Compared to the industrial polysaccharides, which are generally either neutral or anionic, chitosan is the only high molecular weight cationic polyelectrolyte.

The more advanced is the application foreseen (in particular in medicine, cosmetic and healthcare) the highest purity and reliability are required for the products; so biotechnological chitosan has more advantages and potential high-level applications with respect to animal-sourced chitosans, specially in the biomedical field. It is considered as GRAS (Generally Recognized As Safe, GRAS notice: 397, Chitosan from *Aspergillus niger*) and able to be *in vivo* degradated (Di Martino et al. 2005).

Another notable advantage of biotechnological chitosan is that is does not induce the same allergenic response as animal-sourced chitosans (Rahman et al. 2012). In fact, it is well known that proteins (i.e. tropomyosin) contained in shrimp and shellfish in general are among the most important food allergens and the exposure to these substances can cause a variety of health problems, including gastrointestinal and urticarial disorders. In order to avoid these undesired reactions, chitosan obtained from algae and fungi can be used due to its allergenic shrimp-protein free characteristic (Nwe & Stevens 2002). Moreover, fungal chitosan is heavy metal free (i.e. nikel and copper, Ghormade et al. 2017).

Table 18.2 : General comparison between animal-sourced (1st generation) and fungal (3rd generation) chitosan

Chitosan's generations	**Characteristics**	**Biomass**	**Applications**

1st generation	Animal derived (crustaceans) High molecular weight (1.5 x 106 Da) Random patterns of acetylation Low purity Seasonal variation	Marine wastes	Non-advanced applications (i.e. agriculture, wastewater treatment and in general all the applications that not require high volume and/or high purity)
3rd generation	Non animal derived (derived from fungi and algae) Medium-low molecular weight (1-12 x 104 Da) Low molecular weight homogeneity Non-random patterns of acetylation Shrimp-protein and heavy metal free High purity Non-seasonal variation	Wastes from agro-alimentary industries and from Biotech industries	Advanced applications (i.e. medicine, cosmetics, healthcare) and when a high and constant quality is strictly required

Disadvantages of Chitosan

The versatility of chitosan leads to a wide variability in terms of compositions, molecular weight, molecular weight homogeneity, degree of de-acetylation and different acetylation pattern. This structural variability is a typical issue when dealing with copolymers or more in general with a pool of similar molecules that together form a single final product as chitosan is (Bellich et al. 2016). The counterpart of it is in the difficult characterization of the substance and in the unsolved question of how the compositional variability add complexity to the identification of beneficial properties of the final product (Bellich et al. 2016).

Chitosan from fungi and algae shows more homogeneity in terms of chemical composition but at present is less available and is more expensive compared to marine chitosan. To date, small quantities of these molecules are made available on the market (Nano3Bio Project); few attempts have been done in order to obtain chitosan with reliable and predictable biological functionalities in amounts that are appropriate to the martket request. It is currently not feasible for high volume and low cost applications (Ghormade et al. 2017).

Main uses

Chitosan is currently being investigated extensively for its applications in various fields. Examples of potential application are biopharmaceutical and cosmetics (Riva et al. 2011), biotechnological and biomedical, agriculture, and both food and non-food industries.

The most relevant applications are in the medical and pharmaceutical field. In fact, chitosan detains important anti-bacterial, anti-microbial (Goy et al. 2009), antioxidant (Yen et al. 2009), anti-fungal, anti-tumor (Salah et al. 2013) properties, anti-coagulant (Vongchan et al. 2003) in addition to wound-healing activities and immune-enhancing effects on animal health.

Specifically, possible uses include the antibacterial lining for bandages and wound dressings, development of artificial skin and cartilage regeneration (Dash et al. 2011), reconstruction of periodontal tissues, hemodialysis membranes, and drug targeting and delivery (Bellich et al. 2016, Ravi Kumar 2000). Chitosan is able to induce various defense-related cellular responses such as gastrointestinal and urtical disorders (Rahman et al. 2012) that can be ascribed to a pool of proteins contained in shellfish able to induce allergy reactions. To avoid these undesired reactions that can occure when chitosan is in contact with body, chitosan obtained from fungi can be used due to its allergenic shrimp-protein free characteristic (Nwe & Stevens 2002).

As for plants (gardening and agriculture), chitosan serves as coating for seeds to boost disease resistance and it can be considered as a green alternative to chemical additives thanks to its antimicrobial activity (El Hadrami 2010).

Additionally, applications can be found in water treatment (Nisticò et al. 2017, Vijaya et al. 2008) as well as in the paper and textile industries (Gupta & Ravi Kumar 2000; Mourya & Inamdar 2008; Synowiecki & Al-Khateeb 2003). According to Nisticò et al. (2017), chitosan have been investigated to be used in water remediation processes from polycyclic aromatic hydrocarbons. At present the most used techniques for water remediation from hydrocarbons pollution are based on physical (by using booms, skimmers, and adsorbents), chemical (photocatalysis or by using dispersants and solidifiers), thermal (i.e., in situ burning), and biological (i.e., bioremediation) processes (Dave & Ghaly 2011). Vijaya et al. (2008) reports the use of chitosan as green adsorbents for treatment of wastewater polluted by heavy metals (nikel II).

Another example is the use of chitosan as commercial adhesive in substitution of alternatives such as poly(vinyl acetate), epoxy, phenol-formaldehyde and polyurethane based on non-renewable and depleting petrochemical resources. Indeed, several adhesives "consist of residual toxic chemicals and volatile organic compounds that are costly, harmful for the health of living beings as well as are pollutants of environments" (Patel 2015).

In food industries, according to Hamed et al. (2016) which offers a good overview of the chitin and chitosan properties, chitosan can be used for its antioxidant and antimicrobial effects enhancing food safety and quality, and lengthening shelf-life. According to Muzzarelli & Muzzarelli (2009) and Cosgrove (2010), chitosan is a promising natural food additive, used as preservative. Chitosan is also stable at high temperature allowing preventing oxidation in processed food products.

Chitosan can be used as agent to prevent spoilage in winemaking (Romanazzi et al. 2003). In particular chitosan has been considered as a valid substitute of sulphur dioxide, characterized to be unhealthy for human and injurious to most fresh fruit. In the Italian wine industry the chitosan-based alternatives to sulphur dioxide (SO_2) are required in view of damage to bunch due to temperature increase, and of the difficulties in using SO_2 with colored grapes (Romanazzi et al. 2002). Also for post-harvest table grapes, sulphur dioxide has been used during storage and transport to control losses. A sustainable alternative to SO_2 has been pointed in chitosan from the *Cunninghamella elegans* fungus (de Oliveira et al. 2014).

A more controversial use implies supporting diets as it enables the loss of weight by avoiding fat digestion and it helps in cholesterol management (Shields et al. 2003).

Unexplored market area is the bioelectronics as results of advances in biotechnology and microelectronics synergies. As an example, chitosan was recently used for the fabrication of a highly sensitive bioelectronic tongue for water and food analysis, thanks to its chelating capability towards metals sich as mercury (Cetò, 2016).

Production process

As previously mentioned and with reference to the origin and the chemical characteristics, there are three types of chitosan with different production processes.

1st generation chitosan refers to chitosan as raw material derived from marine waste. Marine crustacean shells are widely used as the primary source for the production of chitosan from chitin by partial deacetylation through alkaline method (Hamed et al. 2016). According to the alkaline method, raw materials obtained after chitin demineralization, deproteinisation and discoloration are mixed with 40-50% NaOH. The alkaline treatment hydrolyzes the acetyl groups and chitosans with different degree of deacetylation are generated (the purpose is to remove all the acetyl groups however the N-deacetylation is almost never complete) depending on the reaction temperature, time, and the concentration of the alkali solution. The alkali treatment can cause environmental pollution, requires significant energy, and produces poor quality chitosan (Raval et al. 2013). Therefore enzymatic methods could replace it to overcome those limitations.

2nd generation chitosan refers to chitosan obtained from enzymatic processing of chitin (Hamed 2016). Chitin acetyl groups are removed by the enzyme named chitin deacetylase. This enzyme was first found in *Mucor rouxii* in 1794 (Kafetzopoulos et al. 1993) and the enzymatic methods occurs naturally in the cell walls of some fungi. This method shows some disadvantages, such as a low enzyme activity and a low return of deacetylase-producing strains, in addition to complex fermentation requirements. Currently, the chitin degrading enzymes represent high-cost low volume products (Chavan & Deshpande 2013). In this respect, deacetylase-producing bacteria, such as the *Serritia sp.* and *Bacillus sp.* may represent a more efficient solution (GuoYing et al. 2010) as, for large fermentation systems, bacteria grow faster than fungi (Kaur et al. 2012).

3rd generation chitosan refers to chitosan derived from algae, bacteria and fungi, and available biomass is represented by wastes from agro-alimentary industries. For example chitosan from *Gongronella butleri* fungi has been produced from sweet potato substrate fermentation and carbon source for growth. The chitosan extraction has been done using ɑ-amylase (Nwe & Stevens 2002).

Apart from the cost of inputs to production, different extraction methods (either chemical or biological) may yield different processing costs. Clearly, the estimation of production cost also requires taking into account transportation cost, which is influenced by location and labor. For the chitosan produced from waste, the cost of managing waste should be also considered, such as the disposal cost, which is paid to third parties (Nisticò 2017).

- **Markets**

Current volume, market value, prices

Commercialization of non-animal chitosan is at its first steps, with few attempts to produce at large scale and a contained number of firms selling the products, both in Europe and outside. Chitosans are mainly sold from business to business, with rare exceptions of business to consumers transactions.

The economic potential of chitosan's is only partially exploited. This is mainly due to problems existing with the reproducibility of their biological activities. Indeed, the currently available chitosan's are, generally, poorly defined mixtures. Chitosan's with reliable and predictable biological functionalities barely exist and only few attempts have been done to address this first issue. One has been carried out by the Nano3Bio Project consortium (Nano3Bio, 2017), that have recently tried to favor chitosan market penetration by producing in vitro and in vivo (in microbial and microalgal systems, focusing on bacteria and diatoms) defined oligomers and polymers with controlled and tailor-made degree of polymerization, acetylation degree, and pattern of acetylation.

Most of the chitosans commercially available are produced from chemical isolation of chitin from shrimp or crab shell wastes, rather than from fungi and algae derivation. To date, small quantities of these molecules are made available on the market at excessively high price (Nano3Bio Project).

Price estimates for chitosans and chitin notably vary amongst the studies analyzed and the website analysed. The source of chitosan derivation strongly affects final price. Additional parameters influencing the price are represented by the degree and pattern of deacetylation. For example, the chitosan is available in 10g quantities from Sigma and Aldrich supplier at 7.5 USD/g (https://www.sigmaaldrich.com/). Following Nisticò (2017), chitin has a price of around 500 euros/kg, whereas chitosan’s price strongly depends on the purity and the molecular weight, though it goes around from 1 100 euros/kg to 1 200 euros/kg.

Biomass/yield and feedstock availability

As compared to the marine sources, chitin production using fungi is minor, and the fungi showing the highest portion of chitosan appears to be the *mucoraceous fungi* (Ghormade et al. 2017).

In the case of fungal chitin and chitosan, content strongly varies and depends on the specific species. Table 18.3 reports the amount of chitosan produced by different fungi. According to Ghormade et al. (2017) there exist three major sources of fungi that can be exploited at commercial level. These can be grouped into i) waste fungal biomass from Biotech industries where thousands of tons of waste fungal is produced per year, ii) fungi containing high amounts of these polymers (fungal fermentation), and iii) value addition to existing *mycotech*-products.

Table 18.3 : Amount of chitosan produced by different fungi. (Source Pochanavanich, 2002)

Fungal species	chitosan produced (mg g^{-1})	chitosan content (%)
Aspergillus niger	107	11
Rhizopus oryzae	oryzae	138
Lentinus edodes	33	3.3
Zygosaccharomyces rouxii	36	3.6
Candida albicans	44	4.4

In the first group of sources, it can be mentioned, for example, the more than 80,000 tons of waste *Aspergillus Niger* biomass per year, which is generated from the production of the citric acid. Additionally, it can be estimated that in the brewing and baking industries where *S. cerevisiae* and *S. carlbergenis genuses* are traditionally used, biomass availability is more than 130 tonne yeast lees/year. For penicillin production, 1 tonne of penicillin implies around 8-10 tonne/year of waste that can be used for chitosan production (Ghormade et al. 2017).

In the second group of sources involving fermentation of fungus, major contents can be found in *Gongronella butleri*, *Mucor rouxii*, and *Absidia coerulea*, amongst zygomycetous fungi. More specifically, *Benjaminiella poitrasii*, *Cunnighamella blackesleeanus*, *Gongrenella butleri*, *Mortierella isabelina*, *Rhizopus delemar*, and *Rhizopus stolonifera*, amongst others, show a chitosan content ranging between 6.7 % and 10.4 % productions (Ghormade et al. 2017).

- **Actors**

General setting

The main industries producing chitin and chitosan are located in US (Oregon, Washington, Virginia) Japan, and Antarctic, despite several other countries possess large unexploited crustacean resources. Examples are represented by Europe (e.g., Norway and Poland), India, Mexico, Chile (Ravi Kumar 2000), Senegal (Hardy et al. 2016), and China (Lu et al. 2015). Most of the existing firms, both in Europe and outside mainly produce animal-based chitosan. Fewer realities have been starting to produce non-animal based chitosan in the last decades (Tables 18.4 and 18.5).

Europe

Table 18.4 : Producers/sellers of non-animal chitin/chitosan in Europe

N	Company/group	Location
1	KytoZyme (http://www.kitozyme.com)	Belgium
2	Neweaver (http://www.neweaver.com)	France
3	Chitosanlab vegan (http://www.chitosanlab.com/vegan/)	France
4	PLater Bio (http://www.platergroup.co.uk/plater-bio)	UK
5	Heppe Medical Chitosan GmbH (http://www.gmp-chitosan.com/de/)	Germany
6	Enantia SL (http://www.enantia.com)	Spain

Source: own compilation

4.3 Rest of the world

Table 18.5 : Producers/sellers of non-animal chitin/chitosan outside Europe

N	**Company/group**	**Rest of the world**
1	Qingdao ChiBio Biotech Co., Ltd (http://www.chibiotech.com)	China
2	Xi'an Geekee Biotech Co., Ltd (http://www.geekeebio.com)	China
3	Xian Lukee Bio-Tech Co., Ltd (http://www.lukee-health.com)	China
4	Beinjig Wisapple Biothec Co. Ltd (http://www.wisapple.com)	China
5	Union Agol Company (http://http://www.companiess.com)	Russia
6	Sigma Chemical Co. (http://www.sigmaaldrich.com)	US

7	Mycodev Group (http://www.mycodevgroup.com)	Canada

Source: own compilation

- **Value proposition and sustainability**

Co-products

As reported in Yoon (2005) and Kuk et al. (2005), both chitin and chitosan can be used as starting materials for the production of chemicals, i.e., mono-, di-, and oligosaccharides that are derived with additional hydrolysis processes (Kerton et al. 2013). Examples are the chitobiose, the N-acetylglucosamine (NAG) monomer, and glucosamine (GlcN) salts via enzymatically-catalyzed hydrolysis reactions of the obtained chitin/chitosan.

An important implementation of chitosanase is the preparation of Chitosan Oligosaccharide (COS) from chitosan (Thadathil & Velappan 2014) that is able to prevent the accumulation of fat in internal organs, plays a remarkable role in the liver function and in stimulating the immunological system.

In the mushroom industry waste, where stalks, which represent approximately from 25 % to 33 % of the weight of fresh mushrooms, are normally used as low economic value animal feed, a trade-off exists. Indeed, this material could be utilized to produce vitamin D and chitosan instead of high quality mushrooms (Bilbao-Sainz et al. 2017).

Environmental impacts, benefits, sustainability

One of the most relevant aspects related to the production of chitosan from fungi, is that large amount of wastes can be valorized, and seasonal availability of marine sources can be overcame through the rapid, easy and cheap cultivation of fungal species.

Chitosans, recently used in wastewater treatment to remove heavy metals to polluted sediment (Liu et al. 2016), respond to the increasing need of addressing environmental and pollution problems relative to rivers and lakes showing sediment contamination by heavy metal. On the same path, chitosans with a high deacetyletic degree can support lower food waste as they showed potential for extending the shelf life of refrigerated fish fillets, due to inhibitor properties. On the other hand, on the environmental ground, chitosan extraction may generate pollution problem (J. Cosgrove 2010), especially if animal based (Yosefali Asadpour et al. 2007).

Socio-economic advantages, health impacts, bio vs non-bio based alternative

Research tested that polysaccharides offer diverse therapeutic functions due to their biocompatible, biodegradable to harmless products, nontoxic, and physiologically inert. Specifically, chitin and its derivatives have been determined as potential agents for down regulation of allergic reactions via enhancing innate immune system (Vo et al. 2015).

- **Outlook**

Projected trends (baseline)

The current amount of 3rd generation chitosan produced is currently very low so that market trends are extremely hard to forecast. However, both chitin and chitosan market, at global level, have been growing massively in the last years, due to the expansion of their application domain, which is even larger if co-products are considered. Applications include biopharmaceutical, cosmetics, biotechnological and biomedical, agriculture, and both food and non-food industries.

Some features justify positive expectations for the future, such as low toxicity, excellent biocompatibility, versatile biological activity, complete biodegradability. In addition, the 3rd generation chitosan derived from fungi and algae presents many advantages compared with 1st and 2nd generation, primarily less allergenic. Other factors supporting the market development of chitosan are:

The enhancement of the water treatment sector resulting from high demand for removal of metals and chemicals from wastewater including pesticides, surfactants, phenol and polychlorinated biphenyls.

The demand for the compound in food & beverage application in Europe which is expected to grow at significant rate due to rising demand for the wine processing industry.

The development expected in the cosmetics industry due to the rising demand for bio-derived personal care products. Cosmetic industry was the largest application segment of chitosan in North America in 2015 (https://www.researchandmarkets.com/reports/4076513/chitosan-market-estimates-and-trend-analysis-by)

On the other hand, the growth of value-added chitosan-based products is limited by the availability of a sustainable supply chain: the process chemistry for bulk chitosan manufacturing is currently not very environmentally friendly. Green technologies for chitosan modification are facing the challenge of economic viability which hinders its current development.

The growth rate of the chitin market varies broadly depending on the market segment, with the healthcare registering the higher compound annual growth rate (CAGR). It also depend on the country considered (Asia Pacific excluding Japan is the largest.) according to Future Market Insights (https://www.futuremarketinsights.com/press-release/chitin-market).

According to existing analysis, we can consider reasonable a CAGR of 15.4 %, from 2018 to 2020, and a 14% CAGR afterwards (declining due to a contained effect of market saturation). Assuming a $2.0 billion volume in 2016 and 155,000 metric tons of volume reached in 2022 (Jardine and Sayed 2016).

Price estimates for chitosans and chitin are not clear and notably vary amongst the studies analysed. According to Sigma and Aldrich (https://www.sigmaaldrich.com/) a price of 7.5 USD/g currently applies. In Europe, the price is slightly lower and ranges between 1.2 to 1.4 USD/g (Nisticò 2017). However, the source of chitosan derivation strongly affects final price; also, chitosans derived from non-animal sources are notably more expensive. Chitosan from fungal sources is less available compared to marine chitosan sources, which implies higher production costs and therefore very high sale price: i.e., it is currently not feasible for high volume low-cost applications (Ghormade et al. 2017). For this reason, a current share of 0.2% of non-animal chitin is envisaged on total chitin market, slightly growing in time as soon as production costs are able to decrease.

Overall price dynamics could mainly depend on two opposite forces. On the one hand, the increasing demand for high-quality chitosan products will put pressure on their prices. On the other hand, expected improvements in technologies and chemical processes will reduce marginal production costs and limit the price increase. A modest annual price increase is therefore expected in time (1%).

Competitiveness and role of Europe in global production

Europe has some leading companies in product development related to 3rd generation chitosan, compared with animal chitosan. Countries mainly involved in non-animal chitosan production in EU are located in Germany, the U.K., Spain, Belgium, and France. Research projects involving partners from additional EU countries are under development. The role of Europe in global production is expected to have a great margin of growth.

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19 PHAs from urban wastes

- **General information**

Product Name	PHAs from urban wastes
Technology readiness Level (TRL)	6
Biomass Platform	Urban biowaste
Business to Business (BtB) or Business to Consumer (BtC)	BtB

- **Product description**

Polyhydroxyalkanoates (PHAs) are bio-polyesters synthetized and accumulated like carbon or energy storage by various microorganisms.

A variety of waste streams has been utilized in last decades to produce PHAs with less expensive carbon sources (Wolf et al., 2005). Urban wastewater sludge (UWWS), and the organic fraction of the municipality solid waste (OFMSW) are both economically viable carbon substrates for PHAs production (Colombo, 2017). The possibility to use these biomass fractions for the preparation of PHAs at the industrial level, is mainly related to the costs associated to the biomass pretreatments needed to increase their carbon content through concentration, in order to increase production yields and to reduce fermentation volumes. This aspect is particularly relevant for UWWS, in which carbon concentration may be relatively low.

In fact PHAs are accumulated as high-molecular weight polymers through bacterial methabolism, and carbon sources are used in the same way by living cells to accumulate and store energy independetly from their specific origin. The kind of bacterial stream and the specific conditions of fermentation, including the carbon content of the substrate, will ratify the type of PHA produced.

The copolymer poly-hydroxybutyrate-co-hydroxyvalerate (PHB/HV) is the most common type of PHAs that can be obtained by urban wastes. It's obtained by tuning the preliminary biowaste acidogenic fermentation to get a volatile fatty acids (VFAs) fraction with both even and odd number of carbons (*e.g.*, propionic and valeric acids). In fact, the latter lead to the obtainment of the HV monomer, as detailed below. PHB/HV is a high molecular weight aliphatic polyester that shows very interesting engineering properties and allows for the substitution of the most common polyolefins, such as PP and HDPE.

Chemical-physical characteristics

Please, refer to the same section in the case study dealing with PHAs derived from renewable oils and fats.

Production process

PHAs are obtained through bacterial fermentation process (Bhuwal et al., 2013) of prokaryotic microorganism with different nutrition conditions (Jiang et al. 2016) and more than 150 monomers can be combined within PHAs. The PHAs general production process is carried out in three steps: fermentation, isolation and purification, compounding with additives and pelletizing (Wolf et al., 2005).

In case biowaste is used as the process feedstock, a preliminary fermentation step is carried out under anaerobic conditions in order to bioconvert the organic fractions into volatile fatty acids (VFAs) as much as possible (Pittmann & Steinmetz 2017). In fact, VFAs represent the precursors for PHAs cell storage. More in details, VFAs with an odd number of carbons are converted into the hydroxyvalerate monomer very commonly. Thus, this anaerobic-aerobic strategy can lead to the production of the PHB/HV co-polymer. This material offers interesting properties in terms of industrial applicability since it is less brittle and thougher than the most common PHB homopolymer, which is currently produced at the industrial level from molasses extracted from sugar beets and sugar canes. PHB/HV can also be obtained through sugar-based processes, by feeding bacteria with additional sources of monomers with four carbons, such as levulinic acid. But this route is usually more expensive than the route through VFAs described above.

In the case of UWWS, several studies have been carried out on PHAs production under the aerobic dynamic feeding technique by activated sludge. This has been reported as one of the most promising opportunities because of efficient PHAs accumulation. In most studies *acetate* fatty acid has been individuated as the sole substrate used for enrichment of the mixed cultures (Chen & Li 2008).

In the case of OFMSW, fermentation also generates VFAs as in the case of UWWS, in addition to other low molecular weight organic compounds such as alcohols or lactic acid (Bolzonella et al., 2005). These can be used for the co-production of methyl and ethyl-esters useful as additives for gasoline, and again as carbon source for the production of PHAs (Korkakaki et al., 2016).

There are different factors affecting production costs of PHAs, 50% of which represented by raw material costs (Castilho et al. 2009). In this view, the valorization of urban waste streams using them as carbon substrates to feed PHA-producing bacteria is particularly attractive, because it represents a viable route to reduce the actual price of PHAs, which is approximately 4 to 6 folds higher that the price of the competing fossil-based counterpart, which is polyprolylene.

Another limiting factor is the fact that PHA production generates a large amount of biomass waste: in general terms, about 5 kg of raw material is required to obtain 1 kg of final polymer; this can generate additional disposal costs (Wolf et al., 2005) negatively impacting on the final price of PHAs. Organic residues, including cell walls remaining from the recovery actions, are partially reintroduced in the next production batches as carbon sources. They usually do not find alternative uses.

- **Markets**

Current volume, market value, prices:

To date, PHAs are exclusively produced at the industrial level starting from sugars (Bio-on in Italy, Kaneka in Japan are the main actors). There is no industrial production nor commercialization of PHAs obtained from urban biowaste at the global level.

In general terms, today PHAs price is much higher than competing fossil based counterparts such as polypropylene or high-density polyethylene, but also with respect to bio-based starch polymers and other bio-based polyesters such as PLA and PBS. This is mainly due to major processing expenses (particularly purification of the fermentation broth), substrate costs (only sugar used at present), and small production volumes (Wolf et al, 2005). Price quantification varies substantially across sources and time horizon considered.

In a European project, the market price of PHAs from sugars was quantified as 10,000 €/ton (Bioref-integ 2010) in 2010, while in 2014 the price was around 4-5€/kg (Kootstra et al. 2017). This should be compared with prices of fossil based commodity polymers such as polyethylene at 0.80-1.20 €/kg or polypropylene at 1.5-2.0 €/kg (Gunter FestelSarai KolleDieter Sell 2005).

- **Biomass/yield and feedstock availability:**

Being solid and water waste abundant (about 10 million tons dry matter of sewage sludge is estimated as produced in Europe every year. The main issue worth to be considered within the production process is that PHAs yield depends on microorganism reaction capacity and on the carbon content (i.e. concentration) of the substrate. For example, in the production of PHAs by Activated Sludge Treating Municipal Wastewater the polymer content achieved by *Alcaligenes latus* and recombinant *Escherichia coli* have been reported to reach 88% and 76% of cell dry weight, respectively (Chua et al. 2003).

For the case of wastewater, the sludge acclimatized with acetate-supplemented municipal wastewater was estimated to produce PHA up to 31% of sludge dry weight while sludge acclimatized with municipal wastewater around 21% of PHA content (Chua et al. 2003).

In general terms, according to a recent study, using data for the 2016 year, Europe-28 could in principle produce 120% of the worldwide biopolymer production due to the capacity of European waste water treatment plants (Pittmann & Steinmetz 2017).

- **Actors**

General setting

PHAs is currently produced in large volumes by a few companies, such as Procter & Gamble Co., Ltd. (Cincinnati, OH, USA), Tianjin Green Bioscience Co., Ltd. (Tianjin, China) and Kaneka (Japan) and Bio-on (Italy); all these actors use sugars as feedstock for their fermentation processes.

As concerns PHAs from OFMSW and UWWS, production strategy in large volumes is at a very early stage, and apart from pilot plants, there are no industrial facilities which use urban waste materials to generate PHA.

Europe

Below, firms and ongoing projects and experiments producing PHAs from OFMSW/UWWS are reported.

Bio-on plants, Italy. Is an Italian firm founded in 2007 and operating in the sector of biotechnologies producing general and tailored PHAs from agricultural waste and municipal organic fraction. The firm has 6 laboratories in Italy and USA, 8 patents and 2 certifications. http://www.bio-on.it/production.php

WW treatment Plant, Italy, Treviso. The Horizon2020 Innovation actions have funded the SMART-plant in Italy, an innovation system for the waste water treatment for biopolymers from sewage. http://smart-plant.eu/index.php

Res Urbis Partners. Is an ongoing project working on the possible conversion of urban bio-wastes also in PHAs. https://www.resurbis.eu/

NOVA ID FCT, Caparica, Portugal. The Association for Innovation and Development of FCT is working on high quality researcher (both fundamental and applied) also in production and characterization of PHAs from wastewater treatment. To date is one of the partner of the RES Urbis project. http://watintech.eu/

Bio-Based Europe Pilot Plant, Belgium. Is an independent, state-of-the-art facility that operates from a laboratory level to a multi-ton scale providing process development of bio based products. With the AFTERLIFE project, Europe Pilote Plan will separate solids in wastewater in order to obtain high-pure extracts and metabolites or, alternatively, value-added biopolymers like PHAs. http://www.bbeu.org/pilotplant/afterlife/

Rest of the world

Full cycle Bio plastic, California. The company is working on the plastic transformation from organic matter, such as food and agricultural waste. http://fullcyclebioplastics.com/

Centre of Sustainable polymers, University of Minnesota, USA. The Center mission is to transform plastics through innovative research, engaging education, and diverse partnerships that together foster environmental stewardship. https://csp.umn.edu/about/

Mango Materials, San Francisco, USA. It is a start-up that produces PHA from CH4, derived as a waste gas from sites like landfills and abandoned coal mines. From waste biogas (methane) it produces a natural biopolymer that is economically competitive with conventional oil-based materials. http://mangomaterials.com

Newlight, Huntington Beach, California, USA. In a perspective of waste stream use for biopolymer production, the startup Newlight developed a patent and commercialized a carbon capture technology. This combines air with methane emissions to produce a plastic material: a long chain PHA-based thermoplastic material (i.e., AirCarbon). https://www.newlight.com/technology/

- **Value proposition and sustainability**

Co-products

Polyhydroxyalkanoate (PHA) bio plastics represent a co-product that would be compatible with either production of biofuel by hydrolyzing the dry biomass after the extraction of PHAs by thermochemical processes. In this scenario, a new value added co-product could be produced being compatible with biofuel and bioenergy in general (Kristi et. al, 2009).

In addition, according to Pagliano et al. (2017) a simultaneous process for PHAs and bioenergy from organic wastes is possible. The co-production of CH_4 and carbon dioxide and H_2 and bio plastic (from volatile fatty acid) is conceivable due to the multiple step process of bio waste degradation from different bacterial species.

In the case of OFMSW, the organic fraction of municipal solid waste by fermentative process could also generate valuable products such as volatile fatty acids and other low weight organic compounds such as alcohols or lactic acid (Bolzonella et al. , 2005). Subsequently, these can be used for methyl and ethyl-esters to be added to gasoline (using fatty acids), or as external carbon source for the production of biopolymers, like PHAs production (Korkakaki et al., 2016).

Environmental impacts, benefits, sustainability

Environmental impacts of PHAs production are different depending on the carbon substrate used. Compared with PHAs from food crops, such as corn or soy affected by agricultural land use, little to no land competition impacts is registered if the carbon substrate is a waste by-product stream (Pagliano et al. 2017; Momani 2009).

The optimization of OFMSW acidic fermentation results a key step for the success of PHA production because it allows the production of a large amount of OA to be used to produce PHA. Moreover, the high concentrations of OA acted to prevent biogas (methane) production from consuming the substrate to be used to produce PHA. This kind of process could be rapidly implemented in a full-scale plant by adapting dry anaerobic digestion that is commonly used to produce biogas from household wastes (Colombo, 2017).

In terms of energy requirements of PHAs production, the Institute for Prospective Technological Studies have registered energy use two to three times higher than for petrochemical polymers (European Commission JRC 2005). On the other hand, as reported above, PHAs production favors the reduction of solid waste produced by industries, commercial, and residential activities given that allows reusing and recycling around 1 kg product from 5kg of waste (Kootstra et al. 2017).

Socio-economic advantages, health impacts, bio vs non-bio based alternative

In terms of socio-economic advantages of the entirely bio-plastic industry, only Europe in 2013, an accounted for around 23,000 jobs has been created with direct and indirect economic impacts (European Bioplastic; Nova Institute 2017). The European Association for bio industries (EuropaBio) claim that with right framework conditions in place, the market jobs could increase more than tenfold by 2030, with up to 300,000 high-skilled jobs being created in the European bio plastics sector (Debergh et al. 2016). Finally, unlike petroleum-based plastics, bio plastics like PHAs have not been implicated in any health problems (Momani 2009). PHAs are polymers entirely synthesised through bacterial methabolism, therefore they do not contain contaminants possibly present in the biomass feedstock used for the fermentation process. For the same reason, PHAs also do not contain any kind of residual polymerization catalyst. All this make PHAs particularly pure and chemically clean polymers, suitable for biomedical use also and implantation in-vivo as bioresorbable surgical materials.

The entry of PHAs into the commodity market has been limited in last decades by high production costs, PHAs availability and failure to meet the demands of the applications required to replace petroleum-based plastics (Philip et al. 2007).

- **Outlook**

Projected trends (baseline)

Following current trends highlighted above (starting from 2.05 Mt in 2016) and assuming the value of CAGR registered for late years (12 %), production and its value will reach 13,7 Mt and 14 billion USD in 2030.

Costs are still too high for most applications where PHAs can be technically proposed as sustainable substitutes for fossil-based commodity plastics. The packaging sector, which could be a main target for PHAs, is mainly dominated by polyethylenes, polypropylene, polystyrene and poly(ethylene terephthalate); in general terms, their prices are 3 to 5 folds lower than commercial price for PHB. On the other hand, while conventional plastic are obtained using expensive substrates of nutritional importance, bio-derived plastics using PHAs can circumvent this controversy using agro-waste and surplus material.

Also, costs are of the same magnitude of competing products, implying the possibility to increase sharply production via achieving important economies of scale. The latter are possible as PHA still represents a small proportion of total plastic market. Most of these perspectives are in common with PHA from oil and fats.

As for legislation, PHA-based products show similarity in performance with petroleum-derived commodity polymers (such as polypropylene and polyethylene), which, added to biodegradability and/or compostability, makes PHAs particularly attractive. In addition, PHAs production allows creating high added-value products by using material that would otherwise represent just waste. Still raw material represent about half of the cost so that the future cost-competitiveness will depend sharply on the availability of cheap wastes.

Competitiveness and role of Europe in global production

Europe is the second continent after Asia for the production of PHA. The sensibility of EU markets of characteristics of the final products will help boosting the use of PHA-based products in the EU; at the moment Europe is also producing a large amount of wastes, which represent the basis for this product.

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20 Volatile fatty acids (VFAs) mixture

- **General information**

Product Name	Volatile fatty acids (VFAs) mixture
Technology readiness Level (TRL)	7
Biomass Platform	Urban biowaste
Business to Business (BtB) or Business to Consumer (BtC)	BtB

- **Product description**

Volatile fatty acid (VFAs) include short and medium chain saturated carboxylic acids depending on the carbon atoms they have (conventionally, VFAs have 2 to 7 C atoms). The main VFAs have a linear chain and between C2 and C6 carbon atoms (namely, acetic, propionic, butyric, valeric and caproic acids). They are different from fatty acids, which are carboxylic acid having a long aliphatic chain, which is either saturated or unsaturated. While all fatty acids are carboxylic acids, not all carboxylic acids are fatty acids.

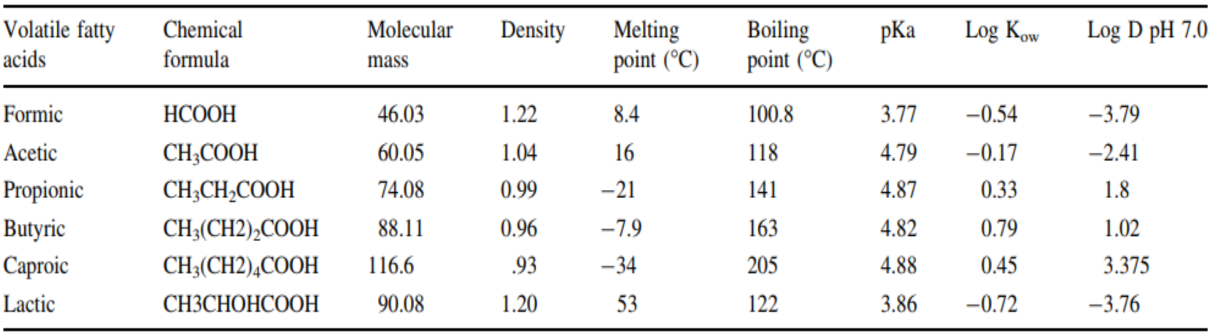
They can be produced both by petroleum based synthesis and via microbial fermentation and biological routes, utilizing renewable carbon sources as raw material (Wang *et al.*, 2014; Bhatia and Yang, 2017).

A large varieties of organic waste streams could be converted in VFAs by the application of conventional biotechnological anaerobic fermentations carried out under acidogenic condition. Among them, solid and liquid materials like organic fraction of municipality solid waste (OFMSW), sludge and livestock effluent (Cavinato *et al.*, 2017; Garcia-Aguirre *et al.*, 2017) or agricultural by-product such as cheese whey (Calero *et al.*, 2017) were used efficiently as the feedstock of acidogenic processes. In most of these cases, and especially with waste stream like a carbon substrate for VFAs production, mixed cultures are essential in the process of waste treatment, because they can tolerate the complexity and variability of substrates (Agler *et al.*, 2011).

Chemical-physical characteristics

Several operational parameters affect the composition of VFAs produced under anaerobic condition such as the PH, the Solid and Hydraulic Retention Time (SRT) (HRT), and temperature. All these operational parameters may affects the VFAs concentration, yield, and composition of VFAs produced from industrial wastes.

According to Calero et al. (2017), the optimal PH values to produce VFA are dependent on the type of raw material used as substrate, varying in the range 5–8. The chemical-physical characteristics for each of volatile fatty acid are explained in Figure 20.1.



Volatile fatty acids	Chemical formula	Molecular mass	Density	Melting point (°C)	Boiling point (°C)	pKa	Log K_{ow}	Log D pH 7.0
Formic	HCOOH	46.03	1.22	8.4	100.8	3.77	−0.54	−3.79
Acetic	CH_3COOH	60.05	1.04	16	118	4.79	−0.17	−2.41
Propionic	CH_3CH_2COOH	74.08	0.99	−21	141	4.87	0.33	1.8
Butyric	$CH_3(CH2)_2COOH$	88.11	0.96	−7.9	163	4.82	0.79	1.02
Caproic	$CH_3(CH2)_4COOH$	116.6	.93	−34	205	4.88	0.45	3.375
Lactic	CH3CHOHCOOH	90.08	1.20	53	122	3.86	−0.72	−3.76

Figure 20.1: VFAs chemical proprieties (Source: Zacharof & Lovitt, 2013)

One of the VFAs disadvantages is mostly related with the actual production costs relative to with the use of chemicals. Presently, the bottleneck for an economically sustainable VFAs industrial production is represented by the costs associated to the separation/purification downstream processes. Several efforts are being carried out in order to define green and cheap VFAs purification processes (Liu *et al.*, 2018).

Main uses

Volatile Fatty Acids could be considered a performing start material for the entire chemical industry. The main VFAs are linear short-chain aliphatic carboxylate compounds with a carbon chain consisting of C2 (acetic acid) to C6 (caproic acid). Because of their functional groups, VFAs represent suitable precursors for the production of biopolymers, such as polyhydroxyalkanoates (PHAs) and polylactate (PLA), reduced chemicals and derivatives (esters, ketones, aldehydes, alcohols and alkanes) as well as biofuels like CH_4 and H_2 (Agler *et al.*, 2011; Zacharof and Lovitt, 2013).

Their application is recognized in several industries such as the cosmetics, food and beverage), textiles, bioenergy and pharmaceutical (Bhatia and Yang, 2017). VFAs are widely used building block chemicals, and employed in the manufacturing of a wide range, pharmaceuticals, and materials, or they are used as free acids for feed conservation in the agro-food industry (Baumann and Westermann, 2016).

The VFAs or generically the carboxylate platform, could be considered as one of the three best known bio refinery platforms. This platforms are used to convert organic feedstock's derived from agro-industrial wastes, to short-chain carboxylates as intermediate feedstock chemicals, using hydrolysis and fermentation with undefined mixed cultures in engineered systems under anaerobic conditions (Agler *et al.*, 2011). The VFAs could also be used as biological remover of nutrients from wastewater as carbon sources (Liu *et al.*, 2018).

Production process

Short chain organic acid including VFAs can be produced through the anaerobic fermentation of organic matter. Their production is based on the carbohydrates, lipids and protein fermentation. Three steps are involved in the anaerobic digestion to produce the VFAs: hydrolysis, acidogenesis, and methanogenesis (Calero *et al.*, 2017).

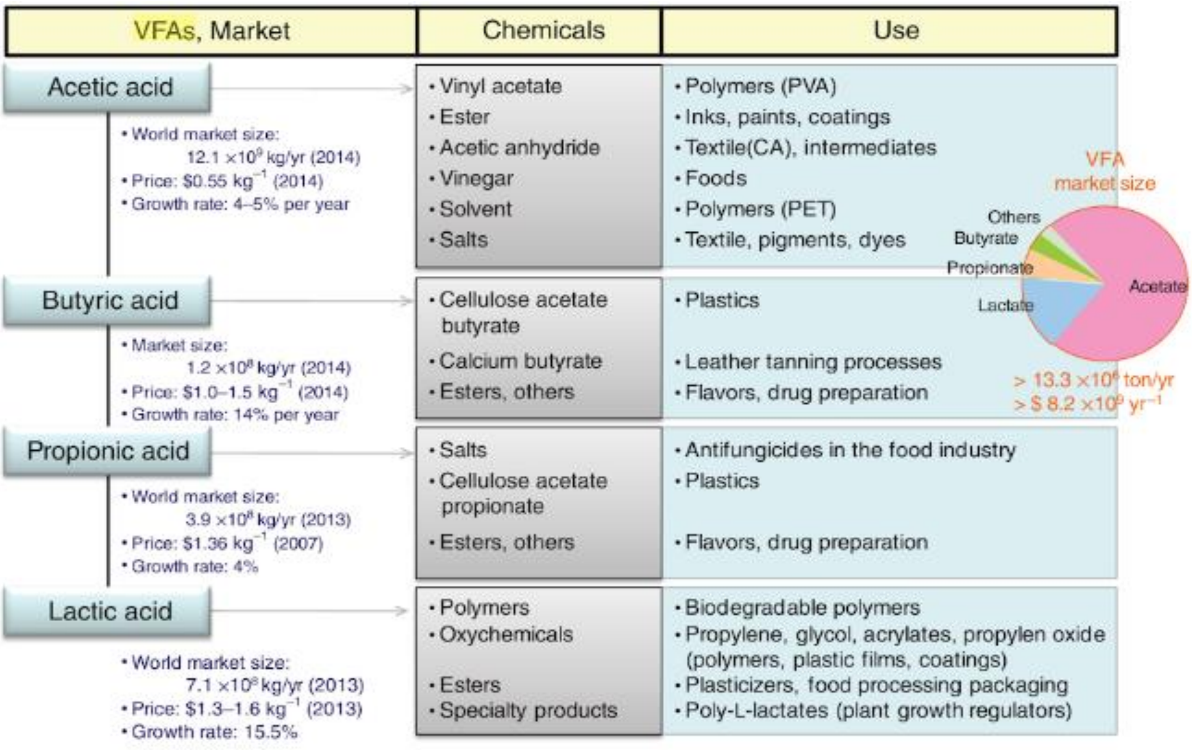
Bio-hydrogen gas production results from dark and light anaerobic fermentations during the VFAs production.

- **Markets**

Current volume, market value, prices.

Amongst the VFAs, the acetic acid is most commercialized as reported in Figure 2 and Table 1. According to Zacharof & Lovitt (2013), one third of the consumption took place in 2013 in United States and global production of acetic acid was approximately 6.5-7 million tonne per year, with the United States demand alone being 1.9 million tons per year at a price of USD 600–800 per tonne.

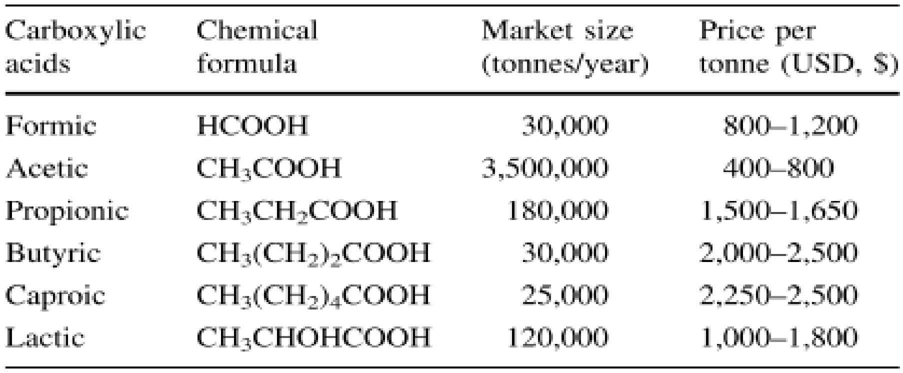
Of the global demand of acetic acid, 1.5 millions of tonne/year is met by recycling; the remainder is manufactured from petrochemical feedstock, produced by oxidation of acetaldehyde, the oxidation of liquid phase hydrocarbons, the carbonization of methanol or from biological sources (Zacharof and Lovitt, 2013)



VFAs, Market	Chemicals	Use
Acetic acid • World market size: 12.1 ×10^9 kg/yr (2014) • Price: \$0.55 kg^{-1} (2014) • Growth rate: 4–5% per year	• Vinyl acetate • Ester • Acetic anhydride • Vinegar • Solvent • Salts	• Polymers (PVA) • Inks, paints, coatings • Textile(CA), intermediates • Foods • Polymers (PET) • Textile, pigments, dyes
Butyric acid • Market size: 1.2 ×10^8 kg/yr (2014) • Price: \$1.0–1.5 kg^{-1} (2014) • Growth rate: 14% per year	• Cellulose acetate butyrate • Calcium butyrate • Esters, others	• Plastics • Leather tanning processes • Flavors, drug preparation
Propionic acid • World market size: 3.9 ×10^8 kg/yr (2013) • Price: \$1.36 kg^{-1} (2007) • Growth rate: 4%	• Salts • Cellulose acetate propionate • Esters, others	• Antifungicides in the food industry • Plastics • Flavors, drug preparation
Lactic acid • World market size: 7.1 ×10^8 kg/yr (2013) • Price: \$1.3–1.6 kg^{-1} (2013) • Growth rate: 15.5%	• Polymers • Oxychemicals • Esters • Specialty products	• Biodegradable polymers • Propylene, glycol, acrylates, propylen oxide (polymers, plastic films, coatings) • Plasticizers, food processing packaging • Poly-L-lactates (plant growth regulators)

Figure 20.2: VFAs market size (Source: Chang, 2017)

Table 20.1: Market size and price by acid (figures relative to 2013)



Carboxylic acids	Chemical formula	Market size (tonnes/year)	Price per tonne (USD, $)
Formic	$HCOOH$	30,000	800–1,200
Acetic	CH_3COOH	3,500,000	400–800
Propionic	CH_3CH_2COOH	180,000	1,500–1,650
Butyric	$CH_3(CH_2)_2COOH$	30,000	2,000–2,500
Caproic	$CH_3(CH_2)_4COOH$	25,000	2,250–2,500
Lactic	$CH_3CHOHCOOH$	120,000	1,000–1,800

Source: Zacharof & *Lovitt* (2013)

Biomass/yield and feedstock availability

The potential added value of VFAs and its production is correlated with the bio-refineries sector. In a technical report from the European project BIOREF-INTEG one billion tonne/year of VFAs from biomass have been produced with a price around 1 500 euro/tonne (Bioref-integ, 2010).

- **Actors**

General setting

Several realities have been started working on the VFAs production and development based on the use of organic bio-waste material and renewable feedstock's. The VFA production is already related with oil and chemicals and most activity are still at the R&D stage.

Europe

InnovEN, (Italy), The Italian spinn-off at the Department of Biotechnology of the University of Verona, which operates in the development and validation of new processes and technologies in the field of environmental technologies. They are mainly interested in the treatment of wastewater, waste and biodegradable waste, with recovery of organic matter and energy. (http://www.innoven.it/)

Afyren (French): The Company operating since 2006 in the valorization of non-food biomass (wastes) into bio-melocules with high energetical and chemical value. They return-to-earth the fermentation residues. Non-food biomass transformed by Afyren allows to obtain synthons (from 2 to 6 carbons), which will lead, via green chemistry, to a variety of high added-value compounds. (http://www.afyren.com)

OWS, (Belgium): The Company which developed innovative and patented designs for biogas plants, with a pretreatment, digester concept and post-treatment adapted to each type of feedstock. (http://www.ows.be)

Twence, (Netherland): The Company is working since 1986 in processing waste. (http://www.twence.nl)

Rest of the world

Earth Energy Renewable, (US): was formed in 2012 and is developing a hybrid biological/chemical process in order to produce VFAs from raw materials (food wastes). Their technology underwent successful scale up from laboratory to demonstration scale, and has been able to process over 3 dry ton/day of municipal solid waste. They acquired intellectual propriety, data and asset of Terrabon Inc., using the technology that has been originally developed at Texas A&M University. (http://www.ee-renewables.com)

- **Value proposition and sustainability**

Co-products

VFAs represent one of the possible products deriving from the anaerobic digestion process. Recent studies have proven that the anaerobic process could be designed to produce volatile fatty acid, biohydrogen and/or bio-methane separately or simultaneously (Khan *et al.*, 2016). After the anaerobic digestion process and VFAs production, this could be used such as suitable precursor for the production of biopolymers (PHA) and other valuable products like biofuels, alcohols, aldehydes or ketones.

Environmental impacts, benefits, sustainability

One of the prominent advantages in terms of environmental benefits of the VFAs use is its direct substitution of fossil carbon substances with more sustainable sources such as waste or biomass. For that reason the recovery material represents a key factor in guaranteeing the VFAs supply (Zacharof and Lovitt, 2013).

In addition, the enormous quantity of waste existing and which is increasing in time, is becoming a global concern. The transformation of wastes into VFAs could provide an alternative route to address the persistency of this problem (Zhou *et al.*, 2014). At the same time, it has been highlighted that VFA production from oil creates hazardous wastes such as heavy metals and organic solvents in addition to the emission of greenhouse gasses (Baumann and Westermann, 2016).

Socio-economic advantages, health impacts, bio vs non-bio based alternative

As for the health impacts, being the VFAs BtB products requiring additional processing to be used by retailers, no specific concerns can be envisaged.

Currently, most VFAs used in industry are produced by petrocatalysis from refined heavy oil and natural gas; naphtha and syngas are examples of such refined products. In the next future, these products may be refined by organic matter and synthetized in VFA to be used such as platforms for other bio-based products (Baumann and Westermann, 2016).

On the other hand, the high raw material costs have been partially solved as a problem, with the use of abundant and cheaply carbon sources as a raw material, like organic waste (Bhatia and Yang, 2017).

- **Outlook**

Projected trends (baseline)

The global market for chemicals is massive and the market volume rose by around 10% from 2012 to 2016 (American Chemistry Council, 2015). The majority of the chemicals produced are fossil based compound and carbon-containing compounds. However, there exist a great potential for increasing the Volatile Fatty Acids (VFAs) from bio-based feedstocks.

VFAs could be considered a performing start material for the entire chemical industry, it represents a suitable precursor for the production of biopolymers and biofuels. Due to their vast applications, US market Analysis Company MarketsandMarkets foresees that the industry for renewable chemicals will be grow rapidly in the coming years. They estimate that the global market for renewable chemicals will increase from USD 57 billion in 2013 to USD 83.4 billion by 2018, delivering a CAGR of 7.7% during the period.

According to the report (Market Research, 2017), the global acetic acid market (wich is the most commercialized volatil fatty acid) accounted for USD 8.37 billion in 2015 and is expected to reach USD 13.65 by 2021, growing at a CAGR of around 8.5 % between 2016 and 2021. Assuming the same CAGR for 2025 and 2030, the acetic acid market value would reach USD 20.52 and 30.67, respectively.

The global production of acetic acid was approximately 6.5-7 million tonnes per year, with the United States demand alone being 1.9 million tonnes per year at a price of USD 500–850 per tonnes. According to Zacharof & Lovitt (2013) compared to butyric VFA, the acetic acid market price is lower.

Competitiveness and role of Europe in global production

Several realities have been started working on the VFAs production and development based on the use of organic bio-waste material and renewable feedstock’s.

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SECTION 7 R&D GAPS

This section gives an overview of identified R&D gaps in the top 20 BBPs, recalling what resulted from previous sections and further elaborating that. This is done by platform first, to then give additional insights at the level of product.

Lignin

Currently, lignin is available on an industrial scale in modified forms as a by-product of the pulp and paper industry and it is used almost exclusively for energy generation (Ragauskas et al., 2014). However, lignin harbours a much higher potential for value creation: its unique structure and chemical properties enable the production of a wide variety of green alternatives to petroleum-derived substances, ranging from chemicals to composite materials, dispersants and carbon fibres, among others. Furthermore and most importantly, lignin is also considered to be a major aromatic resource of the bio-based economy. Therefore, both research and the private sector are addressing lignin valorisation approaches, in order to exploit this resource beyond energy generation (Kathaira et al., 2018). However, the full potential lignin offers for the bio-based economy, is currently still underexploited, due to various R&D challenges:

- **Improved understanding of the chemical structure of lignin:** A large number of studies have focused on lignin's chemical structure, either for the purpose of determining lignin purity, or for studying the native lignin structure in order to understand its formation and decomposition, respectively. However, the *whole* chemical structure has not yet been fully understood, which is critical for developing more robust and effective lignin valorisation processes (Kathaira et al., 2018).

- **Lignin isolation processes:** Multiple processes have been developed to generate lignin or a lignin-enriched residue. They are applied to analyse lignin structure (see above), or to remove lignin, mostly in the pulp and paper industry. However, they are largely impractical for large-scale use or change the lignin structure in a way that significantly reduces its potential as a chemical feedstock. A biorefinery requires different processes for lignin isolation and fractionation in order to generate lignin streams of high yield and purity, suitable for further transformation to bio-based chemicals. More research is necessary to select optimal isolation processes suitable for a biorefinery and to narrow down the multitude of processes down to a few that are practical and economically and environmentally viable. This also requires a conceptual shift for biorefineries from focussing on fermentable sugars coupled to low quality lignin, towards generating lignin as a separate process stream early in the operation that is better suited to further valorisation: Further research is needed on ionic liquid processes to decrease their cost, and Organosolv processes should be studied with the aim to carry out biomass fractionation, lignin dissolution, and lignin conversion simultaneously at early stages of the biomass conversion process (Bozell et al., 2018). Other R&D goals include a high solvent recyclability as well as tolerance for high solid-to-solvent loadings in order to yield an economically feasible process (Jensen et al., 2018).

- **Catalytic upgrading of lignin-derived monomers**: Numerous options for the catalytic upgrading of lignin-derived monomers already exist, but new catalytic methods need to be developed (Lancefield et al., 2018). One goal should be to establish lignin-derived platform molecules that can be used to produce a broad range of upgraded molecules. Further R&D activities are needed especially regarding bio-BTX aromatics and lignin-based phenolic resins: Low monomer yields and low selectivity represent a significant bottleneck (Shuai and Saha, 2017) that should be overcome. Lower process costs are necessary when converting lignin into bio-based products, especially for BTX aromatics, lignin-based carbon nanofibers and PHAs.

TOP bbps under development	Key markets and applications
1. Lignin-based carbon nanofibres	• Alternative to PAN-based carbon fibers. Composites
2. Bio-BTX aromatics	• Bio-based raw chemicals
3. Lignin bio-oil	• Green chemicals and biofuels
4. Lignin-based phenolic resins	• Alternative to phenolic resins. Constructions.
5. High-purity lignin	• Thermosets. Composites. Additive for plastics.
6. Biobased phenol and alkylphenols	• aromatic chemicals and monomers

1. Lignin-based carbon nanofibres

At present, the main R&D challenges when producing lignin-based carbon fibres (CF) is the need to purify lignin to make it suitable for melt spinning and carbon fibre production. The goal is to produce lignin-based carbon fibres at relatively competitive prices. Therefore, the process must be cost-efficient, if the Carbon Fibre Reinforced Plastic (CRFP) market is to expand considerably. Lignin is a low-cost raw material compared to (Polyacrylonitrile) PAN, and can offer mechanical properties suitable for commercial grade CFs (Warren, 2006; Maradur et al., 2012). There have been many R&D activities here including studies of various types of lignin, chemical modifications and the production of CFs (Kadla et al., 2002; Qin, 2012). The next step seems to be the construction of a pilot plant. Another major R&D challenge is recycling. Up to now, carbon fibre cannot be recycled like other materials; it can be chopped and thermically treated. However, the resulting material loses its strength and is not suitable for reuse.

2. Bio- BTX aromatics

Lignin-based BTX aromatics production is still in the R&D phase and there is no mature technology available. Much progress is required to overcome the relatively high production costs and identify the economically most feasible routes to produce BTX aromatics from lignin (Bazzanella and Ausfelder, 2017; Hu et al. 2018).

R&D is needed on lignin depolymerisation techniques to improve yield and selectivity. Furthermore, the aromatic units that make up lignin, and therefore the monomers available from lignin, are highly functionalized, i.e. oxygenated and alkylated (Lancefield et al., 2018). Currently, one of the biggest R&D difficulties in producing BTX from lignin is to selectively de-oxygenate and de-alkylate the C6 aromatic structures (i.e. achieve the desired defunctionalization), without hydrogenating and destroying the C6 aromatic ring of lignin (Bruijnincx et al., 2016). Improved technologies are required that allow a selective cleavage of bonds by preserving the structures of monomeric lignin (Crestini et al., 2011).

3. Lignin Bio oil

Research gaps remain with respect to understanding and improving bio-oil production. Fields of interest for optimising the fast pyrolysis process include feedstock pre-treatment, reaction conditions, reactor design, catalysts and upgrading processes (Perkins et al., 2018; Roy and Dias, 2017). Wang et al. (2017), for instance, provide a list of recommendations for further efforts like the development of fast reliable technologies to typify pyrolysis-based compounds. A second area concerns the reliability, cost and efficiency of the bio-oil production process (Perkins et al. 2018). Bio-refinery technologies (Dhyani and Bhaskar, 2018; Wang et al., 2017; Xiu and Shahbazi, 2012) and lignin feedstock logistics (Roy and Dias, 2017) must be tackled to bridge gaps linked to the process's economic viability.

4. Lignin Based Phenolic Resins

Lignin based phenolic (LBP) resins production faces a number of R&D challenges. First, using unmodified lignin directly is not considered attractive to produce bio-based phenolic resins because of the low bonding properties of resins produced from unmodified lignin (Hu et al., 2011). Pre-treatment modifications are needed to increase lignin's reactivity (Siddiqui, 2013), but these require additional energy and chemicals, making LBP production by currently available technologies economically less attractive to manufacturers.

The properties of LBP resins represent another challenge, because 100 % LBP resins are currently not produced on a commercial scale, apart from the first attempts by UPM Biochemicals (WISA BioBond, 2018). Lignin content in current production methods of more than 70% has a negative impact on LBP resins' performance (i.e. adhesive strength) (Kalami et al., 2017). Other R&D challenges regarding LBP resins include reduced reactivity and thermal stability compared to phenol-based resins and curing issues (Siddiqui, 2013).

5. High-purity lignin

High-purity lignin is the starting point for the development of further formulations suited for use as raw chemicals and advanced materials. It can be considered as a platform chemical from which a wide variety of high-added-value products can be derived.

The current challenges relative to high-purity lignin relate to its processing and costs. Lignin cannot be readily separated in a high quantity and high purity without significant alterations of its native structural properties (Alvarez-Vasco et al., 2016). Also, at present, technical lignin presents large heterogeneity in terms of purity and chemical structures. Therefore, the first major step crucial to add value to the unconverted lignin is its separation from other biomass constituents, such as hemicelluloses, cellulose, ashes to give high purity lignin (Cotana et al., 2014).

Similarly, the high cost of purification of commercial lignin, formed as a by-product of the pulp and paper industry, represents a major drawback. Today the extraction of lignin from black liquor is quite expensive and is not developed at industrial scale (Nilsson, 2017). Several processes for recovering lignin from black liquor have been recently developed, despite additional R&D would support the creation of novel extraction methods, which are more efficient and cost effective.

To be cost effective, lignocellulosic biorefinery for production of biofuel requires valorization of all fractions (Huber et al., 2006). In this respect, various strategies are under development, despite a key point remains the valorization of residual lignin, as well as the possibility to use economically it as value-added co-product at commercial scale (Dong et al., 2011).

Finally, new technological developments are required to breakdown the chemical structure of lignin into commodity chemicals, including vanillin.

6. Biobased phenol and alkylphenols

Phenols are raw chemicals suitable for several industrial needs: solvents and fuel additives, plastics, bio-pesticides or insecticides, dietary supplements and drug components (Bruijnincx, 2016), and cosmetic formulations (Ugartondo, et al., 2008).

Lignin can serve as bio-based source for aromatic chemicals, especially phenols: lignin is an abundant phenolic polymer that can be used as a substitute for toxic and expensive raw materials, such as phenolic monomers. Aromatic building blocks derived from lignin are particularly attractive for use in polymerization, as substituent of oil-derived phenols, e.g. phenol formaldehyde resins or epoxy resins.

Despite the enormous quantity of lignin renders excellent opportunities for production of aromatic monomers and polymers, such as phenols, the full potential of lignin is still underutilized. A first drawback of lignin utilization is its heterogeneity, leading to unpredictable and uncontrollable reactions, odor, and color (Gosselink, 2011). A second issue relates to its low quality (Qu et al., 2015), which derives mostly from the difficulty in obtaining pure aromatic chemicals from lignin. New technological developments are required to breakdown the chemical structure of lignin into commodity chemicals, including phenols. The replacement of petrochemical-based routes for the production of bulk aromatic compounds, such as phenol, by renewable routes has received relatively little attention (Van Haveren et al., 2008) and should be further explored in future research.

As for phenols and phenol derivatives from lignin, the main problem in the production process relates to the cost to obtain pure phenol, which can be associated to an immaturity of the technology (LigniMATHC, 2010).

Renewable Oils and fats

Oils and fats of vegetable and animal origin (plant oils, animal fats, and marine oils) have been the most important renewable feedstock of the chemical industry in the past and in the present. Fats and oils multifunctional chemical composition allows their exploitation through a number of different synthetic methods (Bierman, 2011), giving rise to an almost infinite range of bio-based chemicals.

- **Processing cost**: From a chemical and technical viewpoint, most O&F are interchangeable; however, costs for processing and specific end-use requirements may differ considerably and remain quite high. The production process should then become more efficient and release higher yields.

- **Processing methods:** When considering the methods to produce fatty acids and glycerol, the most relevant include Hydrolysis of triglycerides, Microencapsulation, Microbial Oils Fermentation, and additional Novel polymerisation techniques.

  While in the case of Hydrolysis of triglycerides R&D can help better understanding and comparing the efficiency of using validated heterogeneous catalysis, in addition to find new ones, research on the Microencapsulation method can help improving the shelf-stability and quality of an oil-containing product and avoiding the development of unpleasant tastes and off-flavors, or the generation of free radicals. In the case of Microbial Oils Fermentation, research should push further the development of suitable microbial platforms (or enzymes) to increase the yield of products and to use waste oils and fats. Additionally, more effort could help producing polyunsaturated fatty acids long-chain omega-3 (n-3 LCFAs) to be used in intensive fish farming to replace fish oil, which has become a limited oceanic resource and be increasingly expensive. Additional investigation is also needed to improve novel polymerisation techniques, such as those based on the principles of olefin metathesis to both fatty acid esters and triglycerides using Grubbs and other ruthenium-base catalysts, and the click chemistry to plant oils and fatty acid derivatives for the preparation of highly crosslinked and hyperbranched polyesters (Montero De Espinosa, 2011).

- **New feedstocks:** Overall, it is of crucial importance to introduce and to cultivate more and new oil plants containing fatty acids with desired properties for chemical utilization while simultaneously increasing the agricultural biodiversity. This will support the industrial utilization of food plant oils aiming at creating valid alternatives to the costly coconut, palm kernel, groundnut and cottonseed (Biermann, 2011).

TOP bbps under development	Key markets and applications
1. Biolubricants	• automotive and industrial field
2. PHAs from O&Fs	• biodegradable plastics
3. Biobased polyamide 12	• technical plastics

1. Biolubricants

R&D challenges in the field of biolubricants include poor oxidative stability at higher temperatures and high viscosity at reduced operating temperatures. These can be tackled by changing molecule structures or design better additives specifically for plant-based lubricants. The lubricant market is very diverse with thousands of applications (Ullmann, 2012). Bio-based lubricants were developed primary for applications where the lubricant is emitted directly into the environment, such as chainsaw bars, two-stroke engines, and other marine applications.

In addition, improved production technologies are necessary to enable biolubricants production at lower prices. Biolubricants generally cost 1.5 to 2 times more than mineral-oil-based lubricants (Frost & Sullivan, 2014).

2. PHAs

Polyhydroxyalkanoates (PHAs) are polymers of microbial origin completely biodegradable in the environment. At the industrial level, PHAs are currently produced using pure cultures of selected microorganisms (e.g. Cupravidus necator, Pseudomonas oleovorans, Protomonas extorquens, Alcaligenes latus, or Escherichia coli) and high-cost substrates (e.g. glucose) in unbalanced culture media for cell growth (e.g. lack of nitrogen).

These concerns bring to a high production cost, not competitive with that of non-biodegradable plastics and synthesized from non-renewable sources (oil), which is the main limit to the large-scale diffusion of PHAs. The final PHAs yields result still far from the values required for industrial applications (Romanelli et al., 2014).

For the VFA, precursors of PHAs, to improve connection with bio refineries development is a goal to reach and R&D should help reducing the costs associated to the separation/purification downstream processes. Also, in terms of sustainable production technology the disposal still represents a limit due to the uncontrolled release of the methyl ester.

On the reduction of the cost of inputs to production, a variety of waste streams, different from sugars, has been tested in last decades to produce PHAs in economically sound ways. Carbon has been sourced from agro-industrial food waste (Tsuge et al. 2002; Wolf et al., 2005, Chaudhry et al. 2011), organic municipal waste (Pagliano et al., 2017), and activated sludge coming from waste water treatment (Chua et al. 2003), fat wastes from animal industry (slaughterhouse), and glycerol for microorganisms like yeasts.

Research could better address the cost-effectiveness of PHAs production from animal lipids, given that microbes with the combination of substrate-utilization and PHAs production are not currently available (Romanelli et al., 2014). Simultaneously, R&D should search for more affordable carbon sources.

While the production of feedstock for bioplastics may lead to direct and/or indirect land use change, a systematic analysis of associated land use effects and land competition with feed and food does not exist. In this respect, research should investigate whether land use changes can bring to higher GHG emissions (van den Oever et al., 2017), and what are the overall environmental impacts of PHA production, depending on the carbon substrate used.

3. Biobased polyamide 12

Polyamide (PA) are macromolecules with repeating units linked by amide bonds. The PA12 currently commercialized is based on fossil sources - from butadiene - and converted in five steps into lauryl lactam (the monomer for the PA12 polymerization process).

Attempts to produce bio-based polyamides have been few, especially in the case of PA12. Examples are the use of C11 undecenoic acid methyl ester produced from Castor oil, and cross metathesis with acrylonitrile, and the use of bio-based ω-amino lauric acid from fermentation of palm kernel oil. As a result, overall, bio-polymers are still more expensive compared to conventional commodity polymers (Imre and Pukánszky, 2013).

Bio based PA12 only exists, therefore, at lab and pilot-scale plant and its use for industrial applications would require intensive efforts in research and important investments to make it a commercial reality. R&D can also help investigating further the opportunity to create bio-based PA12 from bio-butadiene. This would allow taking advantage of existing production facilities.

Natural rubber

Natural rubber (NR) plays a vital role in the global economy, with major applications in the automotive, consumer goods, manufacturing, and medical industries. Natural rubber is a promising bio-based product but limits in terms of security and diversification in supply exist.

- **Security in supply:** NR is produced from the rubber tree *Hevea brasiliensis*. A major issue is that the unique relevant commercial source of NR at present is mainly harvested in South East Asia (Thailand accounts for nearly 70-75% of the world's global production). From 2014, concerns apply for Europe, in relation to the values of indicators tracing both economic importance and supply risk of NR. The current import dependency is 100% and there is a lack of readily available substitutes for all identified end-use applications. As a result, from 2017 NR entered the list of the critical raw materials for Europe (European Commission, 2017).

- **Diversification in supply:** Diversifying sources of natural rubber from the current feedstock of *Hevea Brasiliensis* is therefore paramount and additional research and investments should be devoted to this objective. In this respect, guayule rubber and Russian dandelion rubber are attracting attention as their grow, in Europe, would mitigate the overconcentration of natural rubber production in a specific place (Tullo, 2015).

While Russian dandelion (Taraxacum kok-saghyz Rodin) has been investigated as feasible alternative sources for the production of NR on the large scale, Guayule rubber (*Parthenium argentatum Gray*) is considered the most promising crop for cultivation in Mediterranean areas. Moreover, whereas both rubber types may be suitable in applications such as tyres and car parts, guayule rubber may also find specific applications in the area of medicine (due to absence of IgE latex allergy).

TOP bbps under development	Key markets and applications
1. Guayule rubber	• Substitute of natural rubber from Hevea Br. in all rubbery goods. Automotive. Biomedical items.

1. Guayule rubber

Guayule has the potential to complement or substitute the natural rubber produced by the *Hevea brasiliensis* in the tropics.

Today, the cost of cultivation, harvesting, extraction, and processing is significant. Existing cultivations are mainly used for research and development of private companies such as the tire company Bridgestone and the start-up Yulex.

Large-scale cultivation of Guayule met some complications during the decades of breeding. Despite molecular genetics and genetic engineering have recently been addressed (EU-PEARLS and DRIVE4EU projects), there is a need for new breeding activities, which can support higher rubber yields. Yields, which are currently significantly below those of optimised cultivars of Hevea rubber, need to be increased to acquire a competitive advantage with respect to rubber from *Hevea Brasiliensis* and become commercially feasible.

This is possible by investing greater effort in developing large-scale production of Guayule rubber, increase yields, and enhance processing methods to overcome economic barriers. In this respect, R&D should focus mostly on improving currently complex extraction, purification, and separation methods to obtain a higher purity product at a lower cost. Also, to make the production process more sustainable, water use should be reduced substantially.

Research is also needed to better meet guayule rubber transportation needs. Harvested Guayule can be pressed into bales with high density but for short transport distances and short storage time to avoid rubber degradation. Exposure to oxygen reduces its mechanical and physical properties so that antioxidants should be added to the rubber formulation to mitigate this tendency towards degradation.

Plant fibres

The use of plant fibres in innovative areas of materials science gained considerable attention because of their bio-renewable character, their ubiquitous availability in a variety of forms, and their low cost.

The industrial interest is primarily focused on using plant fibres as renewable reinforcing fillers for plastic-based composites, mainly for the automotive and packaging applications, or for the production of sustainable textiles and fabrics exploiting fibres from waste residues, to valorise side/waste streams. Main issues in plant fibers can be summarised as follows:

- **Improve and stabilize their properties**: Plant fibres could be characterized by unstable and heterogeneous properties related to mechanical durability and thermal stability: the specific composition and structure of the different plant fibres gives rise to variability in terms of mechanical properties, which in turn influences their potential use as reinforcing fillers in composites. All natural fibres, also present the problem of water absorption. For this reason, a major R&D gap links with the necessity to improve and stabilize their properties.

  Increase in yields and advance technology: Plant fibres, and in particular hemp and flax fibres, can be considered as good substitutes of E-glass-fibres, which serve as a reference because of their great importance in composite technology.

  Within EU, flax is mainly grown in the northern part of France, in Belgium and in the Netherlands. It is also produced in Belarus and Russia but with lower yields due to lack of access to new technologies (USDA, 2017). Research can work out ways to improve biomass yields and productivity both in existing plots and in new cultivations across EU, removing existing technological barriers or fostering production drivers. Conversely, hemp is mainly grown in China and North Korea, and only in the Netherlands within the European context. Restrictive drug laws could represent a major barrier for industrial hemp cultivation (Cherney and Small, 2016). While R&D can help addressing the limits related to agricultural supply chains, breed varieties, harvest equipment, and manufacturing - which have to be modernized - institutional constraints can still hinder the development of a hemp fibre industry in EU.

- **Enhance reproducibility**: A final concern relates the application of plant fibres that can remain restricted due to a lack of reproducibility along with inconsistency in the manufacturing processes.

TOP bbps under development	Key markets and applications
1. Lignin biocomposites reinforced with	• Injection molding of plastic items

plant fibres	
2. Microfibrillated cellulose	Rheology modifier, reinforcing filler, emulsions stabilizer, filtering media, biomedical field.
3. Thermoplastic biopolymers reinforced with plant fibres	Alternative to glass or carbon-fibres reinforced plastics
4. Plant fibres reinforced bioresin pre-pregs	Alternative to glass or carbon-fibres reinforced pre-pregs
5. Self-binding composite non-woven plant fibres	Plastic paper

1. Lignin biocomposites reinforced with plant fibres

Mixing lignin with plant fibres (flax, hemp or other fibre plants) and natural additives produces a fibre composite also called "liquid wood”, which can be processed at raised temperatures and pressure. Many of these composites are designed specifically as ‘green’ alternatives to displace petroleum-based plastics.

A number of advantages exist when using natural reinforcements in composite materials, in comparison with conventional synthetic fibres (Biagiotti, 2004). On the other hand, certain disadvantages limit their application at industrial level on which more R&D is needed. Examples are moisture absorption, limited maximum processing temperature, incompatibility with the hydrophobic polymer matrix and the tendency to form aggregates during processing, lower durability, poor fire resistance.

Finally, most current sources of existing bio-plastics are reported to be 2 to 5 times more costly than oil-based plastics. At a reported price of around 4,5 cents per kg for lignin feedstock (Alberta Finance and Enterprise 2010), lignin could be price competitive with oil-based commodity plastics. R&D should allow increasing cost efficiency in production.

2. Microfibrillated cellulose

Microfibrillated cellulose has great potential in a huge range of applications, including personal care, cosmetics, home care, pharmaceutical excipients, adhesives and sealants, composites and resins, agricultural chemicals, oil field, fish bait, concrete, and CO_2 capture (Kalia, 2014; Mautner et al. 2018).

Major problem with microfibrillated cellulose is its commercialisation, given the hardship in creating industrial quantities with sufficient running efficiency and stability. An additional barrier is represented by the need to dry the microfibrillated cellulose fibres in a cost effective manner, without losing significant performance. These aspects would deserve further analysis. Finally, the bio toxicity potential should be investigated and testing activities should be carried out to construct a Safety Data Sheet. R&D should also help to develop specific applications for the finished products. This is expected to boost market expansion over next years.

3. Plant fibres reinforced thermoplastic biopolymers

Biopolymers reinforced with plant fibres represent an important alternative to glass reinforced composites to be used in the automotive, packaging sector, and in aerospace industries, amongst others (Rusu et al., 2011; Singh et al., 2017).

In the case of biopolymers used to produce bio-plastic (e.g. PLA, PHAs, starch blends), despite the latter are becoming extensively used as substitutes of traditional fossil-based plastics, they often do not meet the desired thermo-mechanical properties for several technical applications. Reinforcement with plant fibres represents therefore a valuable solutions to fill this gap.

However, plant fibres suffer from drawbacks stemming from the inherent nature of plant fibres (Bismarck et al., 2005). R&D can help in this respect and could shed additional light on how experimental methods used to determine the tensile properties of single fibres could affect tensile properties. Finally, a deeper investigation should interest the limited thermal stability of plant fibres with respect to the temperatures needed to process bioplastics in the molten state.

4. Plant fibres reinforced bioresin pre-pregs

In order to support industrial applications of plant fibres as reinforcing fillers in organic and inorganic composites in the aeronautical, automotive, and manufacturing sectors, current efforts are dedicated to the development of plant fibres reinforced prepregs. Plant fibres, rather than glass and carbon fibres (synthetic alternatives) are then subject to pre-impregnation with resin.

Despite technical knowledge about glass-fibre and carbon-fibre prepregs is currently under transfer into the bio-based sector, further investments from the industry is needed to maximize the proportion of renewable resources used while retaining acceptable material properties. Further efforts should be devoted, in addition, to create fully bio-based composites, where bio-based resins are used in replacement of traditional epoxy resins. Indeed, despite current research is concentrating the attention on finding isocyanates from a biological source, synthetic chemical cross-linkers are still used (Knowledge Transfer Networks, 2014).

However, while the availability of raw crop materials for bio-resins production is not an issue, sustainability concerns may arise in relation to the possible alternative uses of food crops and land. Whereas environmental benefits of composites are known, the scientific community should help understanding better the environmental and social implications associated with the manufacture of these composite materials and products.

A final note refers to the quality of plant fibres which may show properties that vary depending on location, plant maturity and how the fibres are harvested and preconditioned (Balakrishnan et al., 2016). Consequently, plant fibres application in structural composites is not yet solved (Niedermann, 2015) and deserve further attention. For what concerns the processing phase, unsolved issues relate to the limited maximum processing temperature, incompatibility with the hydrophobic polymer matrix and the tendency to form aggregates during processing, poor fire resistance and lower durability than synthetic fibres (Väisänen et al., 2017). All these issues, when solved will increase the comparative advantage of plant fibers with respect to synthetic ones.

5. Self-binding composite non-woven plant fibres

The material consists of a resinous matrix reinforced by an embedded non-woven fabric. Composite non-wovens are created by a modern and innovative industry employing non-woven technologies to bring together fibres of different origins.

Currently, the use of plant fibre composites is mainly restricted to non-structural components due to limitations in mechanical properties. The typical performance of a plant fibre composite is inferior in comparison to those of synthetic composites, so that an improvement of the mechanical properties, which are still inferior to substitutes, is required. On the other hand, the specific properties of some plant fibres are close to, or even better than, those of E-glass fibres, which indicates that their composites' performance can be improved.

Additionally, while the European PAPTIC® product (www.paptic.com) is a success bio-based product realized by Paptic Lld in Finland, additional research can support the development of further self-binding materials. Indeed, at present, the market of self-binding composite non-woven plant fibres is still a niche and should be expanded.

R&D should look at how the wide diversity of plant cell walls translates into different performance in a composite good, given that their behaviour may differ drastically from one to another (Bourmaud, 2018). A better understanding is needed with respect to the key criteria that must be considered to select plant fibre behaviour at the source: limits and potential can change with location of the source which affects structure and biochemical composition (Bourmaud, 2018).

Terpenes

Terpenes constitute a main class of organic molecules produced by diverse organisms to perform a collection of biological functions in variable ecological contexts. Although all of them originate from the same five-carbon building blocks, the structures and functions of terpenes vary widely. Several products can result from the use of terpenes, form green propellants to pesticides, antioxidants for food and cosmetic applications, bioplastics, medical products, etc.

- **Supply and properties enhancement:** Because of the commercial significance of terpenes, the application of metabolic engineering strategies is of great societal importance to both increase supply and improve product properties (Bonfill, 2013). Possible strategies to increase terpene content need to be further investigated based on modern genetics and genomics approaches (Mewalal, 2017). Additionally, some researchers are focusing the attention on determining how exactly each terpene works and how they play off each other to understand how to use them in medical contexts. At industrial level, ways to manipulate the plant's terpene profile are being developing despite more specific information is required (Mayfield, 2018). On the other hand, for (non-chemical) synthesis of terpenes via microbial hosts, R&D can help deepening the knowledge about optimization of microbial metabolisms through genetic manipulations.

- **Human use of terpenes**: There exist problems with the procurement and adaptation of terpenes for human use that can be solved using chemical synthesis. In this respect, research can better document possible strategies to reduce time and cost of terpene synthesis for drug discovery. While bioactive terpenes are isolated frequently, medically relevant terpenes are isolated less often (Jansen and Shenvi, 2015).

- **Terpenes isolation:** One benefit related to the terpenes isolation refers to its frequent use of phenotypic assays, rather than target-based assays. Pharmaceuticals industry is increasingly interested in the latter as it provides important information about potency and selectivity in a cell, rather than on a single macromolecule (Kotz, 2012). On the other hand, the downside is that observation of phenotypic response does not resolve the issue of the biomolecular basis for that response. Therefore, use of a phenotypic versus target-based assay neatly divides medicinally relevant terpenes into two subclasses depending on whether the mechanism of action is known or unknown (Jansen and Shenvi, 2015).

- **Research need and funding pressure:** Despite there is not clear answer on what is the best approach to small molecule synthesis a decreasing number of syntheses are undertaken in the laboratory to show how a biologically produced molecule might be synthesized by chemical means (Jansen and Shenvi, 2015). In addition, while limonene has been lately the object of an increased interest to produce monomers for bio-plastics, the use of terpenes for by-polymers production requires more investigation in the years to come. Unblocking funding resources could advance research in this respect.

- **Alternative sources of terpenes:** Apart from terpenes in plants, algae are also prolific sources of secondary metabolites that might represent useful leads in the development of new high value bio-based products, due to their rapid cultivation on a large scale and fast growth and on the possibility to control the production of their bioactive compounds.

TOP bbps under development	Key markets and applications
1. Limonene-based engineering polymers	• bio-based polyurethanes, polyamides, polycarbonate

1. Limonene-based engineering polymers

Limonene is a good substrate for range of chemistries involving double bonds, mainly polymerizations. Since 1960 limonene has been the object of an increased interest to obtain monomers for durable (i.e. not biodegradable) bio-plastics, and polylimonene was developed.

Starting from limonene, technical polymers for engineering use, having elevated thermomechanical properties, are still under development and calls for additional investigation. The current supply of citrus limonene, is affected by high and increasing price if compared to oil price and this could prevent large scale bioplastics production based on this terpene (Lopez-Sanchez *et al.*, 2014).

Partly, this problem can be addressed by making more efficient the citrus manufacturing process. At present, from the annual global production of citrus fruits, a too high amount of processed citrus ends up as citrus waste (Pourbafrani et al., 2013; Wilkins et al., 2007). Rethinking the manufacturing procedure can foster a closed-loop production process with downward effects on costs and prices.

With the same aim to help Limonene-based materials to compete on price with petroleum-based alternatives, at the same time, research can explore how to develop a Limonene production independently on citrus production (Ciriminna, 2017). On the other hand, while microbial production could meet the Limonene demand it still needs important engineering efforts (Jongedijk *et al.*, 2016).

Natural Polyelectrolytes

This platform includes Bacterial Bio surfactants and Biotechnological Chitosan, and both are characterized by the necessity to support technology advancements and solve existing bottlenecks within the production process. Yields by some feedstocks may be improved.

-**Extraction process**: While polyelectrolytes are usually extracted from their natural biomass, there is a great interest in the development of new biotechnological processes to extract them from unconventional biomasses (for example soil sludge or lignocellulose biorefinery recalcitrant by-products). These studies are in their early stages of development and data are not yet available. More research is needed therefore to shed additional light on these aspects.

- **Surface properties**: Research on polyelectrolytes in recent years is focusing on physical insights in surface and interface science, as well as materials engineering. This is because polyelectrolytes strongly affect surface properties and interactions and the systems can have widespread applications in surface modification, water treatment, and controlled drug release (Scheler et al., 2007). In this respect, research will have to release more insights in next years.

- **R&D on chitosan**: As for chitosan, this could be produced from many raw materials, but in order to develop the end generation chitosan, new material should be found. In addition, owing the large variety of chemical composition, improving and stabilising properties of derived products may be necessary.

TOP bbps under development	Key markets and applications
1. Bacterial biosurfactants (sophorolipids and rhamnolipids) 2. Biotechnological chitosan	• medical and pharmaceutical formulations, cosmetics, personal care, food industry

1. Bacterial biosurfactants (sophorolipids and rhamnolipids)

Biosurfactants are surfactants obtained extracellularly or as part of the cell membrane by bacteria, yeasts and fungi (Otzen, 2017; Henkel, 2017). Sophorolipids and rhamnolipids (Otzen, 2017; Henkel, 2017) are surface-active molecules produced by microorganisms and they belong to the family of biosurfactants.

Because of their potent detergent properties, they are produced commercially as soil remediation agents and to combat marine oil pollution. Despite it is evident that rhamnolipids are able to bind to substrates with low degrees of aqueous solubility including hydrophobic pollutants, the underlying exact mechanism is not clear and would require more investigation.

2. Biotechnological chitosan

Chitosan, obtained by partial deacetylation of chitin, is present in significant quantities in some fungi, bacteria and algae, yeasts and the spines of diatoms (Akca, 2018).

A major research gap relates to how the mix between the molecules characterizing chitosan can be responsible for their biological activity and how they work synergistically. These aspects only recently have started to be studied by the research community and greater knowledge is likely to come in next years. The implications of the variability in structure relate to the difficult characterization of how the compositional variability and the molecular weight distribution add complexity to the identification of beneficial properties of the final product (Bellich et al. 2016).

It must be noted that commercialization of non-animal chitosan has just started. To date, small quantities of the chitosan molecules from fungi and algae derivation are made available on the market at very high price (Nano3Bio Project: http://www.nano3bio.eu/start/), and there exist no large-scale chitosan production. This is mostly due to the hard reproducibility of their biological activities and to their poorly defined mixtures. More attempts should be done to identify chitosans having reliable and more predictable biological functionalities.

Amongst future areas of exploration, within bioelectronics, apart from timid attempts (Kim et al., 2015) the use of chitosan to produce bio-device interface has not been deeply investigated. This, applies despite the advances achieved in biotechnology and microelectronics synergies. In addition, more investigation should focus on the advantages and trade-offs existing in the mushroom industry waste, for what concerns the use of stalks. Indeed, costs and benefits could be assessed to identify their best use between chitosan realization versus high quality mushrooms production (Bilbao-Sainz et al. 2017). Finally, in medical areas, more research could be useful to test the diverse therapeutic functions of chitin, for down regulation of allergic reactions via enhancing innate immune system (Vo et al. 2015).

Urban bio-waste

The platform of Urban bio-waste includes Organic Fraction of Municipal Solid Waste (OFMSW) and Urban Waste Water (UWW). Several are the areas where room for improvement exists.

- **Foster the European circular economy**: The use of bio-waste is of crucial importance in building the European circular economy. A systematic research can increasingly support the processes to produce added-value products from waste feedstocks.

- **Fraction sorting strategy**: OFMSW is a complex and heterogeneous feedstock which can lead to different results, when sub-streams of the OFMSW are isolated. OFMSW can be very diverse and inhomogeneous when mechanically-sorted from non-separated collections; conversely, source-sorted matrices may be mainly composed by specific fractions. Given the correlation between main features of such fractions and the waste sorting strategy, more investments are needed to ensure higher levels of source-sorted matrices.

- **Separation process**: in the specific case of PHA from waste and VFAs, while they have a great potential in terms of yield and feedstock availability, the separation process represents a bottleneck, upwards influencing their price.

- **New value-chains:** a valorization of the main components of biomass feedstock is needed to build new value chains for the development of innovative BBPs from urban bio-waste. In this respect further investments are supportive of a faster transition from traditional production to the biorefineries concept. Research is needed to couple new technologies with traditional methods, and with biotechnologies applied to biomass feedstock and different sources of waste streams.

- **Biorefinery schemes for sludge**: Beside urban wastes, the sludge resulting from the biological treatment of urban wastewaters in dedicated plants can be considered as a potential source of organic substances and nutrients. Thus, the development of urban biorefinery schemes may take such wastewaters into consideration.

TOP bbps under development	Key markets and applications
1. PHAs from urban wastes	• biodegradable plastics
2. Volatile fatty acids (VFAs) mixtures	• raw chemicals to produce esters, solvents, polymers.

1. PHAs from urban wastes

Polyhydroxyalkanoates (PHAs) are aliphatic polyesters, which are accumulated by many microorganisms as carbon and energy storage in the lack of a specific nutrient.

In the case of sludge coming from waste water treatment (WWT), activated sludge can not be directly used for the production of polymers, due to the too low concentration of incoming carbon substrate and the consequent low organic load of the process. They must be enriched in microorganisms with high storage capacity. Based on these considerations, research should tend to optimize the biotechnological process for the production of PHA from organic waste substrates.

At the same time, it should be envisaged the development of urban biorefineries on which more research is needed to increase current knowledge by providing additional evidence. Investments are needed to put in place industrial applications, where the multi-feedstock for the production of energy, biopolymers and nutrients can be tested (e.g., combining urban bio-waste and wastewaters).

It is key to understand how the Waste Framework Directive (EU Directive, 2008) and the Landfill Directive (EC Directive, 1999) will affect the waste and landfill disposal in the years to come (Bianchini et al., 2016). For example, only small amounts of sewage sludge are expected to be sent to landfill in the EU-27 by 2020 (Milieu Ltd et al., 2008).

Research can support decision makers in designing Sewage sludge disposal routes according to expected changes driven by policies. In addition, it should explore innovative systems able to favour a more efficient production of PHA from waste, which obtain more with less inputs. This is even more important when considering the large amount of biomass waste that is needed to, and results from, PHA production (Wolf et al., 2005; Castilho et al., 2009).

Reducing processing expenses by dropping the amount of feedstock needed and the cost for recovery and purification downstream process would unlock PHAs potential and foster its use in many industrial applications. These advancements which require technological breakthroughs are key and would likely help reducing production costs, which are, at present, still too high.

2. Volatile fatty acids (VFAs) mixtures

VFAs mixtures can be produced by the application of fermentation processes of organic matrices carried out under acidogenic conditions. VFAs can represent suitable precursors for PHAs production, reduced chemicals and derivatives, and biofuels.

A major issue on VFAs relates to their low concentration in fermentation broths (Yu, 2001), which makes separation and purification of VFAs very challenging. This translates in their costly recover despite VFAs could represent a source of valuable carbon material for chemicals products. Higher attention should therefore be devoted to the study of longer chains VFAs which could potentially show an easier recover (Chen, 2017), and to investigate pros and cons of different separation techniques (Reyhanitash, 2016).

OVERALL CONSIDERATIONS

Given the current low TRL of the majority of selected TOP 20 products, all of them require further R&D to establish a stronger science and technology base. This enables to bring them to marketable solutions, or to optimize further production processes of the products that have been recently introduced to the market (e.g. lignin based phenolic resins).

Most of them explicitly or implicitly show the need to reduce production costs (e.g. bio-lubricants, lignin based nanofibres), which implies both R&D related expenses to some parts of the process and furthermore, investigation of possible market, institutional or regulation needs, which also represents a resources demanding part of the value chain.

Some cases require more focused R&D intervention (e.g. separation technologies of high purity lignin), while others require wider actions, including organisational solutions, more coordinate all along the value chain.

One of the main strategies to allow cost-competitiveness is improving yields in some products (i.e. BTX aromatics, phenolic resins, PHA-s). Another important aspect of the process concerns the pre-treatment of feedstock that is mentioned in several cases, especially regarding lignin based bio-products (lignin based resins)

A very important issue, however, is that most often there is a need to improve properties of derived products in terms of performances related to their uses. This is important as it implies that many bio-based products, currently, are not perfect substitutes of fossil-based products, i.e. drop-in. In addition, this is an improved pre-requisite for allowing a strong marketing action towards final consumers showing higher and higher needs towards sustainability and health properties of final products, as well as awareness of the origin of the product. Depending on a concrete product, this may be also accompanied by willingness to pay higher prices, but this still is limited by income constraints, which implies the need that better quality should be achieved at cost-competitive end product prices and reasonable production costs.

Looking towards the final market (i.e BtC market), several products could benefit from a larger portfolio of potential end-products, derived from them. This would also serve as a way to substitute more fossil-derived products with bio-based alternatives, currently dominating the market.

Currently, a number of technologies for the production of bio-based alternatives to fossil-based products are approaching maturity and have been developed for demonstration at commercial scale. However, production volumes, if existing, are still low, as besides technological hurdles, the production at commercial scale is often not economically feasible. This highlights a need for supportive policy instruments that would enable market creation for bio-based alternatives of fossil-based products.

Finally, in some cases (i.e. chitosan, PA12, limonene), feedstock availability is also an issue. Feedstock availability, in principle, can be achieved with higher ability to pay for the feedstock itself, but also its costs need to be controlled by investigating alternative sources that are not competing with other biomass use. In particular, synergies with wood-based industry and second-generation biofuels should be explored for lignin-related products.

The precise solutions and R&D pathways are largely product-specific, except, in some cases, for products belonging to the same category or using the same feedstock.

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ABBREVIATIONS

AA	Acrylic acid
B2B	Business-to-business
B2C	Business-to-consume
BBP(s)	Bio-based product(s)
BBWN	Bio-based world news
BDO	1,4 butanediol
BTCA	Butanetetracarboxylic dianhydride
CA	Citric acid
CAGR	Compound annual growth rate
CNC	*See NCC*
COM	European Commission
DG RTD	Directorate General for Research & Innovation
DHA	Docosahexaenoic
DMAEMA	Aminization, dimethylaminoethyl methacrylate
DPA	Docosapentanoic
DVS	Divinyl sulfone
ECH	Epichlorohydrin
EGDE	Ethylene glycol diglycidyl ether
EoL	End-of-Life
EPA	Eicosapentaenoic
EPS	Expanded polystyrene
FU	Functional Unit
GG	Guaiacylglycerol-β-guaiacyl ether
GMA	Glycidyl methacrylate
HDI	Hexamethylene diisocyanate
LCA	Life cycle assessment
LVHV	Low volume/high added value
NCC	Nano crystalline cellulose
NFC	Plant fibre reinforced composite(s)

O&F	Renewable oils and fats
OFMSW	Organic fraction municipal solid waste
PBS	Polybutylene succinate
PDI	Pentamethylene diisocyanate
PEF	Product Environmental Footprint
PFA	Polyfurfuryl alcohol
PHA	Polyhydroxyalkanoates
PHB	Poly(3-hydroxybutyrate)
PHBV	Poly(hydroxybutyrate-co-hydroxyvalerate)
PLA	Poly(lactic acid)
TA	terephthalic acid
TRL	Technology readiness level
VFAs	Volatile fatty acid(s)
VG	Veratrylglycerol-β-guaiacyl ether
VOCs	Volatile organic compound(s)
WPC	Wood plastic composite(s)

APPENDIX A - SHORT DESCRIPTIONS OF THE INNOVATIVE BIO-BASED PRODUCTS INCLUDED IN THE DATABASE

1. MAJOR BIOMASS COMPONENTS: NATURAL RUBBER

Butyl rubber

Butyl rubber, also known as Isobutylene-isoprene (IIR), is a synthetic elastomer produced by low temperature cationic copolymerization of 1,1-dimethylethylene (isobutylene) with about 0.5 to 2 percent 1-methyl-1-butenylene (isoprene) using Lewis catalysts in chlorocarbon solvents. The isoprene provides the necessary unsaturation sites for crosslinking (vulcanization). Butyl elastomers can be vulcanized with sulfur. However, the low level of unsaturation requires more acitve accelerators such as dithocarbamate and thiuram. IIR rubber products can also be vulcanized by quinone dioxime and related compounds.

Butyl rubbers are sometimes blended with other ingredients such as oils, fillers, and antioxidants, which allows for a versatile variation of the thermophysical and mechanical properties.

Bio-based butyl rubber is obtained from copolymerisation of ß-pinene with isoolefins. Copolymers may contain significantly lower isoprenoid content than butyl rubber produced in 1 ,1 ,1 ,2-tetrafluoroethane, and are expected to have higher efficiency in subsequent halogenation reactions in order to produce halobutyl rubber.

Mainly employed in the automotive field, as elastomer for tires and inner liners, and other specialty applications.

Guayule rubber

Guayule is an evergreen shrub that originated in the arid zone from the southwestern part of the USA to northern Mexico and therefore can be grown in environments totally different from those suited for para rubber trees (the current primary source of natural rubber). Also, the rubber constituent contained therein is very similar to that of para rubber trees; Guayule is 5 to 10% cis-1,4-polyisoprene by weight. In guayule, the rubber is trapped within the plant’s cells and must be extracted after the plant reaches maturity, which takes two or three years. Given these factors, guayule is expected to become a new source of natural rubber. Guayule rubber delivers high tactile performance, absence of allergenic latex proteins and offers renewable sustainability because it is resourced from a domestic plant-based resource. Guayule rubber meets the critical performance standards necessary for many medical, industrial and consumer applications and exceeds performance standards of many synthetic lattices. Because hypoallergenic rubber and latex products are in high demand, guayule has an extra advantage of Hevea rubber. Guayule rubber is special in that it has a much lower protein content than the H. brasiliensis-based product. In addition, fewer protein species are associated with purified rubber particles from guayule.

Polyisoprene from plant oils and from natural turpentine.

cis-1,4-Polyisoprene is a natural occurring elastomer extracted from the sap of the Hevea Brasiliensis tree grown on plantations; The synthetic equivalent is polyisoprene (IR) which can be produced by polymerization of 2-methyl-1,3-butadiene with Ziegler-Natta catalyst. Both NR and IR rubbers are often mixed with other ingredients such as oils, fillers, crosslinking agents, and antioxidants, which allows for a versatile variation of the elastomer properties.

Natural and synthetic polyisoprene are inexpensive elastomers with good fatigue resistance and are, therefore, an excellent choice for dynamic applications at low and ambient temperatures. The tensile strength, elongation, and abrasion resistance of natural rubber is excellent over its working temperature range of approximately -50°C to +100°C. The chemically similar synthetic polyisoprene has lower strength than natural rubber but better low-temperature properties.
Bioisoprene has been recently developed through a bacterial fermentation platform, based on different sources of plant oils for glycerol and fatty acids. Natural turpentine, constituent of tree resins, is a natural source of isoprene monomer, which can be purposely polymerized to obtain polyisoprene elastomer. Main uses are as rubber applications for footwear, mechanical tools, medical appliances, sporting goods, and most extensively as polyisoprene in rubber tires

Russian dandelion rubber

Along with the guayule, it is the unique Europe-based alternative to natural rubber latex from hevea Brasiliensis. Russian dandelion is considered the second best crop that should be developed in parallel with guayule in northern and eastern European countries, where climate conditions are favourable to its cultuvation. Rubber is contained in the roots of the plant. The chemical structure and the quality of Russian dandelion rubber is comparable to the quality of traditional natural rubber from the rubber tree. For some applications, such as having a good grip on wet surfaces, dandelion rubber even appears to perform better.

2. MAJOR BIOMASS COMPONENTS: PLANT FIBRES

Geotextiles

Geotextiles are permeable fabrics which, when used in association with soil, have the ability to separate, filter, reinforce, protect or drain. As the use of geotextile fabrics has expanded there has been the introduction of geotextile composites and the development of products such as geogrids and meshes. Overall these materials are referred to as geotextiles and related products. All have a wide range of applications and are currently used to advantage in many civil engineering applications including roads, airfields, railroads, embankments, retaining structures, reservoirs, canals, dams, bank protection and coastal engineering. Plant fibres in the form of paper strips, jute nets, wood shavings or wool mulch are being used as geotextiles. In certain soil reinforcement applications, geotextiles have to serve for more than 100 years. But bio-degradable natural geotextiles are deliberately manufactured to have relatively short period of life.

Plant fibres reinforced concrete

Regular concrete is a brittle material which possesses a high compressive strength but on the other side has a low tensile strength. The combined use of regular concrete and steel reinforcing fibres was able to overcome that disadvantage leading to a material with good compressive and tensile strengths but also with a long post-crack deformation. Unfortunately steel-reinforced concrete has a high permeability that allows water and other aggressive elements to enter, leading to carbonation and chloride ion attack resulting in corrosion problems. Plant fibres are a renewable resource and are available almost all over the world, therefore to promote the use of concrete reinforced with plant fibres could be a way to improve concrete durability and also sustainable construction. in the past moisture absorption capacity of plant-based fibres which influence the mechanical and durability properties of reinforced cement composites negatively has remained a factor mitigating their use. There are however scenarios such as hot-weather concreting where water absorption capacity of plant-based fibres can be seen as a bonus. Inability of some of these fibres to resist a high pH cementitious environment also remains a concern and has discouraged their use.

Plant fibres reinforced prepregs

Recently, there has been a rapid growth in research and innovation in the plant fibre composite area. Interest is warranted due to the advantages of these materials compared to others, such as synthetic fibre composites, including low environmental impact and low cost and support their potential across a wide range of applications. Highly ordered textile reinforcements, such as interlaced woven fabrics and unidirectional fabrics made from natural-fibre yarns, perform considerably better than random non-woven mats in natural-fibre composites. Oriented prepregs made of resin pre-impregnated alligned fibres are currently considered as the best technical solution for obtaining high quality composite laminates with optimized mechanical properties. Both thermoplastic and thermoset resins can be used to pre-impregnate plant fibres, and all can be selected as bio-based alternatives.

Wood plastic composites

WPCs are composites containing a wood component in particle form (wood particles/wood flour) and a polymer matrix. They are used in a variety of structural and non-structural applications ranging from component and product prototyping to outdoor decking. However, construction and automotive applications are the most common worldwide. WPCs can be used outdoors as well as indoors, and some common applications include construction materials, garden and yard products, automotive applications (interior and engine), household items, packaging and consumer goods.

Plant fibres reinforced thermoset composites

Plant fibre composites have been developed over the last two decades. Rather than using synthetic fibre and petroleum-based resin, plant fibre composites are comprised of plant fibre reinforcement. Even though plant fibres contribute to a better environment, plant fibre/thermoset resin composites are not sufficiently ecofriendly because of the petroleum-based source and the non-biodegradable nature of the traditional thermoset polymer matrices. Using plant fibres with polymers based on renewable resource resins will allow many environmental issues to be solved. In addition to solving the environmental issues, developing bio-based resin matrix in composite systems may also counter the issues of scarce petroleum sources that also affect the sustainability of thermoset resin use. Thus, the attention paid to developing bioresin from plant oil derivatives is a very clear future prospect.

Plant fibres reinforced thermoplastic granulates and composites

Plant fibres can be widely used to reinforce thermoplastic commodity polymers, such as polypropylene, polyethylene, high impact polystyrene and thermoplastic elastomers, as well as bio-based thermoplastic polymers such as poly(lactic acid), poly(butylene succinate), poly(hydroxyalkanoate)s and others. Main purposes are related to the development of reinforced sustainable materials for injection moulding applications, or other standard processing techniques. The possibility to use a specific thermoplastic polymer matrix is restricted by the thermal stability by the plant fibres. Composite granulates are currently commercialized to support and improve the degree of dispersion of plant fibres inside the polymer matrix, which in turn influences the mechanical properties of the material after processing. Main innovation trends include the exclusive use of bio-based, bio-degradable thermoplastic matrices, to obtain fully-sustainable reinforced composites for technically demanding applications.

Non-woven mats and fabrics for plastic composites

Random non-woven mats usually show good drape (the ability to adapt to complex geometries) and wet out characteristics and are easy to process, but they demonstrate only very limited mechanical properties in making composite laminates due to the short fibre length and the high resin content. Therefore, they are seldom used for high performance applications. However, mats are still used in applications requiring a high resin content layer without high mechanical stability, like the outer skin of boat hulls. Resin transfer molding (RTM) is the major processing method to make random non-woven plant fibre mats reinforced polymer composites.

Woven mats and fabrics for plastic composites

In applications where more than one fibre orientation is required, a fabric combining different fibre orientations is useful. Woven fabrics are produced by the interlacing of warp fibres and weft fibres in a regular pattern or weave style. The fabric's integrity is maintained by the mechanical interlocking of the fibres. Drape (the ability of a fabric to conform to a complex surface), surface smoothness and stability of a fabric are controlled primarily by the weave style. An important criterion in determining the properties of textile composites is the weave pattern. Therefore, weaving plant fibres into different textile forms is important to their final properties. Basically, the manufacturing of plant fibre textile can be summarized as the following steps: growing plants, harvesting, stem or leave collection (depending on where the fibres are extracted), water retting, fibre separation, fibre hackling (several times), fibre weaving. The detailed fibre weaving techniques have been fully developed by the textile or fabric industry. Most of the fibre textile reinforced polymer composites are manufactured by RTM technology.

Micro- and nano fibrillated cellulose (also named nanocellulose)

Microfibrillated cellulose (MFC) is obtained by fibrillating cellulose fibres longitudinally, and thus obtaining a three dimensional network of cellulose microfibrils, which has a much higher surface area than regular cellulose fibres or powdered cellulose. This leads to some very interesting properties like very high water holding capacity and ability to form strong gels at low concentrations due to a larger number of hydroxyl groups, which comes in handy in applications such as controlling drying time of coatings and concrete, stabilizing water based formulations or keeping a surface longer wetted. Microfibrils in MFC have diameters in nanometers and lengths in micrometers, which makes them long and thin. This high aspect ratio makes the material high strength as useful in applications such as reinforcements for composites, films and barriers. Even though MFC is not soluble in water, it can exhibit some properties as water soluble cellulose derivatives. At the same time, it has some advantages over those derivatives such as being stable over the whole pH range, at high salt concentrations and at high temperatures. The first benefit of using this material is that it can strengthen and lighten fibre materials sustainably, obtaining products with reduced material use but with the same performance. For example, using just 1% of MFC can result in a 15% to 20% product performance improvement. The MFC fibres can give a material that is stronger and stiffer than glass or carbon fibre and more lightweight at the same time. Secondly, the material provides excellent oxygen and moister barriers.

Micronized superabsorbent fibres

Superabsorbent product made from the inner core particles(hurd) of kenaf, flax, hemp plants; can absorb extremely quickly up to 200 times its own weight in demineralised water and circa 60 times its own weight in saline. Main uses as loss circulation material and spill absorbents for the oil and gas industries. Animal bedding, garden mulch and specialty fillers.

Lignocellulosic microfibres

Such fibres have high aspect ratios and surface area, enabling improved composite mechanical properties. Lignocellulosic microfibres can be produced in a cost effective manner and from a variety of raw materials. Main use is as functional reinforcing additive for plastic composite material, that additionally supports improved mechanical damping properties. Higher performance than other commercially available biocomposites, such as those made from hemp, flax, wheat straw, and wood traditional fibres. Also used as rheology modifiers.

Crailar® flax and hemp fibres

Once the plants have been harvested the fibre is mechanically stripped from the stem. This raw fibre is rough and tough; the fibre is then transformed via the proprietary CRAiLAR process into a soft and fluffy fibre made up of thousands of individualized bast fibres that — while they resemble cotton in feel and appearance — outperform cotton on almost every level.

Composite non woven fibres

The term 'composite non-wovens' refers to a category of materials different from 'non-woven composites', which consist of a resinous matrix reinforced by an embedded non-woven fabric. These are self-binding fibres, that do not need to be dispersed into a plastic matrix to stick together, because they are polymer surface impregnated. Composite non-wovens are created by a modern and innovative industry employing non-woven technologies to bring together fibres of different origins, different characteristics or a combination thereof. Chopped strand mats are produced fabric like roll form where the fibres are randomly oriented, and held together with a resin specific binder.

Lignin biocomposites reinforced with plant fibres

Mixing lignin with plant fibres (flax, hemp or other fibre plants) and natural additives produces a fibre composite that can be processed at raised temperatures and pressure and made into mouldings on plastic injection moulding machines. It is also called "liquid wood". Depending on the application, these biocomposites contain different biopolymers like e.g. polyhydroxyalkanoate, poly(lactic acid), lignin, starch, cellulose, organic additives, natural resins or waxes and natural reinforcing fibres. These biocomposite granules are 100% biodegradable and show comparable material properties as classic plastics with high impact strength.

Plant fibres reinforced bioresin prepregs

Highly ordered textile reinforcements, such as interlaced woven fabrics and unidirectional fabrics made from natural-fibre yarns, perform considerably better than random non-woven mats in natural-fibre composites. Oriented prepregs made of resin pre-impregnated alligned fibres are currently considered as the best technical solution for obtaining high quality composite laminates with optimized mechanical properties. Both thermoplastic and thermoset resins can be used to pre-impregnate plant fibres, and all can be selected as bio-based alternatives. Bioresin prepregs are formulated with a poly(furfuryl alcohol) bio-based matrix, similar to a phenolic resin, it is a thermosetting system derived from hemicellulose crop waste, such as sugar cane bagasse. Aside from its positive environmental profile, it has been shown to have flame-retardant properties equivalent to that of phenolics, along with excellent chemical resistance.

Wood and plant fibres reinforced thermoplastic biopolymers

Plant fibres can be widely used to reinforce standard thermoplastic commodity polymers, but main innovation trends are related to the use of a bio-based thermoplastic polymer matrix, such as poly(lactic acid), poly(butylene succinate), poly(hydroxyalkanoate)s and others. Main purposes are related to the development of reinforced sustainable materials for injection moulding applications, or other standard processing techniques. The possibility to use a specific thermoplastic polymer matrix is restricted by the thermal stability by the plant fibres. Composite granulates are currently commercialized to support and improve the degree of dispersion of plant fibres inside the polymer matrix, which in turn influences the mechanical properties of the material after processing. The composite granulate is 100% bio-based and 100% bio-degradable.

3. MAJOR BIOMASS COMPONENTS: LIGNINS

Vanillin

Vanillin, a phenolic aldehyde, is the primary component of the extract of the vanilla bean (seed pods of *Vanilla planifolia*). Vanillin is among the most important flavours and fragrances products in the world with a market volume of about 15,000-18,000 tonnes. However, because of the scarcity and expense of natural vanilla extract, synthetic vanillin is now used more often than natural one. Subsequently, different processes have been employed to produce artificial vanillin, especially from lignin. In this field, Borregaard is alone in supplying vanillin from wood, offering a wide range of specially adapted varieties of vanillin for different applications. In addition, by using wood as a raw material, environmentally friendly and sustainable vanillin is produced, replacing oil-based products. Vanillin from lignin finds applications in the food and fragrances industry and also as precursor for pharmaceuticals and agrochemicals. Furthermore, it can be used as additive (antioxidant, antifoaming and vulcanization inhibitor).

Lignin-based thermoplastic biocomposites

Lignin-based thermoplastic biocomposites are thermoplastic elastomers obtained from renewable raw materials such as polylactide, polyhydroxyalkanoates, starch, and polyamides based on dimer fatty acid. Lignin is added and included into the polymer matrix in order to give to the material a relatively high strength and stiffness and a high resistance to UV radiation. These biocomposites ensure the well-known elastic recovery capacity of conventional thermoplastic elastomers, as well as a thermoplastic processability.

Lignosulfonates

Lignosulphonates are by-products from sulphite pulping process, with high content of inorganics and residual carbohydrates. Importantly, the sulphonate functionality increases the water-solubility of the hydrophobic lignin. Lignosulfonates are a very effective and economical adhesive and can prevent the clumping and settling of undissolved particles in suspensions. Lignosulfonates stabilize emulsions of immiscible liquids and can tie up metal ions, preventing them from reacting with other compounds and becoming insoluble. Lignosulphonates are also used as chemical additives: dispersing agent for concrete particles; water-reducing additives (strong concrete) and for the production of gypsum board. In addition, lignosulfonate are used to disperse pesticides, dyes, carbon black, and other insoluble solids and liquids into water.

Bio-phenolic resins

Phenol formaldehyde resins are synthetic polymers. They are used in a wide variety of products, including coatings, adhesives, laminates, and engineered plastics. Comprising many household and industrial goods such as plywood, countertops, brake pads, and bearings. Phenolic resins are traditionally produced by reacting petroleum-based phenol with highly-carcinogenic formaldehyde. Bio phenolic resins can replace fossil-based phenol in the additives and adhesive used in the production of plywood and other goods, mainly for the green constructions sector.

Organosolv lignin

Organosolv lignin, derived from organosolv lignin process, is designed to dissolve lignin from plant cell walls by using a high proportion of an organic solvent in the cooking liquor. Organosolv pulping process is an environmentally benign pathway. The structure of these lignins depends to a large degree on the processing conditions under which they are obtained. Organosolv lignins are of high purity, often with very little carbohydrate and ash impurities. High challenging end uses are expected from organosolv lignins: as source of aromatics, phenolic resins and thermoplastics, polyurethanes, carbon fibres.

BTX aromatics (benzene toluene xylene)

BTX aromatics (Benzene, Toluene and Xylene) are high value molecules and the precursors of many mass-produced goods. These chemical compounds are obtained through catalytic de-oxygenation and de-polymerization of lignin, followed by a purification step and separation of the desired products. The process itself uses hydrogen, generated in situ from the reactions and re-introduced as a reagent during the process itself, together with an off-the-shelf catalyst. Lignin-based BTX would be used as a drop-in chemical and for a wide range of applications such as chemicals, high volume commodity polymers PET, PC, PA (which are in turn used to produce beverage bottles, food packaging, clothing, carpeting, automotive components and and electronic components), jet fuels, marine fuels.

Phenol and alkylphenols (coniferyl, sinapyl, p-coumaryl compounds)

Phenol and alkylphenols are important aromatic compounds. Aromatics are currently extracted from oil, which leads to the emission of CO2. New technologies from lignin reduce dependency on oil, leads to lower CO2-emissions, and provides profitable and sustainable prospects for the chemical industry and the supply industry. These compounds find use in the synthesis of sustainable chemicals and monomers (coatings, resins, adhesives, lubricants, polyesters, and polyurethane).

Lignin bio-oil

Lignin bio-oil is a mixture of guaiacols with different functionalities, i.e. ethyl, methyl, formyl, H. Processes are mainly based on the conversion of lignin waste streams, providing a more environmentally friendly approach to the production of fuels and chemical building blocks. The so-obtained oil is used as source of green chemicals and biofuels, for bioenergy demands and as a biodiesel enhancer.

Dispersants, concrete and mortar plasticizers

Lignin-based concrete and mortar plasticizers are a new sustainable, cost-competitive and high performance plasticizers, which enable the use of a small amount of water, producing a highly workable concrete that hardens into a strong final product. Adding value to underexploited biomass side-stream lignins, improving the sustainability and cost-efficiency of traditional pulping industry.

Thermoplastic lignin polymer (lignin TOFA-ester; lignin esterified with tall oil fatty acid fractions (lignin palmitate, lignin laurate))

Thermoplastic lignin polymers are materials derived from chemical modification of lignin, mainly by reacting at least a part of the hydroxyl groups present in the lignin with a fatty acid composition. In particular, innovative internally plasticised lignin is obtained. The process mix lignin with fine plant fibres made of wood, hemp or flax and natural additives such as wax. In this way, lignin provides a bio-based aromatic side stream for the replacement of plastics in compounds and composites. These lignin-polymers are sustainable materials for the automotive and packaging industries and also for the manufacturer of furniture, toys, musical instruments and shoes.

High purity lignin

Pure lignin is used as reinforcing filler in composites, while fractionating pretreatments will provide streams that will be tested as plasticizers. Lignin is expected to add value to composites also by improving their flame retardancy. The development of composite applications is led by an industrial partner.

Lignin pyrolysis char

Char and pyrolysis oil fractions are obtained through pyrolysis of lignin side-streams from pulp mills and other biorefineries. Lignin pyrolysis char can serve as a bio-based additive or substitute of fossil based compounds in higher-value applications. In detail, application in car tyres and asphalt production will be tested. In addition, the potential for blending with fossil diesel and heavy fuel oil will be also investigated.

Carbon fibres

Carbon fibres (CFs) are a lightweight, strong and flexible materials. Almost 80% of commercial CFs is predicated on using PAN as the starting raw material, but its cost has limited application to high performance materials; lignins permit the production of low-cost CFs. The development of lignin based high performance material will result in real benefits in the contexts of increased energy efficiency and reduced environmental production. In addition, by introducing a cost-effective lignin-based carbon fibre, the market could increase considerably. Main applications are: high mechanical performance light-weight composites materials (sports equipment, marine products, construction, aircraft and automotive industry); structural applications (aviation and aerospace, automotive industry); non-structural applications (Thermal insulation; Electrodes for batteries; Hydrogen gas storage); multifunctional applications (Separators in super capacitors; Load-bearing electrodes in super capacitors and batteries); application in energy and automotive sectors.

Muconic / adipic acid

Muconic acid is a dicarboxylic acid that can be obtained by biochemical conversion of both softwood lignin (mostly guaiacyl-lignin), and hardwood lignin (mostly syringyl- and guaiacyl-lignins). Muconic acid is a versatile platform molecule to produce adipic acid, terephthalic acid, hexamethylenediamine, caprolactam and many other chemicals. *Cis,cis*-muconic acid is a precursor of recognized industrial value for commercial plastics (hydrogenated to adipic acid for nylons; polyesters adipates mainly as plasticizers).

Acrylonitrile-butadiene-lignin (ABL)

Acrylonitrile-butadiene-lignin (ABL) is thermoplastic which has been made by replacing styrene with lignin, a brittle, rigid polymer. The innovative solvent-free production process interconnects equal parts of nanoscale lignin dispersed in a synthetic rubber matrix to produce a meltable, moldable, ductile material that is at least 10 times tougher than acrylonitrile-butadiene-styrene (ABS). ABL is recyclable, as it can be melted three times and still perform well. The technology to enable its commercial exploitation would reduce the need for petrochemicals. ABL can replace ABS in a range of applications from medical devices to car bumpers.

Syringaldehyde

Syringaldehyde is an organic compound that occurs widely in nature. Because it contains many functional groups, it can be classified in many ways - aromatic, aldehyde, phenol. Syringaldehyde is a versatile building block mainly for pharmaceutical applications; as an example, to build dendrimers with high antioxidant potential. It is precursor of 3,4,5-trimethoxy-benzaldehyde, a building block for the antibacterial agents ormetropim and trimethoprim. The oxidation of hardwood lignin to produce syringaldehyde-rich mixtures seems to be very attractive, because more environmental friendly and efficient than traditional chemical routes from gallic acid, vanillin and pyrogallol.

Methylated lignin

Methylated lignin is synthesized by chemical modifications (grafting, methylation, hydroxyalkylation) of bare and pre-treated lignin. Lignin represents an excellent candidate for chemical modifications and reactions due to its highly functional character for the development of new biobased materials. Therefore, fine chemical products can be effectively produced in a cost-competitive way comparable to their synthesis from petroleum derivatives.

BTX from bacterial degradation of lignin

Benzene, toluene and xylene are the source of approximately 60% of all aromatics in volume and are the precursors of many mass-produced goods. Biome group has already identified novel lignin-degrading bacteria and their enzymes which can lead to aromatic feedstock chemicals that would be suitable for bioplastic production. The initial focus is to "isolate" an aromatic chemical from lignin to replace the oil-derived equivalent currently used in the production of a polymer that conveys strength and flexibility in some of

Biome’s products. The production of such a bio-based polymer would reduce the cost and further enhance the sustainability of these products.

Reactive lignin "CatLignin®"

Reactive lignin is produced from pulp industry side streams currently used for energy production. Due to its superior reactivity, CatLignin is an ideal replacement for phenol in phenol formaldehyde resins and could become a new, high-value product for pulp mills. In addition, the CO_2 footprint of lignin is only approximately 20% of the footprint of phenol. Replacing phenol with lignin also reduces formaldehyde usage. The CatLignin material has potential as a substitute for a wide range of fossil-based chemicals in adhesive, rubber and plastic applications. Its antioxidative properties are expected to improve weather resistance reducing the need for fossil-based and expensive additives used today.This new material brings new business opportunities for the entire value chain, from lignin producers to adhesive and wood product manufacturers and end-users.

Lignin hybrid copolymers

Lignin hybrid copolymers consist of lignin copolymerized with non-lignin thermoplastic polymer segments. Integration of the networked lignin and its thermoplastic derivative has resulted in a product with the advantageous properties of both materials, including moldability, elasticity, ductility, strength, durability, and ruggedness. The resulting material is also melt-processible. The components in the lignin formulations, molar ratios, and other variables can be fine-tuned to adjust the final thermoplastic material's characteristics to meet specific needs or purposes. These high-performance lignin-based thermoplastic are useful for industrial plastic resins and commercial materials.

Lignin nanoparticles, nanolignin, colloidal lignin

Nanomaterials offer unique properties and the preparation of lignin nanoparticles and other nanostructures has therefore gained interest as a promising technique to obtain value-added lignin products. In particular, micro- and nanosize lignin has recently attracted attention due to improved properties compared to standard lignin available. The current research’s main focus is on pH and solvent-shifting methods where the latter can yield solid and hollow particles. The fields of application are ranging from improvement of mechanical properties of polymer nanocomposites, bactericidal and antioxidant properties and impregnations to hollow lignin drug carriers for hydrophobic and hydrophilic substances. Also, a carbonization of lignin nanostructures can lead to high-value applications such as use in supercapacitors for energy storage.

Terephthalic acid

Terephthalic acid is a dicarboxylic acid and a commodity chemical used principally as a precursor to the polyester PET, used to make clothing and plastic bottles. Lignin (e.g., purified or native lignin) is first converted into small molecule products having a single phenyl moiety. The single phenyl moiety product is then optionally converted via at least one oxidation step into further desired products, including therephthalic acid.

Anthraquinones

Anthraquinone, is an aromatic organic compound. Several isomers are possible, each of which can be viewed as a quinone derivative. The term anthraquinone, however, almost invariably refers to one specific isomer, 9,10-anthraquinone wherein the keto groups are located on the central ring. It is a building block of many dyes and is used in bleaching pulp for papermaking. Pulping catalyzed by AQ holds the promise of addressing problems with plant bleach effluents by producing pulps that are more easily bleached than standard kraft pulps. However, the appearance of cheap imported AQ from China made application of this technology in the pulp and paper industry less important. Still, the ability to selectively oxidize lignin to quinones suggests that development of next-generation oxidation catalysts for lignin could offer an important opportunity for the biorefinery.

4. MAJOR BIOMASS COMPONENTS: RENEWABLE OILS AND FATS

Polyesters of azelaic acid

Azelaic acid is a 9-carbon dicarboxylic acid obtained from oleaginous lignocellulosic biomass and can be found in seeds (barely, wheat and rye). Totally biobased polyesters of azelaic acid can be prepared by esterification of azelaic acid with diols obtained from sugar fermentation, such as 1,4-butanediol. In alternative even bio-derived polyols (e.g. glycerol) can be used in the polymerization process in alternative to diols. Those polyesters represent a new generation of fully biodegradable and compostable materials for packaging application.

Glycerides from oilve oil

Glycerides are esters obtained from the esterification of fatty acid with glycerol hydroxyl groups. Vegetable and animal fats are constituted by triglycerides, glycerides in which all the three glycerol hydroxyl group have been esterified by a fatty acid. For this reason, glycerides are a common by-product of fatty industry. Olive oil is a vegetable fat and from the waste of its production glycerides can be obtained. Those molecules have interesting properties and can be an attractive chemical compound for cosmetic industry.

Glycerides from lipids

Glycerides are esters obtained from the esterification of fatty acid with glycerol hydroxyl groups. Vegetable and animal fats are constituted by triglycerides, glycerides in which all the three glycerol hydroxyl group have been esterified by a fatty acid. For this reason, glycerides are a common by-product of fatty industry. Glycerides can be so recovered from waste of lipids processing industry, being by-products of those processes. Those molecules have interesting properties and can be an attractive chemical compound for cosmetic industry.

OMEGA-3: EPA (eicosapentaeonic acid), DHA (docosahexaenoic acid)

Omega-3 defined a specific group of polyunsaturated fatty acid (e.g. EPA, DHA, …). Mammals are unable to biosynthesize them even if omega-3 are important for normal metabolism. For this reason, they are interesting chemical compounds for dietary supplement industry but can also show attractiveness for cosmetic industry. Usually they can be obtained from animal source, such as fish or eggs. Recently, efforts were made to obtain those specific fatty acids in a more suitable way. Realization of dedicated algae aquacultures or utilization of other vegetarian sources can improve Omega-3 production. Moreover, wastes of those Omega-3 farms can be utilized, through fermentation processes, for biogas production.

Low-calories oils

Low-calories oils are new type of products with a low calories content that can be an attractive product for dietary industry. They are obtained from medium chain triglycerides (MCT) for food application and, at the present time, coconut oil and palm kernel oil are the main sources for their production. Nevertheless, alternative sources exist (caprylic, caproic, capric and lauric triglycerides).

Polyamide 11

Polyamide are macromolecules with repeating units linked by amide bonds. Nylon design a family of aliphatic polyamide. Polyamide 11 (PA11) is a specific nylon with an aliphatic repeating unit composed by 11-carbon atoms. PA11 is a biobased materials due to the possibility to obtain monomers from castor oil. It is marketed by Arkema with the commercial name of Rilsan®. It has interesting properties, that can also be better then PA12, PA11 counterpart obtained from petroleum sources. For example, PA11 has a higher melting point and a better cold impact strength than PA12 and can be an extremely interesting technical thermoplastic polymer for engineering applications (e.g. tubes, pipes, sheets, …).

Dodecanedioic acid

Dodecanedioic acid is an aliphatic 12-carbon atoms dicarboxylic acid that can be found in crude palm oil. Being a linear long chain diacid, can be an interesting monomer for the realization of particular nylon such as Nylon 6,12, a high-performing resin. Recently, big improve were made in industrial production of biobased diacid. The construction of VerdePalm plant, the first commercial-scale renewable chemicals manufacturing facility of Verdezyne, has officially started. The groundbreaking ceremony was held on July 30th, 2017. The new facility is designed to produce biobased long chain diacids. The first product manufactured at VerdePalm will be dodecanedioic acid (DDDA), starting from crude palm oil.

Esters of Long-Chain Fatty Acids (LCFA)

Esters of Long-Chain Fatty Acid (LCFA esters) are chemical compounds with interesting lubricating properties (high-viscosity lubricants for special application). At the present time, LCFA esters are obtained from paraffins after fermentation mediated by specific yeasts strains. Recently, new production technologies are under development to obtain these esters from renewable resources. Indeed, LCFA esters can be obtained via fermentation from oils and fats, both saturated and unsaturated.

Poly(hydroxyalkanoate)s PHAs

PHAs are a group of 100% biobased polyester with extremely interesting properties (biodegradability, biocompatibility and bioresorbability). PHAs are totally produced by microorganism through fermentation processes and waste from animal fats industry (tallow) or from biodiesel production (glycerol) can be utilized as carbon sources for hydroxyacids (3-hydoxybutyrate, 3-hydroxyvalerate, …) and PHAs production. Various hydroxyacids can be utilized as monomer for the realization of homopolymer, for example Poly(hydroxybutyrate), or copolymer such as Poly(hydroxybutyrae-co-hydroxyvalerate). More then 150 types of PHAs are known, each one characterized by different properties and can be a total bio-alternative to the currently used petroleum-based polyesters.

Glycerol esters

Glycerol is the main by-product of biodiesel production but can also be obtained from oleaginous lignocellulosic biomass or animal fats. Glycerol esters have show compatibility with conventional fuels and anti-knock properties. In addition to this, they are not corrosive. Therefore, they can be employed as bio-based fuel additives. Depending on the type of acid used for the synthesis of the ester, these chemical compounds can be additives for gasoline, kerosene or diesel.

Acrolein

Acrolein is mainly used as a biocide, but due to its bifunctionality can be an attractive chemical precursor of useful compounds (methionine, methylpyridines, acrylic acid, …) or a monomer for polymerization processes. Currently is prepared starting from propylene but can be produced even from glycerol, a by-product of biodiesel production that can also be obtained from oleaginous lignocellulosic biomass or animal fats.

Esters of azelaic acid

Azelaic acid is a 9-carbon dicarboxylic acid obtained from oleaginous lignocellulosic biomass and can be found in seeds (barely, wheat and rye). Esters of azelaic acid are prepared by esterification of azelaic acid with alcohols. Due to azelaic acid diacid nature, both mono and bi-esters can be obtained after reaction with alcohols (e.g. ethylhexanol). These new types of bio-based esters have interesting properties and can be utilized as lubricants, emollients or plasticizers.

Esters of gondoic or erucic acids

Gondoic acid and erucic acid are monounsaturated fatty acids that can be found in camelina and crambe oil. Methyl ester of both gondoic and erucic acid have interesting surfactant properties. Those bio-based surfactants are attractive chemical compounds for personal care and detergent products realization.

Esters of fatty acids

Fatty acids are the main waste of the alimentary industry (cooking oil, restaurant fats, fried oils, …). The acids can be recovered from waste and converted in esters by esterification with alcohols. The resulting esters have surfactant properties with low toxicity. Moreover, compared to the petroleum-based alternatives, they are highly biodegradable. Those bio-based surfactants are attractive chemical compounds for personal care and detergent products realization.

Polyamides C6 from short-chain dicarboxylic acids

Polyamide are macromolecules with repeating units linked by amide bonds. Nylon design a family of aliphatic or semi-aromatic polyamide. They can be prepared starting from an amino acid (minus H_2O) as monomer or by coupling reaction of a diamine and a diacid. In the last case, two types of monomers are necessary for polymer realization. In the last years, big improve were made in industrial production of biobased dicarboxylic acid. Combination of new biotechnologies and utilization of specific microorganism allows production of short-chain dicarboxylic acid from plant oils such as adipic acid (C6), suberic acid (C8) and sebacic acid (C10). Realization of such bio-based chemical compounds can result in the production of bio-based Nylon or other polymer interesting for textile industry.

Polyamide 9

Polyamide (PA) are macromolecules with repeating units linked by amide bonds. PA are classified on the basis of the number of carbon atoms present on the monomer. PA9 is a new polymer currently not present on the market, due to the absence of a fossil-based precursor for the realization of the monomer. Pelargonic acid, a 9-carbon atoms acid also called nonanoic acid, can be obtained from plant oils and converted in 9-aminopelargonic acid ester, the monomer necessary for the realization of PA9. This polyamide is a technical thermoplastic polymer with properties that might be lower than PA11, already available on the market. For this reason, PA9 production will be interesting only if the final price will be lower than PA11. This makes the development of the process a more difficult task.

Polyamide 12

Polyamide (PA) are macromolecules with repeating units linked by amide bonds. PA are classified on the basis of the number of carbon atoms present on the monomer. PA12 is currently produced from butadiene (petroleum-based sources) and converted in five steps into lauryl lactam, the monomer for the PA12 polymerization process. Recently, a completely bio-based PA12 was presented where the monomer, 12-aminolauric acid methyl ester, is obtained from fermentation of palm kernel oil. In an alternative approach, the C12 amino-ester can be produced through metathesis. The resulting polymer have application in transportation, energy, consumer goods, industrial coatings and electronics.

Esters of pelargonic acid with glycerol, diglycerol or other non-biobased polyols (NPG, TMP, PE) (Bio-OILs for COSMETICS)

Pelargonic acid, a 9-carbon atoms acid also called nonanoic acid, can be obtained from plant oils. Esters of pelargonic acid can be prepared by esterification of glycerol (glycerol tripelargonate) or diglycerol (diglycerol tetrapelargonate). These new types of esters are attractive for new products in cosmetics (emollients, thickeners) leading to the realization of a totally bio-based cosmetics, when bio-based polyols are used. Such cosmetics will be fully biodegradable and will present a favorable ecotoxicity profile.

Esters of short- and medium-chain fatty acids with polyols (neopentylglycol NPG 2,2-dimethylpropane-1,3-diol; trimethylolpropane TMP 2-(hydroxymethyl)-2-ethylpropane-1,3-diol; pentaerythritol PE, 2,2-Bis(hydroxymethyl)propane-1,3-diol))

Short chain fatty acids (C5-C9) and medium-chain fatty acids (C10-C14) can be obtained from oleagineous biomass (camelina, crambe, cardoon, etc) or animal oil. Esterification of these acids with bio-based polyols leads to the realization of new type of esters with lubricants properties for automotive. Such lubricants can be employed in specific applications were no toxicity of the product is required (e.g. agriculture or marine).

5. LVHV BIOMASS COMPONENTS: NATURAL POLYELECTROLYTES

Chitin and chitosan as raw materials (1st generation chitosan)

Chitin biopolymer $(C_8H_{13}O_5N)_n$ represents a very abundant natural biopolymer, the second most available polysaccharide after cellulose. It can be obtained from many sources such as exoskeletons of crustaceans, mollusks (endo- skeleton of cephalopods) and cell walls of fungi, microalgae and insects shells, yeasts and the spines of diatoms. Crustacean shells represent the most important source of chitin for commercial uses, due to the availability of marine waste material from the seafood processing industry. Chitosan is the polymer obtained through deacetlyation of chitin. Different levels of deacetylation are possible. Chitin and chitosan share the ability of forming complexes with metal ions, which is technically exploited for a number of diverse applications, such as decontamination of waters. The ability of chitosan to form polyelectrolyte complexes with polyanions, the cooperativity of this reaction and the properties of chitosan-based polyelectrolyte complex membranes, are also industrially exploited. Main applications of chitin and chitosan are in medicine, pharmacy, agriculture, the food industry, cosmetics, among others. Chitosan as raw material derived from marine waste is referred to as the 1st generation chitosan, which are dominating the market for decades and are still widespread. The deacetylation process of chitin is usually performed by chemical method in concentrated alkali solutions at elevated temperatures. However, they were poorly defined mixtures of polymers of varying purity and varying composition - mostly unfit for the development of successfully marketable products.

Enzymatic chitosan (2nd generation chitosan)

If chitosans come from the enzymatic processing of chitin, then they are called as 2nd generation chitosans, which are well defined in terms of their degrees of polymerization and acetylation. Due to their known molecular structure-function relationships, they are more suitable for the development of reliable products; these chitosans typologies are progressively appearing on the market. From the first to the second generation, a strongly reduced quantity of chitosan is required to achieve the same target (e.g., plant protection), and the results are more reliable.

Chitosan from fungi, bacteria and algae (3rd generation chitosan, also named biotechnolgical chitosan)

Due to the health concerns related to animal diseases, terrestrial organisms like fungi such as the mycelium of Basidiomycetes and fungi such as Zygomycetes species were considered as alternative sources for the production of chitin and chitosan. These sources could be used to obtain a pure, rather uniform product with specific characteristics. In addition, the fermentative production of fungi on cheap industrial by-products and wastes appears as an unlimited and a very economic source of chitin/chitosan. Moreover, such sources contribute to secure supply and product quality, which is difficult with crustaceans. This is referred to as "biotechnological chitosan", or "3rd generation chitosan".

Sophorolipids and rhamnolipids

Sophorolipids and rhamnolipids are biosurfactants, i.e. biologically produced surface-active glycolipids. Some yeast species, and in particular Candida (Torulopsis) bombicola, secrete extracellular glycolipids known as sophorolipids (or sophorosides), as they contain the sugar sophorose (β-D- Glc-(1→2)-D-Glc). This is linked glycosidically to the hydroxyl group of a 17-hydroxy-C18 saturated or monoenoic (cis-9) fatty acid, the carboxyl group of which is usually linked to the 4’-hydroxyl group of the second glucose unit to form a lactone, though it can also remain in free form and then have more powerful detergency properties. One or both of the 6-hydroxyl groups on the glucose units are acetylated. These lipids are produced on a commercial scale when the organism is cultured on substrates containing glucose and a source of alkyl moieties, such as alkanes or seed oils, which influence the nature of the fatty acid constituent. Sophorolipids are used in commerce in cosmetics as deodorant, anti-dandruff and bacteriostatic agents, and they are also known to possess antifungal, antiviral and spermicidal properties. The hydroxy acid constituents are in demand for lactonization for use in perfumes.

Pseudomonads are rod-shaped gram-negative bacteria found in soils that produce extracellular lipids known as rhamnolipids. The term is indicative of the fact that these lipids contain one or two rhamnose units, linked glycosidically to a 3-hydroxy acid, thence by an ester bond to a further 3- hydroxy acid. All of these lipids have antifungal and antiviral properties, and they exhibit bactericidal properties to Gram-positive bacteria. Because of their potent detergent properties, they are produce commercially as soil remediation agents and to combat marine oil pollution. Although the exact mechanism is not clear, it is evident that rhamnolipids are able to bind to substrates with low degrees of aqueous solubility including hydrophobic pollutants. Rhamnolipids are also used as a source of L-rhamnose.

Pectin-based (i.e. Muconic acid based) bioplastics

Pectins are a new source (alternative to sugars) of muconic acid, a platform chemical for the synthesis of biobased plastics. Pectin is a side stream obtained from citrus fruit peels or from sugar beet pulp. Muconic acid is obtained from pectins through their transformation into aldaric acid, which is subsequently dehydroxylated to muconic. Muconic acid can be further converted into a number of chemicals suitable as building blocks for the polymerization of bio-based plastics, such as bio-polyamides and bio-PET.
Pectin is currently underutilized as the production is only about 40 000 t/a, with the potential of several tens of million tonnes available annually. Its current use is in the food and beverage industry as, for example, a gelling agent. In addition to pectin, wood- or plant-based glucose can be used in the production of aldaric acid.

Bacterial (biotechnological) pectins, agars and carrageenans

Pectins, agars and carrageenans are polysaccharides having properties such as gelation and emulsion stabilization which make them useful in the manufacture of food, cosmetics, and medicine. Extraction is the most important process in the pectin production. Pectic substances are usually extracted by chemical or enzymatic methods, with a process of physical and chemical multiple stages, in which involves hydrolysis, extraction and solubilization of macromolecules. Extraction with hot water is the simplest and oldest method for recovery of pectic substances from plant tissues. New biotechnological processes for pectins production are based on the mixing of chemical and enzymatic catalyses with microbial bioconversion of feedstock biomass.

6. LVHV BIOMASS COMPONENTS: TERPENES

ß-pinene silane resin

Terpene-based silane-functionalized resins are usable for the formation of high performance, non-miscible tire treads. Generally, tire treads are compounded with high filler loading and resins to achieve specific properties. When used in tires for high speeds or at high internal tire temperatures (as in race car tires) miscible resins tend to suffer from reduced traction and handling but these problems can be solved by adding high softening point immiscible resins and resin blends.

Limonene-based pesticides

Limonene is a naturally occurring chemical which is used in many food products, soaps and perfumes for its lemon-like flavour and odour. Limonene also is a registered active ingredient in pesticide products used as insecticides, insect repellents, and dog and cat repellents.

Algae carotenoid-rich extract

Marine microalgae constitute a natural source of a variety of drugs for pharmaceutical, food and cosmetic applications—which encompass carotenoids, among others. Microalgal biomass is usually processed via solvent extraction, to render carotenoid extracts—with typical contents of 25%; this extract can be used directly in the formulation of supplements or undergo further multistep purification (including hydrolysis to release hydroxylated carotenoids from the accompanying fatty acids), and final recrystallization to polish the product.

Lycopene-containing functional food

As the main carotenoid in tomatoes, lycopene is often assumed to be responsible for the positive health effects seen with increased tomato intake. Particularly, lycopene is the most efficient carotenoid at scavenging singlet oxygen and reactive oxygen species and this antioxidant effect of lycopene is being used to produce food supplements with potential benefits in prevention of cardio-vascular disease (reducing inflammation, inhibiting cholesterol synthesis, or improving immune function) and prostate cancer, among others.

Polymyrcene-based adhesives

Myrcene is a naturally occurring terpene that can be used to replace isoprene or butadiene monomers (petro-derived) in the formulation of styrenic block copolymers for hot-melt pressure sensitive adhesive applications. These adhesives have utility in typical markets such as tapes, labels and printing plates, construction, and hygiene.

Pinene-based medical formulations

β-pinene can be used in the field of therapeutic drugs since it has been scientifically proven to possess medicinal properties, including anti-inflammatory, antiviral, antitumor, cytotoxic, and antimicrobial activities.

p-Cymene

p-Cymene is a naturally occurring aromatic organic compound. This compound is insoluble in water, but miscible with ethanol and diethyl ether. It is a constituent of several essential oils, most commonly the oil of cumin and thyme. Significant amounts are formed in sulfite pulping process from the wood terpenes.

Terephthalic acid

Terephthalic acid is an organic compound with formula $C_6H_4(CO_2H)_2$ industrially produced by oxidation of p-xylene. This white solid is a commodity chemical, used principally as a precursor to the polyester pet, used to make clothing and plastic bottles. Several million tonnes are produced annually. Recently, its production starting from limonene has been reported.

Limonene-based polyurethanes

Polyurethanes are a family of polymers which are essentially different from most other plastics in that there is no urethane monomer and the polymer is almost invariably created during the manufacture of an object. Polyurethanes are made by the exothermic reactions between alcohols with two or more reactive hydroxyl (-oh) groups per molecule (diols, triols, polyols) and isocyanates that have more than one reactive isocyanate group (-nco) per molecule (diisocyanates, polyisocyanates). A greener route to polyurethanes without using diisocyanates (since diisocyanates are usually very toxic) might be the nucleophilic addition of polyamines to polycyclic carbonates. Synthesis of diamines and polycarbonates from limonene to produce polyhydroxurethanes has been recently reported.

Poly(limonene carbonate)s

Poly(limonene carbonate) is a thermoplastic polymer, which can be synthesized by copolymerization of limonene oxide (derived from limonene, which is found in orange peel) and co_2. Poly(limonene carbonate) has one double bond per repeating unit that can be exploited for further chemical modifications. These chemical modifications allow the tuning of the properties of the aliphatic polycarbonate in nearly any direction.

Squalene-based nanoassemblies

Squalene is a triterpene widely distributed in nature that is an intermediate in the cholesterol biosynthesis pathway. It has been discovered that the linkage of squalene to many drugs, confers to the resulting bioconjugates the remarkable property to self-assemble as nanoparticles. This unique approach known as "squalenoylation" may be considered as a generic platform to construct nanomedicines which are even more efficient and less toxic than the parent drugs.

Cyanobacteria-derived terpenoids

Cyanobacteria have generated considerable attention as they might be genetically engineered to produce biofuels and commodity chemicals directly from co_2 using solar energy. A promising group of products for cyano-based production are terpenes and terpenoids. These compounds are of interest to chemical industry due to their potential of producing platform chemicals that are now obtained from fossil fuels.

Farnesene

Farnesene is a sesquiterpene ($c_{15}h_{24}$) used as building block chemical for speciality products, including rubber, plastics and cosmetics. The standard method to produce farnesene usually involves thermocatalytic processes or the use of sugar or plant-based feedstocks. However, it was recently reported the production of this terpene from methane thanks to genetically modified microbes that convert the hydrocarbon to compounds with a higher carbon content.

Limonene-based polyamides

Polyamides are polymers which contain repeating amide, -co-nh-, linkages. The properties of the polyamides (nylons), which include high strength, abrasion resistance, and resilience, make them very important in the manufacture of clothing and carpets. Limonene has been reported recently as a precursor of diamines which are suitable monomers for polyamide synthesis.

Biosynthetic taxadiene

Taxadiene is a diterpene and the first dedicated intermediate in taxol (paclitaxel) biosynthesis, a highly effective anticancer drug extensively used in the treatment of various carcinomas, melanomas and sarcomas. Recent developments in metabolic engineering and synthetic biology offer new possibilities for the overproduction of complex natural products, including diterpenes, by optimizing more technically amenable microbial hosts that can perform consolidated bioprocess (from the biomass to the desired secondary metabolite).

Limonene-based propellant

A propellant or propellent is a chemical substance used in the production of energy or pressurized gas that is subsequently used to create movement of a fluid or to generate propulsion of a vehicle, projectile, or other object. Recently, limonene has been proposed as propellant fuel or propellant stabilizer.

Limonene-based antioxidants

Some monoterpenes such as limonene, have shown to possess antioxidant activity. This property is being explored in the production of active packaging. This novel alternative packaging technology is based on the incorporation of antioxidant agents in the package (instead of directly in the food) as a way of improving the stability of oxidation-sensitive food products.

7. URBAN BIOWASTES

NPK fertilizers

Phosphorus (P)- and nitrogen (N)-minerals represent the most prominent nutrients that can be recovered from sludge resulting from the biological treatment of urban wastewater. Magnesium ammonium phosphate (MAP), calcium phosphate and iron phosphate are among the main phosphate compounds, which can be recovered from the sludge; MAP is more commonly referred to as struvite and it is a slow releasing granular P-fertiliser.

Bioethanol

Bioethanol is the ethyl alcohol obtained by fermentation processes by feeding yeasts or bacteria with simple sugars. The second generation bioethanol considers lignocellulosic fractions as the raw material in the perspective of replacing the costly process feedstock with a more sustainable sugar-based source.

Verming compost

Vermicompost is the product of composting process carried out by using earthworms to decompose biowaste. The vermicast is the end-product of the breakdown of organic matter by earthworms. Vermicomposting systems are considered less energy consuming, more cost effective and economically feasible when compared to conventional composting. Associated advantages to the compost agronomic employment are that earthworms are rich in protein (65%) with all essential amino acids and they can be used for animal feed, and when pulverized they can be exploited for theirmedicinal properties (effective result have been observed by treating thrombotic diseases).

Lubricants

lubricants are substances, which reduce the friction between surfaces in mutual contact. In this way, they lower the heat generated when the surfaces move reciprocally. Biolubricants can be prduced by re-refining treatments of waste oils.

Glycerol (as the by-product of biodiesel production)

Glycerol (or glycerine) is a C3 aliphatic poly-ol including 3 hydroxylic groups. It participates in the structure of triglycerides, where it represents the alcoholic part of the three esteric molecule. It is widely used in the food industry as a sweetener and humectant and in pharmaceutical formulations. Crude glycerol represents the main by-product of the biodiesel production. Its impurities limit the possibility of employing crude glycerol as a ram material. It can find applications as a feed ingredient for animal, as a substrate for microbial conversions to valuable chemicals using various bacteria, yeast, fungi, and microalgae, as substrate or co-substrate in anaerobic digestion, for ethanol production, or microbial fuel cells to generate electricity.

Cellulose

Cellulose is a a polysaccharide d-glucose units-based polymer, which is a structural component of the primary cell wall of vegetable cells. Bacterial cellulose (biocellulose) is secreted by some bacteria to form biofilms. Industrial cellulose is mainly obtained from wood pulp and cotton, and it finds applications as the major constituent of paper, paperboard, and card stock. Fibres from toilet paper represent most of the screened material that can be removed by finescreen installations at the beginning of wastewater treatment processes. This incorporated treatment step increases the processing capacity of the treatment and generates a cellulose-rich residual stream. Recovered cellulose fibres can be used as a fibre source, for instance, for the optimisation of the dewatering installation, or as reprocessed clean cellulose for (road) construction or chemical industry applications.

Volatile fatty acids (VFAs) mixture

VFAs are short- or middle-chain aliphatic carboxylate compounds with a number of carbon atoms ranging between 2 (acetic acid) and 7 (e.g., eptanoic acid). VFAs mixtures can be produced by the application of fermentation processes of organic matrices carried out under acidogenic conditions, leading to effluents wherein an overall VFA concentration of 30 g/L can be obtained. VFAs can represent suitable precursors for PHAs production, reduced chemicals and derivatives (among them, VFAs-based ethyl esters described below), and biofuels.

Polyhydroxyalkanoates (PHAs)

Polyhydroxyalkanoates (PHAs) are aliphatic polyesters, which are accumulated by many microorganisms as carbon and energy storage in the lack of a specific nutrient. The main common PHA monomers are the 3-hydroxybutyrate (3-HB) and 3-hydroxyvalerate (3-HV). Due to their properties, PHAs are considered potential replacers of petrol-based polyolefins. However, their employment in the formulation of plastic materials depends strictly on the polymer composition, which influences the PHAs physical-chemical and mechanical features. Thus, PHAs also can be exploited in higher value-added applications (e.g., in the biomedical field, or in coating applications).

Alginates

Alginates are cell-wall constituents of some algae. They are chain-forming heteropolysaccharides made up of blocks of mannuronic acid and guluronic acid. Seaweed derived alginate is currently used extensively in the medical and food industries. Wastewater derived alginates are potentially cheap; they can find applications in the chemical sector, paper and textile industries or as a soil enhancer in the agricultural sector to improve water retention in semi-arid areas. Furthermore, This polymer binds strongly with water, can thicken or gel liquids and can be used as a basis for coatings.

Microalgae hydrolisated

Microalgae hydrolisated are organic fractions, which can be collected from microalgae cultivations by chemical or biological hydrolytic processes. They can be used as N- and P-rich fractions in the development of bio-based fertilizers, which can be exploited for agronomic uses as biofertilizers (algae extracts are commercialised at TRL9 in the food/feed market).

Lactic acid

the Lactic acid (LA), or 2-hydroxy-propanoic acid, is a hydroxylated C3 carboxylic acid. It represents a platform chemical due to the high number of derivatives, which can be obtained by LA transformations. LA is currently being produced for the most part by chemical synthesis and microbial fermentations by lactic acid bacteria. It is widely used in the polymer science related industries (e.g., as a monomer in the production of bio-based polymers) as well as in value added-chemicals production (e.g., acrylic acid).

Succinic acid

the succinic acid (SA) is the linear aliphatic saturated dicarboxylic C4 acid, which can be produced industrially by a biotechnological approach as a metabolic intermediate of the tricarboxylic acid cycle. SA is a water-soluble crystal that is used as a chemical platform for the production of a high number of chemicals and products. For instance, it has interesting applications as an intermediate building blocks towards the production of polyols for the polymer industry. The production of Succinic acid via fermentation of simple sugar is assessed at the fully industrial scale.

Vivianite

The vivianite is a hydrated iron phosphate mineral, which can dominate amog iron compounds in sewage sludge treatent plants with moderate iron dosing. The recovery of vivianite from sludge represents an easy & cheap approach to collect a P source, which is a direct counteraction to mineral P depletion problem. Furthermore, the vivianite can be exploited as a pigment and as an important source in the manufacture of lithium iron phosphate ($LiFePO4$), which has been extensively applied to fabricate the Li-ion secondary batteries.

Single cell proteins

Single cell protein (SCP) refers to edible microorganisms having a high protein content. The fermentation for proteins production is potentially a cheap process since it could be carried out in open bioreactors without the need of high purification downstram approaches. Edible microorganisms with a high protein content can be used in the food/feed industry for Human/animal human consumption.

Biosurfactants

Biosurfactants are surfactants obtained extracellularly or as part of the cell membrane by bacteria, yeasts and fungi. Biosurfactant applications in the environmental industries are promising due to their high biodegradability and low toxicity compared to petroleum-based counterparts: in fact, they have a high compatibility with natural soils and organic matter. Besides; they have longer shelf life as compared to synthetic products. They found application as household detergents, in the personal care, as industrial cleaners, food processing, oilfield chemicals, agricultural chemicals, and textiles. They can be used in environmental cleanup by biodegradation and detoxification of industrial effluents and in bioremediation of contaminated soil

Nanoparticles

magnet-sensitive nanoparticles (NPs) are smart materials with enhanced magnet-sensitive properties, which are suitable for applications in wastewater purification treatments. In fact, magnetite (Fe(II)/Fe(III) mixed valence oxide), maghemite (γ-Fe_2O_3), and hematite (α-Fe_2O_3) have been successfully verified as alternative sources of iron in heterogeneous advanced oxidation processes (AOPs).

VFAs ethyl esters

Ethyl esters of volatile fatty acids are short chain esters, such as ethyl acetate, ethyl propionate, ethyl butirate etc. They can be obtained by the esterification of VFAs with ethanol. Thus, they can be obtained as renewable bio-based chemicals and they can replace the corresponing fossil counterparts in conventional applications such as polar solvents and diluents. Ethyl acetate is present in confectionery, perfumes, and fruits.

Cyanophycin

Cyanophycin is the third known polymer, the others being polyglutamate and polylysine, consisting of a restricted number of amino acids, that is synthesized by the nonribosomal synthetase enzyme. Bacteria accumulate cyanophycin as storage compound for nitrogen, carbon, and energy when growth is limited by another nutrient. It is a N-rich polypeptide deriving from bacterial wastewater treatment. Although cyanophycin is not suitable for material applications, it is a useful source of polyaspartate, which can be used as a super-adsorbent or antiscalant applications. Cyanophycin could also be used as a valuable source of dipeptide and of amino acids in the nutritional and medical fields.

APPENDIX B - DATA SOURCES AND LITERATURE SURVEY

- CORDIS for EU-funded projects https://cordis.europa.eu/projects
- ESPACENET for Patents https://www.epo.org/searching-for-patents/technical/espacenet.html#tab-1
- SCOPUS and PUBMED for scientific literature https://scopus.com
- Material Data Center: http://www.m-base.de/en/products/material-data-center.html.
- JRC reports and publications https://ec.europa.eu/jrc/en/publications-list
- Bio Base Europe Plant: past and ongoing projects
- Biorizon http://www.biorizon.eu
- Study on the review of the list of Critical Raw Materials, Final Report (2017) for European Commission DG for Internal Market, Industry, Entrepreneurship and SMEs**,** Directorate Industrial Transformation and Advanced Value Chains**,** Unit C.2 — Resource Efficiency and Raw Materials
- Green building blocks for bio-based plastics. IEA Bioenergy, Task 42 Biorefineries
- Nova Institut documents and reports, nova papers and all the top downloads; http://nova-institute.eu
- Biorefineries in Europe 2017 http://bio-based.eu/downloads/biorefineries-in-europe-2017/
- Study on current situation and trends of the bio-based industries in Europe - Full version (pdf). Pilot Study for BBI JU, nova-Institute June 2017
- Flanders Bioeconomy policy https://www.vlaanderen.be/nl/publicaties/detail/bioeconomy-in-flanders
- Interreg North-West Europe
- BioBase Europe Pilot Plant BioBase4SME www.bbeu.org/pilotplant/biobase4sme/
- Tecnon Orbichem: Biomaterials Handbook http://www.orbichem.com/Biomaterials_Handbook.aspx
- Green Chemicals Blog https://greenchemicalsblog.com
- Blog of the commercial Biorefineries in Europe: https://biorrefineria.blogspot.de/p/listado-de-biorrefiern.html?m=1.
- Market study and Trend Reports on "Bio-based Building Blocks and Polymers in the World – Capacities, Production and Applications: Status Quo and Trends Towards 2020" - 3rd edition
- "Industrial material use of biomass, Basic data for Germany, Europe and the world" - Full version
- Bio-based Building Blocks and Polymers – Global Capacities and Trends 2016 – 2021 Nova Institute.
- Can bio-based chemicals meet demand? Global and regional case-study around citrus waste-derived limonene as a solvent for cleaning applications seeds and flowers. Also contains LCA data comparing toluene with limonene. Wiley online library. https://onlinelibrary.wiley.com/doi/abs/10.1002/bbb.1677
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MARKET REPORTS (SAMPLE VERSION):

- Plant fibre Composites Market - Global Forecasts To 2021. Markets and Markets report code CH2984. Free sample version.
- 2017-2022 Global Top Countries Terpenes Market Report. Decision Databases. Free sample version.
- Global Bio Based Lubricants Market Segmented by Product Type and End-user Industry - Analysis of Growth, Trends, and Forecast. Mordor Intelligence. Free sample version.
- Lignin Market Size By Product (Kraft Lignin, Organosolv, Ligno-sulphonates, High Purity) By Application (Aromatics, Macromolecules), Industry Analysis Report, Regional Outlook, Lignin Downstream Potential (Vanillin, Carbon Fibre, Phenol, BTX), Price Trend, Competitive Market Share & Forecast, 2015 – 2022 . Global Market Insights. Free sample version.
- Plant fibre composites Market. Global Industry Analysis 2012-2016 forecast to 2025. Persistence Market Research. Free sample version.
- Polyelectrolyte Market: Global Historical Growth (2012-2016) & Future Outlook (2017-2024) Demand Analysis & Opportunity Evaluation. Researchnester. Free sample version.
- Lignin Market (Lignosulfonates, Kraft Lignin and Others) for Concrete Additive, Animal Feed, Dye Stuff, and Other Applications: Global Industry Perspective, Comprehensive Analysis and Forecast 2014 - 2020. Marketresearchstore. Free sample version.
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- Global Bio-based Lubricants Market, Mordor Intelligence, sample copy.
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The study mapped the most relevant value chains currently under development that originate from: natural rubber, plant fibres, lignin, renewable oils and fats, terpenes, natural polyelectrolytes, in addition to urban wastes. More than 100 innovative BBPs were monitored; lignin was found to be generating the highest number of innovative products, together with terpenes and urban wastes. More than 30 innovative BBPs are approaching full availability on the market, and more than 20 products are now at the pilot plant level. The 20 most innovative BBPs holding the greatest promise for commercial deployment within the next 5-10 years were identified; selection includes engineering materials, new bioplastics, high added-value products for demanding applications in the pharmaceutical and biomedical fields, as well as sustainable substitutes for critical raw materials. Detailed case studies on these TOP20 innovative BBPs were developed.

Studies and reports

Publications Office