Technology Collaboration Programme
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Bio-Based Chemicals

A 2020 Update

This report was issued on behalf of IEA Bioenergy Task 42 biorefining in a Circular Economy. It addresses the main biobased chemicals that could potentially be co-produced with secondary energy carriers in integrated biorefinery facilities. It is an update of the 2011 report

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Bio-Based Chemicals

A 2020 Update

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Ed de Jong, Avantium (The Netherlands)

Heinz Stichnothe, Thuenen Institute of Agricultural Technology (Germany)

Geoff Bell, Microbiogen (Australia)

Henning Jørgensen, University of Copenhagen (Denmark)

With input from:

Isabelle de Bari, ENEA (Italy)

Jacco van Haveren, Wageningen Food & Biobased Research WFBR (The Netherlands)

Johannes Lindorfer, Energieinstitut an der Johannes Kepler Universität (Austria)

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Executive summary

Since the first issue of the IEA Bioenergy Task 42 report on bio-based chemicals in 2011, the importance of a circular economy has become evident. In the transition to a circular economy, chemicals and materials produced from biomass will play a key role. Given the tremendous focus on climate and actions to mitigate climate change, steps are being taken to move from today's fossil-based economy to a more sustainable economy based on renewable energy, biomass and recycling. The transition to a bio-based circular economy has multiple drivers as well as requirements;

- The need to develop an environmentally, economically and socially sustainable circular global economy
- The desire of many countries to reduce an over dependency on fossil fuel imports by diversifying their energy sources
- The global issue of climate change and the need to reduce atmospheric greenhouse gases (GHG) emissions
- That processes and products are "Safe by Design"
- That chemicals and materials are designed for cost-, material- and energy-efficient recycling
- The "End of Life" solution of the products is equal to or preferably better than the incumbent products
- And deployment of biorefineries in rural areas will stimulate regional and rural development

One of the key institutions to drive this transition to a more sustainable bio-based economy is the IEA Bioenergy implementation agreement. Within IEA Bioenergy, Task 42 specifically focuses on Biorefining in a Circular Economy; e.g. the co-production of fuels, chemicals, (combined heat &) power and materials from biomass. A key factor in the deployment of a successful bio-based economy will be the development of biorefinery systems allowing highly efficient and cost effective processing of biological feedstocks into a range of bio-based products, and successful integration into existing infrastructure. This report shows that the global bio-based chemical and polymer production is estimated to be around 90 million tonnes. However, the relatively low price of fossil feedstocks as well as its volatility together with optimized fossil-based production processes has hampered the acceleration of the commercial production of bio-based products as projected in the previous bio-based chemicals report from 2011. In addition to increased recycling, enlarged chemical and polymer production from renewable resources is an essential part of the transition to a circular economy. As is evident from this report, not many major chemical players are actively pursuing this approach and that deployment over the last several years has been much slower than expected.

Nevertheless, within the bio-based economy as a whole and within the operation of a specific biorefinery there are significant opportunities for the development of bio-based building blocks (chemicals and polymers) and materials (fibre products, starch derivatives, etc.). In many cases this happens in conjunction with the production of bioenergy or biofuels. It is estimated that the production of bio-based products, in addition to biofuels, could generate US$ 10 billion of revenue for the global chemical industry. However, current market conditions, uncertainty about trade agreements, future carbon pricing as well as a non-holistic and polarised bioeconomy debate have hampered the deployment as well as the role-out of biobased initiatives.

Within IEA Bioenergy Task 42 "Biorefining in a Circular Economy", a biorefinery classification method for biorefinery systems has been developed. This classification approach relies on four main features, which are able to classify and describe a biorefinery system:

1) Platforms (e.g. core intermediates such as C5 -C6 carbohydrates, syngas, lignin, pyrolytic liquid)
2) Products (e.g. energy carriers, chemicals and material products)
3) Feedstock (i.e. biomass, from dedicated production or residues from forestry, agriculture, aquaculture and other industry and domestic sources but also CO_2)
4) Processes (e.g. thermochemical, chemical, biochemical and mechanical processes)

The platforms are the most important feature in this classification approach: they are key intermediates between raw materials and final products and can be used to link different biorefinery concepts with target markets. The platforms range from single carbon molecules such as biogas and syngas to a mixed 5 and 6 carbon carbohydrates stream derived from hemicellulose, 6 carbon carbohydrates derived from starch, sucrose (sugar) or cellulose, lignin, oils (plant-based or algal), organic solutions from grasses and pyrolytic liquids. These primary platforms can be converted to a wide range of marketable products using mixtures of thermal, biological and chemical processes. In this report, a direct link is made between the different platforms and the resulting biobased chemicals.

The economic production of biofuels and bioenergy is often still a challenge. The co-production of chemicals, materials, food and feed can in principle generate the necessary added value to solve the economic challenges. An example is the co-production of distiller's dried grains with solubles (DDGS) and corn oil in a corn ethanol dry-milling plant. This report highlights all bio-based chemicals with immediate potential as biorefinery 'value added products'. For commercial products, market sizes are given where available. The selected products are either demonstrating potential market growth or have significant industry investment in development and demonstration programmes. This report shows that by far the biggest biochemical produced today is bioethanol with more than 80% share of total combined production capacity. The report introduces companies actively developing bio-based chemicals and provides information on potential greenhouse gas emission savings and how the co-production of bio-based chemicals with biofuel can influence the economics of biofuel production.

The IEA is publishing its World Energy Outlook yearly. In this outlook three different scenario's are discussed in relation to energy usage and global warming: the Current Policy scenario; the Stated Policy scenario and the Sustainable Development Scenario. Since the first publication of the Biochemical Report in 2011, the anticipated growth in biochemicals production capacity (excluding bioethanol) has not materialised yet. The main reasons for this lack of growth include the significantly lower oil prices compared to a decade ago, the different economies of scale of fossil-based plant capacities versus biobased plant capacities, high feedstock costs as well as the lack of policies, which would facilitate the transition to a biobased economy. It can therefore be concluded that the Current Policies as well as the Stated Policies for the chemical industry are not sufficient to reach the goals as defined in the Sustainable Development Scenario in a circular bioeconomy. This report identifies actions in the areas of policy (e.g. High CO_2 price > 100 $/t; fossil subsidies are gone; net CO_2 sequestration incentivised; circular economy is mandatory; sustainable forestry and agriculture is mandatory), technology (e.g. High progress in: up- and downstream processes for bio-based feedstock; ethanol-to-chemicals; Green H_2-production; widespread algae/ seaweed utilisation), feedstock availability (e.g. No restrictions on 1st, 2nd and 3rd generation, all are available) and social acceptance (e.g. High acceptance of climate treat and for climate policy resulting in: agreement on biomass sustainability and biodiversity; willingness to change behaviour; willingness to pay for climate-friendly products; open attitude to locations of facilities, less meat demand (resulting in high feedstock availability), which are in our opinion necessary to align with the Sustainable Development Scenario.

1. Introduction

The production of bio-based chemicals is not new, nor is it an historic artefact (1). Current global bio-based chemical and polymer production is estimated to be around 90 million tonnes (1). Notable examples of bio-based chemicals include fermentation products such as ethanol, lysine and citric acid, and sorbitol, glycerol as well as fatty acids.

However, the majority of organic chemicals and polymers are still derived from fossil based feedstocks, predominantly oil and gas. Non-energy applications account for around 9% of all fossil fuel (oil, gas, coal) use and 16% of oil products (2). Global petrochemical production of chemicals and polymers is estimated at around 330 million tonnes. Primary output is dominated by a small number of key building blocks, namely methanol, ethylene, propylene, butadiene, benzene, toluene and xylene. These building blocks are mainly converted to polymers and plastics but they are also converted to a staggering number of different fine and specialty chemicals with specific functions and attributes. From a technical point of view almost all industrial materials made from fossil resources could be substituted by their bio-based[1] counterparts (3, 4). However, currently the cost of bio-based production in many cases exceeds the cost of petrochemical production. For chemicals with novel functionality, e.g. lactic acid, succinic acid, furandicarboxylic acid, must be proven to perform at least as well as the petrochemical equivalent they are substituting and to have a lower environmental impact.

Historically biobased chemical producers have targeted high value fine or speciality chemicals markets, often where specific functionality played an important role. The low price of crude oil acted as a barrier to bio-based commodity chemical production and producers focussed on the specific attributes of bio-based chemicals such as their complex structure to justify production costs.

The climb in oil prices in the first decade of this century, the consumer demand for environmentally friendly products, population growth and limited supplies of non-renewable resources have opened new windows of opportunity for bio-based chemicals and polymers. However, the general volatility in the oil prices as well as the recent decline in oil prices in recent years have hampered business cases as well as investments in novel technologies.

To become truly sustainable and circular, industry is increasingly viewing (chemical) recycling as well as chemical and polymer production from renewable resources as the future *modus operandi* and an attractive area for investment. However, the price of oil and consumer demand is not the only driver in these areas. Emerging economies such as the BRIC countries require increasing amounts of oil and other fossil based products, and are creating a more competitive marketplace. Also, security of supply is an important driver in biobased products as well as bio-energy.

[1] Bio-based products – chemicals and materials (pre-norm CEN/BT/WG 209: "biobased product = product wholly or partly bio-based (="derived from biomass")") include all kind of bio-based chemicals, bio-based plastics and additives – biodegradable and durable, bio-composites like wood plastics composites and natural fibres reinforced plastics and insulation material, and also the traditional products of the timber industry. Bio-based products are used in construction & insulation, packaging, automotive and consumer goods (3).

Figure 1. WTI (West Texas Intermediate) crude oil daily closing prices over the last 10 years (5).

2. Biorefineries and the bio-based economy

Around the world small but distinct steps are being taken to move from today's fossil based economy to a more sustainable economy based on greater use of renewable resources. The transition to a bio-based economy has multiple drivers: the global issue of climate change and the desire to reduce the emission of greenhouse gases, an over dependency of many countries on fossil fuel imports, the anticipation that oil, gas, and maybe coal production will reach peak production in the not too distant future; the need for countries to diversify their energy sources, and the need to stimulate regional and rural development (6-10).

Biofuels and Bio-based products (chemicals, materials) can be produced in single product processes; however, the production in integrated biorefinery processes producing both bio-based products and secondary energy carriers (fuels, power, heat), in analogy with oil refineries, is probably a more efficient approach for the sustainable valorisation of biomass resources in a future biobased economy (11-13). Biorefining can also be integrated with food or feed production, as is the case with first generation ethanol production.

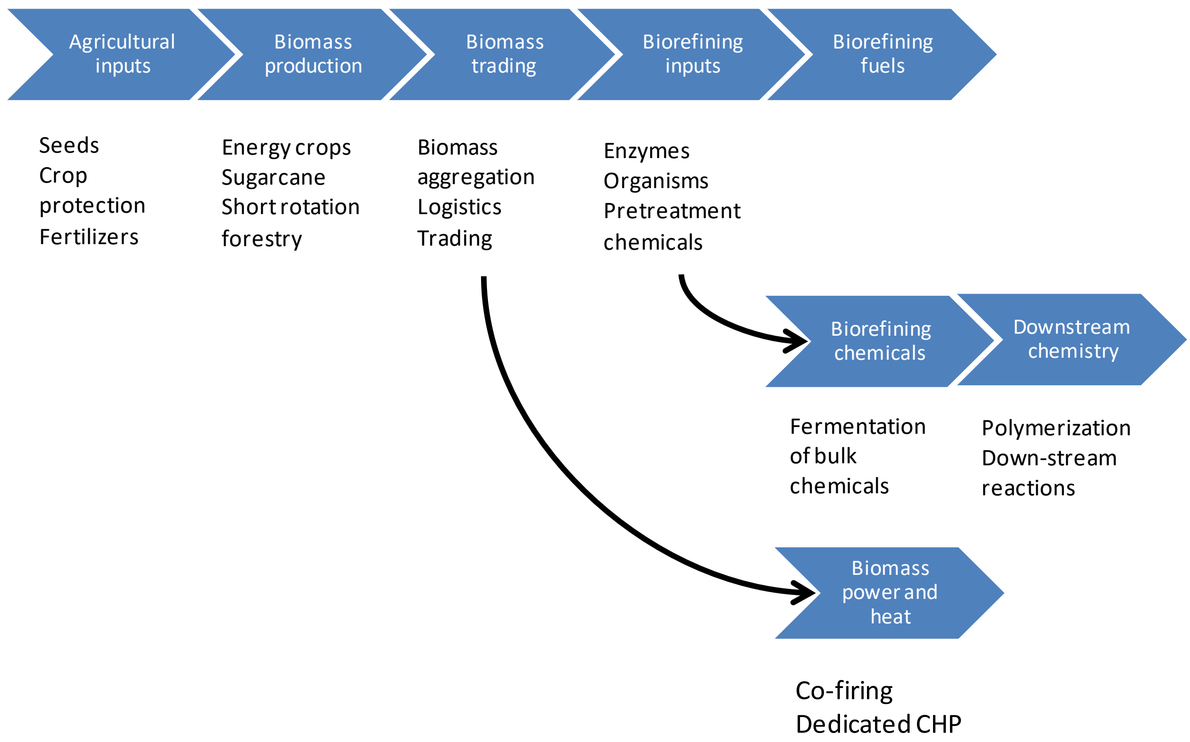


Figure 2. An example of a Bio-based products value chain (12, 13).

However, the main driver for the development and implementation of new biorefinery processes today is the transportation sector. Significant amounts of renewable fuels are necessary in the short and midterm to meet policy regulations both in- and outside Europe. Biofuels, especially from a so-called 2nd generation origin, have to fill in a large fraction of this demand, specifically for heavy duty road transport and in the aviation sector where biofuels are the only reasonable alternative at the moment. Both conventional (ethanol, biodiesel) and advanced biofuels (lignocellulosic methanol, lignocellulosic ethanol, butanol, Fischer-Tropsch-diesel/kerosine, ...) generally cannot be produced in a profitable way at current crude oil prices. This implies that they only can enter the market if they are forced to (e.g. governmental regulation) or if significant financial support is provided (e.g. tax reduction). However, this artificial market will probably not be long lasting. A significant reduction in biofuel production costs as well as a far-ranging carbon tax which is widely applied are required to create a sustainable market.

A promising approach to reduce biofuel production costs is to use so called biofuel-driven biorefineries for the co-production of both value-added products (chemicals, materials, food and feed) and biofuels from biomass resources in a very efficient integrated approach. The added-value of the co-products makes it possible to produce fuels at costs that are market competitive at a given biomass resource price. Wageningen UR (Nl) performed a study in 2010 in which 12 full biofuel value chains – both single product processes and biorefinery processes co-producing value-added products – were technically, economically and ecologically assessed (14). The main overall conclusion was that the production costs of the biofuels could be reduced by about 30% using the biorefinery approach. Figure 2 is a general illustration of an agriculture feedstock based biorefinery that is built around biochemical conversion technologies (12, 13). There are also other models based on forest, marine and solid waste feedstocks, and models built around (thermo-)chemical conversion technologies, such as chemical conversion, gasification and pyrolysis. It should be noted that there are also other models based on forest, marine and solid waste feedstocks, and models built around (thermo-)chemical conversion technologies, such as chemical conversion, gasification and pyrolysis.

Box 1. IEA Bioenergy Task 42 Biorefinery Definition

"Biorefinery is the sustainable processing of biomass into a spectrum of marketable products (food, feed, materials, chemicals) and energy (fuels, power, heat)"

The IEA Bioenergy Task 42 definition of a biorefinery allows it to be viewed as concept, a facility, a process, a plant or even a cluster of facilities. A biorefinery is not a new concept; many traditional users of biomass, sugar, starch and pulp industries run biorefineries today. However, it is the rapid expansion in biofuel production and the need to derive value from all of the co-products which is driving the development of modern biorefineries at the moment. To be a viable proposition, the production of bio-based energy, materials and chemicals alongside biofuel should improve the overall economics of biorefinery operations and, in some cases, may even be the primary revenue stream. One of the main drivers for the establishment of biorefineries is the call for sustainability. Biorefinery development can be designed for environmental, social and economic sustainability impacting the full product value chain. New industrial development also requires a social contract from the communities and countries in which they plan to operate. This can include issues of direct and indirect employment, new skills development, health, noise and nuisance factors, ownership and consultative decision-making. Finally, the biorefinery needs to dovetail with the existing infrastructure. Both the biorefinery and petrochemical industry need to play key parts of future bio-petro hybrid value chains. This is an ongoing development, which is just partly realised, but not deployed in full (15). In the establishment of biomass feedstock supply consideration should be given to possible unintended consequences such as the competition for food and biomass resource, the impact on water use and quality, changes in land-use, soil carbon stocks and long term fertility, net balance of greenhouse gases and impacts on biodiversity. Also, the amount and type of energy used to operate the biorefinery and transport its inputs and outputs needs to be evaluated. The range and balance of products produced in a biorefinery needs to be market competitive and will be critical to its economic sustainability.

Within the bio-based economy and the operation of a biorefinery there are significant opportunities for the development of bio-based chemicals and polymers. At the global scale, the production of bio-based chemicals could generate over US$ 10 billion of revenue for the global chemical industry (12). Examples of some of these opportunities are described as follows.

A key factor in the realization of a successful bio-based economy will be the development of biorefinery systems that are well integrated into the existing infrastructure. Through biorefinery development, highly efficient and cost-effective processing of biological raw materials to a range of bio-based products can be achieved.

3. Biorefinery platforms for chemicals production

Major feedstocks for biorefineries include starch crops (e.g. wheat and maize), sugar crops (e.g. beet and cane), perennial grasses and legumes (e.g. ryegrass and alfalfa), lignocellulosic crops (e.g. managed forest, short rotation coppice, switchgrass), lignocellulosic residues (e.g. forest residues, stover and straw), oil crops (e.g. palm and oilseed rape), aquatic biomass (e.g. algae and seaweeds), and organic residues (e.g. industrial, commercial and postconsumer waste). An overview how various biomasses can be converted into intermediates and value-added products is provided in Figure 3.

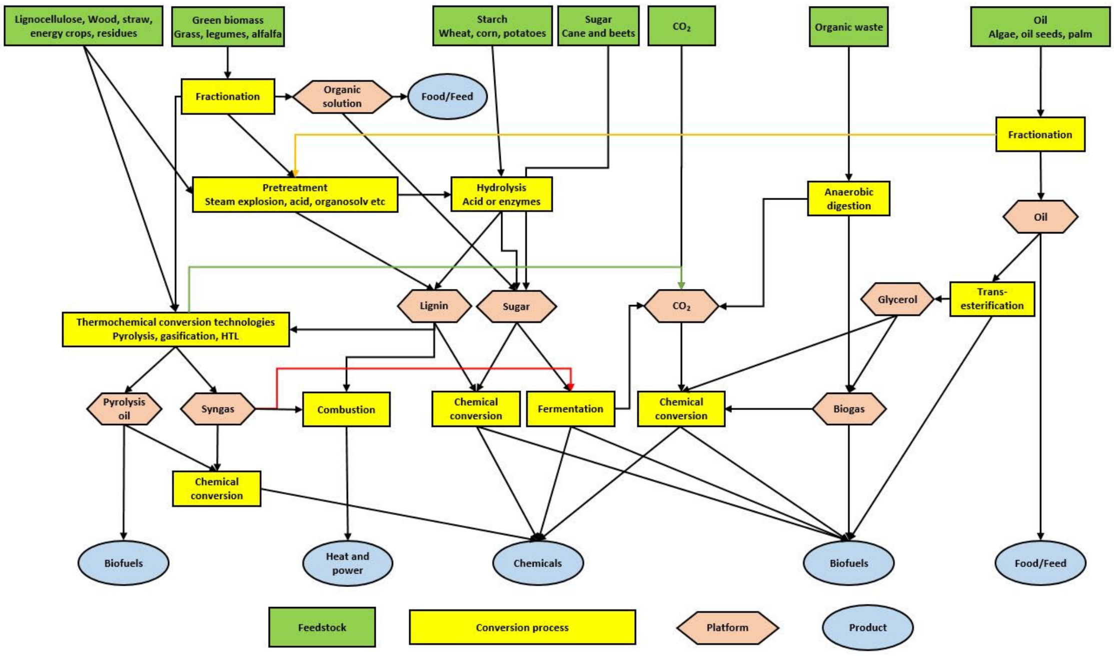


Figure 3. Conversion technologies for biomass based on IEA Bioenergy Task 42 biorefinery classification system (16)

Within the biorefinery, the feedstocks are typically fractionated/processed into a number of key **intermediates.** These intermediates serve as the **platform** for further specific processing and conversion into the final marketable products, e.g. fuels and chemicals, those giving rise to the term platforms, such as syngas platform, sugar platform or oil platform. The intermediates in a platform is not necessarily a single well-defined compound, but often a mixture of compounds of varying purity. Several feedstocks can lead to the same platform, and often a biorefinery will include several platforms. The biorefineries can accordingly be systematically classified on the basis of their key characteristics – feedstock(s) utilized, platform(s) involved, product(s) produced and processes used (16). An overview of possible feedstocks, platforms and products is given in Figure 3. Examples of how operating biorefineries can be classified can be viewed on the IEA Bioenergy Task 42 website (http://task42.ieabioenergy.com/). The following will provide an overview of the most relevant platforms in relation to chemicals production in biorefineries.

3.1 Pyrolysis Oil Platform

Pyrolysis is a thermal process of heating biomass in the absence or with limited supply of oxygen at an elevated temperature (<700 °C) thereby resulting in depolymerization of biomass and generation of pyrolysis oil (major product), char and some gas. The spectrum of products from biomass pyrolysis depends on the process temperature, pressure and residence time (17). The crude oil can be utilized directly for energy generation, but within the biorefinery it is possible to be upgraded or converted into higher value compounds via different catalytic reactions such as cracking, steam reforming, hydrocracking and hydrodeoxygenation. Numerous products can be produced including benzene, toluene, various carboxylic acids and furans (17).

The major advantage of a pyrolysis biorefinery is the possibility of smaller scale decentralized production of the pyrolysis oil in regions where abundant biomass is readily available. The pyrolysis oil is then collected at centralized biorefineries for upgrading and conversion into high value products. Transporting pyrolysis oil rather than bulky biomass provides a cost-effective transportation (18).

3.2 Biomass Balance Approach

In the biomass balance approach, renewable resources such as bio-naphtha/pyrolysis oil or biogas derived from organic waste or vegetable oils are used as feedstock in the very first steps of chemical production. The bio-based feedstock amount is then allocated to specific products sold by means of the certified method. BASF has developed this innovative "biomass balance method" together with TÜV SÜD (19). In the current Production Verbund fossil resources are replaced by renewable resources with sustainability certification. The formulation and quality of the corresponding end products remain unchanged. All of BASF's biomass balanced products are certified according to the new REDcert² scheme for the chemical industry. This independent certification will confirm that a company has replaced the required quantities of fossil resources for the biomass balanced product purchased with renewable feedstock. This approach is already applied for many BASF products, such as super-absorbents, dispersions, plastics and intermediates. The resulting biomass balanced products offer BASF customers a differentiation opportunity such as a quantifiably improved CO_2 footprint and savings of fossil resources. Customers can rely on the identical product quality and performance to which they are accustomed to and benefit from a sustainable drop-in solution, making a conscious contribution to environmental protection. BASF markets its biomass balanced products as BMBcert™ portfolio (19). Recently also the Ellen MacArthur Foundation's CE100 Network published a report (20) that a new approach is needed to fully unlock the circular economy potential of the chemical sector. This report explores how a mass balance method offers a workable set of rules to ensure the traceability of recycled feedstock into new products. It is stated that a mass balance approach to enable the sale of certified recycled products at virgin-grade quality could be very valuable to all users of materials and chemicals in the value chain. It seems desirable that in the future an integration of both biobased content as well as recycled content will be achieved in the mass balance method.

3.3 CO_2-Platform

According to the latest IPCC report net CO_2-sequestration is required to comply with the goal to keep the global average temperature increase below 1.5°C (21). Biobased chemicals and materials used in long-term applications offer that possibility, particularly when biogenic CO_2 from fermentation processes is used (Figure 3). However, that requires enhanced cross-sectorial collaboration and exploration of industrial symbiosis opportunities but can also create synergies and improve energy and resource efficiency beyond sectorial boundaries. The conversion of CO_2 into intermediates is already addressed in various research projects, e.g. Carbon4PUR (22).

Methanol is one of the largest volume chemicals in the world and serves as source for various other compounds, e.g. formaldehyde or acetic acid. Currently, methanol is produced quasi exclusively from synthesis gas. The alternative low-carbon pathway to methanol is based on hydrogen, produced by water electrolysis with low-carbon electricity followed by hydrogenation of CO_2 as carbon source (23).

In 2011, Carbon Recycling International (CRI) started operation of the "George Olah Renewable Methanol Plant" and hereby demonstrated the potential of tapping into Iceland's geothermal energy. The 7.1 € million plant (for a capacity of 1,300 metric tons) was designed to currently produce 4,000 tons of renewable methanol per year (5 million liters). This plant serves as a pilot study for the planned extension to a 40,000 tons plant. The feed consists of CO_2 from geothermal power plant and hydrogen produced by 5 MW water electrolysis fed by a geothermal power plant. All units are operated continuously. The methanol product is mixed into gasoline and substitutes up to 2.5% of Iceland's fuel consumption. Further uses are as feed in biodiesel production or in other methanol-based processes. In comparison to fossil-fuel based methanol, renewable methanol reduces GHG emissions by 90%. Plans for a second plant in China have been announced (24, 25).

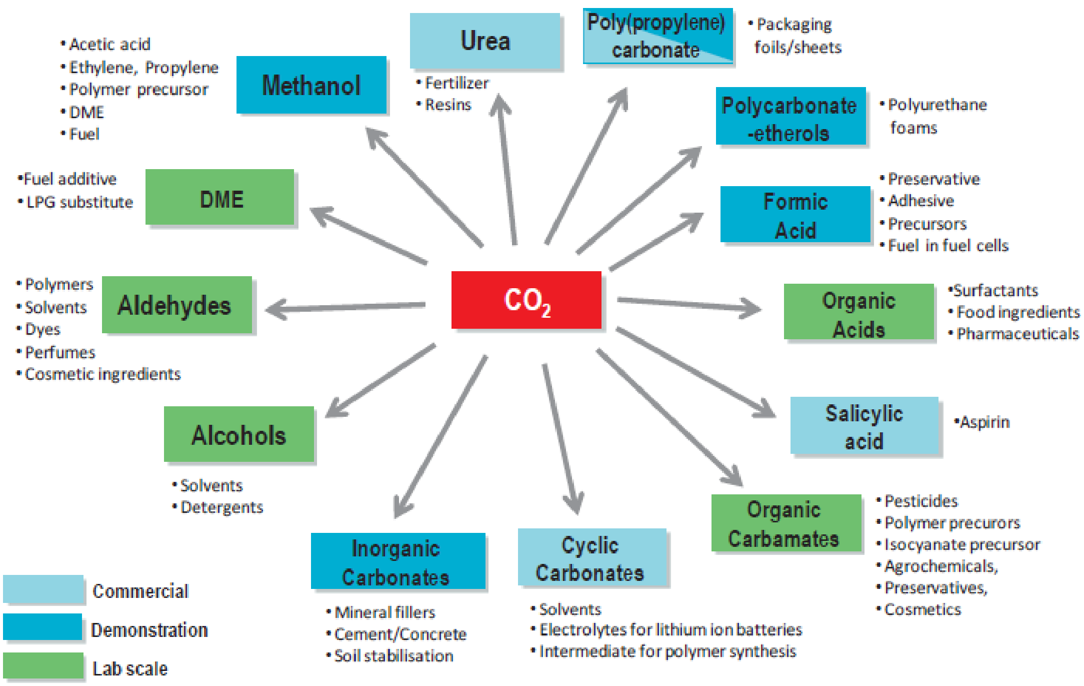


Figure 4. Commercial, demonstration and lab scale utilization routes of CO_2 and their status of deployment.

Methanol is suitable as platform for various bulk chemicals via catalytic conversion, e.g. methanol-to-olefins, methanol-to-propylene, methanol-to-gasoline but also conversions into aromatics (26). However, an absolute precondition is the availability of cost-competitive and low-carbon electricity.

There are also other options to utilize CO_2 with reactants other than hydrogen. The following figure shows various products from CO_2 produced at different scales.

3.4 Syngas Platform

Synthesis gas (syngas) is a gas mixture of carbon monoxide (CO), hydrogen (H_2), methane (CH_4) and carbon dioxide (CO_2) and nitrogen (N_2). It is produced by subjecting biomass to extreme heat, typically in the range 800-1500°C, in the presence of oxygen or air in a process known as gasification. The gasification technology has historically been developed with the main focus on energy generation and many operating gasifiers are used for power generation (27). However, after cleaning, the syngas can be converted by thermochemical catalysis to alcohols (methanol, ethanol), fuels such as Fischer-Tropsch diesel and chemical products (28). The Fisher-Tropsh process for making hydrocarbons has a long history and is operated in large industrial scale. Currently there is also a great interest to use syngas as substrate for microbial fermentation to give alcohols such as ethanol or butanol, and potentially other chemical building blocks, e.g. acetic acid (29).

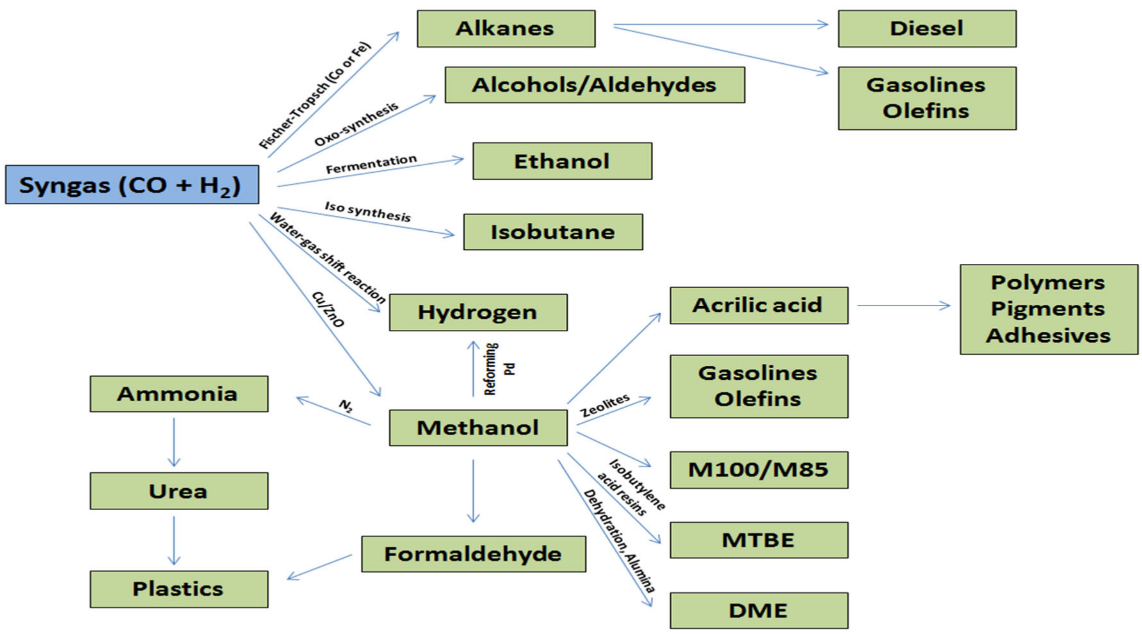


Figure 5. Overview of Syngas derived chemicals (30).

3.5 Sugar platform

The sugar platform is one of the key platforms and considered by volume currently the largest platform for production of chemicals based on biomass. Sugar is the basis for a large number of traditional biorefinery processes and well-established industries. The traditional processes are based on utilizing sucrose (composed of glucose and fructose) derived from sugar crops, e.g. sugar beet or sugar cane, or glucose obtained after hydrolysis of starch from e.g. corn or grain (Figure 3). In advanced biorefineries utilizing lignocellulosic biomass as feedstock, the biomass will typically undergo first pre-treatment followed by enzymatic hydrolysis in order to release the sugars. Glucose will be produced from the cellulose whereas hydrolysis of the hemicellulose will result in a mixture of e.g. xylose, arabinose, mannose and galactose. The composition of the hemicellulose fraction is very feedstock dependent. In a lignocellulosic biorefinery, the sugar platform will often consist of a mix of glucose along with the hemicellulose derived sugars (31).

Glucose serves as the primary substrate for many biological fermentation processes providing access to a variety of important chemical building blocks (alcohols, organic acids, lipids and hydrocarbons) but also very high value fine chemicals and products (amino acids, vitamins, antibiotics, enzymes etc). The mixed sugar platform in a lignocellulosic biorefinery can in theory produce the same products as glucose. However, a number of technical, biological and economic barriers need to be overcome before these opportunities can be exploited. The sugars can also be converted by catalytic processes to useful chemical building blocks such as HMF, furandicarboxylic and levulinic acid (32, 33).

3.6 Fermentation products from sugars

Fermentation has been used extensively by the chemical industry to produce a number of products, with chemical production through fermentation starting around the turn of the 20th century. The number of chemical building blocks accessible through fermentation is considerable, and steadily growing due to constant developments within the biotechnology area, e.g. using genetic engineering of the microorganisms.

Box 2. Innovative fermentation products

Itaconic acid

Adipic acid

3-Hydroxypropionic acid / aldehyde

Isoprene/farnesene

Glutamic acid

Aspartic acid

1,4 BDO (1,4-butanediol)

In 2013, the market size for production of fermentation products was above 110 million tonnes and with a value of 207 billion USD. Alcohols made up the largest share (94% of volume and 87% of value) of which the largest share was ethanol used as transportation fuel. Production of fine chemicals was around 11 million tonnes. The projected market growth for fermentation products until 2020 is 4.6% annually and 6.5% if excluding alcohols as shown in Table 1 (34).

Table 1. Market overview for key fermentation products in 2013 and forecast until 2020 (adapted from 34).

Market overview for key fermentation products in 2013 and annual growth until 2020			
Category	Market size in product output	Market size in value	Market growth until 2020
	Mln tonnes	Bn USD	% CAGR
Alcohols	99.8	110.0	4.4
Amino acids	7.1	11.0	5.6
Organic acids	2.9	3.5	8.8
Polymers	0.2	0.6	13.5
Vitamins	0.2	0.7	2.6
Antibiotics	0.2	0.8	4.0
Industrial enzymes	0.1	0.3	8.0
Total	**110.5**	**126.9**	**4.6**

Modern biotechnology is allowing industry to target new and previously abandoned fermentation products and improve the economics of products with commercial potential. Coupled with increasing fossil feedstock costs, cost reductions in the production of traditional fermentation products such as ethanol and lactic acid will allow derivative products to capture new or increased market shares. Improving cost structures will also allow previously abandoned products such as butanol to re-enter the market. Many see the future abundant availability of carbohydrates derived from lignocellulosic biomass as the main driver. However, sugar prices from lignocellulosic sources have to become cost competitive with 1st generation glucose from starch and sucrose. Fermentation also gives the industry access to new chemical building blocks previously inaccessible due to cost constraints. The development of cost-effective fermentation processes to succinic, itaconic and glutamic acids promises the potential for novel chemical development.

3.7 Chemical transformation products from sugars

Sugars can also be a key intermediate in chemically catalyzed processes. The sugars can undergo selective dehydration, hydrogenation and oxidation reactions to give useful products, such as sorbitol, furfural, glucaric acid, hydroxymethylfurfural (32) and levulinic acid (33). Examples of current industrial processes are production of sugar alcohols such as sorbitol and xylitol. The projected demand for sorbitol in 2018 was over 2 million tonnes (35). Besides direct uses of sorbitol as food ingredients it is an important intermediate in the production of isosorbide, which is among others used as a monomer for the manufacture of bio-based plastics.

An example of a chemical processes converting cellulose or hemicellulose in biomass via sugars as intermediate into chemicals is the production of furfural. The combination of high temperature and use of mineral acids as catalyst results in first hemicellulose hydrolysis followed by dehydration of xylose to yield furfural. This process is operated in industrial scale with annual production volumes exceeding 360,000 tonnes (36). There is also a growing interest in developing new catalytic processes for conversion of sugars to new chemical building blocks such as mono-ethylene glycol and methyl vinyl glycolate that serves as precursors for plastic production (37, 38).

Box 3. Promising sugar chemical derivatives

Levulinic acid

2,5-Furan dicarboxylic acid

Mono-ethylene glycol

Methyl vinyl glycolate

3.8 Lignin Platform

Currently most lignin on the market is a by-product from the pulp and paper industry in the form of lignosulfonates and Kraft lignin. It is estimated that in the order of 50-70 million tonnes of lignin is produced annually, but more than 95% is used internally at pulp mills for energy generation (39). New technologies to recover lignin from the Kraft mills (e.g. Lignoboost technology) have been installed thereby increasing the availability of Kraft lignin for other applications, e.g. chemicals, resins and polymers production (40). In addition, lignin is also produced concurrently with sugars during the biochemical conversion of lignocellulosic biomasses and therefore closely linked to the sugar platform. It is foreseen that large amounts of lignin will be available when industrial scale production of bioethanol for transportation from lignocellulosics is realized (41). The global lignin market size was estimated at USD 733 million in 2015 of which lignosulfonates was by far the biggest segment.

Lignin is an abundant platform molecule and offers a significant opportunity for enhancing the operation of a lignocellulosic biorefinery. It is an extremely abundant raw material contributing as much as 30% of the weight and 40% of the energy content of lignocellulosic biomass (42).

Lignin's native structure suggests that it could play a central role as a new chemical feedstock, particularly in the formation of supramolecular materials and aromatic chemicals (41-43). Almost all lignins on the market contain substantial amounts of sulfur (lignosulfonates and Kraft lignin). Up to now the vast majority of industrial applications have been developed for lignosulfonates and with Borregaard/Borregaard LignoTech as a leading company (44, 45). These sulfonates are isolated from acid sulfite pulping and are used in a wide range applications. Major applications for lignosulfonates are as dispersant, concrete admixtures, binder and adhesive. Major end-use markets include construction, mining, animal feeds and agriculture uses. The use of lignin for chemical production has so far been limited due to contamination from salts, carbohydrates, particulates, volatiles and the wide variability of molecular weight distribution of lignosulfonates (1,000-50,000 g/mo). One of the only industrial exception is the limited production of vanillin from lignosulfonates (45).

Sulfur-free lignin derived from lignocellulosic biorefineries along with the sugar platform for production of e.g. bioethanol or chemicals could result in new forms of lignin becoming available for chemical applications. This could either be in the form of lower quality hydrolysis lignin (the residue after enzymatic hydrolysis of cellulose and hemicellulose) or high purity lignin isolated as part of the pre-treatment. Examples of the later is organosolv lignin. This process was first commercialized by the Canadian company Repap and later further developed by the other Canadian company Lignol and now part of the Brazilian company Suzano (44).

The production of more value-added chemicals from lignin (e.g. resins, composites and polymers, aromatic compounds, carbon fibres) is viewed as a medium to long term opportunity, which depends on the quality and functionality of the lignin that can be obtained. There are currently many research programs working on developing processes for catalytic depolymerization and conversion of lignin. Examples of interesting compounds are the conversion of the lignin-derived phenolics to substituted cyclohexanol and cyclohexanone, which is precursor for novel polymer-building blocks like alkylated caprolactone, caprolactam, or adipic acid. alkylated cyclohexanols (46).

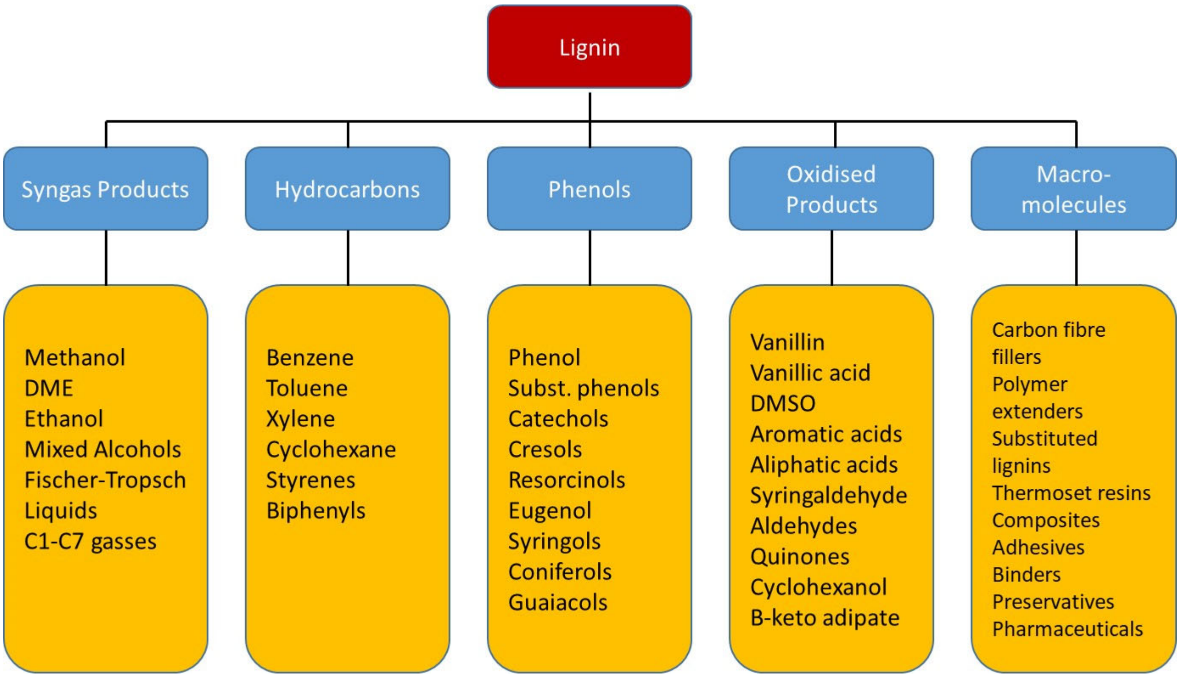


Figure 6. Potential products from lignin (adapted from 46).

Finally, lignin can be used to produce drop-in stocks for jet-fuel (such as the aromatics and cycloalkane hydrocarbons). The WSU lab recently demonstrated the successful conversion of biomass-derived lignin into C7–C18 jet-fuel range hydrocarbons (47). Despite its potential, converting lignin effectively has proven to be challenging, mainly due to the heterogeneous structure of lignin (48).

3.9 Bio-Oil Platform

The oil platform covers fatty acids and triglycerides that are obtained either from various terrestrial oil plants such as palm, coconut, rape seed, sun flower and soybean or aquatic biomasses, typically microalgae. The oleochemical industry is a major producer of bio-based products. In 2016/17, global vegetable oil production was around 184 million tonnes and the largest source of oil was from palm (62 million tonnes (49)). Roughly 80% of the vegetable oil is used for human consumption and 20% for non-food applications (50). The global oleochemicals market size was valued at USD 20.2 billion in 2016 (51). The use of plant oil for biofuels production has increased in recent years with a large percentage being derived from palm, rapeseed and soy oils. The majority of the biofuel is traditional biodiesel (FAME – fatty acid methyl ester), but the market for HVO (hydrotreated vegetable oil) has increased rapidly in recent years. In 2016 biodiesel production (FAME) was around 25 million tonnes and HVO 4 million tonnes (52), which also resulted in production of around 1.4 million tonnes of glycerol.

As a chemical feedstock, the triacylglycerol molecule – the major component of most plant oils - is either (a) cleaved to glycerol and fatty acids or (b) converted to alkyl esters and glycerol by transesterification, e.g. for biodiesel production (FAME). The usage of the fatty acids and esters is determined primarily by their chain length and functionality. The majority of fatty acid derivatives are used as surface active agents in soaps, detergents and personal care products. Major sources for these applications are coconut, palm and palm kernel oil, which are rich in C12-C18 saturated and monounsaturated fatty acids. Important products of unsaturated oils such as soybean, sunflower and linseed oil include alkyd resins, linoleum and epoxidized oils. Rapeseed oil, high in oleic acid, is a favoured source for biolubricants. Commercialized bifunctional building blocks for bio-based plastics include sebacic acid and 11-aminoundecanoic acid, both from castor oil, and azelaic acid derived from oleic acid. Dimerized fatty acids are primarily used for polyamide resins and polyamide hot melt adhesives. In applications such as lubricants and hydraulic fluids, plant oil can act as direct replacement for mineral (petroleum-derived) oil, or require only minor chemical modification.

A recent sector study in Germany shows that approx. 1 million tonnes oils and fats are used annually for chemical production. More than half of that amount is used as feedstock for surfactants (tensides). In health care products the proportion of biobased surfactants was 7% and of partly bio-based surfactants 43%. Thus the oleochemical industry is an already well established sector and one the future bioeconomy can rely on (53).

Box 4. Promising glycerol derived chemicals

Propylene glycol

Epichlorohydrin

1,3-Propanediol

3-Hydroxypropion aldehyde

Acrylic acid

Propylene

Glycerol is an important co-product of fatty acid/alcohol production. It can be purified and sold for a variety of uses. Current markets are pharmaceutical, cosmetic, and food industries. The large availability (over production) of glycerol has encouraged chemical producers to look at technology for its conversion to chemical building blocks. Glycerol can serve as feedstock for fermentation and anaerobic digestion. One of the most promising fermentation products is 1,3-propanediol, but other products include ethanol and various organic acids (54). Chemical modifications include oxidation to glyceric acid and tartronic acid (2-hydroxymalonic acid) or reduction to acrolein or propanediol (23). However, it has been the chemical conversion tartronic acid of glycerol to three carbon chemicals such as epichlorohydrin and propylene glycol that has received particular attention.

There has been tremendous interest in exploiting algae for production of oils and lipids. Generally, the usages and applications will be comparable to those already mentioned for oils derived from terrestrial plants. The main drivers for cultivating algae are that algae has high photosynthetic efficiency potentially allowing for a higher oil productivity compared with terrestrial crops. Some algae can accumulate up to 50-80% of oil/lipids. In addition, microalgae can be cultivated in seawater or brackish water on non-arable land. However, commercial production is challenged by the high cost of cultivating and harvesting algal biomass feedstocks relative to producing terrestrial plant biomass. The inverse relationship between productivity and oil content may prove to be a challenge in overall process optimization. Opportunities do exist to use algae in an integrated biorefinery context to make higher value food, feed, nutraceutical and oleochemical bioproducts (55, 56). Besides algae, oleaginosus microorganisms are of interest as alternative source of oils. They can accumulate lipids, mostly consisting of triacylglycerols (TAG) as reserve compounds. Among heterotrophic microorganisms, oleaginous fungi, are increasingly been reported as good TAG producers. Some oleaginous species, such as *Lipomyces starkeyi*, have the capability to accumulate up to 70% of their cell biomass as lipid under defined culture conditions, and can produce lipids on several carbon sources including sugars and raw glycerol. Microbial oils holds the potential to be used for the production of many chemicals and drop-in fuels, namely hydrocarbons. However some economic estimations indicate that some improvements in the bioconversion process and downstream operations are necessary to make the process feasible.

3.10 Organic Solutions Platform

A green biorefinery processes (wet) green biomass, such as grass, clover, alfalfa or immature cereals (11). The first step involves a fractionation of the green biomass into a nutrient-rich juice "Organic Solution" and a fibre-rich lignocellulosic press cake. This is typically performed mechanically in a screw press. Both intermediates are starting points for various valorisation pathways.

The organic solution (press juice) contains valuable compounds, such as carbohydrates, proteins, free amino acids, organic acids, minerals, hormones and enzymes depending on whether the biomass used as the feedstock is fresh or silage. Soluble carbohydrates and proteins are the main components of organic solution. In juice from fresh biomass, the proteins can be recovered by precipitation and used as feed for e.g. monogastric animals (57) or eventually purified for human consumption. The remaining solution can be used as fermentation medium (58). In the case of silage press juice, production of bio-chemicals (lactic acid and amino acids) have been demonstrated (59).

The press cake fibres can be utilized as green feed pellets, processed to fibre products (60) or potentially used as a raw material for other platforms (e.g. pyrolysis oil, syngas, sugar and lignin platforms (Figure 3). Grass fibre products are currently in a market introduction phase (e.g. insulation material) and some technologies have been implemented at pilot and industrial scale (59).

4. Bio-based Chemicals and Polymers - Opportunities and Growth Predictions

The potential for chemical and polymer production from biomass has been comprehensively assessed in several reports and papers (2, 61-65). In 2004 the US Department of Energy issued a report which listed 12 chemicals building blocks which it considered as potential building blocks for the future. This list was reviewed and updated in 2010 with new opportunities added to the list (Table 2).

Table 2. Promising Bio-based chemical targets as assessed in 2004 and 2010 (64, 65).

Bio-based chemical opportunities	
2004	2010
1,4-Dicarboxylic acids (succinic, fumaric and malic)	Succinic acid
2,5-Furan dicarboxylic acid	Furanics
3-Hydroxy-propionic acid	Hydroxypropionic acid/aldehyde
Glycerol	Glycerol and derivatives
Sorbitol	Sorbitol
Xylitol/Arabinitol	Xylitol
Levulinic acid	Levulinic acid
Aspartic acid	-
Glucaric acid	-
Glutamic acid	-
Itaconic acid	-
3-Hydroxybutyrolactone	-
-	Biohydrocarbons
-	Lactic acid
-	Ethanol

The BREW project (63) analysed the market potential for the group of bulk chemicals produced from renewable resources using biotechnology (Table 3). The study found that with favourable market conditions the production of bulk chemicals from renewable resources could reach 113 million tonnes by 2050, representing 38% of all organic chemical production. Under more conservative market conditions the market could still be a significant 26 million tonnes representing 17.5% of organic chemical production.

Recently European Bioplastic eV / nova Institute (66) gave an overview of the biopolymers market volume which was estimated to be 2.11 million tonnes globally in 2018. The platform biorenewable chemicals ethanol, glycerine and lactic acid make up the bulk of biorenewable chemicals being sold in 2018, accounting for the fast majority of the market. There is a large range in market maturity for platform biochemicals, ranging from mature markets such as lactic acid and mono-ethyleneglycol to nascent markets for chemicals such as succinic acid and 2,5 furan dicarboxylic acid. The strongest growth will be for biopolymers such as polylactic acid (PLA), polyhydroxyalkanoate (PHA) and bio-ethylene that are used to manufacture bio-based plastic products.

The world market for succinic acid was approximately 30,000 tonnes in 2009, of which less than 5% was produced from bio-based feedstock. Biorenewable succinic acid has now entered the marketplace, and accounts for half of the global succinic acid market. Nova Institut has published a report which discusses the significant gap between previous estimations and the current market situation as well as the study highlights the key drivers and inhibitors for growth as well as the necessary framework conditions needed (67). Various companies (primarily in the U.S. and Europe) have moved past the laboratory to the pilot plant stage for isosorbide, isoprene, levulinic acid, and adipic acid. For these platform organic chemicals, production will continue to be a very limited affair, with volumes well below 9,000 tonnes/year for the foreseeable future. The production capacity for polyhydroxyalkanoates (PHA) remains limited (Figure 7). The largest barrier for PHA to gain market share is high manufacturing costs which are still much higher than other polymers, although high-end applications such as in 100% biodegradable microbeads shows good promise (68, 69).

Table 3. Bio-based chemicals assessed for market penetration and reference materials (adapted and updated from reference (63)).

Bio-based chemical	Reference Petrochemical
Acetic acid	Acetic acid
Adipic acid	Adipic acid
n-Butanol	n-Butanol
Ethylene	Ethylene
Bio-MEG	MEG (mono-Ethyleneglycol)
Ethyl lactate	Ethyl acetate
FDCA	Terephthalic acid
PHA	HDPE
PLA	PET and PS
Succinic acid	Maleic anhydride

Currently, commercialised bio-polymers (among others starch blends, PLA, polyethylene, PET) are demonstrating moderate market growth (Figures 7, 8). Market analysis show growth per annum to be in the 9-30% range (66, 70, 71), with especially strong growth numbers for 2023 (Figure 8). Traditionally, bio-based polymer markets have been dominated by biodegradable food packaging and food service applications. However, with durable bio-based polymer items (e.g. biobased polyethylene, polypropylene and (partially) biobased PET) forcefully entering the market resulting in a dominance of the non-biodegradable plastics in 2018 (Figure 7). It is anticipated that this gap will only increase in the upcoming years (Figure 8). It can be rationalised that the production of more stable, stronger and longer lasting biopolymers will lead to CO_2 being sequestered for longer periods and leads to (thermochemical) recycling rather than composting where the carbon is released very quickly without any energy benefits.

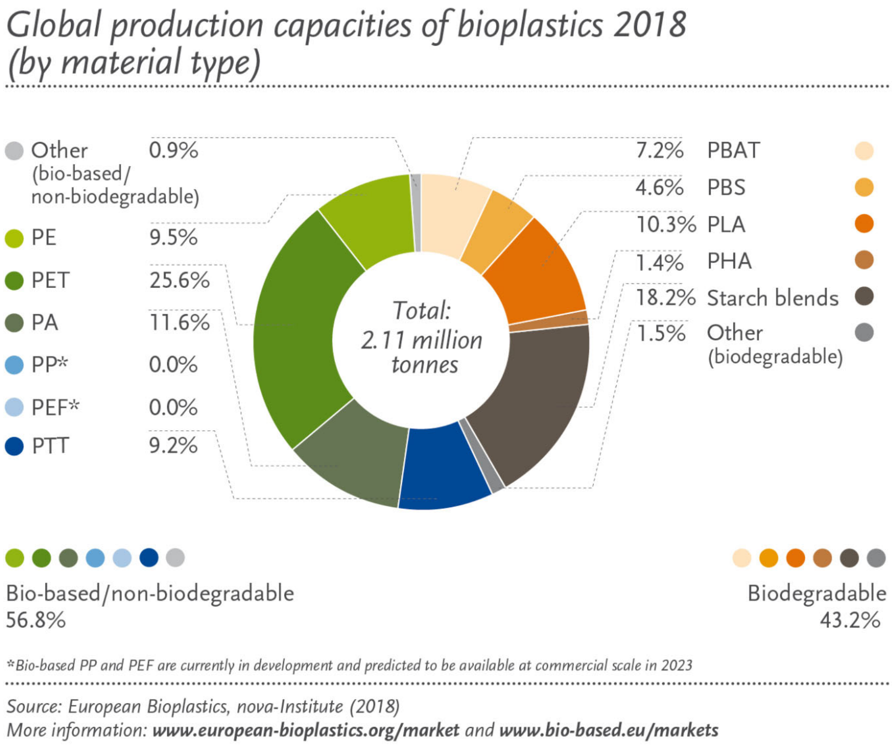


Figure 7. Global production of bioplastics in 2018 (in tonnes/year) by European Bioplastics, nova-Institute (177).

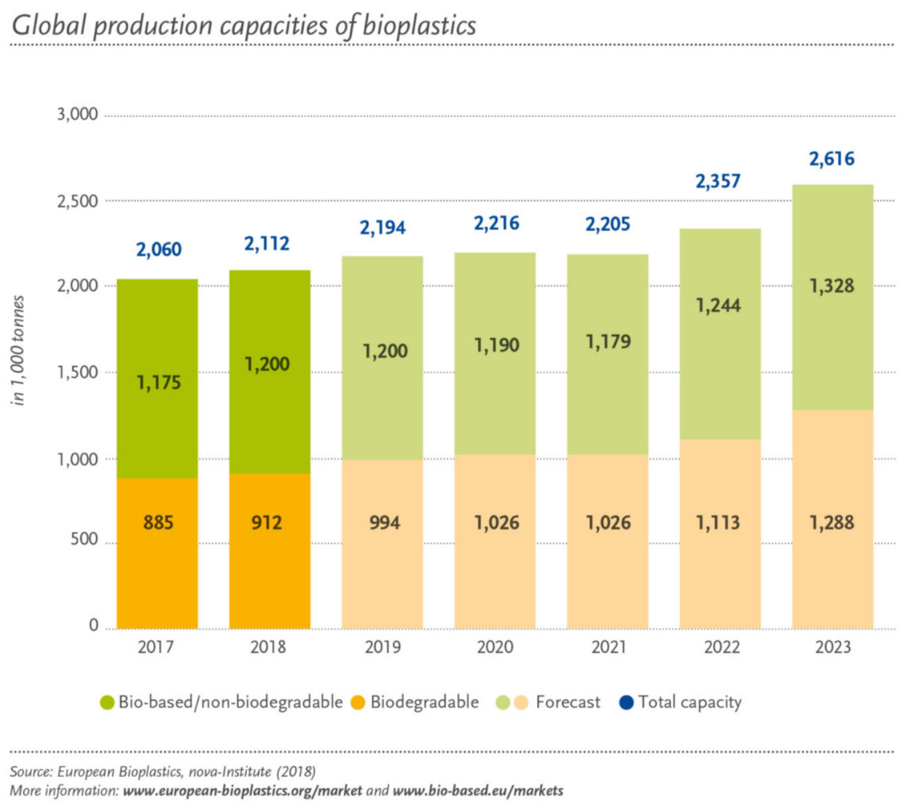


Figure 8. Anticipated growth in the global production of bioplastics in the period 2018-2023 (in tonnes/year) by European Bioplastics, nova-Institute (177).

5. Economic benefit of co-production of fuel and chemicals

A biorefinery should produce a spectrum of marketable products in order to maximise its economic sustainability and to aim for "zero waste". A variety of different biorefinery configurations are already in operation which are being expanded/reconfigured (e.g. pulp and paper industry, starch industry, ethanol industry) or are newly being developed. Biorefineries may be configured around a large volume product to maximize economies of scale and to allow the successful utilisation of all inputs with the integration of process operations. The fuel market offer the scale necessary to support biorefinery operation but without legislation and/or support mechanisms possibly not the necessary economic return. Subsidies and strategic decisions are currently still the drivers not sustainability in its true sense. That is, the three pillars of sustainability consist of three equally weighted sectors, Environmental, Social and Economic. Policies and subsidies may skew the development of biofuels away from one or more of these areas. If subsidies and policy assist in the implementation of these systems, at what point can we truly evaluate the economic viability of biofuels and the environmental or social load of changes in biomass use. Strategic decisions drive the implementation and subsidies make them 'economic'. In order to increase the economic viability for biofuel production, the feedstock and other inputs should be low cost and economic value needs to be derived from its co-products. In the case of a forest based biorefinery, for example, sufficient value should be generated from the entire product portfolio - pulp, biofuel, energy and other chemical production. A cascading product flow is often recommended where the highest value products are extracted first, recovered, reused and recycled, and biofuels and energy are the final use products as the biomass is ultimately valorised for its energy content upon use. However, we might need a paradigm shift within the biorefinery concept. The assumed advantage of biorefineries has often been based upon the need/mandates for liquid or gaseous biofuels. It can be questioned if the use of biomass for biofuels as a primary aim is in the interests of global sustainability. Some might say that the support and subsidies for biofuels has skewed the system of development, and that a strong case should be made that the benefits of biomass utilisation arise from the use of the best materials and technologies for products. Bioenergy is a "final, destructive use" of biomass and should be primarily generated from the waste streams. This will only be possible if there is a level playing field for both biobased chemicals and materials as well as biofuels and bioenergy. Sound evaluations should be performed of the achieved CO_2 savings, energy input and land use for a particular product compared with conventional methods and energy output from waste streams. Carrez et al have made the following statement on biomass use: "Indeed, its use in green chemistry and green materials is saving more CO_2/ (ha*y), is more resource efficient and leads to more employment than using the equivalent land area for the production of bioenergy" (72).

5.1 Integration with bioethanol production

The BIOREF-INTEG study analysed the effect of partitioning the carbohydrate stream in a grain to ethanol plant between ethanol and in a lactic acid production (73). The carbohydrate stream was split 4:1 with the bulk of material feeding the ethanol fermentation (Figure 9). In the reference scenario the required sale price of ethanol, in order for the plant to generate an IRR of 20%, was €775 per tonne. Integration of lactic acid production with ethanol reduced the required ethanol sale price considerably down to €545 per tonne. Rosales-Calderon and Arantes (134) presented a review on commercial-scale high-value products that can be produced alongside cellulosic ethanol.

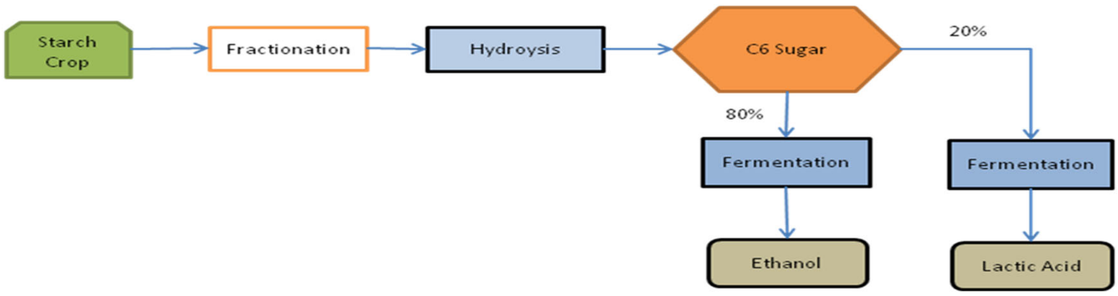


Figure 9. Integrated ethanol and lactic acid production.

Alternative process flowsheets (Figure 10) could include the co-production of xylitol or furfural from C5 sugars deriving from biomass hydrolysis. Some techno economic evaluations indicate that if xylitol or furfural is coproduced together with ethanol the surplus electricity generated through the lignin thermal valorisation decreases by about 30%. From the profitability point of view, xylitol coproduction appears more convenient than both the co-production of furfural or the production of ethanol alone. This result is due to the significantly higher selling price of xylitol which lowers the Payback Selling Price of Ethanol (€/kg) to 0.79 with respect to the base case of 1.62 (74).

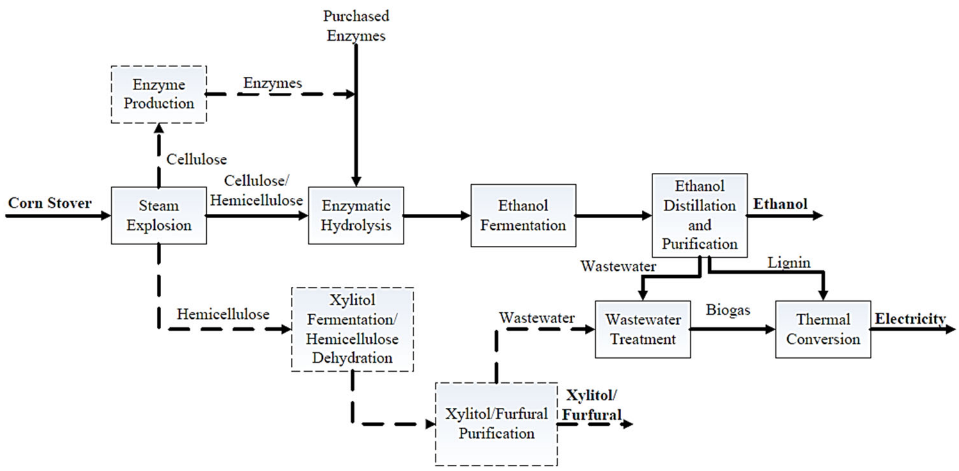


Figure 10. General flowsheet of a multi-product lignocellulosic biorefinery producing ethanol and furfural/xylitol (74).

5.2 Integration with biodiesel production

The BIOREF-INTEG study considered the integration of chemical production with biodiesel production on the basis of upgrading the glycerol co-product to either epichlorohydrin or 1,3-propanediol. A reference plant processing 300 tonnes per day of crude rapeseed oil was considered (Figure 11). In the reference scenario the required sale price of biodiesel, in order for the plant to generate an IRR of 20%, was €765 per tonne. The integration of biodiesel with epichlorohydrin production resulted in a slightly reduced biodiesel sale price of €735 per tonne. The integration with 1,3-propanediol resulted in an increase in biodiesel sales price of €815 per tonne. The difference in economic impacts can be explained by the modelled yield efficiencies for glycerol to epichlorohydrin and 1,3-propanediol. While 35 tonnes of glycerol yields 27 tonnes of epichlorohydrin the same quantity of glycerol was only modelled to yield 14 tons of 1,3-propanediol. Improvements in the efficiency of glycerol to 1,3-propanediol fermentation or finding a value for the "yield difference" would improve the economics of both the fermentation process and the integrated biorefinery (75). The results for the BioRef study indicate that the biorefinery configurations need to be carefully analysed in order to draw conclusions as to their financial viability. Concluding that a bio-based chemical can be as or even be more competitive than its petroleum based counterpart is not possible without an analysis of the biorefinery configuration (73).

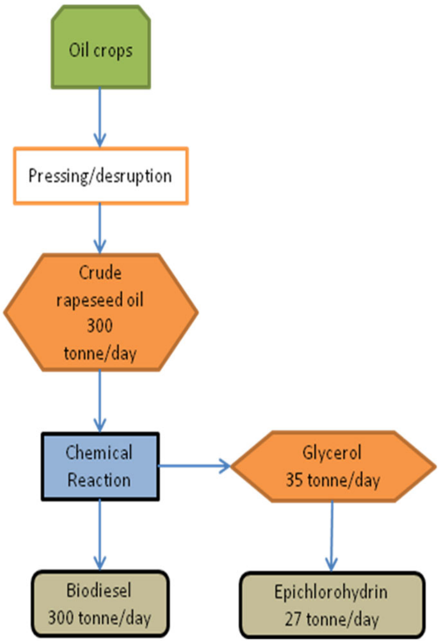


Figure 11. Integrated biodiesel and epichlorohydrin production.

6. Product Commercialisation

Although the production of many bio-based chemicals and materials is technically possible at lab and even pilot scales, a smaller number will actually be commercialised. The key criteria (market and technology) considered for commercialisation are outlined in the box below.

Box 5

Market assessment

Market fundamentals (local, regional, global)
Feedstock availability and price
Utilities (steam, gas, electricity etc.) availability and price
Product(s) profitability
Bankability
Competitive nature of market
Need for partnerships
Downstream development opportunities

Technology assessment

Commercial experience
Necessary capital investment
Process complexity
Access to technology
Environmental and legislative considerations

Once commercialised, a product needs to capture market share in order for production to expand. Establishing a market is considerably easier for recognised chemicals and materials. Novel chemicals as well as innovative materials will require time for supply chain participants and downstream processors to adapt equipment and processes. For example, a new plastic material will typically take 2-3 years to establish early applications, 2-6 years could be required to develop a platform position and over 6 years is typically required to achieve large scale production (76). A plastic with a technical function and complex supply chain could take 20-40 years to achieve production scales over 100,000 tonnes. The easiest market entrance will be therefor for the so called "drop-in" biobased chemicals such as ethylene, propylene and *p*-xylene, which have direct fossil-based counterparts. For these chemicals only price at desired purity and environmental footprint are relevant. They can be processed in already available infrastructure and substantial markets are already established. However, the far majority of chemicals is not economically competitive at recent crude oil prices (Figure 1) and no/low CO_2 taxes. Another point of consideration is the use of 'clip-on' technologies.

These 'clip-on' technologies may consist of processes, or components, that were originally designed for a biorefinery. However, an existing producer of biobased chemicals may find it uneconomic to change the technology before full depreciation of the plant and equipment, and it may be argued that to abandon extant plant and machinery is not sustainable. One approach may be to implement elements of biorefinery technology as required, and dictated, by 'market forces'. An example of this would be the production of carbohydrates from lignocellulose. It may now be economic for such industries to invest in a pre-treatment technology to produce carbohydrates for processing within existing infrastructure. A variety of viable technologies now exists in this area and is becoming economically realistic due to changes in feedstock prices and availability. The sugar and carbohydrate markets are becoming very volatile (Figure 11). This figure indicates a surplus of carbohydrates and an increasing difficult business case for 2nd generation sugars at present, unless they are mandated. However, on the longer term widely available 2nd generation sugars are needed to make the transition in the chemical industry from fossil- to biobased feedstocks.

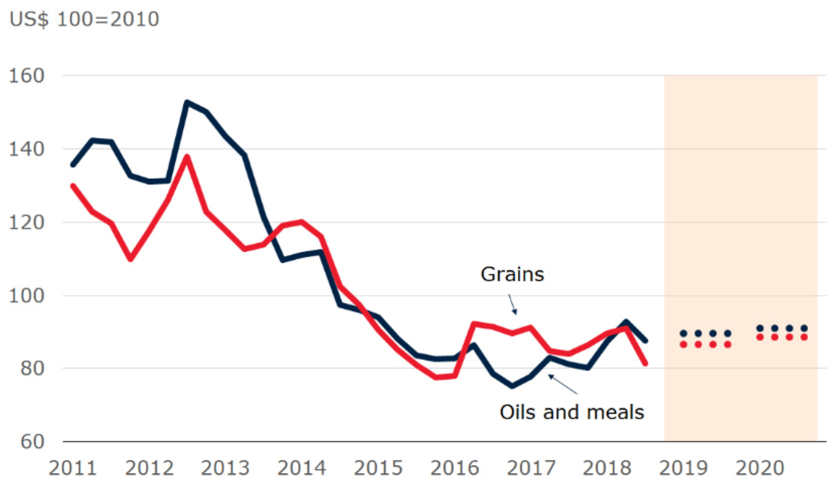


Figure 12. Global Prices of Key Food Commodities (*Source*: World Bank, last observation is 2018Q3. Shaded areas denotes forecasts).

Table 4. Estimates of total EU production, the bio-based share of production and the consumption of bio-based products for each category in 2019 (77).

Product category	EU Biobased production (kt/a)	Total EU production (kt/a)	EU bio-based production share (%)	EU bio-based consumption (kt/a)
Platform chemicals	181	60,791	0.3	197
Solvents	75	5,000	1.5	107
Polymers for plastics	268	60,000	0.4	247
Paints, coatings, inks and dyes [(a)]	1,002	10,340	12.5	1,293
Surfactants	1,500	3,000	50.0	1,800
Cosmetics and personal care products [(a)]	558	1,263	44.0	558
Adhesives [(a)]	237	2,680	9.0	320
Lubricants [(a)]	237	6,764	3.5	220
Plasticisers [(a)]	67	1,300	9.0	117
Man-made fibers	600	4,500	13.0	630
Total	**4,725**	**155,639**	**3.0**	**5,489**

[(a)] No total EU production data were found; it has been assumed that total EU production (fossil- and biobased) equals the total EU market (fossil- and bio-based consumption).

Large companies with huge capital expenditure cannot afford to walk away from existing infrastructure. However, if carbohydrates are produced from lignocellulose for €300/t rather than paying in excess of €600/t on the open market then a clip on technology may be feasible in the near future. The use of 'clip-ons' may occur anywhere within the biobased value chain, from feedstock treatment/variety, to fermentation systems, downstream processing or as an addition to oil refinery technology e.g. the addition of biobased ethylene production usually produced from an oil to ethane stream. A progressive move to full biorefinery configuration may be necessary for existing industries. Start-ups will of course have an advantage, but they have to create their own markets. The Tables 4-6 below gives an overview of the current turnover of biomass in general and biobased products in particular in the EU (77).

Table 5. Prices and turnover figures for bio-based products aggregated to product category level in 2019 (77).

Product category	Price (€/kg)	Turnover (€ million /a)
Platform chemicals	1.48	268
Solvents	1.01	76
Polymers for plastics	2.98	799
Paints, coatings, inks and dyes	1.62	1,623
Surfactants	1.65	2,475
Cosmetics and personal care products	2.07	1,155
Adhesives	1.65	391
Lubricants	2.33	552
Plasticisers	3.60	241
Man-made fibres	2.65	1,590
Total	**1.94**	**9,167**

Table 6. Feedstock and land use for EU production of bio-based products at product category level (77).

	Feedstock use for EU production of bio-based products			Land use for EU production of bio-based products	
Product category	Total (including imports) (kt/a)	Imported feedstock (kt/a) [(a)]	Import dependency (%)	1,000 ha	ha/t product
Platform chemicals	262	90	34	88	0.49
Solvents	87	3	3	42	0.56
Polymers for plastics	284	28	10	95	0.36
Paints, coatings, inks and dyes	593	468	79	351	0.35
Surfactants	1,744	1,179	68	885	0.59
Cosmetics and personal care products	456	306	67	430	0.77
Adhesives	232	14	6	117	0.49
Lubricants	192	149	78	114	0.48
Plasticizers	106	46	44	43	0.64
Man-made fibres	555	19	3	228	0.38
Total	**4,511**	**2,302**	**51**	**2,393**	**0.51**

[(a)] These data refer only to imports of feedstock for EU production of bio-based products, not to imports minus exports, as there are of course no exports of feedstock for EU production of bio-based products.

7. Greenhouse gas GHG emission reductions and other environmental impacts through bio-based chemical production

Bio-based chemicals are perceived to be environmentally sustainable, because they are produced from renewable resources. Unfortunately, the picture is much more complex. Just a limited number of Life Cycle Assessment (LCA) studies using primary data at relevant industrial scale are available, examples are succinic acid, lactic acid, 1,4-butanediol and 1,3-propanediol. Most other studies rely on data at technical scale (TRL 5-6) or even lab-scale (TRL 3-4) (78).

The real greenhouse gas reductions must be estimated by life cycle approaches, using realistic data. There are sometimes huge variations of environmental impact results for the same bio-based or fossil-based product, that can just partly be explained by different scopes and technologies used in the respective studies, but might also be caused by collection and use of not representative data. For any future process optimisation and policy decisions on bio-based products, a robust and transparent benchmark of petrochemical counterparts should be made available. This requires more accessible and transparent data provided by the chemical, particularly plastic, industry as well as LCI data providers (79). It is important that forward looking predictions are made for the petrochemical based molecules because it is anticipated that their LCI data will become less favourable because extraction as well as upgrading will become much more difficult and therefore energy intensive. It also important not to oversell the potential GHG emission reductions of the biobased molecules, as was done with the introduction of biofuels. Some bio-based chemicals might in fact not have a GHG reduction relative to their current fossil-based counterparts (80). Just as not all biofuels are created equally, all bio-based chemicals are not created equally.

In general, the results from different studies are hardly comparable because of different assumptions. For example, in the studies different End-of-Life (EoL) approaches, methodological choices (allocation or subdivision) and considered environmental impact categories within different geographical, spatial and temporal scales are used. The same applies for the environmental impacts of their fossil-based counterparts. Drawing conclusions from published LCA studies is not an easy task and it is recommended to consult expert knowledge in order to avoid misinterpretations. However, that does not imply that general trends cannot be identified.

Several review papers (81-83) on bio-based products have shown that the production of bio-based chemicals has the potential to significantly reduce the greenhouse gas (GHG) emissions and fossil resource demand of the petrochemical industry, and of the downstream users. The conclusions for other environmental impacts, such as acidification, ecotoxicity, stratospheric ozone depletion, etc. or resources such as water are inconclusive (79, 83). Moreover, environmental impacts concerning biodiversity and ecosystem service are hardly investigated (84). The overall environmental performance has to be assessed on a case-by-case basis taking all relevant environmental impacts into account.

Montazeri (81, 85) has investigated the environmental performance of several DOE priority bio-based chemicals and comes to similar conclusions for biomass derived fuels and chemicals in the US. He states: In general, assessment results of bio-based fuels and chemicals were found to be sensitive to process and LCA model parameters, especially the choice of conversion process, coproduct allocation method, and inclusion/exclusion of emissions from land use change. Net GHG emissions results for most sugar-derived chemicals met existing sustainability thresholds, while thermochemical conversions routes typically did not. Smidt has shown for bio-based succinic acid

(86), Jeswani (87) and Munoz (84) for biobased ethanol, Morales (88) for lactic acid and Vink (89, 90) and Groot (91) for Polylactic acid that significant GHG reductions and reduction of fossil resources can be achieved today, relative to their petroleum-derived counterparts. However, that does not hold for all other environmental impacts. Most studies have used sugar from sugarcane or sugar beet or corn starch as feedstock rather than second or third generation feedstock. The impacts of second and third generation feedstock are still uncertain. Also using waste as a resource is not necessary a guarantee for a lower environmental impact of the studied bio-based products; it strongly depends on the type of waste and efficiency of the used conversion technologies (79).

The Joint Research Centre of the EU (JRC) has commissioned a study "Environmental impact assessments of innovative bio-based products" (79, 92). Seven cradle-to-grave LCA case studies were carried out covering three major commercialised bio-based polymers, namely

i) Bio-based polyethylene terephthalate (PET; "Beverage Bottles"; partly biobased only Mono-Ethyleneglycol (MEG) replacement),
ii) Polylactic acid (PLA; "Single-use cups", "Single-use Cutlery", "Packaging films"),
iii) Starch plastics ("Clips", "Mulch films" and "Carrier bags").

Primary data are gathered from industry based on the real supply chain. This also includes the biomass used by the industry presently. The aim of the study is to provide science-based facts and evidences on the environmental impacts of innovative bio-based products and mostly plastic products compared to petrochemical counterparts. Some conclusions of the study are:

- In principle, biomass feedstock production for bio-based products typically requires (more) land than the extraction and use of fossil fuels, and thus land use and associated impacts are often specifically investigated. We found that the impacts from land use and water use are rather limited compared to the impacts from the manufacturing phase.
- The manufacturing phase has the highest contribution of all life cycle stage: it accounts for approximately 50 % of the cradle-to-grave impacts of nearly all seven bio-based products studied.
- The impacts of transportation are in general insignificant. The exceptions are when the global supply chain is very long.
- The impacts of the EoL of the bio-based products studied are highly dependent on the applications. It is not possible for this study to establish a so-called "status-quo" waste management for these newcomers, because the quantity of the bio-based products in the waste stream is still statistically insignificant.

Bio-based industries are a nascent sector. Their production processes are not fully optimised for efficiency and there are on-going efforts to optimise those processes. Also the scale of the biobased processes is currently in general much smaller than for their petrochemical counterparts, this limits the economy of scale benefits. In the future, through process optimisation and decarbonisation of the energy sector, the contribution of the manufacturing phase to the total environmental impact of bio-based products could be expected to decrease. Lower GHG emissions are expected as dedicated industrial biomass feedstocks are developed, processes are further optimized, and renewable energy technologies are further adopted in industrial and transportation applications. Posen et al. showed that ethylene and polyethylene production from switchgrass can result in lower emissions than fossil-based polyethylene, but these results have high uncertainty mainly due to limited data for commercial-scale production (93). Although the traditional petroleum-based processes are also expected to become more GHG-efficient over time, new exploration methods (e.g. tar sands, deep sea drilling, arctic exploration) as well as the extraction of heavier and more contaminated oil will likely create too great a challenge to achieve the same GHG-efficiency as current processes.

Bioplastics show frequently a much better GHG-balance than their fossil-based counter parts, but overall environmental advantages seem often to be limited. It is difficult to judge bio-based chemicals based on the same requirements than biofuels, i.e. 65% GHG reduction from 2021 onwards in the EU. One reason is that bio-based chemicals can often be used multiple times in recycling cascades and incinerated for energy purposes thereafter, although the optimal point when recycling should turn to energetic use depends on many factors and is context- und regional specific. However, prolonged material use followed by energy use of biomass will most likely provide the largest GHG savings.

Table 7. Future GHG savings per tonne and annual savings for bio-based chemicals assuming a 20% replacement of fossil based chemical by biobased chemical as predicted by Hermann et al. in 2007 (95).

Product	GHG savings ($t\ CO_2$/t of product)	Installed world capacity (million t/year)	Annual GHG savings (million t CO_2/year) 15%	Annual GHG savings (million t CO_2/year) 65%
Acetic acid	1.2	8.3	0.3	1.3
Acrylic acid	1.5	2.9	0.1	0.6
Adipic acid	3.3	2.4	0.2	1.0
Butanol	3.9	2.5	0.3	1.3
Caprolactam	5.2	3.9	0.6	2.6
Ethanol	2.7	2.6	0.2	0.9
Ethyl lactate	1.9	1.2	0.1	0.3
Ethylene	2.5	100.0	7.5	32.5
Lysine	3.6	0.6	0.1	0.3
Succinic acid	5.0	1.4	0.2	0.9
1,3-propanediol	2.9	-	-	-
PHA	2.8	57.0	4.8	20.7
PLA	3.3	11.1	1.1	4.8

Albrecht et al. (94) also stated in their 2010 paper that more savings in GHG emissions can be made through the use of biobased products than using the same material for energy. Under these circumstances, the production of biobased products should be favoured over biomass usage before energy production. It should be remembered that a suite of technologies are available and will be used to meet energy needs, even using ‘clip-on, technologies to attenuate existing oil, gas and coal supplies.

Several authors have produced detailed assessments of potential GHG emission savings, which could be made if bulk chemicals and polymers are produced from renewable resources (63, 95, 96). The assessment of GHG-savings is complicated by the large number of potential chemical building blocks and the multiple process routes and feedstocks, however scenario based assumptions can be provided. For the sake of simplicity, we assume that bio-based products can provide GHG savings between 15% to 66% (79, 92) and will replace 20% of their fossil counterparts in the midterm future.

Based on that scenario the GHG-saving potential is between 16 and 67 million tonnes of CO_2eq per year. This estimation carry a high level of uncertainty but the development towards more bio-based chemicals can be triggered by CO_2-pricing. If lignocellulosic feedstocks would be used, even greater GHG reductions can be expected. On a per unit comparison the potential GHG savings from production of bio-based chemicals and polymers often exceed the savings produced from bioenergy or biofuel production.

If climate change is the most serious challenge of humanity then every measure to reduce the GHG-emissions should be taken as long as no problem shifting occur. In order to ensure that, LCA is probably the best suited tool to identify the best options. Recently, the European Committee for Standardization (CEN), has provided guidance how to conduct an LCA for biobased products (97, 98)). These approaches should be used in the future to assess the overall environmental performance of biobased products and for comparison with their fossil counterparts.

7.1 Oxidation state of carbon in the chemical compound

There is a major difference in the starting position of making chemicals from fossil or biobased feedstocks, i.e. the oxidation state of the carbon. Carbon in fossil feedstocks has an oxidation state of -1 (benzene) to -4 (methane) while carbohydrates, in volume by far the biggest biomass feedstock, have an oxidation state of 0. Fatty acids have a much lower oxidation state (-1.78 for stearic acid) but are produced in much lower quantities and have a much higher cost level than carbohydrates. So only the longer chain fatty acids and alcohols are derived from fatty acids while the rest of the chemicals is almost exclusively derived from carbohydrates. Many chemicals, e.g. precursors for plastics, have an oxidation state below 0, meaning that oxygen has to be removed and/or hydrogen needs to be added during the conversion process if carbohydrates are the starting material. This also implies that whereas weight is often added during the conversion of fossil feedstocks, conversion of biomass feedstocks is typically associated with a weight loss. For example, the conversion of fossil-based ethylene (Mw=28) to ethyleneglycol (Mw=64) multiplies the mass by 2.23 due to addition of oxygen.

8. Future scenario's for the role of bio-based chemicals in a sustainable and circular bioeconomy

In this section actions are identified in the area of policy, technology progress and social acceptance, which are, in our opinion, necessary to align with a Sustainable Development.

The IEA publishes an annual World Energy Outlook (WEO). In this outlook three different scenario's are discussed in relation to energy usage and global warming: the Current Policy scenario; the Stated Policy Scenario and the Sustainable Development Scenario (99). In Table 8, these three scenarios are described and in Table 9 corresponding policies, technology progress and social acceptance are compiled.

Table 8. Description of the WEO scenarios from 2019 (99).

Scenario WEO 2019	Sustainable Development Scenario	Stated Policies Scenario	Current Policies Scenario
Scenario description	• Energy demand fully aligned with the Paris Agreement by holding the rise in global temperatures to "well below 2°C … and pursuing efforts to limit it to 1.5°C", and meets objectives related to universal energy access and cleaner air • The breadth of the world's energy needs means that there are no simple or single solutions	• Energy demand rises by 1% per year to 2040 • Low-carbon sources, led by solar PV, supply more than half of this growth, and natural gas, boosted by rising trade in liquefied natural gas (LNG), accounts for 1/3 • Oil demand flattens out in the 2030s, and coal use edges lower • The rise in emissions slows but, with no peak before 2040, the world falls far short of shared sustainability goals	• Energy demand rises by 1.3% each year to 2040 • Relentless upward march in energy-related emissions. Growing strains on almost all aspects of energy security

Figure 13 shows the energy demand versus the energy-related CO_2-emssions for the three scenarios in 2040. It is obvious that the Current Policies as well as Stated Policies for the industry are not at all sufficient to reach the goals as defined in the Sustainable Development Scenario.

There is a widening gap between the ever-higher amounts of greenhouse gas emissions being produced and the insufficiency of stated policies to curb those emissions in line with international climate targets (99). As ever, decisions made by governments remain critical for the future of the energy system and subsequent industrial and private users. This is evident in the divergences between WEO scenarios. These scenarios map out different routes the world could follow over the coming decades, depending on the policies, investments, technologies and other choices that decision makers pursue today (Table 8). Together, these scenarios seek to address a fundamental issue – how to get from where we are now to where we want to go (99). The Stated Policies Scenario incorporates today's policy intentions and targets in addition to existing measures related to biomass in general and biobased chemicals in particular. The future outlined in this scenario is still well off track from the aim of a circular economy and a secure and sustainable energy future.

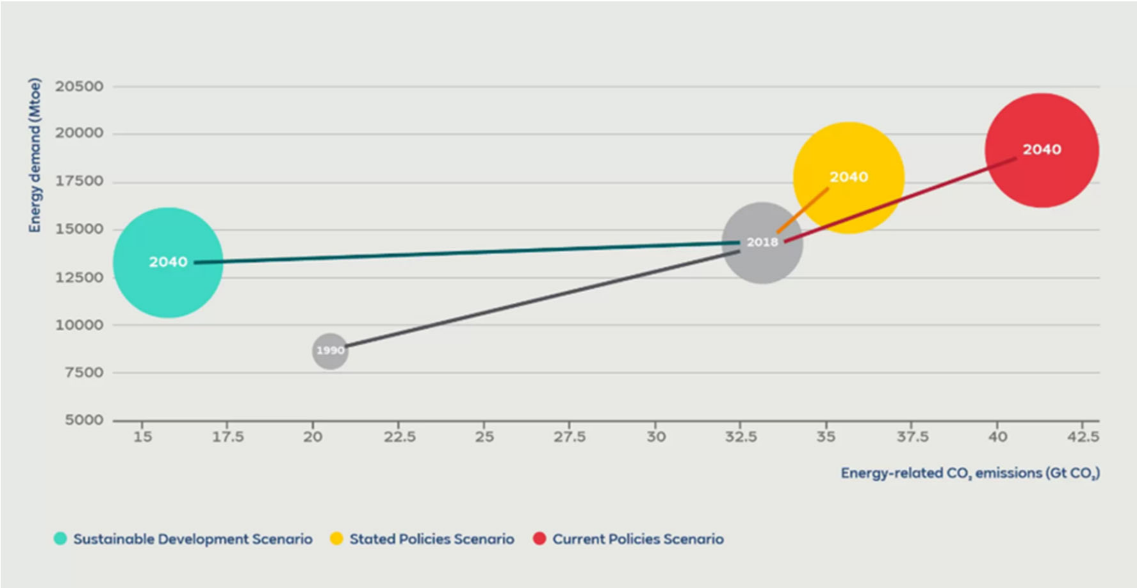


Figure 13. World primary energy demand and energy-related CO_2 emissions by scenario. Bubble size represents size of global economy (99)

In the Sustainable Development Scenario presented in Table 9, IEA Bioenergy Task 42 identified what needs to be done differently to fully achieve a circular bioeconomy. Achieving this scenario – a path fully aligned with the Paris Agreement aim of holding the rise in global temperatures to well below 2°C and pursuing efforts to limit it to 1.5°C – requires rapid and widespread changes across all parts of the energy, chemicals and materials system.

Table 9. Required policy actions, consumer behaviour change and technological progress identified by IEA Bioenergy Task 42.

Scenario	Sustainable Development Scenario	Stated Policies Scenario	Current Policies Scenario
Policy	• High CO_2 price > 100 $/t • Fossil subsidies are gone • Net CO_2 sequestration incentivised • Circular economy is mandatory • Sustainable forestry and agriculture is mandatory	• Moderate CO_2-price >50 - <100 $/t • Fossil subsidies moderately reduced • Net CO_2 sequestration demanded • Circular economy is desired • Sustainable forestry and agriculture is desired	• Current CO_2 price • Fossil subsidies remain • No net CO_2 sequestration demanded • No effective policy in place to achieve circular economy • Current status, no major change
Technology	High progress: • In up- and downstream processes for bio-based feedstock • Ethanol-to-chemicals • Green H_2- production • Widespread algae/ seaweed utilisation	Medium progress: • In up- and downstream processes for bio-based feedstock • Ethanol-to-chemicals • Blue and some green H_2-production • Moderate algae/ seaweed utilisation	Low progress: • In up- and downstream processes for bio-based feedstock • Limited ethanol-to-chemicals • Minimal sustainable H_2 –production • Algae/ seaweed utilisation only for Food and Pharma
Social acceptance	High acceptance of climate treat and for climate policy: • Agreement on biomass sustainability and biodiversity • Willingness to change behaviour • Willingness to pay for climate-friendly products • Open attitude to locations of facilities • Less meat demand (resulting in high feedstock availability)	Moderate acceptance of climate change urgency: • Inconclusive debate about biomass sustainability and biodiversity hampers biomass utilisation • Moderate behaviour change • Only willing to take steps if everybody else take similar steps. • NIMBY (Not In My BackYard) attitude • Moderate reduction of meat consumption	No willingness to change behaviour: • Continuing debate about man-made role in climate change as well as usefulness of mitigation actions • No substantial behaviour change • No willingness to pay for climate-friendly products • NIMBY attitude • Meat consumption continuously growing

The following actions are identified in the area of policy, technology progress and social acceptance, which correspond with the described scenarios. The consequences of the scenario-derived actions regarding feedstock availability, renewable energy availability for industrial processes and biobased chemicals are displayed in Table 10.

Table 10. Consequences for the scenarios with respect to more sustainable biobased economy identified by IEA Bioenergy Task 42.

Scenario	Sustainable Development Scenario	Stated Policies Scenario	Current Policies Scenario
Prices and renewable energy share	• High prices for GHG-intensive products • Share of electricity from renewable sources 100%, surplus electricity available	• Moderate prices for GHG-intensive products • Share of electricity from renewable sources > 50% < 100%	• Relative low prices for GHG-intensive products • Renewable electricity share < 50%
Feedstock availability	• No restrictions (1st, 2nd and 3rd generation are available)	• 2nd and 3rd generation are available	• 1st at current levels. • Non-food biomass predominantly used for bioenergy
Bio-based industries	• Biobased chemicals for all chemical products • Large scale lignocellulosic biomass utilisation • Extensive use of drop-in chemicals from biomass for existing industry • Biogenic CO_2-conversion to chemicals digestion	• Biobased chemicals for high- and moderate-value products • Limited lignocellulosic biomass utilisation • Limited amounts of drop-in chemicals from biomass for existing industry	• Biobased chemicals just for high-value/nice products • No substantial lignocellulosic biomass utilisation • Chemicals from fossil resources as present

To achieve the "sustainable development" scenario as described in Table 8 concerted actions from policy makers, consumers and technology developers are required. Those actions will lead to the co-evolution of renewable energy and advanced technologies for producing bio-based chemicals. Although we will not run out of fossil resources in the near future, the impacts of climate change might trigger environmental and social tipping points, which demands the use of all mitigation options at hand. Environmentally friendly produced bio-based chemicals offers multiple benefits, not just for the reduction of greenhouse gases, but also for the vitalization of rural areas and the development of new biobased production routes.

9. Commercial & Near Market Products

Bio-based bulk chemicals and polymers included historic items with a long history of bio-based production such as citric acid, recently introduced products such as propylene glycol, and products currently in the demonstration stage of development (15). The next section outlines a number of products with the potential for strong growth and supporting industry interest. In addition, various bio-based chemicals are in the pipeline. The scope and flexibility for the production of bio-based chemicals to form the core or add value to biorefinery operation is exemplified in the range of chemicals currently under industrial development. A non-comprehensive list of chemicals currently in development is shown in Table 11 below and a broad selection are discussed in more detail.

Table 11. Global overview of the different chemicals produced by companies at commercial as well as demonstration scale.

Cn	Chemical	Formula	Ox state C	Global Biobased Capacity (kta)[#]	Company	Potential
1	Methane	CH4	-4		Many	Growth[^]
	Methanol	CH4O	-2	43	OCI (BioMCN), Sodra, Carbon Recycling International, *W2C*[*]	Growth
	Formaldehyde	CH2O	0		BASF	Pipeline
	Syn gas	CO	+2	760	Many	Growth
	Formic acid	CH2O2	+3		Avantium	Pipeline
	Carbon dioxide	CO2	+4		Climeworks	Pipeline
2	Ethylene	C2H4	-2	200	Braskem	Growth
	Ethanol	C2H6O	-2	80,800	Many	Growth
	Ethylene oxide	C2OH4	-1	40	Croda, *Biokim*	Growth
	Ethylene glycol (MEG)	C2H6O2	-1	175	India Glycols Ltd, *HaldorTopsoe, UPM, Avantium, ENI/Versalis*	Growth
	Acetic acid	C2H4O2	0	24.5	Sekab, Wacker, Godovari Biorefineries Ltd, Zeachem	Growth
	Glycolic acid	C2H4O3	+1		Metabolic Explorer (Metex)	Pipeline
	Oxalic acid	C2H2O4	+3		Avantium	Pipeline
3	Propane	C3H8	-2.67	40	Neste/SHV	Growth
	Propylene	C3H6	-2		Braskem/Toyota Tsusho, Mitsubishi Chemical, Mitsui Chemicals	Pipeline
	n-Propanol	C3H8O	-2		Braskem	Pipeline
	Isopropanol	C3H8O	-2		Genomatica, Mitsui Chemicals	Pipeline

Cn	Chemical	Formula	Ox state C	Global Biobased Capacity (kta)#	Company	Potential
	Propylene Glycol (1,2-Propanediol)	C3H8O2	-1.33	120	ADM, Oleon, *Avantium*	Growth
	Acetone	C3H6O	-1.33		Green Biologics, Celtic Renewables	Pipeline
	1,3-Propanediol	C3H8O2	-1.33	77	DuPont/Tate & Lyle, *Glory Biomaterial, Shenghong Group*	Growth
	Glycerol	C3H8O3	-0.67	1,500	Many	Growth
	Epichlorohydrin	C3H5ClO	-0.67	540	A.o. Yihai Kerry Group, Jiangsu Yangnong, Advance Biochemical Thailand	Growth
	Lactic acid	C3H6O3	0	>600	Corbion, NatureWorks, Galactic, Henan Jindan, BBCA	Growth
	Acrylic acid	C3H4O2	0		Cargill/Novozymes, ADM/LC Chemicals, Perstorp, Arkema	Pipeline
	3-Hydroxy propionic acid	C3H6O3	0		Cargill/Novozymes	Pipeline
	Malonic acid	C3H4O4	+1.33		Sirrus, Lygos	Pipeline
4	n-Butanol	C4H10O	-2	(10)	Green Biologics, Celtic Renewables	Pipeline
	Iso-Butanol	C4H10O	-2	6-9	Butamax, Gevo	Growth
	Iso-Butene	C4H8	-2		Global Bioenergies	Pipeline
	1,4-Butanediol	C4H10O2	-1.5	30	Genomatica, Novamont, Dupont/Tate & Lyle, Godovari Biorefineries Ltd,	Growth
	2,3-Butanediol	C4H10O2	-1.5		Intrexion	Pipeline
	Tetrahydrofuran	C4H8O	-1.5		Novamont	Growth
	Ethyl acetate	C4H8O2	-1	36	Sekab(JRC), Zeachem, Greenyug	Pipeline
	Butyric acid	C4H8O2	-1		Metex, Kemin, Blue Marble Biomaterials	Pipeline
	Crotonaldehyde	C4H6O	-1		Godovari Biorefineries Ltd,	Growth
	Succinic acid	C4H6O4	+0.5	34	Myriant, Succinity (BASF /Corbion), Reverdia (Roquette)	Growth
5	Isoprene/ Farnesene	C5H8	-1.6		Goodyear/ Genencor, GlycosBio, Amyris	Pipeline
	1,5-Pentanediamine	C5H14N2	-1.6	50	Cathay Industrial Biotech, *CJ Cheiljedang*	Growth

Cn	Chemical	Formula	Ox state C	Global Biobased Capacity (kta)#	Company	Potential
	Methyl methacrylate	$C_5H_8O_2$	-0.8		Lucite/Mitsubishi Rayon, Evonik/Arkema	Pipeline
	Ethyl lactate	$C_5H_{10}O_3$	-0.8		Corbion, Vertec BioSolvents	Growth
	Levulinic acid	$C_5H_8O_3$	-0.4	2-3	Avantium, GFBiochemicals, Circa Group	Pipeline
	Xylitol	$C_5H_{12}O_5$	-0.4	190	a.o. Danisco/Lenzing, Fortress	Growth
	Methylvinyl glycolate	$C_5H_7O_3$	-0.2		Haldor Topsoe	Pipeline
	Furfural	$C_5H_4O_2$	0	360	Many	Growth
	Itaconic acid	$C_5H_6O_4$	+0.4	90	Qingdao kehai, Zhejiang Guoguang, Jinan Huaming	Growth
	Glutamic acid	$C_5H_9NO_4$	+0.4		a.o. Global Biotech, Meihua, Fufeng, Juhua	Growth
6	Caprolactam	$C_6H_{11}NO$	-1		Genomatica / Aquafil	Pipeline
	Lysine	$C_6H_{14}N_2O_2$	-0.67	1,100	a.o. Global Biotech, Evonik/RusBiotech, BBCA, Draths, Ajinomoto	Growth
	Aniline	C_6H_7N	-0.67		Covestro	Pipeline
	Sorbitol	$C_6H_{14}O_6$	-0.33	1,800	a.o. Roquette, Cargill, ADM, Ingredion	Growth
	Adipic acid	$C_6H_{10}O_4$	-0.33		Genomatica	Pipeline
	Isosorbide	$C_6H_{10}O_4$	-0.33	20	Roquette	Growth
	Cyrene	$C_6H_8O_3$	-0.33		Circa Group	Pipeline
	FDCA	$C_6H_4O_5$	+1		Avantium, ADM/Dupont, Corbion, Stora-Enso, Annikki	Pipeline
	Glucaric acid	$C_6H_{10}O_8$	+1		Rivertop renewables	Pipeline
	Citric acid	$C_6H_8O_7$	+1	2,000	a.o. Cargill, DSM, BBCA, Ensign, TTCA, RZBC	Growth
7	Pentamethylene diisocyanate (PDI)	$C_7H_{10}N_2O_2$	0		Covestro (70% biobased content), Mitsubishi Chemical	Growth
8	p-Xylene	C_8H_{10}	-0.25		Annellotech, Origin Materials, BioBTX, Tesoro	Pipeline
	Terephthalic acid	$C_8H_6O_4$	+0.25		UOP, Annellotech	Pipeline
9	Pelargonic acid	$C_9H_{18}O_2$	-1.56	25	Matrica (Novamont/Versalis JV)	Growth

Cn	Chemical	Formula	Ox state C	Global Biobased Capacity (kta)#	Company	Potential
	Azelaic acid	C9H16O4	-0.89	25	Matrica (Novamont/Versalis JV), Emery Oleochemicals	Growth
10	Sebacic Acid	C10H18O4	-1	200	A.o. Arkema (Casda Biomaterials)	Growth
11	UDDA (undecanedioic acid)	C11H20O4	-1.09	24	Arkema	Growth
12	12-Amino-dodecanoic acid	C12H25NO2	-1.5	25	Evonik	Growth
	DDDA (Dodecane-dioic Acid)	C12H22O4	-0.17		Cathay Industrial Biotech	Growth

*Companies in *italic* indicates that the production of that chemical is in the pipeline for that company

Capacity numbers in kilotonnes per annum (kta) are indicative

ˆ Growth means commercial production is in place and there is potential for growth depending on a wide range of dominators (e.g. oil price, carbon tax, consumer wishes)

9.1 C1 containing compounds

Methane

Methane is the main component of Biogas. Biogas is produced by the anaerobic digestion or fermentation of biodegradable materials such as biomass, manure, sewage, municipal waste, green waste, plant material, and crops. Biogas comprises primarily methane (CH_4) and carbon dioxide (CO_2) and may have small amounts of hydrogen sulphide (H_2S), water and siloxanes. The methane in the biogas needs to be cleaned and upgraded for most of the biofuels and chemicals applications. Biogas is produced using anaerobic digesters. There are two key processes: Mesophilic and Thermophilic digestion, which can be operated continuously or batch-wise under wet (5 – 15% dry matter) or dry (over 15% dry matter) conditions in single, double or multiple digesters (100).

Methanol

Methanol can easily be formed from syngas. In the process developed by the Swedish company Chemrec, black liquor was gasified and used for the production of methanol, which was subsequently dehydrated to dimethylether (DME), an interesting biofuels pursuit by Volvo. Currently, the plant is not running. BioMCN also produces methanol but their primary feedstocks are biogas and CO_2, glycerol, the main side-product of biodiesel production has been used before. Enerkem uses domestic waste to produce partly biobased syngas for a wide range of Applications. Air Liquide, Nouryon, the Port of Rotterdam, Shell together with Enerkem are developing an advanced 'waste to chemicals' (W2C) plant in Rotterdam. The aim is that this will be the first plant of this type in Europe that make valuable methanol for chemicals and bio-fuels usage out of non-recyclable waste materials (101). Methanol can also be produced from (atmospheric) CO_2 as demonstrated by the Icelandic company Carbon Recycling International (24, 25).

Formic acid

Formic acid is produced in equimolar amounts in the Biofine process and other C6 based dehydration processes for levulinic acid production (33). At the moment it is mainly produced as a value-adding co-product. Formic acid can also be produced by electrochemical reduction of CO_2.

Carbon Monoxide (CO)

According to the International Energy Agency (IEA) Bioenergy Task 33E—Thermal Gasification of Biomass database (102), there are 114 operational biomass gasification plants globally, 14 idle/on hold biomass gasification plants, and 13 under construction/planned biomass gasification plants. This results in a total number of 141 plants, with the following end use of the syngas produced: 106 plants for power production, with global electric power produced from biomass-derived syngas ~ 356 MW and global thermal power produced from biomass-derived syngas ~ 185 MW; 24 plants for liquid fuel production (methanol, ethanol, DME, FTS, diesel, gasoline), with global production of liquid fuel from biomass-derived syngas ~ 750,000 t/year; 8 plants for gaseous fuel production (SNG and H2), with global production of gaseous fuel from biomass-derived syngas ~ 3.2 × 108 Nm3/year; 7 plants for chemical production (various), with global production of chemical from biomass-derived syngas ~ 9,000 t/year. It is worth highlighting that in four plants, syngas is used for both power production and fuel production (28).

Carbon Dioxide (CO_2)

Carbon Dioxide is a major greenhouse gas and is produced as waste stream in many energy and chemical processes. However, CO_2 is, in addition to biomass, the only renewable source of carbon widely available. The purity of the CO_2 produced can vary a lot and can be restrictive for downstream applications. Climeworks, a Switzerland-based clean technology company, has launched its first commercial plant in Hinwil, Zurich that can capture 900 tons/year of CO_2 directly from ambient air. In this case the CO_2 is supplied to a nearby greenhouse to help grow vegetables. The use of carbon dioxide as chemical feedstock has been extensively discussed in the book edited by Prof. Michele Aresta (103) as well as more recent report (104) and is outside the scope of this overview. However, it is worth mentioning that the German company Covestro has developed several applications (e.g. Mattresses, sports floors, clothing) containing substantial amounts of CO_2 (105).

9.2 C2 containing compounds

Ethylene

Ethylene is the basis for a range of high-volume plastics including polyethylenes (high density polyethylene (HDPE), low density polyethylene (LDPE) and linear low-density polyethylene (LLDPE)), polyvinylchloride (PVC) and polyethylene terephthalate (PET) (Figure 14). Global ethylene production was 150 million tonnes in 2016 and growing to 175 million tonnes in 2021 (106).

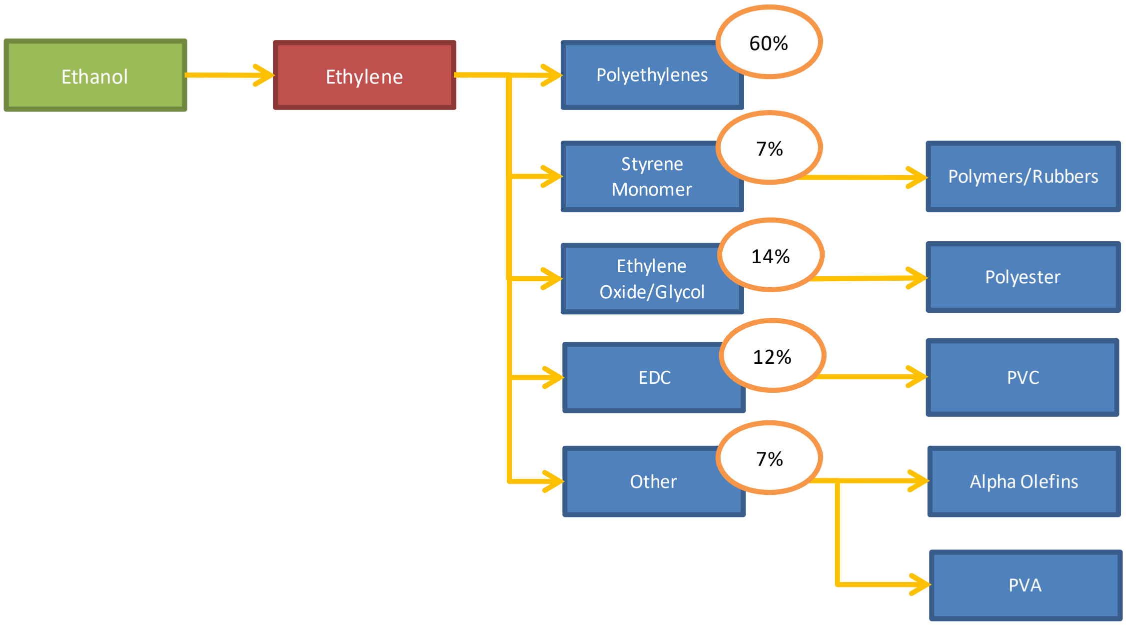


Figure 14. Ethylene value chain (Adapted from Higson et al. (107)).

Ethylene can be readily produced through the dehydration of bioethanol or through the cracking of bionaphtha. Bionaphtha is produced during the processing of renewable feedstocks in processes such as Fischer Tropsch fuel production; it comprises of molecules with a carbon chain length ranging from about C5 to C9. Global ethanol production has been expanded rapidly due to the global demand for biofuels. The leading producers of bioethanol are the USA and Brazil. The vapour phase dehydration of ethanol at 400 °C gives ethylene with >99% conversion and >99% selectivity. The production of 1 tonne of ethylene requires 1.7 tonnes of ethanol. Given the large scale of ethylene plants (>300,000 tonnes) a single ethylene plant would be a considerable consumer of ethanol.

Box 6. Braskem

Braskem is the largest chemical producer in the Americas and a global leader in polypropylene production. In 2007 they launched a bio-based polyethylene produced from sugar cane derived ethanol. The launch was followed by the construction of a 200,000 tonnes capacity plant in Triunfo, Rio Grande do Sul costing R$500 million (~$300 million). The plant will produce a wide range of HDPE and LLDPE grades. Braskem LCA studies show that 2.5 tonnes of carbon dioxide are sequestered for every 1 tonne of polyethylene produced. Braskem are now supplying to a range of companies including TetraPak and LEGO.

http://plasticoverde.braskem.com.br/site.aspx/plastic-green

The largest consumer of ethylene is polyethylene e.g. HDPE and LDPE (Figure 14). In 2010, the Brazilian chemical producer Braskem commissioned a 200,000 tonnes capacity plant to produce polyethylene from sugar cane derived ethanol. Currently, a further significant use of ethylene is in the production of mono ethylene glycol (MEG), see below.

Ethanol

The production of bio-ethanol is by far the most mature biobased chemical produced. The vast majority is used for transportation fuels but significant amounts of ethanol are used for the production of biobased ethylene, ethylene oxide and MEG. Smaller amounts are used for several other products. It is clear that the ethanol market is dominated by the United States and Brasil (Figure 15).

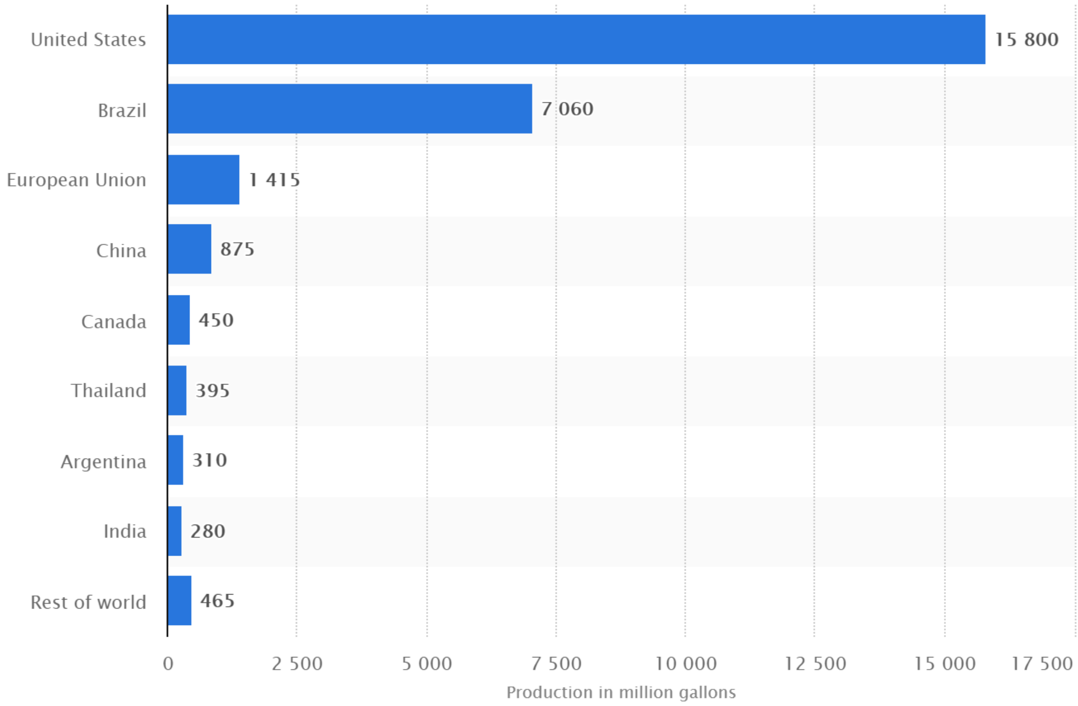


Figure 15. Global ethanol production in million gallons in 2017 (108).

Ethylene Oxide

Biobased ethylene oxide is made via ethanol and ethylene. In addition to be an intermediate for biobased MEG Croda uses biobased ethylene oxide for the production of 100% renewable non-ionic surfactants such as ethoxylated alcohols, ethoxylated fatty acids and ethoxylated quaternary amines. Croda has started up its $170 million bio-based ethylene oxide production facility at its Atlas Point facility in New Castle, Delaware. The facility will use corn-based ethanol as feedstock. It was said that the USDA's BioPreferred Program was a big driver in the US to increase interests in renewable chemicals and bio-based products. The program mandates purchasing requirements for all US federal agencies and their contractors to increase the purchase and use of bio-based products. The program also establishes minimum bio-based content in 97 different product categories and also provides a voluntary USDA biobased certification labelling program (109).

Mono-Ethyleneglycol (MEG)

The current MEG market is around 28 million tonnes/year, growing to 50 million tonnes/year in 2035. To keep up with the growing demand of polyesters, an additional 1.2 million tonnes of annual MEG capacity is required, every year, in the next 15-20 years. More than 90% of the current MEG is co-polymerised with terephthalic acid to produce poly(ethylene)terephthalate (PET), which is commonly used for production of plastic bottles and textile fibres. The production of MEG from renewable resources has allowed several companies to use bio-based PET in product packaging. Coca Cola and Danone are using bio-based PET in their Dasani and Volvic bottled water ranges. However, the conversion of biomass via ethanol into bio-MEG is a 4-step process with poor atom efficiency. This results in a high cost position of ethanol derived bio-MEG resulting in a substantially decreased global production of ethanol derived bio-MEG. At the moment India Glycols Ltd. is the only company making ethanol-derived ethylene glycol for incorporation into PET. Fortunately, several companies (Avantium, HaldorTopsoe/Braskem, UPM, ENI Versalis) are scaling-up carbon efficient, direct routes to bio-MEG.

Acetic Acid

Godavari Biorefineries Ltd. (GBL) restarted its production of bio-based acetic acid at its Sakarwadi facility in Maharashtra from August 2018 (110). GBL will produce acetic acid from molasses-based ethanol, backed by strong demand from customers as they have expressed the need for renewable raw materials adhering to the 'green chemistry principles'. Production capacity will be around 7,000 tons per year. GBL said it has received interest from local and global consumers for niche specialty applications of bio-based acetic acid including applications in food and pharmaceuticals.

Other C2 based building blocks

Several other C2 based building blocks are currently used at scales around 1 million tonnes/year and up. Important examples are dichloroethane (formed by chlorination of ethane), vinylchloride (formed by dehydrochlorination of dichloroethane), and ethylenediamine (reaction of 1,2-dichloroethane and ammonia). As soon as sufficient market volumes of biobased ethylene become available and markets are ready for these chemicals they can easily be produced using traditional chemistry and existent infrastructure.

9.3 C3 containing compounds

Propane

Neste has started up the world's first large-scale renewable propane production facility in Rotterdam in the Netherlands. The renewable propane has been delivered to SHV Energy, who will market and sell the product to its customers across Europe as BioLPG. Neste's new facility has a production capacity of 40,000 tonnes per year and SHV Energy will be the exclusive distributor, supplying 160,000 tonnes over four years. Neste's Rotterdam refinery primarily produces premium-quality Neste MY Renewable Diesel from various waste and residues as well as vegetable oils. The new unit will purify and separate renewable propane from the side-stream gases produced by the refinery (111).

Propylene

Global propylene demand is approximately 50 million tonnes. It is used predominately in the production of polypropylene (60% of propylene demand), but is also consumed in propylene oxide, acrylontrile, acrylic acid and butanol production. Various routes have been suggested for bio-based propylene production (112).

Polypropylene derived from bio-based naphtha, however, has been on the commercial market for several years in a process led by SABIC and Dow at Terneuzen, the Netherlands, using the biomass balance approach (see chapter 3) to market their bio-derived polypropylene. Neste has the ability to supply bio-based naphtha as feedstock for biomass balance-based polyolefins. However, IKEA and Neste recently announced that they are now able to utilize renewable residue and waste raw materials, such as used cooking oil, as well as sustainably-produced vegetable oils in the production of plastic products. The pilot at commercial scale started during fall 2018. It is the first large-scale production of renewable, 100% bio-based polypropylene plastic globally (113).

Table 12. Routes for bio-based production of propylene.

Raw Material	Process
Ethanol	Ethanol is readily produced from carbohydrates. Dehydration of ethanol gives ethylene which can be dimerised to give butenes. In a metathesis reaction butene and ethylene can be reacted to give propylene
Butanol	Butanol can be produced by fermentation of carbohydrates or via the production of syngas by biomass gasification. Dehydration of butanol gives butene which can then be reacted with ethylene in a metathesis reaction to give propylene
Propane	Propane produced as a by-product of biodiesel production can be dehydrogenated to propylene
Vegetable oil	Vegetable oil can be converted to propylene by catalytic cracking
Methanol	Gasification of biomass gives syngas which can be reduced to methanol. Propylene can be produced using methanol to olefins technology.

There have been several initiatives for the production of fermentation-based polypropylene (PP) within the past several years but most of these initiatives have been put on hold due to cost economics. Braskem has developed a technology to produce polypropylene via a fermentation process in collaboration with Novozymes and Cargill but the companies have put this R&D on hold. Global Bioenergies also has the technology to produce propylene from butane but the company is currently focusing on the fuels market for its isobutene.

n-Propanol

A couple of years ago a Braskem patent was published (114) which describes the fermentative production of n-propanol and the subsequent dehydration into propylene.

Isopropanol

France-based Global Bioenergies has started the scale-up phase of a new fermentation process converting sugars to acetone and isopropanol using bacterial strains with an engineered cellular metabolism. These two C3 compounds are extensively used in a wide range of industries such as solvents, cosmetics, and other materials, and can also be converted subsequently into propylene (115). Isopropanol production via fermentation (116, 117) and its conversion into propylene (118) have been reported by Mitsui Chemicals, INC.

Propylene Glycol (1,2-Propanediol)

Propylene glycol has a range of uses, including industrial applications such as unsaturated polyester resins, coolants and antifreeze, hydraulic and brake fluid, aircraft de-icing fluid, heat transfer fluids, paints and coatings. There is a market for higher grade propylene glycol in fragrance, cosmetics and personal care applications, food and flavourings, pet food/animal feed and in pharmaceutical formulations (Figure 16).

The market value of propylene glycol was 3.6 million $ in 2016 with a CAGR estimated at 5.8% per year up to 2021 (119). The future expansion of bio-based propylene glycol will be dependent on the price and availability of glycerol which is in turn linked to the development of the biodiesel industry.

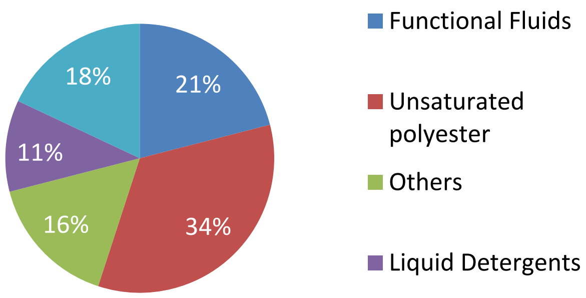


Figure 16. Market breakdown for propylene glycol.

In 2010 the agricultural processor Archer Daniels Midland (ADM) commissioned a propylene glycol plant with a capacity of 100,000 tonnes (see box). A number of companies also hold technology for propylene glycol production from C5 and C6 sugars: HaldorTopsoe/Braskem, Avantium, UPM, Fortress (formerly S2G) (120).

Box 7. Archer Daniels Midland (ADM)

ADM are building on their position as global leader in agricultural processing. Under the brand Evolution Chemicals™, they are developing a chemical portfolio based on renewable raw materials. ADM operates a propylene glycol plant with an annual production capacity of 100,000 tonnes. The plant will produce both industrial and USP grades for use in a range of applications. The feedstock for the process is glycerol derived from soybean or canola. ADM life cycle analysis of their propylene glycol shows an 80% reduction in greenhouse gas emissions when compared with petrochemical based production. Alternative feedstocks for propylene glycol production include sorbitol and dextrose.

https://www.adm.com/products-services/industrials/propylene-glycol

1,3-Propanediol

In 2004 the chemical producer DuPont formed a joint venture with agriculture products company Tate & Lyle (121). The joint venture, DuPont Tate & Lyle BioProducts, has successfully commercialised the production of 1,3-propanediol (PDO) from renewable resources under the trade names Susterra® and Zemea®. Susterra® PDO is targeted at industrial application while Zemea® is aimed at the personal care sector. DuPont Tate & Lyle BioProducts operate a 60,000 tonne capacity production plant in Loudon, Tennessee, US (122). Susterra® PDO has been used in a range of products from textiles to coatings and engineering plastics. Susterra® PDO is co-polymerised with terephthalic acid to produce poly(trimethylene) terephthalate (PTT) sold by DuPont under the trade name Sorona® (123). Sorona® PTT has been targeted at clothing, carpet and automotive textile markets. PDO can also be used for a variety of other applications including personal care products, solvents, and lubricants (124). In China, Glory Biomaterial and Shenghong Group are developing a PDO process with glycerol as feedstock (105).

Acetone

Acetone is widely used chemical, both as a chemical feedstock as well as a solvent. About half of the world production is used for the production of methyl methacrylate. Renewable acetone is part of the Celtic Renewables portfolio (125). Renewable acetone is also part of the portfolio of Green Biologics (126). The acetone is produced through fermentation of sugars from renewable feedstocks.

Epichlorohydrin

With a market size of 1.3 million tonnes, epichlorohydrin is predominately used in the production of epoxy resins (76%) and other resins and polymers. Niche applications include paper reinforcement e.g. tea bags and coffee filters and water treatment. Solvay sold its 58.77% stake in its Thai subsidiary, Vinythai PCL, to the Japanese firm AGC Asahi Glass for €435 million in 2017 (127). With the sale, Solvay has ceased to be a producer of bio-ECH and instead will still be active in licensing its glycerol-to-ECH Epicerol® technology. The fast majority of glycerol based epichlorhydrin production is located in Asia with China be the predominant country. Total glycerol capacity is over 500,000 tonnes annually, but because of low oil prices not all capacity is currently used.

Lactic acid

Lactic acid is a bulk chemical with a global production capacity of over 600,000 tonnes in 2019. Lactic acid has a long history of applications in the food and beverage sector as a preservative and pH adjusting agent. It is used in the pharmaceutical and chemical industries as a solvent and a starting material in the production of lactate ester. Lactic acid is also used as a standard or active ingredient in personal care products, due to its moisturising, pH regulating and skin lightening properties.

Current and predicted large growth rates for lactic acid lie in its use in bio-based polymer production. Polymerisation of lactic acid produces the biodegradable polymer polylactic acid (PLA), which is used in food packaging including rigid containers, shrink wrap and short shelf-life trays, as well as mulch films and rubbish bags. European demand for PLA is currently 25,000 tonnes per year, and could potentially reach 650,000 tonnes per year in 2025. Polylactide may also be used as a fibre for clothing, carpets and in industrial applications.

The global leader in PLA production is NatureWorks based in Blair Nebraska, USA. The Dutch company Corbion is the world leader in lactic acid production and is actively exploiting their technology base through its joint-venture Total-Corbion. The company recently announced the opening of their 75,000 tonnes/year plant in Thailand (128). Other companies active in PLA include Galactic, Henan Jindan and BBCA in China (129).

Box 8. NatureWorks LLC

NatureWorks is a world-leading polylactic acid (PLA) biopolymers supplier and innovator. Its Ingeo portfolio of naturally advanced materials made from renewable, abundant feedstocks with performance and economics can compete with oil-based intermediates, plastics, and fibers. NatureWorks is jointly owned by Thailand's largest chemical producer, PTT Global Chemical, and Cargill, which provides food, agriculture, financial and industrial products and services to the world. NatureWorks manufacturing facility of 150.000 metric tonnes is located in Blair, Nebraska, USA. In 2016, a new fermentation laboratory to develop commercial-scale methane to lactic acid fermentation technology was opened. NatureWorks polymer products span multiple industries and categories, including rigid and flexible packaging solutions; food serviceware; health and personal care; durable products in home, appliance, and electronic categories; and 3D printing filament.

https://www.natureworksllc.com/

The development of PLA applications has been hampered by some of its functional characteristics. These short-comings are now being overcome through the use of additive packages and importantly through the controlled polymerisation of defined isomers of lactic acid (130-135).

Acrylic acid

Acrylic acid is an important chemical building block used in the production of polyacrylates and commodity acrylates. The global acrylic acid market is estimated to reach USD 13.21 Billion by 2020 (136). Commodity acrylates include methyl, ethyl, n-butyl and 2-ethylhexyl acrylate which are used in a variety of industrial applications including coatings, adhesives and sealants, textiles and fibres, polymer additives/impact modifiers and films. Polyacrylates are widely used a super absorbent polymers. The table below shows the potential of acrylic acid and its derivatives (137, 138).

Table 13. The potential of acrylic acid and its derivatives.

Biobased Product	Classifications	Market Opportunity	Market Size
Acrylic Acid	Adhesives, polymers	Acrylates (e.g., coatings, adhesives), co-monomer, superabsorbent polymers, detergent polymers	Markets for acrylic acid derivatives in the previous column are 1 million tonnes per year, at a market price of $1.06 per kg.
Acrylonitrile	Polymers	Acrylic fibers (carpets, clothing), acrylonitrile-butadiene-styrene and styrene-acrylonitrile (pipes and fittings, automobiles, furniture, packaging), nitrile rubber copolymers, adiponitrile, acrylamide	Markets for acrylonitrile derivatives in the previous column are 1.4 million tonnes per year, at a market price of $0.68 to $0.81 per kg.
Acrylamide	Resins	Polyacrylamide, comonomers (styrenebutadiene latex, acrylic resins, and many others)	Markets for acrylamide derivatives in the previous column are 94,000tonnes per year, at a market price of $3.88 to $4.10 per kg.

At least five routes have been reported for the production of bio-based acrylic acid. A well-known route to bio-acrylic acid is through the dehydration of 3-hydroxypropionic acid (3-HP), which is derived via fermentation of sugar. Processes have also been developed to produce 3-HP from glycerol (either via dehydration to acrolein followed by oxidation or in a single step oxydehydration, Evonic has published a patent for converting glycerol into 3-hydroxypropion-aldehyde, which can also serve as precursor for acrylic acid production (139, 140). Novomer has developed a route to acrylic acid via polypropiolactone (PPL) from bio-ethylene oxide (bio-EO) and Genomatica has several patents involving production of bio-based acrylic acid using sugar-based fumaric acid via methathesis transformation (with a sufficient amount of ethylene). Alternatively, sugar-derived lactic acid can be dehydrated to form acrylic acid. Corbion reported the possibility of producing acrylic acid through catalytic cracking of lactide and PLA at low temperatures with up to 58% yield. This transformation is catalysed by strong acids in the presence of bromide or chloride salts. Acrylic acid can be produced directly from PLA or oligolactic acid offering a new route to the chemical recycling of PLA into valuable building blocks (141). It is worth noting that biobased acrylic acid production remains in the early stages and none of the biobased technologies have been successfully proven at commercial scale. In the beginning of 2015 BASF decided to abandon the collaboration with Cargill and Novozymes into biobased acrylic acid.

Malonic acid

Malonic acid is a high-value specialty chemical used in the production of a variety of pharmaceuticals, flavours, fragrances, and specialty materials, and is currently produced using petrochemical-based chloroacetic acid and sodium cyanide and was listed as one of the top 30 chemicals to be produced from biomass by the US Department of Energy (64, 65). Lygos, a California-based synthetic biology company, has pioneered the world's first bio-based production of malonic acid from sugar and has been shipping tonne quantities of its Bio-malonic™ acid to customers. Sirrus Inc., a developer of next-generation crosslinking platforms for coatings and adhesives, and BASF's Coatings Division have formed a collaboration to further develop a new class of high-performance automotive coatings based on Sirrus's proprietary methylene malonate technology. Methylene malonate monomers and their oligomeric crosslinking derivatives reportedly have the unique advantage of polymerising rapidly at ambient temperatures – without the need for ultraviolet light, high temperatures or high solvent loading required by current automotive coating systems.

Other C3 based building blocks

The C3 based chemical building block arena contains the largest, and most diverse, of the commercial, and in the pipeline, activities. Besides the clear importance of these building blocks for industry, the fact that carbohydrates, as well as fats and oils (glycerol), are feedstocks for this class of components has driven the development in recent years. Other C3 based building blocks that are of interest to be replaced by biobased equivalents, include acrolein, 3-hydroyxypropionic (HPA) and propionic acid (reduction of lactic acid). Most are currently used at scales around 1 million tonnes per year and up.

9.4 C4 containing compounds

n-Butanol

A number of companies are commercializing n-butanol and isobutanol production. The bio-based production of n-butanol is an historic process dating back to the early 20th century (142). n-Butanol is produced fermentative and is co-produced with acetone and ethanol, the processes being known as the acetone-butanol-ethanol (ABE) process. Bio-based n-butanol production ceased in the 1980's due to the low cost of crude oil and competing petrochemical routes. However increasing oil prices and the interest in renewably sourced chemicals have renewed interest. The higher energy content and compatibility with existing infrastructure makes butanol an interesting biofuel proposition for the future. Current high production costs lead producers to focus on the development of higher priced chemical applications. n-Butanol is used in a wide range of polymers and plastics and is also used as a solvent in paints and chemical stabilisers (Figure 17). In 2006 n-butanol had a market size of 2.8 million tonnes.

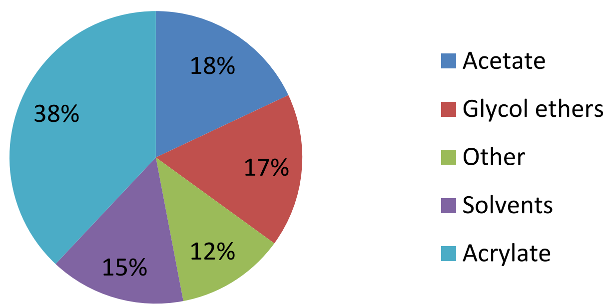


Figure 17. n-Butanol consumption in 2008.

Bio-based butanol production has been re-established in China to supply its growing chemicals market. Cathay Industrial Bio currently produces corn-based n-butanol for chemical applications at its 100,000 tonnes/year biorefinery in Jilin Province, China. The facility, which uses the acetone-butanol-ethanol (ABE) fermentation route, started production in 2009 of about 65–70% butanol, 20–25% acetone and 5–10% ethanol (105). Beginning 2017, Green Biologics started operations of its n-butanol production facility in Little Falls, Minnesota but the facility ceased operation in middle of 2019 due to lack of funding. Green Biologics is now pursuing a new business strategy (126). A major outlet for the n-butanol is as a burning fuel.

iso-Butanol

Butamax™ Advanced Biofuels (143), a joint venture between energy producers BP and the chemical producer DuPont, and Gevo Development (144) are focused on the production of isobutanol. The production of isobutanol creates the opportunity for isobutylene production and a range of downstream products. It is thought that both companies are currently producing well below name plate capacity (145).

1,4-Butanediol

1,4-Butanediol is a versatile chemical intermediate especially for polymer production due to its two alcohol groups. It can react with diacids to polyesters, with di-isocyanates to polyurethanes, or with phosgene to polycarbonates. 1,4-Butanediol is used in the manufacturing of thermoplastic polyurethanes (TPU), Spandex, and polybutylene terephthalate (PBT). It is also used in pharmaceuticals, solvents (THF), coatings, co-polyester ethers and electronic chemicals (124). BDO is currently produced form acetylene or propylene oxide and has a market size of nearly 1 million tonnes. It serves as a raw material for a range of important chemicals including polymers polybutylene terephthalate (PBT) and polybutylene succinate (PBS). BDO also acts as precursor to a number of speciality chemicals used as solvents or as raw materials in pharmaceuticals and agrochemicals (Figure 18). Novamont operates a 30,000 tonnes per year 1,4-butanediol plant in Bottrighe, Italy using Genomatica technology.

THF (Tetrahydrofuran)

Approximately 40% of the fossil-based BDO is consumed in tetrahydrofuran (THF) production. THF is a widely used (342,000 tonnes market in 2006) as a performance solvent and a feedstock for the production of polytetramethylene ether glycol used in the production of polyurethane polymers. It is also used in the pharmaceutical industry. During the polymerization reaction 1,4-butanediol, used as an excess reagent, undergoes a cyclization reaction giving rise to tetrahydrofuran (THF). Water and various organic solvents containing THF are treated in a distillation plant. The pure THF recovered from the plant is transferred to a special storage basin and sold to customers.

Ethyl acetate

Strobel Energy Group announced that it has executed an Engineering, Procurement and Construction (EPC) agreement with Prairie Catalytic, LLC, a subsidiary of Greenyug, LLC, to design such as paints, coatings, pharmaceuticals, adhesives and a variety of consumer goods (124). The Prairie Catalytic production facility will be located adjacent to the Archer Daniels Midland Company's Corn Processing Plant in Columbus, Nebraska which will supply the project with Bio-Ethanol feedstock and other services. The capacity of the plant is believed to be around 50,000 tonnes per year, equivalent to 2% of the world demand (146).

Crotonaldehyde

Crotonaldehyde is an unsaturated aldehyde with the formula (CH3CH=CHCHO) and therefor a versatile intermediate in organic synthesis. It occurs in a variety of foodstuffs, e.g. soybean oils.

Crotonaldehyde can be chemically produced by the aldol condensation of acetaldehyde. Its main application is as a precursor to fine chemicals. Sorbic acid, a food preservative, and trimethylhydroquinone, a precursor to the vitamin E, are prepared from crotonaldehyde. Other derivatives include crotonic acid and 3-methoxybutanol (26). Crotonaldehyde is commercially produced by Godovari Biorefineries Ltd.

Succinic Acid

Succinic acid is currently a high volume speciality chemical produced by catalytic hydrogenation of petrochemical maleic acid or anhydride. However with cost reductions delivered through production based on bacterial fermentation of carbohydrates, large volume commodity markets could be accessed (124). Succinic acid can be converted to 1,4-butanediol (BDO) and other products (Figure 18).

The production of succinic acid has attracted a number of industry players (105). The first to demonstrate their technology at scale was BioAmber, however, unfortunately Bioamber ceased operation. Other companies looking to commercialise succinic acid include Reverdia (Roquette) (147), technology developer Myriant Technologies (now GC Innovation America (148)) and Succinity a J.V. between Corbion and BASF.

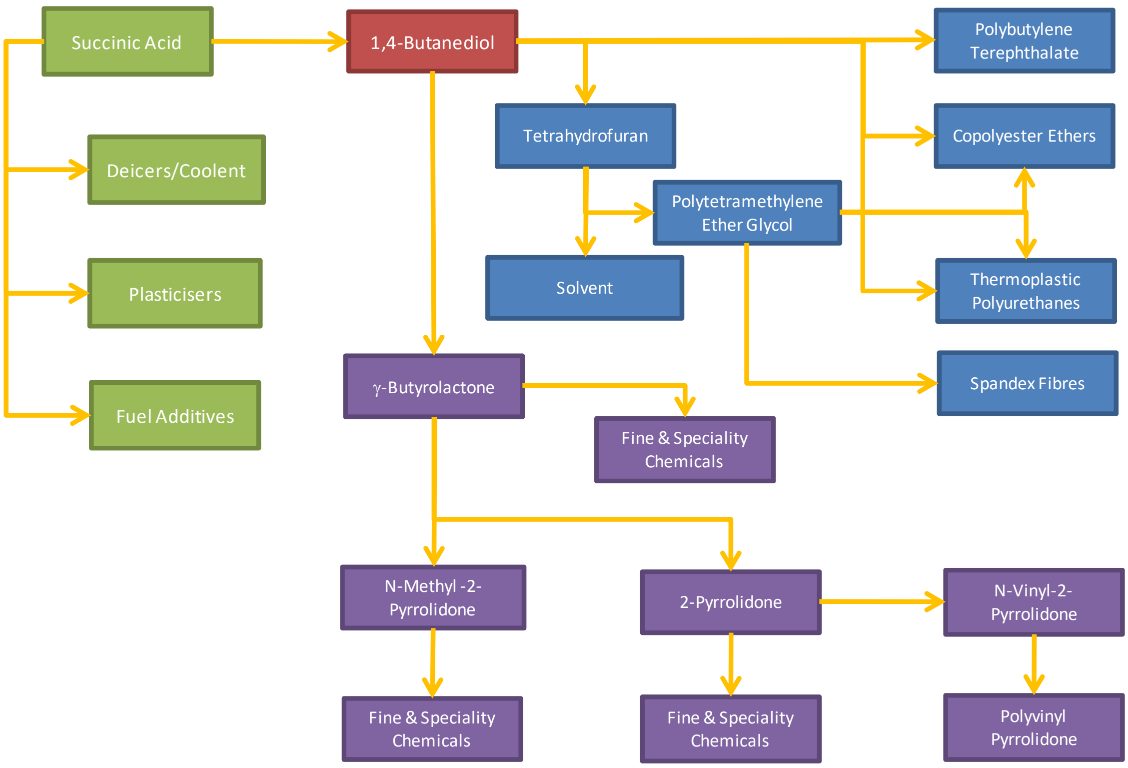


Figure 18. Potential succinic acid and 1,4-butanediol value chain.

Box 9. Reverdia (Roquette)

Reverdia was created for the production, commercialisation and market development of sustainable bio-succinic acid. Biosuccinium® is a leading bio-based chemical building block which offers the chemical industry a real alternative to various oil-based di-acids. Based on a patented fermentation technology with a best-in-class environmental footprint, Reverdia's bio-succinic acid has a broad range of applications, from packaging to footwear as well as cosmetics. In 2012, Reverdia began operating the world's first dedicated, large-scale plant for succinic acid production from renewable resources in Cassano, Spinola, Italy. The 10,000 tonnes/year plant was the first commercial facility of its kind to use low-pH yeast technology. Since those early days, Reverdia has surpassed its planned technical milestones, growing from a biotechnology start-up to a co-development partner (147).

https://reverdia.com/about/company-overview/

Other C4 based building blocks

Several other C4 based building blocks are currently used at scales around 100,000 tonnes/year and up. Important examples are iso-butene, 2,3-butanediol, tetrahydrofuran (THF, from succinic acid), butyric acid and 1,4-butanediamine (formed from succinic acid). Another interesting building block is (*R*)-3-hydroxybutyric acid. This building block can be produced by the (enzymatic) hydrolysis of the biosynthesized PHB or via direct biosynthesis routes (149).

9.5 C5 containing compounds

Isoprene / Farnesene (Biohydrocarbons)

The fermentation of carbohydrates to biohydrocarbons is the latest wave of targets for bio-based chemical production. This opportunity is in part due to the recent advances in synthetic biology, which is allowing industry to design microbes for the production of a new range of molecules (124).

Isoprene is a five carbon hydrocarbon used primarily in the production of polyisoprene rubber, styrenic thermoplastic elastomer block copolymers and butyl rubber. Isoprene is found in products ranging from surgical gloves to car tyres. Isoprene has a market value of $1-2 billion. The production of isoprene from renewable resources (BioIsoprene™) is the target of a joint venture between the Goodyear Tire and Rubber Company and the biotechnology company Genencor (now DuPont Industrial Biosciences). Using development samples of BioIsoprene™ from Genencor, Goodyear have produced a synthetic rubber for incorporation in a concept tyre demonstrating the equivalence of BioIsoprene™ with petroleum derived isoprene (150), the current status of the development is unknown.

The U.S. company Amyris is developing synthetic biology as a technology platform (151). Amyris have developed a process for the production for trans-ß-farnesene under the trade mark Biofene™. Farnesene is a 15 carbon isoprenoid which could be used as a diesel fuel or a speciality chemical. Amyris are introducing Biofene™ into the marketplace through a contract manufacturing agreement with Tate & Lyle.

Methyl methacrylate (MMA)

The principal application, consuming approximately 80% of the MMA, is the manufacture of polymethyl methacrylate acrylic plastics (PMMA). MMA is also used for the production of the co-polymer methyl methacrylate-butadiene-styrene (MBS), used as a modifier for PVC. Lucite International is the world's leading supplier of MMA. Methacrylates polymerize easily to form resins and polymers with excellent performance characteristics including exceptional optical clarity, strength and durability - especially in aggressive all weather or corrosive environments. They can also be co-polymerized with other monomers to form a broader range of products typically used for paints, coatings and adhesives.

Lucite International has developed the Alpha technology, which is a two-stage, high-yield patented process route to MMA that liberates the industry from its traditional dependence on acetone, hydrocyanic acid and isobutylene. Developed and piloted over a 12-year period, the Company's first world-scale Alpha plant in Singapore was commissioned in 2008 and is now fully operational. It has a capacity of 120,000 tonnes per year.

The Alpha technology uses ethylene, methanol and carbon monoxide as readily available and potential biobased raw materials. In addition, Alpha has benefits regarding cost (advantage of around 40% over conventional MMA technology) and lower capital investment and variable costs and low environmental impact (152).

Ethyl Lactate

Ethyl lactate is another lactic acid derivative that has recently been commercialized. It is an environmentally benign solvent with properties superior to many conventional petroleum-based solvents. It can be blended with methyl soyate derived from soybean oil to create custom-tailored solvents for various applications. Until recently, the use of ethyl lactate has been limited owing to high production costs; selling prices for ethyl lactate have ranged between $3.30 and $4.40/kg, compared with $2.00 and $3.75/kg for conventional solvents. With advances in lactic acid fermentation, and separations and conversion technologies, retail costs have been driven down to as low as $1.87/kg (153).

More than 4.5 million metric tonnes of solvents is used in the United States annually, and it has been suggested by industry experts that ethyl lactate could replace conventional solvents in more than 80% of these applications. However, it has to be taken into account that the boiling point for ethyl lactate is at 151- 155 °C and therefore much higher than for most fossil based solvents. Consequently, the application of ethyl lactate as solvent can involve a re- design of products (e.g. paint, glue etc.) and might encounter specific problems, regarding for instance drying time, for specific applications. Therefore ethyl lactate is not a classical "drop-in" bulk chemical because its application is dependent on industry cooperation in order to adopt existing product formulation for replacing petrochemical solvents. From the chemical industry perspective this substitution is often seen as complicated as the development of a new product.

Vertec BioSolvents, Inc. offers a full line of bio-based solvents derived from renewable resources and solvent blends that provide high performance as formulating ingredients, carrier solvents and/or cleaning solvents. The main ingredient in most blended products is VertecBio™ EL ethyl lactate, a corn derived ester solvent with excellent solvating ability for many resins, pigments, gums, soils, greases, etc. In most applications, however, performance can be enhanced by the addition of co-solvents and/or other ingredients. As a formulating ingredient, EL and its blends provide high solvating capacity, thus enabling production of concentrated or high-solids products. As cleaning solvents, they are very effective against a wide variety of contaminants (153). Applications targeted by Vertec Biosolvents include conventional solvents that are under environmental scrutiny such as methylene chloride, methyl ethyl ketone, and *N*-methyl pyrrolidone (153). Corbion has developed a range of L-lactate esters called PURASOLV® that enhance solvency in agrochemical formulations. Besides ethyl lactate also the methyl-, n-propyl, n-butyl-, and ethylhexyl-L-lactate esterss are available (154).

Levulinic acid

Levulinic acid can be produced by acid treatment of starch or the C6-carbohydrates in lignocellulosic biomass via the hydration of HMF, an intermediate in this reaction. A side product of this reaction is formic acid which is produced in equimolar amounts (33, 155). It is also possible to obtain levulinic acid from the five carbon carbohydrates in hemicellulose (e.g. xylose, arabinose) by addition of a reduction step (via furfuryl alcohol) subsequent to the acid treatment. Levulinic acid has been promoted as an important biorefinery building block due to its high yield from six carbon carbohydrates (64). The company GFBiochemicals has taken over the patent portfolio of Segetis and is commercialising levulinic ketals for a variety of applications. Levulinic acid contains two reactive functional groups that allow a great number of synthetic transformations. Figure 19 shows a number of interesting derivates of levulinic acid. In the FDCA production process as commercialised by Avantium, the methyl ester of levulinic acid is formed as a co-product (32, 33). The Biofine process is developed by Maine BioProducts (MBP) and the process works by "cracking" any lignocellulosic feedstock under the influence of dilute mineral acid and moderate temperature. In essence, the Biofine technology is a plug flow reactor running at high temperature and short residence times followed by a CSTR at moderate residence times and temperatures. This novel dual reactor section allows, according to Biofine publications, high throughput and high yields. The cellulose fraction is broken down to form levulinic acid and formic acid as co-product. The hemicellulose fraction is cracked to furfural, which can be delivered as a product, or upgraded to levulinic acid. The lignin, along with some degraded cellulose and hemicellulose and any inerts, comes out of the process as a carbon-rich char mixture which is combusted to produce power for the process and for export (102).

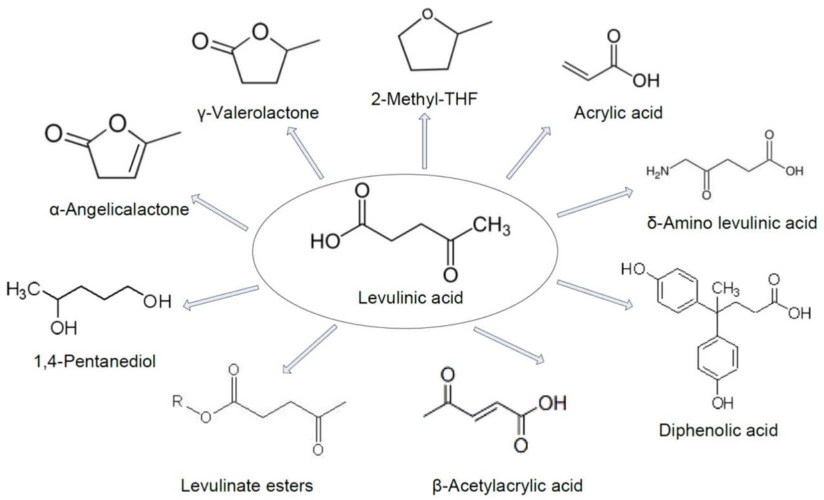


Figure 19. Chemicals derived from levulinic acid.

Xylitol/Arabitol

Xylose and arabinose are the main pentoses or C5-carbohydrates in hemicellulose. Hydrogenation of these carbohydrates yields the isomers xylitol and arabitol. Xylitol is presently used as a sustainable, naturally occurring sweetener with all the sweetness of sugar but with 40% less calories. At the moment there is limited commercial production of xylitol outside China and no commercial production of arabitol. Total production is around 200,000 tonnes per year. Xylose and arabinose can be obtained from lignocellulosic biomass but a major challenge is to obtain clean feed streams of these carbohydrates in a low cost way (64, 65). Fortress Global, which recently acquired S2G Biochemicals, intends to commission the construction of a demonstration plant to produce xylitol at its Fortress Specialty Cellulose Mill, utilizing proprietary process technologies, know-how and expertise developed by S2G (120) and Mondelez International, Inc. The demonstration plant will use C5 sugars extracted from hemicellulose, which is a residue from the FSC Mill, to produce xylitol. The extraction and conversion of this residue will also further debottleneck the FSC Mill and increase its annual production capacity of dissolving pulp. The demonstration plant is expected to commence operation in 2020 and have a production capacity of up to 2,000 tonnes per year of xylitol. The FSC Mill is expected to produce sufficient C5 sugars annually to provide the feedstock for up to an additional 20,000 tonnes per year of xylitol production. Fortress intends to utilize this capacity by constructing an approximately $150 million full-scale plant following successful completion of the demonstration plant. When complete, the full-scale plant would be expected to generate up to $40 million of EBITDA annually (120). The non-purified sugar alcohols have other potential as they can be converted to glycols such as ethylene glycol and 1,2-propanediol.

Box 10. Xylitol (XIVIA™ by DuPont)

Traditionally xylose, the starting material for xylitol production, is extracted from corn cobs, which are what remains of an ear of corn after the kernels have been extracted. In a published white paper DuPont describe the sustainability benefits of the newly developed DWB process, the DuPont Wood Based concept. In this process, the xylose producing facility is integrated with a pulp and paper plant. Pulp and paper plants typically produce a waste side stream – consisting of black liquor – that has a high carbohydrate content and energy value. The side stream is usually combusted to produce heat and electricity which is used internally to fuel the pulp production within the plant. The integration of xylose production with a pulp and paper plant takes advantage of the high carbohydrate content of the side stream and utilises this waste stream as feedstock. The xylose in this feedstock is already in a hydrolysed form, and therefore in the DWB process there is no use of acid for hydrolysis. An LCA assessment demonstrated that the DWB integrated manufacturing process is 84-99% less impactful than the traditional xylose production process, leading to a significantly less impactful and more sustainable product.

https://www.dupontnutritionandbiosciences.com/content/dam/dupont/amer/us/en/products/nutrition-health/documents/2e_XIVIA_White_Paper.pdf

Furfural

Furfural is one of the members of the Furanics class, which also encompass a group of molecules which include 5-hydroxymethylfurfural (HMF), 5-chloromethylfurfural (CMF) 2,5-furandicarboxylic acid (FDCA) and 2,5-dimethylfuran (DMF).

The chemical dehydration of five carbon carbohydrates such as xylose and arabinose yields furfural. Furfural is an established chemical product with a static market (124). World production of furfural has been estimated at around 200,000 -360,000 tonnes per annum of which 60-70% is used for the production of furfuryl alcohol (156, 157). Its production has rapidly declined in the developed world, while production is increasing in developing regions. China is the world's principal producer of furfural, mainly based on corn cobs, followed by the Dominican Republic, based on sugarcane bagasse. It is anticipated that furfural production will increase in the upcoming years probably lowering its costs and making traditional and new outlets of furfural economically attractive again (157).

Itaconic Acid

Itaconic acid is a granulated light yellow powder that can be processed into a polymer. Itcan be used to replace petroleum-based poly-acrylic acids which are used in diapers, feminine pads, detergents, cosmetics, inks and cleaners. Itaconic acid was produced at around 80,000 tonnes per year, mainly in China and little in France (158), however markets are in decline because of the slow rate of development of viable end use applications, its relatively high price and stable and low fossil prices. Current global itaconic acid production capacity is said to be more than adequate to fulfil current market requirements. Recent estimates of global itaconic acid production were between 40,000 and 70,000 tonnes per year, with three large and four smaller facilities in China using C6 feedstock. Over the last 10 years, some itaconic acid producers in China have also quit the market due to the high cost fermentation process and fierce price competition. Qingdao Kehai, Zhejiang Guoguang and Jinan Huaming are the three major producers and are currently producing itaconic acid in China.

Other C5 based building blocks

There are not many other C5 based building blocks that are currently used at scales around 50,000 tonnes/year and up. Important examples are furfuryl alcohol (formed by hydrogenation of furfural) and pentane diamine (cadaverine) used in nylon 5,10 (formed by decarboxylation of lysine). Covestro and Mitsubishi Chemical use biobased pentane diamine to produce partly biobased pentamethylene diisocyanate (105).

9.6 C6 containing compounds

Sorbitol

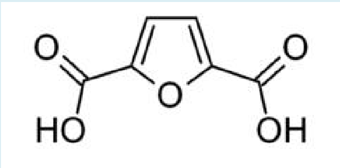
Sorbitol is produced on large industrial scale by catalytic hydrogenation of glucose. It is a batch process with a production volume of around 1.8 million tonnes/year (35, 159). Further development could be the industrial implementation of a continuous process. Other research routes include the development of milder processing conditions and/or other catalysts to replace the nickel catalysts that are used nowadays. Fermentative routes are also suggested (160) but it is unlikely that these routes can replace the technically mature catalytic hydrogenation process. Besides food, sorbitol is also the raw material for other products such as surfactants and polyurethanes (Woodbridge Foams). Sorbitol can also be further derivatised into ascorbic acid (80,000 ton/y by combined biotechnological/chemical process), sorbitan (50,000 ton/y), isosorbide (selective dehydration) and 1,2-propanediol by hydrogenolysis (161).

2,5-Furandicarboxylic acid (FDCA)

Hydroxymethylfurfural (HMF) is produced by the chemical dehydration of six carbon carbohydrates (32, 162, 163). Through chemical conversion, HMF can be converted to a range of furan derivatives (33). Oxidation of HMF gives 2,5-furandicarboxylic acid (FDCA), FDCA has been suggested as a replacement for terephthalic acid in the production of polyester polymers. The range of potential furanic products and the possibilities for use in novel polymer structures suggests the potential for good market growth if commercialisation can be achieved. Avantium is building a platform technology, branded as ‘YXY’, to commercialise bio-based furanics. Recently, the company announced they joined the Paper Bottle Project (164). Other parties involved in the FDCA production via HMF are ADM/Dupont, Corbion and Anniki. Additional routes are developed via the conversion of sugars to chloromethylfurfural (CMF), the chlorinated analogue of HMF. Among others this is developed by Mercurius Biorefining and Origin Materials.

Box 11. Avantium Renewable Polymers FDCA and PEF

Avantium Renewable Polymers mission is to establish world-leading positions in FDCA and PEF. To realize this ambition, it is intended to construct a flagship plant with a capacity of 5,000 tonnes of PEF a year. The next move will be to license the technology for industrial-scale production. Alongside its environmental benefits, the polymer PEF offers increased performance in comparison with PET and other packaging materials, such as fossil-based plastics, aluminum or glass (165). These benefits mean that PEF is viable for a range of additional applications that have so far been beyond the reach of PET.



Furanics: 2,5-Furan-dicarboxylic-acid

Avantium Renewable Polymers produces FDCA at its pilot plant in Geleen, The Netherlands, using the YXY® process developed by Avantium and based on fructose as a renewable raw material. Currently, the polymerizing of FDCA to PEF is done externally at their partners' facilities.

https://www.avantium.com/renewable-polymers/

Adipic acid

Adipic acid (hexanedioic acid or 1,4-butanedicarboxylic acid) is the most important aliphatic dicarboxylic acid, a white crystalline powder. It is primarily used for the production of nylon 6,6. The current market for adipic acid is close to 3 million tonnes per year, worth approximately $8 billion at current market prices. Within the Brew-report several fossil-based processes for the production of adipic acid are described, whereas only one process involves a biomass substrate (63). This is the biosynthesis of cis,cis-muconic acid by fermentation of glucose, followed by catalytic hydrogenation to adipic acid. Besides optimization of production organisms, the recovery of adipic acid from aqueous medium at the purity levels needed for polymer-grade products and catalytic conversion of muconic acid to adipic acid needs to be further investigated (63). Genomatica has entered the adipic acid arena. A recent patent, number 7,799,545, entitled "Microorganisms for the production of adipic acid and other compounds," describes how to produce a "green" version of key intermediate chemicals used to produce nylon, utilising renewable feedstocks such as commercially-available carbohydrates, instead of crude oil or natural gas. These organisms directly produce adipic acid and 6-aminocaproic acid (6-ACA), which can be used to produce nylon 6,6 and nylon 6, respectively (166).

Lysine

Production of nitrogen-containing bulk chemicals from biomass is in a less advanced state compared to oxygenated bulk chemicals such as glycols. Biobased routes from lysine to caprolactam for the production of nylon have perhaps received the most attention (167). In the 1950's, fermentation with *Corynebacterium glutamicum* was found to be a very efficient production route to L-glutamic acid. Since this time biotechnological processes with bacteria of the species *Corynebacterium* developed to be among the most important in terms of tonnage and economical value. L-lysine is a bulk product nowadays with a production volume of 640,000 tonnes/y (161) and a cost price of 1,200 €/ton. Other routes that are currently under investigation are the development of genetically modified plants with elevated levels of certain amino acids such as lysine. In this way amino acids that are naturally produced by plants can be produced at higher concentration levels by over-expression of certain structural genes.

Isosorbide

Isosorbide is a diol obtained by dehydration of sorbitol, (a derivative of glucose), for which Roquette is the leading world producer. Isosorbide is used for the manufacture of specialty polymers in the polyester (f.i. PET-like polymers), polycarbonate, polyurethane and plasticizers families (168). Thanks to its rigid structure, isosorbide is the only biobased diol that improves resistance to heat, UV rays and chemicals, and offers excellent optical and mechanical properties on the materials produced. Roquette's production capacity of isosorbide located in Lestrem (France) will have a nameplate capacity of 20,000 tonnes/year.

Cyrene

Dihydrolevoglucosenone (Cyrene) is a bio-based molecule, derived in two simple steps from cellulose, which demonstrates significant promise as a dipolar aprotic solvent and is developed by the Circa Group (169).

Citric Acid

In the course of the last two decades citric acid global production, mostly located in China, rose from less than 0.5 to more than 2 million tonnes becoming the single largest chemical obtained via biomass fermentation and the most widely employed organic acid (170). Citric acid is used as an acidulant, preservative, emulsifier, flavorant, chelating and buffering agent and is widely used across many industries especially in food, beverage, pharmaceutical, nutraceutical and cosmetic products.

Other C6 based building blocks

Several other C6 based building blocks are currently used at scales around 100,000 tonnes/year and up. Important examples are ascorbic acid (formed by combined biotechnological/chemical process), sorbitan (formed by dehydration of sorbitol), and phenols (from lignin). The development of glucaric acid by Rivertop Renewables and Rennovia has stopped.

9.7 Higher Cn containing compounds

p-Xylene

PET is a polymer built up from the monomers mono-ethyleneglycol (MEG) and purified terephthalic acid (PTA). In 2010 The Coca Cola Company introduced Plantbottle[R], a PET bottle containing 100% renewable MEG (171). The route to ethylene glycol from ethanol is well known and was practiced into the 1960's until oil based MEG became a cheaper route. Ethanol is being produced from sugarcane and India Glycols converts sugarcane ethanol into Ethylene Glycol. Other companies, with PepsiCo (172) as a flagship example, have announced they want to go to a 100% renewable PET bottle, that means also replacing fossil based PTA by renewable PTA. Several companies have announced they are working on this. Gevo is commercializing biobutanol (iso-butanol) and have announced their interest to work with companies to convert this into para-xylene and then to PTA (144, 173). Isobutanol can be converted to para-xylene via isobutylene which can be readily oxidised to terephthalic acid for production of PET. Anellotech claims the technology to convert biomass (i.e. wood waste, corn stover, sugar cane bagasse, etc.) in a fluidized bed reactor in the presence of an inexpensive zeolite catalyst. Biomass is rapidly heated without oxygen and the resulting gases are immediately catalytically converted into aromatic hydrocarbons. The resulting benzene, toluene, xylene (BTX) mixture can be sold to petrochemical companies for processing in existing separation units, or distilled by Anellotech and sold directly into the market. According to Anellotech, other than the reactor, regenerator and the catalyst, the process equipment consists of standard items, simplifying and focusing development. The reaction of dimethylfuran and ethylene to produce *para*-xylene has been disclosed in a patent (WO2010/151346A1) by Honeywell/UOP (174). The dimethylfuran can be produced from carbohydrates such as glucose or fructose. Also US patent application, US2010/0168461A1, claims the use of terpenes such a limonene (found in citrus fruits) as a route to PTA. The latest in line is Virent, now Tesoro, who claims to have produced *para*-xylene in their pilot plant made through a patented, catalytic process which converts plant-based carbohydrates into *para*-xylene molecules (175). However, in spite of all this activity, none of these technologies are close to being commercial, and it seems a long way before they will be cost competitive with fossil based PTA.

Fatty Acid derivatives

Oils and fats and their derivatives are already being used for a long time in the chemical industry. Compared to other major plant constituents such as carbohydrates, proteins and lignin, fatty acid derivatives are the easiest to handle in the current hydrocarbon-based chemical infrastructure, due to their often liquid nature and their low oxygen content. About 10% of the 170 million tonnes of oils and fats produced in 2009/2010 (175) are used as feedstock for the oleochemical industry. Palm, palm kernel and coconut oil, being rich in C12-C18 saturated and monounsaturated fatty acids, are important sources for a broad range of surfactants in soaps, detergents and personal care products. 'Drying oils' such as soybean, sunflower and linseed oil contain high levels of polyunsaturated fatty acids and are major raw materials for thermosetting systems such as coatings and ink resins, lacquers, and linoleum. Epoxidised soybean and linseed oils are used as (secondary) plasticisers and stabilisers in PVC. Rapeseed oil has a high level of oleic acid, and is therefore a favoured source for biolubricants, for which low viscosity combined with high oxidative and thermal stability are important properties.

Although their number is currently relatively small, a few bifunctional building blocks derived from fatty acids are commercially applied. Ricinoleic acid (12-hydroxy-9-octadecenoic acid) from castor oil can be fragmented in two different ways, to obtain either a C10 dicarboxylic acid called sebacic acid, or 10-undecanoic acid. Sebacic acid is used for the preparation of polyamides such as nylon-4,10 (EcoPaXX® by DSM), nylon-10,10 (VESTAMID® Terra DS by Evonik; Zytel RS 6/10 by DuPont) and nylon-6,10 (VESTAMID® Terra HS by Evonik; Ultramid® BALANCE by BASF and Technyl eXten by Rhodia). 10-Undecenoic acid is converted by Arkema to 11-aminoundecanoic acid, the monomer for nylon-11 (Rilsan®). Arkema also produces sebaic acid based nylons-10.10 and 10.12 under the name hiprolon. DSM also produces a thermoplastic copolyester (Arnitel Eco) based on rapeseed oil, while BASF/Elastogran produces castor oil based polyols (Lupranol® BALANCE 50). Cognis produces azelaic acid, a C9 dicarboxylic acid, by ozonolysis of oleic acid. Azelaic acid is used as a monomer in nylon-6,9. A well-known class of branched difunctional oleochemical are the dimerised fatty acids or dimer acids. These are C36 dicarboxylic acids obtained by treating unsaturated fatty acids at high temperature with clay catalysts. Trimers are also formed. Dimer acids are used in polyamide resins for hot melt adhesives, but also as a modifier of polyesters, and in polyester polyols for e.g. polyurethanes. Dimer diols are obtained by reduction of dimer acids (or their dimethyl esters). A recent addition to the fatty dimer family is a C36 diamine (Priamine™ by Croda).

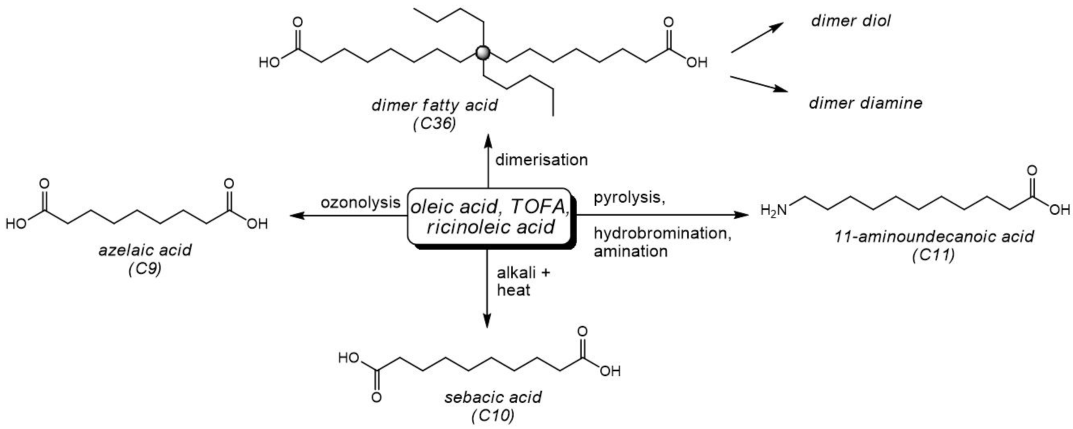


Figure 20. Examples of commercial fatty acid derived monomers. TOFA = tall oil fatty acids.

Other oleochemical monomers for bioplastics described in recent scientific literature include 1,18-octadec-9-enedioic acid, a C18 dicarboxylic acid obtained by self-metathesis of oleic acid (174), dimethyl 1,19-nonadecanedioate, a C19 dicarboxylic acid ester produced by methoxycarbonylation of unsaturated C18 acids (176), and mid- to long-chain dicarboxylic acids obtained by microbial ☐-oxidation of fatty acids (116, 117). In Italy, Novamont has developed a proprietary process to convert oils containing high levels of oleic acid into azelaic and pelargonic acid. The former is used to manufacture ORIGO-BI® biololyesters, components of MATER-BI® compostable bioplastics. The latter is used to produce biolubricants.

Box 12. Croda

Pripol for water resistance – C36 dimer fatty acid or dimer diol. Pripol dimer acid and dimer diol are made from natural fatty acids, resulting in a 100% renewable carbon content. The products bring the following benefits, e.g. enhanced hydrophobicity, (low temperature) flexibility and improved melt flow properties and substrate wetting to PET modification. The Dimer diol is a bi-functional, low viscosity building block, especially suitable for high-end Polyurethane applications. Pripol™ polymerised fatty acids are also used in a variety of industrial and consumer care applications, the highly lipophilic (oil-loving) structure providing unique performance benefits in lubricants, metal-working fluids, fuel additives, personal care products, corrosion inhibitors and rheology modifiers.

Priplast for maintaining hardness – dimer based polyesters. Priplast polyester polyols are made from dimer fatty acids and are ideal as larger soft segments to modify PET. The low polarity Priplast can be built in as an elongated soft segment. This results in a two-phase structure with soft, rubbery Priplast segments distributed in the hard PET matrix. This phase separated structure brings special benefits for PET including no compromise in hardness, improved impact strength, also at low temperatures and resistance to heat, oxidation, UV, hydrolysis and chemicals/petrol.

https://www.croda.com/en-gb

10. Discussion

The continued development of bio-based chemicals and polymers in biorefinery complexes will lead to new feedstock demands, new technology development and new economic opportunities. Although it is difficult to predict which biorefinery model and bio-based chemical targets may ultimately be successful, the current level of research and industrial activity is very encouraging for the sector as a whole. However, the last of couple of years we have seen quite a few companies ceasing operation (Abengoa, BioAmber, Rennovia, Rivertop Renewables) or being taken over by other companies (BetaRenewables/Biochemtex => EniVersalis; Itaconix => Revolymer; Liquid Light => Avantium; Mascoma => Renmatix; Segetis => GFBiochemicals; Virdia => Stora Enso; S2G => Fortress; Virent => Tesoro)). The shutdown of operation is clearly not a good sign. But the acquisition of some companies by other (in general bigger and better capitalized) companies is not necessarily a bad thing. It is however a clear indication that this transition from a fossil-based chemical industry into a biobased industry is expensive as well as time consuming and requires large amounts of resources and capital.

The integration of bio-based chemical production with biofuel production in a biofuel-driven biorefinery or with pulp production in a paper mill will be dependent on a number of factors including the fit with biorefinery business plan, technology and feedstock fit with the biorefinery, the capital cost of integration versus stand-alone chemical production and the biorefinery location and local chemical market dynamics.

The development of a more biobased economy, where biomass replaces traditional sources of feedstock, will incrementally grow in size and complexity. The opportunities are not always clear if all aspects of sustainability are considered.

It is therefore recommended that a true valuation be placed on biomass for future use. Cellulose, hemicellulose and lignin, as well as the other components of plants, are valuable assets and we should examine the opportunities available to maximize the economic, environmental and social benefits of a variety of pathways to their use.

It is incumbent upon us to identify the best apportioning of biomass to biofuels or biobased chemicals based on realistic assessments of requirements, best technology leads and the overall needs of society. This will assist the biomass industry to plan a sustainable industry into the future.

The wide spread development of biorefineries presents opportunities for the development of increasingly sustainable economy however many challenges exist in their development. A strengths, weaknesses, opportunities and threats (SWOT) analysis for biorefineries is summarized below (Table 14).

Table 14. A strengths, weaknesses, opportunities and threats (SWOT) analysis for biorefineries.

Strengths	**Weaknesses**
• Adding value to the use of biomass • Maximising biomass conversion efficiency minimising raw material requirements • Production of a spectrum of bio-based products (food, feed, materials, chemicals) and bioenergy (fuels, power and/or heat) feeding entire bioeconomy • Strong knowledge infrastructure available to tackle technical and non-technical issues • Biorefinery is not new, it builds on agriculture, food and forestry industries	• Broad undefined and unclassified area • Involvement of stakeholders for different market sectors (agriculture, forestry, energy, chemical) over full biomass value chain necessary • Most promising biorefinery processes / concepts not clear • Most promising biomass value chains, including current/future market volumes/prices, not clear • Studying and concept development instead of real market implementation • Variability of quality and energy density of biomass • Drop-in chemicals face difficult market penetration due to low oil prices
Opportunities	**Threats**
• Biorefineries can make a significant contribution to sustainable development • Challenging national and global policy goals, international focus on sustainable use of biomass for the production of bioenergy • International consensus on the fact that biomass availability is limited meaning that raw materials should be used as efficiently as possible – i.e. development of multi-purpose biorefineries in a framework of scarce raw materials and energy • International development of a portfolio of biorefinery concepts, including technical processes • Strengthening of the economic position of various market sectors (e.g. agriculture, forestry, chemical and energy) • Strong demand from brand owners for biobased chemicals • Increased production of plant-based proteins for food and feed	• Economic change and volatility in fossil fuel prices • Fast implementation of other renewable energy technologies feeding the market requests • Bio-based products and bioenergy are assessed to a higher standard than traditional products (no level playing field) • Availability and contractibility of raw materials (e.g. climate change, policies, logistics) • (High) investment capital for pilot and demo initiatives difficult to find, and undepreciated existing industrial infrastructure • Changing governmental policies • Questioning of food/feed/fuels (indirect land use competition) and sustainability of biomass production • Goals of end users often focused on single product

11. Conclusions

The biobased chemicals and materials industry has reached a tipping point, with several processes ready for scale-up in the upcoming years. Several strong forces including mitigating global warming, realising a truly circular economy, consumer preference, corporate commitment, and government mandates and support, are driving development in this area. However, relatively low oil prices, the absence of a carbon-tax in many places, trade wars, as well as lack of consistency in policy and legislation, slows down the deployment. The data in this report show that a shift in the deployment strategy is occurring. Many companies are refocusing on high profits, low volume specialty areas. Areas which are generating special traction are Food and Nutrition, Flavours/Fragrances, Cosmetics/Personal Care, Pharmaceutical, Fine chemicals as well as chemicals needing more Research and Development: lubricants, surfactants, coatings, solvents, high-tech materials (e.g. biomedical, engineering plastics). In addition, also some platform biochemical, with competitive or even better performance than the incumbent molecules, are expected to grow substantially over the next five years. The “drop-in” molecules aiming for a direct replacement of their fossil-based counterparts have a hard time because costs need to be the roughly the same as its fossil equivalent with only a very small green premium acceptable by the market. Although, the growth of the sector is less pronounced than anticipated a decade ago the described development will still generate a strong boost for the cost effective production of biofuels within a biorefinery context.

12. Works Cited

1. Burns, C., Higson, A., Hodgson, E. 2016. Five recommendations to kick-start bioeconomy innovation in the UK. . *Biofuels Bioprod. Bioref.* 10:12-16.

2. Shen, L., Haufe, J., Patel, M.K. 2009. Product overview and market projection of emerging bio-based plastics, PRO-BIP 2009.Utrecht Univeristy, [Online] [Cited: 18 October 2019] http://news.bio-based.eu/media/news-images/20091108-02/Product_overview_and_market_projection_of_emerging_bio-based_plastics,_PRO-BIP_2009.pdf

3. Raschka A., Carus, M. 2012. Industrial material use of biomass. Basic data for Germany, Europe and the world. 28pp. http://bio-based.eu/downloads/industrial-material-use-biomass-basic-data-germany-europe-world/

4. Carus, M. 2018: Renewable Carbon is Key to a Sustainable and Future Oriented Chemical Industry, Hürth 2018-08. [Online] [Cited: 18 October 2019] www.bio-based.eu/nova-papers.

5. WTI Crude Oil prices - 10 Year daily chart. 2019. Macrotrends. [Online] [Cited: October 2019] https://www.macrotrends.net/2516/wti-crude-oil-prices-10-year-daily-chart.

6. The circular bio-society in 2050. 2019. EuropaBio. [Online] June 2019 [Cited: 23 October 2019]. https://www.europabio.org/sites/default/files/Vision%20for%20a%20circular%20bio-society%202050.pdf.

7. A sustainable bioeconomy for Europe: strengthening the connection between economy, society and the environment Updated Bioeconomy Strategy. 2018. European Commission Directorate-General for Research and Innovation Unit F – Bioeconomy. [Online] October 2018 [Cited: 23 October 2019]. https://ec.europa.eu/research/bioeconomy/pdf/ec_bioeconomy_strategy_2018.pdf.

8. The Bioeconomy to 2030: designing a policy agenda. 2009. OECD. [Online] April 2009 [Cited: 22 October 2019]. https://www.oecd.org/futures/long-termtechnologicalsocietalchallenges/42837897.pdf.

9. Meeting Policy Challenges for a Sustainable Bioeconomy. 2018. OECD. [Online] 19 April 2018 [Cited: 22 October 2019]. https://read.oecd-ilibrary.org/science-and-technology/policy-challenges-facing-a-sustainable-bioeconomy_9789264292345-en#page1.

10. Langeveld, H., Sanders, J. Meeusen, M. (ed.). 2010. *The Biobased Economy.* London: Earthscan, ISBN 978-1-84407-770-0.

11. Kamm, B., P. Gruber, M. Kamm (ed.). 2006. *Biorefineries - Industrial Processes and Products.* Weinheim: Wiley-VCH, ISBN-13 978-3-527-31027-2.

12. King, D., Inderwildi, O.R., Williams, A. 2010. The future of industrial biorefineries. World Economic Forum. https://www.iwbio.de/fileadmin/Publikationen/IWBio-Publikationen/WEF_Biorefineries_Report_2010.pdf.

13. World Economic Forum Industry Agenda. 2015. Biorefineries, Biotechnology and Bioenergy in North America. Montreal, Canada 22 July 2015. http://www3.weforum.org/docs/IP/2016/CH/WEF_CH_Biorefineries_BBB_North_America.pdf.

14. Bakker, R., den Uil, H., van Ree, R. 2010. Financieel-economische aspecten van biobrandstofproductie – Desktopstudie naar de invloed van co-productie van bio-based producten op de financiele haalbaarheid van biobrandstoffen. WUR Food and Biobased Research, rapport 1175, Wageningen, Nederland, Oktober 2010 (in Dutch).

15. Advancing the biobased economy: Renewable chemical biorefinery commercialization, progress, and market opportunities, 2016 and beyond. 2016. Biotechnology Innovation Organization (BIO). https://www.bio.org/sites/default/files/BIO_Advancing_the_Biobased_Economy_2016.pdf

16. Cherubini, F., Jungmeier, G., Wellisch, M., Willke, T., Skiadas, I., van Ree, R., de Jong, E. 2009. Toward a common classification approach for biorefinery systems. *Biofuels Bioprod. Bioref.* 3:534-546.

17. Akhtar, A., Krepl. V., Ivanova, T.A. 2018. Combined overview of combustion, pyrolysis, and gasification of biomass. *Energy Fuels.* 32:7294–318.

18. BTG Biomass Technology Group. BTG-BTL [Cited 29 Augustus 2018]. Available from: https://www.btg-btl.com/en.

19. Biomass Balance Approach: Reduce CO_2 emissions and save fossil resources A groundbreaking way of using renewable resources in the chemical industry. 2019. BASF. [ONLINE] [Cited 31 October 2019]. https://www.basf.com/global/documents/en/sustainability/we-source-responsibly/Biomass-balance-approach_2019_Brochure.pdf.

20. Enabling a Circular Economy for Chemicals with the Mass Balance Approach: A White Paper from Co. Project Mass Balance. 2019. Ellen MacArthur Foundation's CE100 Network. [ONLINE] [Sited 30 October 2019] https://www.ellenmacarthurfoundation.org/assets/downloads/Mass-Balance-White-Paper.pdf.

21. Masson-Delmotte, V., Zhai, P., Pörtner, H-O. et al. 2019. IPCC, 2018: Global Warming of 1.5°C. An IPCC Special Report on the impacts of global warming of 1.5°C above pre-industrial levels and related global greenhouse gas emission pathways, in the context of strengthening the global response to the threat of climate change, sustainable development, and efforts to eradicate poverty. https://www.ipcc.ch/site/assets/uploads/sites/2/2019/06/SR15_Full_Report_Low_Res.pdf.

22. Carbon4PUR. Turning industrial waste gases (mixed CO/CO_2 steams) into intermediates for polyurethane plastics for rigid foams/building insulation and coatings. 2017. EU H2020 project. https://www.carbon4pur.eu/

23. Bazzanella, A.M., Ausfelder, F. 2017. Low carbon energy and feedstock for the European chemical industry. https://dechema.de/Low_carbon_chemical_industry.html.

24. Hobson C., Márquez C. 2018. Renewable Methanol Report. Methanol Institute. [Online] December 2018 [Cited: 28 October 2019]. https://www.methanol.org/wp-content/uploads/2019/01/MethanolReport.pdf

25. Agreement signed for CRI's first CO_2-To-Methanol plant in China. 2019. Carbon Recycling International (CRI) [Online] 22 May 2019 [Cited: 31 October 2019]. https://www.carbonrecycling.is/news/co2-to-methanol-plant-china.

26. Schulz, R.P., Blumenstein, J., Kohlpaintner, C. 2005. Crotonaldehyde and crotonic acid. Ullmann's Encyclopedia of Industrial Chemistry. Weinheim: Wiley-VCH. https://doi:10.1002/14356007.a08_083.

27. Hrbek, J. 2016. Status report on thermal biomass gasification in countries participating in IEA Bioenergy Task 33 [Internet]. p. 163. Available from: http://www.ieatask33.org/app/webroot/files/file/2016/Status_report.pdf.

28. Molino, A., Chianese, S., Musmarra, D. 2016. Biomass gasification technology: The state of the art overview. *J. Energy Chem.* 25:10–25.

29. Asimakopoulos, K., Gavala, H.N., Skiadas, I. 2018. Reactor systems for syngas fermentation processes: A review. *Chem. Eng. J.* 348:732–44.

30. Giuliano et al. 2018. Proceedings of the 28th European Symposium on Computer Aided Process Engineering, 2018, Graz, Austria.

31. Jørgensen, H., Kristensen, J.B., Felby, C. 2007. Enzymatic conversion of lignocellulose into fermentable sugars: Challenges and opportunities. *Biofuels Bioprod. Bioref*. 1:119–34.

32. van Putten, R-J., van der Waal, J.C., de Jong, E., Rasrendra, C.B., Heeres, H.J., de Vries, J.G. 2013. Hydroxymethylfurfural, a versatile platform chemical made from renewable resources. *Chem.l Rev.* 113:1499-1597.

33. van der Waal, J.C., de Jong, E. 2016. Avantium chemicals: The high potential for the levulinic product tree. In: Industrial biorenewables, a practical viewpoint. (Domínguez de María, P. ed.) pp. 97-120. https://doi:10.1002/9781118843796.ch4.

34. Opportunities for the chemical industry - An analysis of the market potential and competitiveness of North-West Europe. 2014. Deloitte. [Internet]. 2014. p. 1–50. Available from: https://www2.deloitte.com/vi/en/pages/manufacturing/articles/opportunities-for-fermentation-based-chemical-industry.html.

35. Barbaro, P., Liguori, F., Moreno-Marrodan, C. 2016. Selective direct conversion of C5 and C6 sugars to high added-value chemicals by a bifunctional, single catalytic body. *Green Chem.* 18:2935–40.

36. Shrotri, A., Kobayashi, H., Fukuoka, A. 2017. Catalytic conversion of structural carbohydrates and lignin to chemicals. *Adv. Catal.* 60:59-123. https://doi.org/10.1016/bs.acat.2017.09.002.

37. HaldorTopsoe. 2018. Changing the world of bio-chemicals [Online] [cited 25 June 2018]. Available from: https://info.topsoe.com/biochemicals.

38. Avantium advances its plant-based MEG technology with the opening of its demonstration plant. 2019. Avantium. [Internet] 7 November 2019 [cited 8 November 2019]. https://www.avantium.com/in-the-media/avantium-advances-its-plant-based-meg-technology-with-the-opening-of-its-demonstration-plant/.

39. Aro, T., Fatehi, P. 2017. Production and application of lignosulfonates and sulfonated lignin. *ChemSusChem*. 10:1861-1877.

40. Dessbesell, L., Yuan, Z., Hamilton, S., Leitch, M., Pulkki, R., Xu, C.C. 2018. Bio-based polymers production in a Kraft lignin biorefinery: techno-economic assessment. *Biofuels Bioprod. Bioref.* 12:239–250.

41. Ragauskas, A.J., Beckham, G.T., Biddy, M.J. et al. 2014. Lignin Valorization: Improving Lignin Processing in the Biorefinery. *Science* 344(6185):709-720.

42. Holladay, J.E., White, J.F., Bozell, J.J., Johnson, D. 2007. Top value-added chemicals from biomass - Volume II—Results of screening for potential candidates from biorefinery lignin.

Pacific Northwest Natl. Lab. Richland, WA (United States) [Online] [Cited 25 November 2019] https://www.pnnl.gov/main/publications/external/technical_reports/PNNL-16983.pdf.

43. Laurichesse, S., Avérous, L. 2014. Chemical modification of lignins: Towards biobased polymers. *Prog. Polym. Sci.* 39:1266–1290.

44. Pye, E.K. 2008. Industrial Lignin Production and Applications. In: Biorefineries-Industrial Process. Prod. Weinheim, Germany: Wiley-VCH Verlag GmbH; pp. 165–200.

45. Rødsrud, G., Lersch, M., Sjöde, A. 2012. History and future of world's most advanced biorefinery in operation. *Biomass Bioenergy* 46:46–59.

46. Schutyser, W., Renders, T., Van den Bossche, G., et al. 2017. Catalysis in lignocellulosic biorefineries: The case of lignin conversion. In: Nanotechnology in catalysis (Van de Voorde, M., Sels, B. eds.). Weinheim, Germany: Wiley-VCH Verlag GmbH & Co. KGaA; pp. 537–84. https://doi:10.1002/9783527699827.ch23.

47. Yang, B., Laskar, D.D. 2016. Apparatus and process for preparing reactive lignin with High yield from plant biomass for production of fuels and chemicals. US patent 9 518 076 B2.

48. Shen, R., Tao, L., Yang, B. 2019. Techno-economic analysis of jet-fuel production from biorefinery waste lignin. *Biofuels Bioprod. Bioref.* 13:486-501.

49. Consumption of vegetable oils worldwide from 2013/14 to 2018/2019, by oil type (in million metric tons). 2019. Statista. [Online] [Cited: 22 October2019] https://www.statista.com/statistics/263937/vegetable-oils-global-consumption/

50. Caullet, C., Le Nôtre, J. 2015. Vegetable oil biorefineries. In: Industrial biorefineries and white biotechnology (Ashok Pandey A., Höfer, R., Taherzadeh, M., Nampoothiri, K.M., Larroche, C. Eds) Elsevier; pp. 247–270.

51. Oleochemicals market size, share & trend analysis. Report by product (fatty acid, fatty alcohol, glycerol), by region and segment forecasts, 2019 – 2025. 2018. Grandview Research. [Online] [Cited: 23 October 2019]. https://www.grandviewresearch.com/industry-analysis/oleochemicals-industry.

52. Naumann. K., Billig, E., Millinger, M., Pfeiffer, D., Zech, K. 2018. Data on biofuels production, trade, and demand. In: Biofuels Prod. Process. Technol. (Riazi M.R., Chiaramonti, D. eds.) Boca Raton, FL, USA: CRC Press; 2018. p. 55–99.

53. T+I Consulting Dr. Busch/Fachagentur Nachwachsende Rohstoffe. 2019. Erhebung, Aufbereitung und Analyse statistischer Daten zum Anbau und zur Verarbeitung nachwachsender Rohstoffe und Energiepflanzen in Deutschland sowie Weiterentwicklung von Methoden hierzu (NRstat), Project No FKZ 22004416. [Online] [Cited 22 November 2019, in German only] https://www.fnr.de/index.php?id=11150&fkz=22004416.

54. Pudel. F., Wiesen, S. 2019. Vegetable Oil-Biorefinery. *Adv. Biochem. Eng. Biotechnol.* 166:69-98

55. Laurens, L.M.L., Chen-Glasser, M., McMillan, J.D. 2017. A perspective on renewable bioenergy from photosynthetic algae as feedstock for biofuels and bioproducts. *Algal Research* 24:261-264.

56. Laurens, L.M.L., Markham, J., Templeton, D.W., et al. 2017. Development of algae biorefinery concepts for biofuels and bioproducts; a perspective on process-compatible products and their impact on cost-reduction. *Energy Environ. Sci.* 10:1716-1738.

57. Stødkilde, L., Damborg, V.K., Jørgensen, H., Lærke, H.N., Jensen, S.K. 2018. White clover fractions as protein source for monogastrics: dry matter digestibility and protein digestibility-corrected amino acid scores. *J. Sci. Food Agric.* 98:2557–2563.

58. Corona, A., Ambye-Jensen, M., Vega, G.C., Hauschild, M.Z., Birkved, M. 2018.Techno-environmental assessment of the green biorefinery concept: Combining process simulation and life cycle assessment at an early design stage. *Sci. Total Environ.* 635:100–111.

59. Mandl, M. 2010. Status of green biorefining in Europe. *Biofuels Bioprod. Biorefin.* 4:268-274.

60. Schwinn, V. 2019. Biowert Grass Biorefinery; Biobased Plastics, Germany , IEA Bioenergy Task 37 [Online] [Cited: 28 October 2019]. https://www.ieabioenergy.com/wp-content/uploads/2019/07/IEA_grass-refinery_end.pdf.

61. U.S. Biobased market potential and projections through 2025. 2008. USDA. https://www.usda.gov/oce/reports/energy/BiobasedReport2008.pdf.

62. Golden, J.S., Handfield, R., Daystar, J., Morrison, B., McConnell, E. 2016. An economic impact analysis of the U.S. Biobased Products industry. USDA. https://www.usda.gov/media/press-releases/2016/10/03/usda-report-shows-growing-biobased-products-industry-contributes.

63. Patel, M., Crank, M., Dornburg, V., Hermann, B., Roes, L., Hüsing, B., van Overbeek, L., Terragni, F., Recchia, E. 2006. Medium and long-term opportunities and risks of the biotechnological production of bulk chemicals from renewable resources - The BREW Project. https://dspace.library.uu.nl/bitstream/handle/1874/21824/NWS-E-2006-146.pdf?sequence=1.

64. Bozell, J.J., Petersen, G.R. 2010.Technology development for the production of biobased products from biorefinery carbohydrates - the US Department of Energy's "Top 10" revisited. *Green Chemistry.* 12:539-554.

65. Werpy, T, G. Petersen. 2004. Top Value Added Chemicals from Biomass, Volume 1 Results of Screening for Potential Candidates from Sugars and Synthesis Gas. [Online] [Cited: 17 October2019] https://www.nrel.gov/docs/fy04osti/35523.pdf

66. Bioplastics market data. 2019. European Bioplastics. [Online] [Cited: 23 October 2019]. https://www.european-bioplastics.org/market/.

67. Chinthapalli, R., Puente, A., Skoczinski, P., Raschka, A., Carus, M. 2019. Succinic acid: From a promising building block to a slow seller – what will a realistic future market look like? [Online] [Cited: 29 October 2019. http://www.bio-based.eu/reports/.

68. Natural microspheres from PHA biopolymers for personal care and cosmetic products. 2017. Plastemart.com. [Online] 2 May 2017 [Cited: 23 October 2019]. http://www.plastemart.com/plastic-technical-articles/natural-microspheres-from-pha-biopolymers-for-personal-care-and-cosmetic-products/2354;

69. Bio-on inaugurates in Italy the first bioplastics production plant to produce 100% natural and biodegradable microbeads. 2018. Plastemart.com. [Online] 20 June 2018 [Cited: 23 October 2019]. http://www.plastemart.com/news-plastics-information/bio-on-inaugurates-in-italy-the-first-bioplastics-production-plant-to-produce-100-natural-and-biodegradable-microbeads/49956.

70. Smithers Pira forecasts global bioplastic packaging market to reach $8.8 billion by 2024. 2019. Bioplastics Magazine.com. [Online] 12 July 2019 [Cited: 23 October 2019].

https://www.bioplasticsmagazine.com/en/news/meldungen/20190712Smithers-Pira-forecasts-robust-growth-global-bioplastic-packaging-market-.php.

71. Biodegradable polymers market value. 2018. IHS Market [Online] 2018 [Cited: 23 October 2019]. https://cdn.ihs.com/www/pdf/IHS%20Markit%20Biodegradable%20Polymer%20Infographic.pdf.

72. Carrez, D., Albrecht, J., Cunningham, P., Daroda, L., Mancia, R., Máthé, L., Raschka, A., Carus, M., Piotrowski, S. 2010: The Knowledge Based Bio-Economy (KBBE in Europe: Achievements and Challenges. http://cleverconsult.eu/cleversafe/wp-content/uploads/2010/09/KBBE_A4_1_Full-report_final.pdf.

73. Mozaffarian, H. 2010. Development of Advanced BIOREFinery Schemes to be INTEGrated into Existing Industrial Fuel Complexes. [Online] 2010 [Cited: 23 October 2019]. https://www.bioref-integ.eu/publications/index.html; https://www.bioref-integ.eu/fileadmin/bioref-integ/user/documents/Brochure.pdf.

74. De Bari, I., Cuna, D., Di Fidio N. 2017. Biorefineries: Biofuels, Biochemicals, and Bioproducts. In: Biofuels Production and Processing Technology (Riazi, M.R., Chiaramonti, D. eds) CRC Press. ISBN 9781498778930.

75. Wilkens, E., Ringel, A., Hortig, D., Willke, T., Vorlop, K.-D. 2012. High-level production of 1,3-propanediol from crude glycerol by *Clostridium butyricum* AKR102a. *Appl. Microbiol. Biotechnol.* 93:1057–1063. https://doi:10.1007/s00253-011-3595-6.

76. The new plastics economy: Rethinking the future of plastics & catalysing action. 2016. World Economic Forum, Ellen MacArthur Foundation and McKinsey & Company, The New Plastics Economy – Rethinking the future of plastics (2016); – Catalysing action (2017); – Rethinking the Future of Plastics & Catalysing Action (2017). [Online] 2010 [Cited: 23 October 2019]. https://www.ellenmacarthurfoundation.org/publications.

77. Spekreijse, J., Lammens, T., Parisi, C., Ronzon, T., Vis, M., 2019. Insights into the European market of bio-based chemicals. Analysis based on ten key product categories, EUR 29581 EN, Publications Office of the European Union, Luxembourg, 2019, ISBN 978-92-79-98420-4, https://doi:10.2760/549564, JRC112989.

78. Ögmundarson, O. 2019. Life Cycle Assessment of chosen biochemicals and bio-based polymers, Technical University of Denmark. [Online] [Cited: 16 November 2019]. https://orbit.dtu.dk/en/publications/life-cycle-assessment-of-chosen-biochemicals-and-biobased-polymers(2d344dcf-f880-47b1-b89d-0138386831aa).html.

79. COWI A/S, Utrecht University. 2018. Environmental impact assessments of innovative bio-based product. Task 1 of "Study on Support to R&I Policy in the Area of Bio-based Products and Services". Brussels, European Commission: pp 1-754. doi:10.2777/251887 [Online] [Cited: 16 November 2019]. https://op.europa.eu/en/publication-detail/-/publication/15bb40e3-3979-11e9-8d04-01aa75ed71a1.

80. Lammens, T.M., Potting, J., Sanders J.P.M., De Boer, I.J.M. 2011. Environmental Comparison of Biobased Chemicals from Glutamic Acid with Their Petrochemical Equivalents. *Environ. Sci. Technol.* 45: 8521-8528.

81. Montazeri, M., Eckelman, M.J. 2016. Life Cycle Assessment of catechols from lignin depolymerization. *ACS Sust. Chem. Eng.* 4:708-718.

82. Posada, J.A., Patel, A.D., Roes, A., Blok, K., Faaij A.P.C., Patel, M.K. 2013. Potential of bioethanol as a chemical building block for biorefineries: Preliminary sustainability assessment of 12 bioethanol-based products. *Biores, Technol.* 135:490-499.

83. Weiss, M., Haufe, J., Carus, M., Brandão, M., Bringezu, S., Hermann, B., Patel, M.K. 2012. A review of the environmental impacts of biobased materials. *J. Ind. Ecol.* 16: S169-S181.

84. Muñoz, I., Flury, K., Jungbluth, N., Rigarlsford, G., Canals, L.M., King H. 2014. Life cycle assessment of bio-based ethanol produced from different agricultural feedstocks. *Int. J. Life Cycle Assess.* 19:109-119.

85. Montazeri, M. 2017. Environmental assessment of bio-based fuels and chemicals using LCA Methodology. PhD, Northeastern University Boston. [Online] [Cited: 16 November 2019]. https://repository.library.northeastern.edu/files/neu:cj82q829t/fulltext.pdf.

86. Smidt, M., den Hollander, J., Bosch, H., Xiang, Y., van der Graaf, M., Lambin, A., Duda, J. 2016. Life cycle assessment of biobased and fossil-based succinic acid. In: Dewulf, J., De Meester, S., Alvarenga, R.A.F. (Eds.), Sustainability Assessment of Renewables-Based Products: Methods and Case Studies. Wiley. pp. 307–322. ISBN: 978-1-118-93394-7.

87. Jeswani, H.K., Falano, T., Azapagic, A. 2015. Life cycle environmental sustainability of lignocellulosic ethanol produced in integrated thermo-chemical biorefineries. *Biofuels Bioprod. Bioref.* 9:661-676.

88. Morales, M., Dapsens, P.Y., Giovinazzo, I., Witte, J., Mondelli, C., Papadokonstantakis, S., Hungerbühler, K., Pérez-Ramírez, J. 2015. Environmental and economic assessment of lactic acid production from glycerol using cascade bio- and chemocatalysis. *Energy Environ. Sci.* 8:558-567.

89. Vink, E.T.H., Rabago, K.R., Glassner, D.A., Gruber, P.R. 2003. Applications of life cycle assessment to NatureWorks(TM) polylactide (PLA) production. *Pol. Degrad. Stability* 80:403-419.

90. Vink, E.T.H., Davies, S. 2015. Life Cycle Inventory and Impact Assessment Data for 2014 Ingeo™ Polylactide Production. *Indus. Biotechnol.* 11:167-180.

91. Groot, W.J., Borén, T. 2010. Life cycle assessment of the manufacture of lactide and PLA biopolymers from sugarcane in Thailand. *Int. J. Life Cycle Assess.* 15:970-984.

92. COWI A/S, Utrecht University. 2018. Environmental impact assessments of innovative bio-based product - Summary of methodology and conclusions. Brussels, European Commission: pp 1-131. [Online] [Cited: 16 November 2019]. doi:10.2777/83590. https://op.europa.eu/en/publication-detail/-/publication/9ab51539-2e79-11e9-8d04-01aa75ed71a1.

93. Posen, I.D., Griffin, W.M., Matthews, H.S., Azevedo, I.L. 2014. Changing the renewable fuel standard to a renewable material standard: Bioethylene Case Study. *Environ. Sci. Technol.* 49:93-102.

94. Albercht, J., Carrez D., Cunningham P., Daroda L., Mancia R. 2010. The Knowledge Based Bio-Economy (KBBE in Europe: Achievements and Challenges). http://www.kbbe2010.be/en/kbbe2010/programme/kbbe-report.

95. Hermann, B.G., Blok, K., Patel, M.K. 2007. Producing bio-based bulk chemicals using industrial biotechnology saves energy and combats climate change*. Environ. Sci. Technol.* 41:7915-7921.

96. Buttazzoni, M. 2009. GHG emission reductions with industrial biotechnology: assessing the opportunities. [Online] [Cited: 25 October 2019]. https://d2ouvy59p0dg6k.cloudfront.net/downloads/wwf_biotech_technical_report.pdf.

97. CEN-EN 16760 Biobased products - Life Cycle Assessment. 2015. European Committee for Standardization (CEN), Brussels. [Online] [Cited: 14 November 2019]. https://standards.globalspec.com/std/9972876/EN%2016760.

98. CEN-EN 16760 Biobased products - Sustainability criteria. 2016. European Committee for Standardization (CEN), Brussels. [Online] [Cited: 14 November 2019]. https://standards.globalspec.com/std/10005544/EN%2016751.

99. World Energy Outlook 2019. 2019. Internal Energy Agency. [Online] 13 November 2019 [Cited: 16 November 2019]. https://www.iea.org/newsroom/news/2019/november/world-energy-outlook-2019-highlights-deep-disparities-in-the-global-energy-system.html.

100. Hopwood, L. 2009. Anaerobic Digestion; Renewable Fuels and Energy Factsheet. http://www.nnfcc.co.uk/publications/nnfcc-renewable-fuels-and-energy-factsheet-anaerobic-digestion.

101. Waste To Chemicals Rotterdam. 2019. WtoC. [Online] [Cited: 28 October 2019]. https://w2c-rotterdam.com/.

102. Task 33 Database, gasification of biomass and waste. 2019. IEA Bioenergy Task 33e Thermal gasification of biomass. [Online] [Cited: 5 May 2019.] http://task33.ieabioenergy.com/.

103. Areste, M. 2010. Carbon dioxide as chemical feedstock. Wiley-VCH Verlag GmbH & Co. Weinheim, Germany. ISBN: 978-527-32475-0.

104. Raschka, A., Skoczinski, P., Ravenstijn J., Carus, M. 2019. Carbon dioxide (CO_2) as chemical feedstock for polymers - technologies, polymers, developers and producers. nova-Institute GmbH. [Online] 2019 [Cited: 23 October 2019]. http://bio-based.eu/publication-search/?wpv_post_search=co2&wpv_filter_submit=.

105. Davies, P., de Guzman, D. 2017. Replacing existing petro-chemicals with bio-based alternatives – Tecnon OrbiChem. Powerpoint presentation at Bio World Congress Montreal July 2017. [ONLINE] [Sited 30 October 2019] https://www.bio.org/sites/default/files/0830AM-Philippa%20Davies.pdf.

106. Lewandowski, S. (2016) Ethylene – Global. IHS Markit Asia Chemical Conference. https://cdn.ihs.com/www/pdf/Steve-Lewandowski-Big-Changes-Ahead-for-Ethylene-Implications-for-Asia.pdf.

107. Higson, A. 2013. Global trends in the Bioeconomy. [Online] [Cited: 31 October 2019]. https://www.slideshare.net/AHigson/global-trends-in-the-bioeconomy.

108. Fuel ethanol production worldwide in 2018, by country (in million gallons). 2019. Statista. [Online] 15 February 2019 [Cited: 25 October 2019]. https://www.statista.com/statistics/281606/ethanol-production-in-selected-countries/.

109. Croda completes Ethanol to EO Plant In Delaware. Ribbon-Cutting for First-of-its-Kind Chemical Manufacturer in Delaware. 2017. [Online] 19 October 2017 [Cited: 28 October 2019]. https://everchem.com/croda-completes-ethanol-eo-plant-delaware/.

110. Re-starting production of Bio-based acetic acid from August 2018. 2018. BioBased News. [Online] 25 July 2018 [Cited: 28 October 2019]. http://news.bio-based.eu/re-starting-production-of-bio-based-acetic-acid-from-august-2018/.

111. Renewable propane – a clean fuel made even cleaner. 2018. Neste. [Online] [Cited: 10 October 2019.] https://www.neste.com/companies/products/renewable-fuels/renewable-propane.

112. Nexant Chemsystems. (2012) Evolving Propylene Sources Solution to Supply Shortages? [Online] [Cited: 1 October 2019.] https://www.nexantsubscriptions.com/file/42395/download?token=ZggJiM_s.

113. Neste and LyondellBasell announce commercial-scale production of bio-based plastic from renewable materials (2019) Neste [Online] [Cited: 8 October 2019] https://www.neste.com/releases-and-news/neste-and-lyondellbasell-announce-commercial-scale-production-bio-based-plastic-renewable-materials.

114. Pereira, G.A.G., Perez, J.R., Carazzolle, M.F. et al. 2011. Mircoorganisms and process for producing n-propanol. WO2011/029166 A1.

115. Butagaz and Global Bioenergies announce their first delivery of bio isobutene, a bio-sourced gas, to the Héraclès Winery. 2019. Global Bioenergies. [Online] 12 March 2019 [Cited: 14 October 2019]. https://www.global-bioenergies.com/butagaz-and-global-bioenergies-announce-their-first-delivery-of-bio-isobutene-a-bio-sourced-gas-to-the-heracles-winery/?lang=en.

116. Matsumoto Y., Hirano J., Morishige, T., Shirai, T. et al. 2011. Highly productive isopropyl alcohol-producing bacterium. WO2011/111638A1.

117. Takebayashi N., Wada M., Mochizuki, D., Yoshimi F., et al. 2010. Isopropyl alcohol-producing bacterium and method of producing isopropyl alcohol using the same. US2010/0311135 A1.

118. Ohkubo, T., Fujiwara, K., Fujita T. 2011. Olefin production process. US20110230696A1.

119. Propylene Glycol Market by Source (Petroleum and bio-based), application (unsaturated polyester resin, antifreeze & functional fluid, food, pharmaceuticals & cosmetics), end-use industry (transportation, building & construction) - Global Forecast to 2021. 2019. Markets and Markets. [Online] 15 February 2019 [Cited: 25 October 2019]. https://www.marketsandmarkets.com/Market-Reports/propylene-glycol-market-264488864.html.

120. Lane, J. 2018. The Sweet Four: Fortess acquires S2G, taking xylitol to demo scale. [ONLINE] 21 March 2018 [Sited 24 October 2019] https://www.biofuelsdigest.com/bdigest/2018/03/21/the-sweet-four-fortess-acquires-s2g-taking-xylitol-to-demo-scale-cargill-begins-commercial-production-of-evolvas-stevia/.

121. DuPont Tate & Lyle Bioproducts. Performance is in our nature. 2019. [Online] [Cited: 4 October 2019] http://www.duponttateandlyle.com/.

122. DuPont Tate & Lyle Bio Products Expanding Bio-PDO™ Production in Tennessee by 35 million pounds . 2018. *DuPont Tate & Lyle Bio Products.* [Online] 4 March 2018. [Cited: 13 Augustus 2019] http://www.duponttateandlyle.com/DuPont-Tate-Lyle-Bio6Products-Expanding-Bio-based-Propanediol-Production-in-Tennessee.

123. The SORONA® Story. Dupont Sorona. 2019. [Online] [Cited: 24 October 2019] http://sorona.com/our-story/

124. Biddy, M.J., Scarlata, C., Kinchin, C. 2016. Chemicals from biomass: A market assessment of bioproducts with near-term potential. National Renewable Energy Laboratory. [Online] March 2016 [Cited: 25 October 2019]. https://www.nrel.gov/docs/fy16osti/65509.pdf.

125. Bioacetone: Process; Technology; Products. 2019. Celtic Renewables [Online] [Cited: 29 October 2019]. http://www.celtic-renewables.com/process/technology-products.

126. Green Biologics' UK R&D team are about to enter an exciting new era. 2019. Green Biologics. [Online] September 2019 [Cited: 24 October 2019] https://greenbiologics.com/.

127. Solvay completes the sale of its Vinythai stake to AGC Asahi Glass. 2017. Solvay. [Online] 23 February 2017 [Cited: 25 October 2019]. https://www.solvay.com/en/press-release/solvay-completes-sale-its-vinythai-stake-agc-asahi-glass.

128. Total Corbion PLA celebrates the opening of its 75,000 tons per year bioplastics plant. 2019. Total-Corbion. Corbion. [Online] [Cited: 24 September 2019.] https://www.total-corbion.com/news/total-corbion-pla-celebrates-the-opening-of-its-75-000-tons-per-year-bioplastics-plant/?p=1&q=.

129. Shen, L, Haufe, J. and Patel, M.K. 2009. Product overview and market projection of emerging bio-based plastics. PRO-BIP 2009, Final report, report commissioned by European Polysaccharide Network of Excellence (EPNOE) and European Bioplastics, 243 pp https://www.uu.nl/sites/default/files/copernicus_probip2009_final_june_2009_revised_in_november_09.pdf.

130. PolyOne's exclusive reSound™ biopolymer formulations combine engineering thermoplastic resins with bio-derived polymers such as PLA (2019). Polyone. [Online] [Cited: 10 October 2019] https://www.polyone.com/search?query=pla.

131. AkzoNobel/Nouryon. 2019. AkzoNobel and PURAC develop additives deal for Poly Lactic Acid. [Online] [Cited: 17 January 2011] http://www.akzonobel.com/polymer/news/pressreleases/2009/akzonobel_and_purac_develop_additives_deal_for_poly_lactic_acid.aspx.; [Online] [Cited: 17 January 2019] https://polymerchemistry.nouryon.com/products-applications/thermoplastics-rubber/polymer-modification/.

132. Arkema. Arkema Inc. Sustainability additives group introduces new PLA processing lubricant-Biostrength® 280 . *Arkema.* [Online] [Cited: 17 January 2011] http://www.arkema-inc.com/index.cfm?pag=343&PRR_ID=814; [Online] [Cited: 28 August 2019] https://www.additives-arkema.com/export/sites/acrylicmodifiers/.content/medias/downloads/literature/biostrength-280-impact-modifier.pdf.

133. DuPont. DuPont Packaging introduces FDA-compliant PLA modifier for food packaging. [Online] [Cited: 17 January 2011]http://www2.dupont.com/Press_Club/en_US/food_news/biomax_21052007.html; [Online] [Cited: 15 September 2019] https://www.dupont.com/content/dam/assets/products-and-services/packaging-materials-solutions/assets/biomax_strong_ep9000a.pdf.

134. Rosales-Calderon, O., Arantes, V. 2019. A review on commercial-scale high-value products that can be produced alongside cellulosic ethanol. *Biotechnol. Biofuels* 12:240-298.

135. Total-Corbion Purac develops a PLA compound with engineering plastics properties. [Online] [Cited: 17 January 2011] http://www.purac.com/EN/Green_chemicals/News/Press-release-Development-PLA-compound.aspx; [Online] [Cited: 17 August 2019] https://www.total-corbion.com/media/9325/factsheet-sc-pla-180418-web.pdf.

136. Acrylic acid market by derivative (Esters/Acrylates - Methyl, ethyl, butyl, 2-EH; Polymers - elastomers, superabsorbent polymers, water treatment polymers; other derivatives), by applications & region - Global forecast to 2020. 2016. Markets and Markets. [Online] March 2016 [Cited: 25 October 2019]. https://www.marketsandmarkets.com/Market-Reports/acrylic-acid-market-683.html.

137. 3-Hydroxypropionic Acid (3-HPA). Wisconsin biorefining development initiative (http://www.biorefine.org/prod/3acid.pdf).

138. Energetics Incorporated. 2003. Industrial bioproducts: Today and tomorrow. U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Office of the Biomass Program, Washington, D.C.

139. Haas, T., Klasovsky, F., Krauter, H., Schaffer, S., Schöbel, R., Tacke, T., Vorlop, K-D., Willke, T., Wessel, M. 2010. Enzymatic method for producing aldehydes Patent No. WO 2010/127970 A2]. Genf: WIPO, 43p.

140. Krauter, H., Willke, T., Vorlop, K.-D. 2011. Production of high amounts of 3-hydroxypropionaldehyde from glycerol by *Lactobacillus reuteri* with strongly increased biocatalyst lifetime and productivity. *New Biotechnol.* 29(2):211-117.

141. Terrade, F.G., J. van Krieken, J., B. J. V. Verkuijl, B.J.V., Bouwman, E. 2017. Catalytic Cracking of Lactide and Poly(Lactic Acid) to Acrylic Acid at Low Temperatures, *ChemSusChem* 10:1904-1908.

142. Garcia, V., Päkkilä, **J., Ojamo**, **H., Muurinen**, **E.** (2011.) Challenges in biobutanol production: How to improve efficiency. *Renew. Sust. Energy Rev.* 15:964-980.

143. Butamax®, Announces Next Step in Commercialization of Bio-Isobutanol with Acquisition of Ethanol Facility in Kansas. 2018. [Online] 3 April 2018 [Cited: 14 October 2019] https://www.butamax.com/wp-content/uploads/2017_04_03_ib_butamax_announce-FINAL.pdf.

144. Gevo Announces Breakthrough Development of Low-Carbon No Particulate Renewable Diesel 2019. **Gevo** [Online] [Cited: 24 October 2019] http://www.globenewswire.com/news-release/2019/09/04/1910857/0/en/Gevo-Announces-Breakthrough-Development-of-Low-Carbon-No-Particulate-Renewable-Diesel.html.

145. Eikmanns, B.J., Blombach, B. 2014. Isobutanol. In: Bioprocessing of Renewable Resources to Commodity Bioproducts (Bisaria, V.S., Kondo, A. eds) John Wiley & Sons pp 327-352. https://doi.org/10.1002/9781118845394.ch12.

146. Strobel Energy Group Selected to Design & Construct Prairie Catalytic Ethyl Acetate Facility in Columbus, Nebraska. 2017. PR Newawire. [Online] 28 July 2017 [Cited: 23 October 2019]. https://www.prnewswire.com/news-releases/strobel-energy-group-selected-to-design--construct-prairie-catalytic-ethyl-acetate-facility-in-columbus-nebraska-300495697.html.

147. DSM and Roquette take next step in Reverdia bio-succinic acid joint venture. 2019. Bioenergy International. [Online] 2019 [Cited: 23 October 2019]. https://bioenergyinternational.com/biochemicals-materials/dsm-and-roquette-take-next-step-in-bio-based-succinic-acid.

148. Myriant Technologies now GC Innovation America. 2019. GC Innovation America. [Online] [Cited: 24 October 2019] https://www.gcinnovationamerica.com/about-us/.

149. Tokiwa, Y., Ugwu, C.U. 2007. Biotechnological production of (*R*)-3-hydroxybutyric acid monomer. *J. Biotechnol.* 132:264–272.

150. Whited, G.M., Feher, F.J., Benko, D.A. et al. 2010, Development of a gas-phase bioprocess for isoprene-monomer production using metabolic pathway engineering*. Industrial Biotechnology*, 3:152-163.

151. Amyris announces the execution of strategic supply agreements with Raízen. 2019. Amyris [Online] 21 May 2019 [Cited: 24 October 2019] https://investors.amyris.com/2019-05-21-Amyris-Announces-the-Execution-of-Strategic-Supply-Agreements-with-Raizen-the-Largest-Sugar-Producer-in-the-World.

152. Methacrylate Monomers, Lucite International. 2019. Alpha Technology. [Online] [Cited: 18 October 2019] https://www.luciteinternational.com/monomers-emea-manufacturing-alpha-technology-15/; https://www.luciteinternational.com/monomers-emea-manufacturing-biotechnology-16/.

153. Carole, T.M., Pellegrino, J., Paster., M.D. 2004. Opportunities in the industrial biobased products industry. *Appl. Biochem.Biotechnol.* 113–116:871-885.

154. Vertec Biosolvents. 2019. Bio-Based solvent formulations for your product formulating and cleaning requirements. [Online] [Cited: 20 October 2019] http://www.vertecbiosolvents.com.

154. PURASOLV® Superior solvency for agrochemical formulations. 2017. Corbion – Biobased Chemicals. [ONLINE] October 2017 [Sited 31 October 2019] https://www.corbion.com/media/467624/corbion-purasolv.pdf.

155. Raschka, A., Skoczinski, P., Chinthapalli, R., Puente, A., Carus, M. 2019. Levulinic acid – A versatile platform chemical for a variety of market applications – Global market dynamics, demand/supply, trends and market potential. [Online] [Cited: 29 October 2019]. http://www.bio-based.eu/reports/.

156. Mamman, A.S., Lee, J-M., Kim, Y-C. et al. 2008. Furfural: Hemicellulose/Xylose-derived biochemical. *Biofuels Bioprod. Bioref.* 2:438-435.

157. Hoydonckx, H.E., Van Rhijn, W.M., Van Rhijn, W., De Vos, D.E., Jacobs, P.A. 2007. "Furfural and Derivatives" in Ullmann's Encyclopedia of Industrial Chemistry 2007, Wiley-VCH, Weinheim.

158. Okabe, M., Lies, D., Kanamasa, S., Park, E.Y. 2009. Biotechnological production of itaconic acid and its biosynthesis in *Aspergillus terreus. Appl. Microbiol. Biotechnol.* 84:597-606.

159. **Marques, C., Tarek, R., Sara, M., Brar, S.K.** 2016. Sorbitol production from biomass and its global market. In: Brar, S.K, Sarma, S.J., Pakshirajan, K. (Eds.), Platform Chemical Biorefinery. Elsevier, pp. 217–227. ISBN: 9780128029800.

160. Akinterinwa, O., Khankal, R., Cirino, P.C. 2008. Metabolic engineering for bioproduction of sugar alcohols. *Current Opinion Biotechnol.* 19:461-467.

161. Star Colibri project. 2010. Deliverable 2.1 Background information and biorefinery status, potential and sustainability. http://www.star-colibri.eu/files/files/Deliverables/D2.1-Report-19-04-2010.pdf.

162. van Putten, R-J., van der Waal, J.C., Harmse, M., van den Bovenkamp, H.H., de Jong, E., Heeres, H.J. 2016. A comparative study on the reactivity of various ketohexoses to furanics in methanol*. ChemSusChem* 9:1827-34. DOI: 10.1002/cssc.201600252.

163. Tong, X, Ma, Y. and Li, Y. 2010. Biomass into chemicals: Conversion of sugars to furan derivatives by catalytic processes. *Appl. Cat. A: General* 385:1-13.

164. Avantium joins the Paper Bottle Project. 2019. Avantium [Online] 11 October 2019 [Cited: 12 October 2019] https://www.avantium.com/in-the-media/avantium-joins-the-paper-bottle-project/.

165. de Jong, E., Dam, M.A., Sipos, L., Gruter G-J.M. 2012. Furandicarboxylic acid (FDCA), a versatile building block for a very interesting class of polyesters. *ACS Symposium Series* "Biobased Monomers, Polymers and Materials" (eds Smith, P.B. and Gross, R.) 1-13. https://DOI:10.1021/bk-2012-1105.ch001.

166. Burgard, A.P., Pharkya, P. Osterhout, R.E. 2010. Microorganisms for the production of adipic acid and other compounds. US 7,799,545.

167. Haveren, J., Scott, E.L., Sanders, J. 2008. Bulk chemicals from biomass. *Biofuels Bioprod. Bioref.* 2:41-57.

168. Rose, M., Palkovits, R. 2012. Isosorbide as a Renewable Platform chemical for Versatile Applications—Quo Vadis? *ChemSusChem* 5:167-176.

169. Sherwood J., De Bruyn, M., Constantinou, A. et al. 2014. Dihydrolevoglucosenone (Cyrene) as a bio-based alternative for dipolar aprotic solvents. *Chem. Comm*. 50:9650-9652.

170. Ciriminna, R., Meneguzzo, F., Delisi, R., Pagliaro, M. 2017. Citric acid: emerging applications of key biotechnology industrial product. *Chem Cent J.* 11:22-30.

171. Coca-Cola Expands Access to PlantBottle IP. 2019. The Coca Cola Company. [Online] 25 January 2019 [Cited: 12 October 2019] https://www.coca-colacompany.com/stories/coca-cola-expands-access-to-plantbottle-ip-.

172. PepsiCo. Press release: PepsiCo Develops World's First 100 Percent Plant-Based, Renewably Sourced PET Bottle. (http://www.pepsico.com/PressRelease/PepsiCo-Develops-Worlds-First-100-Percent-Plant-Based-Renewably-Sourced-PET-Bott03152011.html).

173. Peters M.W., Taylor, J.D., Jenni, M., Manzer, L., Henton, D.E. 2011. Integrated Process to Selectively Convert Renewable Isobutanol to P-Xylene. Gevo patent US 2011087000 (A1).

174. Brandvold, T.A. 2010. Carbohydrate route to paraxylene and terephthalic acid. US 20100331568 (A1).

175. Mol, J.C. 2004. Catalytic metathesis of unsaturated fatty acid esters and oils, *Top. Catal*. 27:97–104.

176. Yang, Y., Lu, W., Zhang, X., Xie, W., Cai, M., Gross, R.A. 2010. Two-step biocatalytic route to biobased functional polyesters from ω-carboxy fatty acids and diols. *Biomacromolecules* 11:259–268.

177. Bioplastics market data. 2019. European Bioplastics. [Online] [Cited: 24 October 2019] https://www.european-bioplastics.org/market/.

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