Bio-based Chemicals

Value Added Products from Biorefineries

This report, that was prepared on behalf of IEA Bioenergy – Task42 Biorefinery, addresses the main bio-based chemicals that potentially could be co-produced with secondary energy carriers in integrated biorefinery facilities. Biorefining, i.e. the sustainable processing of biomass into a spectrum of marketable Bio-based Products (chemicals, materials) and Bioenergy (fuels, power, heat) generally is seen as the optimal strategy to sustainably convert biomass into a portfolio of biomass-derived intermediates and products that will form the base for the future Bio-based Economy. The report deals with the current production of bio-based chemicals, chemicals that potentially could be produced from major biorefinery platforms (syngas, biogas, sugars, oils, algae, organic solution, lignin, pyrolysis-oil), market growth predictions for the production of bio-based chemicals, economic benefits of co-producing bioenergy and bio-based chemicals, and an overview of commercial and near market bio-based chemicals (C1-C6, Cn). The purpose of the report is to provide an unbiased, authoritative statement aimed at stakeholders from the agro-sector, industry, SMEs, policy makers, and NGOs.

IEA Bioenergy

IEA Bioenergy – Task42 Biorefinery

Bio-based Chemicals
Value Added Products from Biorefineries

Report prepared by
Ed de Jong, Avantium Chemicals (Netherlands)
Adrian Higson, NNFCC (UK)
Patrick Walsh, Energy Research Group (Ireland)
Maria Wellisch, Agriculture and Agri-Food Canada (Canada).

With input from
Maria Barbosa, Rolf Blaauw, Richard Gosselink, René van Ree WUR Food & Biobased Research (Netherlands)
Henning Jørgensen, University of Copenhagen (Denmark)
Michael Mandl, Joanneum Research (Austria)
Murray McLaughlin, Sustainable Chemistry Alliance (Canada)
Mark A. Smith, National Research Council, Plant Biotechnology Institute (Canada)
Thomas Willke, Johann Heinrich von Thünen-Institut (Germany).

on behalf of

IEA Bioenergy | Task 42 Biorefinery

TABLE OF CONTENTS

SUMMARY

Around the world significant steps are being taken to move from today's fossil based economy to a more sustainable economy based on biomass. The transition to a bio-based economy has multiple drivers:

- the need to develop an environmentally, economically and socially sustainable global economy,
- the anticipation that oil, gas, coal and phosphorus will reach peak production in the not too distant future and that prices will climb,
- the desire of many countries to reduce an over dependency on fossil fuel imports, so the need for countries to diversify their energy sources,
- the global issue of climate change and the need to reduce atmospheric greenhouse gases (GHG) emissions,
- and the need to stimulate regional and rural development.

One of the key institutions to accommodate this transition is the IEA Bioenergy Implementation Agreement. Within IEA Bioenergy, Task 42 specifically focuses on Biorefineries; e.g. the co-production of fuels, chemicals, (combined heat &) power and materials from biomass. A key factor in the realisation of a successful bio-based economy will be the development of biorefinery systems allowing highly efficient and cost effective processing of biological feedstocks to a range of bio-based products, and successful integration into existing infrastructure. Although global bio-based chemical and polymer production is estimated to be around 50 million tonnes, the historic low price of fossil feedstocks together with optimized production processes has restricted commercial production of bio-based products. The recent climb in oil prices and consumer demand for environmentally friendly products has now opened new windows of opportunity for bio-based chemicals and polymers. Industry is increasingly viewing chemical and polymer production from renewable resources as an attractive area for investment. Within the bio-based economy and the operation of a 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. The production of bio-based products could generate US$ 10-15 billion of revenue for the global chemical industry.

Within IEA Bioenergy Task 42 "Biorefinery" a biorefinery classification method for biorefinery systems was 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)
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 and 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 hemicelluloses, 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 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 is often a challenge. The co-production of chemicals, materials food and feed can generate the necessary added value. This report highlights all bio-based chemicals with immediate potential as biorefinery 'value added products'. The selected products are either demonstrating strong market growth or have significant industry investment in development and demonstration programmes. The report introduces companies actively developing bio-based chemicals and polymers and provides Information on potential greenhouse gas emission savings and how the co-production of bio-based chemicals with biofuels can influence the economics of biofuels production.

1. INTRODUCTION

The production of bio-based chemicals is not new, nor is it an historic artefact. Current global bio-based chemical and polymer production (excluding biofuels) is estimated to be around 50 million tonnes (1). Notably examples of bio-based chemicals include non-food starch, cellulose fibres and cellulose derivatives, tall oils, fatty acids and fermentation products such as ethanol and citric acid.
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 (111).

However the cost of bio-based production in many cases exceeds the cost of petrochemical production. Also new products must be proven to perform at least as good as the petrochemical equivalent they are substituting and to have a lower environmental impact.

---

[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 (111).

Historically bio-based 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 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 recent climb in oil prices, the consumer demand for environmentally friendly products, population growth and limited supplies of non-renewable resources have now opened new windows of opportunity for bio-based chemicals and polymers. Industry is increasingly viewing chemical and polymer production from renewable resources as an attractive area for investment. However, not only the price of oil and consumer demand is acting as drivers 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. One reason why the chemical industry in more isolated areas such as Ireland never really became economic was due to the need to import chemical components and additives. Island economies may be scaled up to global economies if the chemical feedstocks are available within a reasonable geographic region. Biomass possesses this inherent possibility.

2. BIOREFINERIES AND THE BIO-BASED ECONOMY

Around the world small but discernable 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: an over dependency of many countries on fossil fuel imports, the anticipation that oil, gas, coal and phosphorus will reach peak production in the not too distant future; the need for countries to diversify their energy sources, the global issue of climate change and the desire to reduce the emission of greenhouse gases, and the need to stimulate regional and rural development (3, 4, 5).

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, probably is a more efficient approach for the sustainable valorisation of biomass resources in a future biobased economy (6, 7). Biorefining can also be integrated with food or feed production, as is the case with first generation ethanol production.

However, the main driver for the development and implementation of 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 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. Both conventional (ethanol, biodiesel) and advanced biofuels (lignocellulosic methanol, ethanol, butanol, Fischer-Tropsch-diesel/kerosine, ...) generally cannot be produced in a profitable way at current crude oil prices. This implicates that they only can enter the market if they are forced to (governmental regulation) or if significant financial support is provided (tax reduction). This artificial market will not be a long lasting one. A significant reduction in biofuel production costs is required to create a sustainable market.

A very 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, feed) and biofuels from biomass resources in a very efficient integrated approach.

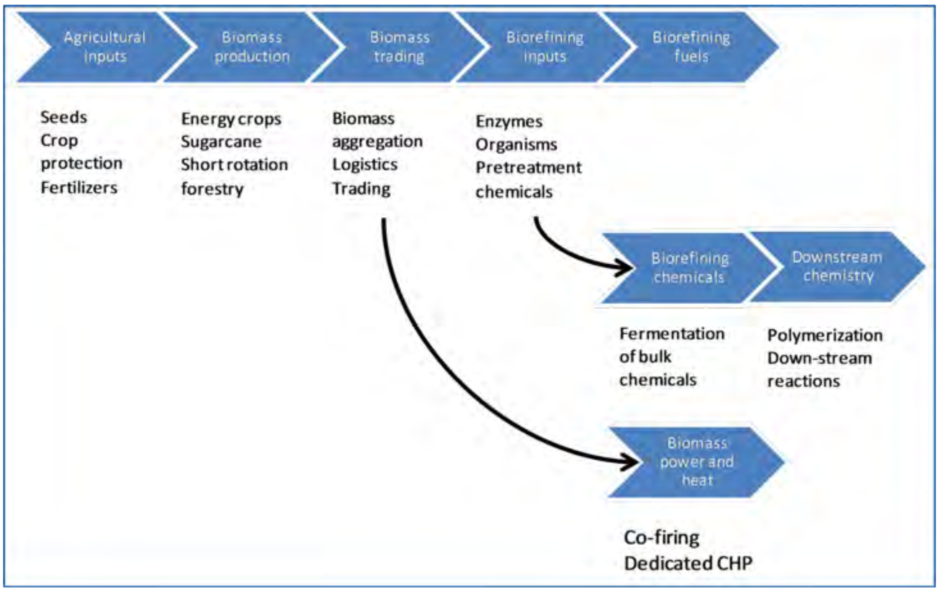


Figure 1. An example of a Bio-based products value chain (source World Economic Forum, The Future of Industrial Biorefineries (7)) which is a general illustration of an agriculture feedstock based biorefinery that is built around biochemical conversion technologies.

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 [8]. The main overall conclusion was that the production costs of the biofuels could be reduced by about 30% using the biorefinery approach.

Figure 1. is a general illustration of an agriculture feedstock based biorefinery that is built around biochemical conversion technologies. 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.

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 biofuels should improve the overall economics of biorefinery operation 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. 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 US$ 10-15 billion of revenue for the global chemical industry (7). Examples of some of these opportunities are described as follows.

A key factor in the realisation 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. BIOREFINERIES - CLASSIFICATION

Biorefineries can be classified on the basis of a number of their key characteristics. Major feedstocks include perennial grasses, starch crops (e.g. wheat and maize), sugar crops (e.g. beet and cane), lignocellulosic crops (e.g. managed forest, short rotation coppice, switchgrass), lignocellulosic residues (e.g. 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 post consumer waste).

Key biorefinery characteristics (69)
Feedstock utilised
Biorefinery Platform
Products
Process

These feedstocks can be processed to a range of biorefinery streams termed platforms. These platforms include single carbon molecules such as biogas and syngas, 5 and 6 carbon carbohydrates from starch, sucrose or cellulose; a mixed 5 and 6 carbon carbohydrates stream derived from hemicelluloses, lignin, oils (plant-based or algal), organic solutions from grasses, pyrolytic liquids. These primary platforms can be converted to wide range of marketable products using combinations of thermal, biological and chemical processes. Knowledge of a biorefinery's feedstock, platform and product allows it to be classified in a systematic manner (69). The classification of biorefineries enables the comparisons of biorefinery systems, improves the understanding of global biorefinery development, and allows the identification of technology gaps. An overview of current feedstocks, platforms and products is given in **Figure 2**.

Examples of biorefinery classification include:

- C6 sugar biorefinery yielding ethanol and animal feed from starch crops
- Syngas biorefinery yielding FT-diesel and naptha from lignocellulosic residues
- C6 and C6/C5 sugar and syngas biorefinery yielding ethanol, FT-diesel and furfural from lignocellulosic crops

Examples of how operating biorefineries can be classified can be viewed on the IEA Bioenergy Task 42 website: http://www.iea-bioenergy.task42-biorefineries.com.

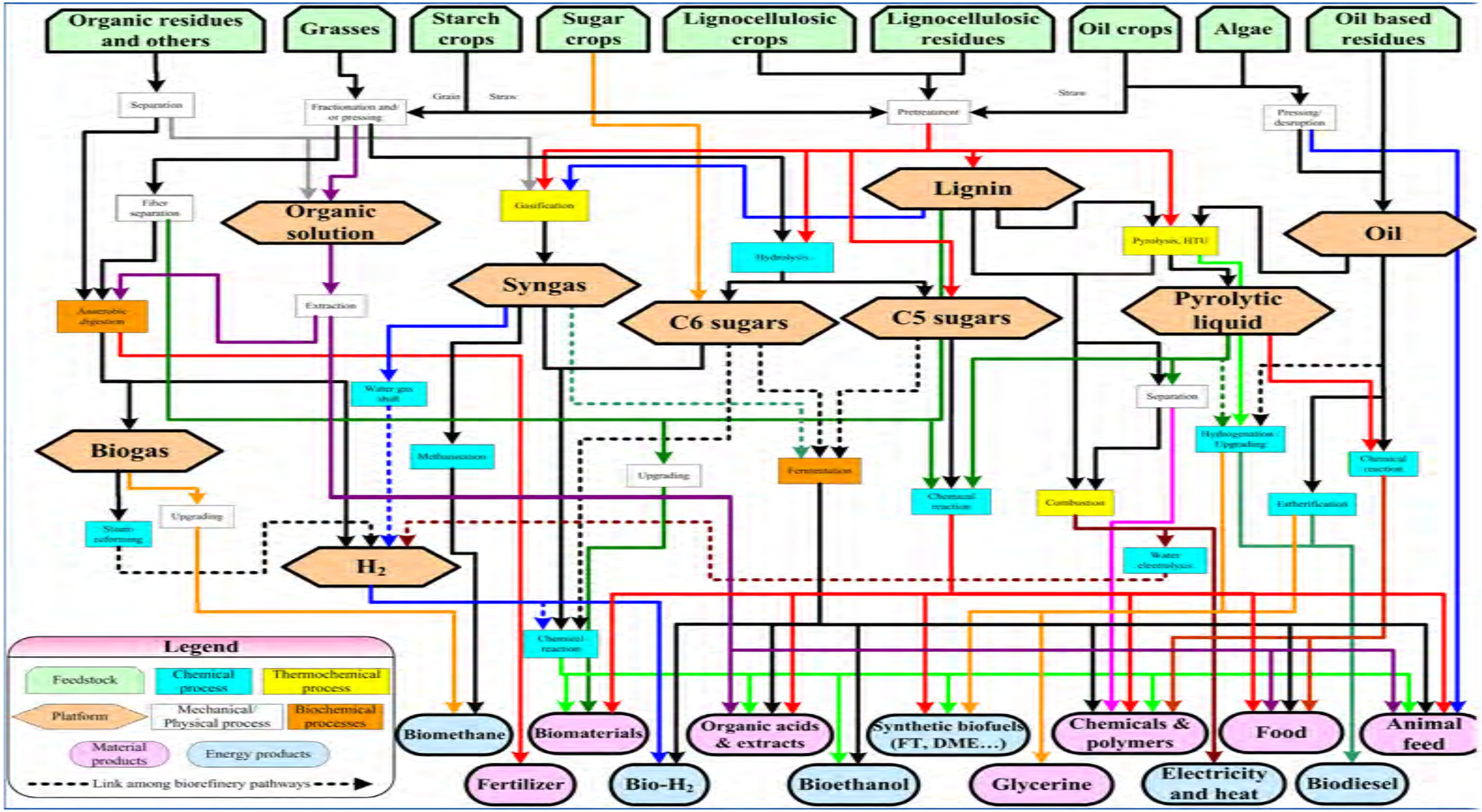


Figure 2. Overview of IEA Bioenergy Task 42 biorefinery classification system (69).

4. POTENTIAL CHEMICALS AND POLYMERS FROM BIOREFINERY PLATFORMS

4.1 Syngas Platform

Synthesis gas (syngas) is a mixture of mainly carbon monoxide and hydrogen. It is produced by subjecting biomass to extreme heat (over 430°C/860°F) in the presence of oxygen or air in a process known as gasification. After cleaning, the syngas can be used to produce power or can be converted into lower alcohols, fuel (e.g. Fischer-Tropsch diesel) and chemical products (83). Syngas can also be fermented to give methanol, ethanol, ammonia and potentially other chemical building blocks (12).

Promising syngas derived chemicals:
Methanol
DME (dimethylether)
Ethanol
Fischer-Tropsch diesel

4.2 Biogas Platform

Currently, biogas production is mainly based on the anaerobic digestion of "high moisture content biomass" such as manure, waste streams from food processing plants or biosolids from municipal effluent treatment systems. Biogas production from energy crops will also increase and will have to be based on a wide range of crops that are grown in versatile, sustainable crop rotations. In addition, more by-products from the agricultural, food and energy industry need to be integrated. Anaerobic digestion results in the formation of methane that is typically scrubbed and used for its energetic value, and solid and liquid digestate. Biogas production can be part of sustainable biochemicals and biofuels-based biorefinery concepts as it can derive value from wet streams. Value can be increased by optimizing methane yield and economic efficiency of biogas production (84), and deriving nutrient value from the digestate streams.

4.3 C6 and C6/C5 Sugar Platform

Six carbon sugar platforms can be accessed from sucrose or through the hydrolysis of starch or cellulose to give glucose. Glucose serves as feedstock for (biological) fermentation processes providing access to a variety of important chemical building blocks. Glucose can also be converted by chemical processing to useful chemical building blocks.

Mixed six and five carbon platforms are produced from the hydrolysis of hemicelluloses. The fermentation of these carbohydrate streams can in theory produce the same products as six carbon sugar streams; however, technical, biological and economic barriers need to be overcome before these opportunities can be exploited. Chemical manipulation of these streams can provide a range of useful molecules.

Fermentation Products

The number of chemical building blocks accessible through fermentation is considerable. 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. Around 8 million tonnes of fermentation products are currently produced annually (8).

- Fermentation derived fine chemicals are largely manufactured from starch and sugar (wheat, corn, sugarcane etc.)
- The global market for fermentation derived fine chemicals in 2009 was $16 billion and is forecasted to increase to $22 billion by 2013 (119), see Table 1.

Table 1. Global market for fermentation derived fine chemicals (119).

Chemical	2009 $ millions	2013 $ millions
Amino Acids	5,410	7,821
Enzymes	3,200	4,900
Organic Acids (Lactic Acid 20%)	2,651	4,036
Vitamins and related compounds	2,397	2,286
Antibiotics	1,800	2,600
Xanthan	443	708
Total	15,901	22,351

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, carbohydrate costs are increasing strongly in recent years and their use for non-food products is under pressure even in China. 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.

Innovative fermentation products:
Succinic acid
Itaconic acid
Adipic acid
3-Hydroxypropionic acid / aldehyde
Isoprene/farnesene
Glutamic acid
Aspartic acid

Chemical transformation products

Six and five carbon carbohydrates can undergo selective dehydration, hydrogenation and oxidation reactions to give useful products, such as: sorbitol, furfural, glucaric acid, hydroxymethylfurfural (HMF), and levulinic acid. Over 1 million tonnes of sorbitol is produced per year as a food ingredient, personal care ingredient (e.g. toothpaste), and for industrial use (9, 82).

Promising glucose chemical derivatives:
Sorbitol
Levulinic acid
Glucaric acid
Hydroxymethylfurfural
2,5-Furan dicarboxylic acid
p-Xylene

4.4 Plant-based Oil Platform

The oleochemical industry is a major producer of bio-based products. A recent study of Taylor indicates that in the 2009–10 cropping year the estimated world production of vegetable oils was close to 140 million metric tonnes. Of this, approximately 20% was used for non-food uses, including biofuel (126). Global oleochemical production in 2009 amounted to 7.7 million tonnes of fatty acids and 2.0 million tonnes of fatty alcohols (10). The majority of fatty acid derivatives are used as surface active agents in soaps, detergents and personal care products (126). Major sources for these applications are coconut, palm and palm kernel oil, which are rich in C12–C18 saturated and mono-unsaturated 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. 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. The utility of the fatty acids and esters is determined primarily by their chain length and functionality. Given advances in plant genetics and oil processing, there is considerable interest in developing plant oils for the manufacture of polymers such as polyurethanes, polyamides and epoxy resins (127). Biodiesel production has increased significantly in recent years with a large percentage being derived from palm, rapeseed and soy oils. In 2009 biodiesel production was around 14 million tonnes; this quantity of biodiesel co-produces around 1.4 million tonnes of glycerol.

Glycerol is an important co-product of fatty acid/alcohol production. The glycerol market demand in 2009 was 1.8 million tonnes (10). Glycerol is also an important co-product of fatty acid methyl ester (FAME) biodiesel production. It can be purified and sold for a variety of uses. The new supply 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. However, it has been the chemical conversion of glycerol to three carbon chemicals, such as epichlorohydrin and propylene glycol, that has received particular attention.

Promising glycerol derived chemicals:
Propylene glycol
Epichlorohydrin
1,3-Propanediol
3-Hydroxypropion aldehyde
Acrylic acid
Propylene
Methanol (via syngas)

There is also an important subcategory of oilseeds that produce natural waxes, such as liquid wax from jojoba seeds and the solid waxes collected from the leaf surfaces of the Carnuba palm and several desert shrubs. These tend to be used in specialized high value applications, such as cosmetics. Their excellent lubricity and stability in lubricant applications has led to interest in engineering wax ester production in commercial oilseed crops (126).

4.5 Algae Oil Platform

There are more than 40.000 different algae species both in seawater and freshwater. Algae biomass can be a sustainable renewable resource for chemicals and energy. The major advantages of using microalgae as renewable resource are:

1. Compared to plants algae have a higher productivity. This is mostly due to the fact that the entire biomass can be used in contrast to plants which have roots, stems and leafs. For example, the oil productivity per land surface can be up to 10 times higher than palm oil.
2. Microalgae can be cultivated in seawater or brackish water on non-arable land, and do not compete for resources with conventional agriculture.
3. The essential elements for growth are sunlight, water, CO_2 (a greenhouse gas), and inorganic nutrients such as nitrogen and phosphorous which can be found in residual streams.
4. The biomass can be harvested during all seasons and is homogenous and free of lignocellulose.

The incorporation of low-volume, high-value chemical products is considered as a step on the way to large-scale algal biochemicals and biofuels production. This may offer a business model for a faster deployment of this technology. The main components of microalgae are species dependent but can contain a high protein content, quantities can be up to 50% of dry weight in growing cultures with all 20 amino acids present. Carbohydrates as storage products are also present and some species are rich in storage and functional lipids, they can accumulate up to 50% lipids, and in very specific cases up to 80 % (the green algae Botryococcus) which accumulates long chain hydrocarbons. Other valuable compounds include: pigments, antioxidants, fatty acids, vitamins, anti-fungal, -microbial, -viral toxins, and sterols.

Microalgae have been grown for decades at small scale for high value compounds, especially in Asia and North America, mainly for application in food and feed. However, this is restricted to a very a small number of species; *Spirulina* and *Chlorella* are well-known examples. The production capacity for microalgae is presently limited in comparison to land-based energy crops.

The current worldwide microalgae manufacturing infrastructure (producing the equivalent of ~5000 tons of dry algal biomass) is devoted to extraction of high value products.

Production of microalgae for medium – low value products (bulk chemicals and energy) needs to take place on a much larger scale at much lower costs. In addition the energy balance should be positive. A leap in the development of microalgae technology is required for the production of biofuels and bulk chemicals; on a practical level, the scale of production needs to increase at least 3 orders of magnitude with a concomitant decrease in the cost of production by a factor 10. In addition a biorefinery infrastructure needs to be established in order to make use of the entire biomass, which is essential to achieve economic viability. Technology needs to be developed/improved for both cultivation and biorefinery. The support from industry will play a major role in this development and will enable the development of new markets (114, 115, 116).

4.6 Organic Solutions Platform

A green biorefinery (6) processes fresh wet biomass, such as grass, clover, alfalfa or immature cereals. First processing of wet biomass involves dewatering (e.g. screw press) to obtain two separate intermediates: a nutrient-rich juice "Organic Solutions" and a fibre-rich lignocellulosic press cake. Both intermediates are starting points for various valorization 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 – main components of fresh plant juice - can be used as fermentation medium or for generating feed products. Silage press juice has been demonstrated as feedstock for the production of bio-chemicals and fuels. Lactic acid and its derivatives as well as proteins, amino acids, bioethanol and energy via anaerobic digestion are the most favorable end-products from the organic solution platform.

The press cake fibres can be utilized as green feed pellets, processed to fibre products or potentially used as a raw material for other platforms (e.g. C6 and C5, syngas and lignin platforms.) Grass fiber products are currently in a market introduction phase (e.g. insulation material) and some technologies have been implemented at pilot and industrial scale (112). The liquid and solid organic residues can easily be used to produce biogas with subsequent generation of heat and electricity. Therefore the integration of an organic solution platform concept with anaerobic digestion is preferable.

4.7 Lignin Platform

Lignin 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 (78). 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 (77, 78), see **Figure 3**. Up to now the vast majority of industrial applications have been developed for lignosulfonates. These sulfonates are isolated from acid sulfite pulping and are used in a wide range of lower value applications where the form but not the quality is important. The solubility of this type of lignin in water is an important requirement for many of these applications. Around 67.5% of world consumption of lignosulfonates in 2008 was for dispersant applications followed by binder and adhesive applications at 32.5%. 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 molecular weight distribution of lignosulfonates. The only industrial exception is the limited production of vanillin from lignosulfonates (135). Besides lignosulfonates, Kraft lignin is produced as commercial product at about 60kton/y. New extraction technologies, developed in Sweden, will lead to an increase in Kraft lignin production at the mill side for use as external energy source and for the production of value added applications (136).

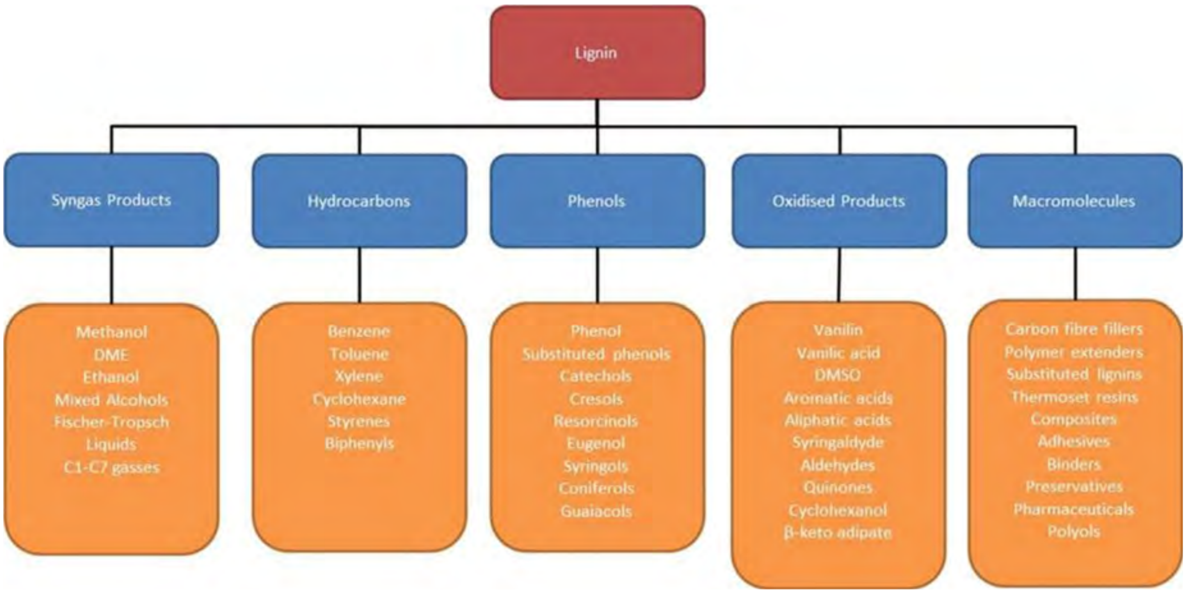


Figure 3. Potential products from Lignin.

The production of bioethanol from lignocellulosic feedstocks could result in new forms of higher quality lignin becoming available for chemical applications. The Canadian company Lignol Energy have announced the production of cellulosic ethanol at their continuous pilot plant at Burnaby, British Columbia. The process is based on a wood pulping process using Canadian wood species but the pilot plant will test a range of feedstocks while optimising equipment configurations, enzyme formulations and other process conditions (11). The Lignol Energy process produces a lignin product (HP-L™ lignin) upon which the company are developing new applications together with industrial partners. Also other lignin types will results from the different biomass pretreatment routes under development and unfortunately there is not one lignin macromolecule which will fits all applications. However, if suitable cost-effective and sustainable conversion technologies can be developed, a lignocellulosic biorefinery can largely benefit from the profit obtained from this side stream lignin (137).

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. The potential of catalytic conversions of lignin (degradation products) has been recently reviewed (79).

4.8 Pyrolysis Oil Platform

Biomass pyrolysis is the thermal depolymerization of biomass at modest temperatures in the absence of added oxygen. The spectrum of products from biomass pyrolysis depends on the process temperature, pressure, and residence time of the liberated pyrolysis vapors (83). A biorefinery based on pyrolysis oil is designed much like a traditional refinery. First biomass is converted into pyrolysis oil which can be a de-centralized process. Second, pyrolysis oil from different installations is collected at the biorefinery where it will be divided into different fractions. Each fraction can be upgraded with a different technology to finally derive the optimal combination of high value and low value products from the pyrolysis oil. The major high value compounds which are foreseen are phenols, organic acids, furfural, HMF and levoglucosan (80, 81, 82). The major advantages of a pyrolysis biorefinery are the possibility of decentralized production of the oil in regions where abundant biomass is readily available, making it possible to keep the minerals in the country of origin and creating the possibility of cost-effective transport of the resulting liquids. The basis for creating high value compounds is the cost-effective fractionation of the pyrolysis oil. Fractionation will result in various qualities of oil needed for further upgrading into fine chemicals, petrochemicals, automotive fuels and energy (80).

5. 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, 13, 14, 15, 16, 17). 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, see **Table 2**.

Table 2. Promising Bio-based chemical targets as assessed in 2004 and 2010 (15,16).

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 (14) analysed the market potential for a group of bulk chemicals produced from renewable resources using biotechnology, see **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 Plastemart (73) gave an overview of the biorenewable market which was estimated to be worth US$2.4 billion globally in 2010. This steadily growing market has experienced a compounded annual growth rate (CAGR) of 14.8%, a growth trend that is going to increase as the world resumes a more normal production pace and new bio-based chemicals such as bio-ethylene come to market, see **Figure 4**. By 2015, the biorenabable chemical market will be worth US$6.8 billion, a CAGR of 22.8% between 2010 and 2015. The largest region for biorenabable chemical sales continues to be the U.S., which captured 21.6% of the market in 2009.

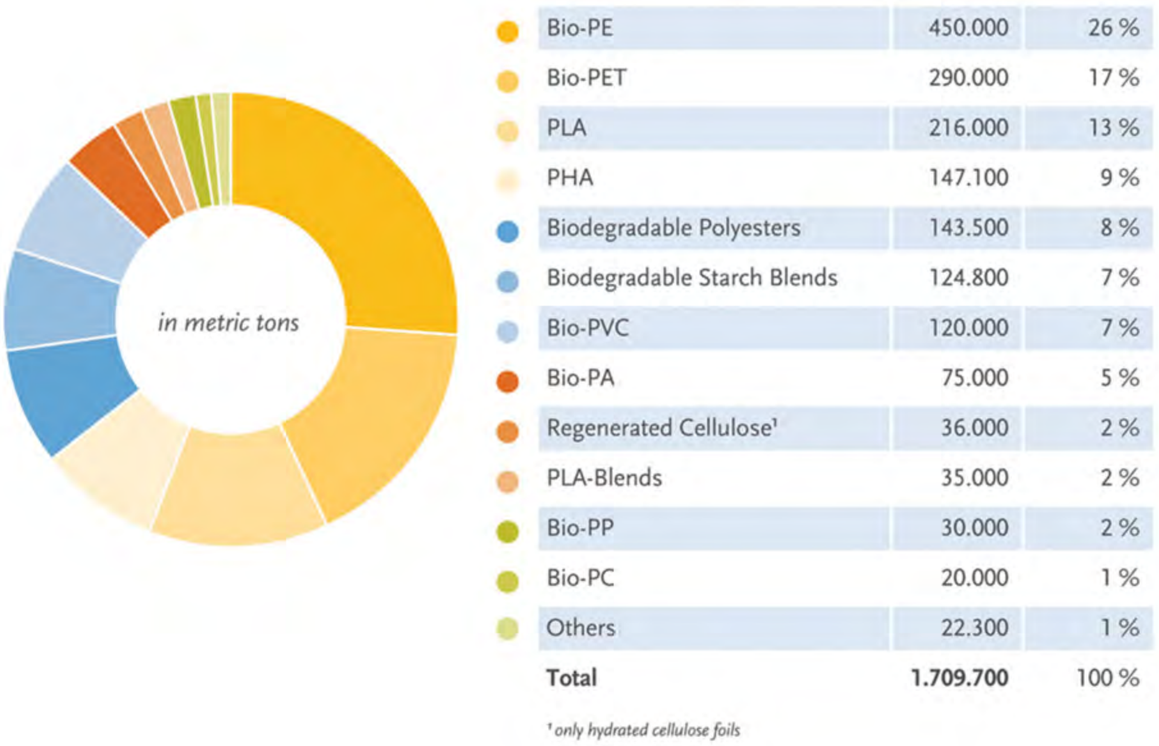


Figure 4. Plastics Europe anticipated biopolymer production capacity (in tonnes/year) by 2015.

The platform biorenewable chemicals glycerine and lactic acid make up the bulk of biorenewable chemicals being sold in 2010, accounting for 79.2% of the market. There is a large range in market maturity for platform biochemicals, ranging from mature markets such as lactic acid to nascent markets for chemicals such as succinic acid. The strongest growth will be for secondary chemicals such as polylactic acid (PLA), polyhydroxyalkanoate (PHA) and bio-ethylene that are used to manufacture bio-based plastics.

The world market for succinic acid was approximately 30 kTon in 2009, of which less than 5% was produced from bio-based feedstock. Biorenewable succinic acid is just entering the marketplace, but by 2015, will account for two thirds of the estimated 90 kTon/year global succinic acid market. SBI Energy expects to see 3-hydroxypropanoic acid (3-HPA) and acetic acid achieving production volumes greater than 20 kTon/year by 2015, primarily due to strong R&D programs from Cargill and WACKER respectively. 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 kTon/year for the foreseeable future. Revenue of PHA worldwide reached an estimated US$107.8 mln in 2009, up 21% from US$89.1 mln in 2008, and is expected to reach US$150.3 mln for 2010.

A steady increase in global production has balanced a decreasing trend in pricing for PHA, giving the PHA market a strong CAGR of 28.3% between 2006 and 2010. The largest barrier for PHA to gain market share is high manufacturing costs which are still much higher than other polymers (73).

Table 3. Bio-based chemicals assessed for market penetration and reference materials (adapted from ref (14)).

Bio-based chemical	Reference petrochemicals
Ethyl lactate	Ethyl acetate
Ethylene	Ethylene
Adipic acid	Adipic acid
Acetic acid	Acetic acid
n-Butanol	n-Butanol
PTT	PTT & Nylon 6
PHA	HDPE
PLA	PET and PS
FDCA	Terephthalic acid
Succinic acid	Maleic anhydride

Currently, commercialised bio-polymers (a.o. PLA, PHA, thermoplastic starch) are demonstrating strong market growth. Market analysis shows growth per annum to be in the 10-30% range (18) (19) (20). 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 over the next 10 years the market share of biodegradable bio-based polymers versus durable bio-based polymers is likely to decrease (ref plastics Europe). 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.

6. ECONOMIC BENEFIT OF CO-PRODUCTION OF FUELS 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 being developed. Biorefineries may be configured around a large volume product to maximise economies of scale and to allow the successful utilisation of all inputs with the integration of process operations. Fuel markets offer the scale necessary to support biorefinery operation but without subsidies possibly not the necessary economic return. Subsidies and strategic decisions are 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 suite - its 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 "destroyed" upon use. However, we might need a paradigm shift within biorefinery concept. However, we might need a paradigm shift within 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 generated from the waste streams. This will only be possible if there is a level playing field for biobased chemicals and biofuels. 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".

The European project BIOREF-INTEG investigated the feasibility and economic impact of integrating chemical production with biofuel production in several biorefinery configurations (21).

6.1 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 lactic acid production. The carbohydrate stream was split 4:1 with the bulk of material feeding the ethanol fermentation, see **Figure 5**. 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.

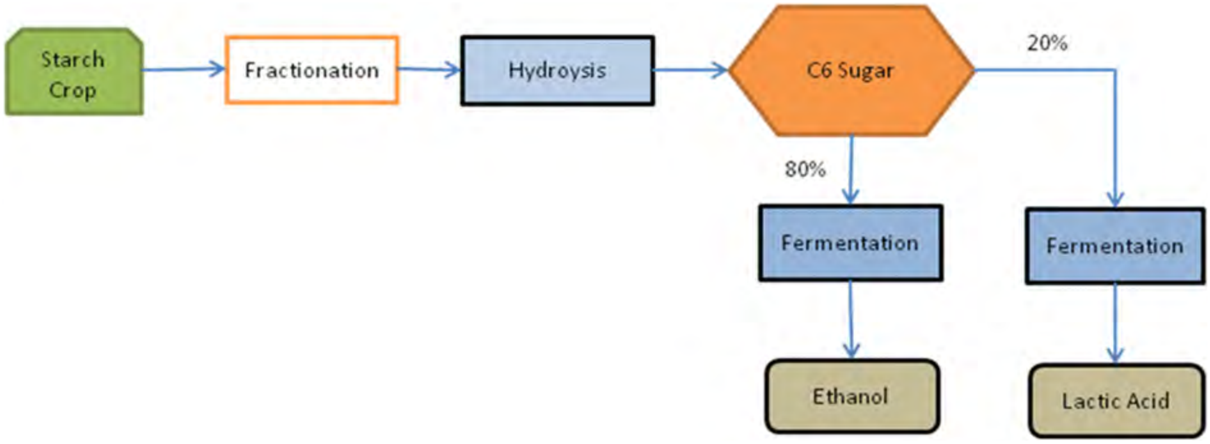


Figure 5. Integrated ethanol and lactic acid production.

6.2 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, see **Figure 6**. A reference plant processing 300 tonnes per day of crude rapeseed oil was considered (Figure 5). 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 for 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 (123). The results for the BioRef study indicate that the biorefinery configurations need to be analysed in order to draw conclusions as to their financial viability. Concluding that a bio-based chemical can be as or more competitive than its petroleum based counterpart is not possible without an analysis of the biorefinery configuration (21).

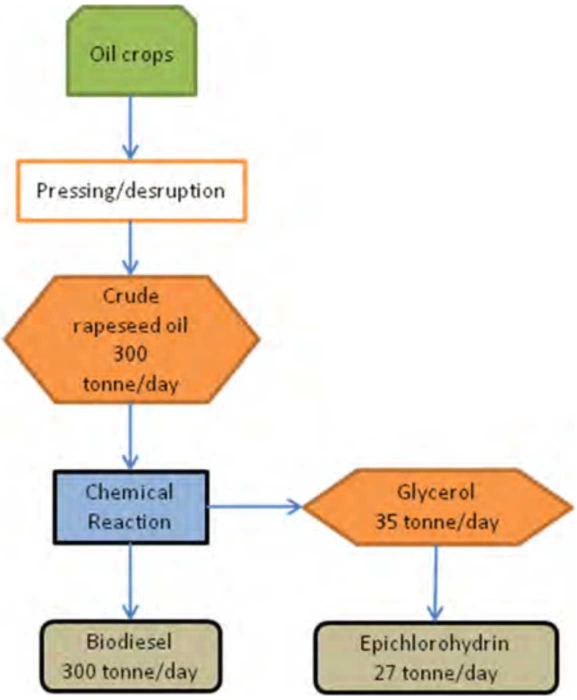


Figure 6. Integrated biodiesel and epichlorohydrin production.

7. 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.

Market assessment

Market fundamentals (local, regional, global)
Feedstock availability and price
Product profitability
Competitive nature of market
Need for partnerships
Downstream development opportunities

Technology assessment

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

Once commercialised a product needs to capture market share in order for production to expand. Establishing a market is considerably easier for recognised materials, innovative materials will require time for supply chain participants and downstream processors to adapt equipment and processes. For example a new plastic 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 (22). 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 for the so called "drop-in" biobased chemicals such as ethylene, propylene and *p*-xylene. For these chemicals only price and environmental footprint are relevant. They can be processed in available infrastructure and substantial markets are already established. 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 pretreatment 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.

Table 4. Turnover of Biomass in food and biobased products.

Sector	Annual turnover (billion Euro)	Employment (thousand)	Data source
Food	965	4400	CIAA
Agriculture	381	12000	COPA-COGECA, Eurostat
Paper/Pulp	375	1800	CEPI
Forestry/Wood industry	269	3000	CEI-BOIS
Biobased products			
Chemicals and plastics	50 (estimation*)	150 (estimation*)	USDA, Arthur D Little, Festel, McKinsey, CEFIC
Enzymes	0.8 (estimation*)	5 (estimation*)	Amfep, Novozymes, Danisco/Genencor, DSM
Biofuels	6**	150	EBB, eBio
Total	2046	21505	

* estimation for Europe for 2009.

** estimation based on a production of 2.2 million tonnes bioethanol and 7.7 million tonnes biodiesel at average market price in Europe.

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. The sugar and carbohydrate markets are becoming very volatile, see **Figure 7.** 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. A progressive move to full biorefinery configuration may be necessary for extant industries. Start-ups will of course have an advantage but they have to create their own markets.

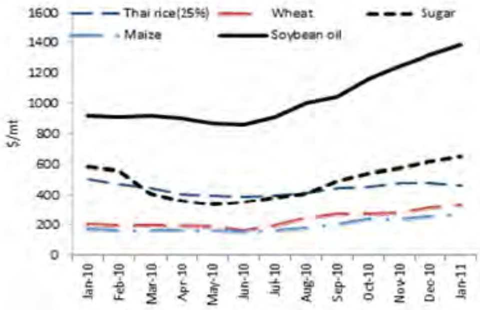


Figure 7. Global Prices of Key Food Commodities (Source: World Bank Development Prospects Group).

Table 4. gives an overview of the current turnover of biomass in general and biobased products in particular.

8. GREENHOUSE GAS EMISSION REDUCTIONS THROUGH BIO-BASED CHEMICAL PRODUCTION

The production of bio-based chemicals has the potential to significantly reduce the greenhouse gas (GHG) emissions of the petrochemical industry, and the downstream users, see **Table 5.** Life cycle assessment of numerous bio-based chemicals produced using current technology shows that significant GHG reductions could be achieved today, relative to their petroleum-derived equivalent. 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. 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) will have a great challenge to achieve the same GHG-efficiency as current processes.

Table 5. Future GHG savings per tonne and annual savings for bio-based chemicals assuming a complete replacement of fossil based chemical by biobased chemical (64).

Product	GHG savings (t CO_2/t of product)	Installed world capacity (million t/year)	Annual GHG savings (million tonne CO_2/year)
Acetic acid	1.2	8.3	9.6
Acrylic acid	1.5	2.9	4.4
Adipic acid	3.3	2.4	7.9
Butanol	3.9	2.5	9.6
Caprolactam	5.2	3.9	20.0
Ethanol	2.7	2.6	7.1
Ethyl lactate	1.9	1.2	2.2
Ethylene	2.5	100.0	246
Lysine	3.6	0.6	2.3
Succinic acid	5.0	1.4	6.8
1,3-propanediol	2.9	-	-
PHA	2.8	57.0	160
PLA	3.3	11.1	36.5

It also important not to oversell the potential GHG emission reductions, as was done with the introduction of biofuels. Just as not all biofuels are created equal, all bio-based chemicals are not created equal. Some bio-based chemicals might in fact not have a GHG reduction relative to its petroleum counterpart. The reductions must be estimated by lifecycle analysis, using realistic data.

Albrecht et al. 2010 (104) raised another important consideration that in some cases more savings in GHG emissions can be made through the use of biobased products than using the same material for energy. In 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 will be used to meet energy needs, even using 'clip-on, technologies to attenuate existing oil supplies.

Several authors have produced detailed assessments of potential GHG emission savings which could be made if bulk chemicals were produced from renewable resources using biotechnology (14, 64, 65). Although assessment of savings is complicated by the large number of potential chemical building blocks and the multiple process routes and feedstocks; savings around 400 million tonnes of CO_2 eq per year could be made based on today's technology and corn starch feedstock. Savings of this magnitude equate to 45% savings across the studied chemicals. If lignocellulosic or sugar cane feedstocks would be used, even greater GHG reductions were estimated. Reductions could more than double to 820 and 1030 million tonnes of CO_2 eq. per year, respectively, for lignocellulosic and sugar cane. 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 (Hermann, Blok, & Patel, 2007).

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. 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 below and a broad selection are discussed in more detail.

In the following chapter the C1 – Cn chemical building blocks will be discussed, see **Table 6**. In several cases these compounds are also end products (e.g. methanol, ethanol) but they represent substantial perspective/use as building block. Key players in the different area's are highlighted with some more detailed information.

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 (113).

Carbon Monoxide

Carbon monoxide is the major component of syngas and therefore an important biobased building block for a.o. Fischer-Tropsch chemistry.

Methanol

Methanol can easily be formed from syngas. Chemrec (70) uses black liquor gasification for the production of methanol and subsequently dimethylether (DME) an interesting biofuels pursuit by Volvo (71). BioMCN also produces methanol but their primary feedstock is glycerol, the main side-product of biodiesel production (72).

Formic acid

Formic acid is produced in equimolar amounts in the Biofine and other C6 based processes for levulinic acid production (MBP). At the moment it is mainly produced as a value-adding co-product.

Other C1 based building blocks

There are only two other C1 based building blocks possible, e.g. carbon dioxide and formaldehyde. The use of carbon dioxide as chemical feedstock has been extensively discussed in the book edited by Prof. Michele Aresta (102) and is outside the scope of this overview while at present there are no initiatives known to produce biobased formaldehyde but can easily be produced starting from biobased methanol.

Table 6. Biomass-derived chemical building blocks.

Cn	Chemical	Company	Potential
1	Methanol	BioMCN, Chemrec	Growth
	Formic acid	Maine BioProducts	Pipeline
	Methane	Many	Growth
	Syngas	BioMCN, Chemrec	Growth
2	Ethylene	Braskem, DOW/Mitsui, Songyuan Ji'an Biochemical	Growth
	Ethyl acetate	Zeachem	Pipeline
	Ethanol	Many	Growth
	Glycolic acid	Metabolic Explorer (Metex)	Pipeline
	Ethylene glycol	India Glycols Ltd, Greencol Taiwan	Growth
	Acetic acid	Wacker	Growth
3	Lactic acid	Purac, NatureWorks, Galactic, Henan Jindan, BBCA	Growth
	Acrylic acid	Cargill, Perstorp, OPXBio, DOW, Arkema	Pipeline
	Glycerol	Many	Growth
	3-Hydroxy propionic acid	Cargill	Pipeline
	Propylene	Braskem/Toyota Tsusho, Mitsubishi Chemical, Mitsui Chemicals	Pipeline
	Epichlorohydrin	Solvay, DOW	Growth
	1,3-Propanediol	DuPont/Tate & Lyle	Growth
	n-Propanol	Braskem	Pipeline
	Ethyl lactate	Vertec BioSolvents	Growth
	Isopropanol	Genomatica, Mitsui Chemicals	Pipeline
	Propylene Glycol (1,2-Propanediol)	ADM	Growth
4	n-Butanol	Cathay Industrial Biotech, Butamax, Butalco, Cobalt/Rhodia	Growth
	1,4-Butanediol	Genomatica/M&G, Genomatica/Mitsubishi , Genomatica /Tate & Lyle	Pipeline
	iso-Butanol	Butamax, Gevo	Growth
	Iso-butene	Gevo/Lanxess	Pipeline
	Methyl methacrylate	Lucite/Mitsubishi Rayon, Evonik/Arkema	Pipeline
	Succinic acid	BioAmber, Myriant, BASF /Purac, Reverdia (DSM/Roquette), PTT Chem / Mitsubishi CC	Growth
5	Furfural	Many	Growth
	Itaconic acid	a.o. Qingdao Kehai Biochemistry Co, Itaconix	Pipeline
	Xylitol	a.o. Danisco/Lenzing, Xylitol Canada	Growth
	Isoprene/ Farnesene	Goodyear/ Genencor, GlycosBio, Amyris	Pipeline
	Glutamic acid	a.o. Global Biotech, Meihua, Fufeng, Juhua	Growth
	Levulinic acid	Maine BioProducts, Avantium, Segetis, Circa Group	Pipeline
6	Sorbitol	a.o. Roquette, ADM	Growth
	Adipic acid	Verdezyne, Rennovia, BioAmber, Genomatica	Pipeline
	Lysine	a.o. Global Biotech, Evonik/RusBiotech, BBCA, Draths, Ajinomoto	Growth
	FDCA	Avantium	Pipeline
	Isosorbide	Roquette	Growth
	Glucaric acid	Rivertop renewables	Pipeline
	Citric acid	a.o. Cargill, DSM, BBCA, Ensign, TTCA, RZBC	Growth
	Caprolactam	DSM	Pipeline
n	PHA	Metabolic Explorer (Metex), Meridian plastics (103), Tianjin Green Biosience Co.	Growth
	Para-Xylene	Gevo, Draths*, UOP, Annellotech, Virent	Pipeline
	Dicarboxylic acids	Cathay Biotech, Evonik	Growth
	Fatty Acid derivatives	Croda, Elevance	Growth

* Draths is recently acquired by Amyris.

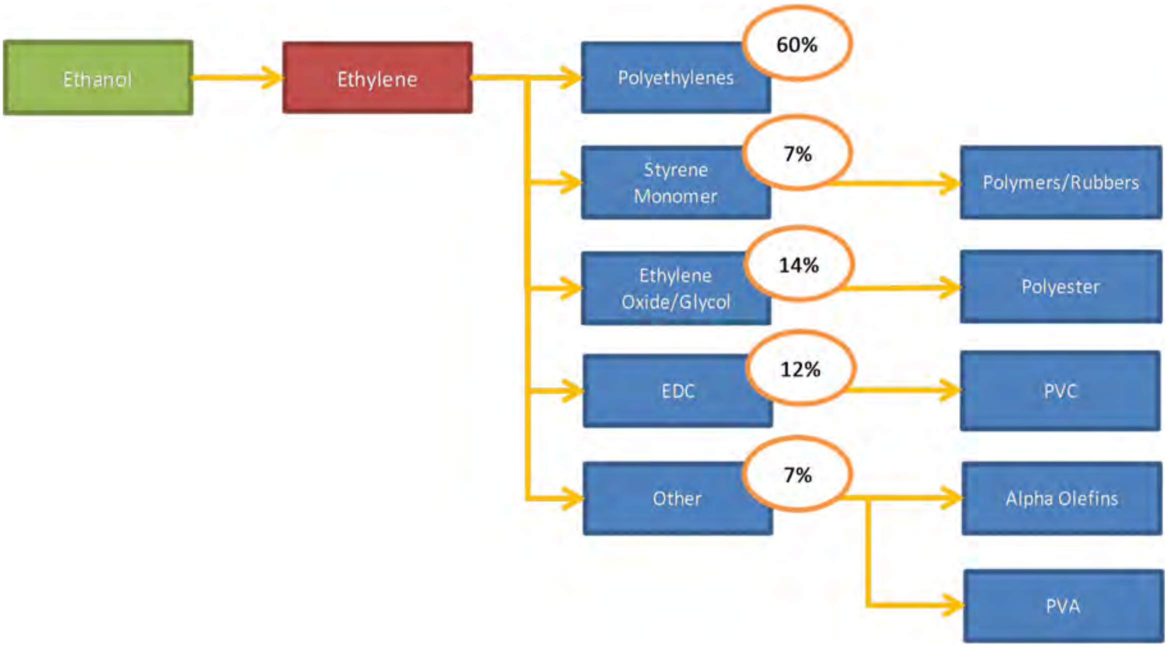


Figure 8. Ethylene value chain.

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), see **Figure 8**. Global ethylene production was 109 million tonnes in 2006 and growing at 4.5% (17).

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 world scale of ethylene plants (>300,000 tonnes) a single ethylene plant would be a considerable consumer of ethanol.

The largest consumer of ethylene is polyethylene e.g. HDPE and LDPE. In 2010 the Brazilian chemical producer Braskem commissioned a 200,000 tonnes capacity plant to produce polyethylene from sugar cane derived ethanol. The American chemical giant DOW has also announced plans for a 350,000 tonnes ethanol to ethylene plant in Brazil.

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 Procter and Gamble, TetraPak and Johnson and Johnson.

http://www.braskem.com/plasticoverde/EN_HOME.html

A further significant use of ethylene is in the production of mono ethylene glycol (MEG), see below. A further 12% of ethylene production is converted to ethylene dichloride for use in the production of polyvinyl chloride (PVC). In 2007 Solvay Inupta PVC announced plans to produced 60,000 tonnes of ethylene from sugar cane for conversion to bio-based PVC (45).

Mono-Ethyleneglycol (MEG)

MEG is co-polymerised with terephthalic acid to produce poly(ethylene)terephthalate (PET) 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 (42) (43). India Glycols Ltd. is making bio-derived ethylene glycol for incorporation into PET. The car manufacturer Toyota is intending to use bio-based PET is in its car production (see box). Teijin Fibers have announced their plans to produce 30,000 tonnes for bio-based PET fibre and textile in 2012, their intention is to increase production to 70,000 tonnes by 2015 (44).

Table 7. The global development of lactic acid consumption is as follows (1,000 metric tons).

1990	1995	2000	2002	2004	2006	2008	CAGR% 1990 – 2008
125	140	175	230	290	390	540	8.5

Toyota Motor Corporation

The car producer Toyota has announced its intention to use bio-based PET for vehicle liner material and other interior surfaces. The bio-based PET has been developed with Toyota Tsusho who has put together a new supply chain for material production. In a joint venture Toyota Tsusho and China Man-made Fiber Corp. have established Greencol Taiwan Corp to produce MEG. The ethanol for MEG production will be sourced from Brazil. Greencol have engaged the engineering contractor Chemtex to build a 100,000 tonnes capacity ethanol to ethylene plant in Kaohsiung, Taiwan.

http://pressroom.toyota.com/pr/tms/tmc-to-use-bio-pet-ecological-173305.aspx

http://www.chemtex.com/templates/news_20101020.html

Other C2 based building blocks

Several other C2 based building blocks are currently used at scales around 1 Mton/year and up. Important examples are acetic acid, dichloroethane (formed by chlorination of ethane), vinylchloride (formed by dehydrochlorination of dichloroethane), ethylene oxide (oxidation of ethylene) 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

Lactic Acid

Lactic acid is a bulk chemical with a global demand of 275,000 tonnes in 2006 and an average annual growth rate of 10% (17). 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.

Table 8. Forecast for growth in lactic acid market (1000 t per annum) (121).

Application	2008	2013	% of total 2013
Food	220	240	34
Pharmaceuticals	50	60	9
Industrial applications			
pH regulation	65	70	10
Biopolymers	165	280	40
Pesticide/other	40	50	7
Total	540	700	100

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, see **Tables 7/8**. 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 Purac is the world leader in lactic acid production and is actively exploiting their technology base through partner collaborations (23). Other companies active in PLA include Futerro (a joint venture between lactic acid producers Galactic and the global energy producer Total), Teijin Fibers in Japan, Toyobo in Japan, HiSun in China and Pyramid Bioplastics in Germany (24).

NatureWorks LLC

NatureWorks is an independent company wholly owned by the agriculture giants Cargill. NatureWorks started producing PLA at their production plant in Blair Nebraska in 2002. The plant capacity now stands at 140,000 tonnes. NatureWorks produce Ingeo resin and Ingeo fiber for a range of applications. According to NatureWorks the production of Ingeo PLA produces up to 60% less greenhouse gas emissions compared to the production of fossil based PET and polystyrene.

http://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 (25, 26,27,28,29).

Ethyl Lactate

Ethyl lactate is another lactic acid derivative that has recently been commercialized. 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 as low as $1.87/kg (89).

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 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^{TM} EL Ethyl Lactate, an ester solvent derived from corn which has 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 (90). Applications targeted by Vertec Biosolvents include conventional solvents that are under environmental scrutiny such as methylene chloride, methyl ethyl ketone, and *N*-methyl pyrrolidone (89).

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 material in fragrance, cosmetics and personal care applications, food and flavourings, pet food/animal feed and in pharmaceutical formulations, see **Figure 9**.

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 have commissioned 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.

http://www.adm.com/en-US/products/evolution/Pages/default.aspx

1,3 Propanediol

In 2004 the chemical producer DuPont formed a joint venture with agriculture products company Tate & Lyle (31). 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 45,000 tonne capacity production plant in Loudon, Tennessee, US and recently announced their intention to increase capacity by 35% (32). 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® (33). Sorona® PTT has been targeted at clothing, carpet and automotive textile markets. Cerenol™ polyols based on PDO can be used in variety of applications from personal care and functional fluids to performance coating and elastomers (34).

The French company Metabolic Explorer (35) have announced the construction of a bio-based 1,3-propanediol plant in South East Asia. With an initial capacity of 8,000 tonnes the plant is expected to have a final capacity of 50,000 tonnes (36).

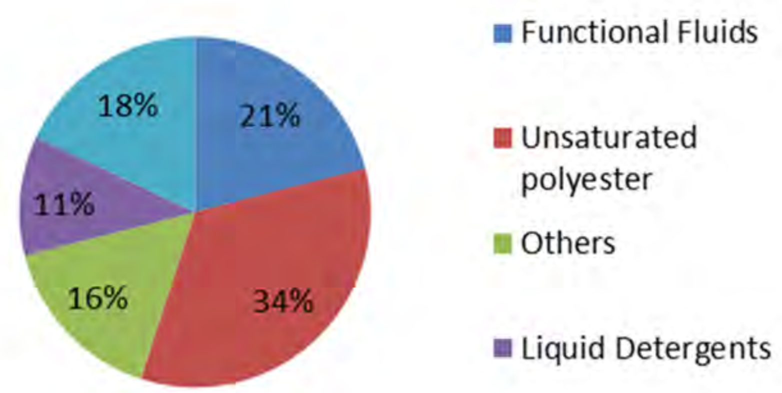


Figure 9. Market breakdown for propylene glycol.

Epichlorohydrin

With a market size of 1.3 million tonnes, epichlorohydrin is predominately used in the production of epoxy resins (76%) (37) and other resins and polymers (38). Niche applications include paper reinforcement e.g. tea bags and coffee filters and water treatment. Global epichlorohydrin consumption is expected to grow at 6% per year out to 2015 with the largest growth seen in Asia (38) (39). Solvay (see box) and a number of chemical producers including Zeachem, Spolchemie and DOW (40) are working to commercialise bio-based epichlorohydrin (41).

Solvay Chlorinated Organics

Solvay is the world's 4th largest producer of epichlorohydrin. They have developed their Epicerol® process to convert glycerol to epichlorohydrin. A 10,000 tonne demonstration plant has been operating in Tavaux, France since 2007. Solvay life cycle analysis shows a 20% reduction in CO_2 emissions along with a 50% reduction in non renewable feedstock requirement. The process reduces the requirement for chlorine and subsequently creates less chlorinated by products than the petrochemical process. The development of a production plant with a 100,000 tonne capacity is underway. Based in Map Ta Phut in Thailand the plant will be owned by Vinythai and is expected to be on stream in 2011.

http://www.solvaychlorinatedorganics.com/info/0,0,1000574-EN,00.html

Isopropanol

Isopropanol production via fermentation (131) and its conversion into propylene (132) have been reported by Mitsui Chemicals, INC.

n-Propanol

Recently a Braskem patent was published (88) which describes the fermentative production of n-propanol and the subsequent dehydration into propylene.

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 (63).

Table 9. Suggested routes biobased 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.

Braskem/Toyota Tsusho strategic partnership has recently announced their plans to jointly set-up a sugarcane-derived bio-polypropylene plant in Brazil. This first of its kind bio-PP plant with output capacity of more than 30,000 t/y and at a cost of about $100 million aims for startup as early as in 2013. Mitsubishi Chemical is developing a new technology in which ethylene or ethanol is converted to propylene directly. Crude ethylene produced by ethane cracker or bio-ethanol is applicable as a raw material. Many patents arguing the modified specific zeolite catalyst and a very unique re-generation of deactivated catalyst have been filed. (Mitsubishi Chemical, W007/114195).

Table 10. Market potential of acrylic acid and main derivates.

BIOBASED PRODUCT	CLASSIFICATIONS	MARKET OPPORTUNITY	MARKET SIZE
Acrylic Acid	Adhesives, polymers	Acrylates (e.g., coatings, adhesives), comonomer, superabsorbent polymers, detergent polymers	Markets for acrylic acid derivatives in the previous column are 2 billion pounds per year, at a market price of $0.48 per pound.
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 3.13 billion pounds per year, at a market price of $0.31 to $0.37 per pound.
Acrylamide	Resins	Polyacrylamide, comonomers (styrenebutadiene latex, acrylic resins, and many others)	Markets for acrylamide derivatives in the previous column are 206 million pounds per year, at a market price of $1.76 to $1.86 per pound.

Acrylic acid

Acrylic acid is an important chemical building block used in the production of polyacrylates and commodity acrylates. The acrylic acid market stood at 3.3 million tonnes in 2006. The global petroleum-based acrylic acid market is worth US$8 billion (2011) and growing 3 to 4 percent per year. 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 (17). Polyacrylates are widely used a super absorbent polymers. **Table 10**. of the Wisconsin Biorefining Development Initiative (75) shows the potential of acrylic acid and its derivatives (74).

Bio-based acrylic acid can be accessed through the fermentation of carbohydrates to 3-hydroxypropionic acid (3-HPA), further dehydration of 3-HPA gives acrylic acid. An Evonic patent for producing 3-hydroxypropionaldehyde from glycerol, which can also serve as precursor has been published (124, 125). 3-HPA could also serve as precursor to other important chemical building blocks such 1,3-propanediol, acrylonitrile and acrylamide. Glycerol can also be chemically converted to acrylic acid, either by dehydration to acrolein followed by oxidation to the final product, or in a one-step oxydehydration. An example of the latter process is described in an Arkema patent publication [WO 2006/114506].

Dow and OPXBio together in Acrylic Acid

The Dow Chemical Company and OPX Biotechnologies, Inc. announced on April 11, 2011 that the two companies are collaborating to develop an industrial scale process for the production of bio-based acrylic acid from renewable feedstocks. Dow and OPXBIO recently signed a joint development agreement to prove the technical and economic viability of an industrial-scale process to produce acrylic acid using a fermentable sugar (such as corn and/or cane sugar) feedstock with equal performance qualities as petroleum-based acrylic acid, creating a direct replacement option for the market. If collaborative research is successful, the companies will discuss commercialization opportunities that could bring bio-based acrylic acid to market in three to five years. During an 18-month pilot-scale program, OPXBIO demonstrated with unprecedented speed and capital efficiency that its EDGETM technology enables the manufacture of acrylic acid using renewable feedstock. A life cycle analysis conducted by Symbiotic Engineering, a greenhouse gas and sustainability consultant, concluded that OPXBIO's production process can reduce greenhouse gas emissions by more than 70 percent when compared to traditional petroleum-based acrylic acid production.

http://www.businesswire.com/news/dow/20110411005906/en

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, acetone (product in ABE fermentations) and proprionic acid (reduction of lactic acid). All are currently used at scales around 1 Mton/year and up.

9.4 C4 containing compounds

Butanol

A number of companies are commercialising n-butanol and iso-butanol production. The bio-based production of n-butanol is an historic process dating back to the early 20th century (46). n-Butanol is produced fermentatively 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. However current production costs are high, leading 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, see **Figure 10**. In 2006 n-butanol had a market size of 2.8 million tonnes.

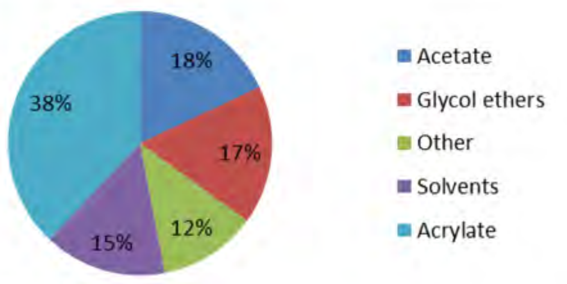


Figure 10. n-Butanol consumption (2008).

Bio-based butanol production has been re-established in China to supply its growing chemicals market. In 2008 Cathay Industrial Biotech began supplying butanol under their BioSol brand, production capacity is now 100,000 tonnes.

Companies seeking to commercialise bio-based butanol include Butamax™ Advanced Biofuels (47), a joint venture between energy producers BP and the chemical producer DuPont, the UK companies Green Biologics (48) and Solvert (49), US technology companies Colbalt Technologies (50) and Gevo Development (51).

Butamax™ and Gevo Development are focused on the production of isobutanol. The production of isobutanol creates the opportunity for isobutylene production and a range of downstream products.

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. Currently the bacterial strain used for succinic acid production is *E. coli*, but necessity for lower costs is moving companies towards other microorganisms such as *Coryne*-type bacteria and yeast. Mitsubishi Chemical has developed a *Coryne*-type bacterium that has a significantly higher productivity compared to *E. coli* (133).

Succinic acid can be converted to 1,4-butanediol (BDO) and other products, see **Figure 11**. 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). Approximately 40% of BDO is consumed in tetrahydrofuran (THF) production. THF is a widely used (342,000 tons market in 2006) performance solvent and a feedstock for the production of polytetramethylene ether glycol used in the production of polyurethane polymers. BDO also acts as precursor to a number of speciality chemicals used as solvents or as raw materials in pharmaceuticals and agrochemicals (Figure 11).

The production of succinic acid has attracted a number of industry players. The first to demonstrate their technology at scale was BioAmber. BioAmber is currently working together with Mitsubishi Chemical to further improve their technology and obtain low cost products (134).

Other companies looking to commercialise succinic acid include technology developer Myriant Technologies (52); Reverdia, a joint venture between Dutch life science and materials producer DSM and the French starch company Roquette (53) and lactic acid producers Purac with chemical giants BASF. In 2010 Myriant Technologies began design engineering of a succinic acid plant. The construction of the plant is supported by a $50 million US Department of Energy grant issued to BioEnergy International LLC.

BioAmber – Mitsui & Co

BioAmber and Mitsui & Co have partnered to build and operate a manufacturing facility in Sarnia, Ontario, Canada. The initial phase of the facility is expected to have production capacity of 17,000 metric tons of biosuccinic acid and commence commercial production in 2013. The partners intend to subsequently expand capacity and produce 35,000 metric tons of succinic acid and 23,000 metric tons of 1,4 butanediol (BDO) on the site. BioAmber and Mitsui also intend to jointly build and operate two additional facilities (Thailand and North America/Brazil) that, together with Sarnia, will have a total cumulative capacity of 165,000 tons of succinic acid and 123,000 tons of BDO. BioAmber will be the majority shareholder in the plants.

http://www.bio-amber.com/img/pdf/BioAmber_Mitsui_PR_final.pdf

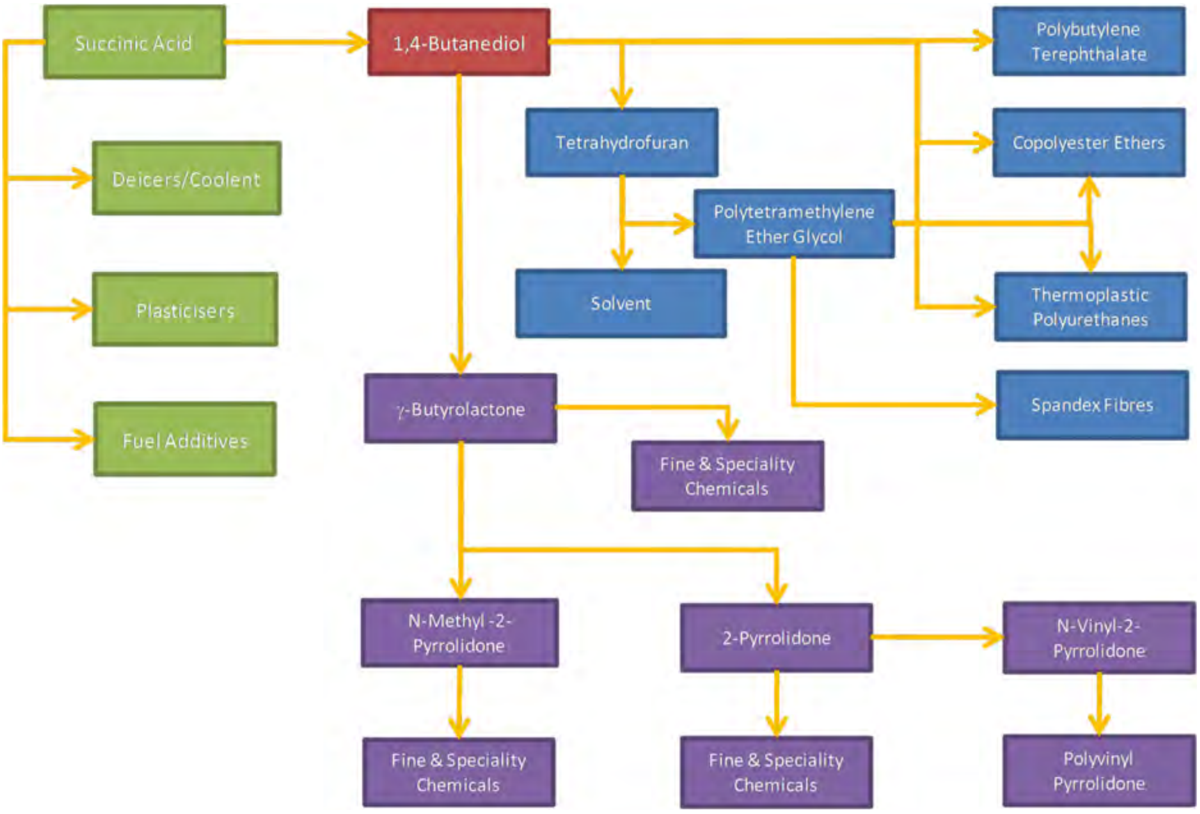


Figure 11. Potential Succinic acid value chain.

Methyl methacrylate

The principal application, consuming approximately 80% of the MMA, is the manufacture of polymethyl methacrylate acrylic plastics (PMMA). Methyl methacrylate 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 Methyl Methacrylate (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 has developed Alpha 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 120kte per annum.

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 (76).

Other C4 based building blocks

Several other C4 based building blocks are currently used at scales around 100 kton/year and up. Important examples are 1,4-butanediol (formed from succinic acid), tetrahydrofuran (THF, from succinic 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 (117).

9.5 C5 containing compounds

Furfural

Furfural is one of the members of the Furanics class, which also encompass a group of molecules which include 5-hydroxymethylfurfural, 2,5-furandicarboxylic acid and 2,5-dimethylfuran.

The chemical dehydration of five carbon carbohydrates such as xylose and arabinose yields furfural. Furfural is an established chemical product with a static market. World production of furfural has been estimated at around 200,000 tonnes per annum of which 60-70% is used for the production of furfuryl alcohol (58, 92). 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, followed by the Dominican Republic. 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 (92).

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. 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 (15). The U.S. company Segetis is commercialising levulinic ketals for a variety of applications (62). Levulinic acid contains two reactive functional groups that allow a great number of synthetic transformations. **Figure 12** below shows a number of interesting derivates of Levulinic acid.

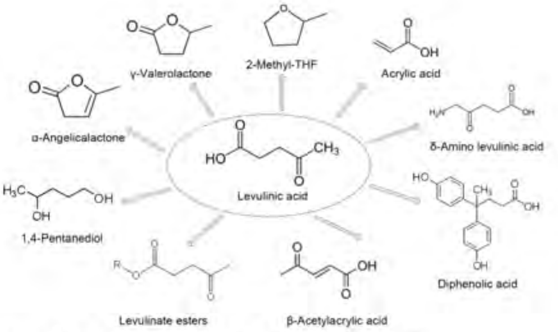


Figure 12. Chemicals derived from levulinic acid.

The Biofine process is commercialised by Maine BioProducts (MBP) and the process works by "cracking" any lignocellulosic feedstock under the influence of dilute mineral acid and moderate temperature, with a novel dual reactor design that allows 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 (72).

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.

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 (55). 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 (56).

The U.S. company Amyris is developing synthetic biology as a technology platform (57). 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.

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 (900.000 ton/y) (118). 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 (15, 16). However, these sugar alcohols have other potential as they can be converted to glycols such as ethylene glycol and 1,2 propanediol.

Xylitol (Danisco/Lenzing)

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 recently published white paper Danisco together with Lenzing describe the sustainability benefits of a newly developed process, the Danisco Wood Based (DWB) process. 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 85-99% less impactful than the traditional xylose production process, leading to a significantly less impactful and more sustainable product.

http://www.xivia.info/multimedia/Danisco_White_Paper_Xylitol_1e2011.pdf

Other C5 based building blocks

There are not many other C5 based building blocks that are currently used at scales around 50 kton/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). Itaconic acid is a granulated light yellow powder that can be processed into a polymer which may be used to replace petroleum-based poly-acrylic acids which are used in diapers, feminine pads, detergents, cosmetics, inks and cleaners. Itaconic acid is currently produced at around 80 kTon per year, mainly in China and little in France (122).

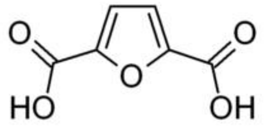
9.6 C6 containing compounds

2,5-Furandicarboxylic acid (FDCA)

Hydroxymethylfurfural (HMF) is produced by the chemical dehydration of six carbon carbohydrates. Through chemical manipulation, HMF can be converted to a range of furan derivatives (59). 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. The Dutch company Avantium is building a platform technology, branded as 'YXY', to commercialise bio-based furanics (60). Dimethylfuran has been proposed as a potential biofuel.

Avantium's YXY Building Blocks

Avantium has created an enabling technology, called YXY, for the economic production of a new category of green products called Furanics. Furanics are green building blocks for a range of materials, chemicals and fuels. The building block as such has been studied for decades by industrial companies such as DuPont (USA), Celanese (USA) and DSM (NL), agricultural companies such as Quaker Oats (USA) and SüdZucker (DE), and research institutes around the world. In the scientific literature, Furanics are referred to as 'sleeping giants' because of their enormous potential for the production of green plastics and chemicals; Furanics were also listed in the top 12 high-potential green building blocks published by the US Department of Energy. Until today, Furanics had not been commercialized because Furanics production was not yet cost-effective.



Furanics: 2,5-Furan-dicarboxylic-acid

Avantium is set to change this by the development of a breakthrough technology that allows for the cost-effective production of Furanics as shown in their recently opened 24/7 pilot plant. Avantium's proprietary process will unlock a whole new field of green materials and fuels. Beverage bottles, fibres, apparel, computer casings, car bumpers, airplane coatings and truck fuels: in future, all these things can be made on the basis of Avantium's green building blocks. Recently co-development agreements were announced within the polyester (The Coca Cola Company – development of PEF bottles for PET replacement) and polyamide (Teijin Aramide and Solvay) space.

http://www.avantium.com; http://www.yxy.com

Sorbitol

Sorbitol is produced on large industrial scale by catalytic hydrogenation of glucose. It is a batch process with a production volume of 1.1 Mton/year (Patel 2006). 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 (107) but are 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 (900.000 ton/y) (118).

Isosorbide (Roquette)

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 and polyurethane families. 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 announced that its production capacity of isosorbide located in Lestrem (France) will attain several thousand tonnes by the beginning of 2011, at the "Bio-Based Chemicals East" congress in Boston, MA, on 13 September 2010. Roquette is consolidating its position as world leader for Isosorbide, a biobased intermediate for new polymers and plasticizers.

http://www.roquette.com

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 (91 - Haveren, Scott et al. 2008). In the 1950s 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 kton/y (118) and a cost price of 1200 €/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.

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 tons 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 (14). 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 purity levels needed for polymer-grade products and catalytic conversion of muconic acid to adipic acid needs to be further investigated (14). Since then several companies have claimed processes for adipic acid. Verdezyne, Inc., a privately-held synthetic biology company developing processes for renewable chemicals and fuels, announced they are developing a new fermentation process for the production of adipic acid. This company achieved proof of concept by demonstrating production and recovery of adipic acid by a yeast microorganism from an alkane feedstock. Using proprietary technologies, Verdezyne discovered and is engineering a proprietary metabolic pathway that can utilize carbohydrates, plant-based oils or alkanes (108). BioAmber, one of the market leaders in biobased succinic acid, has entered into an exclusive licensing agreement with Celexion LLC for technology related to the production of adipic acid and other chemical intermediates (109). Also 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 (110). Rennovia (Menlo Park, CA), an early-stage start up founded by researchers at Symyx Technologies, is developing a chemo-catalytic process for production of adipic acid from renewable raw materials (106).

Glucaric acid

Rivertop has developed a catalytic oxidation to make glucaric acid from glucose. The company claims that while the current market for glucaric acid is very minor, it has huge potential. Rivertop is initially marketing glucaric as a drop-in replacement for phosphates in detergents, a '10 billion market. The U.S. banned phosphates in automatic dishwasher detergents last year, and earlier this month the European Commission proposed restricting phosphates and phosphorus· containing compounds In all domestic laundry detergents across the European Union. Phosphates are blamed for stimulating algae growth, which In turn reduces oxygen supply for other aquatic life. Glucaric acid also has corrosion inhibition properties and Rivertop expects to build a market presence in applications such as cooling towers and boilers. Glucaric acid can also be polymerized, although commercializing a polymer is probably 5-7 years away. Rivertop aims to have a commercial plant on the order of 60 million lbs/year operational by 2013.

Other C6 based building blocks

Several other C6 based building blocks are currently used at scales around 100 kton/year and up. Important examples are ascorbic acid (formed by combined biotechnological/chemical process), sorbitan (formed by dehydration of sorbitol), and phenols (from lignin).

9.7 Cn containing compounds

p-Xylene

In 2011, quite a buzz about 100% biobased PET has started. 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 (42). 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 in Brazil and India is being produced from sugarcane and India Glycols does convert sugarcane ethanol to Ethylene Glycol. Now other companies, with PepsiCo (95) 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 to para-xylene and then to PTA (51, 96). Isobutanol can be converted to para-xylene via isobutylene which can be readily oxidised to terephthalic acid for production of PET. Draths is working to convert glucose via trans, trans-muconate to PTA. 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 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 (61). 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 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 (101). 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.

The Coca Cola Company

The Coca-Cola Company Announces Partnerships to Develop Commercial Solutions for Plastic Bottles Made Entirely From Plants - Breakthrough Technologies from Virent, Gevo and Avantium Selected to Reach Global Scale

The Coca-Cola Company recently announced multi-million dollar partnership agreements with three leading biotechnology companies to accelerate development of the first commercial solutions for next-generation PlantBottle™ packaging made 100% from plant-based materials. This effort to commercialize a plastic bottle made entirely from plants builds on the Company's ground-breaking introduction and roll-out of its first generation PlantBottle™ package which was the first ever recyclable PET beverage bottle made partially from plants. Since introduced in 2009, the Company has already distributed more than 10 billion PlantBottle™ packages in 20 countries worldwide. Agreements with Virent, Gevo and Avantium - industry leaders in developing plant-based alternatives to materials traditionally made from fossil fuels and other non-renewable resources - were signed following an in-depth two year analysis of different technologies by The Coca-Cola Company's R&D team and technical advisory board. "While the technology to make bio-based materials in a lab has been available for years, we believe Virent, Gevo and Avantium are companies that possess technologies that have high potential for creating them on a global commercial scale within the next few years," said Rick Frazier, Vice President, Commercial Product Supply, The Coca-Cola Company. "This is a significant R&D investment in packaging innovation and is the next step toward our vision of creating all of our plastic packaging from responsibly sourced plant-based materials." Agreements with these three companies will help The Coca-Cola Company support its long-term commitments through sustainable practices in sourcing and packaging supply. While Virent, Gevo and Avantium will follow their own route to make bio-based materials, all materials will be developed in line with Company and industry recycling requirements (138).

Polyhydroxyalkanoates

Polyhydroxyalkanaotes (PHAs) are a group of microbial polyesters with a history of production dating back over 50 years. Unlike most bio-based polymers, which are produced by chemical polymerisation methods using bio-based monomers, PHAs are produced directly by fermentation. PHAs are based on renewable materials and are biodegradable attracting the interest of a number of companies. Although over 150 types of PHAs are known only 3* are produced in significant quantities (54). Global capacity for PHA production is around 100,000 to 130,000 tonnes but could expand significantly given the increasing demand for bio-based and biodegradable materials (54) (24). Companies active in the production of PHAs include Mitsubishi Gas Chemical in Japan, PHB Industrial in Brazil, Tianjin Green Bio-Science in China and Metabolic Explorer (24). Telles, the joint venture between agricultural giant Archer Daniels Midland and technology developer Metabolic Explorer has recently been terminated.

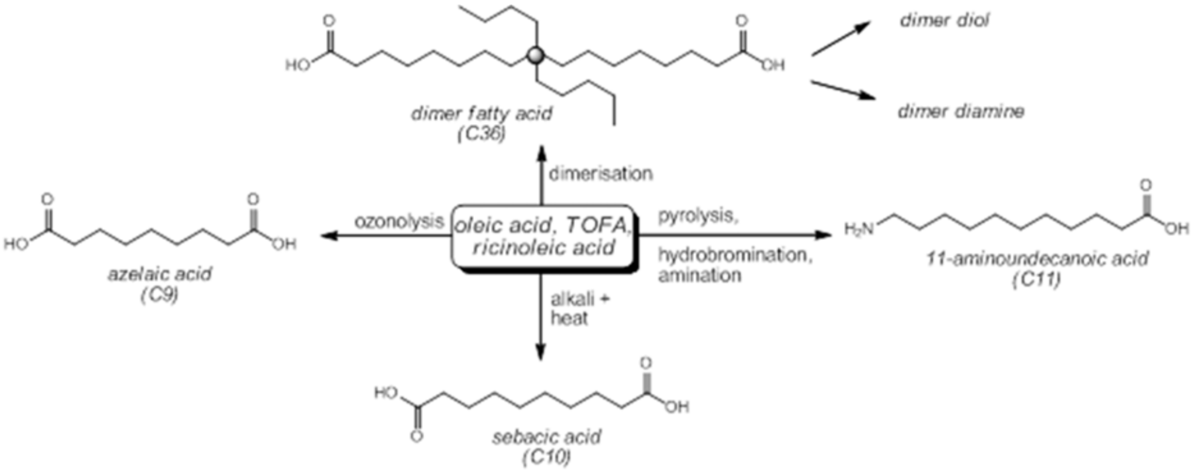


Figure 13. Examples of commercial fatty acid derived monomers. TOFA = tall oil fatty acids.

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 (128) 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).

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 (129), dimethyl 1,19-nonadecanedioate, a C19 dicarboxylic acid ester produced by methoxycarbonylation of unsaturated C18 acids (130), and mid- to long-chain dicarboxylic acids obtained by microbial ω-oxidation of fatty acids (131).

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.

http://www.croda.com/ (86)

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.

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. The emergence of policies to promote the use of a given percentage of liquid biofuels e.g. EU 10% by 2020 ensures a market for a product leading to the execution of easiest to implement technologies. This may not always be a good thing, especially if routes to production and sustainability are not well defined or policed.

This paper highlights the many opportunities available in the Biobased Economy where biofuels are a co-product rather than the main driver.

It is 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 maximise the economic, environmental and social benefits of a variety of pathways to their use.

It is further recommended that a meta analysis of published data on Biofuels and Biobased chemicals is undertaken. Many opportunities exist at present but thorough comparisons are lacking. If we are to avoid the fall and rise of biobased products because of hyperbole and lack of analysis then a roadmap to the most sustainable technologies must be developed.

An example of this could be the emergence of a technology for production of glucose from cellulose without the requirement of enzymatic hydrolysis. If this is implemented commercially then many enzyme companies may lose very large investments and companies in the fermentation industry may have a portion of their technologies become redundant. It must be noted that this is a hypothetical example.

Table 11. SWOT-analysis 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 • Stronger focus on drop-in chemicals facilitating market penetration	• 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
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	• 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

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 in **Table 11**.

11. CONCLUSIONS

The biobased chemicals and materials industry has reached a tipping point, with production expected to double in the upcoming years. Several strong forces including high oil prices, consumer preference, corporate commitment, and government mandates and support, are driving development in this area. The data in this report show that especially the drop-in biobased chemicals sector is very likely to be on the brink of a strong expansion. In addition, platform biochemicals are also expected to grow substantially over the next five years. This will also generate a strong boost for the cost effective production of biofuels within a biorefinery context.

12. WORKS CITED

1. **Higson, A** 2011. **NNFCC.** Estimate of chemicals and polymers from renewable resources. 2010. **NNFCC.** Estimate of fermentation products. 2010. Personnal communication

2. **Shen, L., Haufe, J., Patel, M.K.** Product overview and market projection of emerging bio-based plastics. s.l. : Utrecht Univeristy, 2009.

3. **EuropaBio and ESAB.** Bio-based Economy. [Online] [Cited: 18 January 2011.] http://www.bio-economy.net/index.html.

4[1] **OECD**. The Bioeconomy to 2030: designing a policy agenda. 2009.

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

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

7. **World Economic Forum.** The Future of Industrial Biorefineries. s.l. : World Economic Forum, 2010.

8. **Bakker, Robert, et al.** 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).

9. **ERRMA.** EU-Public/PrivateInnovation Partnership "Building the Bio-economy by 2020". 2011.

10. **ICIS Chemical Business.** Soaps & Detergents Oleochemicals. ICIS Chemical Business. 2010, January 25-February 7.

11. **Lignol Energy.** Lignol Announces Production of Cellulosic Ethanol from New Biorefinery Pilot Plant. Lignol Innovationc. [Online] 8 June 2009. [Cited: 18 June 2009.] http://www.lignol.ca/news/2009-jun08.html.

12. **Ineosbio.** [Online] [Cited: 17 January 2011.] http://www.ineosbio.com/57-Welcome_to_INEOS_Bio.htm.

13. **U.S. Department of Agriculture.** U.S. Biobased Products, Market Potential and Projections Through 2025. s.l. : U.S. Department of Agriculture, 2008.

14. **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. (http://www.projects.science.uu.nl/brew/programme.html)

15. **Bozell, J.J., G.R. Petersen.** 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.

16. **Werpy, T, G. Petersen.** 2004. Top Value Added Chemicals from Biomass, Volume 1 Results of Screening for Potential Candidates from Sugars and Synthesis Gas. (http://www1.eere.energy.gov/biomass/pdfs/35523.pdf)

17. **Nexant ChemSystems.** Biochemical Opportunities in the Uniten Kingdom. York : NNFCC, 2008.

18. **Pira.** The Future of Bioplastics for Packaging to 2020. s.l. : Pira, 2010.

19. **SRI Consulting.** Biodegradable Polymers. [Online] [Cited: 17 January 2011.] http://www.sriconsulting.com/CEH/Public/Reports/580.0280.

20. **Helmut Kaiser Consultancy.** Bioplastics Market Worldwide 2007-2025. [Online] 2009. [Cited: 17 January 2011.] http://www.hkc22.com/bioplastics.html.

21. **ECN.** Development of advanced biorefinery schemes to be integrated into existing industrial (fuel producing) complexes. 2010.

22. Biopolymers- Identifying and Capturing the Value. **McKinsey & Company.** Brussels : s.n., 2009. Bioplastics Forum.

23. **Purac.** Purac. [Online] [Cited: 24 January 2011.] http://www.purac.com.

24. **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 (http://nws.chem.uu.nl/publica/Publicaties%202009/NWS-E-2009-32.pdf)

25. **DOW.** Bio-Plastics - PLA. DOW Plastic Additives. [Online] [Cited: 17 January 2011.] https://www.dow.com/additives/packaging_additives/bio_plastics.htm.

26. **AkzoNobel.** 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.

27. **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.

28. **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.

29. **Purac.** Purac develops a PLA compound with engineering plastics properties. [Online] 1 December 2010. [Cited: 17 January 2011.] http://www.purac.com/EN/Green_chemicals/News/Press-release-Development-PLA-compound.aspx.

30. **Nexant Chemsystems.** Glycerin Conversion to Propylene Glycol . Nexant Chemsystems. [Online] 2008. [Cited: 18 January 2011.] http://www.chemsystems.com/about/cs/news/items/PERP%200607S4_Glycerin.cfm.

31. **DuPont Tate & Lyle Bioproducts.** DuPont Tate & Lyle Bioproducts. DuPont Tate & Lyle Bioproducts. [Online] [Cited: 14 January 2011.] http://www.duponttateandlyle.com/index.php.

32. **DuPont Tate & Lyle Bioproducts.** DuPont Tate & Lyle Bio Products Expanding Bio-PDO™ Production in Tennessee. DuPont Tate & Lyle Bio Products. [Online] 4 May 2010. [Cited: 13 January 2011.] http://duponttateandlyle.com/news_050410.php.

33. **DuPont.** Sorona® renewably sourced polymer. DuPont. [Online] [Cited: 14 January 2011.] http://www2.dupont.com/Sorona/en_US/index.html.

34. **DuPont.** Welcome to DuPont™ Cerenol™ Polyols. DuPont. [Online] [Cited: 14 January 2011.] http://www2.dupont.com/Cerenol_Polyols/en_US/index.html.

35. **Metabolic Explorer.** Metabolic Explorer. Metabolic Explorer. [Online] [Cited: 14 January 2011.] http://www.metabolic-explorer.com.

36. **Metabolic Explorer.** METabolic EXplorer, announces launch of construction work on its first PDO manufacturing plant in Malaysia. Metabolic Explorer. [Online] 02 Decmber 2010. [Cited: 14 January 2011.] http://www.metabolic-explorer.com/images/dynmetex/biblio/fichiers/CPMETEX2010/PR_METabolic_EXplorer_1st_PDO_manufacturing_plant_in_Malaysia_021110.pdf.

37. **DOW.** Dow Epoxy Advances Glycerine-To-Epichlorohydrin and Liquid Epoxy Resins Projects by Choosing Shanghai Site. DOW Epoxy. [Online] 26 March 2007. [Cited: 19 November 2010.] http://epoxy.dow.com/epoxy/news/2007/20070326b.htm.

38. **Solvay.** Chemicals - Opportunites and Challanges. Solvay. [Online] 1 October 2008. [Cited: 19 November 2010.] http://www.solvaypress.com/static/wma/pdf/1/3/8/2/9/081001_SID_Chemicals.pdf.

39. **SRI Consulting.** Epichlorohydrin. SRI Consulting. [Online] September 2010. http://www.sriconsulting.com/CEH/Public/Reports/642.3000.

40. **DOW.** Dow Epoxy Receives Environmental Impact Assessment Approvals for Two Proposed Plants in Shanghai. [Online] 02 September 2008. [Cited: 19 January 2011.] http://www.dow.com/commitments/studies/glycerine.htm.

41. **ICIS Chemical Business.** Oleochemicals: Low glycerin price drives new uses. ICIS Chemical Business. August 15-29, 2010.

42. **Coca Cola.** Introducing PlantBottle™. Coca Cola. [Online] 14 May 2009. [Cited: 12 January 2011.] http://www.thecoca-colacompany.com/dynamic/press_center/2009/05/the-coca-cola-company-introduces-innovative-bottle-made-from-renewable-recyclable-plant-based-plasti-1.html.

43. **Danone.** Volvic's 'Greener bottle' will be made from 20% sugarcane waste. Danone. [Online] 2010. [Cited: 12 January 2011.] http://www.danone.co.uk/News/Media/Volvic-Greener-Bottle.aspx.

44. **Teijin Fibers.** Teijin to Launch Bio-derived PET Fiber in 2012. Teijin. [Online] 10 December 2010. [Cited: 12 January 2011.] http://www.teijin.co.jp/english/news/2010/ebd101210.html.

45. **Solvay.** Polyvinyl chloride (PVC) Derived from Sugar Cane and Salt. Solvay. [Online] 14 December 2007. [Cited: 12 January 2011.] http://www.solvay.com/services/newsfrompo/0,,62016-2-0,00.htm.

46. **Garcia, V., Päkkilä, J., Ojamo, H., Muurinen, E.** 2011, Challenges in biobutanol production: How to improve efficiency. Renewable and Sustainable Energy Reviews, Vol. 15, pp. 964-980.

47. **Butamax Advanced Biofuels.** Butamax Advanced Biofuels. Butamax Advanced Biofuels. [Online] http://www.butamax.com.

48. **Green Biologics.** Green Biologics. Green Biologics. [Online] [Cited: 14 January 2011.] http://www.greenbiologics.com.

49. **Solvert.** Solvert. [Online] [Cited: 7 February 2011.] http://www.solvertltd.co.uk.

50. **Colbalt Technologies.** Colbalt Technologies. Colbalt Technologies. [Online] [Cited: 14 January 2011.] http://www.cobalttech.com/about-cobalt.

51. **Gevo Development.** Gevo Development. Gevo Development. [Online] [Cited: 14 January 2011.] http://www.gevo.com.

52. **Myriant Technologies.** Myriant Technologies. [Online] [Cited: 24 January 2011.] http://www.myriant.com.

53. **DSM.** DSM and Roquette to start bio-based succinic acid joint venture. DSM. [Online] 28 June 2010. [Cited: 24 January 2011.] http://www.dsm.com/en_US/html/media/press_releases/28_10_dsm_and_roquette_to_start_bio_based_succinic_acid_joint_venture.htm.

54. **Chanprateep, S..** Current trends in biodegradable polyhydroxyalkanoates., Journal of Bioscience and Bioengineering, 2010 Vol. 110, 6

55. **Genencor.** Genencor and Goodyear to co-develop renewable alternative to petroleum-derived isoprene. [Online] 16 September 2008. [Cited: 18 January 2011.] http://www.genencor.com/wps/wcm/connect/genencor/genencor/media_relations/news/frontpage/investor_265_en.htm.

56. **Whited, G.M, et al.** 2010, Development of a gas-phase bioprocess for isoprene-monomer production using metabolic pathway engineering. Industrial Biotechnology, pp. 152-163.

57. **Amyris.** Amyris. [Online] [Cited: 24 January 2011.] http://www.amyrisbiotech.com.

58. **Mamman, AS, et al.** 2008, Furfural: Hemicellulose/Xylose-derived biochemical. Biofuels, Bioproducts and Biorefining, pp. 438-435.

59. **Tong, X, Ma, Y. and Li, Y.** 2010. Biomass into chemicals: Conversion of sugars to furan derivatives by catalytic processes. Applied Catalysis A: General, Vol. 385, pp. 1-13.

60. **Avantium Research & Technology.** Avantium Research & Technology. Avantium Research & Technology. [Online] [Cited: 14 January 2011.] http://www.avantium.com.

61. **Brandvold, T.A.** Carbohydrate route to paraxylene and terephthalic acid. US/2010/0331568 A1 U.S., 30 December 2010.

62. **Segetis.** Segetis. Segetis [Online] [Cited: 14 January 2011.] http://www.segetis.com/home.html.

63. **Nexant Chemsystems.** Green Propylene. 2009.

64. **Hermann, B.G., Blok, K. and Patel, M.K.** 2007, Producing Bio-Based Bulk Chemicals Using Industrial Biotechnology Saves Energy and Combats Climate Change. Environmental Science and Technology 41, 7915-7921.

65. **Buttazzoni, M.** GHG Emission Reductions With Industrial Biotechnology- Assessing the Opportunities. s.l. : Novazymes, 2009.

66. **ADM.** Evolution Chemicals by ADM. [Online] http://www.adm.com/en-US/products/evolution/Pages/default.aspx.

67. **Nexant Chemsystems.** Glycerin Conversion to Propylene Glycol. [Online]

68. **International Energy Agency.** Key World Energy Statistics. s.l. : International Energy Agency, 2010.

69. **Cherubini, F., Jungmeier, G., Wellisch, M., Willke, T., Skiadas, I., van Ree, R. and de Jong, E.** 2009. Toward a common classification approach for biorefinery systems. Biofuels Bioproducts Biorefinery 3(5):534-546.

70. **Chemrec.** CHEMREC gasification technology - turns pulp and paper mills into biorefineries (http://www.chemrec.se)

71. **BioMCN.** Our Product – Biomethanol. http://www.biomcn.eu/our-product/bio-methanol.html

72. **Maine BioProducts.** Development of the biofine process for the production of levulinic acid. (http://www.mainebioproducts.com)

73. **Plastemart.com** 30/05/2011. Biorenewable chemicals market to be worth US$6.8 bln by 2015 at a CAGR of 22.8%

74. **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.

75. **3-Hydroxypropionic Acid (3-HP). Wisconsin** biorefining development initiative (http://www.biorefine.org/prod/3acid.pdf)

76. **Lucite International.** The future with Alpha Technology. (http://www.lucite.com/innovation_alphatechnology.asp)

77. **Hatakeyama, H., Hatakeyama, T.** Lignin structure, properties and applications. Adv. Polym. Sci. 2010: 232, 1-63.

78. **Holladay J.E., J.J. Bozell, J.F. White, D. Johnson**, 2007 Top Value-Added Chemicals from Biomass Volume II—Results of Screening for Potential Candidates from Biorefinery Lignin. (http://www.ntis.gov/ordering.htm)

79. **Zakzeski, J., P.C.A. Bruijnincx, A.L. Jongerius, and B.M. Weckhuysen.** The catalytic valorization of lignin for the production of renewable chemicals. Chemical Reviews 110 (6), 3552-3599.

80. **BTG-BTL.** Pyrolysis based Biorefinery. http://www.btg-btl.com/index.php?id=76&rid=47&r=oilapplication

81. **Branca, C., A.Galgano, C. Blasi, M. Esposito, and C. Di Blasi.** H_2SO_4-Catalyzed Pyrolysis of Corncobs. Energy Fuels 2011, 25, 359–369

82. **Vlachos, D.G. J. G. Chen,R. J. Gorte, G.W. Huber, M. Tsapatsis.** Catalysis Center for Energy Innovation for Biomass Processing: Research Strategies and Goals. Catal Lett (2010) 140:77–84

83. **NSF. 2008.** Breaking the Chemical and Engineering Barriers to Lignocellulosic Biofuels: Next Generation Hydrocarbon Biorefineries.Ed. George W. Huber, University of Massachusetts Amherst. National Science Foundation. Chemical, Bioengineering, Environmental, and Transport Systems Division. Washington D.C. 180 p.

84. **Bauer A., Hrbek a, B. Amon, V. Kryvoruchko, V. Bodiroza, H.Wagentristl, W. Zollitsch, B. Liebmanne, M. Pfeffere, A. Friedle, T. Amon.** 2007. Potential of biogas production in sustainable biorefinery concepts. (http://www.nas.boku.ac.at/uploads/media/OD7.1_Berlin.pdf).

85. **Schmid-Staiger, U.** National German Workshop on Biorefineries. 15th September 2009, Worms

86. **Croda.** Coatings & Polymers literature. (Http://www.crodacoatingsandpolymers.com/home.aspx?s=139&r=223)

88. **Pereira, G.A.G. et al.** 2011 Mircoorganisms and process for producing n-propanol. WO2011/029166 A1.

89. **Carole, T.M., J. Pellegrino, M.D. Paster.** Opportunities in the Industrial Biobased Products Industry. Applied Biochemistry and Biotechnology Vol. 113–116, 2004: 871-885

90. **Vertec Biosolvents.** (http://www.vertecbiosolvents.com/tour-home.htm)

91. **Haveren, J., E.L. Scott, J. Sanders.** 2008. "Bulk chemicals from biomass." Biofuels, Bioproducts and Biorefining 2(1): 41-57.

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

93. **Hill, K-H.** Cognis GmbH : 2nd Workshop Fats and Oils as Renewable Feedstock for the Chemical Industry, Emden, March 22-24, 2009

94. **IENICA Summary Report 2000-2005** - www.ienica.net/reports/ienicafinalsummaryreport2000-2005.pdf

95. **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)

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

97. **Draths.** Our first two Commercial Products will be: Caprolactam & Purified Terephthalic Acid (PTA) (http://www.drathscorporation.com/products.aspx)

98. **Annelotech.** Low cost green petrochemicals & fuels from biomass. (http://www.anellotech.com/index.html)

99. **Brandvold, T.** 2010. Carbohydrate route to para-xylene and terephthalic acid. WO2010151346 A1.

100. **Berti C., E. Binassi ,M. Colonna, M. Fiorini, G. Kannan, S. Karanam, M. Mazzacurati, I. Odeh.** 2010. Bio-Based Terephthalate Polyesters. US20100168461 A1.

101. **Virent Energy Systems Inc.** Virent's Chemical Completes Plant-Based PET Bottle (http://www.virent.com/News/press/06-06-11_Virent_Makes_Paraxylene.pdf)

102. **Areste, M.** 2010. Carbon Dioxide as Chemical Feedstock. Wiley-VCH Verlag GmbH & Co. Weinheim, Germany. ISBN: 978-527-32475-0

103. **Meredian plastics** - Danimer Scientific llc. (http://www.danimer.com)

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

105. **Coons, R.** 2010. Industrial Biotechnology, turning chemical engineering into a profit. Chemical week, November 8/15, 2010, pp 22-26. (http://www.genomatica.com/_uploads/pdfs/ChemicalWeek_11_8_101.pdf)

106. **Westerveld, R.** 2010. Rennovia Targets Bio-based Route to Adipic Acid. Chemical Week Oktober 18, 2010. (http://www.rennovia.com/LinkClick.aspx?fileticket=-Q5uwX-Ayhc%3D&tabid=62)

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

108. **Gibson, L.** 2010. Verdezyne proves adipic acid production process. Biomass Magazine 4: 25. (http://biomassmagazine.com/articles/3608/verdezyne-proves-adipic-acid-production-process)

109. **Sheridan, K.** 2011. BioAmber and CELEXION announce exclusive licensing partnership. (http://www.bio-amber.com/img/pdf/BioAmber_Celexion_Press_Release_15MAR2011.pdf)

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

111. **Raschka A., M. Carus.** 2012 Industrial material use of biomass Basic data for Germany, Europe and the world. 28pp. http://www.nova-institut.de/bio/

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

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

114. **Norsker, N., Barbosa, M.J., Vermue, M, Wijffels, R.H.** 2011. Microalgal production–a close look at the economics. Biotechnology Advances. 29, 24–27.

115. **Wijffels, R.H., Barbosa, M.J.,** 2010. An outlook on microalgal biofuels. Science 329, 796-799

116. **Wijffels, R.H., Barbosa, M.J., Eppink, M.** 2010. Microalgae for the production of bulk chemicals and biofuels. Biofuels, Bioproducts and Biorefining. 4, 287–295.

117. **Tokiwa Y, C.U. Ugwu.** 2007. Biotechnological production of (R)-3-hydroxybutyric acid monomer. Journal of Biotechnology 132, 264–272.

118. **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

119. **Frost & Sullivan.** 2011. Advances in Fermentation Technologies - An Industry Overview. http://www.technicalinsights.frost.com

120. **Carrez, D., J. Albrecht, P. Cunningham, L. Daroda, 4R. Mancia, L. Máthé, A. Raschka, M. Carus, S. Piotrowski.** 2010: The Knowledge Based Bio-Economy (KBBE in Europe: Achievements and Challenges. (Free Download: http://cleverconsult.eu/cleversafe/wp-content/uploads/2010/09/KBBE_A4_1_Full-report_final.pdf).

121. A Global Strategic Business Report – October 2008 – Global Industry Analysts, Inc. (http://www.strategyr.com).

122. **Okabe, M., Lies, D., Kanamasa, S., Park, E.Y.** 2009 Biotechnological production of itaconic acid and its biosynthesis in Aspergillus terreus. Applied Microbiology and Biotechnology 84, 597-606.

123. **Wilkens, E., Ringel, A., Hortig, D., Willke, T., Vorlop, K.-D.** 2011 High-level production of 1,3-propanediol from crude glycerol by Clostridium butyricum AKR102a. Applied Microbiology and Biotechnology, 1-7. doi: 10.1007/s00253-011-3595-6

124. **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

125. **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 Biotechnology(0). doi: 10.1016/j.nbt.2011.06.015

126. **Taylor D.C., Smith M.A., Fobert P, Mietkiewska E, Weselake R.J.** 2011 Plant systems - Metabolic engineering of higher plants to produce bio-industrial oils. In: Murray Moo-Young (ed.), Comprehensive Biotechnology, Second Edition, volume 4, pp. 67–85. Elsevier.

126. **Gunstone, F.D.** The Chemistry of Oils and Fats: sources, composition, properties, and uses. Blackwell Publishing, Oxford, 2004. 288 pp. ISBN 1-4051-1626-9.

127. **Taylor D.C., Smith M.A., Fobert P, Mietkiewska E, Weselake R.J.** 2011 Plant systems - Metabolic engineering of higher plants to produce bio-industrial oils. In: Murray Moo-Young (ed.), Comprehensive Biotechnology, Second Edition, volume 4, pp. 67–85. Elsevier.

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

129. **Quinzler, D., Mecking, S.** 2010. Linear semicrystalline polyesters from fatty acids by complete feedstock molecule utilization. Angew. Chem. Int. Ed. **49**, 4306 –4308.

130. **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.

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

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

133. **Yamagishi K.** 2005. Method for producing organic acid. WO2005005649; **Murase, M., Yonekura, M., Kido, D., Aoyama, R., et al.** 2009. Method for production of succinic acid. WO2009025363.

134. **BioAmber.** 2011. BioAmber partners with Mitsubishi Chemical in succinic acid. http://www.bio-amber.com/bioamber/en/news/article?id=459

135. **Evju, H.** 1979. Process for the preparation of 3-methoxy-4-hydroxybenzaldehyde, US Patent 4151207.

136. **Öhman, F., Theliander, H., Tomani, P., Axegard, P.** 2009. A method for separating lignin from black liquor, a lignin product, and use of a lignin product for the production of fuels or materials. W0104995.

137. **Gosselink, R.J.A.** 2011. Lignin as a renewable aromatic resource for the chemical industry. PhD Thesis Wageningen, ISBN: 978-94-6173-100-5, the Netherlands.

138. **Coca Cola.** 2011. The Coca-Cola Company Announces Partnerships to Develop Commercial Solutions for Plastic Bottles Made Entirely From Plants. (2011). http://www.thecoca-colacompany.com/dynamic/press_center/2011/12/plantbottle-partnerships.html

IEA Bioenergy

IEA Bioenergy is an international collaboration set-up in 1978 by the International Energy Agency (IEA) to improve international co-operation and information exchange between national bioenergy RD&D programmes. IEA Bioenergy's vision is to achieve a substantial bioenergy contribution to future global energy demands by accelerating the production and use of environmentally sound, socially accepted, and cost-competitive bioenergy on a sustainable basis, thus providing the increased security of supply whilst reducing greenhouse gas emissions from energy use. Currently, IEA Bioenergy has 24 Members and is operating on the basis of 12 Tasks covering all aspects of the bioenergy chain, from resource to the supply of energy services to the consumer.

IEA Bioenergy | Task 42 Biorefinery

IEA Bioenergy Task42 Biorefinery deals with knowledge building and exchange within the area of biorefining, i.e. the sustainable processing of biomass into a spectrum of marketable Bio-based Products and Bioenergy. The Task was started in 2007, and is now very successfully in operation involving Australia, Austria, Canada, Denmark, France, Germany, Ireland, Italy, Netherlands, Turkey, United Kingdom, United States of America. Within the first triennium (2007-2009) the main focus of activities was on setting a common international framework on biorefining (i.e. definition, classification system, state-of-the-art in participating countries). In the second (this) triennium (2010-2012) the focus of the activities is on the integral technical, economic and ecological assessments of full biofuel-driven biorefineries; the analysis of the types of Bio-based Chemicals that potentially could be co-produced with secondary energy carriers to maximise full biomass valorisation chain economics, and to minimise the overall environmental impact (this report), to study overall sustainability aspects of integrated biorefineries, and to organise a Biorefining Summer School to get both industrial stakeholders, policy makers and students acquainted with the principles, current state-of-the-art, and future possibilities of applying the biorefining approach as base for a Bio-based Economy. Task42 will continue in the next triennium (2013-2015) with main focus on tackling market deployment aspects for integrated biorefineries, supporting stakeholders in the energy sector finding their position within a future Bio(-based) Economy, optimal sustainable use of biomass for Food and Non-food applications, and dissemination & training activities.

Further Information

IEA Bioenergy Task42 Website
www.iea-bioenergy.task42-biorefineries.com

IEA Bioenergy Website
www.ieabioenergy.com

Contact – IEA Bioenergy Task42 Secretariat
Wageningen UR – Food and Bio-based Research
Hilde Holleman – Secretary
P.O. Box 17
6700 AA Wageningen
The Netherlands
Phone: +31 317 481165
Email: hilde.holleman@wur.nl

Leader of Task42
René van Ree
Wageningen UR – Food and Bio-based Research
Phone: +31 317 611894
Email: rene.vanree@wur.nl

Co-leader of Task42
Ed de Jong
Avantium Chemicals BV
Amsterdam
The Netherlands
Phone: +31 20 586 80 80
Email: ed.dejong@avantium.com

Operating Agent Task42
Kees Kwant
NL Agency
Ministry of Economic Affairs, Agriculture and Innovation
Utrecht
The Netherlands
Phone: +31 88 602 2458
Email: kees.kwant@agentschapnl.nl

iea Energy Technology Network

This publication was produced by the Implementing Agreement on Bioenergy Task 42 Biorefinery, which forms part of a programme of international energy technology collaboration undertaken under the auspices of the International Energy Agency.