INTRODUCTION

The call for products based on renewable resources has grown louder in recent years because of the increasing awareness of the public about environmental problems that are caused by the society’s dependence on fossil resources. As a result, the petrochemical industry has been looking for feedstock alternatives and accompanying technologies. For instance, Chevron formed a joint-venture with Weyerhaeuser (a forest products company), in order to produce fuels, and Royal Dutch Shell is a long-time partner of Iogen, a company that is developing technology for producing second generation bioethanol.

Moreover, bio-based industries like the pulp and paper industry are looking for opportunities to revive their commodity-based business by considering the expansion of their product portfolios with added-value products. For instance, a recent study that focused on the Canadian forestry industry identified several products that can be manufactured from wood fibre and have an interesting projected annual growth rate and value (Table 3.1). The goal of this expansion is to increase companies’ profit margins and to make efficient use of the renewable resources that they have traditionally been using.

The biorefinery is a process concept that is a means to produce biobased products that are both economically and environmentally beneficial. The biorefinery includes the use of many kinds of biobased feedstocks and makes use of several technological concepts that are based on chemical, biochemical and thermochemical...
The purpose of this chapter is to give an overview of some of the products that can be manufactured using biorefinery concepts. First, the biorefinery product platform is discussed. This is followed by a discussion of the products that can be manufactured. A distinction will be made between platform chemicals, added-value chemicals, materials and bioenergy. This chapter will be concluded with some thoughts on how to decide which biorefinery products are feasible for production.

**BIOREFINERY PRODUCT PLATFORM**

A product platform-based approach can be applied to explore the opportunities for manufacturing biorefinery products. A product platform is “the common technological base from which a product family is derived through modification and instantiation of the product platform to target specific market niches.” The biorefinery platform-based approach involves the production of a chemical building block or intermediate and this intermediate is subsequently converted to a larger number of products. Such a product platform can e.g. be added to an existing pulp and paper mill product portfolio (Chapter 5), resulting in a new company product portfolio (Figure 3.2). This approach has successfully been used by the petrochemical industry.

Biomass-based products can substitute for fossil fuel based products. A distinction can be made between replacement and substitution products: replacement products are identical in chemical composition to existing products, but are based on renewable resources, e.g. bioethanol; substitution products have a different chemical composition to existing products, but have a similar functionality, e.g. PLA (polylactic acid) which would substitute PET (polyethylene terephthalate) in the production of e.g. plastic bottles.

The value of biorefinery products is strongly dependent on the volume that is produced (Figure 3.3): commodities (e.g. cellulose-based fibre, ethanol) will typically have low prices, whereas added-value chemicals (e.g. vanillin, aldehydes)

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3. V. Chambost, J. McNutt and P. Stuart. ‘Guided tour: Implementing the forest biorefinery (FBR) at existing pulp and paper mills’. In: Pulp and Paper Canada 109.7–8 (2008), pp. 19–27. In other contexts these concepts might have a slightly different meaning.
operations because it is relatively easy to switch to the production of a different chemical. (See also Chapter 5 for a discussion on factors that influence process choice in pulp mills, Chapter 8 on the value of heat as a byproduct and Chapter 9 on technical and market risks.)

**PLATFORM CHEMICALS**

There are several chemicals that are considered for production of biobased products. The US Department of Energy made an assessment of the most important biobased chemicals based on, among others, market data, properties and the technical complexity of the synthesis pathways. This list of chemicals was recently updated based on the progress that has been made with regard to the production of these chemicals (Table 3.3). Well-known examples in this list are ethanol, lactic acid and succinic acid.

Global fuel ethanol production was about 70

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5 B. Mansoornejad, V. Chambost and P. Stuart (2010). 'Integrating product portfolio design and supply chain design for the forest biorefinery'. In: Computers & Chemical Engineering 34.9, pp. 1497–1506.


Ethanol can be used for the production of ethyl esters such as ethyl acrylate (for polymer production) and ethyl acetate (used as a solvent in industry), and ethylamines that are used in the synthesis of pharmaceuticals, surfactants and agricultural chemicals.

Lactic acid is commercially produced mainly by the fermentation of glucose. The production of bio-based lactic acid is about 350 thousand tonnes (kt) per year. The conventional process is not optimal; for every tonne of lactic acid that is produced, one tonne of gypsum is produced. Furthermore, the separation and purification steps are expensive. Recent advances in membrane-based technologies have however resulted in more cost efficient processes.

Lactic acid can be used as a platform chemical for the production of a wide range of chemicals (Figure 4.4). It is currently mostly used for the production of polylactic acid (PLA). The increased demand for PLA is the main driver for the increasing production of lactic acid. PLA is a

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8 Renewable fuels association (2012).

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Figure 3.3: Illustration of price-market size relationship for biobased products. The squares indicate ranges regarding market volume and price.

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Figure 4.4: Illustration of price-market size relationship for biobased products.
Succinic acid can be produced by the fermentation of glucose and used as a precursor for a range of products (Figure 3.5). For instance, succinate esters are intermediates for the production of 1,4-butanediol, tetrahydrofuran and γ-butyrolactone: 1,4-butanediol is an important building block for the production of polyesters, polyethers and polyurethanes; tetrahydrofuran is used as an industrial solvent for PVC and can be polymerized to form poly (tetramethylene ether) glycol (PTMEG); γ-butyrolactone is another industrial solvent and is an intermediate for the production of agrochemicals and pharmaceuticals. Fumaric acid is currently under investigation for treatment of multiple sclerosis.


Table 3.2 Production and market potential for some promising biorefinery products

<table>
<thead>
<tr>
<th>Biorefinery Products</th>
<th>Biorefinery production (ktones/year)</th>
<th>Year</th>
<th>Market potential (ktones/year)*</th>
<th>Potential value (billion EUR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Platform chemicals</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lactic acid</td>
<td>350</td>
<td>n/a</td>
<td>54 000</td>
<td>8.1</td>
</tr>
<tr>
<td>Succinic acid</td>
<td>15</td>
<td>n/a</td>
<td>245</td>
<td>1.4</td>
</tr>
<tr>
<td>Added-value chemicals</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethylene</td>
<td>200</td>
<td>2008</td>
<td>130 000</td>
<td>130</td>
</tr>
<tr>
<td>Xylitol</td>
<td>45</td>
<td>n/a</td>
<td>75</td>
<td>0.34</td>
</tr>
<tr>
<td>Astaxanthin</td>
<td>0.004</td>
<td>n/a</td>
<td>0.13</td>
<td>0.20</td>
</tr>
<tr>
<td>Materials</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polylactic acid (PLA)</td>
<td>230</td>
<td>2008</td>
<td>54 000</td>
<td>9.0</td>
</tr>
<tr>
<td>TPS/PLA blend</td>
<td>330</td>
<td>2008</td>
<td>14 000</td>
<td>30</td>
</tr>
<tr>
<td>Viscose</td>
<td>3 500</td>
<td>2005</td>
<td>60 000</td>
<td>120</td>
</tr>
<tr>
<td>Transportation fuels</td>
<td>88 000</td>
<td>2008</td>
<td>2 500 000</td>
<td>1200</td>
</tr>
</tbody>
</table>

*The potential market volume is defined as the market volume of the fossil fuel alternative of a given product in the given year (if available).

Table 3.3 US Department of Energy “Top 10” biobased chemicals. The table is arranged such that the similarities and differences between the two lists become apparent

<table>
<thead>
<tr>
<th>Year 2004</th>
<th>Year 2010</th>
</tr>
</thead>
<tbody>
<tr>
<td>Succinic, fumaric and malic acids</td>
<td>Biohydrocarbons (isoprene, other)</td>
</tr>
<tr>
<td>2,5-Furan dicarboxylic acid</td>
<td>Lactic acid</td>
</tr>
<tr>
<td>3-Hydroxypropionic acid</td>
<td>Ethanol</td>
</tr>
<tr>
<td>Leucinonic acid</td>
<td>Succinic acid</td>
</tr>
<tr>
<td>Glycerol</td>
<td>Furans (furfural, HMF, FDCA)</td>
</tr>
<tr>
<td>Sorbitol</td>
<td>Hydroxypropionic acid/aldheyde</td>
</tr>
<tr>
<td>Xylitol/arabinitol</td>
<td>Leucinonic acid</td>
</tr>
<tr>
<td>Aspartic, glucaric, glutamic, itaconic acid</td>
<td>Glycerol and derivatives</td>
</tr>
<tr>
<td>3-Hydroxybutyrolactone</td>
<td>Sorbitol</td>
</tr>
<tr>
<td></td>
<td>Xylitol</td>
</tr>
</tbody>
</table>

Another high-volume derivative from lactic acid is acrylic acid. This is the primary building block for the formation of acrylate polymers which have numerous applications e.g. in surface coatings and adhesives.

Succinic acid is considered an important platform chemical that can be produced from renewable resources and its market size has been projected to be about 250 kt per year.11 Production has recently started at a scale of a few thousand tonnes per year but new larger production plants are planned.12

Succinic acid can be produced by the fermentation of glucose and used as a precursor for a range of products (Figure 3.5). For instance, succinate esters are intermediates for the production of 1,4-butanediol, tetrahydrofuran and γ-butyrolactone: 1,4-butanediol is an important building block for the production of polyesters, polyethers and polyurethanes; tetrahydrofuran is used as an industrial solvent for PVC and can be polymerized to form poly (tetramethylene ether) glycol (PTMEG); γ-butyrolactone is another industrial solvent and is an intermediate for the production of agrochemicals and pharmaceuticals. Fumaric acid is currently under investigation for treatment of multiple sclerosis.

well-known example is astaxanthin which is produced naturally by micro-algae. Astaxanthin has a strong anti-oxidant character and may prevent some cancers. Plant cell cultures can also be used for the production of nutraceuticals. An issue that needs to be addressed is the efficient extraction of the relevant metabolites. Solvent-based extraction has several drawbacks such as low yield and long extraction times. Enzyme-based extraction is an alternative to such conventional extraction methods. For example, the extraction of stevioside, a high intensity non-nutritive sweetener, has been improved by applying an enzyme-based method. Another prominent nutraceutical is xylitol, which is applied as a natural sweetener in mouthwashes, toothpastes or chewing gums. The global consumption of xylitol was about 45 kt in 2005 (Table 3.2).

Xylitol is produced by the hydrogenation of xylose, which itself is the product of the decomposition of xylan. Xylan is a hemicellulose and thus can be found in lignocellulosic biomass (see Chapter 5).

Nutraceuticals (products that promote health) may be extracted from biomass as well. One


MATERIALS

The global production capacity of emerging bioplastics has been estimated at 0.4 Mt in 2007, with projected growth to 4 Mt in 2020. The most important emerging bioplastics in 2007 were PLA (polylactic acid) and starch plastics. PLA, starch plastics, biobased PE and PHAs (polyhydroxy alkanoates) were projected to be the most important ones in 2020. As discussed above, PLA and PE can be produced from lactic acid and ethanol, respectively. In contrast to these two plastics, PHAs are produced directly via fermentation within the microorganism and are stored in granules in the cell cytoplasm. Carbon sources for the production of PHAs include carbohydrates, alcohols, alkanes and organic acids, depending on the type of PHA wanted and the microorganism used in the fermentation. Other emerging biobased plastics include polylactide (PLA), polyamides (nylon), polyurethane and thermosets like epoxy resins.

Besides these emerging bioplastics, there is a range of established biopolymers which include non-food starch (without starch for fuel ethanol), cellulosic polymers and alkyd resins. These polymers comprise a volume of 20 Mt per year. There are several types of starch plastics including thermoplastic starch (TPS). TPS is produced by the extrusion of native starch. However, it is of somewhat limited usefulness due to its hydrophobicity and inferior mechanical properties compared to conventional polymers. Cellulosic polymers include organic cellulose esters and cellulose ethers. Organic cellulose esters replaced cellulose nitrate because of the latter’s flammability. Cellulose esters have been widely applied in packaging films, cigarette filters and textile fibres; cellulose ethers however have only been used in non-plastic applications. Alkyd resins are made from glycol or glycerol, fatty acids or triglyceride oils. The major part of manufactured alkyd resins is used for the coating of industrial goods and infrastructure.

One major application of natural fibres can be found in the production of paper products (380 Mt of paper and paperboard in 2009). Lignocellulosic (woody) biomass is mostly used as the source of fibre. The processing of the wood for producing pulp has a large impact on the application and the properties of the paper.

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 thermo-mechanical pulping retains all of the wood components in the pulp and is used mostly for the production of newsprint; chemical pulping (e.g. the kraft pulping process) on the other hand strives for the separation of lignin, hemicellulose and other compounds in order to free the cellulose fibres for the production of e.g. uncoated free sheet. Besides these conventional types of paper, new applications of paper that are currently in the R&D stage are bioactive paper and “intelligent” paper.

The textile industry also makes extensive use of natural fibres, e.g. wool, cotton and silk. However, textile fibre can also be produced from (wood) pulp. This type of fibre is called man-made or regenerated cellulose fibres, and in 2005 the annual production was approximately 3.5 Mt.\(^\text{18}\) Examples of this type of fibre, which differ from each other in terms of physical properties, are viscose, modal and lyocell. One can note that also PLA (discussed above) can be used for the fabrication of fibre used in textiles.

Biobased composites have already been used in the past. For instance, in 1941, Henry Ford unveiled the “soybean car”, but it was suspended due to the outbreak of World War II. The car had a tubular steel frame with 14 plastic panels attached to it. These panels consisted of soybean fibre in a phenolic resin.\(^\text{19}\)

Biocomposites can be made by mixing plastics and fibres. Examples are a composite from L-poly lactide and jute fibre mats, and composites composed of regenerated cellulose fabric and biodegradable polyesters. Other types of green composites are based on fibre and soy, and fibre and natural rubber. Textile composites have been developed that have superior mechanical properties. For instance, phenolic composites reinforced with jute and cotton woven fabrics have been found to be suitable for the production of lightweight structural applications. Fibre-reinforced biocomposites have been applied extensively. Roof structures have been successfully fabricated from soy oil-based resin and cellulose fibres in the form of paper sheets made from recycled cardboard boxes. Plastic and wood fibre composites are being used in decks, docks, window frames and molded panel components. As well, a wood fibre was found to be the best replacement of asbestos in fibre cement products. Lastly, almost all German car manufacturers now use biocomposites in various applications such as dashboards and door panels (polypropylene and natural fibres) and asbestos has been replaced by flax fibres in disk brakes.\(^\text{20}\)

**BIOENERGY**

Biofuels used as transportation fuels are currently the most prominent products that are produced in biorefineries, bioethanol being the best known. The production of bioethanol (for use as a transportation fuel) is mandated to be 110 Mt per year (3.2 EJ per year) in 2022 in the United States, of which 62 Mt per year (1.8 EJ per year) should be bioethanol from lignocellulosic feedstock.\(^\text{21,22}\) Currently, the major part of the bioethanol produced in the United States is based on corn. Brazil also is a major producer of bioethanol and uses sugarcane as feedstock. The Brazilian production of fuel ethanol was nearly 21 Mt (0.6 EJ) in 2010. Since 1975, a fuel ethanol programme has been in place in Brazil which mandates that the content of ethanol in car fuel is at least 25% (E25).

Biodiesel can be produced from vegetable oils (jatropha, micro-algae) or animal fat feedstocks. The biodiesel is formed via the transesterification of these feedstocks into methyl or ethyl esters. The world-wide production of biodiesel was 16 Mt (0.6 EJ) in 2010, which was a significant increase from less than 4 Mt in 2005.\(^\text{23}\) Biodiesel can be used as a car fuel, as a heating oil, and has been tested for railway and aircraft usage.

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\(^\text{19}\) See the soybean car, [thehenryford.org](http://thehenryford.org).


\(^\text{22}\) The realism of this goal for ethanol from woody biomass can be put into question. See discussion on scale-up of the production of other types of fuels based on woody biomass in Chapter 9.

Other examples of proposed transportation fuels based on renewable resources are hydrocarbons, butanol, Fischer-Tropsch diesel (FT-diesel), methanol, dimethyl ether (DME) and hydrogen. Hydrocarbons can be produced by converting plant-based sugars using catalytic chemistry. Butanol is proposed as a substitute for gasoline due to its energy content (higher than ethanol) and ability to mix with gasoline in high proportions. Biobutanol is typically produced using ABE (acetone, butanol, ethanol) fermentation. However, the current ABE technology is not mature enough yet to be able to compete with conventional ethanol technology.\(^{24}\) There are several pilot and demonstration plants that aim at producing FT-diesel, methanol, DME or hydrogen from gasified biomass or black liquor (see Chapters 2, 5 and 9). Gasification enables that more of the energy content in the biomass feedstock can be converted to the targeted fuel as compared to pathways based on fermentation (see Chapter 2 and 6).

Other bioenergy products are mostly used for the generation of heat and electricity. Examples of such products are wood pellets, bio-oil and lignin. Wood pellets have gained popularity in Europe as a means to reduce CO\(_2\) emissions of heat and electricity generation. In Canada, the amount of deadwood suitable for pellet production has increased significantly due to the pine beetle infestation. Even if the transportation of wood pellets from the west coast of Canada to Europe is taken into account, environmental benefits are expected.\(^{25}\)

Pyrolysis is a means to produce bio-oil, which can be used as an energy resource or as a feedstock for chemicals production. Besides the bio-oil, a pyrolysis process typically also yields char and gas.\(^{26}\) Lastly, lignin can be separated in pulp plants and used as a biofuel (Chapter 5). Lignin has a higher heating value than wood and can either be burned as such or co-fired with other (fossil-based) fuels.

The interest in using biomass, or more generally, renewable resources for energy generation has increased more recently due to environmental concerns. On the one hand, the share of bioenergy is small when compared to energy that is generated from fossil fuels (6% vs. 77% in the EU-27 in 2009, respectively). On the other hand, among renewable energy sources (biomass, hydro, geothermal, wind and solar), biomass supply is dominant accounting for 68% in 2010. In absolute terms bioenergy supply in EU-27 increased from 1.7 EJ in 1990 to 4.7 EJ in 2010 (Figure 3.6).


the portfolio of possible products includes a wide range from high volume low price commodities, such as biofuel and bioplastics, to low volume high price substances, such a specialty chemicals for the pharmaceutical industry.

The successful commercialisation and diffusion of these products do not depend on technical issues only. For instance, the forestry products industry will have a challenge in introducing wood-based biofuel on the market because corn-based ethanol is currently produced at lower cost partly due to sheer production volume. Besides production costs, market size and competition, also policy instruments affect the competitiveness of different products. For example, in many countries there are currently subsidies when biomass is used for biofuels and bioelectricity production, while this not the case for the production of green chemicals and materials. Moreover, the environmental impact of the production of biobased products needs to be taken into account, when assessing the future desirability of individual products. It is not guaranteed that all biobased products are more environmentally friendly than their fossil-based counterparts.

Sweden has a significantly different energy mix (Figure 4.7). The share of biomass in the energy mix has increased from about 10% in the 1980s to 23% in 2010. The growth in biomass use for energy purposes is largely responsible for the increase of the share of renewable energy in the Swedish energy mix during this period.

The examples of the EU and Sweden show that the share of bioenergy (heat and electricity) has been growing steadily in recent years, and that there can be large differences between countries to what extent biomass is used as an energy source.

**CONCLUDING REMARKS**

There is a plethora of potential biobased products and many have a significant growth potential. Biobased products can be classified in different ways, and no matter which classification that is selected there will remain ambiguities. For example, when considering platform chemicals such as ethanol, a relevant question becomes whether or not to consider it as the final (ethanol as fuel) or as an intermediate product (ethanol as a precursor for ethylene and PE production). Nevertheless, it is apparent from this chapter that