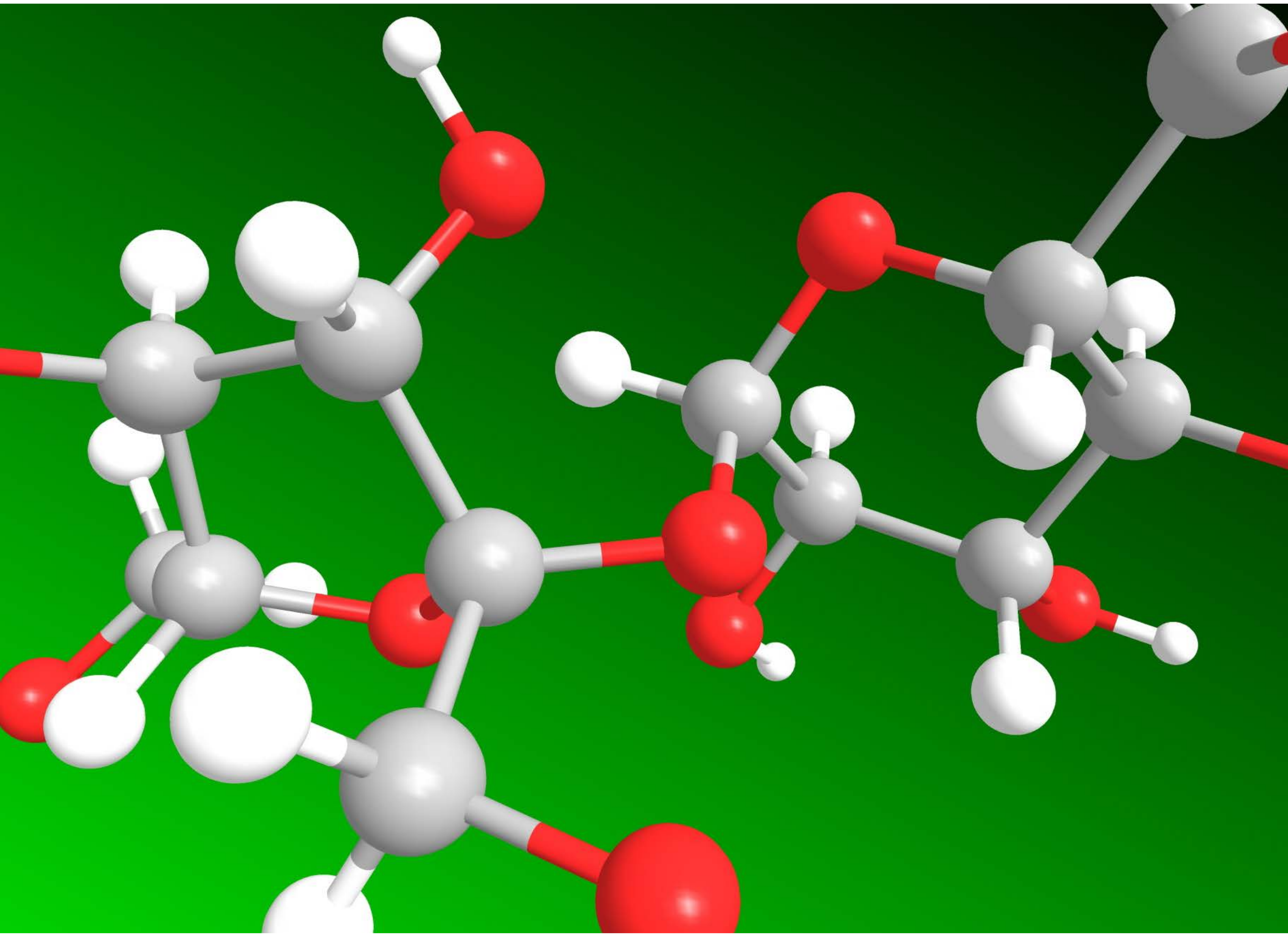
Green building blocks for biobased plastics

PAULIEN HARMSEN AND MARTIJN HACKMANN

WAGENINGEN UR
For quality of life



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Biobased processes and market development

Paulien Harmsen en Martijn Hackmann

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Preface

The Biobased Economy is an economy in which crops and waste streams from agriculture and the food industry, the so-called renewable resources or biomass, are used for non-food applications such as materials, chemicals, transport fuels and energy.

The chemical sector is currently using more and more biomass as raw material to replace increasingly scarce mineral oil. Previous editions in the 'Green Raw Materials' series focused on a range of subjects within the Biobased Economy including biobased plastics. There is considerable interest in this subject and a clear demand for more information about the 'green building blocks' for biobased plastics.

From a chemical perspective, nearly all building blocks for plastics can be made using renewable raw materials. However, not every process is commercially feasible. Processes often remain inefficient, products have insufficient purity or the raw materials are simply too expensive. This publication provides more insight into the processes that are currently under development and the companies involved, as well as the current development stage (from R&D to commercial production).

This study was commissioned by the Dutch Ministry of Economic Affairs, Agriculture and Innovation, and describes the current situation at established industrial companies and start-up businesses. The many developments and leads generated by research institutes have been largely left out of consideration. For many people, the information will serve as an eye opener due to the rapid developments in the field of biobased building blocks. The same developments may also stimulate businesses in their search for opportunities to produce green chemicals from biomass.

Contents

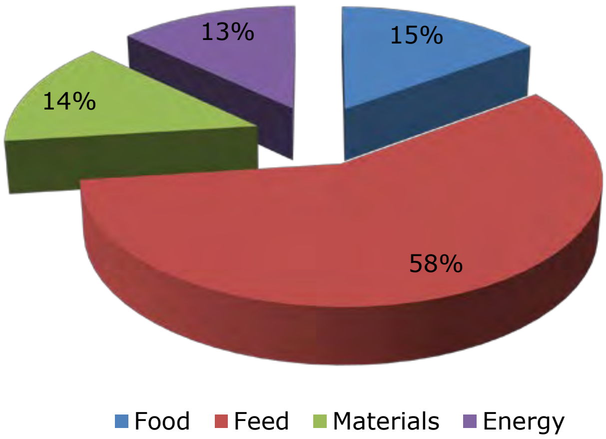
1 Introduction

1.1 Reason for this study

The development of biomass-based ('biobased') chemicals and materials has really taken off over the past decade. Technology has been developed and upscaled from lab scale to demo scale, and for some chemicals the technology has been sufficiently developed to enable commercial production. Current production is often just a fraction of the petrochemical market, but the growth is impressive and it is expected that production will increase considerably in the coming years. There are also examples of chemical building blocks and materials (partly) based on biobased raw materials that have been in production for years.

The Dutch chemical sector would like the Netherlands to be known as the country for green chemistry by 2050. This means that the production of synthetic materials will be mainly based on biomass-based raw materials. The chemical sector is developing clean and sustainable production processes to convert biomass into a wide range of existing and new products. This publication provides an overview of the current situation regarding green chemistry, and takes into account developments in the Netherlands and elsewhere in the world.

As part of the 'Green Raw Materials' series, this publication is focused on green building blocks for biobased plastics. The figure on the next page shows that currently the majority of biomass is used for food and animal feed (73%). The remainder (27%) is used for energy and materials with wood as main raw material. Only a small percentage of the biomass is currently being used as raw material for chemicals; approximately 5% of all chemicals is biobased [1].
In the chemical industry, the market volume of plastics is by far the largest. While raw materials for the chemical sector still mainly have a petrochemical origin, in the plastics sector there are many developments towards taking the step from petrochemical to renewable raw materials.



Global application of biomass
(Source: Nova Institute, data from 2008 with a total biomass volume of 13 billion tons)

This publication describes both well-known biobased processes for chemical production that are currently being applied in the industry and less familiar, often neglected processes. We mainly looked at chemical or biotechnological processes that have retained the functionality of the biobased building blocks in sugar, lignin, oil or protein as much as possible. Thermo-chemical processes that reduce the biomass to non-functional compounds (CO, CO_2, H_2), including incineration, gasification, pyrolysis or torrefaction, are not taken into account (with a few exceptions).

Chemical building blocks that are chemically identical to their petrochemical counterparts (so-called 'drop-ins') can immediately be used in the current industrial infrastructure, and make a material partly or completely biobased. There are also examples of new chemicals and materials from renewable raw materials with unique characteristics that are often impossible or very difficult to produce from petrochemical raw materials, like lactic acid. These building blocks result in the development of new products and markets.
Due to the focus on chemical building blocks, this publication does not describe biobased plastics from natural polymers such as cellulose and starch. So-called PHAs (biobased polymers from micro-organisms) also fall into this category and are excluded from this publication. A previous publication in the 'Green Raw Materials' series (*i.e.* Biobased Plastics 2012) discusses these materials comprehensively.

1.2 Reader's guide

The following chapters discuss the chemical building blocks for each polymer group: Vinyl polymers, polyesters, polyamides, polyurethanes and synthetic rubbers. Polymers consist of monomers with a specific functionality; polyesters, for example, are made up of alcohols and acids, while polyamides are built from acids and amines. For each group of polymers, we provide the main monomers, how they are currently being produced and by whom, and the possible biobased processes.

These biobased processes are pictured for each polymer in diagrams that consist of various blocks which indicate a process or product. This is analogous to the 'International Energy Agency (IEA) Bioenergy Task 42 on Biorefinery' for the categorisation of biorefineries:

The vinyl polymers and the polyesters are such large groups that they are divided in multiple diagrams to ensure a clear overview. Per chapter we discuss chemical building blocks that are applied in the polymer group; if a building block was already discussed in a previous polymer group, you are referred to the relevant group. Building blocks are discussed as part of the polymer group in which they are most relevant. The annexes include a table with the structure of the chemical building blocks and a list of polymer abbreviations.

All the information in this publication is public. We used reports and publications as resources, and consulted internet forums and blogs. These forums and blogs were checked by studying the website of the companies involved. We then used as much information from these company websites as possible, including presentations and press releases.

The diagrams also include the status of the biobased processes (*i.e.* R&D, pilot, demonstration, commercial) in case of available information. In addition, they include the biobased production volumes (in metric tons, indicated in green) and estimations for 2016 based on the plans of the industry. These figures were derived from company reports and press releases. Although it is difficult to obtain reliable figures on production volumes, in this way we hope to provide a reasonable indication and an insight into their growth.

2 Vinyl polymers

2.1 Introduction

Vinyl polymers (or polyolefins) form the largest group in production volume. They are produced by polymerising an alkene monomer (C=C) into a chain. One of the most important monomers for this group is ethylene (C2), with polyethylene being the most common example of a vinyl polymer. Besides polyethylene this chapter discusses polypropylene, poly(vinyl chloride), polystyrene, poly(vinyl acetate) and polyacrylates (in that order).

2.2 Polyethylene (PE)

2.2.1 General information

Polyethylene (PE) is the most commonly used plastic in the world, with a production volume of 88,000 kton/y [2] and a market share of nearly 30%. It is mainly known for plastic bags and as a packaging material, but is also used in, for instance, flexible (water) pipes. There are many different types of PE which each have their own unique characteristics and applications. The main types are high density PE (HDPE), low density PE (LDPE) and linear low density PE (LLDPE). The latter is developed by copolymerising ethylene (C2) with longer polymers such as butylene (C4), hexene (C6) or octene (C8).

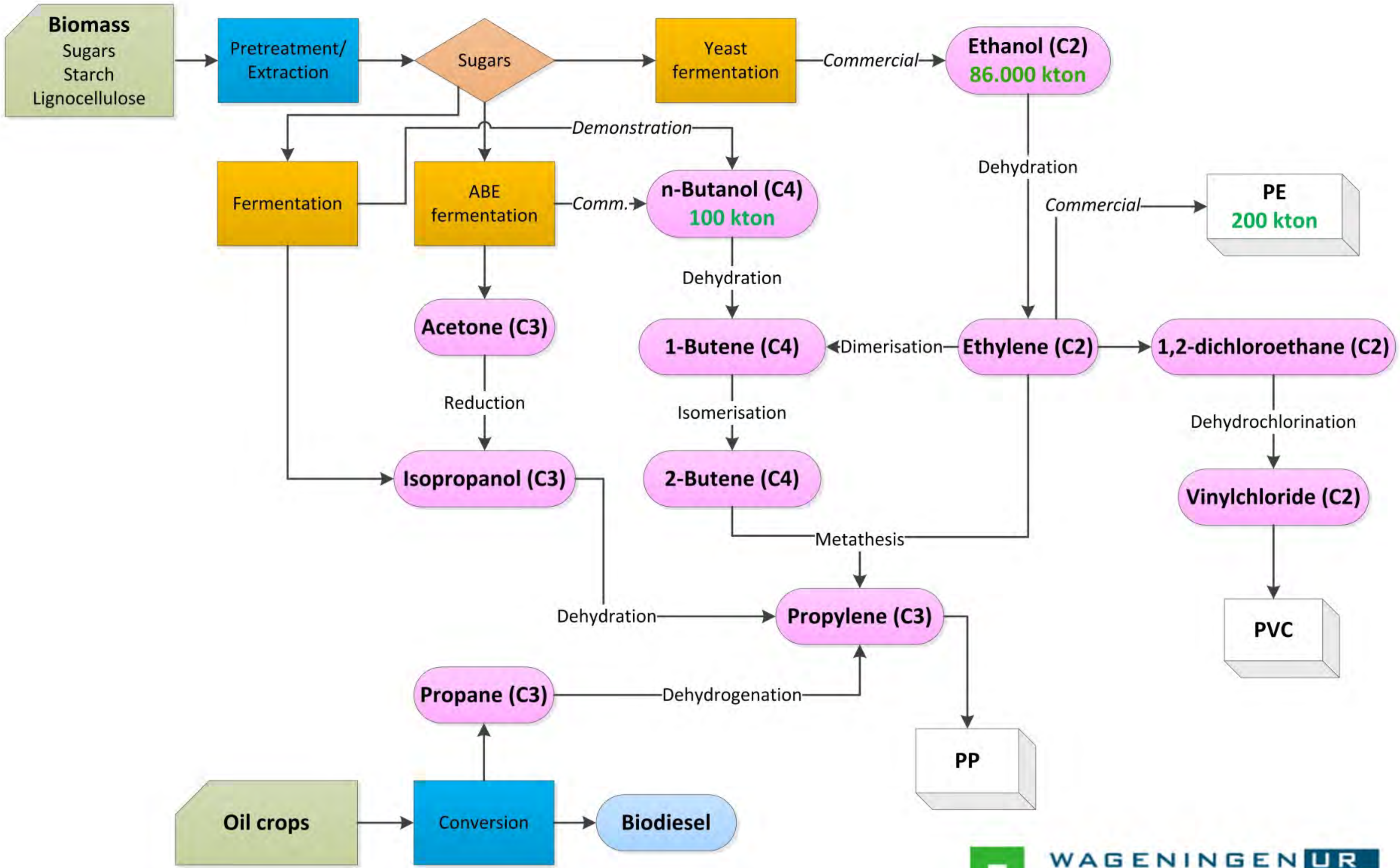
PE from renewable raw materials (bioPE) behaves the same as PE based on petroleum. This means that bioPE cannot be composted or biodegraded. It can easily be recycled, however, and can thus be included in the current waste separation process, and processed into new bioPE products using conventional technologies without requiring extra investments [3].

BioPE is currently sold at an extra cost of 30-50% compared to conventional PE. Companies seem to be willing to pay these extra costs as the material is biobased and more sustainable. Major packaging producers and A-brands in food, drinks and cosmetics have already introduced bioPE in their packaging products (examples include Tetrapak, Danone with Actimel, and Proctor and Gamble with Pantène).

2.2.2 Biobased processes for PE

The monomer ethylene is extracted from mineral oil by breaking down light petroleum fractions (naphtha). Ethylene can also be produced from biomass via ethanol as indicated in the diagram on page 12. Ethanol is produced by fermenting sugars, then converted into ethylene by means of dehydration. This ethylene is polymerised into bioPE with conventional processes.

Vinyl polymers: PE, PP and PVC



BioPE has the same process-technological characteristics as PE from petroleum. It therefore does not require new investments in production and processing equipment. The technical properties of the material are identical to conventional PE. This offers major benefits for the processing industry as it can continue to use the existing infrastructure.

2.2.3 Green building blocks and producers

Building blocks in the process to PE (ethanol and ethylene) are further clarified below:

Ethanol (C2)

Ethanol is a building block that is currently produced mainly by yeast fermentation of sugar-rich and starch-rich biomass like sugar cane (Brazil) or maize (North America), so-called first generation biomass. Globally, some 86,000 kton of bio-ethanol is produced each year, mainly for applications in biofuel [4].
The industrial production of ethanol from second generation biomass such as lignocellulose is rapidly developing. An overview of industrial activities in the field of second generation bio-ethanol is provided by the IEA Bioenergy Task 39 [5]. It shows that there are many facilities around the world currently at the pilot or demonstration stage. The first commercial plant for the production of bio-ethanol from second generation biomass may become operational in 2013, for example the facility of DSM and POET:

DSM and POET

DSM and POET have announced that they will be demonstrating the production of bio-ethanol from lignocellulose at a commercial scale in a joint venture. According to the planning, the production of bio-ethanol from lignocellulose will start in the second half of 2013. Residues from maize crops will be used as a raw material. For the production, a plant will be built adjacent to an existing POET facility in Emmetsburg (US) where ethanol is produced from maize. The initial production capacity will be 75 million litres (60 kton) a year, which they are expecting to expand to around 95 million litres (75 kton) a year [6].

Ethylene (C2)

Ethylene is one of the most important chemical building blocks with a production volume of over 100,000 kton a year. It is the basis for bulk polymers like PE and PVC (and in the future possibly for PP), and can be produced relatively easily by means of dehydration from (bio-)ethanol, which enables a biobased process.

2.2.4 Developments

The developments in the field of biobased PE are progressing rapidly, partly as a result of activities performed by Braskem, DOW and Mitsui:

Braskem

In 2010 Braskem [3] commissioned a production unit in Brazil that produces 200 kton/year of bioPE with bio-ethanol from sugar cane as raw material. This makes Braskem the first and largest global producer of ethylene from bio-ethanol. The produced ethylene is processed directly into PE.
Braskem is planning the construction of a second bioPE production facility of 400 kton/year which should be operational at the end of 2014-2015 [7].

DOW Chemical and Mitsui Chemicals

A joint-venture between DOW Chemical and Mitsui Chemicals is investing in the construction of a production facility for making bioHDPE and bioLLDPE with biobased ethylene as raw material [7, 8]. Although the joint-venture has not yet announced any exact dates, it is expected that the facility with a production capacity of 350 kton/year will be operational in 2015.

With the current production volume of 200 kton/year and the planned activities by Braskem, DOW, Mitsui and (possibly) others, the production of bioPE will increase to 750 kton/year around 2015. If this is indeed realised, it will make bioPE the largest biobased plastic by far in terms of volume.

Future producers of ethanol from lignocellulose may prefer to convert ethanol into ethylene instead of application as a fuel in the (saturated) fuel market. Of the global production of ethanol, 18 % (16,000 kton/year) is currently being used for non-fuel applications [4].

2.3 Polypropylene (PP)

2.3.1 General information

After PE, polypropylene (PP) is the most used plastic worldwide with a production volume of 47,000 kton/year [2]. There has been a considerable increase in the range of applications over the past 20 years, including textiles, cars (dashboards and bumpers), packaging, pipe systems and medical applications.

All these applications require different material characteristics. PP is a versatile plastic of which the material characteristics such as elasticity, viscosity, hardness, stiffness and transparency can be tailored to a wide range of applications. These tailor-made properties are possible by predetermining the structure of the polymer chain at a molecular level and making specific choices in the process conditions.

2.3.2 Biobased processes for PP

Propylene, the monomer for PP and currently derived from petroleum, is an important building block for the chemical industry. Propylene can be produced from biomass via various processes (see also the diagram on page 12):

1. ABE fermentation (fermentation with bacteria) of sugars which produces acetone (in addition to *n*-butanol and ethanol). Propylene can then be produced from the acetone via isopropanol
2. Fermentation of sugars into isopropanol, followed by dehydration into propylene
3. Metathesis of ethylene and 2-butene, with ethylene via the dehydration of ethanol and 2-butene via the dehydration of *n*-butanol into 1-butene followed by isomerisation into 2-butene
4. Metathesis of ethylene and 2-butene, with ethylene via the dehydration of ethanol and 2-butene by the dimerisation of ethylene into 1-butene, followed by isomerisation into 2-butene. In this process, the propylene is entirely derived from ethanol
5. Another process is via propane, a by-product of renewable diesel from natural oils and fats. Dehydrogenating propane can produce propylene

Currently it is unclear which process will be used to produce propylene. The process via ethanol and *n*-butanol or the one entirely from ethanol via dimerisation are the most likely possibilities as both ethanol and *n*-butanol can be produced via biobased routes. A recent development is the production of propylene from renewable raw materials via a biotechnological process developed by the French company Global Bioenergies [9]. The exact process is not yet known.

Propylene can then be polymerised into PP. Like bioPE, bioPP has the same process-technological properties as PP from petroleum, and thus does not require new investments in production and processing equipment. The final properties of the material are also the same as conventional PP.

2.3.3 Green building blocks and producers

Building blocks in the process to PP including ethanol and ethylene were already described in the previous paragraph. Below is a clarification of isopropanol and *n*-butanol:

Isopropanol (C3)

Isopropanol is currently mainly used as a solvent for cleaning and disinfection, but it can also serve as a raw material for propylene. Mitsui Chemicals is working on the fermentation of sugars into isopropanol and this is described in a number of patents [10, 11]. A similar process is currently being developed by Wageningen UR Food and Biobased Research in collaboration with the French company IFP.

n-Butanol (C4)

n-Butanol is a chemical building block with a current production volume of 2,300 kton/year [2]. Like isobutanol it is one of the isomers of butanol.[1] It is used as a solvent in paints and coatings. Most industrial initiatives in the field of *n*-butanol, however, are aimed at the biofuels market in light of the benefits compared to ethanol as a result of lower (CO_2) emissions and a higher energy value. Conversely, *n*-butanol can also be used as a chemical building block for the production of *e.g.* 1-butene. The following companies are involved in the production of *n*-butanol:

Cathay Industrial Biotech

As far as is known, the Chinese company Cathay Industrial Biotech [12] is the only company to produce biobased *n*-butanol on a commercial scale (via the fermentation of maize) at a capacity of 90 kton/year [13].

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[1] Both isomers of butanol are called biobutanol, which often causes confusion as to which isomer is actually intended. There are, however, major differences in the properties, applications and production methods of the two isomers.

Cobalt Technologies, Rhodia and Andritz

Cobalt Technologies and Rhodia recently announced a strategic alliance for the production of *n*-butanol in Latin America [14, 15]. As a raw material they will use sugar cane bagasse, a lignocellulose residue from sugar cane production. Cobalt Technologies and Andritz developed a pretreatment process under diluted acidic conditions to extract the sugar from the bagasse. This sugar solution can then be directly fermented into *n*-butanol without further enzymatic hydrolysis. This technology will be further developed to a commercial scale.

Butamax Advanced Biofuels

Butamax Advanced Biofuels, a joint venture between BP and DuPont, announced plans for the production of *n*-butanol from renewable raw materials on a commercial scale for the transport fuel market, building on bio-ethanol technology. It is expected that the commercial plant will be operational in 2014 [16].

Green Biologics

In 2010, the British biotech company Green Biologics announced an investment of six million euros in the development and commercialisation of biobased butanol for chemical applications and as transport fuel [17]. They currently have a 500-litre pilot facility in the UK and a 1100-litre pilot facility in the US.

Solvert

Solvert, another British company, is focusing on ABE-fermentation for the production of *n*-butanol, in addition to acetone and ethanol. It is not known at which scale they are operating [18].

2.3.4 Developments

Biobased PP is not being produced at the moment but this is likely to start soon. Braskem is investing approximately 76 million euros in the construction of a bioPP production unit [3] in which bio-ethanol from sugar cane is the main raw material. The production capacity of the unit will be 30 kton/year and commissioning is planned in the second half of 2013.

2.4 Poly(vinyl chloride) (PVC)

2.4.1 General information

Poly(vinyl chloride) (PVC) is a plastic of which the properties can be adjusted by means of additives such as plasticisers. PVC without (or with very little amount of) plasticiser is a hard material. Drainpipes, sewage pipes and synthetic window frames are made of PVC. The fact that PVC is extremely sustainable has been proven in practice: PVC frames last over 40 years, and sewage pipes around 100 years.
Plasticised PVC can contain up to 60% of plasticiser and be made so flexible that it can be used for *e.g.* rainproof clothing. Familiar products that are made from plasticised PVC include vinyl flooring, electricity cables and shower curtains. The main application market for PVC nowadays is the construction sector. Although PVC has a negative image, it receives high scores in environmental impact studies due to low energy consumption in the production process and its very long lifespan.
Increasing the sustainability of renewable PVC involves both the polymer PVC and plasticisers. The development of the polymer PVC is explained below; developments in the field of plasticiser are not included in this publication.

2.4.2 Biobased processes for PVC

Like PE and PP, the monomer for biobased PVC is ethylene, which can be obtained by dehydration of bio-ethanol. The ethylene is then converted into 1,2-dichlorethane with chlorine, resulting in vinyl chloride after dehydrochlorination. Vinyl chloride can then be polymerised into PVC (see the diagram on page 12).

2.4.3 Developments

Developments in the field of biobased PVC are limited at the moment. Braskem has been producing bio-ethylene from sugar cane since 2010; Solvay Indupa has plans to produce biobased PVC in Brazil, using bio-ethylene as a building block [19]. Sources report that Solvay Indupa is planning a production facility with a production volume of 120 kton/year but that the start-up, originally planned for 2011, has been delayed [20]. For the moment PVC is not being produced from renewable raw materials.

2.5 Polystyrene (PS)

2.5.1 General information

Polystyrene (PS) is a plastic that is currently being produced only from fossil resources (benzene and ethylene). It is mainly known as disposable packaging like coffee cups and chips containers. Polystyrene can also be foamed by means of CO_2. This expanded polystyrene (EPS or polystyrene foam) is used as packaging or insulation material.

2.5.2 Biobased processes for PS

The monomer for PS is styrene (vinyl benzene), an aromatic compound (ring structure). Styrene is currently produced from petroleum. It is mainly used as monomer for the production of polymers like PS and as a reactive solvent for polyester resins.

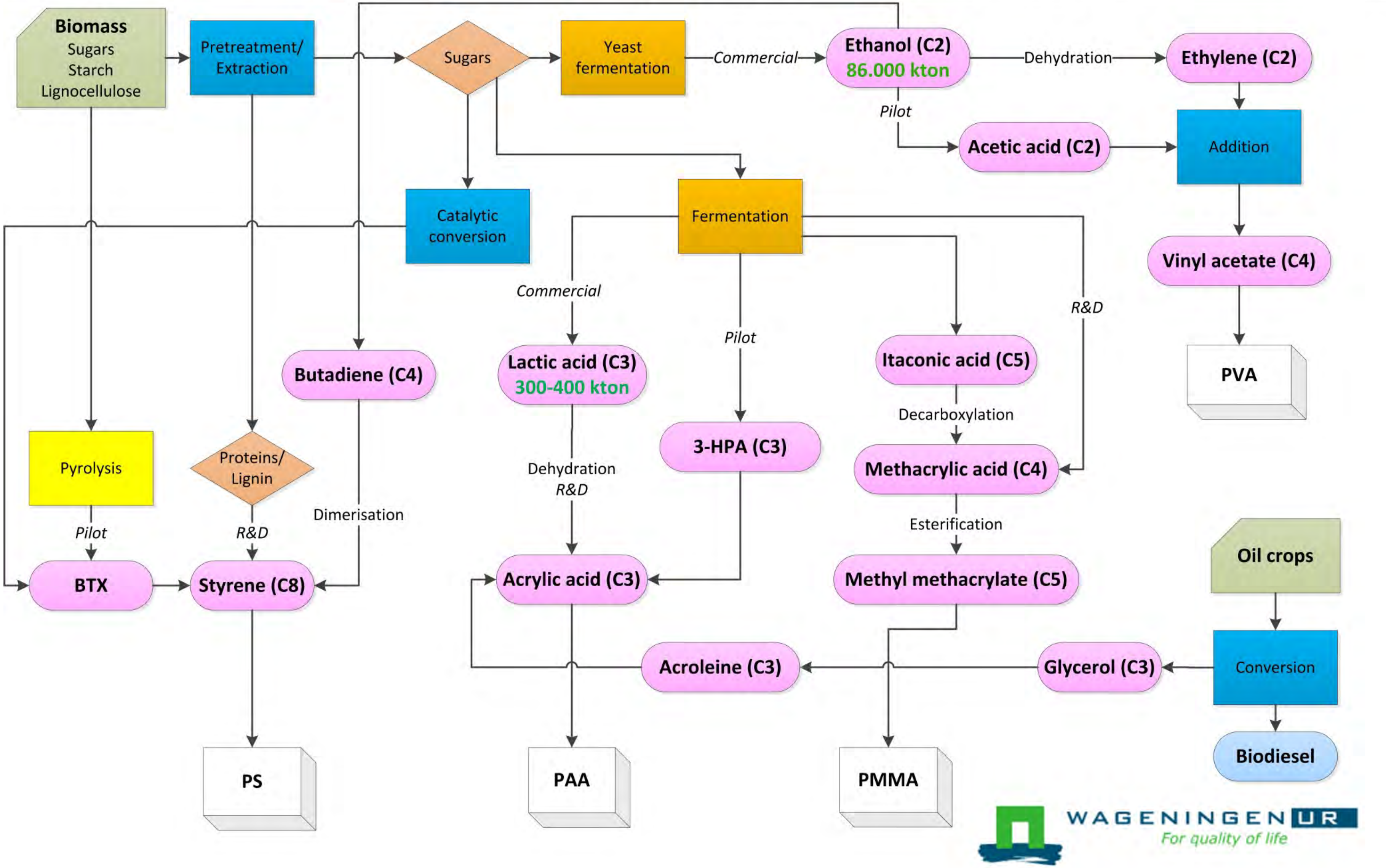
There are various possibilities for the production of styrene from biomass [21]; these processes have been indicated in the diagram on page 20:

1. Yeast fermentation from sugars to ethanol, conversion into butadiene followed by dimerisation into styrene
2. Pyrolysis (heating at a high temperature without the presence of oxygen) of biomass to a mixture of benzene, toluene and xylene (BTX). Benzene can then be converted into styrene via a reaction with ethylene
3. Chemical
(catalytic) conversion from sugars to BTX and further conversion of benzene into styrene via reaction with ethylene
4. Isolation of aromatic compounds from proteins or lignin

For process 4 it may be beneficial if the biomass already contains the functional aromatic structures. Renewable raw materials that contain aromatics are proteins (amino acids) and lignin.

In the Biobased Performance Materials programme, scientists from BASF, GreenICT, Synbra and DSM are cooperating with Wageningen University and Wageningen UR Food & Biobased Research on the development of styrene production from proteins [22]. This process is currently at the R&D stage.

Vinyl polymers: PS, PVA, PMMA and PAA



Another (possible) renewable source for styrene is lignin. Lignin, a natural polymer of aromatic compounds, is present in the cell walls of plants and functions as a kind of glue to provide strength and protection. Despite the fact that there is increasing insight into the chemical composition of the lignin structure [23], a lot of R&D is still required to make styrene from lignin in a profitable way.
As a result of developments in the field of second generation fuels, *e.g.* bio-ethanol from lignocellulose, major residual lignin streams are entering the market. While this lignin is currently being used as fuel, this could all change as soon as lignin can be used as a raw material for (high-quality) aromatic compounds.

2.5.3 Developments

Due to the large market volume, PS can be produced at very low costs at the moment and the biobased alternative will have to compete with this. Although aromatic structures are present in renewable raw materials, it is not yet possible to produce biobased styrene with sufficient purity from protein- or lignin-rich raw materials.

In contrast, the Dutch company Synbra Technology BV has succeeded in producing a biobased version of polystyrene foam; not by replacing the petrochemical styrene by a green alternative, but by making the foam from poly(lactic acid) (PLA), a polymer made from renewable raw materials (see also page 42) [24, 25]. The green foam called BioFoam can be composted and is considered as green waste. Synbra will be producing PLA itself and becomes then the first PLA manufacturer in the Netherlands. As a result, the company is no longer dependent on PLA availability on the market and is able to produce the optimal PLA quality required for the production of BioFoam.

2.6 Poly(vinyl acetate) (PVA)

2.6.1 General information

Poly(vinyl acetate) is a polymer that is mainly applied in adhesive and latex (paint) products. It is produced by polymerising vinyl acetate in water to create a poly(vinyl acetate) emulsion with a milky-white colour. The adhesives are used in products such as wood and paper glue, but also as shiny coatings for paper and textiles.

Vinyl acetate is also the basis for a copolymer with ethylene (ethylene-vinyl acetate copolymer, EVA) which is applied as a transparent adhesive in double glazing and solar panels. Vinyl acetate is also the raw material for the production of poly(vinyl alcohol) (PVOH).

2.6.2 *Biobased processes for PVA*

Biobased possibilities for poly(vinyl acetate) are shown schematically on page 20. Vinyl acetate, the monomer for poly(vinyl acetate), is produced by adding acetic acid to ethylene. Vinyl acetate polymerises into poly(vinyl acetate) under the influence of light (radical polymerisation).

2.6.3 *Green building blocks and producers*

The process of producing biobased PVA involves the building blocks ethylene, acetic acid and vinyl acetate. Developments in the field of acetic acid are described below. Ethylene is described on page 13, and vinyl acetate is not taken into consideration:

Acetic acid (C2)

Acetic acid is used in diluted form as a food ingredient and as a cleaning agent. It is also used in the production of plastics including PVA. Acetic acid can be produced via a synthetic process from methanol as well as by fermentation:

Wacker Chemie

Wacker Chemie has developed three processes for producing acetic acid from biomass, of which one has been further developed to pilot scale [26]. In this process, biomass is converted into ethanol via fermentation which is then converted into acetic acid by means of oxidation. Wacker Chemie has plans to upscale the process to an industrial scale as soon as it is economically feasible [27].

2.6.4 *Developments*

It is technically possible to produce 100% biobased vinyl acetate from ethylene and acetic acid. In addition to acetic acid, Wacker Chemie has the intention to produce bio-ethylene in the future, thereby opening up the route to vinyl acetate and thus poly(vinyl acetate).

2.7 Poly(methyl methacrylate) (PMMA)

2.7.1 General information

Poly(methyl methacrylate) (PMMA) is a plastic that is more widely known as acrylic glass, Plexiglas or Perspex. It is highly transparent, strong, extremely durable and mainly used in the construction sector. PMMA is produced by polymerising methyl methacrylate. In addition to PMMA, methyl methacrylates are also widely applied in other products such as coatings and adhesives through the copolymerisation with other monomers.

2.7.2 Biobased processes for PMMA

There are various processes for the biobased production of methyl methacrylate, the monomer for PMMA. The processes in the diagram on page 20 are both based on fermentation:

1. Fermentation of sugars to methacrylic acid, followed by esterification of methacrylic acid into methyl methacrylate
2. Fermentation of sugars to itaconic acid, followed by decarboxylation to methacrylic acid and esterification to methyl methacrylate

Methyl methacrylate polymerises to PMMA under the influence of light (radical polymerisation).

2.7.3 Green building blocks and producers

The building blocks in the process to biobased PMMA, *i.e.* methacrylic acid and itaconic acid, are seen as important chemical building blocks. The developments in these fields are described below:

<u>Methacrylic acid (C4)</u>

There are various developments in the field of biobased methacrylic acid for the production of methyl methacrylate, and in the end PMMA. These developments are all at R&D stage and not yet ready for production.

In cooperation with Lucite International, Mitsubishi Rayon (MRC) is developing a biotechnical process for producing methacrylic acid via fermentation of biomass with bacteria [28].
In addition to MRC, Evonik is also working on biobased production processes for methacrylic acid. Further details on these processes have yet to be published.

Itaconic acid (C5)

Itaconic acid is seen as a highly interesting chemical building block due to its resemblance to maleic acid, a compound commonly used in acrylates and resins. Itaconic acid can be produced using various processes. The processes described below are currently under development in R&D programmes:

- Fermentation of sugars by means of fungi [29].
- Production of itaconic acid in genetically modified crops. It has been shown that itaconic acid is stored in the tubers of potato plants [30]. Energy crops like switch grass, grown for the production of bio-ethanol, can also produce itaconic acid [31].

2.7.4 Developments

R&D developments in the field of biobased methacrylic acid should eventually lead to the industrial production of biobased methyl methacrylate in 2016 (MRC) and 2018 (Evonik).

2.8 Poly(acrylic acid) (PAA)

2.8.1 General information

Poly(acrylic acid) (PAA) is the polymer made from acrylic acid, in which the double bond in acrylic acid is used for polymerisation and the side chain is formed by an acid group that is negatively charged in water in neutral conditions. PAA is mainly used in adhesives and coatings (like latex and acrylic paint). Copolymers of PAA can absorb a lot of water and are used as super-absorber in incontinence products and as a thickening agent.

2.8.2 Biobased processes for PAA

Acrylic acid, the monomer for PAA, can be produced by means of various processes as indicated in the diagram on page 20:

1. Fermentation of sugars to 3-HPA (3-hydroxypropionic acid), followed by dehydration into acrylic acid
2. Catalytic dehydration of lactic acid
3. Conversion of glycerol (via acrolein) to acrylic acid
4. Oxidation of biobased propylene

PAA can then be produced from acrylic acid via addition polymerisation.

2.8.3 Green building blocks and producers

The building blocks in the processes to biobased PAA are described below, with the exception of lactic acid, the monomer for poly(lactic acid) (PLA). Lactic acid is discussed in the chapter on polyesters on page 43.

Glycerol (C3)

Glycerol is an alcohol with a wide range of applications. It is a by-product of diesel production and a suitable raw material for the production of propanediols and other derivatives.

3-HPA (C3)

3-Hydroxypropionic acid or 3-HPA is, like lactic acid, a molecule with both an alcohol and an acid group. 3-HPA can be produced by the fermentation of sugars. In 2011 the American company OPX Biotechnologies obtained a patent describing the fermentative production of 3-HPA [32].

Novozymes and Cargill

In 2008 Novozymes and Cargill announced the development of a technology for the biobased production of 3-HPA and acrylic acid by means of fermentation [33]. In 2009 Novozymes submitted a patent for the production of 3-HPA with the aid of an *E.coli* strain [34]. According to a press release from 2008, the development of the technology is expected to take approximately five years.

Acrylic acid (C3)

Acrylic acid is used as monomer for PAA as well as ingredient in coatings, paints and adhesives. It is a bulk product that is currently produced via the oxidation of (petrochemical) propylene.

OPX Biotechnologies and DOW

In 2011, OPX Biotechnologies and DOW (a producer of petrochemical acrylic acid) announced a partnership for the production of acrylic acid from renewable raw materials [35]. OPX Biotechnologies recently announced that the technology (fermentation to 3-HPA, conversion to acrylic acid) had been successfully upscaled to 3000-L fermentation and is being further developed for commercial production [36].

Myriant

Myriant, an American producer of biobased lactic acid and succinic acid, has filed for patent protection for its bio-acrylic acid process and initiated scale-up activities to provide product samples to customers in the second half of 2012 [37]. Based on its progress to-date, Myriant expects that biobased acrylic acid will be cost competitive compared to petroleum-based acrylic acid, without the need for government subsidies or green premiums [38].

Arkema

In 2010, the French company Arkema announced their activities on the development of biobased acrylic acid from glycerol [39]. Glycerol is available in large quantities in the French region Lorraine as a by-product of rape seed processing for biodiesel. The programme has a budget of approximately 11 million euros and a running time of three years.

2.8.4 Developments

It is as yet unclear which process is the most promising for the production of biobased acrylic acid for PAA. The process via lactic acid has the benefit that lactic acid is already being produced at a commercial scale, while the process via glycerol has potential because of the wide availability of glycerol as a raw material.

The current process for acrylic acid involves the oxidation of petrochemical propylene. If biobased propylene is produced on a large scale in the future, it is possibly a raw material for acrylic acid as the required infrastructure is already in place.

3 Polyesters

3.1 Introduction

Polyesters are polymers in which the monomers are connected via an ester linkage. They can be produced via polycondensation of a diacid and a dialcohol, hydroxyl acid, or via ring-opening polymerisation of a lactone (cyclic ester). This chapter provides further information on the building blocks for polyesters.

3.2 Poly(ethylene terephthalate) (PET)

3.2.1 General information

Polyethylene terephthalate or PET is one of the five most commonly sold plastics worldwide with a production volume of 50,000 kton/year [40]. PET is mainly known as food packaging material such as PET bottles. PET is also used for the production of fibres (for example in fleece clothing) [41].

PET is a non-degradable polyester that is produced by the polymerisation of a diol (ethylene glycol) and a diacid (terephthalic acid). Developments in the field of biobased PET are proceeding rapidly and the most important ones are described here.

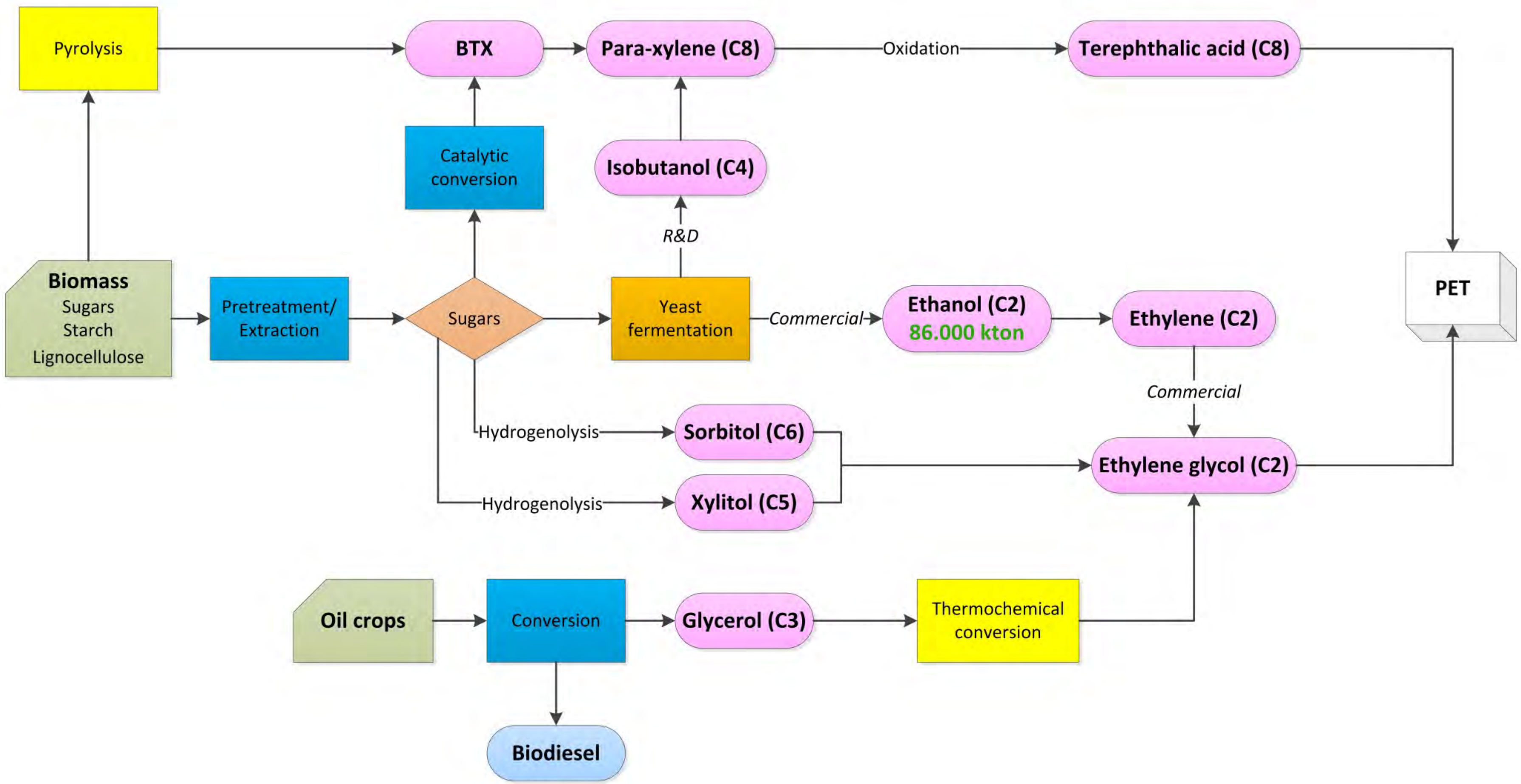
3.2.2 Biobased processes

The monomers of PET are ethylene glycol and terephthalic acid, and both components can be replaced by a biobased alternative. A first step to biobased PET is replacing petrochemical ethylene glycol by ethylene glycol from renewable raw materials. This results in PET that is partially biobased.

The diagram on page 28 shows that there are various possibilities for producing biobased ethylene glycol [42]:

1. The conversion of ethanol into ethylene via ethylene oxide to ethylene glycol
2. Hydrogenolysis (*i.e.* covalent bond cleavage by hydrogen) of xylitol (originating from xylose) to ethylene glycol
3. Hydrogenolysis of sorbitol (originating from glucose) to ethylene glycol
4. Hydrogenolysis of glycerol (a by-product of biodiesel production) into ethylene glycol

Polyesters: PET



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In addition to ethylene glycol also the diacid in PET (*i.e.* terephthalic acid) can be replaced by a biobased version to produce fully biobased PET. Technically, terephthalic acid can be produced from renewable raw materials but this is not as easy as ethylene glycol.

Terephthalic acid is currently produced via catalytic oxidation of petrochemical para-xylene, and it would therefore be a logical step to look for possibilities for the production of biobased para-xylene. The potential global market for terephthalic acid is estimated to be 50,000 kton/year; the current market for para-xylene is an estimated 30,000 kton/year with an increase to 60,000 kton/year in 2020 [43]. There are currently three processes for developing biobased para-xylene:

1. Pyrolysis (*i.e.* heating at high temperature without oxygen) of biomass into a mixture of benzene, toluene and xylene (BTX). Para-xylene can then be obtained from BTX.
2. Yeast fermentation of sugars into isobutanol, which can be converted into para-xylene via isobutylene.
3. Chemical conversion (catalytic) of sugars to BTX followed by isolation of para-xylene.

3.2.3 Green building blocks and producers

The building blocks in the biobased processes for PET are already partially described in the previous chapter (ethanol, ethylene, glycerol); the processes for the building blocks ethylene glycol, isobutanol, BTX, paraxylene and terephtalic acid are described below:

Ethylene glycol (C2)

Petrochemical ethylene glycol is currently being produced on industrial scale by addition of water to ethylene oxide, in which ethylene oxide is produced by the oxidation of ethylene. As it is possible to produce biobased ethylene from ethanol (see page) it is also possible to produce biobased ethylene glycol.

This process is technically feasible and is being applied at a commercial scale, but is not very sustainable. In the process in which glucose ($C_6H_{12}O_6$) is broken down to ethylene (C_2H_4) a lot of carbon and oxygen is lost. Functional groups in the form of two alcohol groups must be added again to produce ethylene glycol. In this regard the processes via xylitol, sorbitol and glycerol are more sustainable, although still requiring further development.

Coca-Cola

The process via ethylene is the most widely used; for instance for ethylene glycol that is used in the 'plant bottle' produced by Coca-Cola [44]. In this bottle 'up to 30 %' of the raw materials is of renewable origin, in this case sugar cane. The process for ethylene glycol from lignocellulose is still at the R&D stage.

India Glycols Limited

India Glycols has been producing ethylene glycol from bio-ethanol since 1989 for applications including PET [13, 45].

Isobutanol (C4)

Isobutanol, like *n*-butanol, is one of the isomers of butanol. In addition to its use as biofuel, isobutanol serves as an important building block in the chemical sector.

Gevo

Gevo is an American producer of bio-ethanol and isobutanol via yeast fermentation of sugars. They produce bio-ethanol from grain, and plan to expand the production of isobutanol from 55 kton/year in 2012 to 1000 kton/year in 2015 [46].
Future developments for Gevo lie in the production of isobutanol from lignocellulose such as energy crops (*e.g.* switchgrass) and residues from forestry and agriculture (*e.g.* wood, maize stems, sugar cane bagasse) in cooperation with Cargill [46].

BTX (benzene (C6), toluene (C7), xylene (C8))

BTX is the abbreviation for the aromatics benzene, toluene and xylene; components that are mainly used as solvent as well as in the production of polyamides, polyurethanes and polyesters. The current production volumes in Europe are around 13,000 kton/year [47]. (Para-)xylene can be isolated from BTX.

Anellotech

The American company Anellotech is developing a process to produce BTX from lignocellulose residues (*e.g.* wood chips, maize stems, straw). The conversion takes place in a one-step catalytic process (pyrolysis) [48, 49]. Anellotech is investing at the moment 15 million euros in a pilot facility with a capacity of two tons of BTX a day. The company aims to have a production facility on commercial scale by 2015. Anellotech is currently focused on the production of BTX for biobased terephthalic acid (C8) as a building block for PET.

Virent

Virent wants to start developing biobased para-xylene for the production of 100% biobased PET. Virent will replace the products from crude oil by chemicals and fuels from a wide range of renewable raw materials. Catalytic chemistry will be used to convert vegetable sugars into various products such as biofuels and chemicals for plastics and fibres. The products will serve as a replacement for their petrochemical counterparts within the existing logistic infrastructure.

Para-xylene (C8)

Para-xylene is one of the three isomers of xylene (the X in BTX). It is an important building block as oxidation of para-xylene yields terephthalic acid. Para-xylene can be produced from BTX but also via fermentation of isobutanol.

Gevo and Toray Industries

Gevo has produced biobased para-xylene from isobutanol via conventional chemical processes at laboratory scale. The company is planning to establish a pilot for the production of biobased para-xylene.

To convert para-xylene into terephthalic acid and eventually to PET, Gevo started a cooperation with the Japanese company Toray Industries. Toray is planning to produce 100% biobased PET from biobased terephthalic acid and ethylene glycol. In 2011, Toray succeeded in doing so on a laboratory scale [50].

Terephthalic acid (C8)

Terephthalic acid is obtained by oxidation of para-xylene. As described above, a large number of companies and research institutes is working on biobased terephthalic acid, and these investments in R&D cause the developments to progress rapidly.

3.2.4 Developments

In December 2011 Coca-Cola announced the development of a 100% biobased ‘plant bottle’ in partnership with Gevo, Virent and the Dutch company Avantium [51]. These companies will each use their own process to produce biobased materials in accordance with the requirements of Coca-Cola and the recycling industry.

3.3 Poly(trimethylene terephthalate) (PTT) and poly(butylene terephthalate) (PBT)

3.3.1 General information

Replacing the ethylene glycol in PET by an alternative diol results in polymers with different characteristics. Two examples are described here.

For poly(trimethylene terephthalate) or PTT, ethylene glycol (C2) is replaced by 1,3-propanediol (C3), which is abbreviated as PDO. Production of PTT, a polymer very similar to PET, was commercialised in 2000. PTT is currently mainly used in carpet and textile fibres.

For poly(butylene terephthalate) or PBT, ethylene glycol (C2) is replaced by 1,4-butanediol (C4), which is abbreviated as BDO. Although this crystalline, thermoplastic polyester is related to PET and PTT, it is more a technical polymer for specialty applications. It has good chemical, thermal and mechanical characteristics, and is mainly used to produce small precision components for car parts or electrical or electronic equipment. PBT can withstand temperatures up to approximately 120 °C as well as petrol, diesel oil, oils and fats, and weak acids.

3.3.2 Biobased processes

The monomers for PTT are terephthalic acid and PDO; the monomers for PBT are terephthalic acid and BDO. Biobased PDO is obtained by sugar fermentation, but for BDO there are multiple processes. These processes are further detailed in the next section due to the relevance of BDO for poly(butylene succinate) or PBS, another promising polyester.

Polycondensation of the monomers yields the polymers PTT and PBT and the biobased processes are indicated in the diagram on page 34.

3.3.3 Green building blocks and producers

Building blocks in the biobased processes for PTT and PBT have already been partly described in the previous chapter; PDO is detailed below.

PDO (C3)

PDO (1,3-propanediol) is a chemical building block with a market volume of 125 kton/year [2]. A large part of this production volume is already biobased: the current global production capacity of biobased PDO is 90 kton with an expected increase to over 100 kton in 2016 [2] of which the largest share is produced by DuPont.

DuPont

Biobased PDO has been an industrial process for quite some time. DuPont produces biobased PDO by fermenting sugars from maize starch in a joint venture with Tate & Lyle and Genencor. This PDO (with the brand name Susterra®) is used as a biobased building block in the production of PTT (brand name Sorona®), a polymer of which 37% of the weight consists of renewable material. Sorona® is used in clothing such as sports clothing and lingerie as well as in carpeting and cars. It is one of the most important polymers developed by DuPont over the past few years [52] which can be spun.

Metabolic Explorer

The French company Metabolic Explorer is planning a production facility for PDO with a capacity of 8 kton/year in Malaysia, with a possible increase to 50 kton/year [53].

Shell

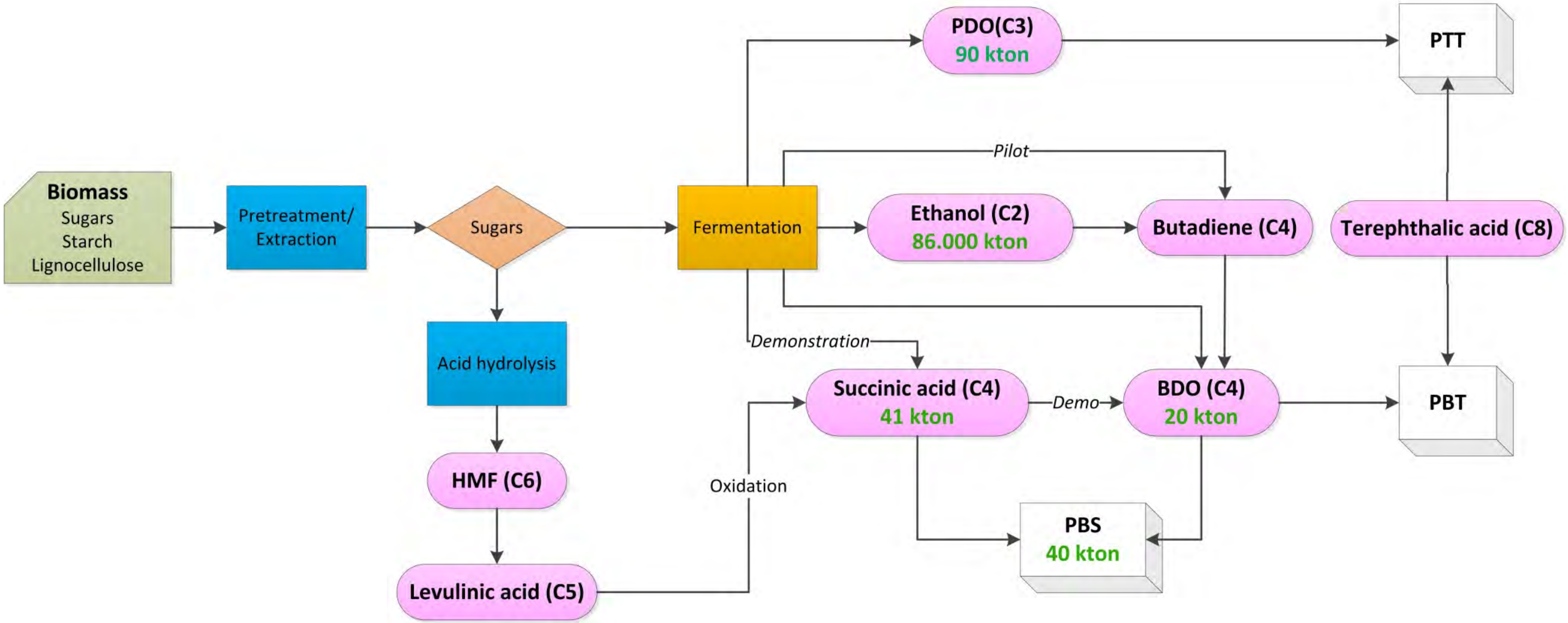
Like DuPont, Shell also used to produce PTT (brand name Corterra) from petrochemical raw materials. The polymer was patented back in 1941, but it was not until 1990 when Shell Chemicals was able to produce PDO with sufficient purity and in a cost-effective way that PTT could be produced on a commercial scale [54]. In 2001 Shell Chemical and SGF Chimie announced plans to build a facility in Montreal (Canada) for the production of PTT. The plant with a capacity of 86 kton/year was due to be operational in May 2004. In March 2009 the facility was closed permanently due to a shortage in demand and global overcapacity [55].

3.4 Poly(butylene succinate) (PBS)

3.4.1 General information

Poly(butylene succinate) or PBS is a polyester that is produced by polymerisation of succinic acid (1,4-butanediacid) and BDO (1,4-butanediol). PBS is biodegradable and can be composted but is not transparent. PBS resembles polypropylene (PP) in terms of mechanical properties. Compared to many other biopolymers such as poly(lactic acid) or PLA, PBS has a higher heat deflection temperature (HDT) and is much tougher. By introducing other monomers (like lactic acid, terephthalic acid or adipic acid) the characteristics of PBS polymers can be altered. PBS is currently being produced mainly from petrochemical raw materials.

Polyesters: PTT, PBT and PBS



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3.4.2 Biobased processes

The monomers for PBS, both succinic acid and BDO, can be produced by means of fermentation of sugars from biomass to create a 100% biobased material. The possible biobased processes for PBS are indicated schematically on the previous page and described below:

1. Fermentation of sugars to BDO
2. Fermentation of sugars to succinic acid, followed by reduction to BDO
3. Fermentation to ethanol, followed by conversion to butadiene and then BDO [48]
4. Chemical conversion of sugars into levulinic acid, followed by oxidation to succinic acid and reduction to BDO

3.4.3 Green building blocks and producers

The main building blocks in the biobased process for PBS are succinic acid, levulinic acid and BDO:

Succinic acid (C4)

The conventional process for succinic acid from petrochemical raw materials is by hydrolysis of maleic anhydride. Petrochemical succinic acid is now mainly being used in niche markets because production is expensive. It is expected that a less costly biobased production of succinic acid will lead to a larger market demand.

Succinic acid can be produced from sugars via fermentation. All existing industrial developments are based on this process. The current global production of biobased succinic acid is estimated at 50 kton/year, with a possible increase to 270 kton/year in the coming years [2]. Possible growth in biobased succinic acid is most likely related to increased use of biodegradable polyesters.

Various major businesses and consortiums are working on the development and upscaling of the production of biobased succinic acid. Recent developments for succinic acid involve the production of micro-organisms that are more productive and produce less by-products. It is important to achieve the highest possible yield of succinic acid with as few by-products as possible, as it is much more difficult to isolate succinic acid (a solid substance) from a fermentation mixture than, for instance, ethanol (a liquid with a low boiling point). In addition, the fermentation process has to be integrated within the existing infrastructure. With regard to sustainability, it is a benefit that the fermentative production of succinic acid requires CO_2.

Myriant and Purac

In 2008 Myriant started producing (*D*)-lactic acid on a commercial scale in Spain in collaboration with Purac (part of CSM) [56]. The process used by Myriant for the production of biobased succinic acid is derived from this lactic acid production, allowing the company to make substantial savings on the development costs of the succinic acid process.

Myriant is currently producing samples for clients on a scale of 1000 kg to verify the quality and specifications of the biobased succinic acid. Starch is being used as raw material. The company is planning to start a production facility of 14 kton/year (in Lake Providence, US) in the first quarter of 2013 with a possible expansion to 77 kton/year in 2014. In addition to succinic acid from starch, Myriant is also working on succinic acid from lignocellulose [57].

Bioamber and Mitsui

BioAmber has been producing succinic acid with a high level of purity (350,000-L scale fermentor, property of ARD) in France since 2010. The raw materials used are sugars from sugar beet and wheat. As of 2013 BioAmber will be producing succinic acid on a global scale in a plant in North America (Sarnia, Ontario) with an initial production capacity of 17 kton/year in a joint-venture with Mitsui. It is expected that the scale benefit and lower costs of, for instance, raw materials for succinic acid will lead to considerably reduced production costs. There are also plans to expand the capacity at the facility in Sarnia to 35 kton/year [58] and at two other facilities (Thailand and North America/Brazil) to achieve a total succinic acid production of 165 kton/year.

DSM and Roquette (Reverdia)

DSM and the French company Roquette have joined forces in the implementation and commercialisation of the production of succinic acid based on renewable raw materials by means of fermentation. The biobased succinic acid will be produced by means of the fermentation of starch.

The new production process was jointly developed by DSM and Roquette. In early 2010, the two companies opened a demonstration factory in the Lestrem (France) for the production of succinic acid from starch; the facility is currently fully operational. In 2010 DSM and Roquette also announced the intention to establish a joint venture for their cooperation (under the name Reverdia) [59].This joint venture is subject to regulatory approval. In May 2011 they announced the construction of a factory at the premises of Roquette in Italy with a capacity of 10 kton/year that was planned to be in operation in the second half of 2012.

BASF and CSM

BASF Future Business GmbH (part of BASF) and Purac are working together on the development of biobased succinic acid. In the second quarter of 2010, they announced the production of succinic acid at an existing CSM facility in Spain. New reports mention a possible start-up in 2013 [60]. The facility is already equipped with machinery for fermentation and downstream processing at an industrial scale [61] and has a fermentation capacity of 25 kton/year.

Levulinic acid (C5)

Levulinic acid can be produced from lignocellulose, as described in the PhD thesis by Girisuta [62]. Acidic hydrolysis of lignocellulose causes the breakdown of polymer sugars to both C5 and C6 sugars (*e.g.* glucose). A degradation product of C6 sugar is 5-hydroxymethylfurfural (HMF), a furan compound that can be converted to levulinic acid and formic acid. Dehydration of C5 sugars results in furfural, which can also be converted to levulinic acid. These processes are being further developed by the company Biofine [63].

Levulinic acid can be oxidised into succinic acid. All processes for succinic acid as described above are based on fermentation. In 2010, Wageningen UR Food & Biobased Research patented a technology that enables the extraction of succinic acid from crude levulinic acid via a simple chemical process.

BDO (C4)

1,4-butanediol (BDO) is a bulk product that is currently being produced in large volumes from petrochemical raw materials. BDO is used for the production of polymers, the solvent tetrahydrofuran (THF) and fine chemicals. BDO can be produced in various ways: a large percentage is being produced from petrochemical maleic anhydride via a process that is owned by the British company Davy Process Technologies.

Biobased processes are challenging and the subject of intensive study. Various large companies and consortiums are working on the development and upscaling of biobased BDO; the current production is still at demonstration level. When biobased BDO is produced it can be used immediately within the existing infrastructure as it has the same characteristics as petrochemical BDO (*i.e.* drop-in).

Myriant and Davy Process Technologies

Myriant has started a partnership with Davy Process Technologies for the production of BDO [64]. Davy Process Technologies produces BDO, THF and γ-butyrolactone from maleic anhydride. Because succinic acid (1,4-butanediacid) is chemically very similar to the commonly used maleic acid (cis-butenediacid) it is a possible replacement for maleic anhydride in the production of BDO. Both companies expect that the combination of the technologies will allow them to take a major leap forward in the production of biobased BDO.

Genomatica, Tate & Lyle, Beta Renewables

Genomatica develops production processes for chemical building blocks based on fermentation. In collaboration with its partner Tate & Lyle, the company has been producing BDO on a demonstration scale since June 2011. It is expected that in 2013 BDO will be produced on a commercial scale in a facility of Novamont in Italy with a capacity of 18 kton/year [65]. In January 2012, Genomatica also obtained the rights for the PROESA technology from Beta Renewables for the production of BDO from lignocellulosic biomass. The production at demonstration level, also in Italy, is due to start 2012-2013.

BioAmber

Bioamber, producer of succinic acid, is planning the production of 23 kton/year of BDO [58] at its site in Sarnia, and 100 kton/year in its facilities in Thailand and North America/Brazil. This would result in a total planned BDO production of 123 kton/year. BioAmber has a license from DuPont to produce BDO and THF from succinic acid.

3.4.4 Developments

The current global PBS production is still small (approximately 40 kton/year) but there are ambitious plans for expansion [41]. Examples of PBS producers are Mitsubishi Chemical Company and Showa Denka (Bionolle®). It is expected that the growth in biodegradable plastics will increase the share of PBS to 150 kton/year (in 2016), with facilities in China and Thailand in particular [2]. It is important to reduce the production costs of PBS as it is still too expensive for large-scale applications. The successful implementation and upscaling of new technologies could lead to a significant price reduction.

PBS polymers are also good components for biobased blends with other polymers like poly(lactic acid) (PLA), polyhydroxyalkanoates (PHAs) or thermoplastic starch (TPS), and polymers such as polystyrene (PS) and polycarbonate (PC). This is underlined by a recently announced collaboration between NatureWorks and BioAmber. In a joint venture called AmberWorks the companies will work together on the production of biobased PLA/PBS blends [66]. Metabolix recently sold a license (a patent titled 'Polylactic Acid-based Blends') to NatureWorks for the production and sale of PLA/PBS blends [67]. Bioamber foresees a rapidly growing market with PBS, PBS blends and PBS composites [60].

3.5 Poly(ethylene furandicarboxylate) (PEF) and poly(butylene furandicarboxylate) (PBF)

3.5.1 General information

In addition to the production of building blocks that are chemically identical to existing petrochemical building blocks, it is also possible to make entirely new monomers based on biobased raw materials. An example is the monomer 2,5-furandicarboxylic acid (2,5-FDCA) that can serve as a replacement for terephthalic acid. As 2,5-FDCA has a different molecular structure than terephthalic acid, the resulting polymer will also have other properties.

For the polymer poly(ethylene furandicarboxylate) (PEF), terephthalic acid is being replaced by 2,5-FDCA. PEF is seen as a possible replacement for PET. With regard to thermal properties, PEF is more interesting than PET as it has a higher thermal stability (higher glass transition temperature) combined with a lower processing temperature (lower melting point). PEF is also seen as a superior material for bottles due to its increased gas barrier properties [40].

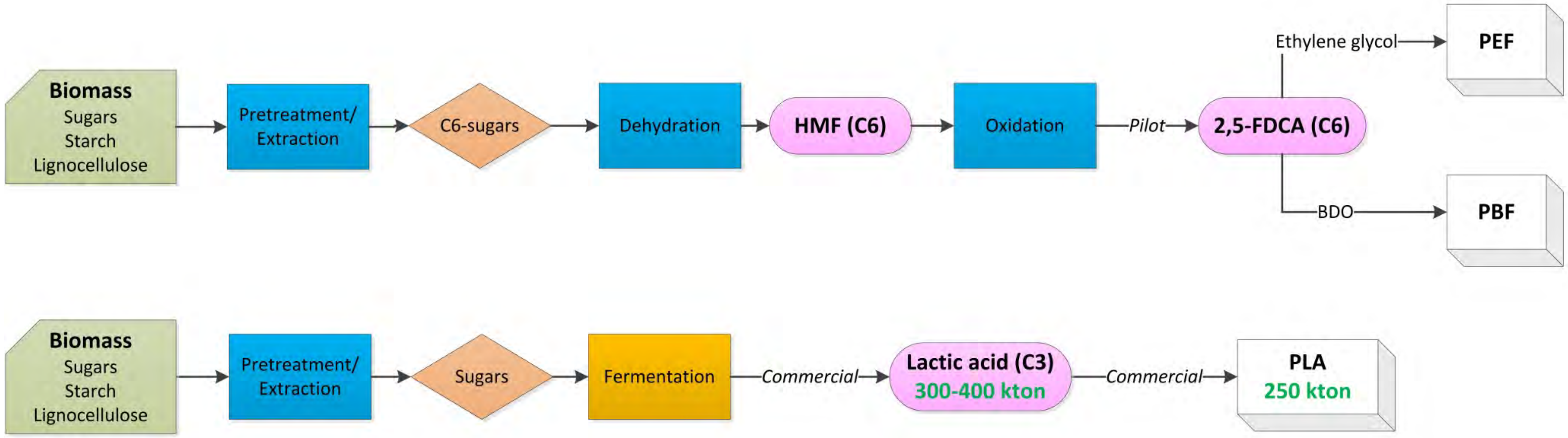
Replacing terephthalic acid by 2,5-FDCA as well as ethylene glycol by 1,4-butanediol (BDO) results in the polymer poly(butylene furandicarboxylate) (PBF).

3.5.2 Biobased processes

The monomers for PEF are 2,5-FDCA and ethylene glycol; the monomers for PBF are 2,5-FDCA and BDO. The process to 2,5-FDCA takes place via dehydration of sugars to 5-hydroxymethylfurfural (HMF), followed by oxidation. The processes for the production of biobased ethylene glycol and BDO have already been described above.

PEF and PBF are then produced by polycondensation of the monomers. The biobased processes for PEF and PBF are described on the next page.

Polyesters: PEF, PBF and PLA



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3.5.3 Green building block and producer

2,5-FDCA (C6)

Sugars can be converted into 2,5-FDCA in several steps. Fructose is used as a raw material and is converted via dehydration to the furan compound HMF, which can then be converted into 2,5-FDCA via oxidation.

Avantium

The Dutch company Avantium (spin-off from Shell since 2000) is working on the production of 2,5-FDCA for polyester applications, and PEF in particular. They expect a potential market for biobased 2,5-FDCA of more than 100,000 kton/year with a price of less than €1000/ton on a commercial scale. In comparison, petrochemical terephthalic acid currently costs €1200/ton [68].

For the construction of a pilot plant in Geleen (Netherlands), Avantium raised 30 million euros from investors and five million euros from the Dutch Ministry of Economic Affairs, Agriculture and Innovation (EL&I) in June 2011. The factory was opened in December 2011. The company will use the pilot plant to further upscale the production of furan building blocks ("YXY building blocks") to 40 ton/year. The plant will facilitate optimisation of the process and later the production of polymeric materials from these furan building blocks (such as PEF). It will be scaled-up to 400 ton/year in 2013, and a commercial plant with a capacity of 30-50 kton/year is planned in 2015 [69].

Avantium will grant licenses for the YXY-technology to industrial companies for the production and application of furan-based building blocks. For PEF these companies can include producers of fibres, bottles, packaging materials, thermosets (resins, coatings, adhesives) and plasticisers. Avantium has also proven the possibilities for developing PEF from recycled PEF and depolymerising it into monomers [68].

3.5.4 Developments

For replacement of petrochemical terephthalic acid the production process for 2,5-FDCA is probably cheaper than the process for biobased terephthalic acid [70]. The production of 2,5-FDCA currently uses fructose, a first generation raw material, but glucose from second generation raw materials such as lignocellulose could also be used. In this case glucose must be converted into fructose first, a C6 sugar with a C5 ring structure, by means of enzymatic isomerisation [42].

There are many major research programmes and various research institutes in the Netherlands currently working on the process from lignocellulose. Within the framework of the BE-Basic research programme [71], for example, various parties are

working on a process for producing HMF from lignocellulose HMF. The HMF can then be converted into 2,5-FDCA via a biotechnological process.
From an environmental perspective, the production of furan-based polymers from lignocellulose offers countless opportunities. An LCA study that compared PEF to PET showed possible savings of 40 to 50 % on the consumption of non-renewable energy and CO_2 emissions. Potential savings could even run up to 50-90 %, although this very much depends on the raw material and processes used [72].

3.6 Polylactic acid (PLA)

3.6.1 General information

Polylactic acid (PLA) is currently the most important biobased polyester and one of the most attractive examples of a fully biobased material. It is produced from lactides (cyclic diester of lactic acid) using ring-opening polymerisation. The global production of PLA is around 250 kton/year.
Current benefits of PLA compared to other biopolymers are its relatively low costs, com mercial availability of various grades (for many processes and applications), transparency, and a high level of gloss and stiffness (comparable to polystyrene). Disadvantages of PLA are the low heat deflection temperature (HDT) and melt strength; another drawback is the fact that the material is naturally bri ttle and has a low tear strength.
PLA is mainly used in packaging materials and textile fibres; in the same approximate volumes. Examples of available packaging materials based on PLA include foils, bottles, cups and foam trays. PLA fibres are also used for the production of clothing and furniture textiles. A new application is the use of PLA-foam as an insulation material in construction, an alternative for PS-foam (BioFoam from Synbra, see also page 21).
There is an increasing demand for PLA for use in sustainable applications such as electronics and car parts. Heat-resistant PLA helps to make these applications possible [41].

3.6.2 Biobased process for PLA

Lactic acid, building block for PLA, is obtained via fermentation of sugars (see the diagram on page 40). While various micro-organisms can produce lactic acid, *Lactobacillus* is most commonly used in commercial applications. During the fermentation process, two molecules of lactic acid are formed from one molecule of glucose via glycolysis; this results in a theoretical yield of 100 % [73]. This is in contrast to ethanol, in which two molecules of ethanol produce two molecules of CO_2, reducing the theoretical yield to 51 %.

Lactic acid is then dimerised into lactide, followed by ring-opening polymerisation to PLA. PLA is an example of a polymer that is only produced from renewable raw materials via a biotechnological process.

3.6.3 Green building blocks and producers

Lactic acid (C3)

Lactic acid is a bulk product with applications originally in the food, pharmaceutical and personal care market. As a building block for PLA, lactic acid has the potential to grow considerably in terms of market volume.
Global producers of lactic acid include Purac (NL, global market leader), Galactic (Belgium), NatureWorks (US) and ADM (US). The current production of lactic acid is around 300-400 kton/year with a market price of 1000-1200 €/ton [74].
Purac produces lactic acid and lactide as an end product, and sells it to clients such as Synbra which uses it to make PLA foam (Biofoam). Galactic and NatureWorks LLC produce lactic acid which is then polymerised to PLA. Galactic is also active in the recycling of PLA by collecting PLA products and subsequent degradation to lactic acid [75]. NatureWorks LLC, a joint venture of Cargill and Teijin, is the largest producer of PLA with a capacity of 140 kton/year.
There is currently a shift in the production of lactic acid to countries with low wages and low sugar prices. No lactic acid is currently being produced from Dutch crops. In view of the fast growing PLA market, other companies are also starting PLA production.

3.6.4 Developments

Lactic acid is currently produced from sugar-rich and starch-rich biomass, such as sugar cane, maize and tapioca. For a sustainable production process on a scale that meets future demands for bioplastics like PLA, however, the use of non-food biomass such as lignocellulose is crucial. Compared to biomass that is rich in sugar and starch, lignocellulose is a complex source of sugars, and several steps (like a pretreatment) are required to isolate the sugar and make it suitable for fermentation into lactic acid. Several companies are working on this process within the BE-Basic research programme [71].
The fact that lactic acid and PLA have great potential is also indicated by the strategy change at CSM: the company announced it will start a divestment process for the bakery supplies businesses and shifts its focus to Purac for the production of biobased lactic acid and PLA [76].

4 Polyamides

4.1 Introduction

Polyamides, better known under the generic name nylons, are a major class of engineering plastics. They are produced via polycondensation of a diacid and a diamine, or ring-opening polymerisation of a lactam (cyclic compound with an amide group) [41]. Polyamides are named after the number of carbon atoms of each of the monomers, in which the first number corresponds with the diamine, and the second with the diacid. The biobased processes for the various polyamides are indicated schematically on the next page.

4.2 General information

4.2.1 Polyamide 11

Polyamide 11 is an example of a fully biobased material that has been in production on a commercial scale for many years. The monomer of PA 11 is 11-amino-undecanoic acid (C11), a derivative of castor oil. PA 11 is a high-quality plastic. Arkema is the only producer of PA 11 under the brand name Rilsan® with a production volume of 10 kton/year [77].

4.2.2 Polyamide 6,6 and polyamide 6

Very well-known polyamides or nylons are polyamide 6,6 (from hexanediamine (C6) and adipic acid (C6)) and polyamide 6 (from caprolactam (C6)). Both polyamides are used in a wide range of applications.

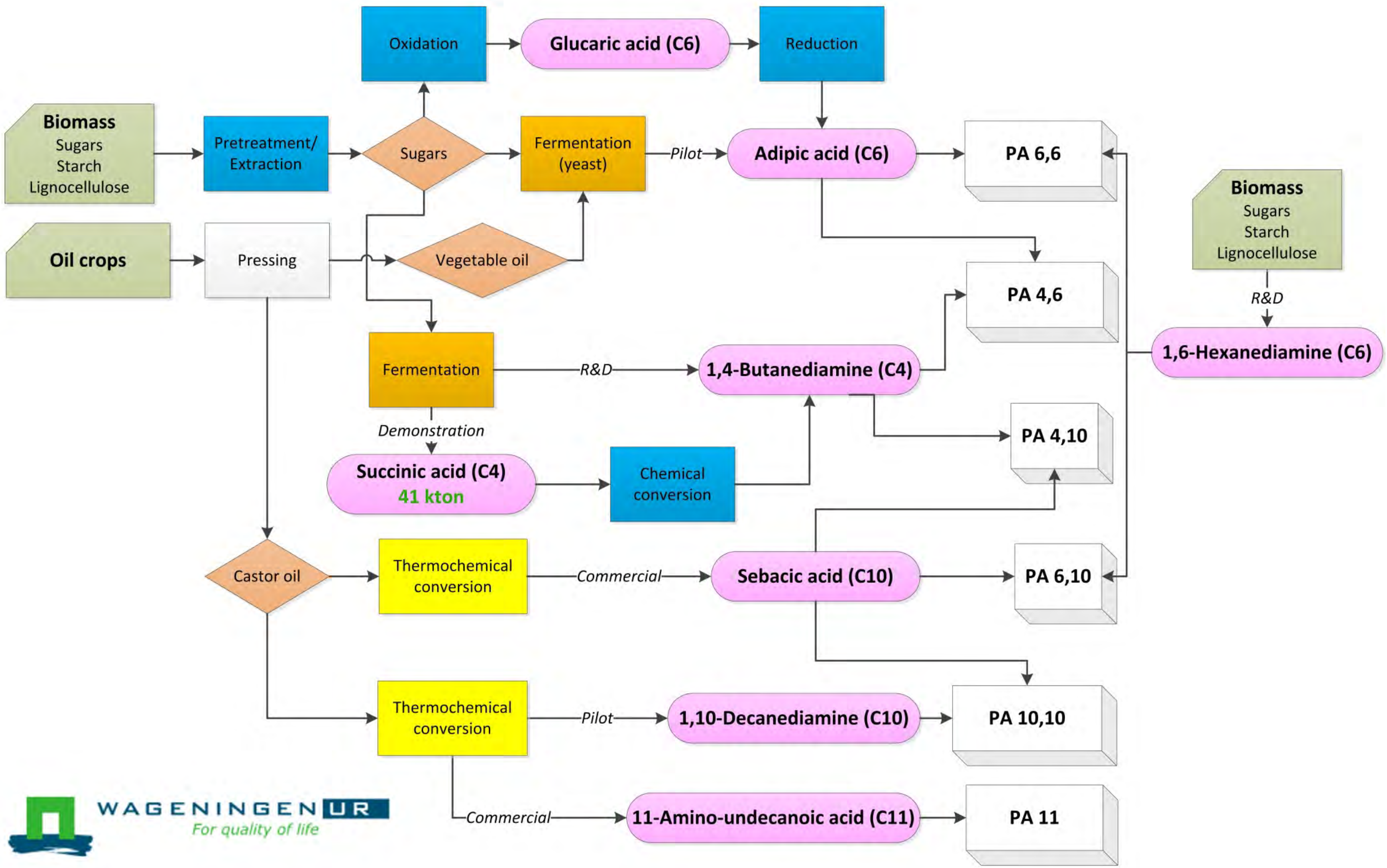
4.2.3 Polyamide 4,6

Polyamide 4,6 is produced by polycondensation of butanediamine (C4) and adipic acid (C6). Polyamide 4,6 is produced by DSM from petrochemical raw materials under the brand name Stanyl®, an engineering plastic with a high crystallinity and melting point [78].

4.2.4 Polyamide 6,10

Polyamide 6,10 is an engineering plastic for niche markets. The monomers for polyamide 6,10 are hexanediamine (C6) and sebacic acid (C10). Polyamide 6,10 is produced on a commercial scale by several companies (DuPont [79], BASF, Toray). Due to the use of castor oil as raw material for the diacid, this polymer is partially biobased (approximately 60% of the carbon).

Polyamides



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4.2.5 Polyamide 10,10

Polyamide 10,10 is obtained via the polymerisation of decanediamine (C10) and sebacic acid (C10). The diacid is already produced from castor oil (see polyamide 6,10) but decanediamine is a derivative of castor oil as well. This results in a polyamide that consists for 99% of biobased materials (% biobased carbon in the polymer) [80]. The material is produced by EMS-Grivory under the brand name Grilamid® 1S, and by Evonik under the brand name TEGOLON® ECO 10-10 [81].

4.2.6 Polyamide 4,10

Polyamide 4,10 is produced by the polymerisation of butanediamine (C4) and sebacic acid (C10). Both components can be obtained by a biobased process. DSM produces polyamide 4,10 under the brand name EcoPaXX™ [82] with sebacic acid as biobased component.

4.3 Green building blocks and producers

An important raw material for polyamides is castor oil, extracted from the tropical plant *Ricinus communis* that grows in India, Brazil and China. The seeds of the plant contain around 45 % castor oil.

Castor oil consists for a large part (85%) of ricinoleic acid, an unsaturated fatty acid with one hydroxyl group. It is the raw material for components in various polyamides such as those described previously. There are also other vegetable oils (besides castor oil) and sugars that serve as raw materials for polyamides. The biobased processes for polyamides are indicated schematically on page 46.

Butanediamine (C4)

The biobased production of butanediamine is possible via the chemical conversion of succinic acid [83]. Research is also being performed on the biotechnical production of butanediamine by fermentation with bacteria (*E.coli)* [84].

Hexanediamine (C6)

Hexanediamine is currently produced from petrochemical butadiene or propylene. In view of the developments surrounding biobased propylene and butadiene, there are opportunities for the production of biobased hexanediamine.

BioAmber

BioAmber has plans to produce biobased hexanediamine from renewable materials. It is looking to further extend the succinic acid (C4) platform to C6 building blocks for chemicals including hexanediamine, adipic acid and caprolactam for the production of polyamide 6 and polyamide 6,6 [85].

Adipic acid (C6)

Adipic acid is one of the most important aliphatic acids with a global production of 4,000 kton/year [2] and is currently produced from benzene. Biobased processes are possible via fermentation or chemical conversion. Biobased adipic acid is currently not in production, but it is expected that the commercial production will be approximately 450 ton/year in 2016, mainly by companies such as Verdezyne, Rennovia and DSM, although other companies are also expected to enter this market (*e.g.* BioAmber).

Verdezyne

The American biotech company Verdezyne [86] has developed a yeast that can produce adipic acid from vegetable oils [87] and sugars [88] in a single step. Verdezyne opened a pilot facility in California (US) for the production of adipic acid in order to produce polyurethane resins (see next chapter). A number of major industrial parties including DSM and BP are partners in this project. Verdezyne claims that the new yeast it developed has enabled the production of adipic acid at lower costs than the current petrochemical production processes. Additionally, DSM announced in 2011 that it would explore other processes for the development of biobased adipic acid [89].

Rennovia

The fact that (in addition to fermentation) adipic acid can also be produced via the chemical conversion of sugar is illustrated by the activities of Rennovia. The company is working on the chemical-catalytic conversion of glucose into adipic acid via oxidation to glucaric acid followed by reduction [90].

Decanediamine (C10), sebacic acid (C10), amino-undecanoic acid (C11)

Decanediamine, sebacic acid [1] and 11-amino-undecanoic acid are all produced from castor oil.

4.4 Developments

Polyamide 6 is being produced by a large number of companies by means of ring-opening polymerisation of caprolactam, a cyclic amide from petrochemical raw materials (*e.g.* Arkema, BASF, DSM, DuPont [1]). There is also a great deal of research going on in the field of biobased processes for caprolactam, for example by BioAmber [85].

5 Polyurethanes

5.1 Introduction

Polyurethanes are a family of polymers with a wide range of characteristics and applica tions. They are formed by the polymerisation of polyols (compound with two or more hydroxyl groups) with (di)isocyanates (compound with two or more isocyanate groups). The final properties of polyurethanes are determined by the characteristics of the polyols and isocyanates. Current applicati ons vary from soft and hard foams to coatings, adhesives and sealants.
The total production of biobased polyurethanes worldwide, with polyols from renewable sources, is estimated at 28 kton. This is a relatively limited volume compared to the total production of petrochemical-based polyurethanes, which is 14,000 kton [2].

5.2 Biobased processes

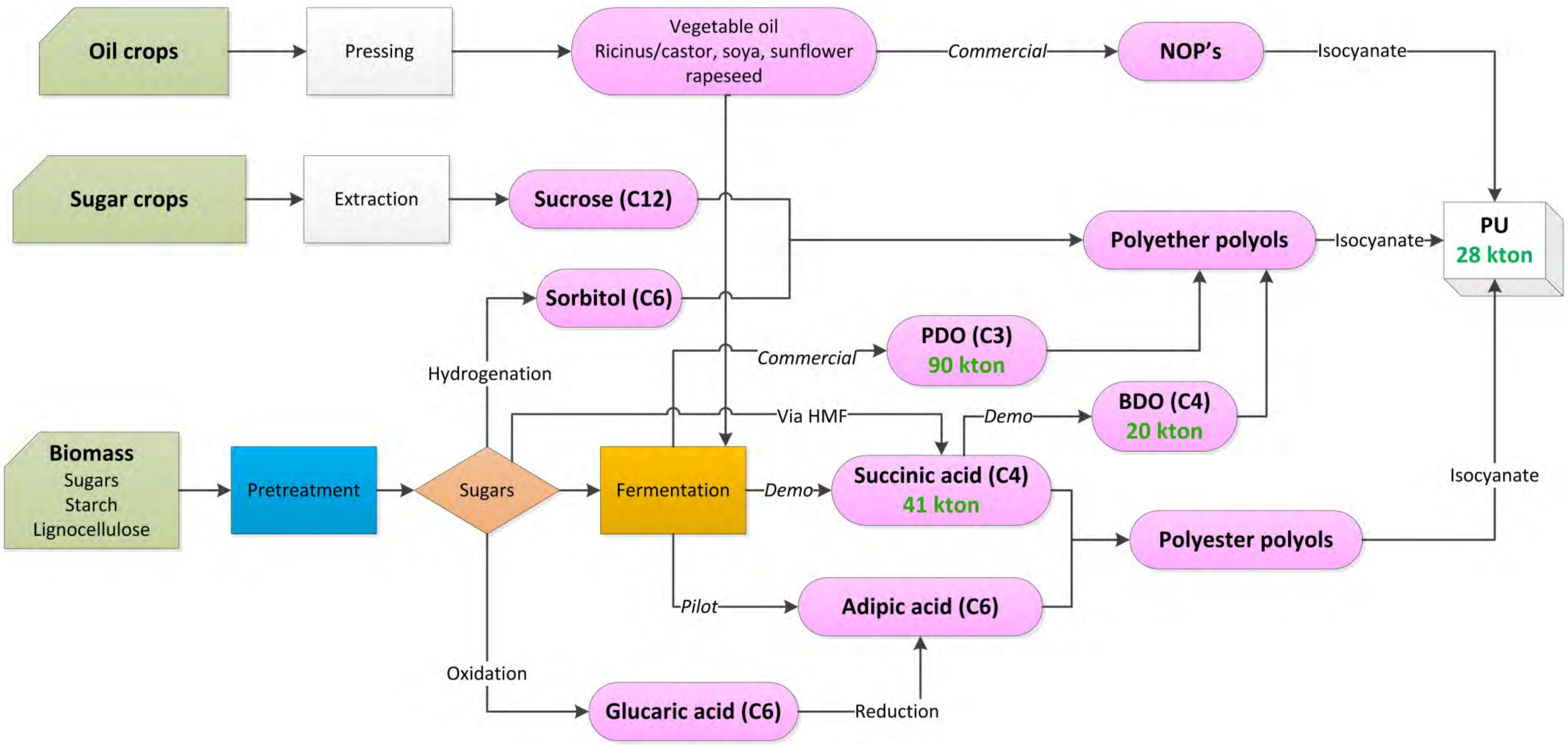
Developments in the field of biobased polyurethanes are focused on both biobased pol yols and isocyanates, with the emphasis on polyols.

Various major international producers are marketing biobased polyols that are specifically suited for the application in polyurethanes. They have the following biobased origin:

- Polyols from natural oils (NOPs, Natural Oil Polyols)
- Polyether polyols from the diols PDO and BDO
- Polyether polyols based on sugars (sorbitol and sucrose)
- Polyester polyols from the diacids succinic acid and adipic acid

The biobased processes for PU are indicated in the diagram on page 50. In addition to polyols, there are also developments on biobased isocyanates but these are limited. The production of isocyanates usually starts by making the amine compound, which is then converted into an isocyanate via the reaction with phosgene. It is also possible to produce isocyanates from fatty acids, but production via this route is still limited due to a very low reactivity of the isocyanates and high costs [91].

Polyurethanes



5.3 Green building blocks and producers

Polyols from NOPs

Natural (vegetable) oils are esters of glycerol (see page 25) and fatty acids. An important raw material for polyurethanes is castor oil (see page 47). Castor oil consists for a large part of unsaturated fatty acid. This fatty acid has a double bond in the middle of the carbon chain as well as a hydroxyl group. This reactivity makes it very suitable as an ingredient for polyurethanes.
Work is also being carried out on the development of polyols from other, possibly chea per, vegetable oils such as soy bean oil, sunflower oil or rape oil. The possibilities for p roducing polyols from vegetable oils are almost limitless.

Companies like Cargill, Dow, Bayer, Urethane Soy Systems and BASF are commercially marketing PU based on polyols from vegetable oils. The market volume of these products is growing, and the application thereof is mainly focused on hard insulation foam applications in construction, refrigerators and pipelines.

Cargill

Cargill produces biobased polyols (BioOH) based on soy bean oil [92]. These BioOH-polyols are mainly used in flexible polyurethane foams for furniture and cars.

Bayer

In July 2011 Bayer announced an investment of 8.5 million euros in the expansion of their polyol-activities in South Charleston (US), where it produces polyols from castor oil [93]. The focus is on improving the downstream processes and reducing the amount of chemical residues in the polyols.

Polyether polyols via PDO and BDO

Another building block is PDO, a diol produced by fermentation of sugars, especially m aize (see page 32). PDO is used for the production of polyether polyols for polyurethanes. Besides PD O, also BDO (see page 37) can be used.

The conversion from PDO to polyether polyols and the subsequent polymerisation with isocyanates results in polyurethanes that are extremely suitable for applications in text iles, coatings and engineering plastics. Among many other companies, the Spanish Mer quinsa is a producer of polyurethanes based on Susterra®

(PDO by DuPont), of which the renewable share is 60 %, with a production volume of 10 kton/year.

Polyether polyols based on sugar

For the production of hard polyurethane foams based on polyether polyols, the sugars sorbitol (Huntsman, Cargill) and sucrose (Bayer) are often used as the alcohol component. Both substances can easily be extracted from sugar crops. The reaction of the polyether polyol with isocyanate results in hard polyurethane foams.

Polyester polyols via succinic acid and adipic acid

Another major process in addition to polyether polyols are the polyester polyols. These esters are made by the esterification of diacids with diols. The biobased diacids that are being used most commonly are succinic acid (see page 35) and adipic acid (see page 48). The polyester polyols give different mechanical properties to the polyurethane, such as a higher level of durability, higher solvent resistance and higher scratch resistance.

5.4 Developments

Various laboratories worldwide are performing research on isocyanate-free processes for the production of polyurethanes, especially for coatings and adhesives, with similar properties. These processes do form a urethane compound but via a different chemical reaction.

Research shows that making biobased isocyanates is possible at a laboratory scale. However, considerable R&D will be required to upscale the development to the pilot and industrial scale and enable the production of 100% biobased polyurethanes.

6 Synthetic rubbers

6.1 Introduction

Rubbers are elastic materials (elastomers) that adapt under pressure or when stretched, before returning to their original dimensions or geometric shape. This elastic behaviour is caused by the long polymer chains that are (slightly) cross-linked, making deformations reversible. Rubber is elastic at normal application temperatures and becomes hard at lower temperatures.

The global production of rubber is approximately 22,000 kton/year, of which around on e-third is natural rubber. Natural rubber (*i.e.* polyisoprene) is mainly produced in Southeast Asia and is a polymerisation produc t of cis-1,4-isoprene. Although polyisoprene can also be produced synthetically, natural rubber has maintained a substantial market share. As a result of the dependence on latex from th e Hevea tree as the only source of natural rubber, there is an ongoing search for altern ative resources. This chapter describes the biobased processes for the synthetic rubber s polyisoprene, polyisobutene and polybutadiene.

6.2 Polyisoprene

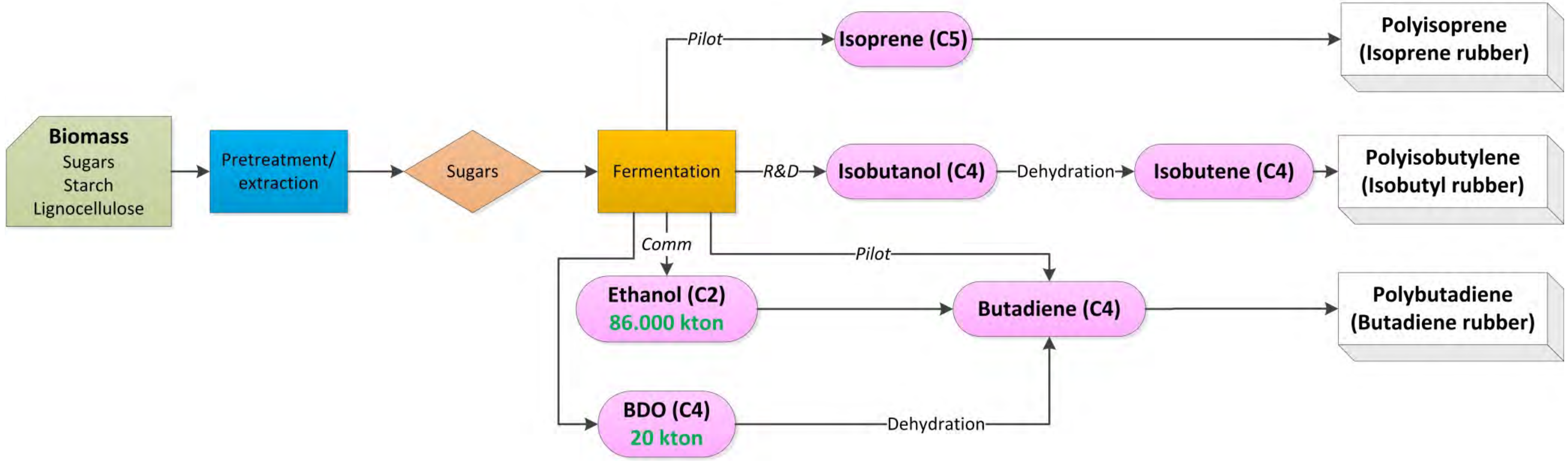
6.2.1 General information

Polyisoprene or isoprene rubber is mainly used for making car tyres, but also other products like medical gloves, golf balls and adhesives are made from polyisoprene. The car tyre industry is therefore the driving force behind the development of biobased processes for polyisoprene. In the past years various car tyre manufacturers have established partnerships with the chemical industry for the production of biobased polyisoprene.

6.2.2 Biobased processes

Isoprene, the monomer for polyisoprene, can be produced via fermentation of sugars. This has been indicated schematically on the next page. The polymerisation of isoprene then results in polyisoprene.

Synthetic rubbers



6.2.3 Green building blocks and producers

Isoprene (C5)

Isoprene is mainly used in synthetic rubbers. The following companies are working on the biobased production of isoprene:

Goodyear and Genencor

Goodyear started a partnership with Genencor (part of DuPont) [94, 95]. The development is well underway and has led to the demonstration of a ‘proof of technology’ biobased polyisoprene car tyre at the International Motor Show in Geneva in 2012. Genencor is developing the process for producing isoprene, while Goodyear then polymerises the isoprene into polyisoprene and produces tyres. The companies hope to market the tyre in the coming years. A challenge in the aerobic (with oxygen) fermentation process for biobased isoprene is to ensure that the oxygen is entirely converted by micro-organisms as low concentrations of oxygen with isoprene result in an explosive mixture [96].

Amyris and Michelin

In 2011, the American company Amyris started a collaboration with Michelin. Amyris has the ambition to produce biobased isoprene on a commercial scale in 2015 [97]. Further information about the production volume and timeline have yet to be published by either company.

Ajinomoto and Bridgestone

The Japanese chemical company Ajinomoto will be producing biobased isoprene for tyre manufacturer Bridgestone. The current state of developments is that isoprene is being produced on laboratory scale by Ajinomoto, and that Bridgestone has polymerised this to polyisoprene. They have not yet succeeded in manufacturing a tyre, however. Both companies have plans to continue the developments in 2013 [98, 99], but are not yet providing information about capacity and timeline.

6.3 Polyisobutylene

6.3.1 General information

Polyisobutylene or isobutyl rubber is characterised by a very low permeability for gas and fluids. This property makes isobutyl rubber very suitable for applications such as inner tubes, gas-tight layers on the inside of car tyres and in special applications like protective clothing and pharmaceutical packaging.

6.3.2 Biobased process

Polyisobutylene can be produced from biomass by fermenting sugar into isobutanol, which is then converted into isobutene via a dehydration process.
The polymerisation of isobutene results in polyisobutylene [100, 101].

6.3.3 Green building blocks and producers

Building blocks in the production of polyisobutylene are isobutanol and isobutylene. Isobutanol was already described in the section on polyesters for the production of paraxylene for PET (see page 30); isobutylene is described below:

Isobutylene (C4)

Isobutylene can be produced from isobutanol via dehydration. The following companies are active in this field:

Gevo and Lanxess

The development of biobased polyisobutylene is taking place within a partnership between Gevo and Lanxess. The American company Gevo is supplying the isobutanol to Lanxess, the second largest rubber manufacturer in the world. Lanxess, in turn, is working on the development of the dehydration process to convert isobutanol into isobutylene. The process has already been upscaled successfully from laboratory to a small-scale production reactor. Tests show that the biobased polyisobutylene meets the strict requirements for rubber products applied by the tyre industry [102].

Global Bioenergies

The French company Global Bioenergies is developing a biobased process by means of fermentation of sugars from biomass into isobutylene [103]. Global Bioenergies is planning to take a pilot facility with a capacity of 10 ton/year into use in 2013. Its aim is to upscale the production to demonstration scale in 2015, and commercial scale by 2017-2018. Global Bioenergies is also looking into the possibility of producing isobutylene from carbon monoxide, but the realisation of such a process lies further into the future.

6.4 Polybutadiene

6.4.1 General information

Polybutadiene or butadiene rubber is characterised by a high level of wear resistance and low rolling resistance but also results in less grip on wet surfaces. As a result, for tyre applications it is usually blended with other polymers into rubber compounds. Butadiene is also copolymerised with acrylonitrile and/or styrene to produce a high-impact material. Pure polybutadiene is used in golf balls due to its elasticity.

6.4.2 Biobased process

The monomer for polybutadiene is butadiene (1,3-butadiene). While the current production is based on petrochemical raw materials, butadiene can also be produced from renewable raw materials via the following processes (see diagram on page 54):

1. Via ethanol to butadiene (see page 35)
2. By fermentation of sugars into dialcohols like BDO, followed by dehydration to butadiene
3. By fermentation of sugars to butadiene

6.4.3 Green building blocks and producers

Butadiene

Butadiene is currently being produced from petrochemical raw materials for application in polymers (such as synthetic rubbers) and the production of hexanediamine and BDO in a capacity of around 11,000 kton/year. The following companies are working on the production of biobased butadiene:

Genomatica

Genomatica has developed a biobased process for the production of butadiene via the fermentation of sugars [104]. At the moment Genomatica is able to produce biobased butadiene on kilogram scale. The company is also planning to develop a commercial process for the production of butadiene, in addition to the production of BDO. No further details have been released [105].

Synthos and Global Bioenergies

The Polish rubber manufacturer Synthos has started a partnership with Global Bioenergies to develop biobased butadiene and the further development into polybutadiene [106]. Information about the process, planned capacity and timeline is not yet available.

6.5 Developments

The current biobased developments for butadiene (but also for ethylene, propylene and styrene) will make it possible in the future to produce all other kinds of rubbers and plastics like EPDM rubber (ethylene-propylene-diene), SBR (styrene-butadiene rubber) and ABS (acrylonitrile-butadiene-styrene). This will require much larger investments in time and money, however.

7 Developments & prospects

Green building blocks are experiencing enormous growth as a result of government funding for sustainable production and CO_2 reductions, as well as consumer demands for environmentally-friendly products and their willingness to pay for them. The so-called drop-ins, building blocks that are chemically identical to their petrochemical counterparts, are especially booming. A major benefit of the new generation of biobased plastics based on green building blocks is that they are able to compete with petrochemical plastics in terms of performance; the characteristics are sometimes identical and occasionally even better.

As the price of crude raw materials remains one of the main factors in the economic feasibility of biobased products, capacity increases on locations where low-cost biomass is available. North America has maize starch, South America sugar cane and Asia both crops, for example. Low wages and strategic alliances are also essential for success. In addition to these first generation crops, there are also rapid developments in technologies involving second generation biomass as a raw material for chemical building blocks. This includes the design of factories that integrate the first and second generation (residue streams, mainly lignocellulose) for optimal biomass efficiency. Examples include sugar from grain and straw, from sugar cane and sugar cane bagasse, or from maize and maize straw.

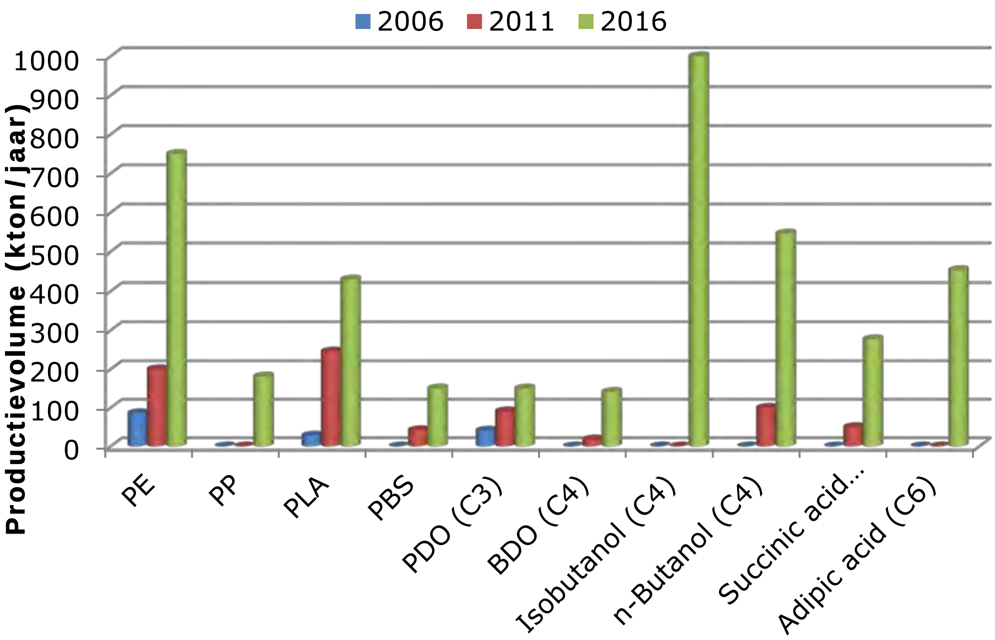
This publication has provided an overview of the technological possibilities for the production of chemical building blocks from renewable raw materials. It does not make a distinction between first and second generation biomass. Most examples of industrial production are based on first generation raw materials as the second generation are yet to become profitable. Press releases regularly report that the second generation is in an R&D stage (with exception of ethanol which is close to commercial production).

The transition from petrochemical raw materials to renewable raw materials is a step-by-step process. Companies initially work with raw materials that are as pure as possible, like sugar from sugar cane, and starch from wheat or maize. If this is successful they can take the next step; for example, sugar from lignocellulosic biomass. These sugar streams, however, are often less pure which makes producing chemical building blocks far more challenging. Additionally, using lignocellulosic biomass as source for sugars results in residues such as lignin, for which an application to ensure an economically feasible process has yet to be found.

The table below shows a summary of companies that are planning to or are actively producing biobased polymers or chemical building blocks from renewable raw materials. Considerable growth is expected in particular for the production of alcohols like ethanol, *n*-butanol and isobutanol, partly due to the production of biofuels. In addition to this application as biofuel, these components are important building blocks for the chemical sector. The most well-known example is the production of ethylene for vinyl polymers like PE and PP. With a saturated bio-ethanol market, other possibilities such as the conversion of bio-ethanol plants to isobutanol or *n*-butanol are also being considered.

Companies with (planned) biobased production	
Polymers	
PE	Braskem, Dow Chemical, Mitsui
PP	Braskem, Mitsui, Toyota, Sinopec
PLA	Galactic, NatureWorks, Synbra
PBS	Mitsubishi, Showa Denka, Anqing Hexing, PTT
Polyesters	Avantium (PEF), DuPont (PTT)
Polyurethanes	Cargill, Dow, Bayer, Urethane Soy Systems, BASF, Metabolic Explorer
Polyamides	DSM, DuPont, BASF, Toray, EMS-Grivory, Evonik, Arkema
Chemical building blocks	
Acetic acid (C2)	Wacker Chemie
Ethylene glycol (C2)	India Glycols
PDO (C3)	DuPont-Tate &Lyle (joint venture)
Lactic acid (C3)	PURAC, Myriant, Galactic, NatureWorks, ADM
Acrylic acid (C3)	Myriant, OPXBio, DOW, Novozymes, Cargill, Arkema
Butadiene (C4)	Genomatica, Global Bioenergies
BDO (C4)	Myriant, Davy Process Technologies, Genomatica, Tate & Lyle, Novamont, Mitsubishi, Beta Renewables
n-Butanol (C4)	Eastman (Tetravitae), Cathay Industrial Biotech, Cobalt Technologies en Rhodia, Cobalt Technologies en Andritz, Green Biologics, Jilin Jian New Energy Group, Butamax (joint venture BP and DuPont)
Isobutanol (C4)	Gevo
Isobutene (C4)	Lanxess, Global Bioenergies
Succinic acid (C4)	BASF, BioAmber, DSM, Roquette, Mitsui, Myriant, PURAC, Reverdia (DSM & Roquette)
Levulinic acid (C5)	Biofine
Methyl methacrylate (C5)	MRC (Mitsubishi Rayon), Evonik
Isoprene (C5)	Genencor (DuPont), Amyris, Ajinomoto
Adipic acid (C6)	DSM, Rennovia, Verdezyne, Bioamber
2,5-FDCA (C6)	Avantium
Terephtalic acid (C8)	Toray Industries, Virent
BTX	Anellotech

In addition to the current biobased production (2011) and the situation in 2006, the figure below also makes an estimate of the production volumes of a number of polymers and chemical building blocks in 2016 [2]. This diagram is partially based on verified data from companies as indicated in this publication.



Biobased production of various polymers and chemical building blocks in 2006, 2011 and an estimate for 2016

The diagram shows a substantial growth of vinyl polymers PE and PP, although it is still only a fraction of the current (petrochemical) global production of 88,000 kton/year for PE and 47,000 kton/year for PP. The relatively new polymers PLA and PBS are also expected to see considerable growth.

Chemical building blocks that are identical to their petrochemical counterparts can immediately be integrated into the current industrial infrastructure and make a material completely or partially biobased. Examples include BDO, *n*-butanol and adipic acid. These building blocks are currently being produced in large volumes from petrochemical raw materials and can be replaced by their biobased counterparts.

There are also examples of new chemicals and materials from renewable raw materials with unique characteristics which are difficult or impossible to produce from petrochemical raw materials. Examples include lactic acid, PDO, isobutanol, succinic acid and furans. New markets are developing around these building blocks. Especially building blocks that can be used in many different polymer groups due to their chemical structure are especially promising and will undergo substantial growth.

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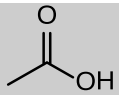
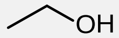
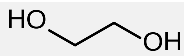
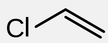
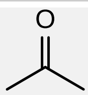
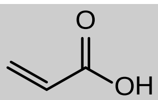
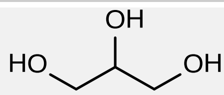
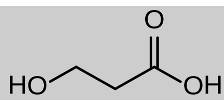
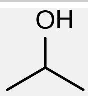
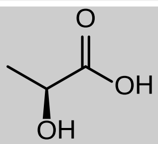
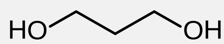
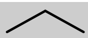
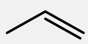
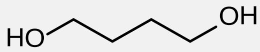
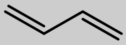
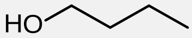
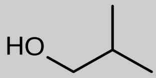
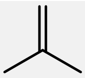
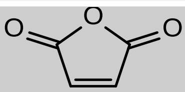
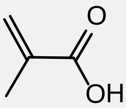
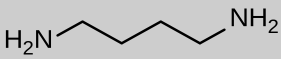
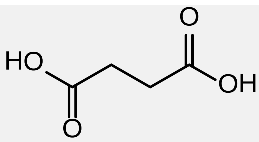
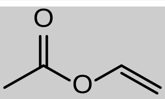
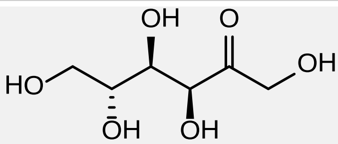
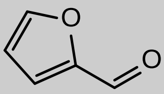
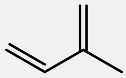
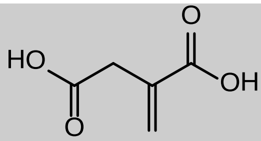
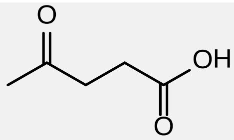
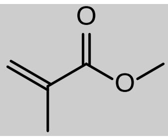
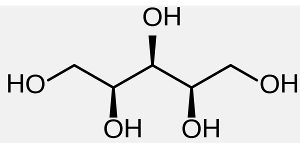
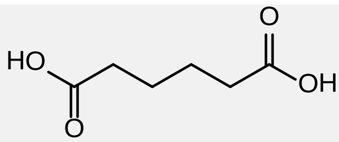
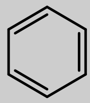
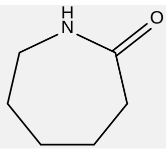
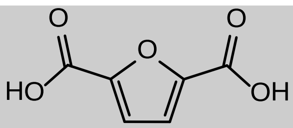
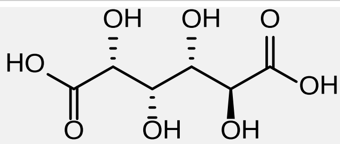
Structure chemical building blocks

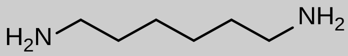
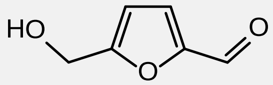
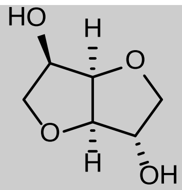
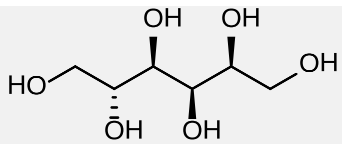
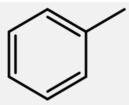
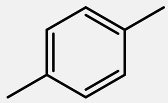
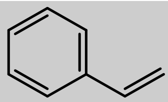
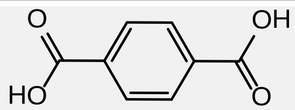
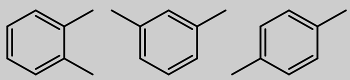
Building block	Alternative name	Structure	Application
		C2	
Acetic acid	Ethanoic acid		Vinyl polymers
Ethanol	Ethyl alcohol		Vinyl polymers Polyesters
Ethylene	Ethene		Vinyl polymers
Ethylene glycol (MEG)	1,2-Ethanediol Glycol		Polyesters
1,2-Dichloroethane			Vinyl polymers
Vinyl chloride	Chloroethene		Vinyl polymers

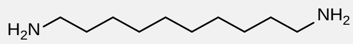
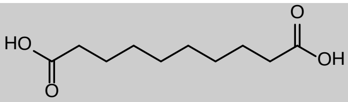
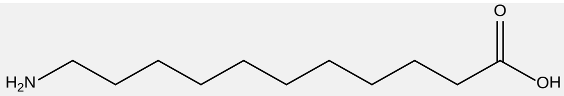
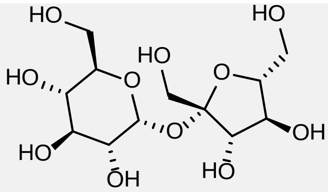
		C3	
Acetone	Propanone		Vinyl polymers
Acrylic acid			Vinyl polymers
Glycerol	Glycerine		Polyesters
3-HPA	3-Hydroxypropionic acid		Vinyl polymers
Isopropanol	2-propanol, Isopropyl alcohol		Vinyl polymers
Lactic acid	2-Hydroxypropionic acid		Polyesters
PDO	1,3-propanediol		Polyesters Polyurethanes
Propane			Vinyl polymers
Propylene	Propene		Vinyl polymers

	C4		
BDO	1,4-Butanediol Butane-1,4-diol		Polyesters
Butadiene	1,3-Butadiene		Polyesters Synthetic rubber
n-Butanol	1-Butanol		Vinyl polymers
1-Butylene	1-Butene		Vinyl polymers
2-Butylene	2-Butene		Vinyl polymers
Isobutanol	2-methyl-1-propanol		Polyesters Synthetic rubber
Isobutylene	Isobutene 2-methylpropene		Synthetic rubber
Maleic anhydride			Polyesters
Methacrylic acid			Vinyl polymers
Butanediamine	1,4-Diaminobutane Butane-1,4-diamine		Polyamides
Succinic acid	Butanedioic acid		Polyesters Polyurethanes Polyamides
Vinyl acetate			Vinyl polymers

	C5		
Fructose			Polyesters
Furfural			Polyesters

Isoprene	2-methyl-1,3-butadiene		Synthetic rubber
Itaconic acid	Methylenesuccinic acid		Vinyl polymers
Levulinic acid			Polyesters Polyamides
Methyl methacrylate			Vinyl polymers
Xylitol			Polyesters
C6			
Adipic acid	Hexanedioic acid		Polyurethanes Polyamides
Benzene			Vinyl polymers
Caprolactam			Polyamides
2,5-FDCA	2,5-Furandicarboxylic acid		Polyesters
Glucaric acid	Saccharic acid		Polyurethanes Polyamides

Hexanediamine	1,6-Diamino hexane Hexane-1,6-diamine		Polyamides
HMF	5-hydroxymethyl-furfural		Polyesters
Isosorbide			Polyesters Polyurethanes
Sorbitol			Polyesters Polyurethanes
		C7	
Toluene			Vinyl polymers
		C8	
Para-xylene	1,4-dimethyl-benzene		Vinyl polymers Polyesters
Styrene			Vinylpolymers
Terephthalic acid	Benzene-1,4-dicarboxylic acid		Polyesters
Xylene (mixture)	1,2-, 1,3-, 1,4-dimethyl-benzene		Vinyl polymers

C10			
Decanediamine	1,10-decanediamine Decane-1,10-diamine		Polyamides
Sebacic acid	1,8-octane dicarboxylic acid		Polyamides
C11			
11-Amino undecanoic acid			Polyamides
C12			
Sucrose	Saccharose		Polyurethanes

Polymer abbreviations

PE	Polyethylene
HDPE	High density polyethylene
LDPE	Low density polyethylene
LLDPE	Linear low density polyethylene
PP	Polypropylene
PVC	Poly(vinyl chloride)
PS	Polystyrene
PVA	Poly(vinyl acetate)
PMMA	Poly(methyl methacrylate)
PAA	Poly(acrylic acid)
PET	Poly(ethylene terephthalate)
PTT	Poly(trimethylene terephthalate)
PBT	Poly(butylene terephthalate)
PBS	Poly(butylene succinate)
PEF	Poly(ethylene furandicarboxylate)
PBF	Poly(butylene furandicarboxylate)
PLA	Poly(lactic acid)
PA	Polyamide
PU	Polyurethane

Colophon

Green building blocks for biobased plastics
Biobased processes and market development

Paulien Harmsen and Martijn Hackmann

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BioBased Economy