Green building blocks for biobased plastics

Paulien F. H. Harmsen[1], Martijn M. Hackmann, Harriëtte L. Bos
Wageningen UR-FBR, P.O. Box 17 6700 AA Wageningen, the Netherlands

Abstract

In this paper we investigate the possible routes to produce the most commonly used polymers from biomass. This includes vinyl polymers, polyesters, polyamides, polyurethanes and synthetic rubbers. Also the most promising newly developed polymers that can be produced from biomass are investigated. Approximately 80% by weight of all chemicals produced by the petrochemical industry are applied in polymer materials. Producing these materials from biomass instead of fossil resources thus significantly contributes to the development of the biobased economy.

We show that it is technically possible to produce all major bioplastics from biomass. In many cases even more than one process can be envisioned. Essential chemical building blocks involved in the biobased production routes are presented, including state of the art production routes and production volumes. If we assume that processing costs for biobased processes will lower with further development of the biobased technologies, feedstock costs will start to weigh more heavily on the total production costs in the future. In that respect efficient use of biomass will become more important. Building blocks with acid- and alcohol functionalities, such as lactic acid and succinic acid, can be well produced from biomass like sugars since the oxygen atoms needed for these building blocks are already present in the biomass. Building blocks that can be applied in many polymer groups due to their chemical structure are promising and are expected to undergo substantial growth. We show that there are various developments on these versatile building blocks.

[1] *Corresponding author, paulien.harmsen@wur.nl; tel +31 317480224*

Introduction

The Biobased Economy is an economy in which biomass from crops and side-streams from agriculture, forestry, marine sources and the food industry is used for food, feed and non-food applications such as materials, chemicals, transport fuels and energy. The petrochemical sector is currently using more and more biomass as raw material to replace increasingly scarce mineral oil; plastics are, in terms of volume, by far its largest output. From a chemical perspective, nearly all chemical 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. Presently, only circa 5% of all chemicals is biobased [(1)]. Nevertheless, in the plastics sector there are many developments taking the step from petrochemical to renewable raw materials. In figure 1 the estimated plastics production worldwide is presented, whereas the global plastics production is correlated to the European plastics demand per resin type for 2012 (data adapted from Plastics Europe [(2)]

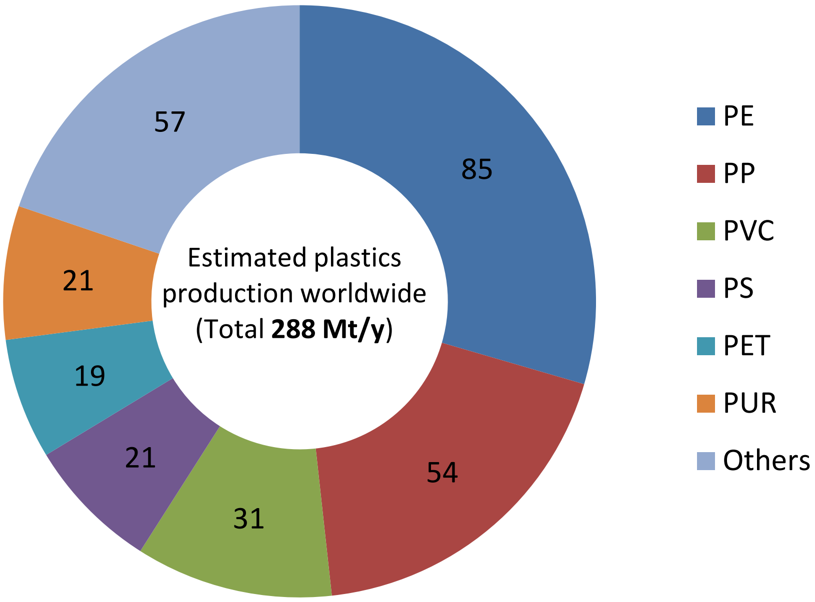

Figure 1. Estimated plastics production worldwide for 2012. Total worldwide plastics production correlated to European demand for the different types of plastics [(2)]PE=polyethylene, PP=polypropylene, PVC=poly(vinyl chloride), PS=polystyrene, PET=poly(ethylene terephthalate), PUR=polyurethane, others includes a.o. polyamides and synthetic rubbers.

This paper investigates the possibilities to produce presently known plastics from biomass, the processes that are currently under development, as well as the current development stage (ranging from R&D to commercial production). The paper focusses on the current situation at established industrial companies and start-up businesses, since these are expected to generate the new materials for the coming decade. Developments and leads generated by research institutes, which may take longer to actually lead to established materials, have been largely left out of consideration. Furthermore, mainly chemical or biotechnological processes that retain the functional groups, that are present in building blocks originating from sugar, lignin, oil or protein fractions, as much as possible are taken into account. Thermo-chemical processes that reduce the biomass to non-functional compounds (e.g. CO, CO_2, H_2) prior to synthesis of building blocks, including incineration, gasification, pyrolysis or torrefaction, are not presented with a few exceptions.

Many studies report on the developments of biobased chemistry and biobased building blocks (3-6). This study focusses on chemical building blocks for plastics, and the options for biobased alternatives. 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. These (partly) biobased materials have the same processing characteristics and general properties as their petroleum based counterparts. They can be recycled with the petrochemical plastic and can be included in the current waste separation process and processed into new products without requiring extra investments.
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, such as lactic acid. These building blocks result in the development of new products and markets, and key examples are included in this publication. Due to the focus on chemical building blocks, this paper does not describe biobased plastics from natural polymers such as cellulose- and starch derivatives and PHAs.

In the next sections the possible routes to produce the most commonly used polymers from biomass are described, starting from vinyl polymers, polyesters, polyamides, polyurethanes and ending with synthetic rubbers. The 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 categorisation of biorefineries by the 'International Energy Agency (IEA) Bioenergy Task 42 on Biorefinery' (7).

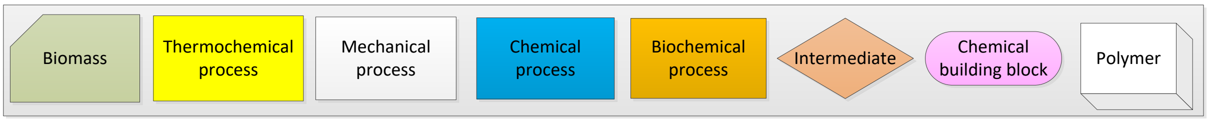

Figure 2. Legend to the diagrams.

The diagrams also include the status of the biobased processes (*i.e.* R&D, pilot, demonstration, commercial) in case the information was available. In addition, they include the present biobased production volumes (in metric tons, indicated in green). Estimations and future plans of the industry are included in tables. The data were derived from company reports and press releases. Although it is difficult to obtain reliable figures on production volumes, the data provide a reasonable indication and an insight into the growth of biobased plastics.

1 Vinyl polymers

Introduction

Vinyl polymers (or polyolefins) form the largest group of plastics in production volume globally. They are produced by polymerising an alkene monomer into a chain. The most important monomer for this group is ethylene (C2), with polyethylene being the most common example of a vinyl polymer. Besides polyethylene, also polypropylene, poly(vinyl chloride), polystyrene, poly(vinyl acetate) and polyacrylates are discussed (see table 1).

Table 1. Overview of vinyl polymers and biobased activities.

Polymer	Applications	Monomers	Biobased developments and development stage	Remarks
Polyethylene (PE)	Bags, foils, tubes etc.	Ethylene	Commercial production, circa 200 kton/year of bioPE from bio-ethanol from sugar cane [8]. Several other plans for production facilities [9, 10]. Expected production of 750 kton/year around 2015, making bioPE the largest fully biobased plastic by far in terms of volume.	Biobased ethylene and propylene (once in place) can also serve as basis for several other polymer building blocks via currently applied chemical conversions.
Polypropylene (PP)	Wide range of applications, including food containers, kitchen utensils, car parts, foam, fibres.	Propylene	Production unit of bioPP under construction [11] Biobased production of propylene is proven ; exact process not known [12]	
Poly(vinyl chloride) (PVC)	Drainpipes, sewage pipes, window frames, shower curtains, rain clothing, flooring.	Vinyl chloride	Plans for production facility of biobased PVC delayed [13]	
Polystyrene (PS)	Coffee cups, fries containers, packaging foam (EPS), disposables.	Styrene	No current activities planned for commercial production of biobased styrene or PS.	Styrene is also used as the reactive solvent in unsaturated polyester resins.
Poly(vinyl acetate) (PVA)	Adhesive and latex (paint).	Vinyl acetate	Biobased route to fully biobased PVA is in theory possible.	Vinyl acetate is also the basis for EVA, (ethylene-vinyl acetate copolymer) and for PVOH (poly (vinyl alcohol)).
Poly(methyl methacrylate) (PMMA)	Construction sector	Methyl methacrylate	Production of biobased methyl methacrylate expected in 2016-2018 [14, 15]	
Poly(acrylic acid) (PAA)	Adhesives, coatings, (copolymer) superabsorbers, thickening agents.	Acrylic acid	No current commercial production of PAA. Development of biobased acrylic acid is at pilot scale [16] with plans for commercial production in nearest future [17, 18]	

An overview of the biobased processes for vinyl polymers from biomass is presented in figure 3. The biobased building blocks involved in these processes are described in more detail in the next section.

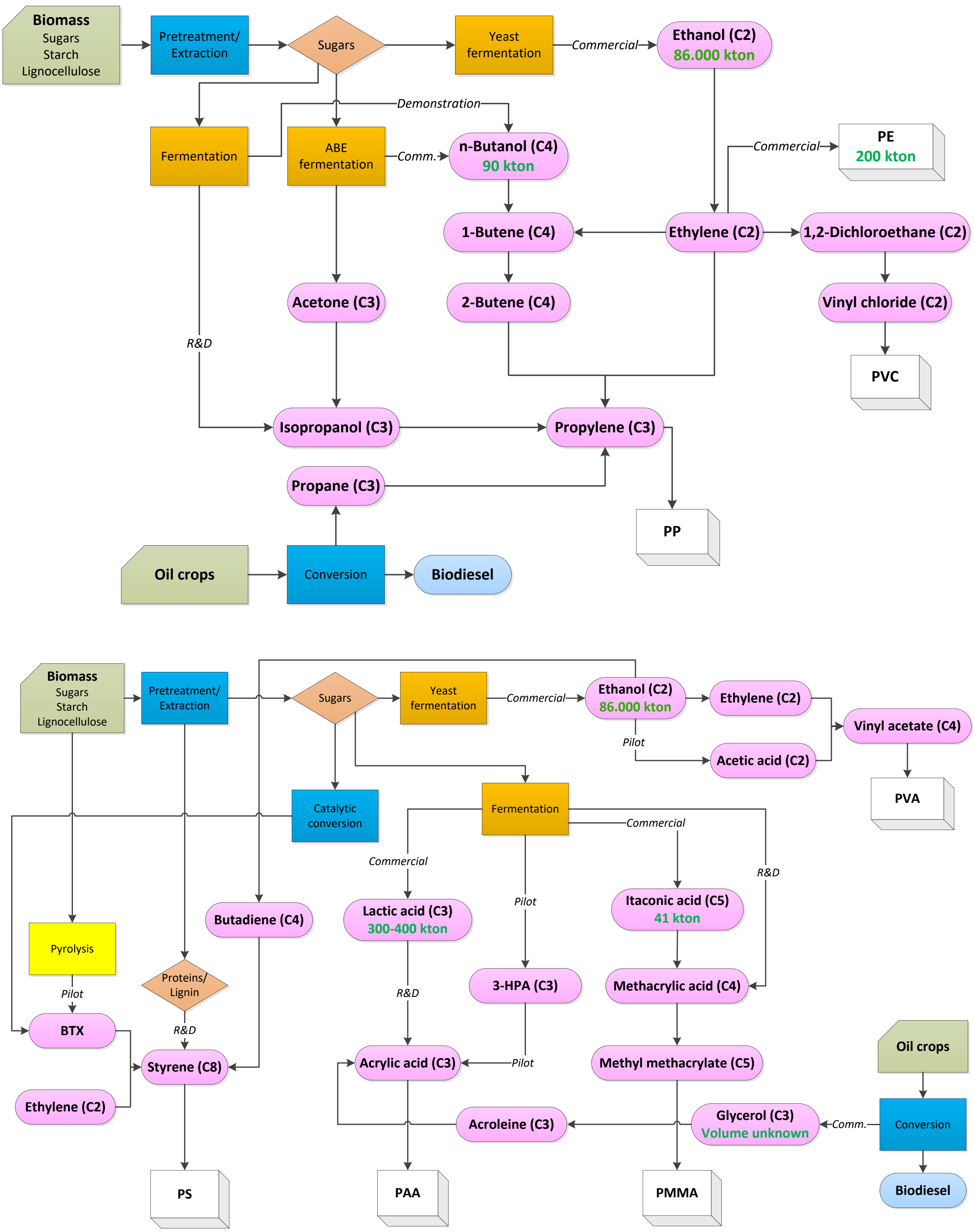

Figure 3. Overview of biobased processes and building blocks for vinyl polymers

Biobased building blocks for vinyl polymers

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. Three processes for producing acetic acid from biomass were recently developed, one of which has been further developed to pilot scale [19]. In this process, biomass is converted into ethanol via fermentation which is then converted into acetic acid by means of oxidation. The process will be scaled-up to an industrial scale as soon as it is economically feasible [20].

Ethanol (C2)

Ethanol is currently produced mainly by yeast fermentation of sugar-rich and starch-rich biomass like sugar cane (Brazil) or maize (North America). Globally circa 86,000 kton/year is produced primarily for applications in biofuels [21]. The industrial production of ethanol from second generation biomass such as lignocellulose is rapidly developing [22]. The first commercial plant for the production of bio-ethanol from second generation biomass (residues from maize crops) may become operational early 2014 [23].

Ethylene (C2)

Ethylene is one of the most essential chemical building blocks with a production volume of over 100,000 kton/year (mainly from petrochemical resources). It can be produced by means of dehydration of (bio-)ethanol, which enables a biobased process.
Future producers of ethanol from lignocellulose may prefer to convert ethanol into ethylene instead of directing it towards the (saturated) fuel market. Of the global production of ethanol, 18% (16,000 kton/year) is currently being used for non-fuel applications like conversion to ethylene as chemical building block [21].

Vinyl chloride (C2)

Vinyl chloride can be obtained by conversion of ethylene (from ethanol by dehydration) with chlorine into 1,2-dichloroethane, followed by dehydrochlorination (known chemical processes).

Acrylic acid (C3)

Acrylic acid is used as monomer for PAA as well as an ingredient in coatings, paints and adhesives. Various developments towards the production of biobased acrylic acid are underway:

- Fermentation of sugars to 3-hydroxypropionic acid (3-HPA) and subsequent conversion to acrylic acid. This route is now at pilot scale [16-18].
- Fermentation of sugars to lactic acid and subsequent conversion to acrylic acid. This route is claimed to be cost competitive compared to petroleum-based acrylic acid, without the need for government subsidies or green premiums [24, 25].
- From glycerol via acroleine [26].

The current process for acrylic acid involves the oxidation of petrochemical propylene. Biobased propylene (possibly produced on a large scale in the future) is thus also a potential raw material for acrylic acid as the required infrastructure is already in place.

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 a molecule with both an alcohol and an acid group. 3-HPA can be produced by fermentation of sugars [27],[28]. Various industrial parties are developing fermentation processes for the production of 3-HPA (see acrylic acid).

Isopropanol (C3)

Isopropanol is currently mainly used as a solvent for cleaning and disinfection, but it can also serve as raw material for propylene. Presently the fermentation of sugars into isopropanol is under development [29, 30].

Propylene (C3)

Propylene, an essential building block for the chemical industry, can be produced from biomass via various processes:

- Dimerisation of ethylene into 1-butene, followed by isomerisation into 2-butene. Metathesis of ethylene and 2-butene yields propylene. In this process, the propylene is entirely derived from ethanol
- Dehydration of *n*-butanol into 1-butene, followed by isomerisation into 2-butene. Metathesis of ethylene and 2-butene yields propylene
- ABE fermentation of sugars to acetone. Reduction of acetone to isopropanol, followed by reduction to propylene
- Fermentation of sugars into isopropanol, followed by dehydration into propylene
- Dehydrogenation of propane from glycerol, a by-product of diesel production from natural oils and fats

Currently it is unclear which process will be used to produce biobased propylene. The processes, entirely from ethanol or ethanol and *n*-butanol, via metathesis of ethylene and 2-butene are the most likely possibilities.

n-Butanol (C4)

n-Butanol is a chemical building block with a current production volume of 2,300 kton/year, mainly from mineral oil [31]. Like isobutanol (a building block for polyesters and synthetic rubbers) it is one of the four isomers of butanol.[2] 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 due to its benefits compared to ethanol: lower (CO_2) emissions and a higher energy value [32]. *n*Butanol can also be used as a chemical building block for the production of *e.g.* 1-butene.
Biobased *n*-butanol is produced on a commercial scale (via the fermentation of maize) at a capacity of 90 kton/year [33][34]. Investment for the production of *n*-butanol from lignocellulose (sugar cane bagasse) is planned [35, 36]. The sugar can be extracted from the bagasse under diluted acidic conditions. This sugar solution can then be directly fermented into *n*-butanol without further enzymatic hydrolysis. The production of *n*-butanol from renewable raw materials on a commercial scale for the transport fuel market, building on bio-ethanol technology, is also planned [37]. Another initiative is the development and commercialisation of biotechnological produced butanol for chemical applications (besides transport fuel) [38]. Furthermore, ABE-fermentation for the production of *n*-butanol, in addition to acetone and ethanol is being developed [39].

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[2] *Both isomers of butanol (n-butanol and isobutanol) 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.*

Methacrylic acid (C4)

There are various developments in the field of biobased methacrylic acid for the production of methyl methacrylate. For instance, a biotechnical process for producing methacrylic acid via fermentation of biomass with bacteria is under development[14, 15]. Methacrylic acid can also be produced by decarboxylation of itaconic acid (see below) or by oxidation of isobutylene, a building block for synthetic rubbers that is being produced at pilot scale from sugars (see section on synthetic rubbers).

Itaconic acid (C5)

Itaconic acid is an important chemical building block for the chemical industry. For instance, it can replace chemicals like acrylic acid and maleic acid which are commonly used in acrylates and resins. Current production, by fermentation of sugars, is 41 kton/y and is concentrated in China[40]. The winning application for itaconic acid can potentially be the production of biobased methyl methacrylate for PMMA, although there are also other routes explored to produce methyl methacrylate[15].

Styrene (C8)

Styrene, currently produced from fossil oil, 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[41]:

- Ethanol conversion into butadiene followed by dimerization into styrene.
- Pyrolysis of biomass to a mixture of benzene, toluene and xylene (BTX) (see next paragraph). Subsequent reaction of benzene with ethylene into styrene.
- Chemical (catalytic) conversion from sugars to BTX and reaction of benzene with ethylene into styrene.
- Isolation of aromatic compounds from proteins[42] or lignin[43].

2 Polyesters

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 section provides further information on the building blocks for polyesters and an overview of the most important polyesters is given in table 2.

Table 2. Overview of polyesters and biobased activities.

Polymer	Applications	Monomers	Biobased developments and development stage	Remarks
Poly(ethylene therephthalate) (PET)	Packaging materials (bottles, containers), fibres (fleece).	Ethylene glycol Terephthalic acid	Partially biobased productionof PET by application of biobased ethyleneglycol [44][45]	Development towards fully biobased PET [46]
Poly(trimethylene terephthalate) (PTT)	Carpet and textile fibres.	1,3-propanediol (PDO) Terephthalic acid	Partially biobased production of PTT since 2000 by application of biobased PDO [47].	Petrochemical PTT production 2004-2009 stopped due to demand shortage and global overcapacity [48] .
Poly(butylene terephthalate) (PBT)	Specialty applications, precision components for car parts, electrical and electronic equipment.	1,4-butanediol (BDO) Terephthalic acid	Production of partial biobased PBT in commercial plant by application of biobased BDO [49].	
Poly(butylene succinate) (PBS)	Wide range of applications (e.g. food packaging, mulch films). Similar to PP, very suitable for blending.	BDO Succinic acid	Developments towards fully biobased PBS [50-53]	Current production of petrochemical PBS is ca. 40 kton/year) [54]
Poly(ethylene furandicarboxylate) (PEF)	Bottles, packaging materials increased gas barrier properties [55].	Ethylene glycol 2,5-FDCA	Development towards fully biobased PEF by 2016 [56]	For replacement of petrochemical terephthalic acid the production process for 2,5-FDCA is probably cheaper than the process for biobased terephthalic acid [57].
Poly(butylene furandicarboxylate) (PBF)	Under development	BDO 2,5-FDCA	Development expected to follow up on PEF development	
Poly(lactic acid)	Packaging materials and textile fibres, insulation foam, electronics and car parts. (heat-resistant PLA)	Lactic acid	Commercial, global PLA production is circa 250 kton/year	PLA is only produced from renewable raw materials via a biotechnological process. It can be recycled by degradation to lactic acid [58, 59].

An overview of the biobased processes for these polymers from biomass is presented in figure 4. The biobased building blocks involved in these production processes are described in more detail in the next section.

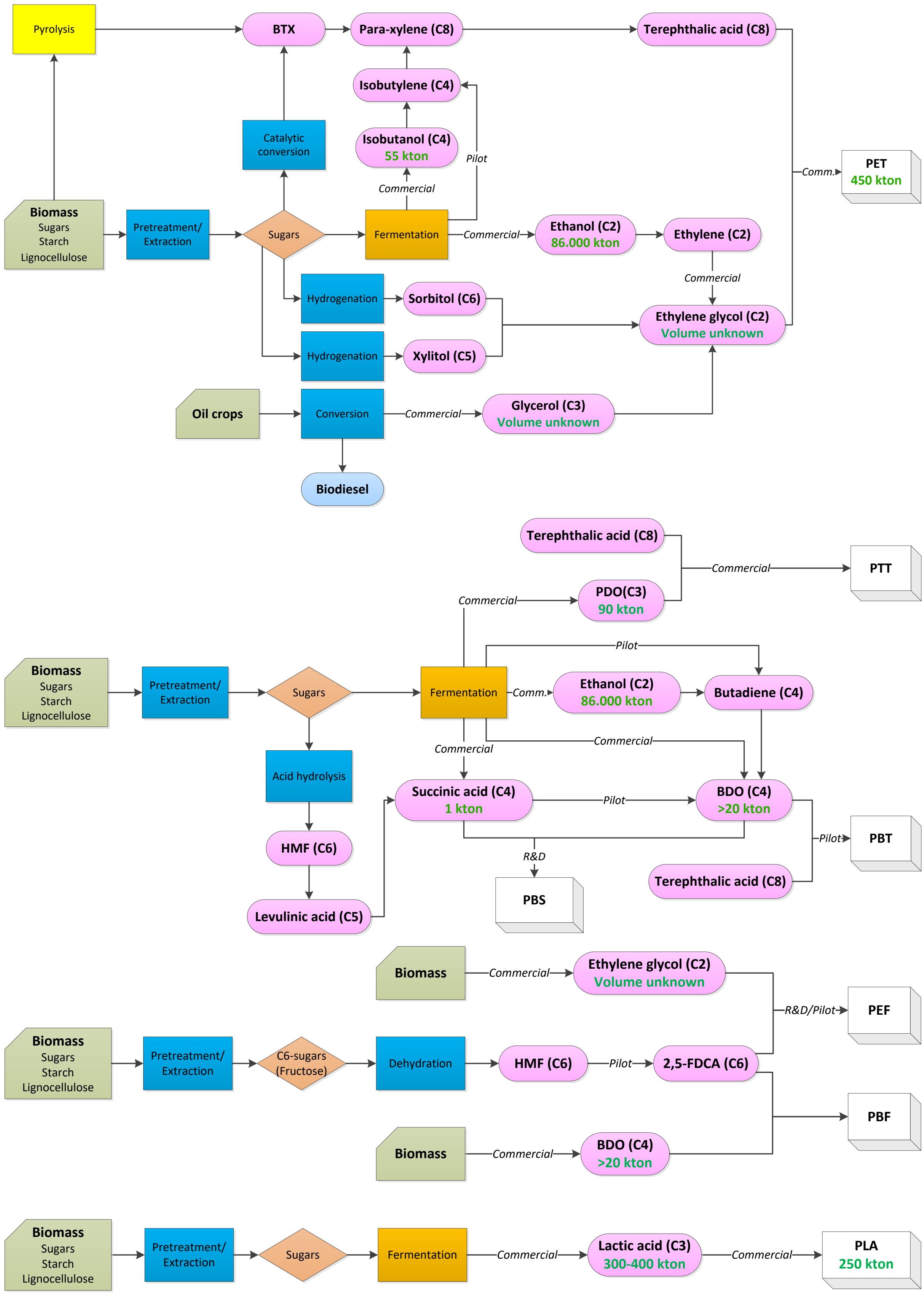

Figure 4: Overview of biobased processes and building blocks for polyesters

Biobased building blocks for polyesters

Ethylene glycol (C2)

Petrochemical ethylene glycol is currently being produced on industrial scale by addition of water to ethylene oxide (produced by oxidation of ethylene). As it is possible to produce biobased ethylene from ethanol (see the previous section), it is also possible to produce biobased ethylene glycol. This process is commercial with a volume of 500 kton/y and for instance used for the production of the "Plant Bottle" (44) and other partial biobased PET-materials (6, 60).
Besides the ethanol route there are also other possibilities via hydrogenolysis (*i.e.* covalent bond cleavage by hydrogen) of xylitol (originating from xylose), sorbitol (originating from glucose) or glycerol (a by-product of biodiesel production) into ethylene glycol (41).

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. The current production of lactic acid is around 300-400 kton/year with a market price of 1000-1200 €/ton (61). For food packaging PLA has an advantage over other polymers since it does not contain, and thus will not leak, any potentially harmful chemical building blocks.
Lactic acid is currently produced from sugar-rich and starch-rich biomass such as sugar cane, maize and tapioca. Several companies are working on developing a production process of lactic acid with lignocellulose as raw material (62).

PDO (C3)

PDO (1,3-propanediol) is a chemical building block with a market volume of 125 kton/year (31). 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 (31). Biobased PDO has been an industrial process for years(47) and new investments are planned (63).

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 (64).
Various large companies and consortia are working on the development and upscaling of biobased BDO (65). Biobased BDO can be used immediately within the existing infrastructure to replace petrochemical BDO (*i.e.* drop-in). It can be produced by:

- Fermentation of sugars to BDO(66), now on commercial scale.
- Fermentation of sugars to succinic acid, followed by reduction to BDO(67). This technology is expected to be commercial in 2014(68).
- Fermentation to ethanol, followed by conversion to butadiene and subsequent BDO(69)
- Chemical conversion of sugars into levulinic acid, followed by oxidation to succinic acid and reduction to BDO

Isobutanol (C4)

Isobutanol, like *n*-butanol, is one of the four isomers of butanol. In addition to its use as biofuel, isobutanol serves as an important building block for the chemical sector. At the moment isobutanol is being produced via yeast fermentation of sugars in a commercial plant with a capacity of 55 kton/y[70, 71]. Also the use of lignocellulose (*e.g.* switchgrass) and residues from forestry and agriculture (*e.g.* wood, maize stems, sugar cane bagasse) for isobutanol is under development [72].

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 will lead to a larger market demand. Succinic acid can be produced from sugars via fermentation and all existing industrial developments are based on this process.
The current global production of succinic acid is estimated at 40 kton/year of which 39 kton is petrol-based and 1 kton/y is biobased. The current production *capacity* of biobased succinic acid is estimated at 4 kton/y and is expected to grow to 225 kton/y in 2014 and 637 kton/y in 2020 in case planned production plants are actually built [40].
Many different parties are further developing succinic acid production by fermentation from various feedstock including lignocellulose [73][74][75]. Also a chemical pathway to succinic acid is possible; it runs through acid hydrolysis of sugars to levulinic acid (see section below).

Levulinic acid (C5)

Levulinic acid can be produced from lignocellulose [76]. Acidic hydrolysis of lignocellulose causes the breakdown of polymeric sugars to both C5- and C6-sugars (*e.g.* glucose). A degradation product of C6sugar 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. Levulinic acid can also be oxidised into succinic acid by extraction of succinic acid from crude levulinic acid.[77]

2,5-FDCA (C6)

2,5-Furandicarboxylic acid (2,5-FDCA) is a diacid that can serve as replacement of several petroleum based chemicals such as terephthalic acid and adipic acid. Sugars can be converted into 2,5-FDCA in a numberof steps. Fructose is used as a raw material and is converted via dehydration to the furan compound HMF, which can be converted into 2,5-FDCA via oxidation. 2,5-FDCA is expected to be less expensive than petrochemical terephthalic acid [78] and this process is being scaled up to commercial production (currently 40 tons/year up to 30-50 ktons/year in 2015) [79].
The production of 2,5-FDCA currently uses a first generation raw material (fructose) but glucose from second generation raw materials such as lignocellulose could also be used. In this case glucose must be converted into fructose first by means of enzymatic isomerisation [80].
From an environmental perspective, the production of furan-based polymers like PEF 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 applied [81].

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 petrochemical production volumes in Europe are around 13,000 kton/year [82].

Biobased BTX can be produced in a one-step catalytic process (pyrolysis) [69, 83] from lignocellulose residues. This process is currently scaled up for the production of BTX for biobased terephthalic acid as a building block for PET. A process via aqueous phase reforming is also under development [84]. In this process sugars are converted to BTX for the production of para-xylene.

Para-xylene (C8)

Para-xylene is one of the three isomers of xylene and can be isolated from BTX. It is an important building block as oxidation of para-xylene yields terephthalic acid. Development of biobased routes for commercial production of para-xylene are still in R&D phase.
Besides the production of para-xylene via BTX (either via pyrolysis or aqueous phase reforming) there is also a fermentative route being developed via isobutanol and isobutylene [72].

Terephthalic acid (C8)

Terephthalic acid is obtained by oxidation of 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 expected increase to 60,000 kton/year in 2020 [85].
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 towards the production of biobased PET [86].

3 Polyamides

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). 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. An overview of the most important polyamides is given in table 3.

Table 3. Overview of polyamides and biobased activities.

Polymer	Applications	Monomers	Biobased developments and development stage	Remarks
Polyamide 6,6 (PA 6,6) and polyamide 6 (PA 6)	The most widely used nylons with many applications	1,6-Hexanediamine Adipic acid Caprolactam	Pilot production of fully biobased PA 6,6 (87)	Biobased process for caprolactam at R&D stage (88)
Polyamide 4,6 (PA 4,6)	Engineering plastic with a high degree of crystallinity and melting point (89)	1,4-Butanediamine Adipic acid	No current activities known	
Polyamide 6,10 (PA 6,10)	Engineering plastic for niche markets.	1,6-Hexanediamine Sebacic acid	Commercial production of partially biobased PA 6,10 (90) by application of biobased sebacic acid.	
Polyamide 10,10 (PA 10,10)	Technical applications, cosmetics	1,10-Decanediamine Sebacic acid	Commercial production of fully biobased PA 10,10 (91)(92)(93)	
Polyamide 4,10 (PA 4,10)	High performance engineering plastic	1,4-Butanediamine Sebacic acid	Commercial production of partially biobased PA 4,10 (94) by application of biobased sebacic acid	
Polyamide 11 (PA 11)	Technical applications	11-Amino-undecanoic acid	Commercial production of fully biobased PA11, 10 kton/year (95)	This material has always been biobased

An overview of the biobased processes for these polymers from biomass is presented in figure 5. The biobased building blocks involved in these production processes are described in the next section.

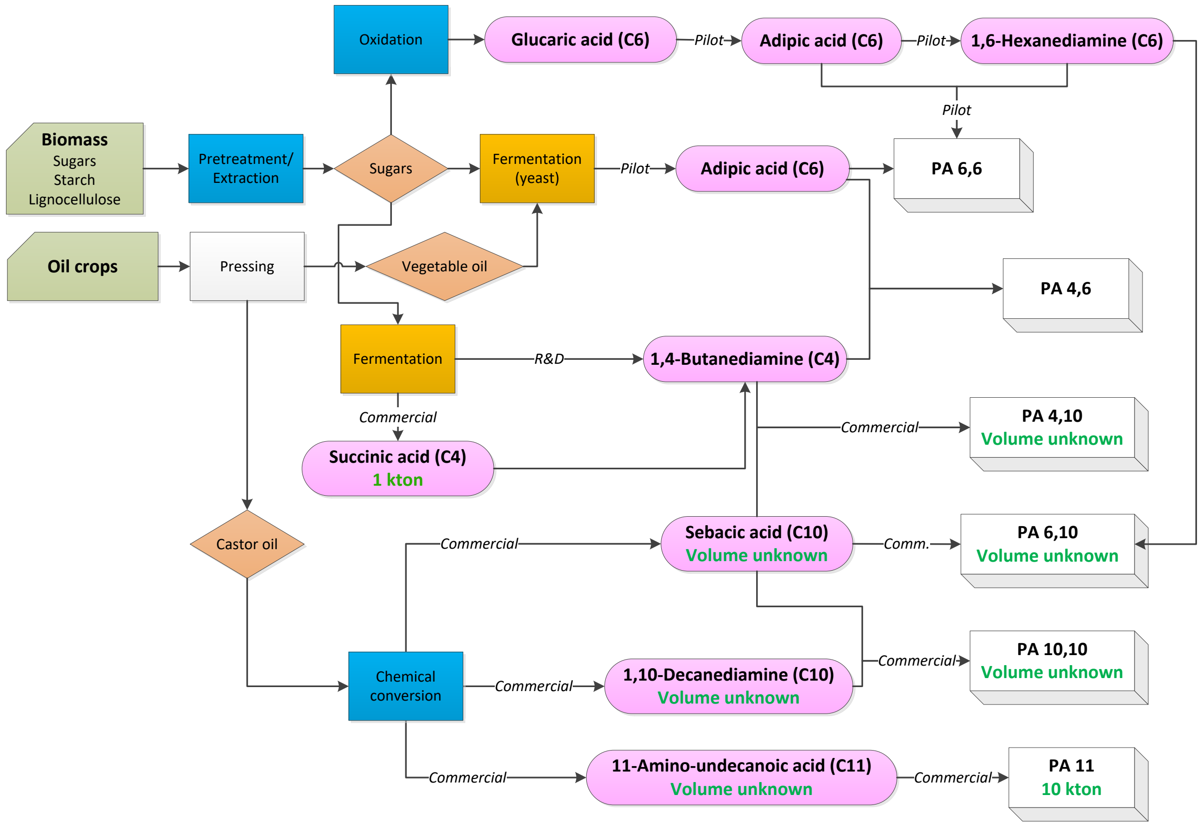

Figure 5: Overview of biobased processes and building blocks for polyamides

Biobased building blocks for polyamides

1,4-Butanediamine (C4)

The biobased production of butanediamine is possible via the chemical conversion of succinic acid [3]. Research is also being performed on the biotechnical production of butanediamine by fermentation of sugars with bacteria (*E.coli)* [96].

Caprolactam (C6)

Biobased processes via fermentation for the production of caprolactam, the monomer for the production of Polyamide 6, are presently being developed [88].

Adipic acid (C6)

Adipic acid is one of the most important aliphatic acids with a global production of 4,000 kton/year and is currently produced from petrochemical cyclohexane. Biobased processes are possible via fermentation or chemical conversion as shown in figure 5. A yeast has been developed that can produce adipic acid from vegetable oils [97, 98] and sugars [99] in a single step. The chemical–catalytic conversion route (i.e. oxidation of glucose into glucaric acid followed by reduction to adipic acid) is also under development[100]. Both routes are on pilot scale and are being evaluated at the moment [101, 102]

Hexanediamine (C6)

Hexanediamine is currently produced from petrochemical butadiene or propylene. Recent developments showed the production of biobased hexanediamine on pilot scale by chemical-catalytic conversion of adipic acid from glucose [100, 103] .In view of the developments on biobased propylene and butadiene there are also opportunities for the production of biobased hexanediamine by fermentative routes [88].

1,10-Decanediamine (C10), sebacic acid (C10), 11-amino-undecanoic acid (C11)

Decanediamine, sebacic acid and 11-amino-undecanoic acid are all produced from castor oil [1]. Castor oil is 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 main raw material for components in various polyamides. There are also other vegetable oils (besides castor oil) and sugars that serve as raw materials for polyamides.

4 Polyurethanes

Introduction

Polyurethanes (PU) are a family of polymers with a wide range of properties and applications. They are formed by the polymerisation of polyols (compounds 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 applications vary from soft and hard foams to coatings, adhesives and sealants.

The total production of biobased polyurethanes worldwide, with polyols from renewable sources and petrochemical-based isocyanates, 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 [(31)].

Main developments in the field of biobased polyurethanes are focused on biobased polyols. Various major international producers are marketing biobased polyols that are specifically suited for the application in polyurethanes[(104, 105)]. 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

In addition to polyols, there are also developments on biobased isocyanates but these are limited [(106)]. 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 laboratory scale. However, considerable R&D will be required to upscale the development to pilot or industrial scale and enable the production of 100% biobased polyurethanes.

The biobased processes for polyurethanes and the biobased building blocks involved in these production processes are indicated in figure 6; the biobased building blocks are described in the next section.

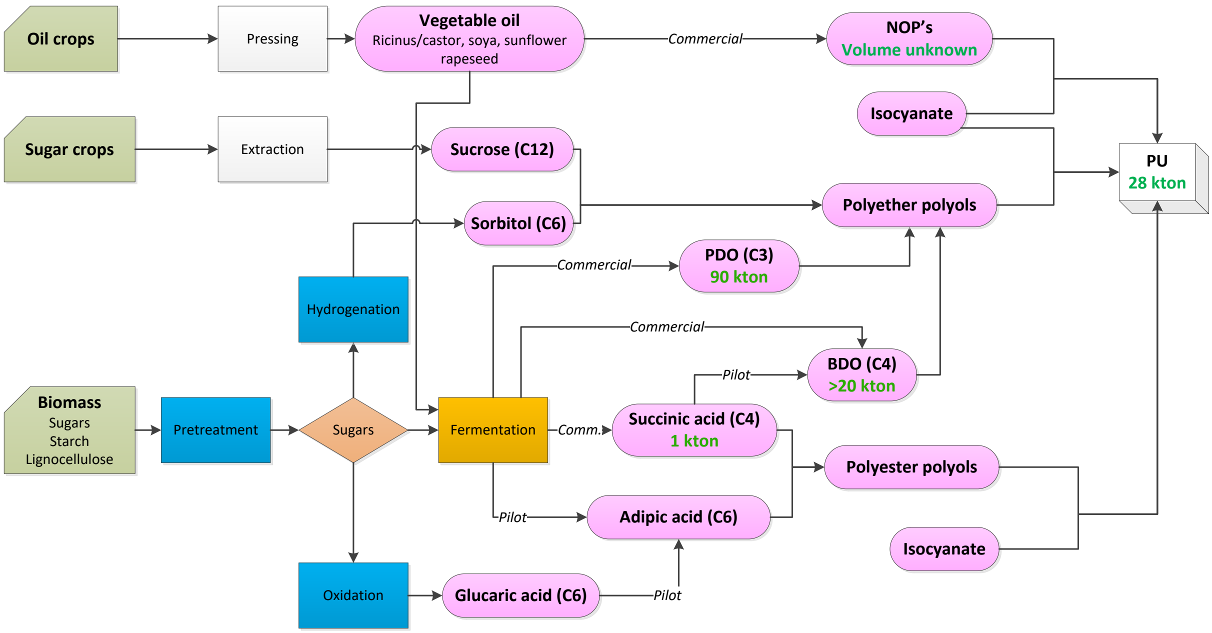

Figure 6: Overview of biobased processes and building blocks for polyurethanes

Biobased building blocks for polyurethanes

Polyols from NOPs

An essential raw material for polyurethanes is castor oil (see the previous section on polyamides). 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 cheaper, vegetable oils such as soy bean oil, sunflower oil or rapeseed oil. PU based on polyols from vegetable oils are presently in the market (104) and the production is expanding (105).

Polyether polyols via PDO and BDO

Also PDO and BDO (see the section on polyesters) can be used for the production of polyether polyols for polyurethanes. The conversion from PDO to polyether polyols and the subsequent polymerisation with isocyanates results in polyurethanes that are extremely suitable for applications in textiles, coatings and engineering plastics.

Polyether polyols based on sugar

For the production of hard polyurethane foams based on polyether polyols, the sugars sorbitol and sucrose are often used as the alcohol component. Both substances can easily be extracted from sugar crops.

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 and adipic acid (see the section on vinyl polymers). 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 Synthetic rubbers

5.1 Introduction

Rubbers are elastic materials (elastomers) that deform under pressure or tension and return to their original dimensions or geometric shape when the force is relieved. 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 one-third is natural rubber. Natural rubber (i.e. polyisoprene) is mainly produced in Southeast Asia and is a polymerisation product of cis-1,4-isoprene. Although polyisoprene isbeing produced synthetically, natural rubber has maintained a substantial market share due to its outstanding properties. As a result of the dependence on latex from the Hevea tree as the only source of natural rubber, there is an ongoing search for alternative resources. This chapter describes the biobased processes for the synthetic rubbers polyisoprene, polyisobutylene and polybutadiene (see table 4).

Table 4. Overview of the rubbers and biobased production options.

Polymer	Applications	Monomers	Biobased developments and development stage	Remarks
Polyisoprene or isoprene rubber	Car tyres, medical gloves, adhesives	Isoprene	Many R&D activities following up on isoprene developments [(107)]	The current developments for butadiene (and 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) from renewable resources
Polyisobutylene or isobutyl rubber	Inner tubes, gas-tight layers, protective clothing, pharmaceutical packaging	Isobutylene	Activities following on isobutylene developments [(108)]	
Polybutadiene or butadiene rubber	Tyre applications, usually blended into rubber compounds. Also constituent of ABS (acrylonitril-butadiene-styrene copolymer, used for lego bricks, computer housing, etc.)	1,3-Butadiene	Polymerisation into polybutadiene [(109)] is in R&D phase	

An overview of the production options for the rubbers from biomass is presented in figure 7. The biobased building blocks involved in these production processes are described in the next section.

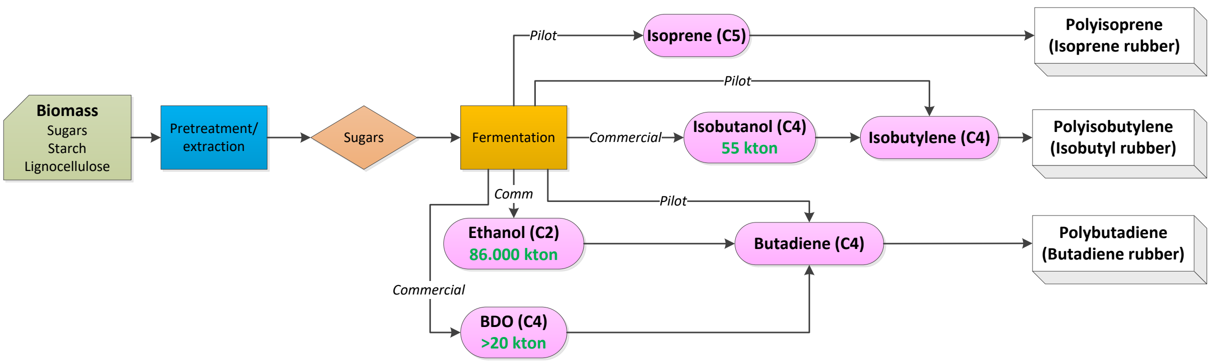

Figure 7: Overview of biobased processes and building blocks for rubbers. Routes to BDO and isobutanol are described in the polyester section.

Biobased building blocks for synthetic rubbers

Isoprene (C5)

Isoprene is mainly used in synthetic rubbers. Many parties are working on the biobased production of isoprene by aerobic fermentation {[107, 110]. The developments on isoprene are in advanced R&D/pilot phase.

Isobutylene (C4)

Isobutylene can be produced from isobutanol via dehydration. Another route is direct fermentation of sugars from biomass into isobutylene, and this route is currently in pilot production phase [108, 111].

Butadiene (C4)

1,3-Butadiene is currently being produced from petrochemical raw materials at a capacity of around 11,000 kton/year, for application in polymers (such as synthetic rubbers) and the production of hexanediamine and BDO.
A biobased process for the production of butadiene via the fermentation of sugars is developed [112]. Biobased butadiene is produced on kg-scale and there are plans for scale-up to a commercial process[113]. Also other processes are being investigated, including the subsequent polymerisation of biobased butadiene into polybutadiene [109]. Development of biobased butadiene is attracting a lot of investments at the moment [114].

6 Developments and prospects

Green building blocks are experiencing enormous growth as a result of active industrial and academic developments and government funding for sustainable production and CO_2 reductions. Also consumer demands for environmentally-friendly products and their willingness to pay for them accelerates this growth. 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 often 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 [(31)]. North America has maize starch, South America sugar cane and Asia has 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 (residual 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 corn stover. 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 has to be found to ensure an economically feasible process. Most examples of industrial production are based on first generation raw materials as second generation materials are yet to become profitable. Press releases regularly report that second generation is in an R&D stage with exception of lignocellulosic ethanol which is commercially produced.

On basis of the figures 2-7 we can conclude that in principle it is or will be possible to produce all presently used plastics from biomass. In these figures all the necessary building blocks for these production routes are given and also we can identify the processes that will produce these building blocks from biomass. In many cases even more than one process can be envisioned.

Chemical building blocks that are identical to their petrochemical counterparts (‘drop-ins’) can immediately be integrated into the current industrial infrastructure and established market and make a material completely or partially biobased. Examples include ethylene for PE, ethylene glycol for PET and adipic acid for PA 6,6. 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 for PLA, PDO for PTT and polyurethanes, isobutanol for isobutylrubber, and succinic acid and furans for polyesters (PBT, PBS, PEF, PBF). New markets are developing around these building blocks. Building blocks that can be used in many different polymer groups due to their chemical structure are especially promising and are expected to undergo substantial growth.

We see that the shift from fossil to renewable raw materials for the production of bioplastics occurs in stages. It starts with the production of mainly drop-ins from first generation biomass for large-volume plastics like PE and PET and expands gradually to the production of chemical building blocks for biobased plastics with a smaller volume. Next step is the conversion of these building blocks to polymers which is a challenge as the requirements in relation to purity are demanding. Examples here include recent developments in the pilot or commercial production of a number of partially or fully biobased polyamides (PA 6,6, PA 4,10, PA 6,10 and PA 10,10). Also within the group of polyesters there are recent developments, for example the R&D/pilot production of partially biobased PBT and fully biobased PBS and PEF.

The fact that it is technologically possible to produce building blocks that are identical to their petrochemical counterparts does not imply that this is also desirable. Not all products and processes are equally feasible from an economic point of view. Up till now, a limited number of biobased building blocks and polymers is on the market. Biobased PE is on its way to become the largest fully biobased polymer of the coming years (if all plans are realized), which is particularly caused by the large production of bioethanol for biofuels and the fact that bioethanol can easily be transformed into ethylene. In addition, partially biobased PET from biobased ethylene glycol (via ethylene and bioethanol) is expected to grow with a factor of 10 [45]. However, as shown by Bos et al.[115] the conversion of sugar into ethylene has a rather low mass efficiency which implies that a relatively large amount of feedstock will be needed. Assuming that processing costs for the processes under development will lower with the further development of the biobased technologies, feedstock costs will start to weigh more heavily on the total product costs in the future. Also the wish to efficiently use scarce agricultural area will favour products that show a higher mass efficiency. Especially the production of ethylene glycol from ethanol is not very efficient with respect to feedstock, although being technically feasible and applied at commercial scale. 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, and functional groups in the form of two alcohol groups must be added again to produce the ethylene glycol ($C_2H_6O_2$).

We believe that the relatively high feedstock demand of biobased materials like PE and PET may become limiting in the future. This opens possibilities for classes of polymers that can be produced more efficiently from sugars, for example other polyesters and polyamides. The polyester family is a versatile class of polymers since by exchanging the building blocks new ranges of properties may be reached, which makes them a potential replacement for many presently used polymers. Polyester building blocks can be well produced from biomass like sugars, since the oxygen atoms needed for the acid- and alcohol functionalities are already present in the biomass. This makes the production of these building blocks from biomass relatively easy compared to their production from fossil oil [116]. An early example of this is the production of partially biobased PTT from biobased PDO (dialcohol) and terephthalic acid. PDO is successfully being produced from fermentable sugars for years and this has presumably led to the closing down of the fossil-based PDO production plant.[117] An example of a polyester based on a single building block that is converted from sugar with a high mass efficiency is PLA. PLA is a prominent example of a new biobased polymer that has shown large growth in production capacity over the last years. Whereas PLA has a properties profile that may be limitative to a number of applications, the fact that it is made from lactic acid makes it very well suited for use as a food packaging material. We expect therefore that PLA will strengthen its already strong position in this field and has the potential to become a cost effective polymer with a reasonably large application area. Also within the polyamide family there are numerous developments that speed up the transition towards (fully) biobased polymers. A number of fully biobased polyamides are already commercially produced from castor oil, and the pilot scale production of adipic acid and hexanediamine from sugars accelerates this process tremendously.

By expanding current polymers with new members from renewable materials more properties can be reached which might eventually lead to a competition between the large family of fossil based polymers and biobased alternatives. For polymer scientists the introduction of new building blocks brings new elan for interesting new developments after many years where no fundamentally new polymers were developed and brought to market. For the development and introduction of these new polymers finding markets, where their specific properties give an advantage, will be key.

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