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D 2.1 Background information and biorefinery status, potential and Sustainability

– Task 2.1.2 Market and Consumers; Carbohydrates –

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D 2.1 Background information and biorefinery status, potential and Sustainability

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Content

Management summary

This report was produced to give an overview of present and future market for biorefinery products based on carbohydrates.

Various studies show that there is a wealth of possible molecules and products that can be produced from carbohydrates. Carbohydrates already find significant application in starch products and cellulose plastics and fibres.
However, for a biorefinery to operate in an economically sustainable way, applications for (preferably all) biomass ingredients need to be found. Presumably the optimal mix of applications will be a combination of larger volume/smaller value and smaller volume/higher value applications. For this study we therefore have taken a molecular approach.

Looking at the size of possible end markets for the molecules that can be based on carbohydrates a number of main products come into view:

- **Dialcohols**: dialcohols can be used in a variety of end products, they are one of the building blocks for polyesters, they find applications in polyurethanes and in thermoset resins. From carbohydrates usually the shorter dialcohols are produced (C2 – C4). The C2 and C4 dialcohol produced from petrochemical resources already find ample application in a variety of products and these can be replaced by the biomass based variant. The C3 dialcohol is easier to produce from biomass than from petrochemical resources and this is one of the building blocks that is presently being commercialized from biomass. A special case of diol is isosorbide which can replace the phthalic acid group in phthalate plasticisers (in combination with carboxylic acid side chains) and other applications.
- **Dioic acids**: dioic or dicaboxylic acids find broad applications as one of the two building blocks for polyesters and also one of the two building blocks for polyamides. From biomass the C2, C4 and C6 dioic acid can be produced. The C6 dioic acid made from petrochemical feedstock already finds ample application. Itaconic acid is a very interesting candidate because it can serve as the basis for (methyl) methacrylate, the building block for PMMA. The longer diacids, like sebacic acid (C10) and longer are often produced from natural oils.
- **2,5 Furan dicarboxylic acid:** 2,5 FDA is a molecule that is not used in commercial applications yet. However, its steric shape is rather comparable to terephthalic acid. Terephthalic acid is found in a very broad range of applications. In many applications 2,5 FDA might be a good candidate to replace terephthalic acid as the building block.
- **Ethanol:** ethanol is a base chemical that can (and is) very easily be produced from biomass. Of course it can be used as transport fuel, but it can also serve as the building block for polyethylene, the most produced polymer and for a number of other polymers, and as a solvent.

These molecules with a wide application range can serve as basis targets for the carbohydrate stream of a biorefinery, provided the production processes are optimised to make them competitive to the petrochemical counterparts. Speciality applications for the resulting side streams will then need to be found on a case by case basis.

1 Introduction

1.1 Task description in DOW

Market and consumer data: A list of products and side-streams commonly produced today will be produced. Additionally, suggestion made by the finished previous projects and CSAs concerning interesting products and side-streams that might not be produced today, but could address future niche markets, contribute to competitiveness or be produced by biomass components that today are discarded will be summarised. Gathered information will be available for Tasks 3.3; 3.4 and 3.5. (UoY, A+F, IAR and VTT)

2 Methodology

In collecting the market and consumer data for carbohydrates we have taken the following approach:

- Compiling from known studies (e.g. NREL, BREW, etc) a long list (see chapter 3) of chemicals (i.e. molecules) that have been identified as interesting intermediates or building block to be produced from carbohydrates (including also some chemicals that might be produced from other sources, oils or protein). For this list we try to find data on present production volume based on biomass/carbohydrates. (some of these molecules are today also or exclusively made from petrochemical resources).
- Making a long list (see chapter 4, paragraph 4.1 to 4.6) of products that are these days made from petrochemicals and identifying the monomers (building blocks) that are used to produce these products. As the majority of today's petrochemical molecules end up in plastics, we have started with making an inventory of plastics and their building blocks. For the plastics and the building blocks we have compiled known production volumes and prices for EU-27 from the Eurostat Prodcom database, which lists data of over 4000 intermediary products. Data of 2007 are used, since this is the most recent complete listing.
- Listing (see paragraph 4.9) today's known polymers and building blocks that are made exclusively or partly from carbohydrates/biomass and collecting data on production volume, source etc.
- By comparing the data from chapter 3 and 4, we can identify today's petrochemical building blocks that can also be produced from biomass, and because we have information of present volume produced and price we can identify the most promising building blocks to be produced via biorefinery.
- Some of the building blocks used today might be replaced by a biomass building block that is not identical, but resembles the petrochemical one. Starting from our knowledge on polymer science we can identify the promising candidates. These biomass building blocks might become interesting biorefinery candidates on a longer timescale than the previous group.
- To complete our listing we also identify the most promising molecules with interesting production volumes or price that have other applications than in polymers (paragraph 4.7 and 4.8), and compare this listing with list 1 to identify additional interesting building blocks.
- In chapter 5 we have compiled known data on present applications and volumes of carbohydrates in non-food, non-feed applications.

Since it is our believe that a biorefinery can only successfully be installed as there is a significant output in volume of molecules that are needed on the market, our focus will be on molecules/building blocks that have a sufficiently large market in terms of volume, and we will add to this some interesting products with small volume but high value.

In taking molecules instead of end products as a basis, we believe we are able to make a more thorough estimation of the interesting biorefinery candidates. There are obviously far more end products than there are intermediate building blocks, which makes the link between interesting biorefinery output (which clearly can be defined in terms of molecules) and the end markets more tangible. An additional advantage is that production volume and price of these molecules are known, which makes the identification of the interesting candidates easier and better founded.

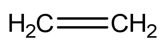
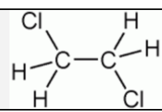
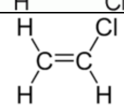
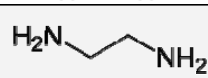
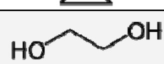
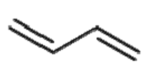
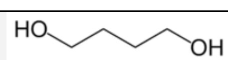
3 Chemical building blocks

3.1 C2 Building blocks

3.1.1 Ethanol

Nowadays less than 10% of the world ethanol production is produced by chemical synthesis starting from crude oil or gas and coil, while more than 90% is derived from fermentation using agricultural biomass as feedstock (Patel 2006). The latter process is considered technically mature, although still many challenges can be defined (e.g. shift from sugar crops to lignocellulose). There are three major uses of ethanol: food industry (10%, mainly beverage), chemical industry (21%, as solvent or building block for chemical synthesis) and fuel (69%, fuel or fuel additive).
Ethanol was not considered a top 30 candidate in the PNNL report; in fact no C2-building block at all are (Werpy and Petersen 2004). However, substantial growth can be expected if bioethanol could be used to synthesize bulk polymers and other (bulk) chemicals from biomass.

Table 3.1 Derivatives of ethanol

Chemical building block		Route from ethanol	World production (t/a)	Biobased world production (t/a)
Ethanol		-	31.500.000 (2003)	30.000.000
Ethylene		Dehydration	107.000.000[1]	150.000 (1980-1990)
1,2 Dichloroethane		Dehydration to ethylene, chlorination	20.000.000	-
Vinyl chloride		Dehydrochlorination of dichloroethane	31.100.000	-
Ethylenediamine		Reaction of 1,2-dichloroethane and ammonia	500.000 (1998)	-
Ethylene oxide		Oxidation of ethylene	15.000.000[a]	-
Ethylene glycol		Hydrolysis of ethylene oxide	6.700.000	-
Butadiene		Dehydrogenation of ethanol, condensation, dehydration[2]		-
1,4-butanediol		Via butadiene[2]		-

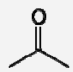
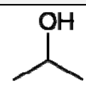
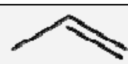
1. Source: Wikipedia
2. Source: (Haveren, Scott et al. 2008)

3.2 C3 Building blocks

3.2.1 Acetone

Acetone is an important chemical compound and more than 3 million tonnes are produced annually. It is possible to obtain acetone via fermentation in the ABE (acetone-butanol-ethanol) fermentation process. The ABE process is now widely studied with different organisms and feedstocks and it will take probably 5-10 years before this process is economical viable for the production of acetone, butanol and ethanol (Haveren, Scott et al. 2008).

Table 3.2 Derivatives of acetone

Chemical building block		**Route from acetone**	**World production (t/a)**	**Biobased world production (t/a)**
Acetone		-	3.000.000	?
2-propanol		Reduction of acetone	50.000.000	-
Propylene		Dehydration of 2-propanol		-

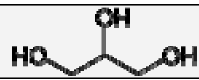
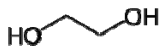
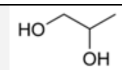
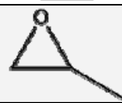
Comparable to ethylene, propylene could in theory be derived from 2-propanol by dehydration. Propylene is the raw material for a wide variety of products including polypropylene, a versatile polymer used in packaging and other applications. Total world production of propylene is currently about half that of ethylene, approximately 50 Mt/a. Currently biochemical production of isopropanol by fermentation processes has not been widely explored (Scott, Haveren et al. 2010), but one patent has described the production of isopropanol by engineered microorganisms (Subbian, Meinhold et al. 2008). It is also possible to produce isopropanol from biobased 1,2 propanediol (see section below).

3.2.2 Glycerol

Glycerol is a byproduct from biodiesel production. It is a very attractive starting material for the production of propanediols and other derivatives.
An example of industrial activities on this subject is the announcement in May 2007 of the joint venture between Cargill and Ashland to produce 1,2-propanediol from glycerol in Europe (www.cargill.com). At this moment no more additional information is provided on the progress.

Thermo-chemical conversions of glycerol to propylene glycols as presented in table 3.3 have been studied to quite some extent over the past decades. However, it is also possible to produce 1,3-propanediol by means of fermentation from biomass sources such as glucose or glycerol. This process is used by Du Pont for the production of PDO for polyester synthesis.

Table 3.3 Derivatives of glycerol

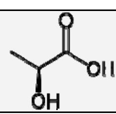
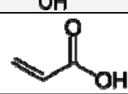
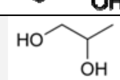
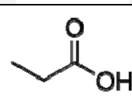
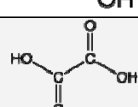
Chemical building block		Route from glycerol	World production (t/a)	Biobased world production (t/a)
Glycerol		-	950.000[1]	
Ethylene glycol		Conversion of glycerol[2]		
1,2-propanediol		Conversion of glycerol[2]	1.500.000	65.000 (planned by Ashland/Cargill)
1,3-propanediol (PDO)		• Conversion of glycerol[2] • Fermentation	80.000	45.000 (Du Pont) via fermentation process.
Epichlorohydrin		Conversion of glycerol		• Solvay (Epicerol) • Dow (150.000 Mton/a)
Ethylene oxide		Via 1,2-propanediol[3]		
Propylene oxide		Via 1,3-propanediol[3]		

1. Source: wikipedia
2. Thermo-chemical conversions; result in general in a mixture of products depending on the type of catalyst used.
3. Source (Haveren, Scott et al. 2008)

3.2.3 Lactic acid

Lactic acid is a bifunctional molecule as it has both a carboxylic acid and a hydroxyl group, which makes it a very interesting molecule for the production of e.g. polymers. World production of lactic acid and -salts and esters is around 260.000 t/a (Jim Jem, van der Pol et al. 2010), and nearly this entire production is by fermentation of sugar-rich crops.
Major uses of lactic acid include food (48%), industrial applications (39%) and pharma/personal care (13%) (Patel 2006). Annual growth is around 10% and is expected to result primarily from lactic acid based biodegradable polymers (i.e. PLA) and lactate solvents.

Table 3.4 Derivatives of lactic acid

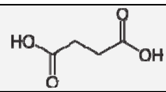
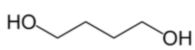
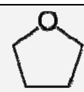
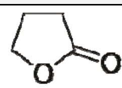
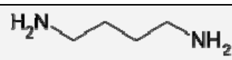
Chemical building block		Route from lactic acid	World production (t/a)	Biobased world production (t/a)
Lactic acid		-	See biobased production	260.000
Acrylic acid		Dehydration of lactic acid	2.000.000	-
1,2-propanediol		Reduction of lactic acid	1.500.000	-
Propionic acid		Reduction of lactic acid	130.000	-
Ethanedioic acid (oxalic acid)		Oxydation of lactic acid, decarboxylation	124.000	-

3.3 C4 Building blocks

3.3.1 Succinic acid

At the moment succinic acid is mainly produced from butane/butadiene via maleic acid with a production volume of 30-50 kt/y. Derivatives of succinic acid are announced to have a potential of hundreds to thousands tons.
Biobased production of succinic acid is possible though fermentation processes. Key challenges include significant reduction of production costs in order to become competitive with the petrochemical route. A number of industrial activities has been undertaken for the production of biobased succinic acid. In France the biobased succinic acid plant of Bioamber produces renewable succinic acid from wheat derived glucose (www.bio-amber.com).

Table 3.5 Derivatives of succinic acid

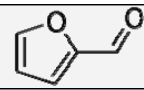
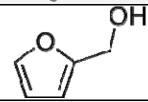
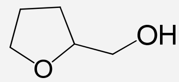
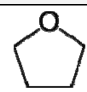
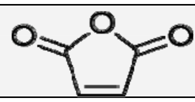
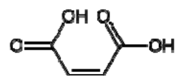
Chemical building block		Route from succinic acid	World production (t/a)	Biobased world production (t/a)
Succinic acid		-	30.000-50.000	2000 t/y (Bioamber, France)
1,4-butanediol (BDO)		Comparable to conversion from maleic acid	1.000.000	?
Tetrahydrofuran (THF)		Comparable to conversion from maleic acid	200.000	-
γ-butyrolactone (GBL)		Comparable to conversion from maleic acid	?	-
1,4-butanediamine			?	-

3.4 C5 Building blocks

3.4.1 Furfural

Furfural is the starting material for industrial production of furan compounds. It is produced from (waste) biomass that is rich in C5-sugars. Furfural is a degradation product from sugar hydrolysis, and besides furfural also other degradation products are formed such as alcohols and organic acids. Removal of these impurities is expensive, and optimization of the furfural production process is necessary (Patel 2006). The chemistry of converting furfural to its derivatives is well developed.

Table 3.6 Derivatives of furfural

Chemical building block		**Route from furfural**	**World production (t/a)**	**Biobased world production (t/a)**
Furfural		-	See biobased production	200.000-300.000
Furfuryl alcohol		Hydrogenation of furfural	120.000-180.000	-
Tetrahydrofurfuryl alcohol		Hydrogenation of furfuryl alcohol	?	-
Tetrahydrofuran (THF)		Hydrogenation of furfural[1]	200.000[2]	-
Maleic anhydride		Ring cleavage of furfural	?	-
Maleic acid		Hydrolysis of maleic anhydride	?	-

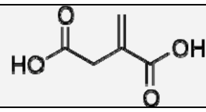
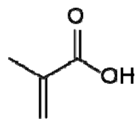
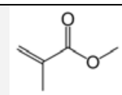
1. Is a biobased alternative for THF production via 1,4-butanediol. THF could in the future also be produced from succinic acid or fumaric acid
2. Source: Wikipedia

3.4.2 Itaconic acid

Itaconic acid is an interesting building block as its chemistry is similar to that of maleic acid and maleic anhydride. Maleic acid and maleic anhydride are for example used as monomers in the production of acrylate based polymers (see section 4.2) and thermoset resins (see section 4.6).
Itaconic acid can be produced via the following routes:

- Itaconic acid is an intermediate in the production of methacrylic acid from citric acid (Carlsson, Habenicht et al. 1994). However, this route requires very high pressures and temperatures and is not economically viable.
- At this moment itaconic acid is produced by fermentation of fungi with a market volume of about 15,000 t/a (in 2001) and with a cost price of 2500 €/ton. New biotechnology approaches could lead to higher productivity and the use of alternative substrates may reduce costs and thus open the market for new and increased applications (Willke and Vorlop 2001).
- As the fermentation route has a vary high cost price, the route via production of itaconic acid in genetically modified plants may have more potential. Itaconic acid can be produced in starch potato plants where the itaconic acid is accumulated in the storage organs (Koops, De Graaff et al. 2009). Also plant-based production systems are developed where methacrylate or methacrylate equivalents such as itaconic acid are produced by genetically engineering existing metabolic pathways in cellulosic ethanol biomass crops such as switchgrass (Van Beilen and Poirier 2008). Challenges for the production of itaconic acid in plants are isolation and purification routes to isolate the itaconic acid from the plant tissue.

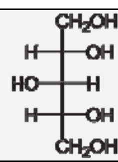
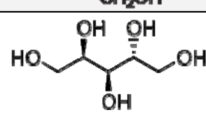
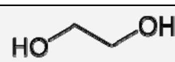
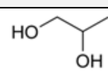
Table 3.7 Derivatives of itaconic acid

Chemical building block		Route from itaconic acid
Itaconic acid		-
Methacrylic acid		Decarboxylation of itaconic acid
Methyl methacrylate		Methyl ester of methacrylic acid

3.4.3 Xylitol/Arabitol

Xylose and arabinose are the main pentoses or C5-sugars in hemicellulose. Hydrogenation of these sugars yields the isomers xylitol and arabitol. At the moment there is limited commercial production of xylitol and no commercial production of arabitol. Xylose and arabinose can be obtained from lignocellulosic biomass but a major challenge is to obtain clean feed streams of these sugars in a low-cost way (Werpy and Petersen 2004).
However, these sugar alcohols have major potential as they can be converted to glycols such as ethylene glycol and 1,2 propanediol.

Table 3.8 Derivatives of xylitol/arabitol

Chemical building block		Route from xylitol
Xylitol (from xylose)		-
Arabitol (from arabinose)		-
Ethylene glycol		Hydrogenolysis of xylitol
1,2-propanediol		Hydrogenolysis of xylitol

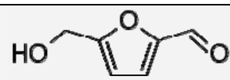
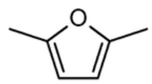
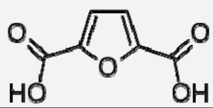
3.5 C6 Building blocks

3.5.1 HMF

HMF or 5-hydroxymethylfurfural can be obtained by dehydration of C6-sugars with fructose as preferred substrate. Because fructose can be readily obtained on bulk scale by enzymatic isomerisation of glucose, cellulose hydrolysate could also be used as feedstock.
Processes for the production of HMF are still on lab scale (one pilot scale?) and reaction media used range from organic solvents to water. A major problem in HMF production are the numerous side reactions that reduce yields and complicate purification. Main side

products are formic acid and levulinic acid, and as such HMF can be regarded as intermediate in the conversion of C6-sugars to levulinic acid.
HMF can be polymerised to form special phenolic resins but moreover it is an attractive building block for further derivatisation to difunctionalised molecules that can be used as monomers for bulk polyesters and polyamides. Of special interest is 2,5-furan dicarboxylic acid as it has structural similarities to terephthalic acid, the most important aromatic dicarboxylic acid.

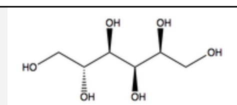
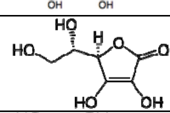
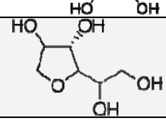
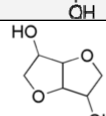
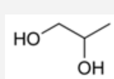
Table 3.9 Derivatives of HMF (Patel 2006)

Chemical building block		**Route from HMF**
HMF		-
2,5-dimethylfuran (DMF)		?
2,5-furan dicarboxylic acid		Oxidation

3.5.2 Sorbitol

Sorbitol is produced on large industrial scale by catalytic hydrogenation of glucose. It is a batch process with a production volume of 1.1 Mton/y (Patel 2006). Further development could be the industrial implementation of a continuous process. Other research routes include the development of milder processing conditions and/or other catalysts to replace the nickel catalysts that are used nowadays. Fermentative routes are also suggested (Akinterinwa, Khankal et al. 2008) but is unlikely that these routes can replace the technically mature catalytic hydrogenation process.
Besides food, sorbitol is also the raw material for other products such as surfactants (Von Rybinski and Hill 1998) and polyurethanes (see section 4.4).

Table 3.10 Derivatives of sorbitol

Chemical building block		**Route from sorbitol**	**World production (t/a)**	**Biobased world production (t/a)**
Sorbitol		-	1.100.000	
Ascorbic acid		Combined biotechnological/chemical process	80.000	
Sorbitan		Dehydration	50.000[1]	
Isosorbide		Selective dehydration	800	High potential[2]
1,2-propanediol		Hydrogenolysis	900.000	Medium to long-term goal; development of efficient catalyst

1. Production volume of sorbitan esters; Sorbitan is esterified with fatty acids to sorbitan esters and used as lipophilic non ionic surfactants
2. Isosorbide has potential as plasticizer building blocks and as monomer for polyesters and polyurethanes (polysorb p),), f.i. PET-like polymers. Roquette has a demonstration unit for isosorbide diesters (plasticizer) with a capacity of 100 ton/y.

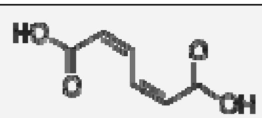
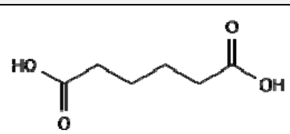
3.5.3 Lysine

Production of nitrogen-containing bulk chemicals from biomass is in a less advanced state compared to oxygenated bulk chemicals such as glycols. Biobased routes from lysine to caprolactam for the production of nylon have perhaps received the most attention (Haveren, Scott et al. 2008).
In the 1950s fermentation with *Corynebacterium glutamicum* was found to be a very efficient production route to L-glutamic acid. Since this time biotechnological processes with bacteria of the species *Corynebacterium* developed to be among the most important in terms of tonnage and economical value. L-lysine is a bulk product nowadays with a production volume of 640 kton/y (Hermann 2003; Hermann, Blok et al. 2007) and a cost price of 1200 €/ton.
Other routes that are currently under investigation are the development of genetically modified plants with elevated levels of certain amino acids such as lysine. In this way amino acids that are naturally produced by plants can be produced at higher concentration levels by over-expression of certain structural genes. An example is the production of lysine in starch potato plants (Van Der Meer, Bovy et al. 2001; Vorst, Van Der Meer et al. 2002)

3.5.4 Muconic acid

Adipic acid (hexanedioic acid or 1,4-butanedicarboxylic acid) is the most important aliphatic dicarboxylic acid. It is primarily used for the production of nylon 6,6 (see 4.5).
In the Brew-report several processes for the production of adipic acid are described, whereas only one process involves a biomass substrate. This is the biosynthesis of cis,cis-muconic acid by fermentation of glucose, followed by catalytic hydrogenation to adipic acid.
Besides optimization of production organisms, also recovery of adipic acid from aqueous medium at purity levels needed for polymer-grade products and catalytic conversion of muconic acid to adipic acid needs to be further investigated (Patel 2006).

Table 3.10 Derivative of muconic acid

Chemical building block		**Route from muconic acid**
Cis,cis-muconic acid		-
Hexanedioic acid (Adipic acid)		Hydrogenation of muconic acid

4 Potential markets

4.1 Introduction

Today's petrochemical industry produces a wide range of chemicals from naphtha, which can be considered a side stream of the production of fuels from crude oil. The larger part of these chemicals are used for the production of polymer materials. In Europe more than 50 Mton of polymers are produced each year (figure 4.1), of which polyethylene and polypropylene are the largest products. Most of these polymers can in principle also be made from biomass. The volume sold of the various polymers thus gives an indication of the potential size of demand for the various building blocks that can be produced from biomass. In this chapter the different current polymers, the building blocks from which they are produced and the volume

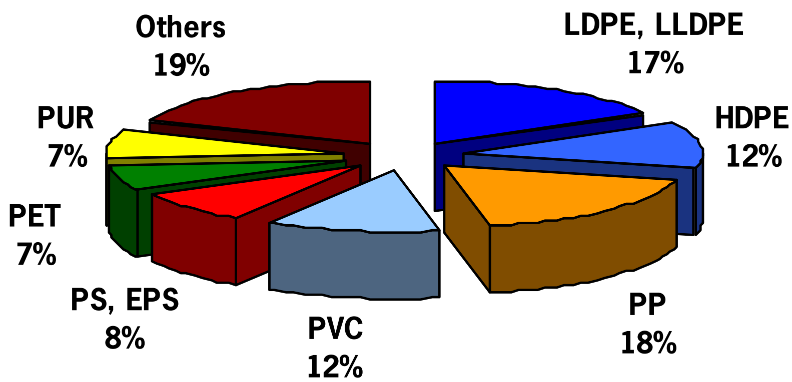


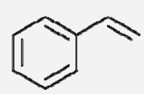
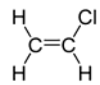
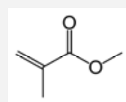
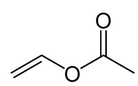
Figure 4.1. Plastics production in Europe, total 52.5 Mtonnes, EU 27 + Norway and Switzerland. APME 2007

sold in the EU are listed. The 'volume sold' as listed in the tables refers to the total volume of these building blocks sold, not the volume used for that specific application.
The various building blocks are linked to the inventory made in the previous chapters. Next to the polymers also solvents and plasticisers are treated.

4.2 Vinyl polymers

Vinyl polymers are in terms of volume by far the largest group of polymers applied. Table 4.1 lists the most common vinyl polymers. As can be seen over 15 Mton of polyethylene is produced in Europe. The feedstock for polyethylene is ethylene. In Europe over 22 Mton ethylene is produced. Ethylene not only serves as the building block for polyethylene, but also for a large number of other chemicals and polymers. For instance for the production of styrene it is combined with benzene and for the production of vinylchloride it is combined with chlorine.
Ethylene is a C2 building block that can be made from biomass (see chapter 3.2)

Table 4.1 Vinyl polymers and their building blocks. Production data for EU-27, 2007 (Eurostat PRODCOM)

Polymer	Polymer (ton/y)	Monomers		Monomer (ton/y)	Possible (bio)synthetic route
PE	15.406.627	Ethylene	$H_2C{=}CH_2$	22.756.632	Via ethanol, see 3.1.1
PP	10.449.207	Propylene		10.449.207	Via acetone, see 3.2.1
PS	4.391.619	Styrene		6.277.404	Most conceivable route via lignin; outside scope of this report
PVC	6.608.755	Vinylchloride		6.163.573	Via ethanol, see 3.1.1
PMMA	292.633	Methylmetha crylate		no data[a]	Via itaconic acid, see 3.4.2
PVA	293.591	Vinylacetate		no data	Via ethylene or acetic acid

[a] World production in the order of 2.4 Mton/y (van der Meer and Bovy)
PE polyethylene
PP polypropylene
PS polystyrene
PVC polyvinylchloride
PMMA polymehtylmethacrylate
PVA polyvinylcetate.

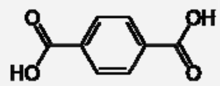
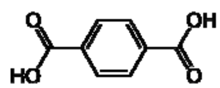
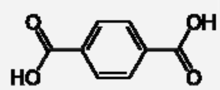
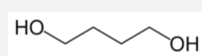
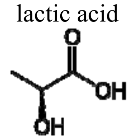
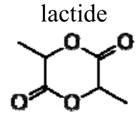
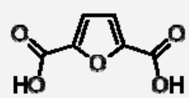
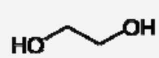
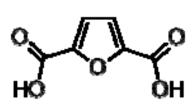
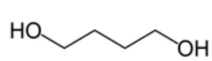
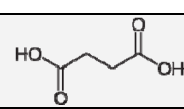
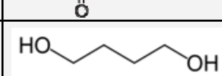
4.3 Polyesters

Polyesters are usually made by combining two different monomers, a diol, containing two alcohol groups and a diacid containing two carboxyl groups. Just like carbohydrates, the building blocks for polyesters contain a number of oxygen groups. Polyesters are therefore a very interesting candidate to be produced from biomass. The most important polyesters produced today, including their building blocks are presented in table 4.2.

A major building block for the polyesters is terephthalic acid. The production volume reported also includes the production of phthalic anhydride, which is a building block for aramid fibres (NOMEX, used for fireman suits etc.) but is mainly used for the production of phthalate plasticizers. Phthalic acid and terephthalic acid are not likely to be produced from carbohydrates, but a molecule with similar structure is 2,5 furandicarboxylic acid. This building block might lead to polymers with similar properties as the major polyesters.

Especially the dialcohols are of great interest. Ethylene glycol, of which 1.5 Mton is produced, but also 1,3 propanediol and 1,4 butanediol are building blocks that can relatively easily be produced from biomass and have potentially a wide application range, and can penetrate into an existing market.

Table 4.2 Thermoplastic polyesters and their building blocks. Production data for EU-27, 2007 (Eurostat PRODCOM)

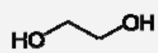
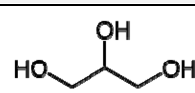
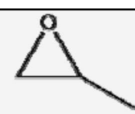
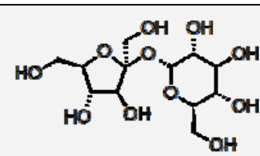
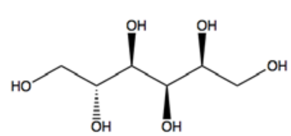
Polymer	**Polymer (ton/y)**	**Monomers**		**Monomer (ton/y)**	**Possible (bio)synthetic route**
PET	3.226.436	Terephthalic acid		4.374.145[a]	None
		Ethylene glycol		1.516.698	• Via ethanol, see 3.1.1 • Via glycerol, see 3.2.2 • Via xylitol, see 3.4.3
PTT or PPT		Terephtalic acid		4.374.145[a]	None
		1,3 propanediol (PDO)		no data	Via glycerol, see 3.2.2
PBT		Terephthalic acid		4.374.145[a]	None
		1,4 butanediol			• Via ethanol, see 3.1.1 • Via succinic acid, see 3.3.1
PLA		lactic acid 	lactide 		See 3.2.3
PEF (Furanics)	potential market related to PET	2,5 furan dicarboxylic acid			Via HMF, see 3.5.1
		Ethylene glycol		1.516.698	• Via ethanol, see 3.1.1 • Via xylitol, see 3.4.3
PEF (Furanics)	potential market related to PET	2,5 furan dicarboxylic acid			Via HMF, see 3.5.1
PBF		1,4 butanediol			• Via ethanol, see 3.1.1 • Via succinic acid, see 3.3.1
PBS	GS Pla[b] Bionolle	Butanedioic acid (Succinic acid)			See 3.3.1
		1,4 butanediol			• Via ethanol, see 3.1.1 • Via succinic acid, see 3.3.1

[a] This figure is for ‘phthalic anhydride, terephthalic acid and its salts’
[b] (Bechthold, Bretz et al. 2008)
PET polyethylene terephthalate,
PTT polytrimethylene terephthalate
PBT polybutylene terephthalate
PLA polylactic acid
PEF polyethylene furandicaboxylicacid
PBF polybutylene furandicaboxylicacid
PBS polybutylene succinate

4.4 Polyurethanes

Polyurethanes are applied in a wide range of applications, for instance as rigid foams for building applications, and as flexible foams for mattresses. Polyurethanes are produced by combining an isocyanate with an alcoholic building block (see table 4.3). The alcohol build ing blocks can easily be replaced by biobased building blocks.

Table 4.3: Polyurethanes and their building blocks. Production data for EU-27, 2007 (Eurostat PRODCOM)

Polymer	Polymer (ton/y)	Monomers		Monomer (ton/y)	Possible (bio)synthetic route
Polyurethanes	3.931.318	Ethylene glycol		1.516.698	• Via ethanol, see 3.1.1 • Via glycerol, see 3.2.2 • Via xylitol, see 3.4.3
		Glycerol		332.836	See 3.2.2
		Propylene oxide		2.760.231	Via glycerol, see 3.2.2
		Ethylene oxide		2.362.358	• Via ethanol, see 3.1.1 • Via glycerol, see 3.2.2
		Sucrose		130.000.000[1]	Extraction of sugar cane and sugar beet
		Sorbitol[2]		600.000	See 3.5.2

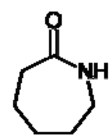
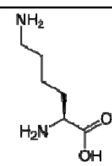
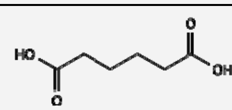
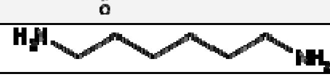
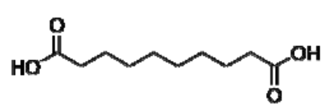
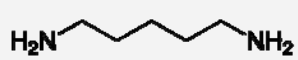
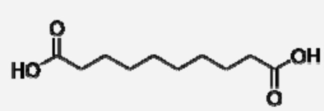
1. Source (Patel 2006)
2. Sorbitol can be polymerised to polyetherpolyols that can be used as intermediate for the synthesis of polyurethanes (Patel 2006).

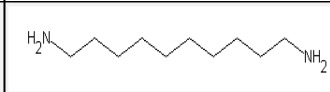
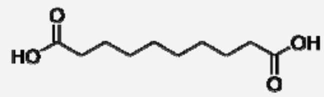
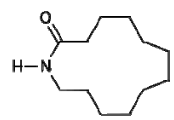
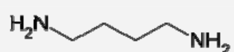
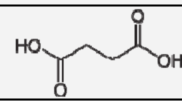
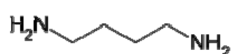
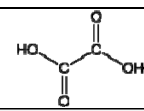
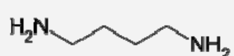
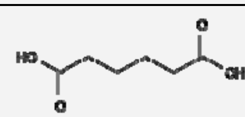
Also for this type of polymer ethylene glycol is an interesting building block. Furthermore glycerol is used, but also other alcohol containing molecules, like sucrose and sorbitol. These are of course already based on biomass. Propylene oxide and possibly ethylene oxide are used in rigid polyurethanes.
Another product that is produced from ethylene oxide is polyethyleneglycol. Production in Europe of this group of polymers is 1.9 Mton.

4.5 Polyamides

Polyamides or nylons are produced from a dicarboxylic acid and a diamine or a molecule that contains both a carboxylic acid group and an amine group. Nylon 11 has always been produced from biomass, from castor oil. Many of the other nylon building blocks however can be made from carbohydrates.

Table 4.4 Polyamides and their building blocks. Production data for EU-27, 2007 (Eurostat PRODCOM)

Polymer	Polymer (ton/y)	Monomers		Monomer (ton/y)	Possible (bio)synthetic route
Polyamides total	2.553.682				
PA 6	[a]	Caprolactam			Via lysine, see 3.5.3
		Lysine (precursor to caprolactam)		125.670	See 3.5.3
PA 6,6		Hexanediamine		879.549	None
		Hexanedioic acid (adipic acid)		1.042.038	Via muconic acid, see 3.5.4
PA 6,10		Hexanediamine		879.549	None
		Decanedioic acid (sebacic acid)			Derivative of castor oil (DuPont (Zytel))
PA 5,10		Pentanediamine (cadaverine)			Via decarboxylation of lysine, see 3.5.3
		Decanedioic acid (sebacic acid)			Derivative of castor oil (DuPont (Zytel))

Polymer	**Polymer (ton/y)**	**Monomers**		**Monomer (ton/y)**	**Possible (bio)synthetic route**
PA 10,10		Decanediamine			
		Decanedioic acid (sebacic acid)			Derivative of castor oil (DuPont (Zytel))
Nylon 11		Undecane aminoacid			Derivative of castor oil (Arkema Rilsan)
Nylon 12		Lauryllactam			
PA44 (Bechthold, Bretz et al. 2008)	Experimental stage	Butanediamine			Via succinic acid, see 3.3.1
		Butanedioic acid (succinic acid)			See 3.3.1
PA42 (Bechthold, Bretz et al. 2008)	Experimental stage	Butanediamine			Via succinic acid, see 3.3.1
		Ethanedioic acid (oxalic acid)			Via lactic acid, see 3.2.3
PA46 (Bechthold, Bretz et al. 2008)	Stanyl (DSM)	Butanediamine			Via succinic acid, see 3.3.1
		Hexanedioic acid (adipic acid)		1.042.038	Via muconic acid, see 3.5.4

[a] World production 4 M ton/y (van der Meer and Bovy)

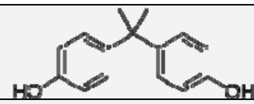
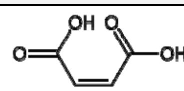
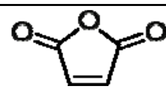
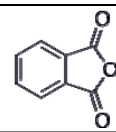
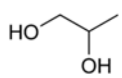
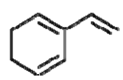
Next to these polyamides also a class of aromatic polyamides (aramides) exists, which are based on phenylenediamines and (tere)phthtalic acids. No biobased routes are presently identified for the production of these materials, but possibly the furane based molecules could be a precursor.

Also various polyesteramides, in which ester as well as amide bonds are present can possibly be produced from a variety of biobased derived molecules(Bechthold, Bretz et al. 2008). Polyesteramides are presently used for instance in rubber-like insulating materials. They can be biodegradable, but not necessarily produced from biomass. They do not at present form a large market.

4.6 Thermoset resins

Thermoset resins are often applied in combination with glass or other fibres to form composite materials. These composite materials are used in all kinds of structural applications, like bridges, bicycles, exterior panels for buses, wind turbines etcetera. The main thermoset resins are unsaturated polyesters and epoxies. They are made from a combination of different building blocks, of which some can easily be replaced by biomass building blocks.

Table 4.5 Thermoset resins and their building blocks. Production data for EU-27, 2007 (Eurostat PRODCOM)

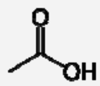
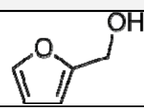
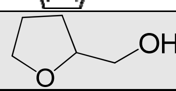
Polymer	**Polymer (ton/y)**	**Monomers**		**Monomer (ton/y)**	**Possible (bio)synthetic route**
Epoxies		Bisphenol-A		772.334	-
		Epichloro-hydrin		No data	Via glycerol, see 3.2.2
Unsaturated polyesters		Maleic acid		119.493	Via furfural, see 3.4.1
		Maleic anhydride			Via furfural, see 3.4.1
		Phthalic anhydride		4.374.145[a]	-
		Diethylene-glycol		80.907	-
		1,2-propanediol		794.229	• Via glycerol, see 3.2.2 • Via lactic acid see 3.2.3 • Via xylitol, see 3.4.3 • Via sorbitol see 3.5.2
		Styrene		6.277.404	Most conceivable route via lignin; outside scope of this report

[a] This figure is for 'phthalic anhydride, terephtalic acid and its salts'

4.7 Solvents

Some of the industrially important solvents can be produced from biomass. The most important are presented in table 4.6.

Table 4.6 Solvents that can be produced from biobased feedstock. Production data for EU-27, 2007 (Eurostat PRODCOM)

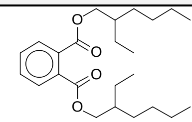
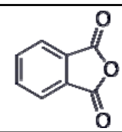
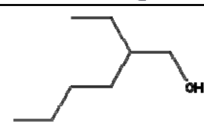
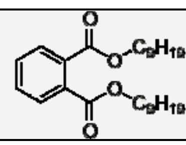
Solvent		**Volume (tonnes)**	**Possible (bio)synthetic route**
Ethanol		No data[a]	Via fermentation, see 3.1.1
Acetic acid		1.105.833	Via fermentation of ethanol
Acetone		1.667.381	Via fermentation (ABE process)
1-Butanol		381.002	Via fermentation (ABE process)
Furfuryl alcohol		No data	Hydrogenation of furfural
Tetrahydrofurfuryl alcohol		No data	Hydrogenation of furfuryl alcohol
THF (tetrahydrofuran)		No data	Via succinic acid, see 3.3.1

[a] world production 31.500.000 tonnes (2003)

4.8 Plasticisers

Plasticisers are used to soften polymers, mostly PVC. More than 90 % of the plasticisers are applied in PVC. 84 % of the plasticisers are phthalate plasticisers, 5 % are aliphatic esters. Of the phthalate plasticisers DEHP and DiNP are the most applied.

Table 4.6 Plasticisers. Production data for EU-27, 2007 (Eurostat PRODCOM)

Plasticiser	**Plasticiser (ton/y)**	**Monomers**		**Monomer (ton/y)**
Pthalate plasticisers	3.870.000			
DEHP (DOP)				
		Phthalic anhydride		4.374.145[a]
		2 ethyl hexanol		
DiNP				

[a] This figure is for ‘phthalic anhydride, terephtalic acid and its salts’
DEHP: di-ethylhexyl phthalate
DiNP: di-isononyl phthalate

The phthalic anhydride group of these plasticisers can be replaced by an isosorbide group (which is a dialcohol, see 3.5.2). Fatty acids, derived from natural oil, can be used as the long side chains.
Wageningen UR has shown that these alternative plasticisers perform equal in a variety of applications compared to the phthalate plasticisers *.

Roquette launched last June 2008 at Lestrem (France) a demonstration unit for Isosorbide Diesters with a capacity of over 100 tonnes a year (www.roquette.com/isosorb).

4.9 Current markets

Some polymers are already made from biomass, they are summarised in table 4.7.

Table 4.7 Polymers that are already (or in the near future) made from biomass. Data from Pro-bip (Shen, Haufe et al. 2009).

Polymers	Volume (world) 2007 (tonnes)	Volume (world) 2009 (tonnes)	Planned production (t/y)
PLA	74.000	154.000	
PTT	10.000	10.000	
PHA	2	80.000	
green PE	5.000	200.000	• 200.000 (Braskem 2011) • 350.000 (Dow/ Crystalsev 2011)
green PVC	not yet biobased production		60.000 ethylene for PVC production (Solvay Brazil)
PBT	no biobased production		
PBS	not yet		
green PET	not yet biobased production		
PUR	13.300	19.900	
Biobased thermosets (oil and/or carbohydrate based)	1.000.000		

PLA polylactic acid
PTT polytrimethylene terephthalate
PHA polyhydroxyalkanoate
PE polyethylene
PVC polyvinylchloride
PBT polybutylene terephthalate
PBS polybutylene succinate
PET polyethylene terephthalate,
PUR polyurethane

Non-biobased PE has a world production of 80.000.000 tonnes per year
Non-biobased PVC has a world production of 40.000.000 tonnes per year.

5 Substances current markets

5.1 Carbohydrates

Carbohydrates have a wide range of non-food applications. In these applications the carbohydrates are not so much broken down to building blocks, but are used more or less as they are produced by nature, with eventually an additional chemical modification. This approach takes advantage of the chemical structure that was built by the plants. The two main groups of carbohydrates applied in this way are the cellulosics and the starches.

Table 5.1 Technical applications of carbohydrates. Data from Pro-bip (Shen, Haufe et al. 2009) and Eurostat PRODCOM

Carbohydrates	volume (EU 27) (tonnes)	volume (world) 2007 (tonnes)	volume (world) 2009 (tonnes)	source	remarks
Cellulosics					
Cellulose and its chemical derivatives, n.e.c., in primary forms	581.465			prodcom	
Cellulose nitrate		150.000		pro-bip	
Carboxymethyl cellulose		230.000		id	
Hydroxyethyl cellulose		60.000		id	
Hyproxypropyl cellulose		10.000		id	approx. less than 10.000
cellulose plastic fibres (including regenerated cellulose and cellulose acetate)		3.500.000		id	more than 60% of global chemical grade pulp is used for regenerated cellulose; about 20% of global chemical grade pulp is used for organic cellulose esters
other cellulosics (including cellophane and rigid cellulose plastics)		500.000		id	max: ranges over the years between almost 0 and 500.000
Starches (traditional non-food use 33%, starch for ethanol 17%)					
Corrugating and paper making		2.600.000		pro-bip	
Pharmaceuticals and chemicals		700.000		id	
Other non-food (including plastics ?)		400.000		id	
Starch plastics	130.000	153.000	323.000	id	

5.2 Proteins

A number of proteins have applications in non-food markets.

Table 5.2 Production value of a number of proteins in EU 27. (source Eurostat PRODCOM)

Protein	**k €**
Casein and caseinates	900.000
Casein glues	51.028
Bone glues; other glues of animal origin (excluding casein glues)	25.519
Caseinates and other casein derivatives (excluding casein glues)	300.000
Gelatin and its derivatives; isinglass (excluding casein glues and bone glues)	762.544

No volume data are given in the PRODCOM database.

6 Conclusions

Various studies show that there is a wealth of possible molecules and products that can be produced from carbohydrates. Carbohydrates already find significant application in starch products and cellulose plastics and fibres.
However, for a biorefinery to operate in an economically sustainable way, applications for (preferably all) biomass ingredients need to be found. Presumably the optimal mix of applications will be a combination of larger volume/smaller value and smaller volume/higher value applications.

Looking at the size of possible end markets for the molecules that can be based on carbohydrates a number of main products come into view:

- **Dialcohols**: dialcohols can be used in a variety of end products, they are one of the building blocks for polyesters, they find applications in polyurethanes and in thermoset resins. From carbohydrates usually the shorter dialcohols are produced (C2 – C4). The C2 and C4 dialcohol produced from petrochemical resources already find ample application in a variety of products and these can be replaced by the biomass based variant. The C3 dialcohol is easier to produce from biomass than from petrochemical resources and this is one of the building blocks that is presently being commercialized from biomass. A special case of diol is isosorbide which can replace the phthalic acid group in phthalate plasticisers (in combination with carboxylic acid side chains) and other applications.
- **Dioic acids**: dioic or dicaboxylic acids find broad applications as one of the two building blocks for polyesters and also one of the two building blocks for polyamides. From biomass the C2, C4 and C6 dioic acid can be produced. The C6 dioic acid made from petrochemical feedstock already finds ample application. Itaconic acid is a very interesting candidate because it can serve as the basis for (methyl) methacrylate, the building block for PMMA. The longer diacids, like sebacic acid (C10) and longer are often produced from natural oils.
- **2,5 Furan dicarboxylic acid:** 2,5 FDA is a molecule that is not used in commercial applications yet. However, its steric shape is rather comparable to terephthalic acid. Terephthalic acid is found in a very broad range of applications. In many applications 2,5 FDA might be a good candidate to replace terephthalic acid as the building block.
- **Ethanol:** ethanol is a base chemical that can (and is) very easily be produced from biomass. Of course it can be used as transport fuel, but it can also serve as the building block for polyethylene, the most produced polymer and for a number of other polymers, and as a solvent.

These molecules with a wide application range can serve as basis targets for the carbohydrate stream of a biorefinery, provided the production processes are optimised to make them competitive to the petrochemical counterparts. Speciality applications for the resulting side streams will then need to be found on a case by case basis.

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