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Bulk chemicals from biomass

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Abstract: Given the current robust forces driving sustainable production, and available biomass conversion technologies, biomass-based routes are expected to make a significant impact on the production of bulk chemicals within 10 years, and a huge impact within 20–30 years. In the Port of Rotterdam there is a clear short-term (0–10 year) substitution potential of 10–15 % of fossil oil-based bulk chemicals by bio-based bulk chemicals, especially for oxygenated bulk chemicals, such as ethylene glycol and propylene glycol, iso-propanol and acetone, butylene and methylethylketone and for the replacement of methyl tertiary butyl ether (MTBE) by ethyl tertiary butyl ether (ETBE). Glycerin, as a byproduct of biodiesel production, is a very favorable short-term option for the production of ethylene and propylene glycols in the Port of Rotterdam. In the mid-term (10–20 years) there is clear potential for a bio-based production of ethylene, acrylic acid and N-containing bulk chemicals such as acrylonitrile, acrylamide and ε-caprolactam. Technologies involving direct isolation of aromatic building blocks from biomass, or the conversion of sugars or lignin to aromatics are still in their infancy. Biorefineries that are being started up today will form the stepping stones toward the chemicals mentioned above if we learn to upgrade their side streams. For main ports like the Port of Rotterdam, these developments imply that it has to consider in much closer detail those facilities it has to offer for a more bio-based chemistry and economy. © 2007 Society of Chemical Industry and John Wiley & Sons, Ltd

Keywords: bulk chemicals; biomass; Port of Rotterdam; bio-based glycols; substitution potential; biorefineries

Introduction

Being faced with the emerging economies of Asia and elsewhere and the limited success of finding new, vast, easily accessible crude oil reservoirs, the perception is growing that the end of the cheap fossil oil era is already here and that prices for crude oil and transportation fuels are likely to further increase in the years to come. This, together with the desire to become more independent with regard to feedstock supply to fulfil our energy and materials need, and the need for more sustainable (CO_2 neutral)

production methods, urges society to develop alternative sources for energy carriers and materials.

Numerous scenarios predict an increasing role for natural gas, coal and biomass at the expense of mineral oil in the first half of the twenty-first century (*www.shell.com –scenarios*). Therefore technologies, such as gas-to-liquid processes, direct alkane functionalization and biomass conversion, will be studied much more intensively than heretofore. These technologies are expected to take another 20–30 years to fully mature. Furthermore, in the long term, biomass will be the *only* reliable resource for organic carbon-based chemicals

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and materials. It may be expected that during this transition the impact of biomass and bio-based chemistry will already significantly affect the production of bulk chemicals in the short to mid-term (0–20 years). Whereas gas-to-liquid processes, using syngas based on biomass, are likely to have an impact on the production of bulk chemicals in the next 20–30 years and will lead to additional bio-based bulk chemicals. this route (and potential products stemming from pyrolysis oils) is not taken into account within the scope of this study. We give an overview of potential routes to bulk chemicals based on biomass, wherein – in so far as possible – the functionality present in the biomass is kept intact in order to produce the bulk chemical.

While crude oil is predominantly being processed by oil refineries to energy carriers and chemicals (natural gas and coal are mostly used for generating heat and/or electricity), we may assume that in a more bio-based society we will see the establishment of biorefineries coproducing energy carriers and feedstocks that can serve for the production of (bulk) chemicals.[1,2]

In recent years, numerous review articles have appeared that give an overview of the potential of biomass as a source of alternative energy carriers or as a source of alternative feedstock for chemicals and materials. Huber and Corma's recent review gives an overview of the options of using biomass for the production of energy carriers.[3] Most of the reviews or roadmaps related to the production of chemicals are rather general in nature and focus on converting lignocellulosic (mostly carbohydrate-based) materials into bio-based platform chemicals, having a *unique structure* different from today's bulk chemicals.

In that respect the DOE/NREL report, *Top Twelve Building Blocks from Biomass*, is one of the better known roadmaps.[4] It chiefly describes carbohydrate-based building blocks with a unique structure. From a technological point of view, such building blocks could be used for the production of new generation bio-based (bulk) chemicals and polymers with a unique structure. Such building blocks already have shown their versatility in products such as surfactants, biolubricants and (thermoplastic) resins suitable, for example, as powder coating or resins for decorative paints.[5,6] In these developments, the aim will be to optimize production chains of both building blocks and materials to ultimately render these materials price competitive with petrochemical-based products present in the market.

With regard to bulk chemicals in the short to mid-term, a much larger impact might be expected from the production of bio-based bulk chemicals with a structure identical to today's bulk chemicals. This could, for example, lead to bio-based ethylene, butadiene, acrylic acid or styrene. If society succeeds in developing effective bio-based synthesis routes into these bulk chemicals, the chemical industry could largely profit from the existing infrastructure in which the production of bulk chemicals, polymers and materials based on crude oil as a feedstock has been already optimized to a very large extent.

In this review we look at the potential production of bio-based chemicals with a structure identical to today's platform chemicals and bulk chemicals. Within this overview, platform chemicals are defined as chemicals that serve as a platform for the synthesis of numerous bulk chemicals. Bulk chemicals are defined as chemicals being produced in quantities larger than 50,000 tonnes/annum. The current state of technology is briefly described and a judgement is made about further technology improvements needed to develop economically viable processes. We include a case study of how bio-based routes might influence the currently produced petrochemical based bulk chemicals in the Port of Rotterdam.

Current production of bulk chemicals in the Port of Rotterdam

Today's chemical industry processes crude oil into a limited number of base fractions.[7] Using numerous cracking and refining catalysts and using distillation as the dominant separation process, crude oil is refined into fractions such as naphtha, gasoline, kerosene, gas oil and residues. The relative volumes of the fractions formed depend on the processing conditions and the composition of the crude oil. The naphtha fraction is subsequently used as a feedstock for the production of just a few platform chemicals from which all the major bulk chemicals are subsequently derived. An important characteristic of the naphtha feedstock is that, unlike biomass, it is very low in oxygen content. The majority of bulk chemicals, such as those produced in the Port of Rotterdam, can be produced based on just six platform chemicals (ethylene, propylene, C4-olefines, and the aromatics benzene, toluene and xylene [BTX]).

In the Port of Rotterdam, approximately 12 million tonnes of platform chemicals and bulk chemicals derived thereof, are produced annually (Fig. 1); aromatic building blocks represent the largest part with 4.9 million tonnes. Compared to a worldwide production volume of about 250–300 million tonnes of base chemicals, the Port of Rotterdam produces as much as 4–5 % of the total world production of these chemicals!

These hydrogen- and carbon-containing platform chemicals are subsequently used for instance as solvents (benzene, toluene), starting material for polymers (ethylene, propylene, butadiene) or are further functionalized via the introduction of elements such as oxygen, nitrogen or chloride.

The quantities of ethylene produced based on naphtha are as high as ca. 4 million tonnes/annum in the Netherlands as a whole (approximately 1 million tonnes of which is produced in the Port of Rotterdam). Ethylene is subsequently converted into various other chemicals (Fig. 2) as well as being used for the synthesis of various grades of polyethylene. In the Port of Rotterdam, products like ethylene oxide, ethylene glycol and vinyl chloride based on ethylene are being made in quantities of approximately 1,000,000 tonnes/annum. These base chemicals are used for the production of a whole variety of different products including polyvinylchloride, surfactants and constituents of polyesters and polyurethanes.

Based on naphtha propylene is also obtained, which subsequently acts as platform chemical to derive bulk chemicals

Figure 2. Summary of the ethylene platform.

such as propylene oxide, propylene glycol (1,2-propanediol), allyl alcohol and 1,4-butanediol (Fig. 3), via chemical processes known as ethoxylation, hydroxylation, isomerization, hydroformylation and hydrogenation.

As with ethylene-based products, these bulk chemicals function as building blocks for a variety of products including polymers and solvents (for example, tetrahydrofuran based on butanediol). Chemicals produced via this route in the Port of Rotterdam amount to more than 2.6 million tonnes/annum.

Besides the bulk chemicals produced from ethylene and propylene in the Port of Rotterdam, ethylene and especially propylene, also act as raw materials for important other chemicals such as acrylic acid, acrylonitrile and acrylamide (Fig. 4). Acrylic acid, acrylonitrile and acrylamide are important feedstocks for the production of polymers such as poly(acrylate)s, rubbers and poly(acrylamide)s. These products are not produced by the Port of Rotterdam; propylene is used by companies in Europe to produce chemicals such as acrylonitrile.

A relatively small amount – about 450,000 tonnes – of C4 olefines (Fig. 5) is produced from naphtha in the Port of Rotterdam.

Next to ethylene, propylene and butylene, bulk aromatic compounds such as benzene act as platform chemicals.

Based on naphtha, a mixture of aromatic bulk chemicals consisting of benzene, toluene and different xylenes, known as B,T,X is produced (Fig. 6). These aromatic platform
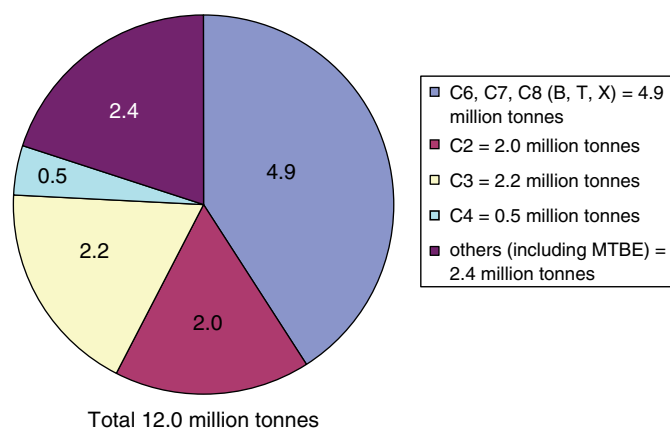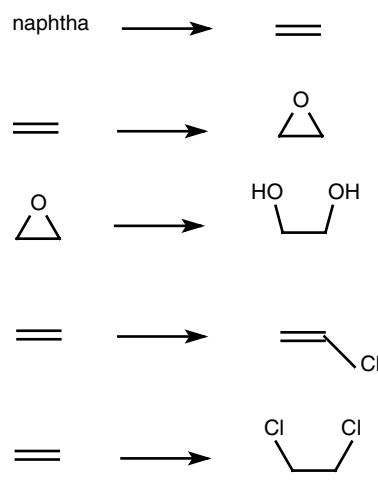

Figure 1. Production of platform chemicals by the Port of Rotterdam divided by category (production of MTBE is planned to be replaced by ETBE within a few years).
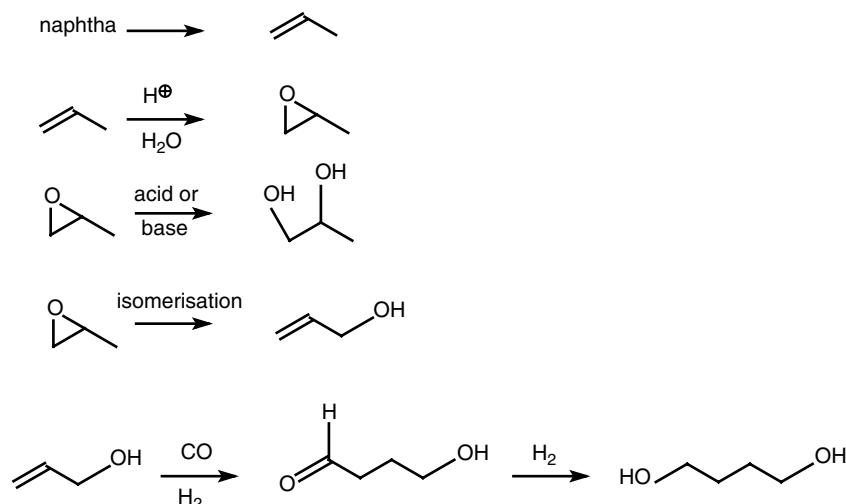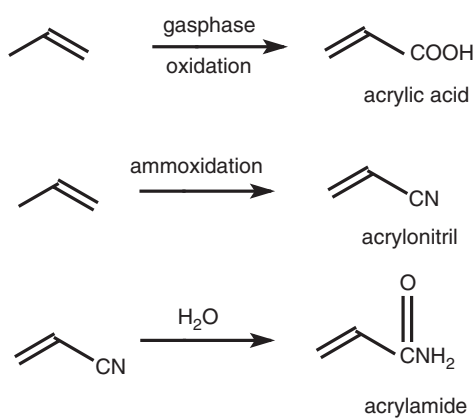
Figure 3. Summary of the propylene platform.

Figure 4. Formation of acrylic acid, acrylonitrile and acrylamide starting from propylene.
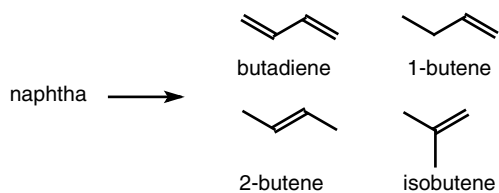

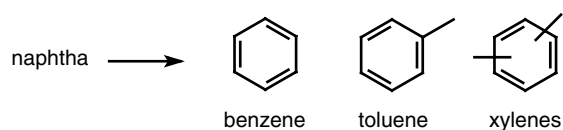Figure 5. Formation of different C4 olefines from naphtha.

Figure 6. Generation of first-generation aromatics based on naphtha.

chemicals are subsequently either converted into other bulk chemicals (Fig. 7), or used directly as solvents. In the Port of Rotterdam overall about 4.9 million tonnes of aromatics are produced and converted into bulk chemicals.

Although, in principle, almost all organic bulk chemicals produced in the Port of Rotterdam can to a very significant extent potentially be based on biomass, in 2007 the production of these bulk chemicals from biomass is negligible.

Potential production of bio-based platform and bulk chemicals

Next to technological developments, price differences between their respective feedstocks will, to a large extent, determine whether part of our bulk chemicals will be based on biomass instead of crude oil in the near future. Table 1 gives an overview of recent prices of several important
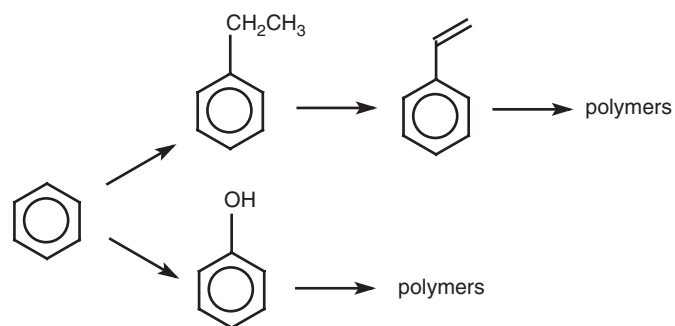

Figure 7. Conversion of benzene into styrene and phenol and subsequent uses.

Table 1. Market prices of selected bulk chemicals (Chemical Marketing Reporter Sample reports Europe-November 2006) in €/Metric tonne. Bio-based feedstocks serving as a potential source for the production of the bulk chemicals are put at the same row in the table.

Bulk chemical	Price	Potential bio-based feedstock	Price
Ethylene	900	Sucrose/Sugar	200–400
Ethanol	700	Sucrose/Sugar	200–400
Ethylene glycol	770	Glycerine	200–400
Ethylene oxide	1370		
Vinyl chloride	800		
Propylene	865		
Propylene glycol	1200	Sorbitol	300–400
Propylene oxide	1430		
Isopropanol	910		
1,4-butanediol	1850	Glycerin	200–400
Acrylic acid	1450–1600	Lactic acid	1350
Methyl Methacrylate	1500–1700	Citric acid*	800
Butadiene	890		
Methylethylketone	950		
Benzene	780	Lignin	<200
o-p-Xylenes	830		
Toluene	700		
Styrene	1000–1100		
Phenol	1220		
Phthalic acid anhydride	1200		
Caprolactam	1700	L- Lysine*	2000

*: From: "Industrial Biotechnology and Sustainable Chemistry", Royal Belgian Academy Council of Applied Science", 2004.

petrochemical-based bulk chemicals, compared to prices of important potential bio-based feedstocks. Of the bulk chemicals mentioned in Table 1, potential bio-based routes are described in the subsequent paragraphs of this review. As a general rule it can be said that prices of fossil oil-based feedstocks have increased whereas prices of biomass-based feedstocks have slowly and steadily decreased.[8]

Biomass production and potential use

Estimates of the amounts of biomass produced annually depend on the resource. According to Eggersdorfer *et al.,* the world biomass production amounts to 170,000 million tonnes per annum of which only 3% is used for human consumption (food and non-food).[9] In fact, there is agreement that biomass production is sufficient to feed all people, to provide the population with the required organic materials and to make a contribution to our energy needs.[10]

The current usage of biomaterials is by no means restricted to food and feed. Even neglecting the massive use of wood as a construction material, the amount of biomass used for materials clearly already surpasses the total combined usage of all synthetic thermoplastic and thermoset materials.

For the majority of these materials there is no competition between food or feed or non-food uses. This demonstrates that when it comes to material production, the production of more bio-based materials, as such, will not have a price-enhancing effect on food products. This effect is probably restricted to the production of first-generation biofuels. Despite the massive use of biomass for non-food applications by the timber or paper industries, for example, the current petrochemical industry relies heavily on fossil feedstock containing only carbon and hydrogen as elements.

Biomass consists of lignocellulosic and related materials (70–75% of biomass), comprising C, H, O as elements; oils

and fatty acids (15–20% of biomass) comprising C, H, (O) as elements; and proteins (about 5% of biomass) comprising C, H, O, N (and S) as elements. This implies that, in principle, today's important organic bulk chemicals could be completely, or to a very significant extent, based on biomass. Unlike naphtha or syngas, when synthesizing bulk chemicals from biomass, the elements are already present, and do not have to be introduced. Instead, functionalities present in biomass have to be selectively removed or altered to render those bulk chemicals that the traditional petrochemical industry has learnt to deal with very efficiently.

Current state-of-the-art and perspectives with regard to platform chemical and bulk chemical production from biomass

Ethylene from biomass

Ethylene is directly produced in nature, for example, during the ripening of fruits. The amount of ethylene produced this way, however, is so limited that an economical process would be practically impossible reach. Production of ethylene via bioethanol in contrast seems to be very promising. In the 2004 report, *Top Value Added Chemicals from Biomass,* production of ethanol, ethylene glycol and ethylene oxide from biomass, was not taken into consideration; according to this study the economic hurdles of large capital investments and low market price competitors would be very difficult to overcome.

Nonetheless, since mid-2004, fossil oil prices have increased substantially and bioethanol production has significantly increased. *Chemical Marketing Reporter* indicated prices varying between €400 and €900/tonne for ethylene in recent years with a price of €900/tonne at November 2006. This suggests a widening gap between the price of bioethanol and ethylene in years to come. The conversion of bioethanol to ethylene can be carried out via established technology and comprises a dehydration step of ethanol to ethylene. This dehydration (at temperatures varying from 300–600°C) can be carried out over a wide variety of heterogeneous catalysts, including alumina, activated clays, zeolites and mordenite.[11-16] There are no technological hurdles left for the production of ethylene from biomass. The current production capacity

of bioethanol (estimated at 30 million tonnes/annum) is attaching increased interest in the conversion of bioethanol to bio-based ethylene (bioethylene). Currently bioethanol is produced based on the fermentation of sugar (at about €0.14–€0.20 /kg of sugar), and there is much research and development devoted globally to the establishment of conversion routes to bioethanol starting from much cheaper lignocellulosic- based agro (waste) materials (at < €0.10/kg). Thus, with further development, it may be expected that the production of ethylene based on biomass (*via* bioethanol) will become price-efficient very soon.

In fact, in June 2007, Braskem announced that it had successfully developed a high-density polyethylene based on bioethanol and that production on an industrial scale was expected to start in late 2009 with a potential annual production capacity of 200,000 tonnes (www.braskem.com). Also DOW recently announced (www.chemweek.com July 25, 2007) that it will form a joint venture with Crystalsev, one of Brazil's largest ethanol producers, with the aim of starting production of bio-based polyethylene at a 350,000 mt/year scale in 2011.

The Braskem and DOW announcements demonstrate that production of ethylene from biomass is initially most likely to happen in regions with cheap access to bioethanol (production), where stand-alone production of bioethylene is most economically attractive. This is much more likely to happen in countries like Brazil than in the Port of Rotterdam as in the latter case stand-alone production of bioethylene is likely to severely disrupt the concomitant coproduction of ethylene, propylene, C4 olefins, and B,T,X from naphtha. Development of more efficient routes to bioethanol will continue and production of bioethanol will increase. As a consequence it is likely that bio-based ethylene production will significantly increase in the short to medium term and that, eventually, after the establishment of lignocellulosic-based ethanol, bioethylene will also be produced in regions like the USA and Europe.

Production of bio-based ethylene will also lead to short-term possibilities for the production of bio-based vinyl chloride. This implies that in 10 years from now a significant part of two of worlds most dominant thermoplastic materials (polyethylene and polyvinylchloride) could completely, or to a very significant extent, be bio-based!

Propylene from biomass

Research on the direct biotechnological production of propylene has also been carried out. According to a publication of Fukuda, C3-hydrocarbon-producing strains are widely distributed.[17] Among 178 strains tested, 49% produced propane and propylene from glucose media, together with butane, butene, pentene, etc. Production of propylene, however, is extremely low. The highest productivity reported was 3.0 nl/ml of propylene per hour.[17] This implies that production of propylene should be increased by orders of magnitude to render a price-efficient process. As major technological hurdles still exist, economic production of propylene via this route is unlikely to happen within the next 30–50 years.

As for bioethylene, propylene in principle could be derived from bio-chemically produced 1-propanol or 2-propanol (iso-propanol). The biochemical production of 1-propanol or 2-propanol via fermentation processes is neither very well advanced, nor widely explored. The technologically most advanced route would probably involve dehydration of bio-chemically produced 2-propanol to propylene. The 2-propanol could then be derived from the 1,2-propanediol production or by reduction of acetone obtained via the acetone, butanol, ethanol (ABE) fermentation process. The ABE process is now widely studied with different micro-organisms and feedstocks.[18-22] In addition to butanol, which could be used as a biofuel, the process produces significant amounts of acetone (and ethanol). It will take probably another 5–10 years before this process is economically viable for the production of butanol as a biofuel, but once it is in operation it will also generate large amounts of acetone that could be used as such in the chemical sector or converted into 2-propanol (isopropanol), or ultimately propylene.

Glycols from biomass – end products or pre-cursor chemicals

Based on the platform chemicals ethylene, propylene and butylenes, the chemical industry produces a variety of glycols. Glycols are defined as components containing two hydroxyl groups. Examples are 1,4-butanediol, 2,3-butanediol, ethylene glycol, 1,2-propanediol (propylene glycol) and 1,3-propanediol. Propylene glycol and ethylene glycol belong to the bulk chemicals that are produced on a significant scale within the Port of Rotterdam. Glycols can be seen either as end products or as pre-cursor chemicals to other products, such as, for example, ethoxylated surfactants. Synthesis of these components from biomass is described using both fermentation and more conventional chemical (thermal) conversion technology.

Propylene glycol production and its uses

Two different C-3 propylene glycols are produced by the chemical industry: 1,2-propylene glycol and 1,3-propylene glycol. The propylene glycol produced in Rotterdam is 1,2-propylene glycol and is currently produced by acid or base catalysed ring opening of propylene oxide (Fig. 3). Approximately 80,000 tonnes/annum are produced in the Rotterdam area by companies such as Shell and Lyondell. It is used as a humectant, antifreeze or brake fluid or as a component of polyesters and alkyd resins. For part of its application propylene glycol is in direct competition with glycerol (e.g. its use as a humectant).

The other propylene glycol (1,3-propanediol) is produced from petrochemicals via processes patented by companies such as Shell and Degussa. 1,3-propanediol is used as a building block for polymers. An important use of 1,3-propanediol is as a monomer for the production of PPT fibers (poly (propanediol terephthalate)) (www.dupont.com).

Propylene and other glycols synthesized with the aid of fermentation

The biotechnological production of 1,3-propanediol has received a lot of attention in recent years.[23-27] DuPont has announced that the biotechnological production of 1,3-propanediol, from biomass sources such as glucose or glycerol, is price effective and can be used for its PPT (Sorona) fibers. Further development will be done by DuPont in cooperation with companies like Genencor and Tate & Lyle. Formation of glycols, such as propylene glycol (1,2-propanediol), has also been described using fermentation as a tool. Altara described the conversion by fermentation of sugars such as glucose, xylose and galactose using *Thermoanaerobacterium thermosaacharolyticum HG-8* as the micro-organism.[28] Fermentations were carried out at 60ºC under anaerobic conditions. Upon total conversion of glucose, 12% of 1,2-propanediol

could be obtained with a larger coproduction of ethanol, lactate and CO_2.

Conversion of biomass to glycols by thermochemical processes

Thermo-chemical bio-based processes to 1,2-propanediol are currently much further developed than fermentative ones. Conversion of (purified) carbohydrates to mixtures of glycols, including propylene glycol, has been studied relatively intensively. In the majority of publications and patents, glycerol or purified alditols (reduced monosaccharides) such as sorbitol or xylitol have been used as bio-based starting compounds. The thermo-chemical conversion routes described usually consist of a hydrogenolysis reaction in which the starting compound is catalytically converted, under heating and reducing conditions, into a mixture of glycols. Basic technologies based on different carbohydrate or polyol resources are described below.

Propylene glycol from glycerol

Thermo-chemical conversion of glycerol to propylene glycols (including both 1,2-propanediol and 1,3 propanediol) has been studied to some extent over the past decades. Celanese, in 1987, patented the conversion of aqueous glycerol solutions, at 300 bar of syngas and 200°C, forming 1,3-propanediol and 1,2-propanediol in 20 and 23% yield, respectively.[29] As catalysts, a homogeneous rhodium complex and tungsten acid were used. Also the hydrogenolysis of glycerol is described in a patent application to Shell.[30] In a recent paper by Chaminand et al., the hydrogenolysis of glycerol is studied over a wide variety of heterogeneous catalysts.[31] Depending on the specific catalysts and conversion of glycerol up to 20–30%, high selectivities can be obtained to 1,2-propanediol or 1,3-propanediol, respectively. A patent application (WO03035582) to Werpy et al., describes the conversion of

biomass – including glycerol – into propylene glycol.[32] Using a Ni-Re bi-metallic catalyst, at 60% conversion of glycerol, a selectivity of 78–88% toward the production of propylene glycol (Fig. 8) was obtained, together with the production of lactate (8–10%) and ethylene glycol (12%).

The dramatic increase in biodiesel production over the last few years and the concomitant production of glycerol (glycerin) as a byproduct, have led to a dramatic drop in glycerol prices, making glycerol a very attractive starting material for the production of ethylene glycol and propylene glycol.

In May 2007, Ashland and Cargill (www.Chemie.DE) announced that they have agreed to create a new joint venture to develop bio-based chemicals. The venture's first product will be propylene glycol. Using both licensed and proprietary technology, the joint venture will start producing propylene glycol from glycerin, from a location yet to be finalized in Europe.

Propylene glycol from sorbitol

Sorbitol has also been mentioned as a source for glycol production. Sorbitol can be obtained by hydrogenation of glucose and is commercially produced at 300–400,000 tonnes scale in Western Europe by companies such as Cerestar–Cargill, Roquette and Tate & Lyle. For a significant part of its applications, sorbitol is in direct competition with glycerol. Thus prices have come down, from €600–€700/tonne some years ago to its current €300–€400/tonne (70% sorbitol solutions in water). It is used in food but also for non-food applications such as polyols in polyurethanes, as components of heat stabilizers and alkyd resins in varnishes, paints and inks. The conversion of sorbitol to propylene glycol has also been the subject of various studies. The patent application to Werpy describes the conversion of pure sorbitol, by hydrogenolysis, into propylene glycol. At about 50% conversion using a Ni-Re catalyst, selectivities of up
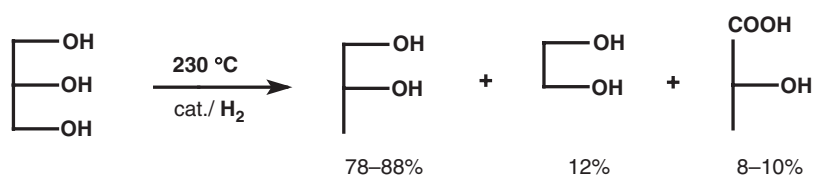
Figure 8. Conversion of glycerol to ethylene-and propylene glycol according to WO 03035582.[32]

to 30% propylene glycol could be obtained (with the other main products being ethylene glycol (16%), glycerol (19%) and lactate (13%).

Based on the availability of sorbitol it is clear that this technology, under current circumstances, also has strong commercial potential. This was confirmed by an announcement that a group of companies called International Polyol Chemical Inc (ICPI) is going to invest in a 200,000 tonne plant starting up in 2007, producing glycols such as propylene glycol, ethylene glycol, glycerin and butanediol, starting from sorbitol/glucose (www.agbob.com). In addition to using sorbitol as a feedstock, ICPI announced its plans to use molasses as a feedstock or waste streams such as various pentoses (xylose/arabinose) and lactose derived from whey.

Propylene glycol from lactic acid

In an alternative biomass-based route, propylene glycol could be derived from lactic acid. Lactic acid in its turn can be produced from all kinds of sugars by fermentation processes.

The patent application to Werphy *et al.*, describes not only the hydrogenation of C6-carbon sugars including sorbitol, but also describes the conversion of lactic acid into propylene glycol (Fig. 9). Using an Ru/Re/C catalyst, reduction of lactic acid to propylene glycol with a yield of 92.3% is reported.[32] Currently, prices of lactic acid (€1.2–€1.5/kg) are of the same order as that of propylene glycol. With further technological development of lactic acid production projected, together with increasing crude oil prices, it may be expected that biotechnologically produced lactic acid will become cheaper than petrochemical-based propylene glycol, offering a third biomass-based route to produce propylene glycol when the price difference becomes large enough.

The literature on hydrogenolysis of glycerol and sugar alcohols does not specifically mention or aim at the formation of 1-propanol or 2-propanol (or acetone). It is clear, however, that with further technology development subjecting

Figure 9. Propylene glycol from lactic acid.

propylene glycol to hydrogenolysis conditions offers potential for the production of either 1-propanol or 2-propanol (and acetone).

Epichlorohydrin from glycerol

Whereas until just 5–10 years ago, a significant part of glycerol was produced synthetically using epichlorohydrin as an intermediate, Solvay has recently announced that it will start producing epichlorohydrin from glycerol. Solvay starts producing epichlorohydrin from glycerol from mid-2007 using the new Epicerol™ process (www.solvaychemicals.com). A 10–50 ktonne production plant will be based in Europe and 100 ktonne production potential is planned in China.

The Epicerol technology relies on the known conversion of glycerol into 1,3-dichloro, 2-propanol (Fig. 10). Solvay claims to have developed improved technology leading to less byproduct formation and less water consumption.[33,34]

Ethylene oxide and propylene oxide based on biomass

Ethylene oxide and propylene oxide can be produced via two known processes: the chlorohydrin process or the direct oxidation process (Fig. 11).[7] The chlorohydrin process has
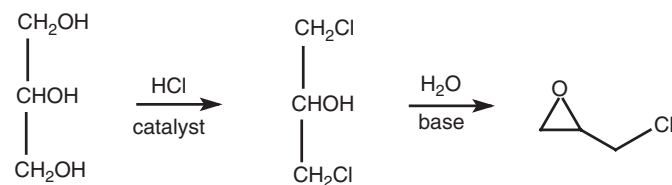

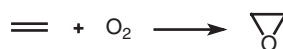Figure 10. Conversion of glycerol into epichlorohydrin according to Solvay Epicerol™ process.

Figure 11. Current processes for the production of ethylene oxide (or propylene oxide); the direct oxidation is the dominant process.

now been replaced to a very large extent by the direct oxidation process as the older chlorohydrin process led to too many byproducts and was too expensive for chlorine. The Solvay Process for the production of epichlorohydrin from glycerin, however, now claims to use less chlorine and water and therefore potentially can also be used for the production of ethylene oxide and propylene oxide from biomass via biomass-based ethylene glycol or propylene glycol; bio-based ethylene glycols and propylene glycols could be converted into their chlorohydrins and subsequently into ethylene oxide and propylene oxide, respectively (Fig. 12).

Obviously these processes would have to compete with the current production of ethylene oxide or propylene oxide by direct oxidation with air in the gas phase, which seems a much easier process.

Selectivities in the direct oxidation process are limited to about 80%, however, with the possibility of over oxidation and costs for transition metal ion-based catalysts also rising. In years to come, bio-based ethylene glycol and propylene glycol are likely to become cheaper than ethylene and propylene, creating a window of opportunity for the short-to-mid-term production of ethylene oxide and propylene oxide from biomass.

Butadiene and butane diols from biomass

Shell Chemicals currently produces about 115,000 tonnes/annum of butadiene from butane or butanes in the Port of Rotterdam. Starting from biomass, butadiene potentially can
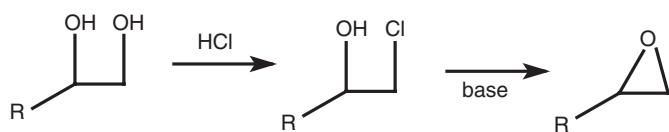

Figure 12. Potential production of ethylene oxide and propylene oxide from their respective glycols (R = CH_3 for propylene oxide, H for ethylene glycol).
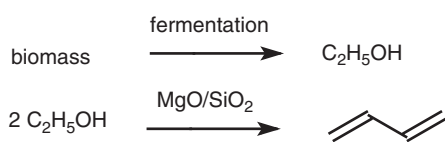

Figure 13. Production of butadiene from bioethanol.

be produced from ethanol by a reaction sequence as depicted in Fig. 13. Dehydrogenation of ethanol to acetaldehyde, followed by aldol condensation and dehydration leads in a one-pot process over a MgO-SiO_2 catalyst (known as the Lebedew process), to an overall yield of 70% of butadiene, offering a very attractive option.[7] This process was commercially operated by Hüls in the early 1950s, using French surpluses of bioethanol.[22] Given current prices of bioethanol at €400/tonne and butadiene prices at €700/tonne, increasing bioethanol production and further technology optimization will make this an attractive short-term option.

Butadiene can subsequently be converted into tetrahydrofuran and 1,4-butanediol, via a butadiene epoxidation process. In the Port of Rotterdam, 1,4-butanediol is presently produced by Lyondell in 126,000 tonnes /annum quantities.

Biomass-derived butadiene can also serve as a feedstock for the production of all kinds of elastomers, for example, styrene butadiene rubbers.

2,3-butanediol and methylethylketone (MEK) from biomass

2,3-butanediol as such is not a bulk chemical produced in the Port of Rotterdam, but can be regarded as a potential precursor in the production of butadiene or MEK (Fig. 11). MEK (or 2-butanone) is produced in the Port of Rotterdam in quantities of about 85,000 tonnes/annum.

The production of 2,3-butanediol by fermentative techniques has been described.[36,37] Various bacterial species such as *Bacillus polymyxa* and *Klebsiella pneumoniae* have been described to convert effectively both glucose and xylose into mixtures of predominantly 2,3-butanediol and ethanol. Qin *et al.,* recently reported a butanediol yield of 98% of its theoretical value at a productivity of up to 2.1 g.L^{-1}.h^{-1}.[38] The
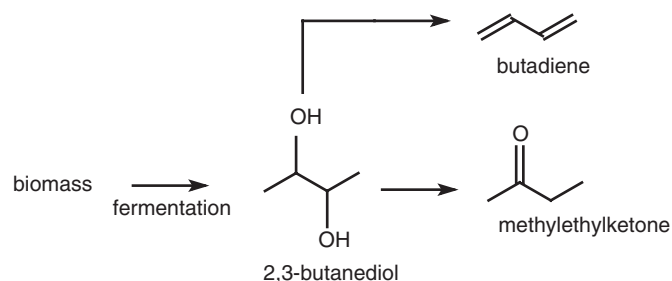

Figure 14. Production of butadiene and MEK from biomass.

production of 2,3-butanediol by the fermentation of sugars is not limited to glucose or xylose. Saha *et al.*, described a production of 40% of 2,3-butanediol using arabinose as a feedstock.[39] Manitto *et al.*, described the synthesis of 2-butanone (methylethylketone) from 2,3-butanediol using a diol-dehydratase enzyme obtained from a strain of *Lactobacillus brevis*.[40]

Chemical dehydration of 2,3-butanediol has not been studied intensively since the 1950s, but is known to result in mixtures of 2-butanone and 1,3-butadiene.[41] Using Morden Bentonite clays, at temperatures lower than 350°C, an 86% yield of MEK from 2,3-butanediol was reported as early as 1947.[42] In a more recent paper of Emerson *et al.*, dehydration of 2,3-butanediol to MEK using catalysts such as alumina or direct reaction with sulphuric acid has been studied.[43]

Conversion of butadiene from 2,3 butanediol has also been described; for example, by pyrolysis of 2,3-butane-diol diacetate or by first converting 2,3-butanediol to the dibromide. As these methods use stoichiometric amounts of either acetic acid or bromides, it is unlikely that they can be transformed into an economical process in the short to medium term. Here, the development of improved catalytic dehydration steps to butadiene would be a prerequisite for commercial production opportunities. A patent application to Compagnie Francaise de Raffinage (1974) mentions the possibility of deriving butadiene from 2,3–butanediol but only describes the synthesis of isoprene from 2-methyl-2,3 butanediol over pyrophosphate catalysts.[44]

Production of acrylic acid from biomass

Next to the bulk chemicals produced by the Port of Rotterdam, biomass-based routes to other important bulk chemicals offer perspectives. One such chemical is acrylic acid. It is currently produced by the gas phase oxidation of propylene and used for the production of polyacrylates used in applications such a super absorbent materials and water-borne coatings and adhesives. The biotechnological produc-tion of acrylic acid from either 3-hydroxypropionic acid or lactic acid (Fig. 15) is under investigation in the USA.[45]

The production of lactic acid from biomass consists of a widely studied biotechnological process. Acid catalyzed dehydration of lactic acid will lead to acrylic acid. At current lactic acid prices of €1.2–€1.5/kg and €1.5–1.7/kg for acrylic
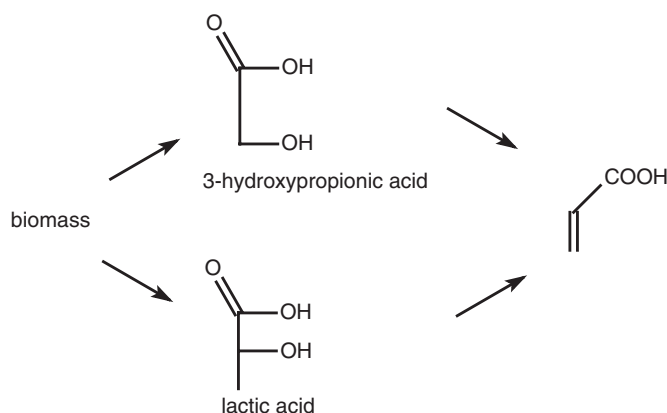

Figure 15. Production of acrylic acid from biomass.

acid (based on a crude oil price of $57/barrel), this could turn out to be an economically attractive route, provided an efficient route for the dehydration of lactic acid into acrylic acid can be established. So far, this has proven to be unex-pectedly difficult; the secondary hydroxyl is quite resistant toward hydrolysis, and further technology development is needed.[45] In an alternative approach, the biotechnological production of 3-hydroxypropionic acid is being studied.[46] This 3-hydroxypropionic acid has shown to be more easily dehydrated into acrylic acid than lactic acid.

Although there are some remaining technological bottle-necks, given the expected price decreases of specific sources of biomass, the expected decrease of lactic acid prices, improved technology for the production of 3-hydroxy propionic acid and increasing acrylic acid prices, economic potential for production of acrylic acid might be expected within 10–20 years.

Production of methacrylic acid

Methacrylic acid is related to acrylic acid. The production of methacrylic acid from biomass, via citric acid conversion to itaconic acid followed by decarboxylation, is described in literature (Fig. 16).

Above temperatures of 180–250°C, citric acid decom-poses to mixtures of predominantly (>90%) of itaconic and citraconic acid. At higher temperatures (360°C), itaconic acid decarboxylates into methacrylic acid. The yield of methacrylic acid is dependent on temperature, pH and buffer strength; yields of 70 mole% of methacrylic acid were reported.[47]
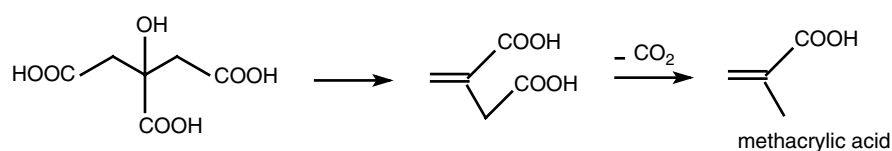
Figure 16. Potential production of methacrylic acid from biomass.

Alternatively, it may be more useful to produce itaconic acid directly by fermentation methods. This then reduces the number of steps and potential costs of this approach for the synthesis of methacrylic acid.

With prices of citric acid (produced by biotechnology from glucose) at about €800/tonne and €1500–€1600/tonne for (methyl) methacrylate, here is definitely an interesting opportunity for the price-effective production of methacrylic acid from biomass in the short to mid-term (even taking the considerable mass loss during conversion of citric acid to methacrylic acid into account).

Production of N-containing bulk chemicals using amino acids

N-containing bulk chemicals are not produced in the Port of Rotterdam and the development of nitrogen-containing bulk chemicals based on biomass is also in a less advanced state than that of oxygenated bulk chemicals such as glycols. Among the nitrogen-containing bulk chemicals, bio-based routes to caprolactam have received most attention.

Frost reported the use of lysine to prepare ε-caprolactam.[48] Here lysine, derived from fermentation, is used. The lysine (salt) upon heating cyclises to form the lactam α-amino-ε-caprolactam. This is followed by deamination (Fig. 17). Both steps are reported to give 75% yield. Given the prices of lysine and ε-caprolactam (Table 1), it can be concluded that improvement or alternative processes are needed to render economic potential. Literature describing the synthesis of intermediates for ε-caprolactam such as the use of (biotech-nologically derived) lysine to form 6-aminohex-2-enoic acid as well as the bio-chemical production of 6-aminohex-2-enoic acid and its conversion to 6-aminocaproic acid, have also been reported.[49,50]

Awareness of large volumes of glycerol generated as a waste stream from biofuel production is apparent. However, an immense concomitant waste stream of protein will also be generated from biofuel production. Bioethanol from wheat and corn and biodiesel from rape and palm will give rise to an additional amount of protein of around 100 million tonnes/annum if these biofuels substitute 10% of the transportation fuel demand. Some of the amino acids present in such proteins could be very suitable raw materials for preparing nitrogen-containing (functionalized) bulk chemicals traditionally prepared by the petrochemical industry.

The literature for the use and transformation of amino acids is extremely diverse and generally focuses on use of amino acids in nutrition, medicine or impact on physiological function. The common characteristics of amino acids are the presence of carboxylic acid and amine functionalities and indeed most of the (bio-) chemical information is focused on the reactivity of these groups. For example, the decarboxylation of α-amino acids is well reported in the literature and where enzymatic decarboxylation is carried out, amino-acid-specific decarboxylase enzymes may be used.

Recently reactions involving a range of amino acids where the impetus is the overlap of the end products of these reactions with chemicals currently produced in the petrochemical
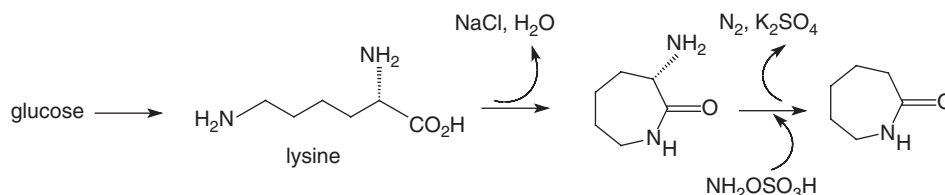

Figure 17. Conversion of lysine into caprolactam.[48]

industry, for example ethanediamine and ε-caprolactam, have been described in the open literature.[51]

Production of aromatic compounds from biomass

Based on recent and earlier studies using fermentation technology and catalytic thermochemical conversions, it is evident that there is a clear short-term potential for the production of oxygen containing C2, C3 and C4 bulk chemicals based on biomass and a mid-term potential for nitrogen-containing bulk chemicals. However, one important area of significant interest that has received relatively little attention with limited success so far is the replacement of petrochemical-based routes for the production of bulk aromatic compounds such as benzene, toluene, xylene and phenol.

This is of special interest for the Port of Rotterdam and similar industrial chemical complexes, as an important part (>40%) of the bulk chemicals is of an aromatic nature.

Fermentation of glucose to a number of aromatic structures has been described in the patent literature.[52] However, these aromatic structures themselves were neither bulk products nor the desired end product of the fermentation process (adipic acid).

Utilization of specific terpenes could offer potential for the production of aromatic compounds such as, for example, substituted phenols or terephthalic acid. The aromatization of terpenes, such as limonene-using zeolites, has been described in literature (Fig. 18).[53] Yields of p-cymene described so far were moderate and next to α- and γ-terpinenes substantial amounts of unidentified products were formed.

Furthermore, current production volumes of terpenes are rather in the range of hundreds of thousand of tonnes instead of the million tonnes needed to substitute a significant amount of aromatics production. Also prices of limonene and related terpenes are relatively high compared to aromatics. Therefore, although from a technological point of view terpenes might certainly, if further developed technologically, offer interesting potential, from an economical point of view they currently do not seem to offer a short- to mid-term potential for bulk aromatic chemicals, but rather selected ones, having a higher market price and smaller market volume.

By far the most available bio-based feedstock that seems feasible for the preparation of aromatic (bulk) chemicals
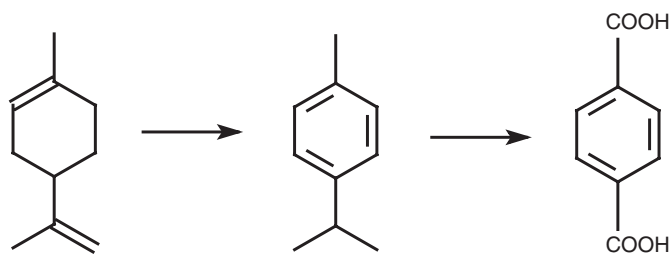
Figure 18. Potential production of terephthalic acid from limonene.

is lignin. Lignin is found in trees and other lignocellulosic plant-based materials.[54]

The increasing demand for ethanol as a biofuel means that increasing amounts of (residual) lignin will be generated and become available. Traditionally, the use of lignin (from rest streams in the pulp and paper industry) has been as a fuel source in the pulp mills, component in binders, or additive in cement. However, due to its chemical nature, and in particular the presence of large amounts of aromatic structures, lignin may be an attractive raw material for the production of aromatic compounds, reducing the need for fossil resources and CO_2 emission.

Some high-temperature thermal processes for the 'cracking' of lignin have been described (Fig. 19). This has resulted, next to tar formation and volatile components, in a complex mixture of polyhydroxylated and alkylated phenol compounds.[55-59] This, of course, provides the challenge of further upgrading these mixtures to a higher content of phenol and of downstream processing of these streams in order to separate the phenolic-like compounds that are derived. The highest percentages of phenol reported (based on total lignin feed) are in the range of 5–10%. Here it seems a prerequisite that in addition to the production of phenol, outlets for all side products formed should be developed.

In conclusion due to its complexity (inhomogeneity, complex structure(s)) and undesirable impurities (sulfur) it is clear that major technology breakthroughs will be needed to be able to isolate pure phenols from lignin. Therefore usage of lignin as a biomass feedstock for the production of phenols should be regarded as a longer-term option.

With regard to lignin conversion, so far most attention has been paid to the production of phenol, because it is more expensive than benzene. Although functionalized aromatics, such as phenols and styrene, are produced in
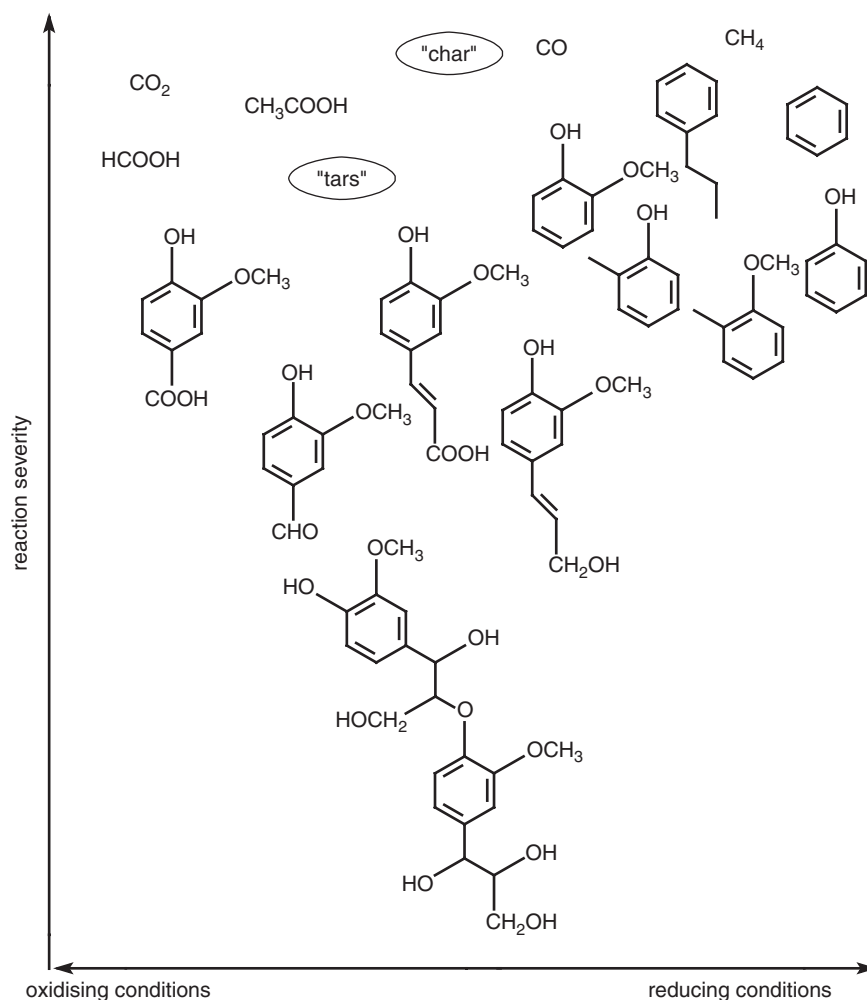
Figure 19. Potential reaction products from the decomposition of lignin.

impressive amounts, 60% of all aromatics produced by a typical integrated chemical complex such as in the Port of Rotterdam are first-generation *unfunctionalized* aromatics (B,T,X). Therefore conversion of lignin into benzene or B,T,X certainly deserves more attention.

One of the most feasible routes to aromatic building blocks based on biomass is probably the sequence as shown in Fig. 20:

The (Diels-Alder) cyclo-addition of butadiene over Cu(I)-zeolites has been described in literature.[60] US Patent 5,196,621 to Dow Chemical Company, claims selectivities for conversion of 1,3-butadiene into 4-vinylcyclohexene of over 99% at 100ºC and 30–50% conversion, using a variety of different catalysts including Cu(I)-zeolites.[61] It is also claimed that crude C4 hydrocarbon feed streams obtained
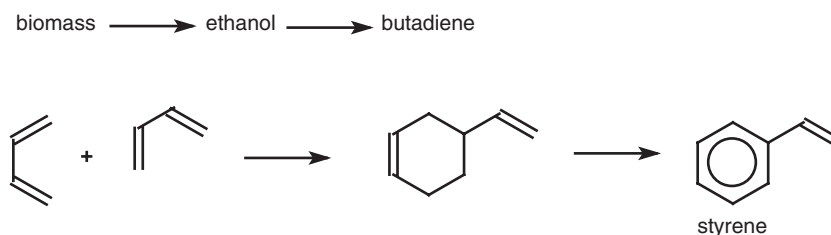

Figure 20. From biomass to styrene.

from petroleum crackers are suitable. The vinylcyclohexenes thus obtained are useful starting materials for the production of styrene.

Obviously this route heavily relies on economic production routes to butadiene from biomass and a further optimization of the production of vinylcyclohexenes from butadiene.

Based on the necessity to optimize at least three intermediate steps, this at best is judged as an intermediate (10–20 year) option toward bio-based styrene.

Conclusions

Based on the evaluation of the bulk chemicals produced by a typical integrated chemical complex such as the one based in the Port of Rotterdam as a case study, it is concluded that biomass-based routes are going to make a significant impact on the production of bulk chemicals within 10 years and a huge impact within 20–30 years.

- There is a clear short-term (0–10 year) substitution potential for oxygenated bulk chemicals such as ethylene glycol and propylene glycol, iso-propanol and acetone, butylene and MEK and for replacement of MTBE by ETBE. This implies that given an estimated production volume of 12,000,000 tonnes of bulk chemicals in the Port of Rotterdam, there is a short-term substitution potential of about 10–15% of fossil-based bulk chemicals by biomass-based bulk chemicals. As glycerol, as a byproduct of biodiesel production, is a highly suitable starting material for the production of ethylene glycol and propylene glycol, this is a very favorable short-term option.
- In the mid-term (10–20 years) there is a clear potential for a bio-based production of acrylic acid and N-containing bulk chemicals such as acrylonitrile, acrylamide and ε-caprolactam. As proteins, a byproduct from biofuel production, become increasingly available at decreasing prices, they can become good starting points for such N-containing chemicals.
- In the short to mid-term (0–20 years) there is surely a huge potential for a bio-based production of ethylene and vinylchloride. Commercial implementation most probably will first take place in areas with access to cheap ethanol and where production of ethylene is not largely integrated with the production of other platform chemicals.

- Direct isolation of aromatic building blocks from biomass or conversion of sugars to aromatics is technologically still in its infancy and is mostly related to functionalized aromatics (e.g., phenols, styrene) instead of B,T,X. Here, further development of biomass-based gas-to-liquid processes is likely to influence the current production of aromatics (benzene, toluene, xylene) in the next 20–30 years.
- Biorefineries that are being started up today, such as ethanol from wheat and biodiesel from rape, will form the stepping stones toward the chemicals mentioned above if we learn to upgrade their abundant side streams.

The Port of Rotterdam, as well as other major integrated chemical complexes, will have to consider in much closer detail which raw materials will be needed in the new situation, how will they be processed, how they will be made available in Rotterdam, what kind of storage facilities are needed, how the production of bio-based bulk chemicals can be integrated, how products will be shipped to the (geographic) area covered by the Port, and which are the most likely companies to produce new bio-based (bulk) chemicals.

Acknowledgements

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