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An Overview of Biorefinery Derived Platform Chemicals from a Cellulose and Hemicellulose Biorefinery

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Abstract

Until recently, most of energy and industrially produced chemicals were derived from fossil fuel-based resources. This along with the continued depletion of finite fossil resources and their attributed adverse environmental impacts, alternatively sourced and more sustainable resources are being pursued as feedstock replacements. Thus, biomass has been identified as an alternate renewable and more sustainable resource as a means to reduce this sector's dependence on fossil fuel-based resources and to alleviate their environmental impacts. As such, lignocellulosic biomass has been further identified and demonstrated as an abundant renewable resource for the production of biofuels, platform chemicals, and their respective value-added products. This review article provides an overview of the techniques developed for the valorization of biomass in the production of platform chemicals within a biorefinery, and the status for commercialization.

Summary:

As demonstrated and discussed, various platform chemicals can and are being produced in biorefineries and are utilizing a renewable biomass as a resource. This is exemplified by the industrial production of platform chemicals such as ethanol, lactic acid, succinic acid, levulinic acid, sorbitol, and 2,5-furandicarboxylic acid from biomass. In addition, several value-added chemical products and polymers produced in a biorefinery have been commercialized. However, still there are challenges in the valorization of lignocellulosic biomass to produce chemicals with high selectivity and yields. Various large chemical companies such as DuPont, BASF, and the Dow Chemical Company are actively pursuing valorization of lignocellulosic biomass. The production of renewable chemicals from biorefineries is expected to increase substantially in the coming years with an increased market share. Although chemicals and materials can be produced in a single product process in a biorefinery, the production in an integrated biorefinery producing both the bio-based products and energy such as fuel, power and heat will be a superior approach for the sustainable valorization of biomass. The biobased products produced in a biorefinery should be market competitive for their economic sustainability. Thus, to develop a sustainable biorefinery, it is critical to produce high value-added bioproducts along with bio-energies in an integrated biorefinery. The production of biobased chemicals in a biorefinery can significantly reduce the

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greenhouse gas emissions, thus stimulating innovative advancements in the area of biorefining processes and expanding the bio-based economy will lead to a more environmentally benign chemical manufacturing industrial sector.

Keywords

Biorefinery; biomass; platform chemicals; lignocellulose; gasification; fermentation

Introduction:

Currently, the majority of chemicals and energy are produced from finite fossil fuel-based resources. The world's societies and commercial markets are dependent on these depleting fossil fuels for the production of approximately 80% of its energy and 90% of its chemicals (Fernando et al. 2006). The large-scale production and use of these fossil fuels have contributed to negatively impacting the environment due to the emission of harmful greenhouse gases and toxic materials. With a growing world population, the demand for energy and chemicals is increasing considerably. Along with a growing world population, the corresponding amount of waste generated is also gradually increasing. In 2014, approximately 258 million tons of municipal solid waste (MSW) was generated in the United States alone. Approximately 35% of this MSW is recycled/composted, 13% of it is utilized for generation of energy, through incineration processes, and about 53% of MSW is discarded into landfills (U.S. EPA 2016). Because of the increasing demands for energy and chemicals and to overcome the issues associated with depleting fossil fuels and its related environmental impact, it is imperative to identify alternate resources to produce energy and chemicals. In this process, biomass has been identified as a renewable resource for the production of chemicals and energy, along with addressing the generation of waste issue. Although biomass is available from natural resources, alternatively it can be obtained from various waste sources such as agricultural waste (corn stover, rice husk, and sugar cane bagasse), municipal solid waste (MSW), and industrial waste, such as pulp and paper mills. Biomass waste valorization also has a very high importance in resource recovery within an integrated waste management approach. A biorefinery, which utilizes a renewable biomass as a feedstock resource, may offer a more sustainable solution for the conversion of harvested and waste biomass into platform chemicals (Esposito and Antonietti 2015). A biorefinery could also bring about sustainable growth, along with environmental advantages in the reduction of overall greenhouse gas emissions (NREL) and air toxics.

Biorefinery:

The concept of the biorefinery evolved during the late 1990's. The US Department of Energy defines a biorefinery as an overall concept of a processing plant where biomass feedstocks are converted and/or extracted into a spectrum of valuable products (Kamm et al. 2006). According to National Renewable Energy Laboratory (NERL), a biorefinery integrates biomass conversion processes and equipment to produce power, chemicals, and fuels (NREL). The International Energy Agency (IEA) Bioenergy Task 42 has defined a biorefinery as "the sustainable processing of biomass into a spectrum of marketable products (food, feed, materials, chemicals) and energy (fuels, power, heat)". Thus, a biorefinery can be a facility, a process, a plant, or a cluster of facilities for the conversion of biomass (de Jong et al. 2013). Furthermore, a biorefinery can be assimilated to a petroleum-based refinery. In petroleum-based refinery fossil-based resources such as oil and natural gas are used to produce energy and chemicals, whereas, in a biorefinery, biomass is used as the feedstock to produce energy and chemicals (Kamm and Kamm 2004; de Jong and Jungmeier 2015). To expand on this concept, biorefineries are further classified based on the type of feedstocks used, the type of intermediates generated (syngas or sugar), conversion processes (thermochemical, biochemical, two platform) and the status of technology execution (conventional, advanced, etc.). Thus, biorefineries are classified into three different types (Kamm and Kamm 2004; Clark and Deswarte 2008).

***Phase I Biorefinery*:**

This type of biorefinery utilizes only one feedstock material, has fixed processing capability and produces a single primary product. Examples of this type of biorefinery are biodiesel from vegetable oil, pulp and paper mills, and the production of ethanol from corn grain (Naik et al. 2010).

***Phase II Biorefinery*:**

Is similar to a Phase I Biorefinery and uses only one feedstock, but is capable of producing various products. Examples of Phase II Biorefineries are the production of various chemicals from starch and the production of multiple carbohydrate derivatives and bioethanol from cereal grains.

***Phase III Biorefinery*:**

Phase III Biorefineries are advanced biorefineries and can utilize various types of feedstocks, processing technologies and produce multiple types of products. There are four classes of Phase III Biorefinery systems (Clark and Deswarte 2008). These are identified as: 1. Whole-crop biorefinery, 2. Green biorefinery, 3. Lignocellulosic biorefinery, 4. Two-platform concept biorefinery.

A whole-crop biorefinery uses an entire crop, such as cereal grains, as raw materials. In this class of biorefinery, a cereal grain crop is first separated into corn and straw, and the corn subsequently converted into starch. The starch upon hydrolysis provides glucose, which serves as a substrate (feedstock) for the production of various chemicals. The cellulosic straw can be processed in a lignocellulosic biorefinery. In a green biorefinery, natural biomass such as grass, green crops or plants are utilized as feedstocks. Whereas, in a lignocellulosic biorefinery the main feedstock is a dry biomass, such as cellulose-based biomass. Recently NREL has introduced the two-platform concept biorefinery. This type of biorefinery consists of two different types of platforms, i.e. sugar platform and syngas platform. The sugar platform employs biochemical conversion methodologies (fermentation of sugars obtained from biomass), whereas the syngas platform depends on thermochemical methods (gasification of biomass to produce syngas). Both of these platforms can produce energy and chemicals as the end products.

A biorefinery can be further classified, based on the chemical nature (composition) of feedstock, into three categories (Octave and Thomas 2009).

1. ***Triglyceride Biorefinery*** **(TGB):** This biorefinery utilizes vegetable oils, animal fats, oil from algae, and waste cooking oil as feedstocks, and has received considerable attention due to the scientific advancements made in the production of biofuels. Triglycerides are converted into a biofuel *via* a transesterification reaction with methanol in the presence of an acid, base, or enzyme acting as a catalyst. In this reaction, glycerol is formed as a byproduct, which is also considered as a platform chemical, and has the potential of adding commercial value to this process.

2. ***Sugar and Starchy Biorefinery*** **(SSB):** This biorefinery for sugar and starch is also well recognized due to the well-developed and executed fermentation process for sugar and starch into the production of ethanol (Serrano-Ruiz and Dumesic 2011). Feedstocks for a SSB are sugar beet, sugar cane, wheat, corn, and maize. In the fermentation process, the starch is first enzymatically degraded into its respective monomer sugars and then the resulting mixture is fermented by *Saccharomyces cerevisiae* at ambient temperature to produce ethanol (Naik et al. 2010). Currently, ethanol accounts for 94% of global biofuel production (Demirbas 2011).

3. ***Lignocellulosic Biorefinery*** **(LCB):** The LCB utilizes a lignocellulosic-based feedstock (LCF) and can produce a wide spectrum of products through various processing approaches. Lignocellulosic feedstocks (LCF) include wood, straw, grasses, etc. and LCFs are composed of 40-50% of cellulose, 25-30% hemicellulose and 15-20% lignin (Alonso 2010). The chemical composition of LCFs also varies considerably, depending on its source (Jorgensen et al. 2007). Cellulose is a high molecular weight linear polymer composed of β-glucose (5000-10000 units) and linked by β-1,4-glycosidic bonds. It is a highly crystalline material, and because of this crystallinity, not soluble in water. This attribute makes it challenging to convert into monomer sugars through hydrolysis (Brethauer and Studer 2015). When hydrolyzed cellulose yields D-glucose, which acts as a substrate for the production of chemicals. Hemicellulose is an amorphous branched polymer and contains both C_5 (xylose, arabinose, and rhamnose) and C_6 sugars (glucose, mannose, and galactose), as well as uronic acids components. Hemicellulose contains approximately 150 repeating monosaccharide units, and the type of monomer sugars present varies depending on the type of material. For example, in hardwood and agricultural plants, hemicellulose contains mainly xylan, (Maki-Arvela et al. 2011), a polymer of xylose, whereas in softwood hemicellulose its main building block is glucomannan, a polymer of D-mannose and D-glucose linked by β-1,4-glycosidic bonds. Hemicellulose is amorphous in nature, highly soluble in water, and thus readily hydrolyzes to the corresponding monomer sugars as opposed to cellulose.

International Energy Agency (IEA) Biorefinery Classification:

In 2008, the IEA Bioenergy Task 42 developed a biorefinery classification system based on feedstocks, biorefinery platform, products, and processes (Cherubini et al. 2009, de Jong et al. 2013). The biorefinery feedstocks include: grasses, starch crops (wheat and maize), sugar crops (beet and cane), lignocellulosic crops, lignocellulosic residues (stover and straw), oil crops, aquatic biomass (algae and seaweeds) and organic residues (industrial, commercial and post-consumer waste). The IEA classified the processes used in a biorefinery into four groups. 1. Mechanical/Physical, such as pre-treatment, milling, pressing, separation and distillation, which perform size reduction or a separation of feedstock components without effecting the nature of chemical components of the biomass. 2. Biochemical, those processes carried out by enzymes or microorganisms, such as fermentation, anaerobic digestion, etc. 3. Chemical, hydrolysis, synthesis, hydrogenation, oxidation, etc. and 4. Thermochemical, where feedstocks are subjected to very high temperature and/or pressure, such as gasification, hydrothermal upgrading, and pyrolysis.

These biomass feedstocks can be processed into a variety of biorefinery platforms, which are the key intermediates linking the feedstocks and their respective final product(s). Examples of important platforms in the energy sector are syngas from gasification, biogas from anaerobic digestion, C_5 and C_6 sugars from starch, cellulose and hemicellulose, lignin from lignocellulosic biomass, pyrolysis liquid from pyrolysis, oil from oilseed crops and algae, organic juice from wet biomass, and electricity and heat. These platforms are then further transformed into a variety of products using a thermal, biological or chemical process, or a combination of these processes. Based on the type of products produced, biorefineries are classified into energy-driven or material-driven biorefinery systems. In an energy-driven biorefinery system, biomass is used mainly for the production of biofuels, power and heat. Whereas, in a material-driven biorefinery system biobased products such as food, feed, chemicals, biomaterials, etc are produced. The process residues, in both systems, can be further utilized to produce energy, thus minimizing waste generation

A few examples of this IEA biorefinery classification system are:

1. One-platform C_6 sugar biorefinery for the production of bioethanol and animal feed from corn crops.
2. One-platform syngas biorefinery for biofuels and chemicals generation from lignocellulosic residues.
3. Two-platform (biogas and organic juice) biorefinery for biomethane, chemicals, biomaterials (fiber products) and fertilizer from grasses.
4. Four-platform (lignin/syngas, C_5/C_6 sugar) biorefinery for liquid biofuel, bioethanol, and animal feed from lignocellulosic crop such as switchgrass.

Valorization of Lignocellulosic Biomass in a Biorefinery

In the valorization of a lignocellulosic biomass, the first step is pretreatment, which aids in the isolation of the cellulose, hemicellulose and lignin components. Biorefineries, which utilize polysaccharides from cellulose/hemicellulose portion of lignocellulosic biomass to produce platform chemicals and materials, generate a substantial amount of lignin as a by-product. Many of the traditional biorefineries, which use polysaccharides, have utilized the resulting byproduct lignin for generation of the power that is needed to achieve the transformation of the biomass. However, there are efforts underway for the valorization of lignin for the production of potential high-value products such as carbon fiber, engineered plastics, thermoplastics elastomers, polymeric foams, membranes and a variety of aromatic chemicals (Ragauskas et al. 2014). These achievements are focused on the valorization of the cellulose and hemicellulose portions of lignocellulosic biomass in a biorefinery to produce platform chemicals and their high value-added products.

Pretreatment of Lignocellulosic Biomass

Conversion of biomass into higher-value chemicals in a biorefinery involves the hydrolysis of lignocellulose to fermentable sugars. However, before this can occur, a biomass pretreatment step is needed to facilitate the efficient hydrolysis of cellulose into its respective monomer sugars (Agbor et al. 2011). The hydrolysis step is carried out using acids or enzymes, followed by the fermentation process being done by either a bacteria or yeast. Various factors can influence the hydrolysis of cellulose, which include the porosity of the biomass material, crystallinity of the cellulose and the content of hemicellulose and lignin (McMillan 1994). The presence of hemicellulose and lignin hinders accessibility of the enzyme and/or acid in reaching the cellulose and thus limits the extent of the hydrolysis process. Pretreatment will help alter the size, structure and chemical composition of biomass, which enhances the hydrolysis process produce monomeric sugars in high yields. There are several types of pretreatment methods. These include physical (milling, grinding etc.), chemical (steam explosion and ammonia fiber explosion), physicochemical (acid pretreatment, alkali pretreatment, oxidative methods and organosolve methods), biological, or a combination of these methods. These pretreatment methods were reviewed by Kumar et al. (2009), and Singh et al. (2015) and provide insight into the different types of lignocellulosic biomass and the requirements of each with varying pretreatment processes.

Platform Chemicals:

A platform chemical is defined as a chemical that can serve as a substrate for the production of various other higher value-added products. In 2004, the Department of Energy (DOE) identified 12 chemical building blocks, that can be obtained from biomass, as potential platform chemicals (Werpy et al. 2004). In 2010, the DOE updated the Platform Chemical List (Bozell and Petersen 2010) which includes ethanol, furfural, hydroxymethylfurfural, 2,5-furandicarboxylic acid, glycerol, isoprene, succinic acid, 3-hydroxypropionic acid/aldehyde, levulinic acid, lactic acid, sorbitol, and xylitol. All these identified platform chemicals, except glycerol and isoprene, can be produced from biomass-derived carbohydrate sources. According to McKinsey & Co. (BIO 2016) estimates, bio-based product sales in 2012 were $252 billion and renewable-based chemical sales were approximately 9% of worldwide chemical sales and are expected to grow by 4% annually. The bio-based product sales are expected to increase with an annual growth rate of 8% to $375 to $441 billion by 2020.

Ethanol:

There are two different types of processes employed to produce ethanol from lignocellulosic biomass. The first utilizes a thermal gasification process to generate syngas, which is then converted to ethanol by either chemical catalytic methods or biochemical fermentative methods. The second is based on the biochemical fermentation process.

Gasification:

Gasification is the process of converting an organic mass into a high-energy gas *via* partial oxidation at a temperature ranging from 500-800°C (Arena 2012). There are three steps in the conversion of biomass to syngas, pre-treatment of feedstock, gasification, and syngas cleaning/conditioning. Syngas consists of a mixture of carbon monoxide (CO) and hydrogen (H_2). Raw syngas also contains some other impurities such as CO_2, tars and a small amount of other gases such as methane, ethane, oxygen, ammonia, HCl (hydrochloric acid) and H_2S (hydrogen sulfide) (McKendry 2002). Since the impurities present in the syngas can affect process efficiency, it is necessary to purify prior to its conversion into ethanol. Initially, particulates from syngas are removed by cyclone separators. If any tars are present in the raw syngas, they can be decomposed by catalytic steam reforming utilizing Ni-based catalysts (Magrini-Bair et al. 2012). The purified syngas can then be converted into ethanol *via* two different methods. The first is based on a catalytic chemical process (Subramani and Gangwal 2008) and the second based on a biological fermentation process (Abubackar et al. 2011; Mohammadi et al. 2011). The catalytic chemical conversion of syngas into ethanol has been carried out utilizing various homogeneous (Co, Ru, and Rh) metal complexes and heterogeneous catalysts (Rh, Cu, Mo, Ni-based, Hayes 2009). For the biological-based conversion of syngas into ethanol microbial fermentation is used. The gas fermentation process is a hybrid thermochemical/biochemical process where syngas can be generated by the gasification process, which is then converted into ethanol *via* a microbial reaction (Mohammadi et al. 2011). This fermentation of syngas takes place at ambient temperatures and results with very high selectivity to ethanol. Although this process is slow when compared to chemical catalytic process, it’s very high specificity results in a higher yield of the desired product.

Biochemical Fermentation:

This process is comprised of three steps. 1. Pretreatment, 2. Saccharification and 3. Fermentation (Sarkar et al. 2012).

***Pretreatment*:** This is an important aspect in the processing of biomass for the production of ethanol. As described earlier, the pretreatment process aids in increased susceptibility of the biomass to hydrolysis and results in generating higher yields of monomer sugars.

***Saccharification*:** In this second step, complex carbohydrates are converted into simple monomers by hydrolysis using cellulase and hemicellulase enzymes (Naik et al. 2010; Talebnia et al. 2010). The hydrolysis of the cellulose starting material yields glucose, whereas the hydrolysis of hemicellulose generates several isomers of pentoses and hexoses.

***Fermentation*:** The biomass sugars obtained upon saccharification are then used for fermentation by various microorganisms. An ideal microorganism for the commercial production of ethanol should be capable of utilizing various types of sugars which can be used to produce ethanol in high yields (Talebnia et al. 2010). Since naturally occurring microorganisms cannot ferment both pentose and hexose sugars, genetically modified microorganisms are needed to ferment these sugars completely, thus providing higher yields of ethanol. There are two types of processes normally employed in this fermentation. In the first type, simultaneous saccharification and fermentation (SSF) occurs and in the second type being the separate hydrolysis and fermentation (SHF) processes. Although the SHF process is traditionally utilized, the SSF process is found to be superior for producing ethanol in higher yields, as well as eliminating the need for separate reactors. To date, several companies are adopting the biochemical method for production of bioethanol (Schwab et al. 2016). Although most of the bioethanol produced in the US is used as a fuel additive, a small percentage is also used as a platform chemical for production of higher value-added products. Bioethanol can serve as a renewable source for production of ethylene, propylene, and butadiene, which are critical building blocks for polymer synthesis. Dow, Solvay, and Braskem have built plants to convert bioethanol to ethylene. With Dow and Braskem then converting the ethylene into green polyethylene (320,000 tons/year, 180,000 tons/year respectively); whereas Solvay uses bio-based ethylene for the production of polyvinyl chloride, 55,000 tonnes/year. Additionally, bioethanol can be readily converted into other commodity chemicals such as acetaldehyde, and acetic acid.

Furfural:

Furfural is produced in a lignocellulosic biorefinery from various renewable agricultural resources (Dutta et al. 2012). Worldwide production of furfural is estimated to be approximately 300,000 tonnes/year. Bio-based furfural is commercially produced *via* the acid catalyzed dehydration of xylose, (Fig.1, Gravitis et al. 2001). First, C_5 polysaccharides present in biomass hemicellulose are hydrolyzed by mineral acids to produce monosaccharides, primarily xylose, which is then converted into furfural by an acid catalyzed dehydration (Machado et al. 2016, Verma et al. 2017). Furfural production from corn stalk, sugarcane bagasse and eucalyptus wood using varying concentrations of mineral acids has also been reported (Barbosa et al. 2014). Several solvents, such as ionic liquids, organic solvents and supercritical fluids were investigated in the monophasic system, whereas water/organic solvent mixtures were tested in a biphasic system (Mariscal et al. 2016). Among the organic solvents tested in a biphasic system, a renewable solvent 2-methyltetrahydrofuran, was found to increase the selectivity and yield of furfural.

Approximately 70% of furfural manufactured is a chemical feedstock for the production of furfuryl alcohol (Yan et al. 2014). In addition, furfural can also be transformed into other 5-membered oxygen-heterocycles, succinic acid and levulinic acid (Mariscal et al. 2016). Furfural has been extensively used in plastics, pharmaceutical and agrochemical industries, adhesives and flavor enhancers.

Hydroxymethylfurfural (HMF):

The production of HMF from mono- and polysaccharides and pretreated biomass is reported (Rout 2016) using various acid catalysts (Fig. 2, Dutta et al. 2012). HMF is produced in high yields by the acid catalyzed dehydration of fructose (Verma et al. 2017). Various organic solvents have been evaluated for production of HMF, and among the solvents tested dimethyl sulfoxide (DMSO) was found to be most suitable for conversion of sugars into

HMF (Esposito and Antonietti 2015). However, the high boiling point of dimethyl sulfoxide poses a challenge in the separation of the product.

Water has been tested as a reaction medium in the presence of a variety of acid catalysts. When water was used as a solvent, the product yield was found to be only about 50% (Wang et al. 2014). This is attributed to problems associated with the degradation of the product in water monophasic solvent system. To overcome this effect, biphasic solvent systems have been explored. In a biphasic system, the product formed is continuously extracted into the organic layer, thus avoiding any degradation of the desired HMF product (Saha and Abu-Omar 2014). Additionally, the biphasic solvent system helps in facilitating separation of the product from the reaction medium, improving HMF selectivity and the yield of the product. HMF can then be converted into other value-added polyester building blocks (Fig. 2) (Dutta et al. 2012; Isikgor and Becer 2015) such as 2,5-furandicarboxylic acid (FDCA), and 2,5-bis(hydroxymethyl)furan, and potential biofuels 2,5-dimethylfuran, 5-ethoxymethylfurfural, ethyl levulinate, and γ-valerolactone (Li et al. 2016; van Putten et al. 2013). HMF can also be converted to 1,6-hexanediol (1,6-HDO), which is used in the preparation of polycarbonatediols for production of polyurethanes for use in coatings, elastomers, and adhesives. In addition, 1,6-HDO can be converted to 1,6-heaxanediamine and ε-caprolactone, which are used in the synthesis of various polymers (Isikgor and Becer 2015).

2,5-Furandicarboxylic acid (FDCA):

FDCA has been extensively investigated due to its potential as a substitute for petrochemical-based adipic acid and terephthalic acid. FDCA is produced by the oxidation of HMF in high yields (Fig. 2, Rass et al. 2013) utilizing various homogeneous and heterogeneous systems (van Putten et al. 2013; Chatterjee et al. 2015). The synthesis of FDCA is also accomplished by starting from fructose in a two-step dehydration followed by oxidation, without needing to isolate the HMF intermediate. FDCA has many potential applications in polyesters, polyamides, and plasticizers. It has also been demonstrated polyethylene furanoate (PEF) polymers produced from FDCA and ethylene glycol have similar physical, chemical and mechanical properties of the petroleum-based polymers polyethylene and terephthalate (Isikgor and Becer 2015). Avantium is operating a pilot plant for production of FDCA and polyethylene furanoate polymers, and has formed a joint venture with BASF to build a commercial production plant with an annual capacity of up to 50,000 metric tons/year (Avantium 2016). Dupont and Archer Daniels Midland (ADM) have developed a high yielding process for production of FDCA methyl ester directly from fructose (DuPont press release 2016).

Glycerol:

Although microbial production of glycerol has been known for more than 100 years, recent developments in the biodiesel industry have led to the production of vast amounts of glycerol. Approximately 10% (w/w) of glycerol is formed during the biodiesel manufacturing process, this has led to about 90% of total glycerol produced. (Okoye and Hameed 2016). In 2012, glycerol production was estimated to be at more than 2×10^6 tons and expected to increase its growth by approximately 6% a year between 2012 and 2018 (Transparency Market Research). In terms of revenue, its demand is predicted to reach

$2.1B by 2018. Because of its ready availability and its potential to act as a primary building block in a biorefinery, glycerol has received significant attention in its conversion to the higher value-added chemicals (Schultz 2014; Zheng et al. 2008). One such method is the catalytic hydrogenation of glycerol in the presence of Ru/C or Pt/C to provide ethylene glycol, propylene glycol (Dasari et al. 2005; Nakagawa et al. 2014), and acetol (Chiu et al. 2006). When the corresponding reduction of glycerol was carried out, in the presence of hydroxide bases, lactic acid is produced as the primary product (Maris et al. 2007).

Archer Daniels Midland (ADM), Dow Chemical Company (Dow press release 2007), Huntsman (Huntsman news 2006), and Cargill (Cargill 2006) are producing renewable propylene glycol from glycerin. The use of glycerol as a feedstock (Fig. 3) in biochemical transformations for production of 1,3-propanediol (1,3-PDO) is being explored by various research groups (Yang et al. 2012). Fermentation of glycerol with genetically modified *Clostridium acetobutylicum* provides a higher yield of 1,3-PDO (Gonzalez-Pajuelo et al. 2006). Glycerol is also utilized in the production of 1,2-propanediol by an *Escherichia coli* fermentation process (Altaras and Cameron 1999). Another derivative of glycerol is glycerol carbonate which is produced either by reacting glycerol with urea or ethylene or propylene carbonate (Okoye 2016) or carbon dioxide (Ma et al. 2012). Glycerol carbonate has a wide range of applications in the synthesis of industrially important chemicals such as glycidol, and in polymers, coatings, adhesives and lubricants. Glycerol has also been utilized in the commercial production of epichlorohydrin. Glycerol is reacted with 2 equivalents of HCl in the presence of acetic acid and primarily forms 1,3-dichloro-2-propanol, which on a further base-catalyzed cyclization provides the product with the elimination of NaCl (Santacesaria et al. 2010). Solvay and Dow Chemical Company (Bell et al. 2008) are manufacturing epichlorohydrin utilizing a similar process. This process is found to be superior when compared to traditional manufacturing methods and produces less chlorinated waste and uses 90% less water overall. When glycerol is subjected to the selective oxidation of the primary hydroxyl groups, the commercially useful compounds glyceraldehyde (Kim et al. 2014), glyceric acid (Kondamudi et al. 2012) and tartronic acid (Behr et al. 2008) are obtained. Oxidation of secondary hydroxyl group provides dihydroxyacetone (DHA), while oxidation of all three hydroxyl groups yields ketomalonic acid (Ciriminna and Pagliaro 2003; Pagliaro et al. 2007; Gil et al. 2014). Glycidol, another glycerol derivative, has the enormous potential for production of other industrially valuable chemicals, epoxy resins, polyurethanes and polyglycerol esters. A bio-based process for the synthesis of glycidol from glycerol has been recently reported (Bai et al. 2013). Glycerol can be converted into polyols and various organic acids by yeast and filamentous fungi fermentation. The anaerobic fermentation of glycerol to various alcohols and acids has been reviewed by Clomburg and Gonzalez (2013). Similarly, 1-butanol, 2,3-butanediol, 1,3-propanediol, ethanol, lactic acid, succinic acid, propionic acid, and dihydroxyacetone can be produced utilizing various microorganisms (Almeida et al. 2012; Abad and Turon 2012).

Succinic acid:

The synthesis of succinic acid is traditionally accomplished by the hydrogenation of petroleum-based maleic acid or via the oxidation of butanediol. However, recently some companies have started manufacturing succinic acid *via* the biochemical fermentation of biorefinery sugars. Roquette/DSM (Press release 2008), as well as Bioamber (Press release 2015) are producing succinic acid at the commercial scale by the *E. coli* fermentation of glucose. Succinic acid, as a platform chemical (Fig. 4), can be converted into succinate esters, which are precursors for 1,4-butanediol, tetrahydrofuran, and γ-butyrolactone (Delhomme et al. 2009; Luque et al. 2009). Dehydrogenative cyclization of succinic acid provides succinic anhydride, which acts as a key starting material for production of fumaric acid and maleic acid (Delhomme et al. 2009). NatureWorks and Bioamber formed an alliance to explore the production of completely bio-renewable polyester copolymers of succinic acid and 1,4-butanediol (Adkins et al. 2012). Among various polyesters that can be prepared, poly(ethylene succinate) (PES), poly(propylene succinate) (PPS), poly(butylene succinate) (PBS) are widely studied, with PES and PBS having been successfully commercialized ((Isikgor and Becer 2015). The market value of succinic acid in 2013 was approximately $115 million and it is expected to reach to $1.1 billion by the year 2020.

Lactic acid:

Lactic acid (LA) is commercially produced *via* the fermentation of various sugars such as glucose, sucrose, or lactose (Datta and Henry 2006; John et al. 2007; Ghaffar et al. 2014). Corbion manufactures L-lactic acid by fermenting carbohydrates (Corbion). The yield of calcium lactate produced in the fermentation process is approximately 90%, which upon neutralization provides lactic acid. The neutralization process produces one equivalent of $CaSO_4$, which poses a disposal problem. To overcome the issue of neutralization other technologies such as nanofiltration and ion-exchange resins have been evaluated (Ghaffar et al. 2014; Datta and Henry 2006). Recently other processes have been developed to convert xylose to lactate using engineered yeast (Ilmen et al. 2007). In addition, Direvo industrial biotechnology has recently produced lactic acid on a pilot scale directly from lignocellulose in a single-step utilizing a consolidated bioprocessing technology (Direvo press release 2013). Lactic acid global production is approximately 350,000 tons/year and is expected to grow considerably in the next decade. Lactic acid (Fig. 5) upon esterification provides lactate esters, which can be used as green solvents (Pereira et al. 2011). Reduction of lactic acid provides propylene glycol, which on dehydration yields propylene oxide. Dehydration of lactic acid affords acrylic acid and esters; whereas hydrogenolysis of the secondary hydroxyl group yields propanoic acid (Maki-Arvela et al. 2014). Lactic acid can also be converted into a biodegradable polylactic acid either by polymerization of lactic acid or its cyclic dimer lactide (Maki-Arvela et al. 2014, Yao and Tang 2013). The polylactic acid polymer exhibits performance properties similar to polystyrene or polyethyleneterephthalate with excellent barrier properties for flavors and good heat stability. Due to its low price and availability, polylactic acid has an extremely high potential among the biodegradable polymers (Erickson et al. 2012). There are several companies that are currently manufacturing polylactic acid at commercial scale, with most of the polylactic acid produced being used in the packaging market and textiles (Isikgor and Becer 2015).

Levulinic acid:

Levulinic acid is produced in high yield by the acid-catalyzed hydrolysis of C_6 sugars. Recently, the large-scale production of levulinic acid from lignocellulosic feedstock has been demonstrated (Pileidis and Titirici 2016). Maine Bioproducts utilizes an acid catalyzed dehydration of lignocellulosic feedstock (Rose and Palkovits 2011) using a two-stage process for production of levulinic acid. GF Biochemicals has started commercial production of levulinic acid from cellulosic biomass in 2015 using their proprietary technology (GF Biochemicals press release 2015).

Levulinic acid acts as a building block in many applications such as pharmaceuticals, plasticizers, fragrances and cosmetics. Avantium has developed a process for the synthesis of levulinic acid methyl ester starting from plant carbohydrates (Avantium). Several other companies have also demonstrated the production of levulinic acid based bio-polymers. For example, Segetis (acquired by GF Biochemicals in 2016) investigated the use of levulinic acid based ketals in polyurethane and thermoplastic applications (Rose and Palkovits 2011). Levulinic acid also has the potential for substituting petroleum-based chemicals. For example, levulinic acid derived diphenolic acid (DPA) (Guo et al. 2008) can serve as a substitute for bisphenol-A (BPA) in food containers and consumer products. In addition, levulinic acid can also be converted into various higher value-added products (Fig. 6, Pileidis and Titirici 2016) such as levulinic acid esters, 5-aminolevulinic acid, valeric acid, γ-valerolactone, and 2-methyltetrahydrofuran.

3-Hydroxypropionic acid (3-HP) and 3-hydroxypropionaldehyde (3-HPA):

3-HP and 3-HPA are important platform chemicals which can be converted to various higher value-added chemicals. Although considerable research is in progress, currently there are not any commercial production processes for 3-hydroxypropionaldehye and 3-hydroxypropionic acid production from renewable sources. One of the challenges associated with the biological production of 3-hydroxypropionaldehyde is the toxicity of 3-HPA itself (Zheng et al. 2006). Currently, 3-hydroxypropionaldehyde is produced by the fermentation of glycerol, which upon oxidation yields 3-hydroxypropionic acid. 3-Hydroxypropionic acid is produced directly from glycerol by using the *Klebsiella pneumoniae* and *E. coli* strains. It is also produced from glucose at neutral pH by *E. coli* (Kumar et al. 2013), or at lower pH by yeast *S. cerevisiae*. Since 3-HP has a pKa of 4.51, carrying out the fermentation process at low pH improves the economics and reduces the amount of waste generated in the process (Kildegaard et al. 2015), thus the yeast-based process is preferable.

As a platform chemical 3-HP and 3-HPA can be converted to various value-added chemicals (Fig. 7) (Corma et al. 2007) such as acrolein, acrylic acid, acrylic acid esters and amides (Craciun et al. 2009), 1,3-propanediol, malonic acid and 3-hydroxypropionic esters. Acrylic monomers are used in the synthesis of various polymers. Polyacrylic acid is commercially produced by The Dow Chemical Company, AkzoNobel, Lubrizol and BASF. Acrylamides are produced by the treatment of 3-HPA with an amine. Although the acrylamide monomer is toxic, its polymer polyacrylamide is not toxic and is used in various applications (Huang et al. 2001) such as in water treatment, paper manufacture, mining, oil recovery, absorbents and as electrophoresis gels. Acrolein and acrylonitrile are two other industrially essential derivatives which are used in the synthesis of various polymers.

Sorbitol:

Sorbitol is the most commonly used sugar substitute with an approximate annual global production of 800,000 tons, and it is widely used in food, beverages, drugs, cosmetics and to produce value-added chemicals (Banu et al. 2012; Zhang et al. 2013). Sorbitol is commercially produced by a transition metal catalyzed hydrogenation of D-glucose (Kamm 2007; Ortiz et al. 2013). In the industrial process, raw materials such as corn, cassava and wheat are converted into glucose by enzymatic hydrolysis, and in a second step the glucose is subjected to hydrogenation to yield the desired sorbitol. Although Ni catalysts have been used in the earlier industrial processes, Ru catalysts have been found to be superior at converting glucose into sorbitol with very high selectivity (Zhang et al. 2013). Currently, Roquette Freres is the most prominent producer of sorbitol, and shares approximately 70% of the market volume with Cargill and SPI Polyols. Recently, there have been reports on the conversion of cellulose and cellobiose to sorbitol by hydrolysis followed by hydrogenation (Chen et al. 2013; Ribeiro et al. 2015). The conversion of cellulose to sorbitol has also been reported using catalysts containing an acid or heteropolyacid with supported metal catalysts such as Pt, or Ru (Zhu et al. 2014; Wang et al. 2016; Zhang et al. 2016). Approximately, 15% of the sorbitol produced is utilized in the industrial conversion into ascorbic acid by fermentation (Kobayashi and Fukuoka 2013). Isosorbide (Fig. 8) is produced by dehydration of sorbitol (Rose and Palkovits 2012) in the presence of a Cu catalyst. Hydrogenolysis of sorbitol with multifunctional catalysts produces lower carbon number alcohols (glycerol, propyleneglycol, ethylene glycol, ethanol and methanol) and these lower alcohols can then be further converted to higher value-added products (Isikgor and Becer 2015). Sorbitol can also be utilized in the synthesis of polymers, which have a wide range of applications as biodegradable polymers and in biocomposites and biomedicines. Similarly, the isosorbide polymer, poly(isosorbide carbonate) is considered as a promising alternative to the petroleum-based BPA polycarbonate due to its superior properties (Roquette). Roquette is also manufacturing polymer grade isosorbide and isosorbide diesters as phthalate-free plasticizers (Roquette).

Xylitol:

Xylitol is a naturally occurring five-carbon sugar alcohol which is 20% sweeter than sucrose, but with 40% the calories. In addition, the metabolism of xylitol is not dependent on insulin, thus it is an ideal sugar substitute for people with diabetes (Lugani et al. 2017).

Industrial production of xylitol (Figure 10) is accomplished *via* the catalytic reduction of pure D-xylose obtained from hardwood hemicellulosic hydrolysate in the presence of Ni catalyst at high temperature and pressure (Rafiqul and Sakinah 2013). Although it is commercially produced by chemical reductive methods, several reports have appeared describing biochemical reductive methods utilizing either enzymes or microorganisms (Chen et al. 2010). Recently a one-pot procedure for the conversion of hemicellulose to xylitol using an acid in combination with Ru on carbon catalyst has been reported (Dietrich et al. 2017). Similarly, the conversion of corncob derived hemicellulose to xylitol is accomplished using a ruthenium catalyst supported on carbon nanotubes (Ribeiro et al. 2016).

Isoprene:

Isoprene is a 5- carbon building block for the synthesis of a variety of polymers. The majority of isoprene produced is converted into the polyisoprene polymer, which is used in a variety of products such as footwear, mechanical instruments, medical appliances, sporting goods, and rubber tires.

Although commercial production of isoprene is currently carried out from petroleum-based feedstocks, manufacturing processes based on renewable resources are in development. Dupont-Genencor and the Goodyear Tire Company are co-developing (DuPont) an integrated process to manufacture bio-isoprene from renewable raw materials on an industrial scale (Genencor). Their technology utilizes a genetically engineered *E. coli* for the fermentation process (Whited et al. 2010). Amyris in partnership with Michelin and Braskem is also exploring the development and commercialization of isoprene from plant sugars (Amyris).

A transition from today’s fossil-based economy towards a more sustainable bio-economy is emphasized by International Energy Agency (IEA), Organization for Economic Co-Operation and Development (OECD), and the World Economic Forum (WEF), as well as several national government entities (e.g. NREL). Each emphasizing the drivers for the transition to a bio-economy being, the need to develop an environmentally, socially and economically more sustainable global economy, the reduction in greenhouse gas emissions, and to reduce the dependence on nonrenewable fossil fuel resources (de Jong et al. 2013). The expansion of a successful bio-economy will depend on the development of robust biorefinery systems each with advanced technologies, which can process biological feedstocks into a variety of bio-based products with efficient, and cost-effective processes. In a bio-economy, the basic building blocks for chemicals, materials and energy are derived from renewable sources and are considered as an integral part of the development toward a more sustainable economy. Lignocellulosic biomass is the most widely available renewable source of biomass with less competition in terms of food and feed production. For the lignocellulosic biorefineries to be successful and to achieve fruitful results, major investment in the development and the application of highly efficient conversion technologies are needed. Advanced biorefineries, which can use lignocellulosic raw materials as the feedstocks, can produce large quantities of biofuels, as well as higher value-added products. These biorefineries can be integrated into the existing industrial infrastructures, such as pulp and paper mills and chemical production facilities. Thus, synergies can be achieved in energy, material flows along with processes, logistics, product and raw material markets (Nanda et al. 2015). Advanced biorefineries when developed at commercial scale will create and drive new business opportunities. However, the most advanced biorefineries are not yet commercialized and the development of these biorefineries depends on the progress made in the thermochemical and biochemical platform technologies (Pandey 2011).

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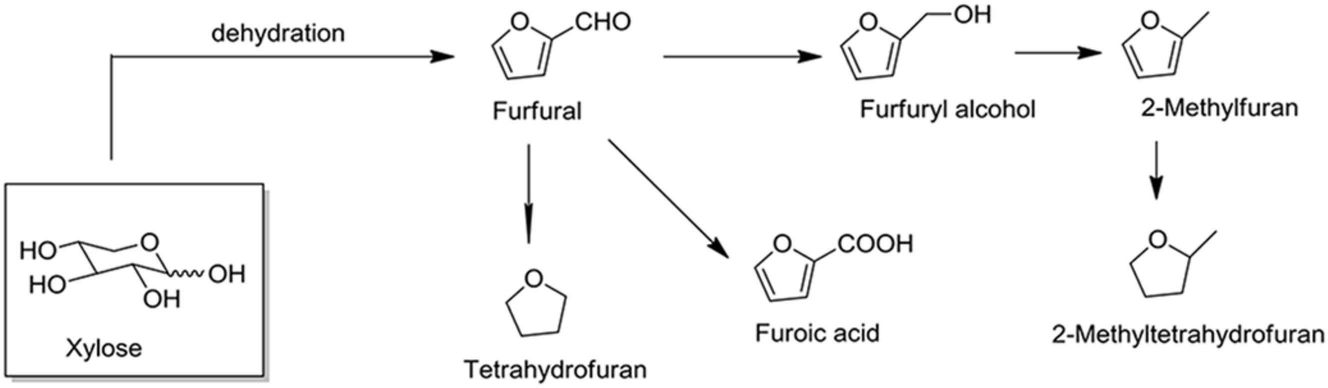

Fig. 1.

Synthesis of Furfural and its derivatives

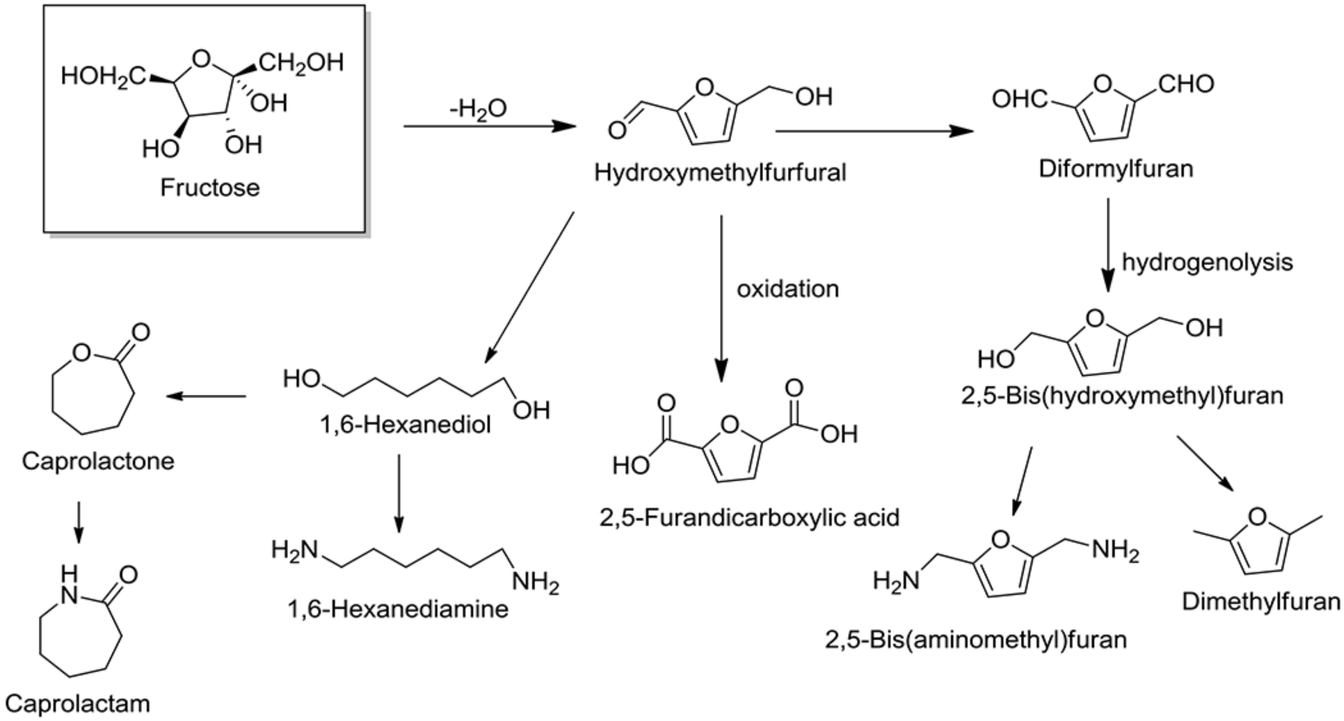

Fig. 2.

Synthesis of Hydroxymethylfurfural and its derivatives

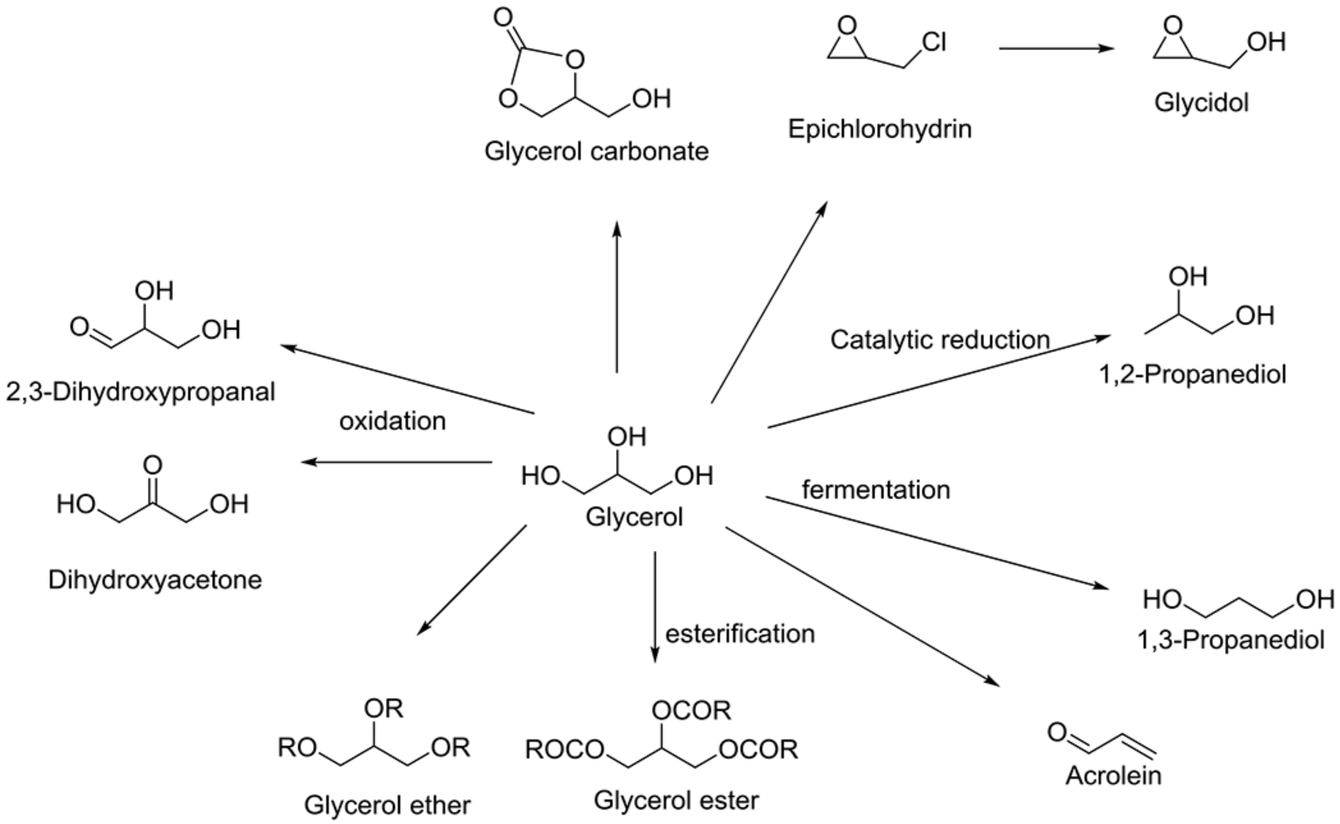

Fig. 3.

Glycerol as a Platform chemical

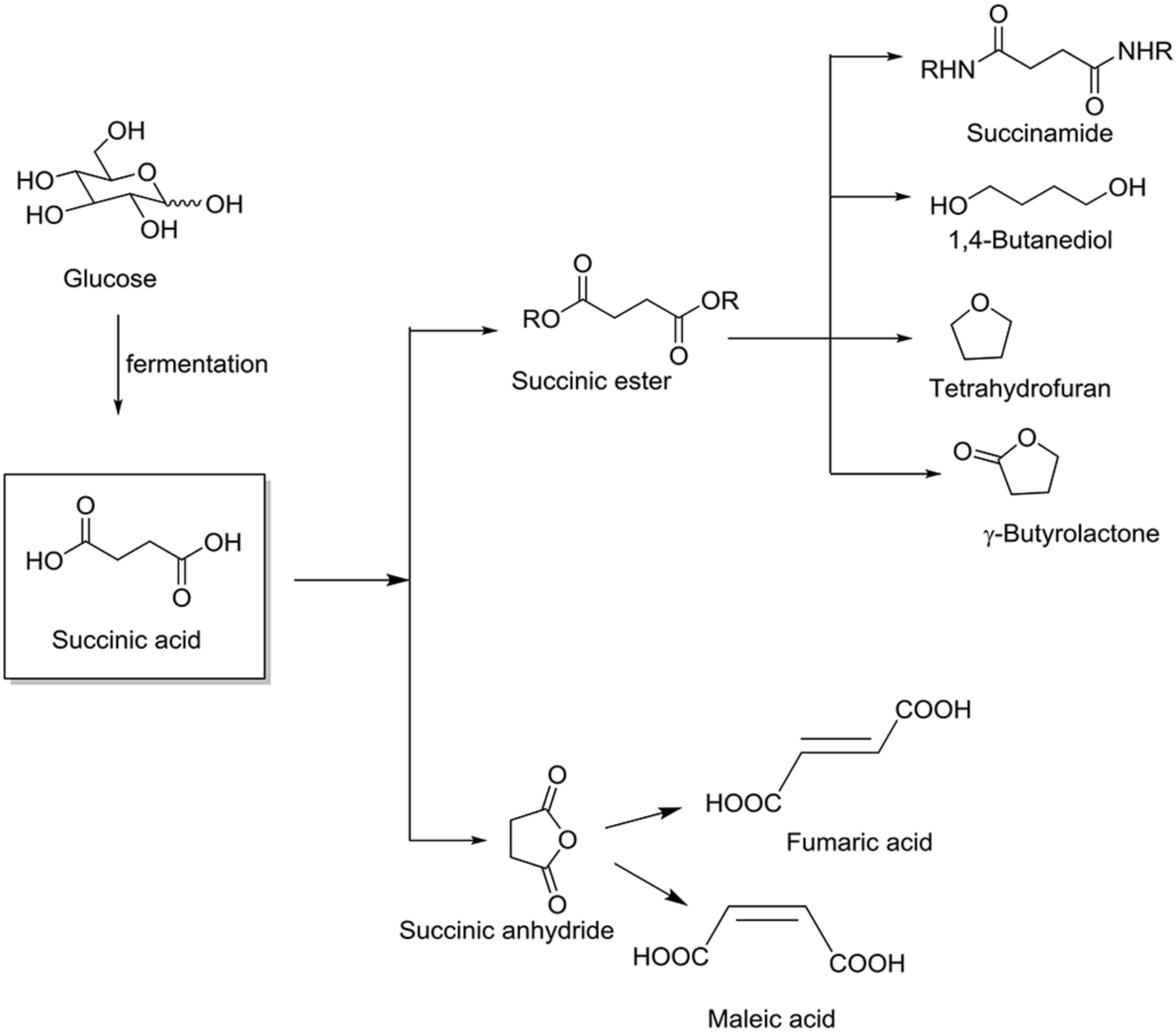

Fig. 4.
Synthesis of Succinic acid and its value-added products

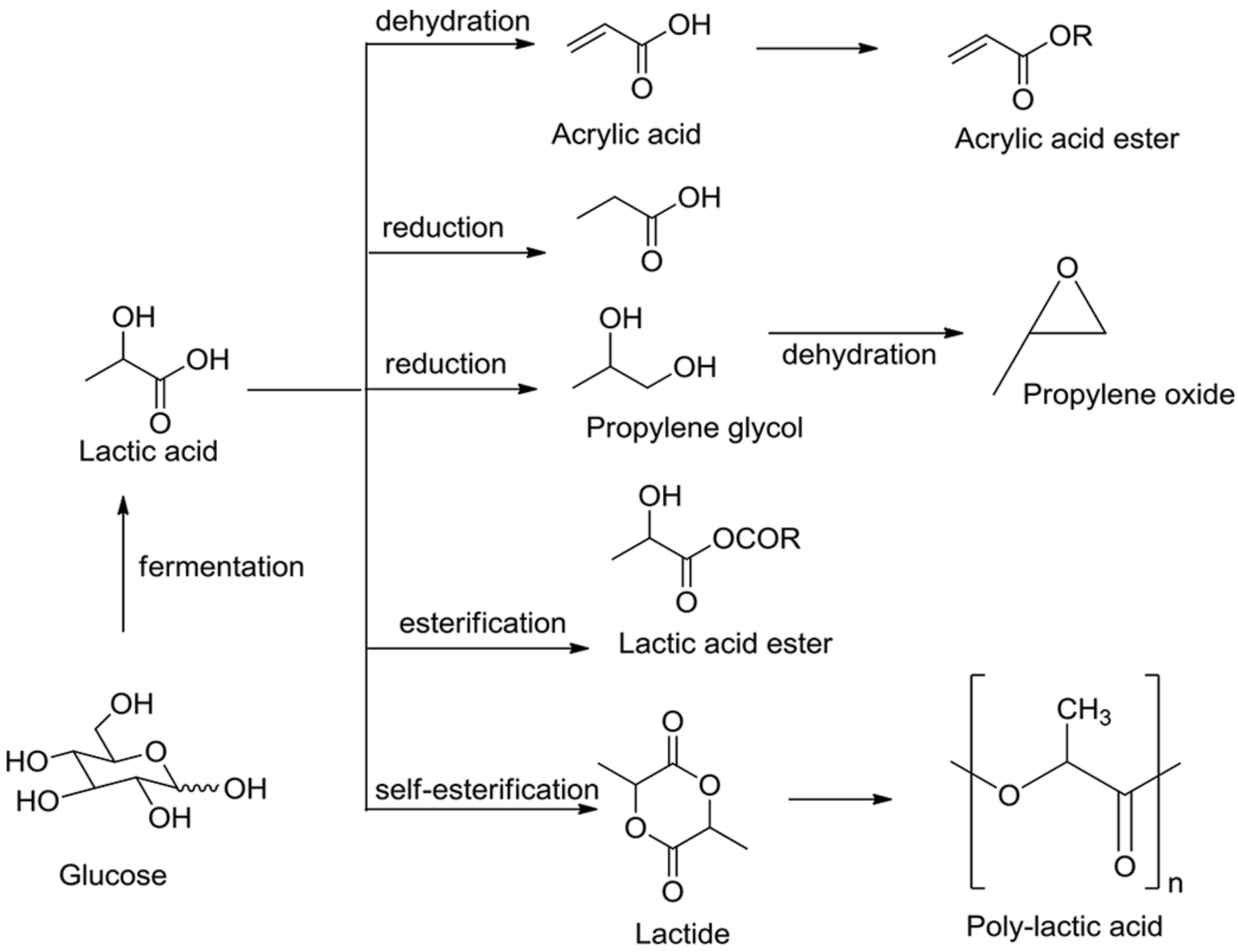

Fig. 5.

Synthesis of lactic acid and its value-added products

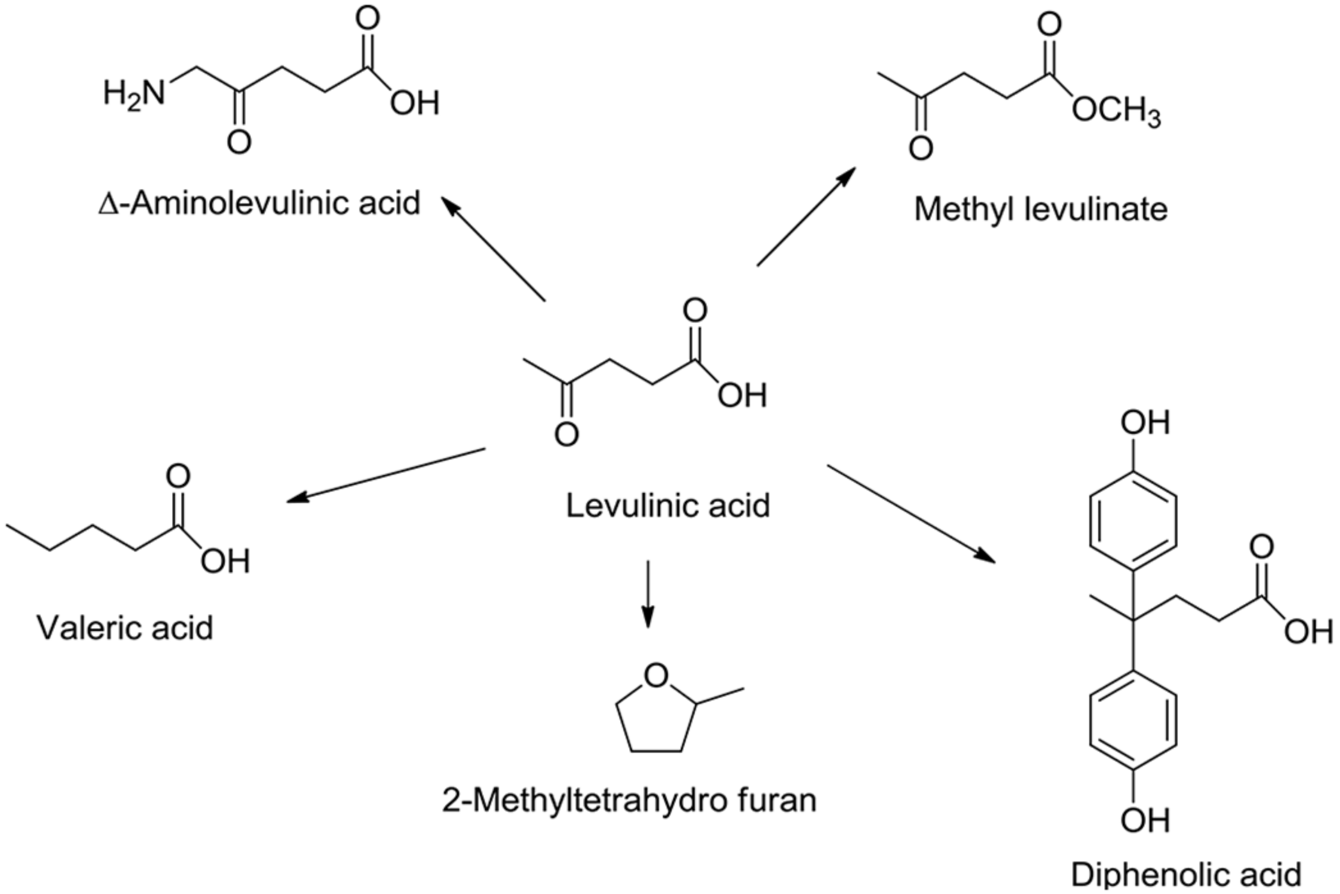

Fig. 6.
Levulinic acid value-added products

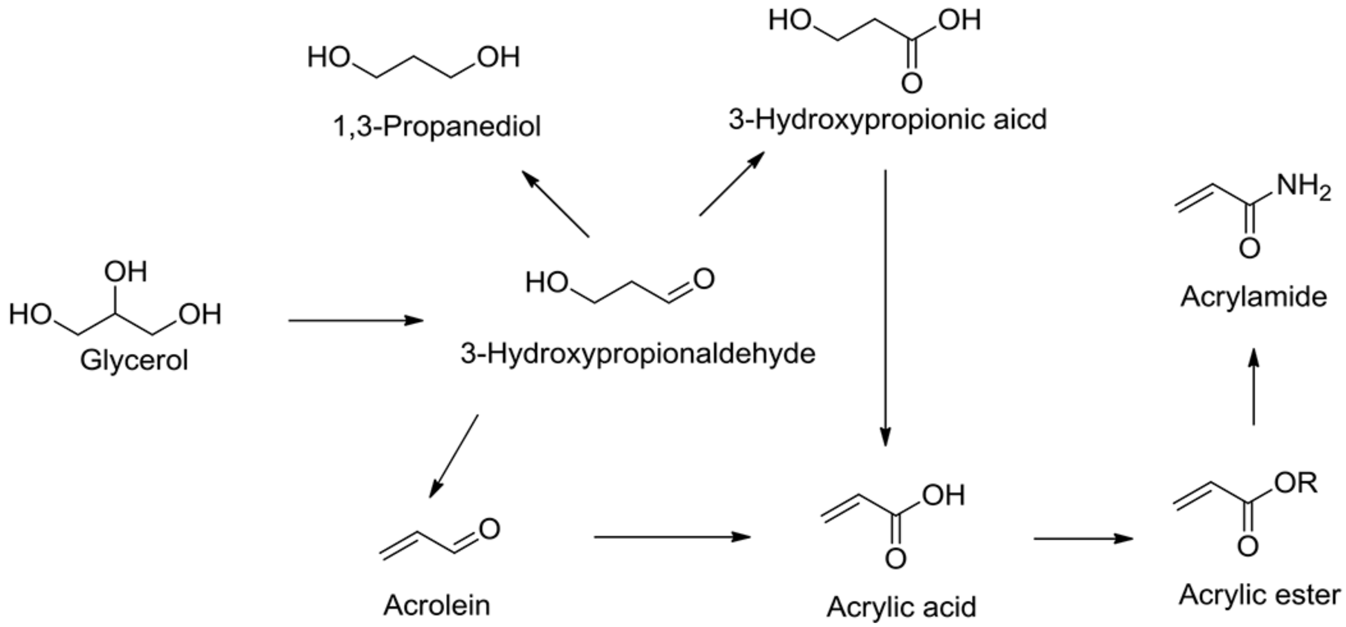

Fig. 7.

3-Hydroxypropionaldehyde and 3-hydroxypropionic acid value-added chemicals

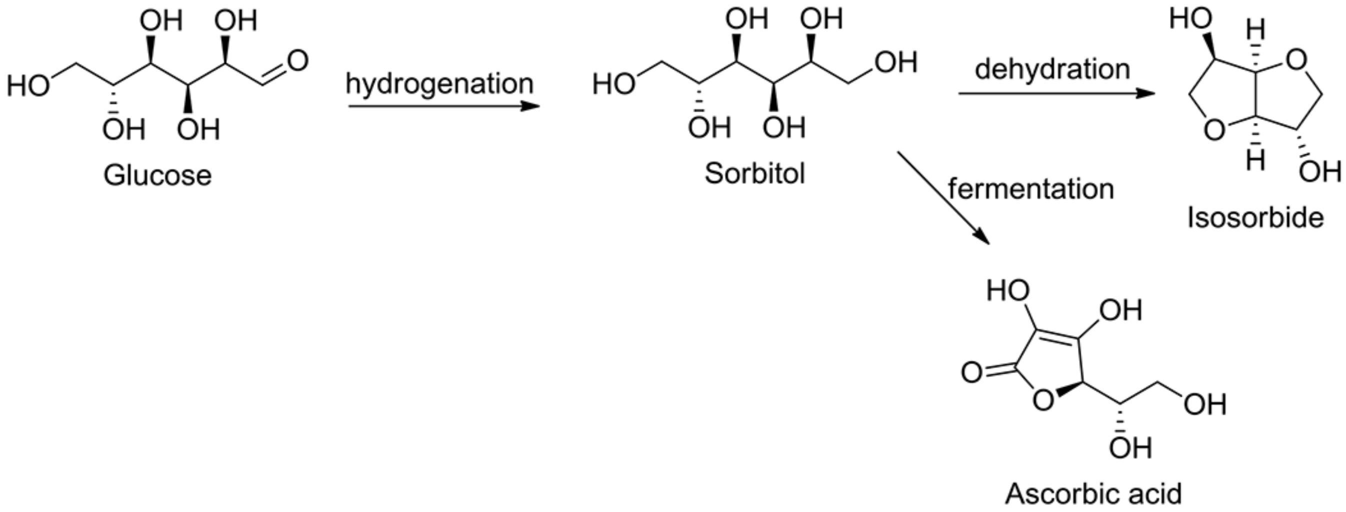

Fig. 8.

Synthesis of Sorbitol and its value-added products

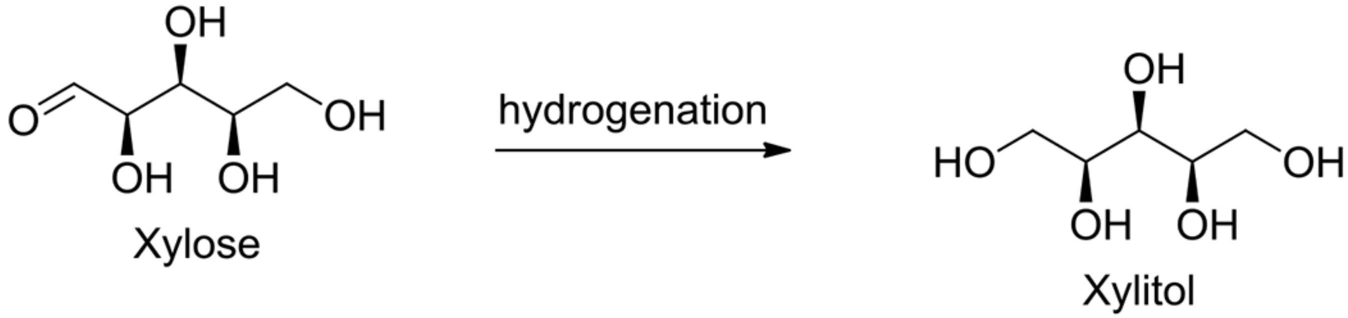

Fig. 9.

Synthesis of Xylitol from Xylose

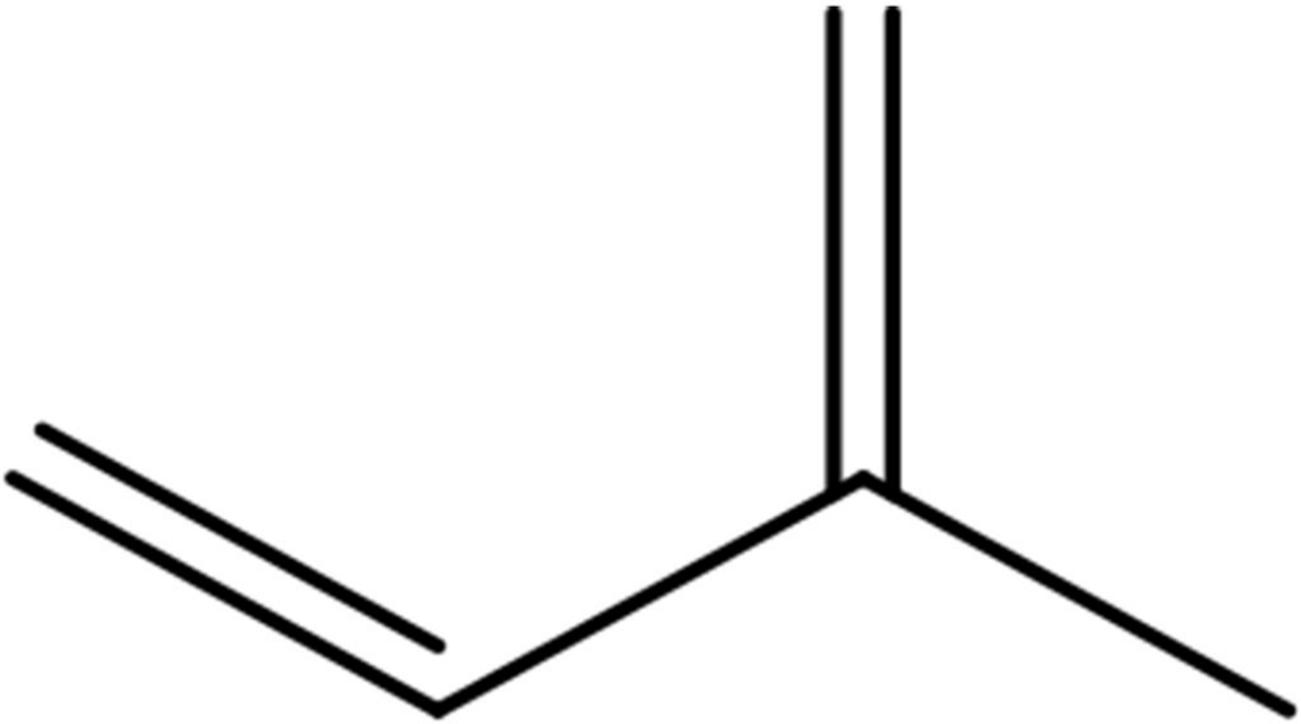

Fig. 10.
Structure of Isoprene