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Review

Bio-Based Chemicals from Renewable Biomass for Integrated Biorefineries

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Abstract: The production of chemicals from biomass, a renewable feedstock, is highly desirable in replacing petrochemicals to make biorefineries more economical. The best approach to compete with fossil-based refineries is the upgradation of biomass in integrated biorefineries. The integrated biorefineries employed various biomass feedstocks and conversion technologies to produce biofuels and bio-based chemicals. Bio-based chemicals can help to replace a large fraction of industrial chemicals and materials from fossil resources. Biomass-derived chemicals, such as 5-hydroxymethylfurfural (5-HMF), levulinic acid, furfurals, sugar alcohols, lactic acid, succinic acid, and phenols, are considered platform chemicals. These platform chemicals can be further used for the production of a variety of important chemicals on an industrial scale. However, current industrial production relies on relatively old and inefficient strategies and low production yields, which have decreased their competitiveness with fossil-based alternatives. The aim of the presented review is to provide a survey of past and current strategies used to achieve a sustainable conversion of biomass to platform chemicals. This review provides an overview of the chemicals obtained, based on the major components of lignocellulosic biomass, sugars, and lignin. First, important platform chemicals derived from the catalytic conversion of biomass were outlined. Later, the targeted chemicals that can be potentially manufactured from the starting or platform materials were discussed in detail. Despite significant advances, however, low yields, complex multistep synthesis processes, difficulties in purification, high costs, and the deactivation of catalysts are still hurdles for large-scale competitive biorefineries. These challenges could be overcome by single-step catalytic conversions using highly efficient and selective catalysts and exploring purification and separation technologies.

Keywords: renewable biomass; hydrodeoxygenation (HDO); dehydration; hydrogenation; biomass-derived chemicals; biorefinery; catalytic conversion

1. Introduction

A dependence on fossil-based energy sources, decreasing accessibility to crude oil, motivation to protect the environment from disastrous carbon emissions, and an increasing world population have led to increased interest in becoming less energy dependent than in the past. These concerns have motivated researchers to develop technologies for renewable resources to substitute petroleum derivatives. The best approach to compete with fossil-based refineries is the processing of biomass in integrated biorefineries. The integrated biorefineries employed various biomass feedstocks and conversion technologies to produce biofuels and bio-based chemicals. From an industrial point of view, a biorefinery should require the most efficient conversion processes for the production of high valued chemicals and biofuels [1–3]. Biomass feedstocks, such as agricultural residues and wood chips, constitute an inexpensive renewable resource for commercial large-scale biorefineries, as these waste products are widely available and can sequester carbon. The target chemicals include alcohols [4], organic acids such as formic acid and levulinic acid [5], and furanics such as 5-hydroxymethylfurfural (5-HMF) and furfurals [6]. These chemicals can further be converted to a range of derivatives that have potential applications in biofuels, polymers, and solvent industries. The possible scheme for a chemo-catalytic biorefinery is shown in Figure 1.

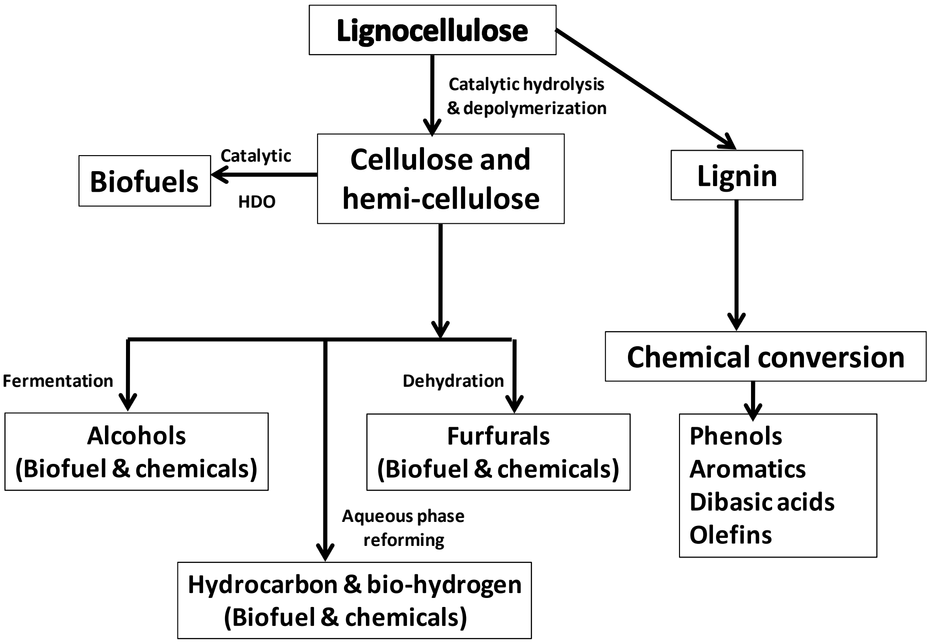

Figure 1. The possible scheme for a chemo-catalytic biorefinery.

Lignocellulosic biomass is mainly composed of cellulose (34–54 wt %), hemicellulose (19–34 wt %), and lignin (11–30 wt %) [7]. Cellulose, the major component of biomass, is present as half of the organic carbon in the biosphere [7–9]. The development of processes and technologies to convert lignocellulosic biomass to fuels and value-added chemicals (given in Figure 2) remains a significant challenge. In this context, the major difficulty in producing a high yield of target chemicals and fuels is the complex chemical composition of lignocellulosic biomass feedstocks. Structurally, cellulose contains anhydrous glucose units and hemicellulose consists of different C5 sugar monomers. On the other hand, lignin is a complex, three-dimensional, and cross-linked biopolymer having phenylpropane units with relatively hydrophobic and aromatic properties [10,11]. Due to these differences in their chemical composition and structure, cellulose, hemicellulose, and lignin have different chemical reactivities. In addition to the complex nature of bio-resources, the inert chemical structure and compositional ratio of carbon, hydrogen, and oxygen in molecules in biomass present difficulties in the chemo-catalytic conversion of biomass to fuels and chemicals. Therefore, besides using the natural lignocellulosic biomass as a reactant, researchers often use model compounds for conversion process studies. In addition, the development of highly active and selective catalysts for the chemo-selective catalytic conversion of lignocellulosic biomass to desired products remains a daunting challenge.

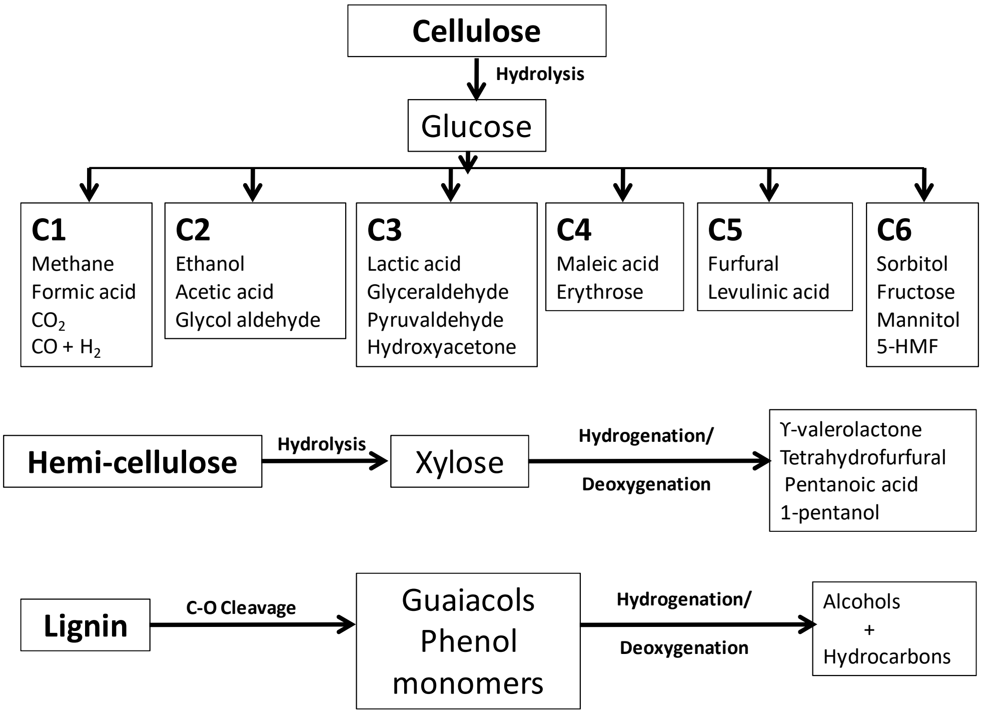

Figure 2. Potential chemicals and fuels obtained from lignocellulosic biomass.

Many review articles on chemicals obtained from bio-resources have been published, such as those focused on a large variety of biomass feedstocks/substrates and reaction types, as well as those dealing with specific feedstocks such as carbohydrates, triglycerides, cellulose, hemicellulose, lignin, 5-hydroxymethylfurfural [12], furfural [13], and lignocellulosic biomass [14]. Some reviews were dedicated to biomass conversion to selected chemicals [15,16]. In other reviews, the requirements to develop cost-effective catalytic processes for highly functionalized biomass molecules and the need for process intensification have been highlighted [17–19]. Thermo-chemical processes such as pyrolysis, gasification, and aqueous phase reforming are widely reported for the production of chemicals from biomass feedstocks [20]. Syngas production from biomass gasification was also reported [2,21,22]. Produced syngas can be selectively converted to hydrocarbons, such as dimethyl ether, methanol, and even higher alcohols, depending on the nature of the heterogeneous catalysts used [2,21,22]. A fast pyrolysis results in the production of complex oxygenates, and these can be used to obtain chemicals. However, the recovery of pure chemicals would be difficult and costly [23]. Ru/C and Pt/C catalysts used for the hydroprocessing of pyrolysis oils leads to the formation of alcohols and polyols [24]. The aqueous phase reforming of carbohydrates was mainly employed to alkane and hydrogen production [25]. Dehydration and coupling reactions have been found to be effective for the production of oxygenates as intermediates [2,26–28]. Biochemical conversion processes such as anaerobic digestion and fermentation were also reported in the literature for converting biomass feedstocks into biomass-based energy fuels [29].

To date, the reviews related to the conversion of biomass to chemical value chains were mainly centered on specific chemicals from one component (carbohydrate sugars). A major objective of this review is to address the production of chemicals and further their derivatives from sugars as well as lignin components of biomass. This basic review is helpful for beginners entering the field. For this purpose, the review is divided into two parts: chemicals obtained from cellulose and hemicellulose (sugars) and lignin feedstocks based on selected publications. In addition, our understanding of the basic reactions involved during biomass processing is explored.

2. Common Reactions Involved in Biomass Processing

Basic knowledge of the mechanisms of common reactions such as dehydration, hydrogenation, and hydrodeoxygenation involved in biomass upgradation processes is discussed in the following section.

2.1. Dehydration

Dehydration is a reaction in which a water molecule is removed from the substrate, mainly alcohol, forming an alkene or other unsaturated product depending on the substrate [30]. The reaction is commonly catalyzed by Lewis or Bronsted acids, as the hydroxyl group is a poor leaving group. Dehydration in the presence of a Bronsted acid catalyst occurs by first protonating the hydroxyl group (Figure 3, step 1), as the protonated hydroxyl group (R-H_2O^+) is a better leaving group than the hydroxyl group. As a result, the catalyst is eliminated as water (Figure 3). Simultaneously, a C=C bond is formed in the C skeleton of the substrate, as per Zaitsev's rule (Figure 3, step 2). In Lewis acid catalyzed reactions, however, the reaction proceeds through the bonding of Lewis acid to the lone electron pair of hydrogen-oxygen [31] (Figure 3, step 1). The electrophile nature of the Lewis acid lowers the electron density in the alcohol C—O bond, which results in the cleavage of the alcohol C—O bond and the formation of alkene and Lewis acid hydroxide species (Figure 3, step 2). The Lewis acid hydroxide reacts with the released β-proton, forming water and the original catalyst species (Figure 3, step 3).

Due to the abundances of hydroxyl groups in a wide variety of natural resources, dehydration reactions are the most common and important ways to valorize biomass. As a result, different dehydration products can be obtained from biomass, and are used as high-value chemicals. In the present review, the dehydration of sugars to furfurals (5-HMF and furfurals) [32], their synthesis, and their applications were explored.

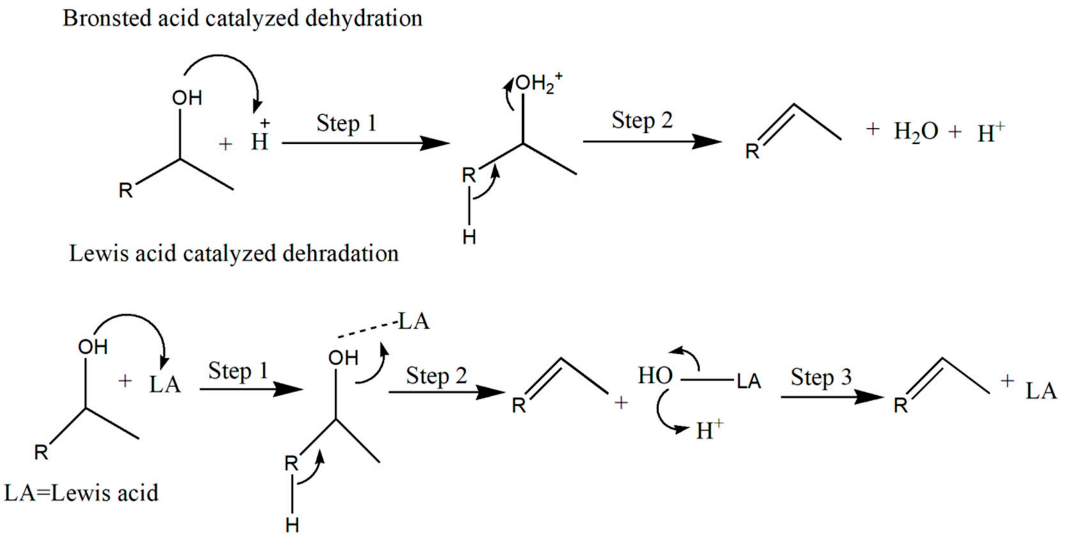

Figure 3. Dehydration mechanism with Bronsted and Lewis acid catalysts [30].

2.2. Hydrogenation

Hydrogenation is a reaction in which hydrogen atoms are added to an unsaturated compound to reduce the double and triple bonds. Molecular hydrogen (H_2, gaseous) and other compounds (transfer hydrogenation) can be used as a hydrogen source in the reaction. However, the addition of hydrogen does not take place without a catalyst; therefore, the reaction is catalyzed by homogeneous and heterogeneous catalysts to increase the feasibility of reactions at the laboratory and industrial scales within short time durations. Most commonly, heterogeneous systems with solid metal hydrogenation catalysts and molecular hydrogen are used as catalysts for biomass conversion reactions.

Hydrogenation with a heterogeneous solid metal catalyst and hydrogen follows the Horiuti–Polanyi mechanism [33]. First, the hydrogen molecule is chemisorbed on the surface of the catalyst, followed by the scission of an H-H bond producing two adsorbed hydrogen atoms (Figure 4, step 1). Next, the unsaturated reactant is adsorbed on the catalyst (Figure 4, step 2). The opening of a double bond through chemisorption (Figure 4, step 3) follows this. The hydrogen atoms are transferred to the chemisorbed reactant on the surface of the catalyst in a stepwise manner of which the first hydrogen transfer is reversible (Figure 4, step 4, and step 5). The second hydrogen transfer forms the reduced reaction product, and then it is desorbed from the surface of the catalyst, thus completing the reaction cycle.

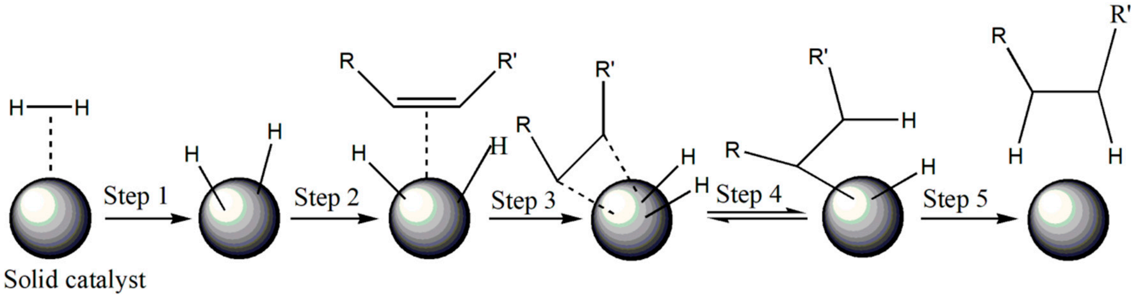

Figure 4. Heterogeneous hydrogenation mechanism according to Horiuti–Polanyi mechanism [33].

Hydrogenation is the most fundamental reaction in chemistry. Nature produces many different unsaturated products including C=C double bonds, in carbonyl groups, in the structural aldoses and ketoses of cellulose and hemicellulose. The hydrogenation of these biomass-derived monosaccharides in lignocellulosic biomass produces sugar alcohols. For example, hydrogenation of glucose and xylose, the main components in lignocellulosic biomass, produces sorbitol and xylitol, respectively. In addition, the dehydration products can be further upgraded through hydrogenation. These hydrogenation products can be used as solvents, monomers, and biofuels [34–36]. The synthesis and uses of hydrogenation of biomass-derived substrates will be covered in more detail.

2.3. Hydrodeoxygenation (HDO)

HDO is a hydrogenolytic reaction in which the removal of the oxygen atom from the reactant occurs in the presence of hydrogen (H_2). The removal of oxygen-containing functionalities can occur through direct hydrogenolysis (C—O bond cleaved with H_2), dehydration (C—O bond cleaved through the removal of water), decarbonylation (removal of CO), and decarboxylation (removal of CO_2) [37]. The most common HDO pathways, depending on the oxygen moieties, are reported in Figure 5. HDO also needs selective catalysts to facilitate the formation of the desired reaction products. Catalysts typically contain noble metals as the hydrogenation catalyst, as well as Bronsted or Lewis acidic sites for cleavage of the C—O bonds. The HDO mechanisms of different oxygen functionalities depend on the reaction conditions and catalysts used. The review article on HDO reported by He and Wang [37] summarized different HDO mechanisms for carboxylic acids, ketones, aldehydes, and alcohols. The relative HDO reactivities have been proposed as alcohols > ketones > alkyl ethers > carboxylic acids [38].

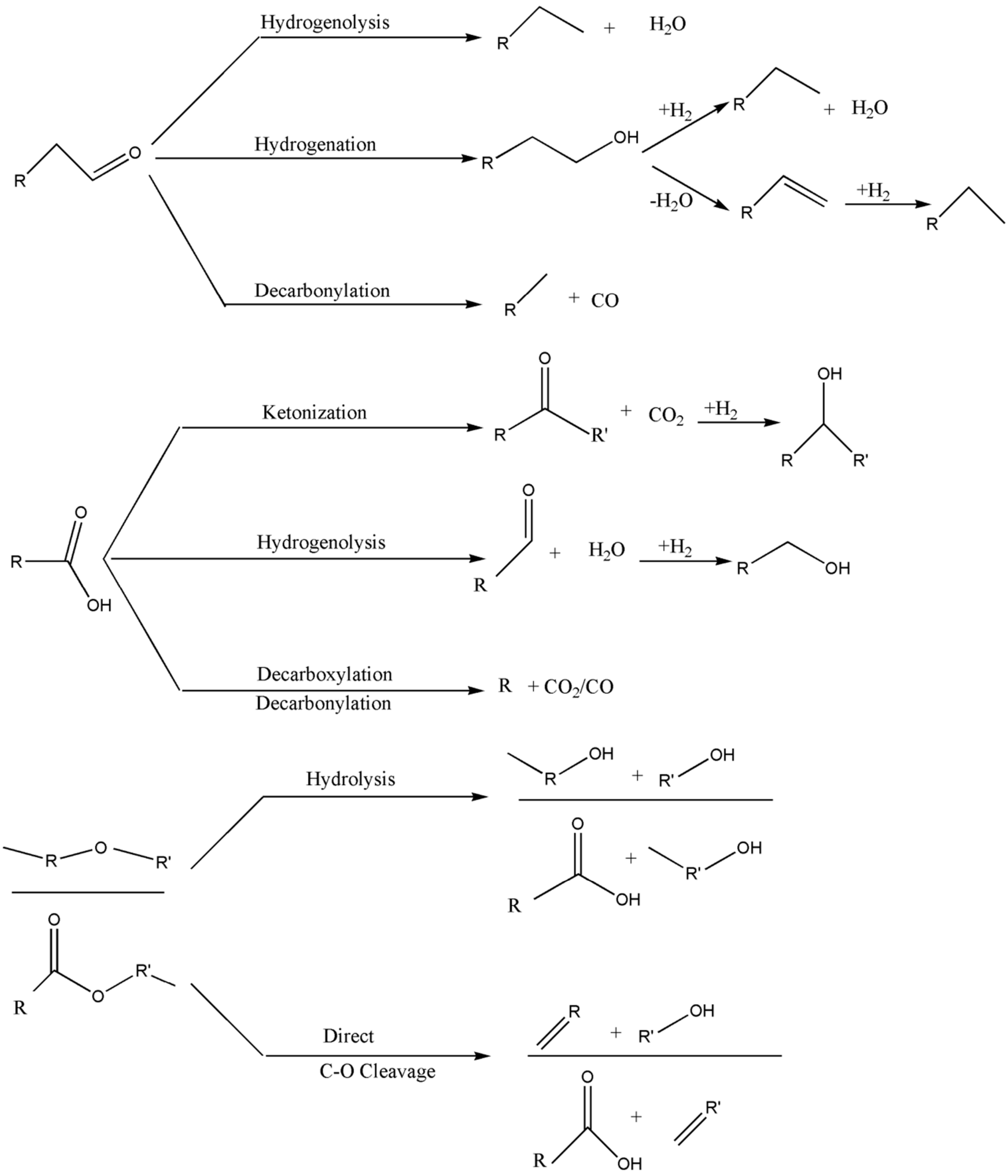

Figure 5. Hydrodeoxygenation (HDO) pathways depending on the oxygen moieties [37,38].

In the case of biomass or biomass-derived substrates, HDO reactions are used to reduce high oxygen content [38]. Typically, these HDO reactions require a high temperature and high pressure, possibly resulting in the formation of product mixtures through cleavage of C—C bonds and carbon skeleton rearrangements. In this context, new catalytic systems need to be developed to remove the oxygen-containing functionalities.

3. Sugars as Feedstocks

Cellulose and hemicellulose are the polymers of C6 and C5 sugar units that are linked by ether bonds. Cellulose consists of D-glucose units connected by β-1-4 linkages and extensive hydrogen bonding which makes the hydrolysis process difficult [39]. Acid and enzymatic hydrolysis are commonly used to liberate the monosaccharide glucose units [40]. Hemicellulose contains C5-sugars, such as xylose, galactose, mannose, and arabinose [41]. The dehydration of C5 sugars can yield furfural, which is a platform chemical that has applications ranging from solvents to resin and fuel additives [42]. The large scale synthesis of organic and furanic chemicals from sugars is an important alternative to petroleum-based energy resources. Therefore, the following discussion focuses on a survey of chemo-catalytic methods for the production of 5-HMF, levulinic acid, furanic chemicals, and alcohols from sugars.

3.1. Hydroxymethylfurfural (5-HMF)

Hydroxymethylfurfural (HMF), also 5-(hydroxymethyl)furfural (5-HMF) is the most important platform chemical from renewable feedstock for the next-generation plastic [1] and biofuel [2] production. The derivatives such as levulinic acid, 2,5-bis(hydroxymethyl)furan (2,5-BHF), 2,5-dimethylfuran (2,5-DMF), and 2,5-diformylfuran (2,5-DFF) were synthesized from 5-HMF (shown in Figure 6). Other derivatives are 1,6-hexanediol [43], 5-hydroxymethyl-2-furan carboxylic acid (HMFCA) [44], 2,5-furfuryldiamine, 2,5-furfuryldiisocyanate, and 5-hydroxymethylfurfurylidenester [45]. These derivatives have found applications as precursors for the synthesis of materials such as polyesters, polyamides, and polyurethane [46,47]. The synthesized polymeric materials exhibit good properties. Polyurethane demonstrates very high resistance to thermal treatments; photoreactive polyesters have been used for ink formulations, and Kevlar-like polyamides exhibit liquid crystal behavior. Therefore, 5-HMF is considered a “sleeping giant” in the field of platform chemicals from renewable feedstocks [48]. Despite the versatile applications of 5-HMF, sustainable synthetic routes for its production in scalable quantities have yet to be developed.

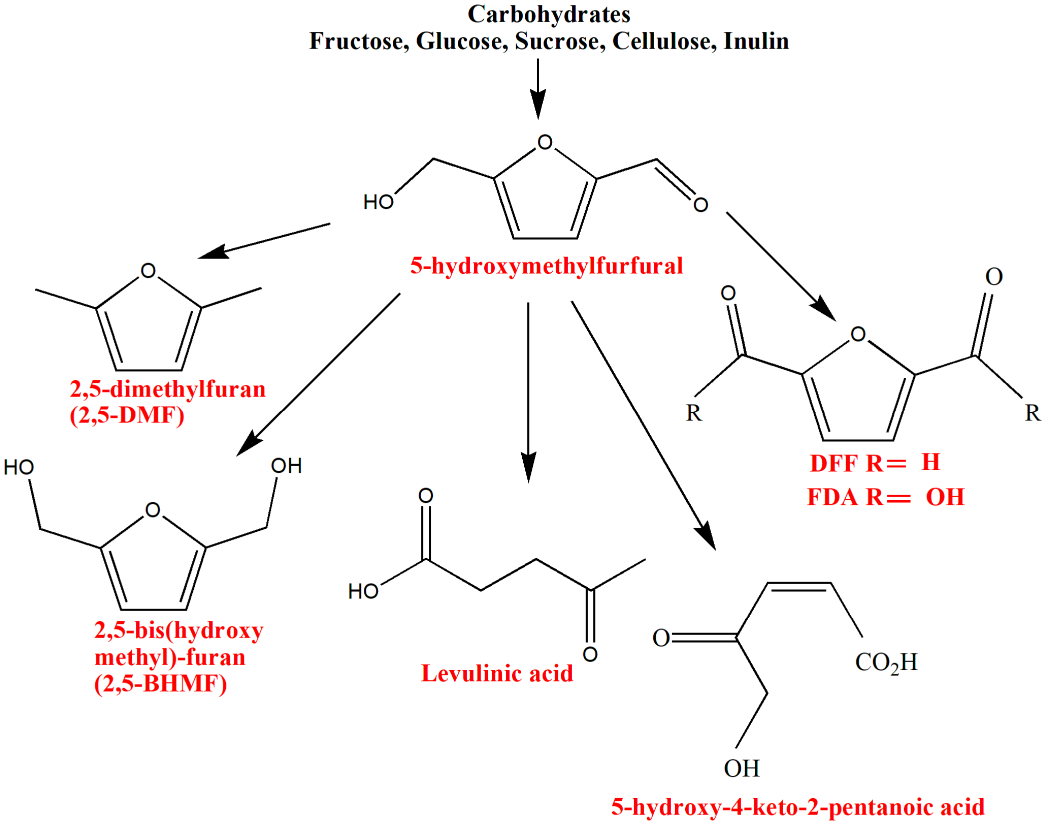

Figure 6. Hydroxymethylfurfural and its derivatives [DFF: 2,5-diformylfuran and FDA: 2,5-furan dicarboxylic acid] [15].

In 1895, Kiermayer first obtained 5-HMF using sucrose and fructose as substrates in the presence of oxalic acid with a 20% yield [49]. Later on, Fenton and co-workers conducted extensive research on 5-HMF [50]. The actual structure for 5-HMF was designated in 1909 [49]. In subsequent years, several synthesis methods were reported using homogeneous and heterogeneous acid catalysts, both in aqueous media [50–52]. Several important reviews on 5-HMF have been published [12,45,53]. The synthetic method used to prepare 5-HMF is shown in Figure 7. The method involves multistep routes: hydrolysis of cellulose to glucopyranose, isomerization of glucopyranose to fructofuranose, and dehydration of fructofuranose to 5-HMF. The catalysts used are an organic acid, mineral acid, solid acid, and metal-containing catalysts. The 52% yield of 5-HMF from inulin was produced in a CuCl/betaine hydrochloride/H_2O system [54]. Lee et al. [55] reported the immobilized enzyme for the conversion of cellulose-to-glucose-fructose. An efficient acid-free and metal-free solid catalyst for the dehydration of fructose to 5-HMF was developed. These catalysts were based on 4-methylpyridinium (ionic polymers) cross-linked with divinylbenzene and 77% of 5-HMF yield was obtained [56]. However, a high yield of 5-HMF was achieved in the presence of sulfonated carbon-based solid acid catalyst [57]. The reaction was performed in the dimethyl sulfoxide (DMSO) solvent at a reaction temperature of 160 °C and reaction time of 1.5 h.

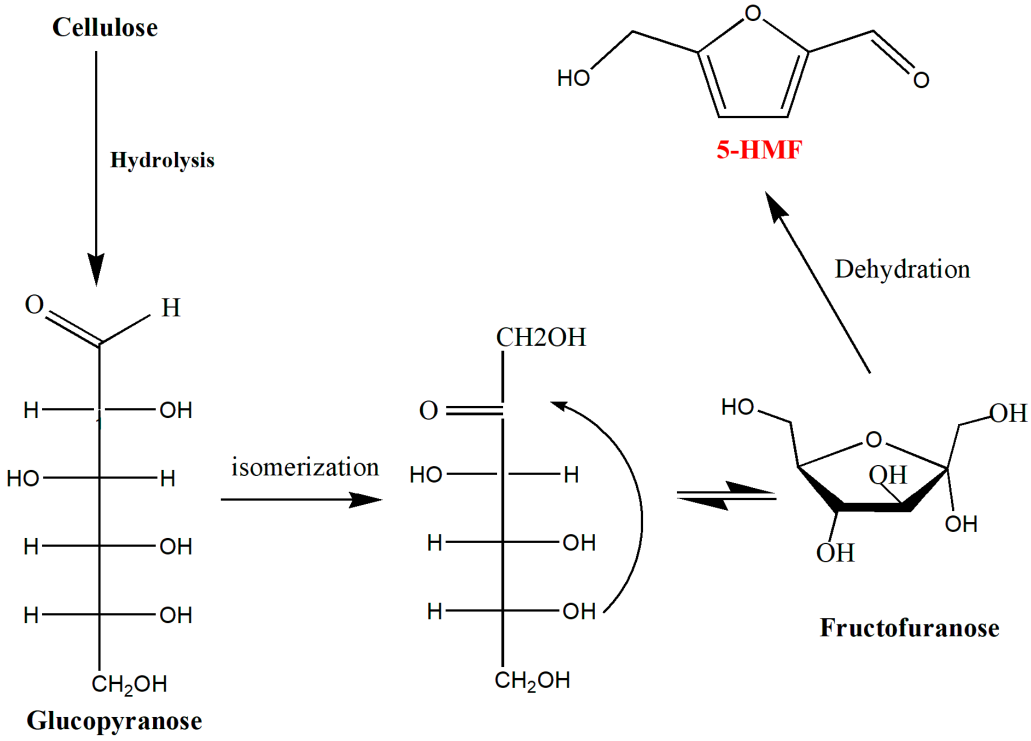

Figure 7. Pathways for cellulose transformation to 5-hydroxyfurfural (5-HMF) (Resketched from reference [12]).

The use of ionic liquids for the conversion of carbohydrates to 5-HMF was extensively reported and thoroughly reviewed [39]. Binder and Raines [58] demonstrated that the $CrCl_2$ catalyzed conversion of corn stover and purified cellulose can produce 48% and 54% 5-HMF, respectively. The authors used *N*,*N*-dimethyl acetamide (DMA) solvent containing LiCl and 1-ethyl-3-imidazolium chloride at reaction temperature of 140 °C. The use of Bronsted-Lewis surfactant-combined heteropolyacid, $Cr[(DS)H_2PW_{12}O_{40}]_3$ ($DS-O-SO_3C_{12}H_{25}$, dodecylsulfate) was reported for the conversion of cellulose to 5-HMF with a 53% yield [59]. Other significant progress has included reports using metal halides in ionic liquids, which are efficient dehydration catalysts [60–63]. Among the metal halides reported, $CrCl_2$ was found to be the most promising. The transformation of D-fructose and glucose with $CrCl_2$ produces 5-HMF with ~70% yield. The proton transfer occurs in the presence of $CrCl_3^-$ anion which promotes the isomerization of glucose to fructose in a [EMIM] $^+$ Cl$^-$ solvent. Further, the use of $CrCl_2$-NHC-carbene/zeolite/ionic liquid and combined $CrCl_3$/$RuCl_3$ as a catalyst system for the transformation of cellulose to 5-HMF has been investigated [64,65]. The cellulose transformation in the presence of $CrCl_2$-NHC-carbene/zeolite/ionic liquid was reported to occur via hydrolysis of cellulose followed by dehydration of the resulting glucose [64]. The use of ytterbium based catalysts such as $YbCl_3$ and $Yb(OTf)_3$ in alkylimidazolium chlorides for the transformation of glucose to 5-HMF was disclosed by Stahlberg et al. [66]. The efficient hydrolysis of cellulose in an ionic liquid-water mixed solvent [67,68] is also reported. Researchers also investigate the Sn-Beta zeolite [69,70], a catalyst containing Lewis and Bronsted acid sites [71,72], and chemo-enzymatic catalytic systems [73–75] for the production of 5-HMF from glucose. Most recently, Xu et al. [76] investigated Bronsted acidic ionic liquids 1-(3-sulfonic acid) propyl-3-methylimidazolium phosphotungstate ($[MIMPS]_3PW_{12}O_{40}$), and various alkaline ionic liquids, 1-ethyl-3-methylimidazolium hydroxide ([EMIM]OH), 1-butyl-3-methylimidazolium hydroxide ([BMIM]OH), 1-butyl-3-methylimidazolium carbonate ($[BMIM]HCO_3$), hydroxy-functionalized ionic liquid, and 1-hydroxyethyl-3-methylimidazolium tetrafluoroborate ($[AEMIM]BF_4$) as catalysts for the conversion of disaccharides (sucrose and cellobiose) to 5-HMF. The maximum catalytic activity and selectivity of 5-HMF were achieved with $[AEMIM]BF_4$ ionic liquid. Amin et al. [77] studied the kinetics of glucose decomposition by a 1-sulfonic-acid-3-methylimidazoliumtetrachloroferate ($[SMIM][FeCl_4]$) in the temperature range of 110 to 170 °C. Most of these reactions were performed under thermal heating and hence required long reaction times. At longer reaction times, the side reactions giving oligomeric species from 5-HMF and sugars are known to become dominant. In this context, the microwave-assisted rapid synthesis of 5-HMF from cellulose is also investigated. These produce a 62% 5-HMF yield in 2 min using ionic liquids as the reaction medium. The $Zr(O)Cl_2$/$CrCl_3$ catalyst in DMA LiCl solvents in the presence of 1-butyl-3-methylimidazolium have been disclosed for the synthesis of 5-HMF from cellulose and lignocellulosic biomass using the microwave-assisted method [78]. No doubt, ionic liquids are the preferred solvent for the synthesis of 5-HMF because of their inherent characteristic properties, such as good thermal stability, low vapor pressure, and range of tunable hydrophobicity/hydrophilicity, but these cannot be considered industrial solvents. The major issues with ionic liquids are their high costs, lack of long-term recyclability, and complex extraction/purification of products. To overcome these issues, in 2004, Abott and co-workers reported new solvents named deep eutectic solvents (DESs) [79]. These DESs were obtained by mixing of the hydrogen-bond donor (HBD) and hydrogen-bond acceptor (HBA). They used safe and biodegradable components such as choline chloride (ChCl), glycerol, renewably sourced carboxylic acids, and carbohydrates. For biomass processing, DESs have advantages over conventional solvents, including an inhibited water reactivity (to some extent), decreased polyol viscosity, compatibility with few enzymes, and the stability of carbohydrates and furanic derivatives. Jerome et al. [80] recently reviewed the contribution of DESs for biomass processing with their limitations. Hong [81] and Konig [82] studied the catalytic conversion of fructose to 5-HMF in the presence of various DESs. The author found low yields of 5-HMF (<30%) at 100 °C in the presence of $AlCl_3$, $FeCl_3$, and $CrCl_3$ catalysts. This may occur because of the side reactions of fructose and urea. Following these reports, more investigations are reported in the literature [54,82–85]. Al-Duri et al. [83] investigated the use of DESs made of ChCl and p-toluenesulfonic acid (p-TSA) in an equimolar amount. The findings suggest that a DES can dissolve the fructose and promotes the dehydration of 5-HMF with a 90% yield. Zhao et al. [84] used a series of bifunctional acid-base heteropolyacids (HPAs) for the conversion of fructose to 5-HMF in a ChCl/fructose DES. A 92% yield of 5-HMF was obtained within 1 min of reaction time at 110 °C. Later, Konig et al. [82] reported the production of 5-HMF in a ChCl/glucose DES using 10 mol% of a $CrCl_2$ catalyst. Besides ChCl, betaine hydrochloride (BHC) has also been tested as a Bronsted acid catalyst in an aqueous solution of different carbohydrates/ChCl DESs [54]. The 80% yield of 5-HMF was obtained from fructose. However, betaine was unable to convert glucose or cellulose to 5-HMF. Despite the many advantages, DESs still face the major issue of long-term recycling and extraction of chemicals from a DES. The long-term recycling of ChCl in biomass processing is hampered by the accumulation of water and side products that modify the physicochemical properties of DESs. Extraction of chemicals from DESs is another major problem that dramatically impacts the cost efficiency of the process. Therefore, the search for recyclability and extraction processes for the use of DESs on a large scale is highly desirable for integrated biorefineries.

5-HMF derivatives

The formation of furan-based derivatives from the 5-HMF by catalytic oxidation and hydrogenation processes is reported in Figure 8. The chemicals obtained include 2,5-diformylfuran (2,5-DFF), 2,5-dimethylfuran (2,5-DMF), 2,5-furan dicarboxylic acid (2,5-FDCA), and 2,5-bis(hydroxymethyl)furan (2,5-BHF). 2,5-DFF is produced by the selective and partial oxidation of 5-HMF. It is used in the synthesis of fungicides, drugs, and polymeric materials [85]. Several promising catalytic routes for 2,5-DFF production are reported in the literature [85–91]. The complete transformation of 5-HMF with a 90% yield of 2,5-DFF was achieved with V_2O_5/TiO_2 catalyst in the presence of air and toluene or methyl isobutyl ketone (MIBK) as the solvent. In another attempt, the aerobic oxidation of 5-HMF to 2,5-DFF was tested by Navarro et al. [85]. The immobilized organic catalyst prepared by pyridine-VO(acac)$_2$ supported on an organo-functionalized SBA-15 support was used. With a vanadyl-acetylacetonate/PVP catalyst, 99% selectivity and 82% conversion of 2,5-DFF was achieved. Halliday and co-workers [86] reported the use of an acidic resin and a vanadium catalyst for the conversion of fructose in DMSO solution. A 45% yield of 2,5-DFF was observed without recovering the 5-HMF intermediates. Researchers also disclosed the potential of iron as a cheap catalyst for the production of 2,5-DFF from 5-HMF [87,88]. Mittal et al. [89] reported the use of magnetic bi-functional WO_3HO-VO (salen)-SiO_2@Fe_2O_3 nano-catalyst to directly synthesize 2,5-DFF from fructose. In this work, an 82% yield of 5-HMF was obtained in 1 h and if a co-oxidant (H_2O_2) was added, 71% 2,5-DMF was synthesized after 15 h in the presence of ambient air. As in this one-step conversion process, in-situ oxidation of 5-HMF occurs by the activated oxoperoxovanadium species. A heterogeneous catalyst 2,2,6,6-tetramethylpiperdine-1-oxyl (TEMPO) on ordered mesoporous silica SBA-15 leads to a 73% 2,5-DFF yield from 5-HMF oxidation in ethylacetate with the addition of [bis(acetoxy)ido]benzene (BAIB) and acetic acid as co-oxidants in an oxygen-rich environment [88,89]. In a most recent work, the V_2O_5 ceramic powder catalyst was investigated for the production of 2,5-DFF from 5-HMF in the presence of oxygen as an oxidant in DMSO with an 85.7% yield [90].

The 2,5-FDCA is a potential substitute for terephthalic or isophthalic acids in the manufacture of polyamides, polyesters, and polyurethanes [2,91]. The oxidation of 5-HMF leads to the production of 2,5-FDCA, and the use of mainly noble metal catalysts was reported [92,93]. In the presence of oxygen pressure and a controlled pH, the oxidation reaction proceeds to form a diacid. The high yields were obtained with Pt/Pb bimetallic catalysts [92]. However, when Pt-based catalysts were used alone, with oxygen as an oxidant in water, a high catalyst to the substrate (weight ratio) could be required [93]. Ribeiro and Schuchardt [94] studied the one-step conversion of D-fructose using a bifunctional redox catalyst. In this, both dehydration and oxidation of D-fructose were achieved over a catalyst containing cobalt acetylacetonate encapsulated in sol-gel silica. Gold dispersed as nanoparticles also proved to be an efficient catalyst for selective oxidation with molecular oxidation [95,96]. The use of Au/TiO_2 catalyst for the oxidation of 5-HMF to 2,5-FDCA was reported by Gorbanev et al. [96]. Gold nanoparticles supported on ceria (Au/CeO_2) were tested by Casanova et al. [97] to selectively convert 5-HMF into 2,5-FDCA with a 99 mol% yield. Fu et al. [98] reported the synthesis of 2,5-FDCA from 5-HMF under base-free conditions. The author prepared an oxidation catalyst using atomic layer deposition (ALD) to deposit Pt nanoparticles on low surface area ZnO_2. It has been suggested that the enhanced adsorption property of Pt/ZnO_2 facilitated stronger adsorption between the catalyst and reactant intermediates, which is associated with the high dispersion and uniform particle size distribution of Pt nanoparticles; thus, the adsorbed reactant can be effectively converted to 2,5-FDCA.

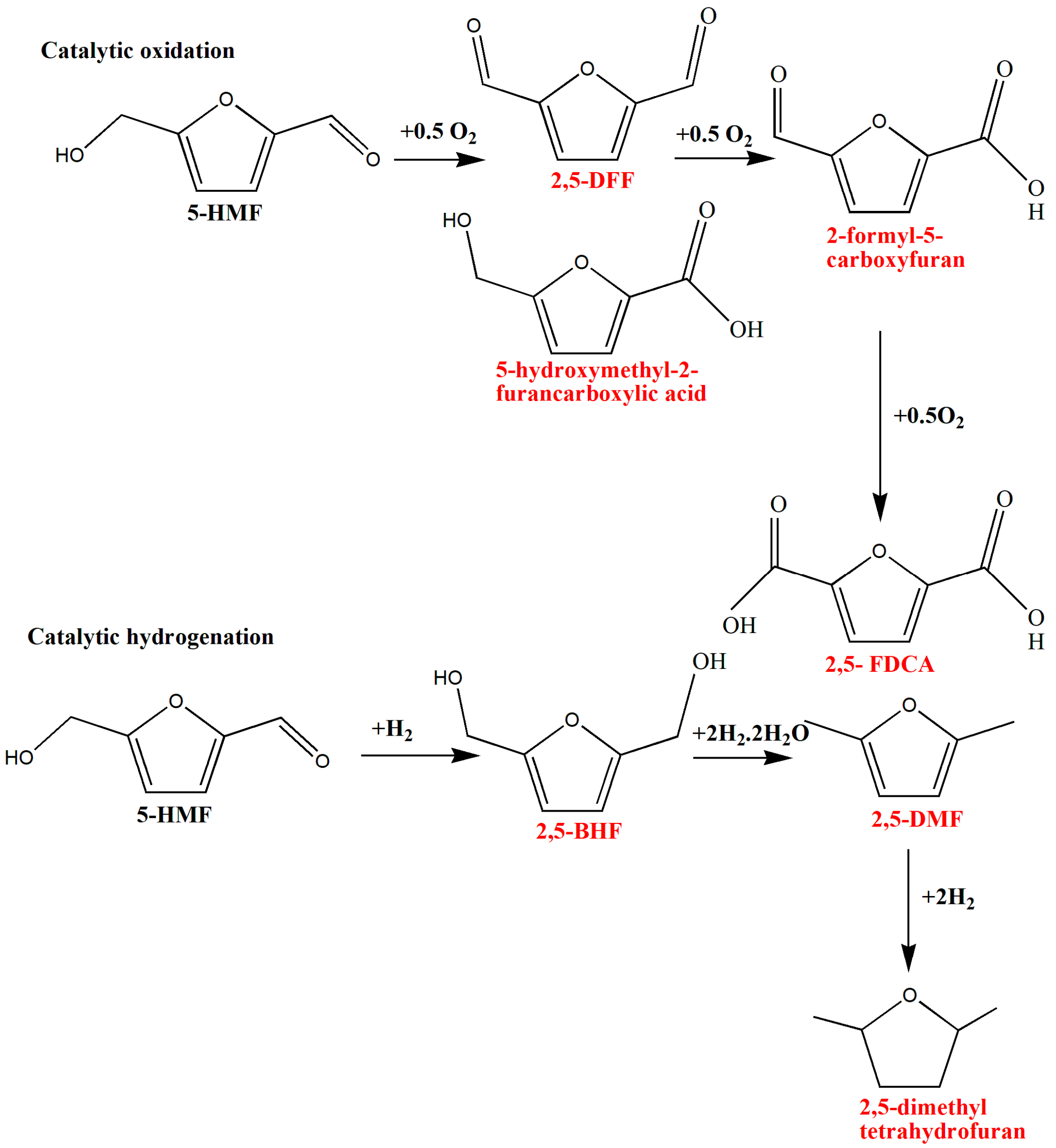

Figure 8. Catalytic oxidation and hydrogenation routes of 5-HMF [2,5-DFF: 2,5-diformylfuran; 2,5-BHF: 2,5-bis(hydroxymethyl)furan; 2,5-DMF: 2,5-dimethylfuran; and 2,5-FDCA: 2,5-furandicaroxylic acid] [86].

The hydrogenation products of 5-HMF, i.e., 2,5-BHF and 2,5-DMF, are important fine chemicals and can be used in the manufacturing of polymeric materials [99–101]. The reaction involves hexoses dehydration and then catalytic hydrogenation reactions. In this process, catalytic hydrogenation of the –CHO group and furan ring takes place, and careful control of the conditions allows an improvement of the selectivity of 2,5-BHF. The conventional hydrogenation catalysts such as Raney Ni and supported metal catalysts (Cu, Pt, Pd, Co, Cr, Mo) with water as a solvent at a high temperature and high hydrogen pressure leads to the production of 2,5-BHF [102,103]. The selective removal of five oxygen atoms from hexoses molecules leads to the production of 2,5-DMF. A two-step process for the synthesis of 2,5-DMF from D-fructose was proposed by Roman-Leshkov et al. [104]. In this process, first dehydration of 5-HMF was carried out in the presence of acid in a biphasic reactor and 5-HMF was extracted in the organic phase. Later, 5-HMF was converted to 2,5-DMF with CuRu-catalyst by hydrogenolysis of C–O bonds. Although a huge number of studies in the literature have been published, the processes involved in the production of these promising chemicals would require a complete environmental assessment view.

The recalcitrance nature of cellulose towards hydrolysis to glucose and its subsequent isomerization to fructose makes the 5-HMF synthesis from cellulose challenging. More sophisticated methods should be developed to obtain high yields of 5-HMF from cellulose or pure lignocellulosic biomass substrates. This requires efficient catalysts for hydrolysis, isomerization, and dehydration in combination with high-performance reaction systems such as continuous flow reactors, microwave reactors, and so forth.

3.2. Levulinic Acid

In 2004, the Biomass Program of the US Department of Energy listed levulinic acid as one of the most promising value-added bio-derived chemicals [105,106]. Levulinic acid contains a carbonyl and a carboxyl group [107] and hence can take part in reactions such as oxidation, reduction, esterification, substitution, and condensation that make it a valuable platform chemical. The chemicals produced from levulinic acid are listed in Figure 9. Levulinic acid is widely applied in the preparation of lubricants, chiral reagents, resins, biologically active materials, adsorbents, batteries, and electronics [108,109]. Certain select chemicals are also produced from levulinic acid, such as succinic acid, methyltetrahydrofuran, diphenolic acid, δ-aminolevulinic acid, 1,4-butanediol, different esters of levulinic acid, γ-valerolactone (GVL), α-angelicalactone, sodium and calcium levulinates, and valeric (pentanoic) acid [110–112].

In 1985, a detailed mechanism for the formation of levulinic acid was disclosed using ^{13}C NMR analysis [113]. After several acid-catalyzed hydrations, 5-HMF opens the furan cycles to form levulinic acid. A Bronsted acid catalyst plays an important role for the conversion of 5-HMF into levulinic acid. The Biofine renewable process was developed at the industrial scale for the production of levulinic acid from cellulose and hemicellulose [108,114]. This process used two reactors. In the first reactor, the substrates are hydrolyzed and dehydrated using acids which yields 5-HMF and in the second reactor, 5-HMF was converted to levulinic acid. The yields (60%) were obtained based on the monomers present in the starting cellulosic materials. In 2013, Yang et al. [115] reported the production of levulinic acid using cotton stalks as the raw material through a continuous hydrolysis acidification method. Most recently, Fachri et al. [116] disclosed the highest 5-HMF and levulinic acid yields of 56% and 74%, respectively, using sulfuric acid as catalysts. They found that the highest yields were obtained with high acid concentrations, and levulinic acid yields are higher from D-fructose than from D-glucose. The reports related to the use of solid acid catalysts for levulinic acid production are very few. As catalysts and reactants both exist in the solid phase, it is difficult to achieve uniform contact. This will greatly reduce the reaction efficiency [117]. Weingarten et al. [118] reported that resin-bearing SO_3H (Amberlyst 70) was efficient in the formation of levulinic acid. It was a two-step process for the conversion of cellulose with 29 wt % Amberlyst 70 in water. The solid acid catalyst having SO_3H groups leads to the production of levulinic acid with high yields. However, leaching of the acidic groups diminished their industrial applications. The levulinic acid production using ionic liquids in the presence of metal-ion, acidic, and co-solvents is also reported [119–121]. In 2012, Zhong and his colleagues [119] tested the single-step synthesis of levulinic acid from cellulose using heteropolyacid ionic liquid catalysts. The authors used water-MIBK (biphasic) as the solvent system. Later on, Ren et al. [120] disclosed a microwave-assisted transformation of cellulose into levulinic acid in SO_3H-functionalized ionic liquids. The use of $[C_4mim]HSO_4$ as a solvent for the conversion of the bamboo-shoot shell (BSS) to levulinic acid was reported [121]. A drawback of the processes reported is the sensitivity of ionic liquids to moisture content; additionally, complex preparation processes and a high cost limits their large-scale applications.

γ-valerolactone (GVL) obtained by hydrogenation of levulinic acid is an important chemical that can be converted to valeric biofuels by esterification to pentenoate esters. Horvath and colleagues [122–124] disclosed the unique physical and chemical properties of GVL, as it is an ideal liquid for use as a solvent and intermediate in the chemical industry or energy storage. The hydrogenation of levulinic acid at 150 °C with a 5 wt % Ru/C catalyst leads to a 97% yield of GVL [125]. Levulinic acid converted to pyrrolidones can be used as solvents and surfactants [126]. α-methylene-γ-valerolactone (MGVL) is an attractive acrylic monomer obtained from the gas phase reaction of GVL with formaldehyde in the presence of alkaline hydroxide supported on silica [127]. Wettstein et al. [127] reported the synthesis of levulinic acid and GVL from cellulose using GVL as a solvent. In 2013, Gallo et al. [128] reported on the conversion of hemicellulose to 5-HMF using a solid acid catalyst in GVL. Ru-based catalysts show high activity for the selective conversion of levulinic acid to GVL [129–132]. With 1 wt % Ru/OMS [Manganese octahedral molecular sieve (OMS)] catalyst, the highest GVL yield of 99.8% was reported [129]. In the most recent work, dendrimer-encapsulated Ru and Pt nanoparticles immobilized on supports TiO_2/SiO_2 for the hydrogenation of levulinic acid to GVL was investigated [131]. The highest conversion was obtained with unsupported catalysts. The tartaric acid-NaBr modified nickel catalyst as an enantio-selective modified heterogeneous catalyst was used by Osawa et al. [133] for the conversion of levulinic acid and alkyl-levulinates to GVL. The optically active GVL with 66%ee (enantiomeric excess) was produced. The production of transportation fuels such as pentanoic esters [122,134] and butenes [122,135] from levulinic acid derivatives are also reported in the literature. However, problems remain in the preparation process of levulinic acid and GVL, including low yields, multi-step synthesis processes, extraction of pure chemicals, and the deactivation of catalysts, which limits their application on a large scale. Further research is still required.

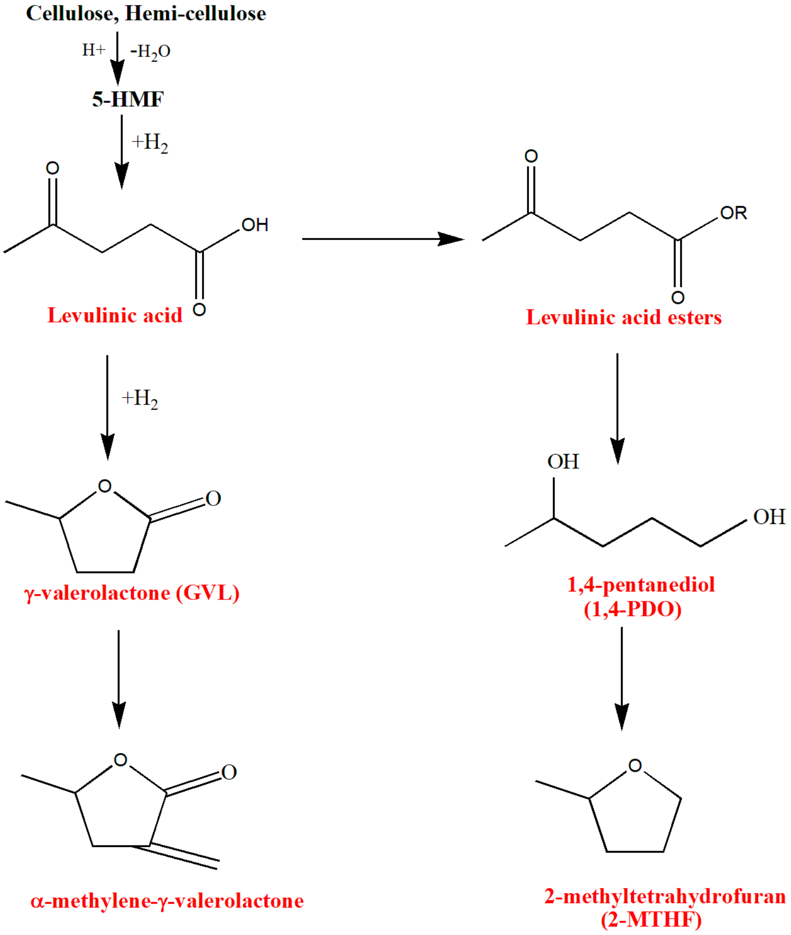

Figure 9. Levulinic acid and derivatives [125–128].

3.3. Furfural

Furfural is also considered a key chemical produced in lignocellulosic biomass refineries [101]. Hemicellulose, which contains a large amount of C5 sugars xylose and arabinose, can serve as a raw material for the production of furfural [136]. This industrial chemical is mainly obtained from xylose by dehydration. Furfural has been used as a foundry sand linker in the refining of lubricating oil.

The use of furfural as an intermediate for the production of chemicals such as furan, furfuryl alcohol, and tetrahydrofuran (THF) has been reported [137]. Reviews have been published on the chemistry of furfural [138]. The catalytic conversion of furan to commodity chemicals is described in Figure 10.

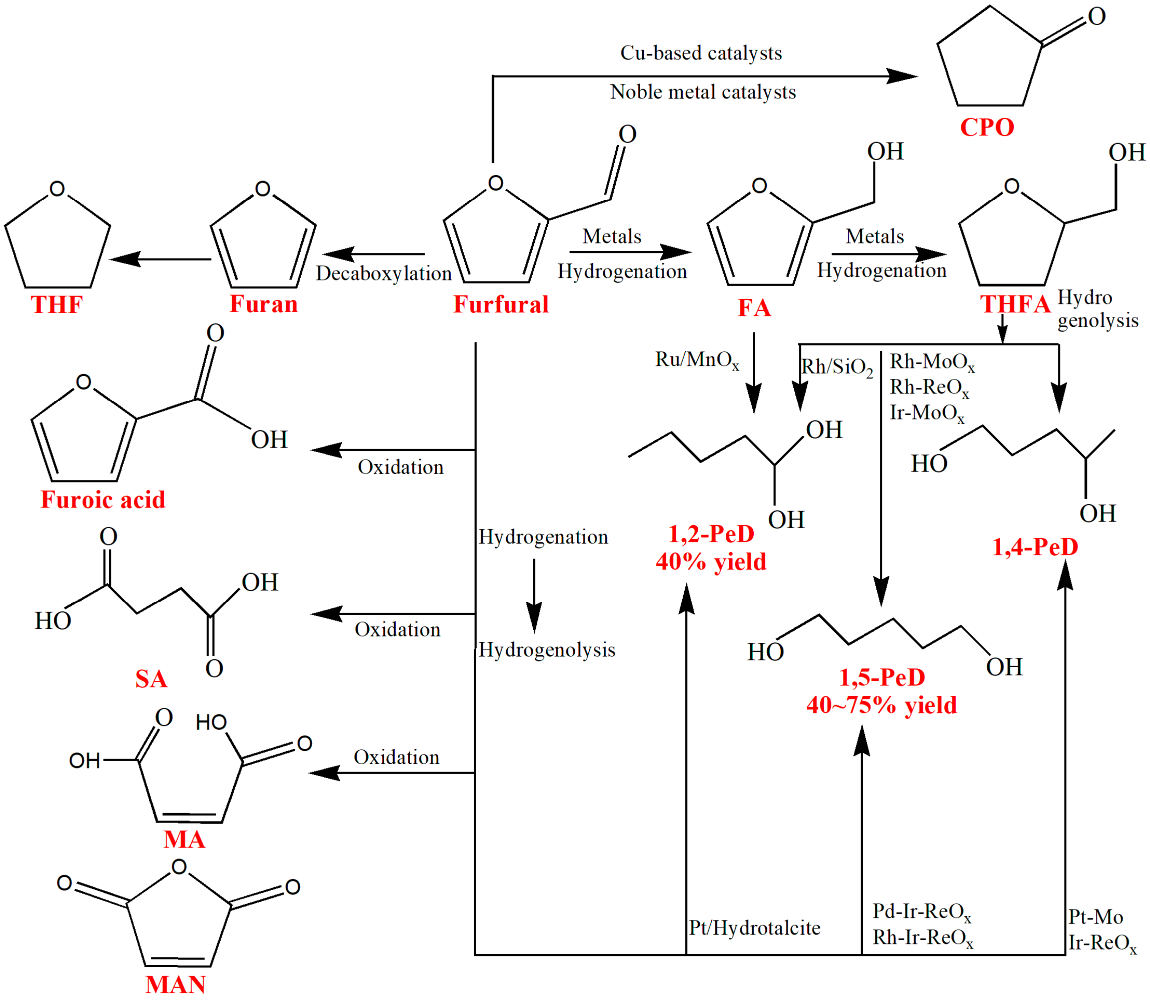

Figure 10. Catalytic conversion of furfural to chemicals [FA: furfuryl alcohol; THFA: tetrahydrofurfuryl alcohol; CPO: cyclopentanone; 1,2-PeD: 1,2-pentanediol; 1,4-PeD: 1,4-pentanediol; 1,5-PeD: 1,5-pentanediol; THF: Tetrahydrofuran; SA: Succinic acid; MA: Maleic acid; and MAN: Maleic anhydride].

The first industrial production of furfural was performed by Quaker Oats Company in 1921. The company used oat hulls as raw material. However, the drawbacks include a limited demand, high maintenance costs, low yields, and production methods that have not improved significantly since 1980 [138,139]. Presently, about 300–700 Ktons of furfural is produced worldwide annually, the majority of which originates from China [140,141]. Commercially, furfural is produced by the acid-catalyzed transformation of pentosan sugars; C5 polysaccharides are first hydrolyzed by H_2SO_4 to monosaccharides (mainly xylose), which are subsequently dehydrated to furfural. Furfural is then recovered from the liquid phase by steam stripping to avoid further degradation and purified by double distillation [142]. Several reports on the conversion of raw biomass into C5 sugars and furfural using mineral acid and solid acid catalysts were published [128,143,144]. The use of these catalysts makes the reaction system more corrosive, which increases the capital costs of the processes [145–149]. The use of ionic liquids for furfural manufacture has been widely discussed [150–155]. An ionic liquid plays a role as an acidic catalyst for pentose dehydration in aqueous media, eventually in the presence of organic solvents. These can also acts as additives for improving the furfural yields in the reaction media comprised of xylose or xylan, organic solvent and acidic catalysts. Ionic liquids can also serve as a reaction medium for furfural manufacturing from pentoses, higher saccharides made up of pentoses, or pentosans. Most recently, Parajo [45] published a review on furfural production using ionic liquids. The utilization of [emim]Cl, [bmim]Cl, or [bmim]PF_6 as solvents in the presence of metal halide solid acid catalysts, Bronsted acids, or a mixture of them was reported for the furfural production from pentoses [150–154]. In 2017, Matsagar et al. [155] reported the one-pot conversion of raw biomass into C5 sugars and furfural with Bronsted acidic ionic liquids [C_3SO_3HMIM][HSO_4].

The important chemical obtained from furfural is furfuryl alcohol (FA), and approximately 65% of the overall furfural produced is consumed for the production of FA [156]. FA is currently manufactured industrially by hydrogenation of furfural in the gas or liquid phase over Cu-Cr catalysts. However, chromium in these catalysts causes serious environmental problems because of its high toxicity [156–160]. Therefore, current studies are focused on exploring more environmentally acceptable catalysts that could selectively hydrogenate the carbonyl group while preserving the C=C bonds [156–160]. The hydrogenation of furfural over Raney Ni modified by impregnation with heteropolyacid (HPA) salts, such as $Cu_{3/2}PMo_{12}O_{40}$, that produced a 96.5% yield of furfuryl alcohol was reported [158]. Recently, novel catalyst synthesis methods such as Atomic Layer Deposition (ALD) and encapsulation in metal organic frameworks have been reported [159,160]. 2-methylfuran (2-MF) is another industrial chemical that can be synthesized from furfural. 2-MF is also a biofuel component [161,162]. Another one, tetrahydrofurfurylalcohol (THFA), is typically produced from furfural via furfuryl alcohol as an intermediate. The hydrogenolysis of THFA to 1, 5-pentanediol (1, 5-Ped), a promising biofuel component, was disclosed using Rh-MoO_x/SiO_2 and Rh-ReO_x/SiO_2 catalysts with 85% and 86% yields respectively [163,164]. FA and THFA are widely used as green solvents for the synthesis of resins. These can also be used as raw materials for the synthesis of fuels and fuel additives. Cyclopentanone (CPO) is another C5 chemical that can be synthesized from furfural. CPO can be widely used in the production of fuels and polymeric materials [165,166]. Mainly, Cu-based catalysts are used for the transformation of furfural to CPO. Wang et al. [167] synthesized a $CuNi_{0.5}/C$ bimetallic catalyst and obtained a 96.9% yield of CPO. In addition to Cu-based catalysts, the use of several noble metals was also reported. The use of Ru/MIL-101 [168] and Au/TiO_2 [169] was reported with good CPO yields.

The decarboxylation of furfural leads to the production of furan. The hydrogenation of furan produced tetrahydrofuran (THF). Furan and THF are also important industrial chemicals. Furfural can be decarboxylated in both gas- and liquid-phase reactions. Supported noble metal catalysts (Pd, Pt, Rh) [161,170] and mixed metal oxides, such as Zn-Fe, Zn-Cr, Zn-Cr, and Mn [171–173] were investigated. The decarboxylation has been found to be most efficient with Pd-based catalysts at a high H_2 pressure and reaction temperature [161]. These rigorous reaction conditions result in catalyst deactivation. Additionally, the noble metals used are expensive and limited in abundance. Therefore, alternate active and selective catalysts need to be explored.

Furoic acid has applications in the pharmaceutical, agrochemical, flavor, and fragrance industries. Li and Ozer [172] reported the production of furoic acid from furfural with a 5 wt % Pt/C catalyst promoted by lead. A number of catalysts based on noble metals (Ag, Pt, Pd, Au) supported on metal oxides (CuO, Fe_2O_3, Co_2O_3, NiO, TiO_2, CeO_2, Bi_2O_5, Sb_2O_5) have been explored, and the highest selectivity (96%) was achieved with Ag/CuO-CeO_2 [173]. The complete conversion of furfural to furoic acid was achieved using a Pd-Pt/C catalyst in the aqueous phase under the condition of 65 °C, 1 h, and 0.36 M furfural concentration [174,175]. Au-based catalysts as an oxidant were also investigated by Signoretto et al. [176–178]. Furoic acid can also be obtained from methyl furoate through the hydrolysis of the ester.

The oxidation of furfural can also lead to the production of C4 chemicals such as maleic anhydride (MAN), maleic acid (MA), and succinic acid (SA). The use of vanadium oxide-based catalysts has been studied for gas-phase oxidation of furfural to maleic anhydride with oxygen [179]. Li et al. [180] reported aerobic oxidation of furfural over a Mo_4VO_{14} catalyst with a 65% maleic anhydride yield. The use of oxidants such as oxygen and hydrogen peroxide (H_2O_2) was also discussed for the oxidation of furfural [181,182]. The combination of copper nitrates with phosphomolybdic acids selectively converts furfural to maleic acid with a 49.2% yield or maleic anhydride with a 54% yield in a liquid medium using oxygen as an oxidant [181]. Fagundez et al. [182] disclosed the aqueous oxidation of furfural to maleic acid in the presence of H_2O_2 (oxidant) and titanium silicate (TS-1). The yield obtained in this report was 78 %. The findings discussed above allow the production of maleic acid under moderate conditions and no catalyst deactivation was observed. However, undesired dicarboxylic acids may be produced, leading to difficulties in the separation process.

3.4. Sugar Alcohols

Lignocellulosic-based sugar alcohols, such as sorbitol, mannitol, xylitol, and erythritol are potential fuels and chemicals widely used for polymer, food, and pharmaceutical applications. These are extensively used as moisturizers, sweeteners, softeners, texturizers, and food for diabetic patients. Currently, sorbitol and mannitol can be synthesized through hydrogenation of fructose and glucose [183]. Xylitol and erythritol can be prepared by the conversion of xylose and glucose, respectively [15,184,185] (Figure 11). Many catalytic systems and methods have been reported for the conversion of cellulose into sorbitol and mannitol via hydrolysis followed by hydrogenation. The use of noble metal-based catalysts Pt/SBA-15 [186–189] and Ru-PTA/MIL-100(Cr) for the conversion of glucose and cellulose into sorbitol, respectively, were reported. However, cheaper non-metal catalysts (supported on TiO_2, Al_2O_3, SiO_2, MgO, ZnO, and ZrO_2) have been found to be effective in converting cellulose into sorbitol and mannitol [189]. Liang et al. [190] prepared a unique flower-shaped, highly effective Ni/ZSM-5 catalyst for hydrolytic hydrogenation of cellulose to sugar alcohols. An activated carbon-supported nickel phosphide ((Ni_2P) catalyst has been found to be effective for the conversion of cellulose into 60% sorbitol and 4.5% mannitol at 230 °C under 5 MPa hydrogen pressure [191]. Pang et al. [192] reported the use of a bimetallic Rh-Ni/MC [MC-mesoporous carbon] catalyst and obtained 51.5% sorbitol and 8.3% mannitol yields. Almeida et al. [193] synthesized a bi-functional RuNPs/A15 catalyst by impregnating Ru nanoparticles (RuNPs) with Amberlyst-15 (A-15). More than an 80% yield of sorbitol was obtained in 5 h using this catalyst. Different micro- and mesoporous materials supported on Ru were used for the hydrolytic hydrogenation of cellulose [194]. The Ru/CNT showed comparatively more effective selectivity (60%) for sorbitol within 5 h. Most recently, Wang et al. [195] used a partially reduced Ru/C catalyst for the direct transformation of lignocellulosic biomass to liquid alkylcyclohexanes and polyols. This catalyst contains RuO_2 species that promote the cleavage of lignin-carbohydrate linkage and help in the conversion of cellulose and hemicellulose fractions into polyols via retro-aldol condensation. Sorbitol can be dehydrated into 1,4-anhydrosorbitol (1,4-AHSO), which can be dehydrated into isosorbide using acidic catalysts such as sulfuric acid, sulfonated zirconia, and zeolite. The one-pot conversion of Japanese cedar into isosorbide using Pt/C and Ru/C catalysts with Amberlyst 70 has been reported [196].

Industrially, xylitol is synthesized by the hydrogenation of pure xylose, while xylose can be obtained through acidic hydrolysis of hemicellulose biomass (corncobs and hardwoods) [197]. The first report on the synthesis of xylitol through the hydrogenation of xylose over a Raney Ni catalyst was carried out in a three-phase slurry reactor in 2012 [198]. The major problem with this process is the catalyst deactivation. The acid-transition metal or bi-functional catalysts were used for the hydrolysis and hydrogenation of cellulose to sugar alcohols in the presence of hydrogen pressure [199]. In recent investigations, Liu et al. [200] reported the one-pot conversion of hemicellulose (xylan) into xylitol in a bi-phasic solvent system over an Ir-ReOx/SiO_2 catalyst along with sulfuric acid. It was found that increasing the acid quantity favors the hydrolysis. Ribeiro and colleagues [201] used a Ru/CNT catalyst for one-pot conversion of corncob xylan (hemicelluloses) into xylitol. Dietrich et al. [202] tested the commercially available Ru/C catalyst in combination with different heteropolyacids for one-pot conversion of hemicelluloses into xylitol. Among these acids, phosphotungstic acid, silicotungstic acid, and lactic acid can enhance the hydrolysis step.

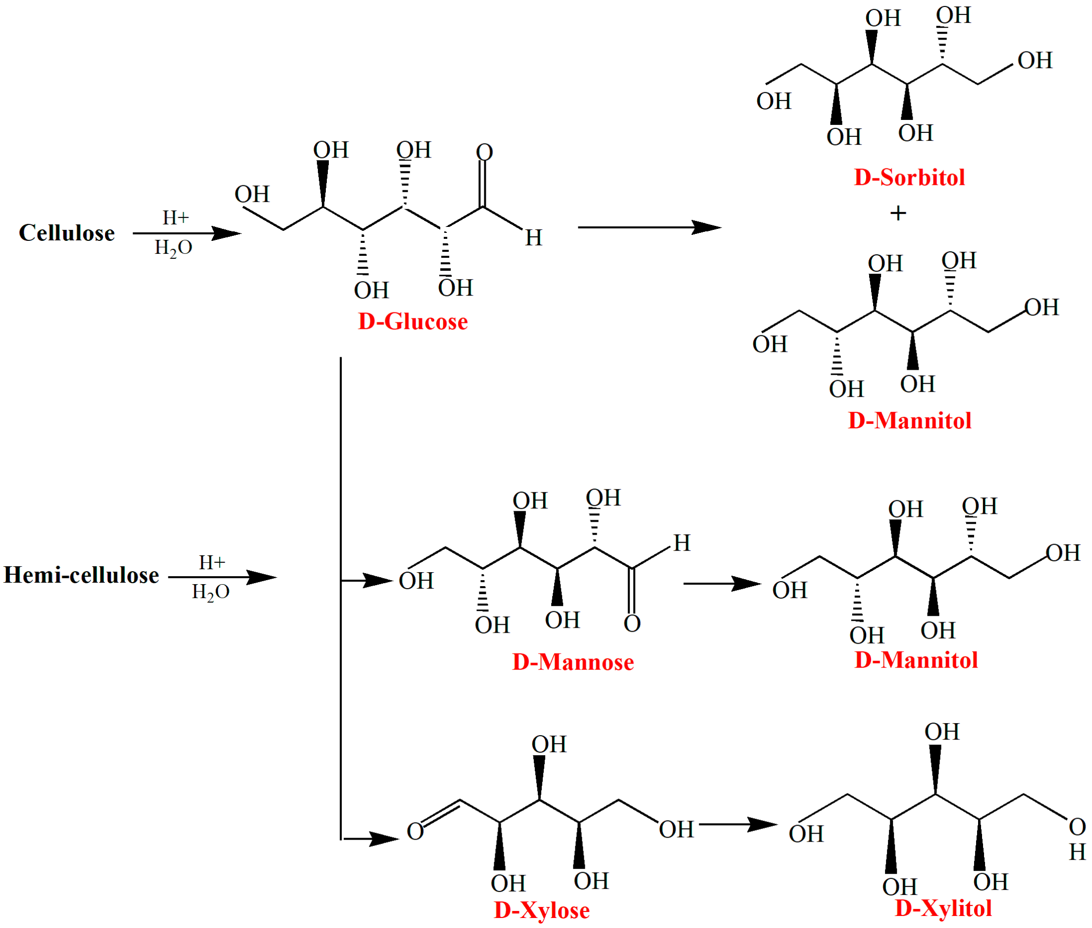

Figure 11. Sugar alcohols from cellulose and hemicelluloses [185,186,195,198].

Erythritol is a C4-sugar alcohol, mainly found in food ingredients. It occurs as a metabolite or storage compound in fruits, such as grapes, pears, seaweed, and fungi [203,204]. Pentose sugars (arabinose and xylose) are the precursors for producing C4-sugar alcohols. The most efficient route for the synthesis of erythritol from pentose sugars is selective cleavage of a C-C bond. The production of erythritol and threitol is mostly carried out at a high temperature range of 200–240 °C in a high hydrogen pressure of 6–10 MPa in alkaline conditions [205,206]. Very few findings relate to the selective bond cleavage to produce erythritol. Fabre et al. [207,208] disclosed the reduction of arabinoic acid to arabitol using Pd, Pt, and Ru based catalysts supported on C, HY, and TiO_2. Sun et al. [209] reported the conversion of xylitol to polyethylene glycol (PG) and ethylene glycol (EG) in a temperature range of 160–240 °C and a hydrogen pressure of 0–10 MPa. Nobel metals (Pt, Pd, Ru, and Rh) based carbon supported catalysts and a catalyst supported on Al_2O_3, TiO_2, Mg_2AlO_x, and ZrO_2 were investigated. The Ru/Mg_2AlO_x catalyst showed only a 7% yield of C4-sugar alcohols (erythritol and xylitol) at 200 °C and 4 MPa hydrogen. The selectivity towards PG, EG, and C4-sugar alcohols followed the order of: $C < TiO_2 < ZrO_2 < Al_2O_3 < Mg_2AlO_x$.

3.5. Succinic Acid

Succinic acid is one of the 12 high-value bio-based chemicals investigated by Werpy and Peterson [210] as a compound that has the potential to improve the profitability and productivity of biorefineries. The key producers of bio-based succinic acid are Riverdia, Bio-Amber, Myriant, and Succinity GmbH (BASF + Purac). Conventionally, succinic acid is produced from maleic acid using Pd/C heterogeneous metal catalysts [211]. Other methods reported for succinic acid production are: oxidation of 1,4-butanediol with nitric acid [212]; the carbonylation of ethylene glycol, acetylene, and dioxane [213]; hydrogenation of fumaric acid in the presence of Ru catalyst [214]; and the condensation of acetonitrile to produce butanedinitrile, which can be subsequently hydrolyzed to succinic acid [215]. The oxidation of levulinic acid using H_2O_2 can also produce succinic acid [216]. Choudhary et al. [217] reported the use of the Amberlyst 15 catalyst for oxidation of furan derivatives to carboxylic acids, such as succinic acid. Dalli et al. [218] disclosed the conversion of the hemicellulose perhydrolysate, which has xylose to succinic acid using Amberlyst 15 and H_2O_2 in a biphasic system.

Chemicals produced from succinic acid are 1,4-butanediol (BDO), γ-butyrolactone (GBL), *N*-methyl-2-pyrrolidone, tetrahydrofuran (THF), and succinic acid esters, as described in Figure 12. BDO has found potential application as a green solvent in the synthesis of polymer materials. The use of Pd-Re bimetallic catalysts supported on activated carbon and TiO_2 with high molar selectivities (~83%) was reported [219–223]. Re nanocatalyst supported on Cu-containing mesoporous carbon (Re/XCu-MC) was tested for the hydrogenation of succinic acid to 1,4-butanediol [224]. Vardon et al. [225] reported the use of Ruthenium-tin based catalysts supported on activated carbon for the reduction of succinic acid (aqueous-phase) to BDO. GBL is an important building block molecule for use in agrichemicals, petrochemicals, dyes, textile processing, and epoxides [226]. The aqueous phase hydrogenation of succinic acid to GBL and THF was discussed using Pd/C, Re/C, and Pd-Re/C catalysts [227]. Most recently, Patnakar et al. [228] carried out the selective synthesis of GBL from succinic acid using 2.5% Pd-2.5% Cu/AX (AX-alumina xerogel) catalyst using isopropyl as an alcoholic solvent. The microwave-assisted thermolytic (MAT) method has been used for the preparation of the Re/C catalyst, and it exhibits good performance for aqueous phase hydrogenation of succinic acid to THF [229,230]. The MAT method was also mentioned for the preparation of bimetallic Re-Ru/C catalysts [231].

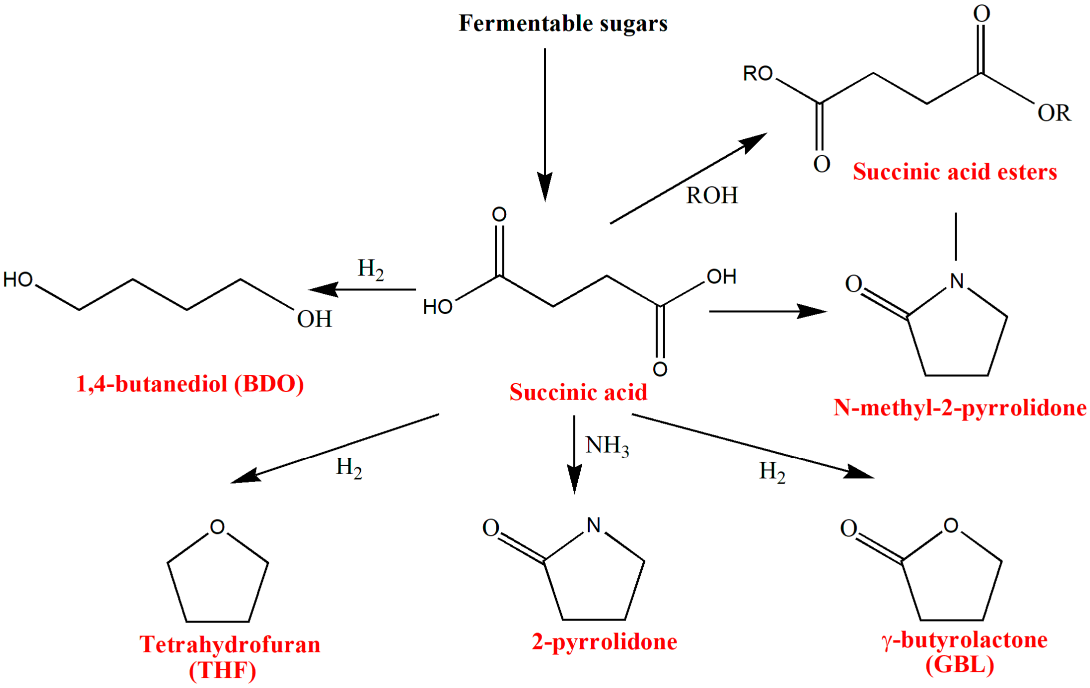

Figure 12. Succinic acid and its derivatives [224–230].

3.6. Lactic Acid (LA)

Lactic acid (2-hydroxypropanoic acid) is an important chemical. It is an alternative for producing alkyl lactates, propylene glycol, propylene oxide, acrylic acid, and poly (lactic acid). Lactic acid has applications in food, pharmaceuticals, and cosmetics [232,233]. In particular, the biopolymers from lactic acid have created a strong interest. Conventionally, lactic acid is produced via fermentation from carbohydrates. However, the process produces a low-purity lactic acid with low productivity

(0.3–5.0 g/L/h) [234–236]. Lactic acid can be made from different reagents such as lignocellulosic materials, cellulose, carbohydrates, sugars, trioses, glycolaldehyde, and glycerol. The production of lactic acid involves complex reactions of several types of transformations such as aldol condensation, retro-aldol condensation, dehydration, and 1,2-hydride shifts [237]. Few reviews have been devoted to lactic acid or its derivatives [232,237,238]. Several homogeneous and heterogeneous catalysts have been reported for the production of lactic acid from biomass. The catalysts such as alkali metal ions [239,240], tin chloride [241], SnO_2 [241,242], acidic resins [242], zeolites [241,243,244], metal-modified zeolites [241,245], mesoporous materials, tungstated alumina [244], mixed-oxides [245,246], and carbon-silica hybrid materials [247] have been reported in the literature. The use of Rh/C, Ru/C, Ir/C, Ir/$CaCO_3$, and Pt/C catalysts for the transformation of glycerol to lactic acid was discussed [248,249]. Typically, the highest yield of lactic acid has been achieved in the presence of an inert gas and alkaline medium ($CaCO_3$) [250]. An alkaline Pt/$CaCO_3$ catalyst has been shown to be an efficient catalyst for glycerol transformation to lactic acid, with 54% selectivity for lactic acid at 45% conversion in the presence of borate esters at 200 °C [251]. The Rh/Al_2O_3 catalyst also gives high selectivity for lactic acid, i.e., 69% in the presence of borates [251].

Figure 13 presents the chemicals obtained from the conversion of lactic acid. Chemicals such as pyruvic acid, acrylic acid, 2,3-pentanedione, polylactic acid (PLA), lactic acid esters, and 1,2-propanediol (1,2-PDO) can be synthesized from lactic acid. PLA was mainly produced by NatureWorks Co. (USA). The synthesized PLA was used mainly in packaging applications. The PLA can be synthesized by two ways: direct polycondensation of LA and ring-opening polymerization (ROP) of the lactide monomer (cyclic). The direct polycondensation of LA is a difficult process because of the strong equilibrium between PLA, water, and lactide that limits the synthesis of high molecular weight products. The most commonly used process is using the lactide intermediate. The lactide intermediate was polymerized via a homogeneously catalyzed ROP (absence of water), which produces two lactoyl units in the growing chain [252]. This process suffers from racemization. Consequently, when commercial L-lactic acid was used, a 5% to 12% yield of undesired product (meso-lactide) was produced [253]. The properties of PLA depend mainly on the stereo-composition of the feed used. Therefore, stereopure L,L-lactide is used to obtain stereopure poly-L-lactic acid. As a result, improvements in catalysts, process parameters, and configuration have been reported [254,255]. Yoo et al. [254] reported the use of SnO as a catalyst for the conversion of a pre-polymer to lactide. A range of homogeneous and heterogeneous metals in the form of oxides, halides, and alkoxides was screened by Noda et al. [255]. The intramolecular transesterification activity was found to be Sn > Zn > Zr > Ti > Al [255]. For the synthesis of lactide, research studies related to the use of heterogeneous catalysis are few. The homogeneous Sn-based catalysts played a vital role in ring-opening polymerization of lactide, which leads to the formation of high molecular weight PLA. The utilization of metal catalysts such as tin(II)bis(2-ethylhexanoate) and Al(III)isopropoxide was also reported [256,257].

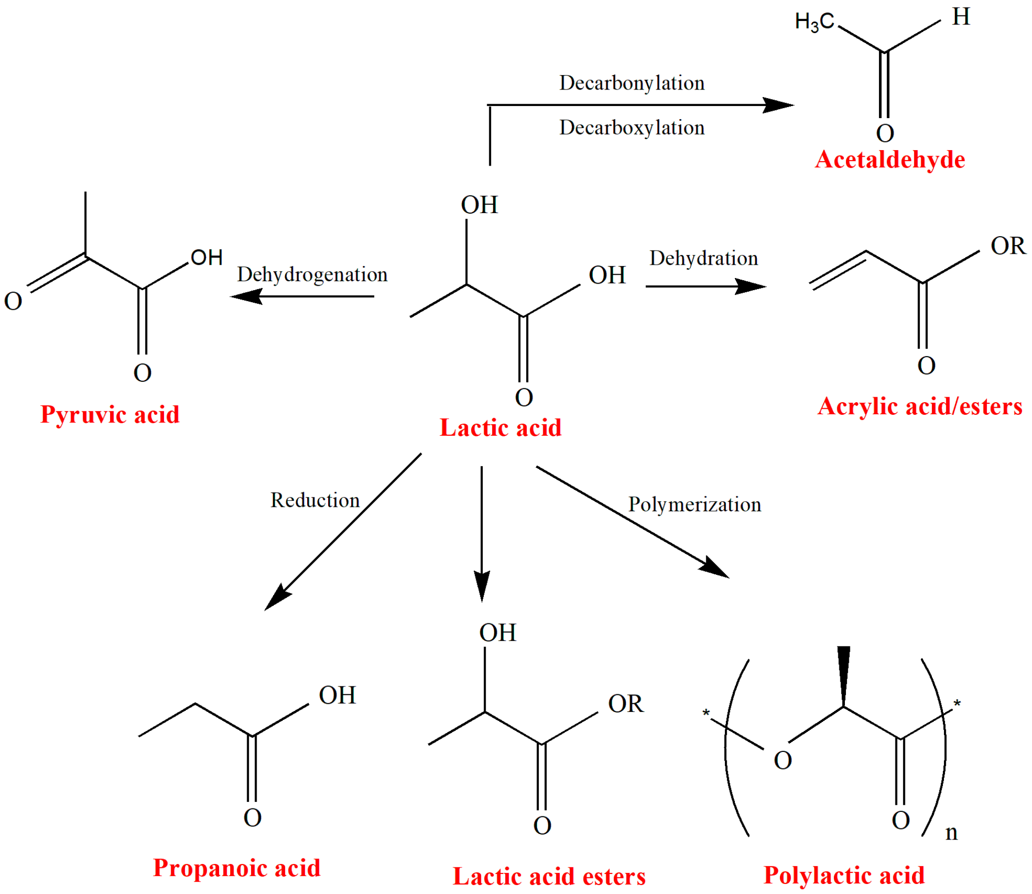

Figure 13. Conversion of lactic acid to chemicals (Redraw from ref. [15]).

Catalytic dehydration of lactic acid leads to acrylic acid, while propanoic and pyruvic acids were obtained by lactic acid reduction and dehydrogenation, respectively. 2,3-pentanedione can be produced by condensation and acetaldehyde by either decarbonylation or decarboxylation [232,258,259]. The lactic acid conversion to acetaldehyde was investigated by Katryniok et al. [247] on silica-supported heteropolyacid with an 83% yield. Zhai et al. [258] obtained high (acetaldehyde + CO) yields from lactic acid conversion using metal sulfate catalysts. Researchers also used aluminum phosphate and magnesium aluminate spinels for lactic acid conversion to acetaldehyde [259,260]. Sad et al. [261] used zeolite-based catalysts (HMCM22, HZSM5, NaZSM5) and reported that the selective formation of acetaldehyde from lactic acid depends on both zeolite pore structure and acid strength. Propionic acid production from lactic acid and biomass using Co catalysts in the presence of Zn under hydrothermal conditions has been reported by Jin et al. [262].

Hydrogenation of lactic acid to 1,2-propanediol was performed in both the liquid as well as the vapor phase using Ru/C and Cu/SiO_2 catalysts, respectively. The direct hydrogenolysis of lactic acid seems an attractive option but deactivation of catalyst makes the process undesirable. The catalyst deactivation occurs as a result of the polymerization of lactic acid and formation of the side-products, propionic acid. Therefore, to avoid this problem, carboxylic acids are usually converted into more readily reducible esters. Xue et al. [263,264] investigated the use of a bi-functional Ru/TiO_2 catalyst for the conversion of lactic acid or lactates to propylene glycol in the liquid phase. The addition of some additives such as boron, tin, and iron to Ru-based catalysts has been reported in the literature [265]. Feng et al. [266] hydrogenated ethyl lactate with Ru catalysts over TiO_2, SiO_2, Al_2O_3, NaY, and active carbon and found Ru/SiO_2 to be an effective catalyst [266–268]. Xu et al. [264] tested the Co/SiO_2 catalyst for liquid-phase hydrogenation of ethyl lactate. The authors also studied the effect of additives, such as Fe, Zn, Sn, and Cu on the activity of Co/SiO_2 catalyst. For the cost-effective production of lactic acid and chemicals from lactic acid, the primary barriers are in separation and purification processes. Efficient purification technologies for high yield and purity for produced key intermediates is a very important aspect and should be considered in all economics calculations.

In summary, the catalytic conversions of sugars to commodity chemicals are widely discussed but the industrial applications are limited. Therefore, further research for the improvements of the catalytic conversion and selectivity are still required for achieving the goal of integrated biorefineries. The areas that need attention are the search for novel reaction media to use efficient catalysts for the biomass conversion processes and the extraction/purification steps to isolate the chemicals with high yield and purity.

4. Lignin as Feedstock

Lignin is the key constituent of the lignocellulosic biomass and responsible for the structural and mechanical integrity of plants. Lignin is a polymer with wide variability in structure. Its components depend on the biomass source and are most often combined with cellulose and hemicelluloses. It is considered the least susceptible to chemical and biotransformation techniques. Therefore, lignin often becomes a low-value waste product of biomass processing technologies, such as in the conventional paper and pulp industry and in the modern bioethanol-fuel-production industry. Therefore, lignin valorization in relation to energy, chemical, and biotechnological application is creating considerable interest to researchers.

Structurally, lignin is a three-dimensional amorphous phenolic polymer that consists of monomers such as phenyl-propane unit, C3C6 including p-coumaryl, sinapyl, and coniferyl alcohol. It contains β-O-4 (40% to 60%), biphenyl (3.5% to 25%), α-O-4 (3% to 5%), and β-5 (4% to 10%) linkages [269]. The chemical transformations of lignin and the products obtained are given in Figure 14. The different structural and chemical properties of lignin lead to the production of a wide variety of aromatic chemicals. Therefore, lignin was observed as the major aromatic source of the bio-based economy. Dimethyl sulfide, vanillin, and dimethyl sulfoxides are the chemicals, manufactured from lignin on a large scale [270]. Several researchers [271,272] have summarized the applications of lignin as a renewable resource, such as emulsifier, bio-dispersant, polyurethane foams, wood panel products, resins, automotive brakes, and precursors for the synthesis of thermoplastic materials in the industry. In addition, the production of aromatics from depolymerization of lignin is considered as the most promising process for the sustainable utilization of lignin [270,273,274]. Aromatics can be derived from monomeric C6 fragments from depolymerized lignin. The maximum theoretical obtainable yield of benzene, toluene, and xylene (BTX) from lignin is about 36% to 42%, as lignin contains 60% to 65% carbon in C6 aromatic rings. The main challenge in producing aromatics is to selectively deoxygenate and dealkylate the C6 aromatic structure (typically with hydrogen) without hydrogenating C6 aromatic rings. The difficulty in the valorization of lignin originates from its complex polymeric structure, which differs from one lignin to another depending on the botanical origin and the pretreatment used for its separation from carbohydrates (cellulose and hemicellulose).

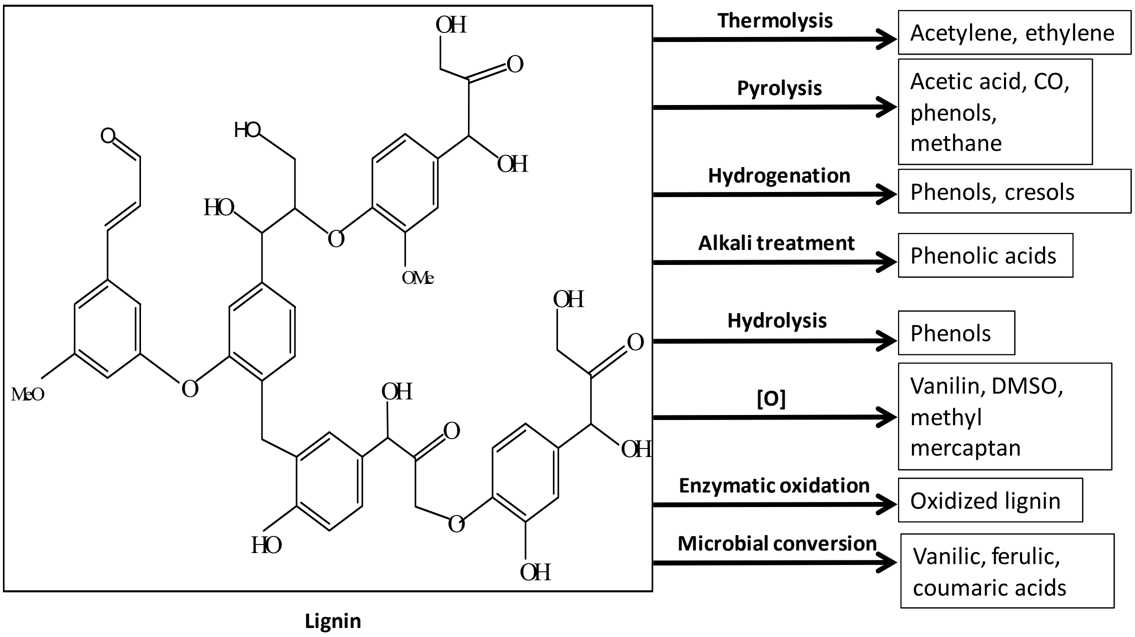

Figure 14. Chemical transformations of lignin and their products [270–272].

The catalytic pathways, including base-catalyzed depolymerization, pyrolysis, and Lewis acid catalyzed solvolysis, have been investigated and studied for the conversion of lignin to valuable compounds [274]. Low product yields and severe treatment conditions, as well as complex product mixtures, have been major drawbacks for lignin conversion. However, lignin's aromatic nature and its versatile functional groups suggest that it can be a valuable source of chemicals, particularly monomeric phenolics. Hydrothermal liquefaction of lignin in the presence of water as the solvent leads to the production of bulk aromatic compounds [275]. Bio-oil obtained after lignin decomposition contains monomeric phenols and oligomeric polyphenols [276]. The monomeric phenols are valuable chemicals, however the oligomeric polyphenols that existed in bio-oils were volatile and viscous, which makes them more difficult for conversion into useful products [277]. As a result, the conversion of lignin to monomers instead of oligomers is highly desirable.

The thermo-chemical conversions such as catalytic fast pyrolysis and microwave pyrolysis were commonly used processes in the presence of effective catalysts to enhance reactions, including cracking, decarbonylation, deoxygenation, and decarboxylation. Recently, several studies have been reported for lignin depolymerization to obtain monomeric phenols [278–282]. The monomers of phenols such as alkylated phenol and guaiacol have found applications as intermediates for the production of polymers, antioxidants, resins, medicines, and pesticides [283]. The preparation of phenolic resins such as phenol-formaldehyde using phenolic-rich pyrolysis oils is well known.

Phenolic compounds are obtained from lignocellulosic biomass after treatment with alkali. A large number of different methods have been discussed, but the processes reported are complex, low yielding, cost-ineffective, and energy inefficient. Liu et al. [284] reported the production of phenolic derivatives (methoxy phenolic compounds) using the walnut shells by the hydrothermal process. The catalyst used was 0.5 M KOH at 300 °C. The use of $Ba(OH)_2$ and Rb_2CO_3 catalysts were also reported for the direct liquefaction of lignocellulosic wastes (saw-dust, cornstalks, and lignin model compounds) [285]. Lercher et al. [286] reported a method of catalytic depolymerization of lignin in the liquid phase. It has been suggested that monomers are the primary products of base-catalyzed hydrolysis, while oligomers are found in the secondary re-condensation steps. They used boric acid to suppress the condensation reactions. The catalyst amount is considered a crucial factor for producing a good yield of monomeric phenols from lignin. An excessive dosage caused side reactions, resulting in decreased monomeric phenol yields [287]. Recently, the mechanism of phenol formation has been proposed by Mukarakate et al. [288]. The upgradation was performed using HZSM-5 with vapors from fast pyrolysis of biomass. They found that phenols did not only arise from phenolic compounds formed during pyrolysis of lignin, but phenols were also formed by the reaction of water molecules with aromatic intermediates formed during the transformation of all pyrolysis products. Others investigated activated carbon as a catalyst on the catalytic microwave pyrolysis of palm kennel shells for phenol production [289]. Zhang et al. [290] reported the use of a magnetic solid base catalyst (potassium phosphate ferroferioxide) for catalyst fast pyrolysis of popular wood species to selectively produce phenolic-rich bio-oil. Kim et al. [287] investigated the effect of alcohol solvents (ethanol, methanol, and propanol) and catalyst types on the physic-chemical properties of lignin-oil (obtained from depolymerization of Asian lignin). The results revealed that the combined ethanol and Pt/C catalyst leads to the 77.4% yield of lignin oil and selectivity to the top four monomeric phenols (4-ethylphenol, guaiacol, 4-ethylguaiacol, and syringol). Wang et al. [291] investigated the pyrolysis of larch sawdust using Cu/C, Pd/C, Pd-Ag, and HZSM-5 catalysts.

Pandey and Kim [8] reviewed the production of chemicals from lignin-derived monomeric phenols using catalytic hydrotreatment. The most challenging is the synthesis of catalysts that can perform deoxygenation without saturating the aromatic rings in the phenol deoxygenation processes. This will help to decrease the hydrogen consumption. For this process, mainly conventional metal sulfide, metal oxide, transition metal phosphide, metal carbides, and bi-metallic catalysts were used. Bi-metallic catalysts are found to be more suitable than monometallic catalysts for deoxygenation of phenols. Products obtained from hydrodeoxygenation (HDO) of guaiacol are shown in Figure 15. The addition of Cu to active metals for deoxygenation of phenolics showed appealing results. Zhang et al. [292] studied the deoxygenation of guaiacol with CuNi bi-metallic catalyst. The addition of 5 wt % of Cu to a Ni catalyst decreased the selectivity towards cyclohexane from 97% to 80.8%. Huynh et al. [293] investigated the replacement of nickel with copper on a 19% Ni/HZSM-5 catalyst, as the copper forms a separate layer with a large particle size. Cu-rich catalysts were found to be more selective towards hydrogenolysis reactions than the Ni-rich catalysts [294]. The addition of Fe also showed good results. Nie et al. [295] reported the use of NiFe with m-cresol. Sun et al. [296] tested a PdFe/C catalyst for the deoxygenation of vapor-phase guaiacol. Other bi-metallic catalysts such as PtSn, PtNi, PtCo, Pt Re, and NiCo [297,298] are also reported in the literature.

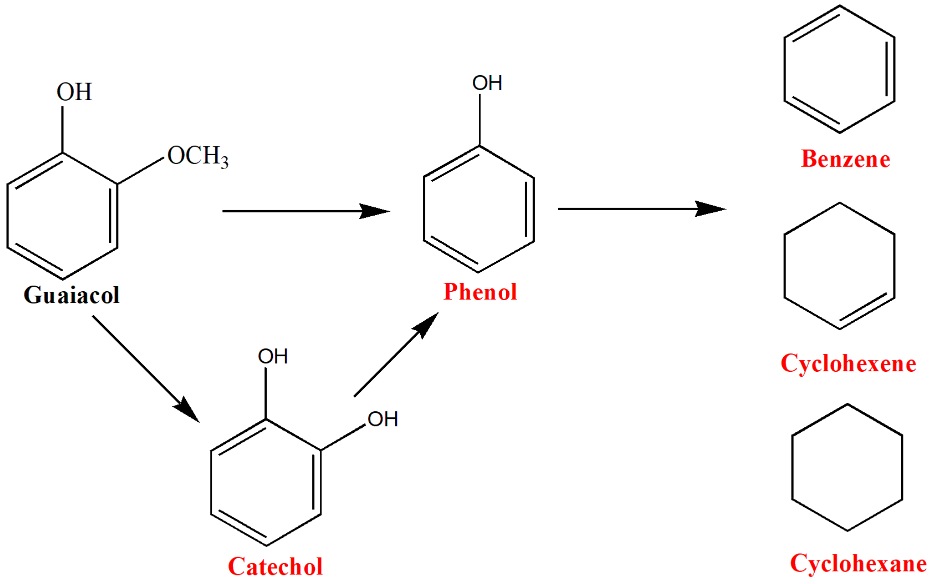

Figure 15. Hydrodeoxygenation (HDO) of guaiacol [214].

Ni-based catalysts were used for lignin hydrogenation/hydrogenolysis in 1940 [299]. Ni catalysts supported on carbon and magnesium oxide were found to be active for C-O bond cleavage of model compounds as well as selectively hydrogenolyzing the aryl ether C-O bonds of β-O-4 without disturbing the arenes [278,300,301]. The alcohol solvents were used as a hydrogen donor for the hydrogenolysis of lignin [278]. Zhang and colleagues [302] investigated the carbon supported Ni-W_2C catalyst for the hydrogenolysis of lignin (from woods) into monomeric phenols with a 46.5% yield. The platinum group metals (Pd, Pt, Ru, Rh, and Ir) bear higher intrinsic activity than Ni catalysts and hence were widely reported for hydrogenolysis of lignin. Zn in Pd-based catalysts was found to be far more effective than the Pd/C catalyst by Abu-Omar et al. [303]. Zn-based catalysts were effective for the cleavage of β-O-4 bonds in lignin model compounds. The depolymerization can be increased by adding small amounts of mineral acids [304] or solid acid [305].

Oxidative depolymerization of lignin leads to the production of polyfunctional aromatic compounds. These compounds include aromatic aldehydes and carboxylic acids, such as 4-hydroxybenzaldehyde, vanillin, muconic acid, and syringaldehyde, which are good alternatives to petroleum-based chemicals. The depolymerization of lignin in 1-ethyl-3-methyl-imidazolium trifluoromethanesulfonate with $Mn(NO_3)_2$ catalysts yielded 11.55 wt % of pure 2,6-dimethoxy-1,4-benzoquinone [306]. The catalytic systems for lignin oxidation involve organometallic catalysts, metal-free organometallic catalysts, acid or base catalysts, metal salt catalysts, photocatalytic, and electrocatalytic oxidation. Methyltrioxorhenium (MTO) in combination with H_2O_2 catalyzed lignin oxidation reactions is the most promising [307,308]. This catalytic system leads to extensive oxidation on the aliphatic side-chain and aromatic-ring cleavages. This results in the production of more soluble aromatic fragments. Salen(*N*,*N*′–bis(salicylidene)ethylenediamine) complexes of transition metals such as [Co(salen)] [309–313] and [Co(salen)]/SBA-15 [313] are also reported for lignin oxidation. Metal-free organometallic systems that are composed of 2,2,6,6-tetramethylpiperidine-1-oxyl-radical, NaBr, and NaClO were used for the lignin oxidation [314–317]. Alkaline media (NaOH, KOH, and Na_2CO_3) exhibit remarkable activity for lignin hydrolysis and in lignin oxidation reactions [317,318]. The oxidation of Kraft lignin in the presence of an acidic medium was reported for the production of vanillin [319]. H_2O_2 oxidation of guaiacol with Ti silicate (acidic zeolite) leads to the production of maleic acid with a 20% to 30% yield.

Lignin-Derived Polymers

After the depolymerization and production of aromatic compounds from lignin, the consequent processes do not require much advancement. The mature technologies already exist for the transformations of aromatic compounds into commodity monomers and polymers. The commodity polymers that can be derived from lignin are polyethylene terephthalate (PET), Kevlar, polystyrene, polyanilines, and unsaturated polyesters. The alternatives to fossil-based aromatic polymers could be accomplished by the full valorization of lignin. The synthesis of bio-based PET can be realized by the preparation of ethylene glycol (EG) and p-terephthalic acid from renewable biomass. Bio-based p-xylene can be used as the raw material for p-terephthalic acid to produce a 100% plant-based PET. Kraft lignin was used to manufacture phenol-formaldehyde binders for wood panels [320]. Sulfur-free organosolv lignins have been widely used as a raw material for wood panel products, polyurethane foams, automotive brakes, biodispersants, and epoxy resins for printed board circuits [321]. Cornstalk-derived bio-oils were used to synthesize phenol-formaldehyde resins [322]. Production of these products depends on the development of new lignin valorization technologies.

An integrated biorefinery approach will optimize the utilization of renewable biomass for the production of bioenergy, biofuels, and bio-derived chemicals for the short- and long-term sustainability. For an integrated biorefinery, the concept of usage of platform intermediates as precursors to different products by chemo-catalytic routes will be of highest importance. This will offer the refinery the necessary adaptability to product demand. This review summarizes the production of platform chemicals from lignocellulosic biomass components. The three main components of lignocellulosic biomass, cellulose, hemicellulose, and lignin are valuable precursors for numerous chemicals having valuable applications. The target chemicals include furanics, such as 5-hydroxymethylfurfural (5-HMF), 2,5-dimethylfuran (2,5-DMF), sugar alcohols and organic acids, such as levulinic acid, lactic acid, succinic acid, and aromatic chemicals. These chemicals can be further converted to a range of derivatives that have potential applications in the polymer and solvent industries. The chemo-catalytic routes were found to be most promising ones for the conversion of biomass feedstocks to these high-value chemicals. To date, various studies involving structural and mechanistic interactions between the several catalyst and feedstocks/substrates and development of novel catalysts have been reported. Many of studies have mainly focused on model compounds. Despite these studies, the complexity of biomass and catalyst selectivity limits the applicability of various catalysts in the commercial production of chemicals from biomass and its derivatives. There are other problems associated with these conversion processes, such as high cost of solvents and catalysts used, catalyst deactivation, low product yields, the high cost of separation and purification processes to obtain high purity chemicals, and transfer of technology to a large scale. Indeed, recent advances in the application of novel catalysts are highly appreciable. However, further efforts should be focused towards developing clean, single-step and high yield process. Further, mechanistic studies should be performed, which would ultimately lead to the design of better catalysts systems for the production of high-value chemicals. The search for novel reaction media is also a promising strategy to be explored for the high-value chemical production from biomass. Efficient separation and purification/extraction methods that can provide high yielding and highly pure intermediates and chemicals are the most important aspect for consideration. For this, advanced membrane-based separation technologies, distillation, and supercritical CO_2 extraction processes need to be explored. The research on recycling/recyclability of the catalyst and solvents used in the conversion processes on a large scale is also desirable for integrated biorefineries.

5. Conclusion and Future Perspectives

The development of a sustainable and environmentally benign solution for the valorization of lignocellulosic biomass using cost-effective and sustainable processes is necessary for forest-based biorefineries so that they could be integrated into industrial supply chains. This paper reviewed the major platform chemicals obtained from lignocellulosic biomass. Special attention was focused on the production of chemicals from sugars and lignin as feedstocks separately because published studies mainly utilized these feedstocks obtained from certain pre-treatments of raw biomass. The target molecules included 5-HMF, levulinic acid, furfurals, sugar alcohols, succinic acid, and lactic acid from sugar feedstocks and aromatics from lignin. The recently reported integrated strategies were also discussed, in which the valorization of raw lignocellulosic biomass for high-value products was a central theme to fully utilize raw feedstocks and improve process economics. Overall, advances are still needed to improve our understanding of the underlying chemistry of chemical formation. We have noticed that despite significant advances, low yields, multistep synthesis processes, purification difficulties, high costs, and catalyst deactivation are still hurdles for large-scale competitive biorefineries. These challenges could be overcome by implementing single-step catalytic conversions using highly efficient and selective catalysts and exploring purification and separation technologies.

Based on current research, efforts in the development of catalysts should be more orientated toward the production of bio-derived chemicals in economically feasible and environmentally benign routes. The multi-functional catalysts such as those from transition metals with solid acid or base catalysts are highly desirable as they allow the reactions to be feasible in single-step. The resulting processes will limit the costly intermediate separate purification process. In addition, recycling of the catalysts and the efficient separation of target products are necessary for inclusion in catalyst process research.

The major challenges to be addressed are the

- Search for novel reaction media;
- Catalyst development and optimization;
- Mechanism of the conversion reactions and the structure-property relationship of catalysts;
- Multi-functional catalysts and suitable solvent systems;

- Efficient processes for purification and separation processes; and
- Process composition and large-scale production.

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