

Sustainable Production of Chemicals and Energy Fuel Precursors from Lignocellulosic Fractions

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Abstract From time immemorial, bioprocessing of lignocelluloses via chemical catalysis has been an impressive methodology of numerous value added commodities and energy fuel precursors (drop-in-fuel) synthesis. The most common technique for biomass fragmentation is catalytic hydrolysis using various acid catalysts covering inorganic or organic liquid acids as well as solid acids (heterogeneous). Most research in the past decade has been focused on cost-effective production of such biomass derived commodities with the aim of their commercialization. Till date, in order to improve final product yields and minimize production costs, various improvised production schemes have been developed like pretreatment methods for improved saccharification and displacement and/or reconstruction of recalcitrant biomass constituents, such as lignin to improve accessibility, employing multi-functional catalysts to promote single stage transformations, continuous extraction of desired product by use of specific solvents to improve product stability as well as to inhibit by-product formation, integration of physical processes for example microwave and ultrasonic irradiation resulting in decreased residence time, etc. With these technological advancements, researchers have overcome substantial limitations associated with lignocellulose transformation including mass-transfer hindrances and expensive downstream processing; as a result a wide array of commercially important chemicals and fuel precursors have been synthesised. The chapter provides an account of value addition to biomass via chemical catalysis of cellulosic, hemicellulosic and lignin fractions towards product chemicals synthesis.

Keywords Lignocellulose • Chemical catalysis • Biorefining • Fuel precursors • Value-added chemicals

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1 Introduction

Till date, most of the worlds' energy requirements are met from one or the other form of conventional petroleum derived fossil fuels. Apart from its main application in the transportation sector and machinery energy resources, fossil reserves also play an important role in synthesis of industrial chemicals and solvents. However, regrettably, near depleting fossil reserves increases energy insecurity along with excessive greenhouse gas emissions (GHCs), evolved due to incombustible hydrocarbons. In order to tackle this fast energy crisis, worldwide many scientists have believed that biomass derived fuel chemicals (second generation cellulosic fuels) are the sustainable energy source to satisfy both energy replacement and net zero carbon emissions. With expectation, over the past few decades, biorefining of lignocellulose feedstock is attracting worldwide interest. According to the recent survey, global biomass production is estimated to be $1.7\text{--}2.0 \times 10^{11}$ tons per year [27]. Considering the current policy scenarios of India, its primary energy demand is postulated to double in the next two decades i.e., from 750 MTOE in 2011 to 1469 MTOE in 2030 [32]. Contrarily, India's biofuel production currently accounts for nearly 1% of global production, which estimates for approximately 127.7 billion litres. The major source of first-generation bio-ethanol in India remains molasses, a by-product of sugar industry. While for second generation biofuels, sugarcane bagasse and leaves, rice straw and husk and wheat straw accounts most of the agricultural residues (crop residues) generated in India [16].

Around world, the abundance of lignocellulosic biomass is widely distributed as energy crops (e.g., switchgrass and short rotation woody crops), forestry residues (e.g., branches and unused trees), agricultural residues (e.g., straws and stover), and industrial residues (e.g., sawdust and brewers spent grains). In general, the inherent biomass comprises up to 75% carbohydrate sugars in the form of cellulose and hemicelluloses, and therefore, represents a store of abundant sugar polymers labile to be converted into specialty chemicals. Thus, making it an ideal feedstock for sustainably renewable energy applications [75]. In broad classification, lignocellulosic conversion methodologies are thermal, thermochemical and biochemical conversions, and in specific each method is employed for appropriate feedstock types and resulting specific end product yield. Although most of these technologies are at pre-commercial stage, production of bio-ethanol from biomass feedstocks is well established (biochemically) and fully commercialized. Industrial-scale synthesis of lactic acid via fermentation of glucose is also established on the market. Undoubtedly, the usefulness of biomass-based chemicals is realized in biorefineries (Fig. 1), where transformation of lignocellulosic feedstocks into value-added products is envisaged by sequential transformations of a set of biomass derivative molecules, the so-called platform molecules (or building blocks). The US Department of Energy (DOE) in 2004 identified top 12 building blocks as 1,4-diacids (succinic, fumaric and malic), 2,5-furan dicarboxylic acid, 3-hydroxy propionic acid, aspartic acid, glucaric acid, glutamic acid, itaconic acid, levulinic acid, 3-hydroxybutyrolactone, glycerol, sorbitol, and xylitol/arabinitol, which can

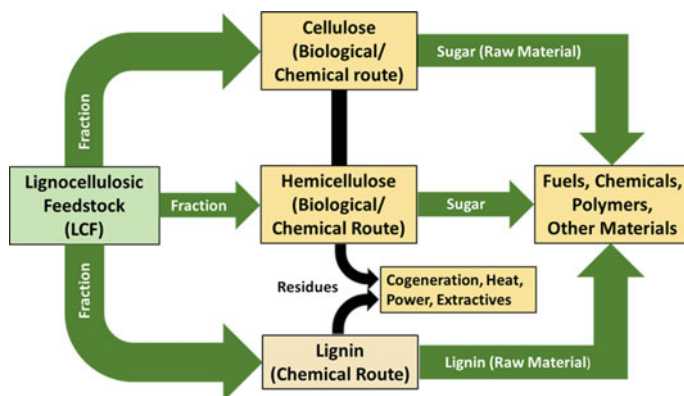


Fig. 1 Schematic illustration of concept of LCF based biorefinery for energy and product chemicals

be produced from biomass derived sugars via sequential chemical or biochemical processing steps [81]. Later, few other important platform molecules have been included in the list, such as fatty acids, fatty acid alkyl esters and triglycerides [21]. Thus, this chapter takes into account production strategies of few important platform molecules which could be chemically catalyzed and their potential applications as industrial chemicals and energy fuel precursors [88].

2 Lignocellulosic Biomass: Fraction and Its Structure

Inherently, lignocellulosic biomass is known as a polymeric material comprised predominantly of three biogenic polymers, namely cellulose (30–50% wt.), hemicellulose (20–30% wt.) and lignin (20–30% wt.) along with other trace components including organic and organic extractives (phenolic substituents) and ash (10–15% wt.). In understanding, the structural characteristics of lignocellulose are governed by composition and alignment of its polymeric constituents [63]. These polymers are clustered to form microfibrils, as depicted in Fig. 2, which mediate structural stability in the plant cell [69].

Typical lignocellulosic biomass is of recalcitrant nature to resist microbial degradation, which stems from the high crystallinity of cellulose, hydrophobicity of lignin, and encapsulation of cellulose by strong lignin–hemicellulose matrix. Based on the constituent representation, cellulose consists of only anhydrous glucose units imparting high crystallinity due to interlinked hydrogen bonding between same and adjacent cellulose chains, while hemicelluloses is a polymer of different sugar monomers and therefore, hemicellulose has a random, amorphous structure. Likewise, lignin is composed of complex, cross-linked, three-dimensional biopolymers with phenylpropane units imparting relative hydrophobic and

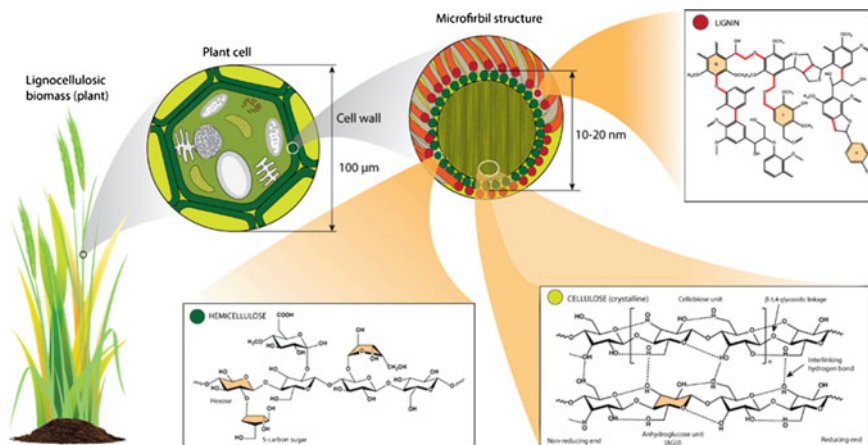


Fig. 2 Schematic representation of lignocellulose microfibril assembly consisting predominant biogenic polymer constituents [69]

aromatic properties. Adversely, the most difficult and energy-consuming step in the conversion of lignocellulosic biomass is the decomposition and degradation of cellulose structure due to its high crystallinity. The intrinsic molecular structure of cellulose is comprised of linearly connected β -D-anhydroglucopyranose units (AGUs), covalently linked through acetal functions (known as β -1,4-glycosidic linkages) between the equatorial hydroxyl groups of C4 and C1 carbon atoms [11] (Fig. 3).

Owing to the abundance of hydroxyl groups and oxygen atoms of AGUs, extensive networks of intra- and inter-molecular hydrogen bonds are formed, aligning cellulose fibrils together in a highly ordered fashion forming a crystalline

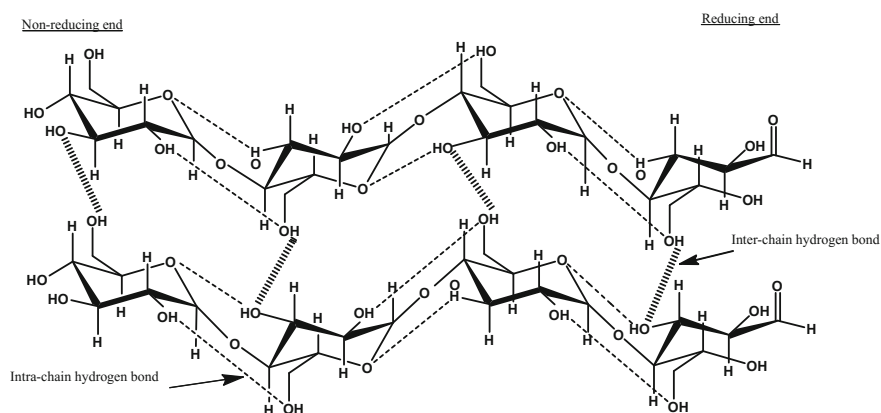


Fig. 3 Biomass cellulose alignment representing intra-and inter-linked hydrogen bonding [18]

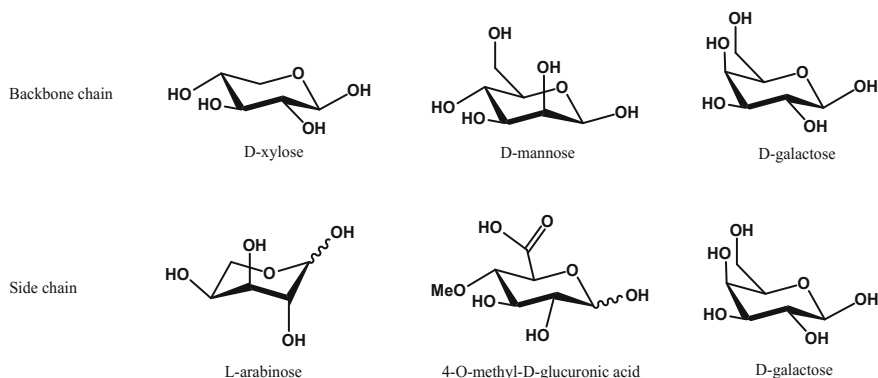


Fig. 4 Chemical structure of hemicellulose backbone monomers including C5- and C6-sugars as backbone and side chain molecules [3]

region, which is water insoluble and very resistant to chemical or enzymatic cleavage. Based on its crystalline structure, cellulose can be categorized into seven known allomorphic forms, denoted as cellulose I_α, I_β, II, II_{II}, III_{II}, IV_I, and IV_{II}.

Although cellulose I is the naturally occurring form (native cellulose), its crystal structure is thermodynamically less stable than that of cellulose II. Four other polymorphs of cellulose (II_{II}, III_{II}, IV_I and IV_{II}) are less commonly encountered and less relevant from commercial perspectives.

Unlike cellulose, hemicellulose has a random and amorphous structure, which is composed of several heteropolymers of different 5- and 6-carbon sugars or sugar acids including xylans (arabinoxylans and 4-O-methyl-glucuronoxylans), galactomannans, glucuronoxylans, arabinoxylans, glucomannans and xyloglucans (4- linked β-D-glucans with attached side chains) (Fig. 4).

These polysaccharides backbone usually consists of one repeating sugar unit linked through β-(1 → 4) with branch points (1 → 2), (1 → 3), and/or (1 → 6). In addition, it consists certain side groups, such as uronic acids and acetyl- and methyl-substituted groups [7].

Pectins, another group of polysaccharides made up of polycarboxylic acid, also account for minor fraction of carbohydrates in some plants. Pectins function together with hemicelluloses as a matrix component providing structural support to the cell walls. However, hemicellulose polymers have a low degree of polymerization (only 50–300 dp) as compared to cellulose. The predominant polysaccharide in hemicellulose is the glucuronoxylans, comprised of a xylan backbone of β-D-xylopyranose units linked through β (1 → 4) with acetyl groups at C-2 or C-3 of the xylose units [18]. Therefore, xylan is generally considered to be the simplest representation of a typical hemicellulose. It functions as the cellular glue which provides compressive strength to the plant tissue and the individual fibres, stiffness to the cell wall and resistance against insects and pathogens.

Similarly, lignin is a three-dimensional, highly cross-linked polymer composed of three types of phenylpropanoid units viz. trans-p-coumaryl, trans-coniferyl, and

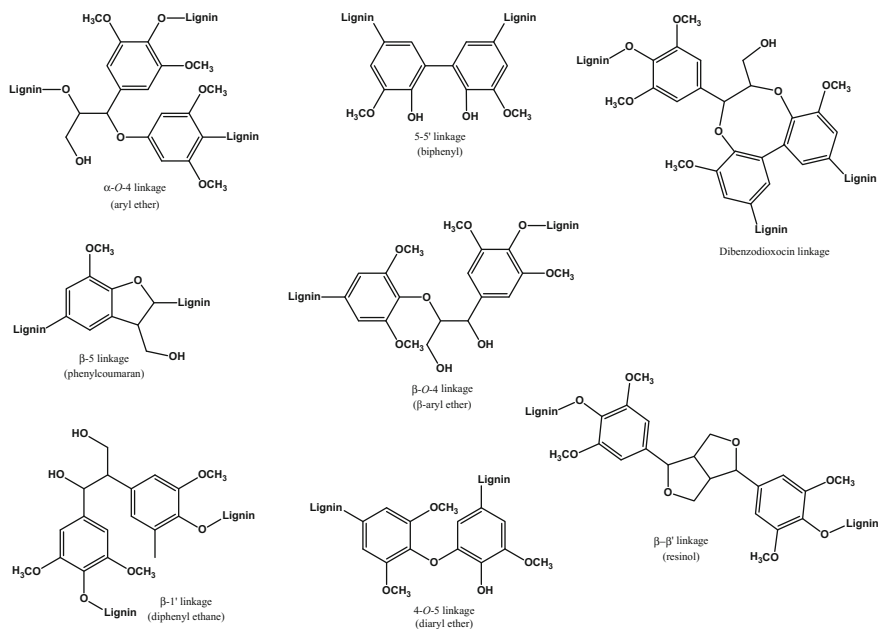


Fig. 5 Representation of major linkages present in biogenic lignin polymer [4]

trans-sinapyl alcohols formed by oxidative coupling, yielding a number of functional groups and linkages.

These precursors are aligned variedly to form three main type of lignin units in plants i.e., p-hydroxyphenyl-propane (H), syringylpropane (S) and guaiacylpropane (G) units. Within the lignin polymer, the phenylpropane units (S, G and H units) are bonded together by a set of linkages include β -O-4, α -O-4, 5-5', β -5, β -1', β - β' and dibenzodioxocin linkages, as depicted in Fig. 5. The crosslinked, lyophilic nature of lignin makes it insoluble and stable in water and acts as the “cellular glue” that connects the polysaccharides, such as cellulose and hemicellulose together providing comprehensive strength to plant tissue. The most common linkage between the lignin monomer units is recognized as the β -O-4 linkage, accounting for 50–60% of total linkages. Lignin also consists of additional functional groups, such as hydroxyl, methoxyl, carboxyl and carbonyl, which play an important role during delignification and lignin fragmentation reactions [46].

3 Hydrolysis of Lignocellulose

Hydrolysis of cellulose commonly refers to breakdown of glucan polymer to its monomer units, is a pre-requisite step in utilization of lignocellulosic biomass and can be accomplished via acidic catalysis using most common mineral acids or

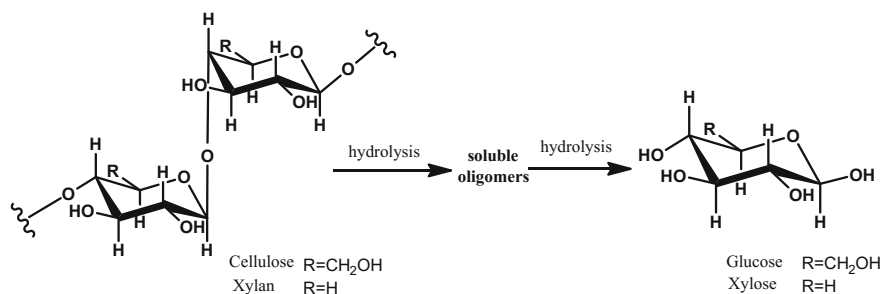


Fig. 6 Proposed reaction scheme of cellulose and hemicellulose hydrolysis [2]

biocatalyst (cellulase complex). Presumably, cellulase comprised of three major enzymes depending on their mode of action and end-product i.e., (i) endoglucanase attacks low crystallinity regions in the cellulose fibers, creating free chain-ends, (ii) exoglucanase or cellobiohydrolase hydrolyze the 1,4-glycosidyl linkages to form cellobiose, and (iii) β -glucosidase converts cello-oligosaccharides and dimers (cellobiose) into glucose residues. At the same time, breaking down of hemicellulose polymers into monomer mixtures consisting 5- and 6-carbon sugars) can be achieved via enzymatic reactions using enzyme cocktails include glucuronide, acetylsterase, xylanase, β -xylosidase, galactomannase and glucomannase [75]. Figure 6 depicts general reaction scheme for hydrolysis of cellulosic and hemicellulosic fraction of lignocellulosic biomass. These enzymes work synergistically to hydrolyse cellulose and hemicellulose. Enzymatic hydrolysis of lignocellulosic biomass is considered to be more effective than the use of acid catalysts owing to their highly specific action and operation at mild process conditions. In spite of these advantages, the use of enzymes in lignocellulosic hydrolysis is still limited due to several associated factors for example their relative instability at high temperature conditions, high costs of enzyme isolation and purification as well as difficult recovery and reusability. When considering the advantages offered by acidic catalysis, various aspects of chemically mediated hydrolysis are briefly discussed in the following sections.

The concept of utilization of lignocellulosic biomass, specifically carbohydrate based fuels and specialty chemicals rely heavily on availability of monomeric C5 and C6 sugars. It is well established that lignocellulose resist any changes in their structural integrity owing to its complexity. Therefore, the first and foremost step in the biorefineries is fragmentation of lignocellulose into its fractional components i.e., cellulose, hemicellulose and lignin. Often termed as pretreatment, the objective of this step is to disrupt the matrix structure to relieve lignin and decrease cellulose crystallinity, enabling enhanced chemical or enzyme accessibility to the cellulose during hydrolysis [56].

Though number of methods have evolved for lignocellulose pretreatment, intrinsic drawbacks, such as development of undesired byproducts, components loss and high processing cost have to be kept in mind while selecting appropriate

approach. For instance, pretreatment severity has to be sometimes reduced to reduce overall economic cost (normally accounts for about 30% of operating cost) as well as inhibitory degradation products. However, low severity factor corresponds to low sugar yields. Therefore, a balance has to be stroked out between various factors. Many different pretreatment methodologies viz. biological, physical, chemical and physico-chemical pretreatments have been employed during the last few decades. Since the chapter focus on chemical catalysis of lignocellulose biomass, pretreatment via chemical methods is discussed in the perspective of integration of pretreatment and production step with the aim of reducing overall production cost in future.

3.1 Homogeneous Hydrolysis Strategy

Mineral acid pretreatment is generally carried out with aim of hemicellulose solubilization and thereby, rendering cellulose more accessible for further processing [75]. A key advantage of acid pretreatment is that subsequent hydrolysis step could be sometimes over-stepped, as the acid itself hydrolyses the biomass to yield fermentable sugars by careful modulating reaction conditions. Most studies have employed strong acids like sulfuric, hydrochloric, nitric and phosphoric acids for biomass pretreatment with favored use of sulfuric acid, owing to being relatively less expensive than other acids and promising yield results [2]. Typically, both dilute (1–2% wt.) and concentrated (30–70% wt.) preparations of acid are evaluated for pretreatment; however, latter strategy is prone to intense formation of inhibitory compounds (poison to microbes), excessive corrosion problems and expensive product downstream. Nevertheless, literature cites that concentrated acid treatment (up to 50% wt.) causes apparent swelling of cellulose leading to the dissolution of cellulose to glucose, whereas dilute acid treatment offers the advantage of solubilizing hemicellulose, mainly xylan and subsequent conversion of solubilized hemicellulose to fermentable sugars depending upon reaction severity.

At the same time, organic acids such as fumaric, maleic and trifluoroacetic acid have emerged as hydrolyzing agents with comparable monosaccharide yields as sulfuric acid along with limited sugar degradation and corresponding furfural production [40, 52]. With time, various types of reactors have been developed and applied for large-scale acidic pretreatment of lignocellulosic materials such as percolation, plug flow, shrinking-bed and counter-current reactors [77]. Voluminous amount of literature is available on acidic pretreatment of lignocellulose biomass [10, 87] and it has been summarized that optimum conditions for the acid pretreatment are highly dependent on the purpose of pretreatment in terms of targeted sugars [49]. For instance, Saha and co-workers [71] achieved maximum carbohydrate content of 76% and 60% wt. from mild acid pretreated wheat straw and rice hull substrates, respectively, after enzyme saccharification and reported less or no formation of sugar degradation products (furfural and HMF) under typical reaction conditions (1.0% v/v H_2SO_4 at 121 °C for 1 h) [71]. Alternatively, several

other studies have proposed for addition of supplementary agents during acidic hydrolysis, in order to improve the direct conversion of cellulose into glucose. For example, Ragg and co-workers [62] employed HCl (6–7 M) supplemented with LiCl or CaCl_2 in aqueous phase for conversion of cellulose to glucose and yielded ~85% fermentable sugar release [62]. Later, in a similar fashion Cao and co-workers [5] employed ZnCl in a homogeneous cellulose pretreatment system followed by hydrolysis with dilute HCl, resulting in improved glucose yield (up to 91.5%) [5]. In modified study, Luterbacher and co-workers [50] evaluated the applicability of biphasic reaction system consisting aqueous (0.05% by wt. H_2SO_4) and organic (γ -valerolactone, a biomass derived green organic solvent) phase for the conversion of various cellulosic substrates to glucose and reported 70–90% conversion yield [50].

Likewise, studies have also been conducted on C5 sugar production from hemicellulosic fraction of lignocellulose via dilute acid hydrolysis. Herrera and co-workers [30] evaluated the production of xylose (16.2 g/L) which corresponded to 71.6% of theoretical yield from sorghum straw using 6% wt. HCl at 122 °C for 70 min [30]. Later, Rita and co-workers demonstrated further improved xylose yield (~74% wt.) from sugarcane bagasse using sulfuric acid (100 mg acid/g dm) under comparatively low severity conditions (130 °C for 10 min) [65]. In modified study, Zhang and co-workers [85] investigated combined dilute acid-catalyzed hydrolysis of palm oil empty fruit bunch by employing both dilute H_2SO_4 (0.5% w/v) and H_3PO_4 (0.2% w/v) to achieve 91.3% xylose yield. The apparent improved yields is mainly attributed to the synergistic action of acids under the modest reaction conditions (160 °C within 10 min) [85].

It is profound that typical alkaline pretreatments increase cellulose digestibility through fiber swelling and are known to be more effective for lignin solubilization, exhibiting minor cellulose and hemicellulose solubilization (less sugar loss) than acid or hydrothermal processes [6]. In perception, alkalis viz. sodium, potassium, calcium and ammonium hydroxides generally enables degradation of ester and glycosidic side chains, resulting in structural alterations of lignin, cellulose swelling and increase its internal surface area, partial decrystallization of cellulose, and partial solvation of hemicellulose [53]. In support, several early studies have revealed for the improved digestibility of lignocellulose (for example hardwood substrate) after pretreatment using NaOH yielded up to 55% wt. glucose, due to enhanced enzyme accessibility through recalcitrant lignin removal [41]. Similarly, numerous comparative studies have established for the better delignification capabilities of NaOH (up to 59% wt.) than sulfuric acid (31% wt.) while increasing its concentration from 0.05 to 0.2% g/g solids [19].

Alongside, studies have also demonstrated using weak base (for example CaOH) for biomass hydrolysis through removal of acetyl groups in hemicellulose and reducing steric hindrance, resulting in enhanced cellulose digestibility. Indeed, biomass pretreatment using lime offers the advantages of lower cost and less safety requirements compared to NaOH or KOH pretreatments, and easy recovery from hydrolysate by reaction with CO_2 . Consequently, application of this approach has resulted in 89% wt. glucose recovery from leafstar rice straw [59]. Furthermore,

supplementation of oxidative reagents, for example O_2 or H_2O_2 to alkali during biomass pretreatment could improve cellulose and hemicellulose hydrolysis by favoring lignin removal and more importantly, decreased furfural and HMF formation [6]. Apparent studies have witnessed for no obvious furfural or HMF formation during alkaline peroxide pretreatment, which favors further microbial fermentation of sugars to ethanol [77]. Several other chemical pretreatment methods like ozonolysis, organosolv and wet oxidation have been practiced with considerably high delignification yields, however, these methods restricted for use in cellulose to bioethanol transformations, due to high expenses involved as well as subsequent enzymatic inhibition by chemical agents employed [58, 75, 86]. Table 1 summarizes few examples of lignocellulosic biomass processing for C5 and C6 sugars production.

In advancement of bioprocessing, ILs functionalized with acidic groups are new-types of thermally stable catalysts having special properties like providing high-density active sites as liquid acids, non-volatile, easily recyclable and exist as solids even above 100 °C [26]. Several mechanistic studies on cellulose hydrolysis proposed that hydrolysis of cellulose involves breakdown of the hydrogen bond in cellulosic network by the high activity of chloride concentration in ILs [76]. However, water acts as an inhibitor for the dissolution of cellulose and hence can be used to regenerate the cellulose dissolved in ILs. Fascinatingly, during dissolution and regeneration by precipitation of cellulose, its crystallinity reduces significantly and thus, exposing the amorphous part which is much easier to hydrolyze compared with the native cellulose. Furthermore, various ILs specifically hydrophilic imidazolium-based, such as 1-butyl-3-methylimidazolium chloride ([BMIM]Cl), 1-allyl-3-methylimidazolium chloride ([AMIM]Cl), 1-benzyl-3-methylimidazolium chloride ([BZMIM]Cl), and 1-ethyl-3-methylimidazolium acetate ([EMIM] CH_3COO), have been demonstrated for significant dissolution of lignocellulosic materials with remarkable glucose conversion yields (>80%) [14, 45, 64]. Another aspect of ILs in lignocellulosic processing was demonstrated when Lee and

Table 1 Examples of monomeric sugar production from lignocellulosic biomass (adapted from Ref. [88])

Catalyst	Lignocellulose	Operating parameters	Hydrolysis Product	Yield (% wt.)	Ref.
H_2SO_4 (0.175% wt.)	Wood chips	210 °C, 2 min, ~ 1.9 MPa	Xylose	54	[20]
H_2SO_4 (0.5% wt.)	Corn cobs	125 °C, 165 min	Xylose	25	[66]
H_2SO_4 (6.2 % wt.)	Sugar maple wood extract	95 °C, 50 min, 0.1 MPa	Xylose	161.6 g.L ⁻¹	[31]
SO_2 Impregnation	Aspen chips	205 °C, 3 min, 1.62 MPa	Glucose Xylose	37 10	[15]
HCl (20% wt.) + [EMIM]Cl	Cellulose	105 °C, 2–4 h	Glucose	~ 90	[2]

co-workers [44] discovered for dissolution of lignin in ILs, however, exhibited a limited affinity toward cellulose and other constituents of wood flour [44]. These ILs were [MMIM]-[CH₃OSO₃], 1,3-dimethylimidazolium trifluoromethanesulfonate ([BMIM][CF₃SO₃]), [EMIM][CH₃COO], [AMIM][Cl], [BMIM][Cl], or 1-benzyl-3-methylimidazolium chloride ([BZMIM][Cl]). Despite the advantages offered by ILs, the high cost of ILs limits their large-scale application in biomass pretreatment. However, it can be expected that research will be focused on dropping down the production cost of ILs so as to enable its application in commercial hydrolysis and pretreatment processes for cellulose conversion.

3.2 Heterogeneous Hydrolysis Strategy

Although homogeneous acids have been quite successful in cellulose hydrolysis to yield monomeric glucose, the handling and operational issues associated with these approaches led to the research and development of heterogeneous acid catalysts. However, most heterogeneous catalytic studies are based on commercial cellulose due to difficulties in separation of cellulose and lignin in biomass; nevertheless, few researches have demonstrated for direct lignocellulose conversion. Table 2 summarizes potential applications of heterogeneous solid acid catalysts towards cellulose hydrolysis to glucose.

In modified study, Jiang and co-workers demonstrated self-derived carbonaceous solid acid (CSA) catalysts giving rise to a close loop recycle procedure,

Table 2 Popularly used heterogeneous solid acid catalysts for bio-derived component transformation reactions [29]

Example solids	Class
Zeolite and zeolite-like	X-, Y-zeolites (faujasite), chabazite, ferrierite, beta-zeolite, mordenite, erionite, HZSM-5, MCM-22, metalloaluminophosphate (e.g., silicoaluminophosphate, gallosilicate, beryllosilicate, titanosilicate, stanosilicate)
Clay	Montmorillonite, saponite
Metal oxide and mixed metal oxide	Al ₂ O ₃ , TiO ₂ , SiO ₂ , Nb ₂ O ₅ , WO ₃ , SiO ₂ -Al ₂ O ₃ , SiO ₂ -ZrO ₂ , SiO ₂ -MgO, TiO ₂ -SiO ₂ , WO ₃ -ZrO ₂ , WO ₃ -Al ₂ O ₃ , WO ₃ -SnO ₂ , Nb ₂ O ₅ -Al ₂ O ₃ , B ₂ O ₃ -Al ₂ O ₃
Acid supported	H ₃ PO ₄ /SiO ₂ , HClO ₄ /SiO ₂ , SO ₃ H/SiO ₂ , SO ₃ H/C, AlCl ₃ /SiO ₂ , BF ₃ /SiO ₂ , SbF ₅ /SiO ₂ -Al ₂ O ₃ , SbF ₅ /TiO ₂ , CF ₃ SO ₃ H/SiO ₂ , heteropoly acids/SiO ₂
Sulfated oxide	SO ₄ ²⁻ /ZrO ₂ , SO ₄ ²⁻ /TiO ₂ , SO ₄ ²⁻ /SnO ₂
Layered transition metal oxide	HNBMoO ₆ , HTaWO ₆ , HNbWO ₆
Metal salt	AlPO ₄ , Nb ₃ (PO ₄) ₅ , FePO ₄ , NiSO ₄
Heteropoly compound	H ₃ PW ₁₂ O ₄₀ , H ₄ SiW ₁₂ O ₄₀ , H ₃ PMo ₁₂ O ₄₀ , H ₄ SiMo ₁₂ O ₄₀ , and their salts (e.g., H _{0.5} Cs _{2.5} PW ₁₂ O ₄₀)
Ion exchange resin	Amberlyst-15, Nafion, Nafion-silica composite/nanocomposite

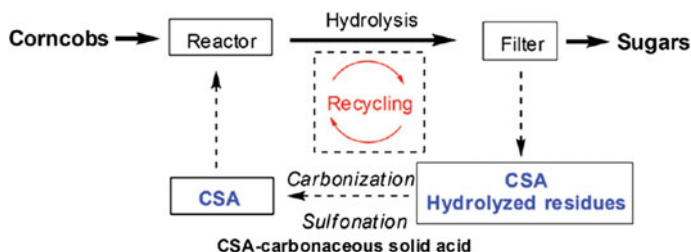


Fig. 7 Process scheme of corncob hydrolysis by CSA derived from the hydrolysis residue [35]

where CSA is prepared under microwave irradiation from hydrolyzed corncob residues and re-used for the hydrolysis of corncob, as illustrated in Fig. 7 [35]. The obvious advantages of this process are two end products as output, first is the sugars derived from cellulose and hemicelluloses and secondly, CSA coming from the unconverted solid residue. Considering the use of inexpensive solid acid catalyst, moderate reaction conditions (130 °C) and appreciable yields of xylose and arabinose (78% wt.) the overall process is postulated to yield good economics. Therefore, it is evident that heterogeneous catalysis offers economic conversion of lignocellulosic biomass into platform sugar compounds. However, efforts are to be made in the direction of overcoming mass-transfer limitations associated with substrate-catalyst interactions without incorporating additional physical pretreatment costs.

4 Thermochemical Catalysis of Carbohydrate Sugars

Depending on the intended end-use of the product, lignocellulosic biomass can be processed in numerous ways like liquefaction, solvo-hydrolysis, pyrolysis, hydrolysis, hydrothermal hydrolysis etc. For instance, synthesis of transportation fuels and chemicals require less oxygen content and consequently, lignocellulosic biomass is depolymerized and deoxygenated prior to catalytic hydrolysis. In favorable, presence of oxygen often provides valuable physical and chemical properties to other value-added chemicals and therefore, require much less deoxygenation. In accordance, with the recent literature cites that 5-hydroxymethylfurfural, lactic acid, acetone-butanol-ethanol (ABE) and lignin has been identified as platform molecules in addition to the previously defined platform chemicals by the US-DOE, which could be obtained from lignocellulose-derived C5 and C6 sugars and also, lignin fraction by any of the chemical or biological processing techniques. Because these molecules can be further processed into value-added chemicals by employing appropriate processing approaches [33].

5-Hydroxymethylfurfural (HMF): A versatile ‘value-added’ additive molecule, gaining much attention in petroleum and chemical industries due to its reactive features (heterocyclic furan), consisting hydroxide and aldehyde functionalities at

2,5-positions, and moreover, it is relatively an unsaturated aromatic compound [12]. Thus, HMF is susceptible to many chemical reactions, depending upon the synthesis route (Fig. 8) undergoing favorable changes leading to the production of commercially important chemicals [79].

It is generally produced through acid-catalyzed dehydration of hexose sugars preferably fructose. Synthesis of HMF from biomass-derived glucose is essentially a two-step process i.e., a base and/or Lewis acid catalyzed reaction for isomerization of glucose to fructose followed by Brønsted acid mediated catalysis to the end product. Due to the unstable character of HMF, obtaining high yield and selectivity from glucose is challenging from industrial point of view. In a typical reaction conditions, HMF is more likely to rehydrate to levulinic acid and formic acid at equal proportion under same prevailing reaction conditions. The earliest reports on synthesis of HMF in aqueous phase reaction system employing cheap raw material like wood chips, were restricted by meager selectivity towards HMF owing to instability of HMF in water under acidic conditions. In order to avoid the complications and further product yield improvement, Kuster and Der Van Steen in 1977 [42] attempted to introduce organic solvents, as extracting agents, resulting achieved remarkable conversion yield under modest reaction conditions with appreciable synergistic effects on HMF's rate of formation along with limiting its decomposition to humin species and other side products [42]. Since then numerous solvents including DMSO (dimethyl sulfoxide), DMF (dimethyl formamide), DMA

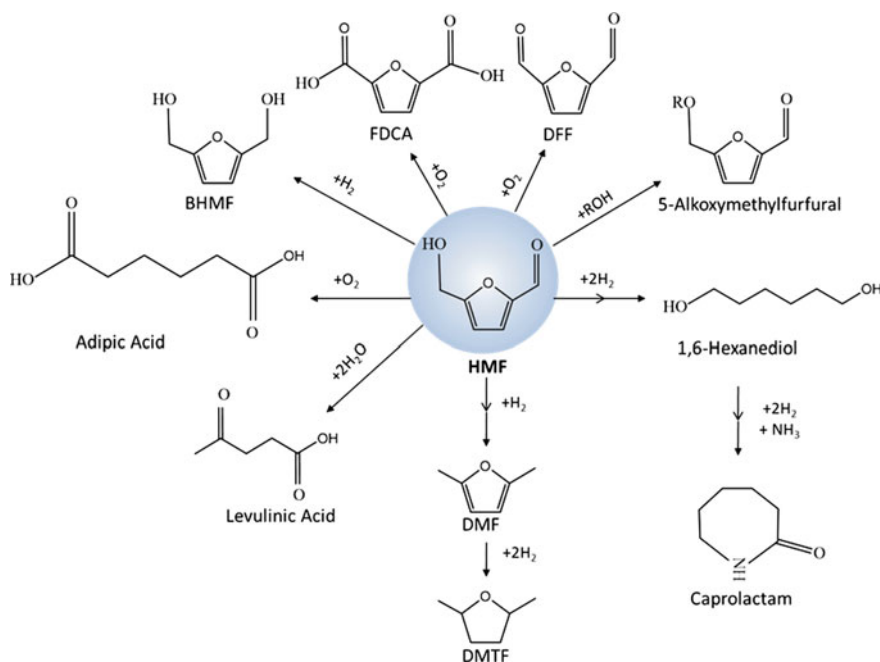


Fig. 8 Potential application of 5-hydroxymethylfurfural as platform molecule

Table 3 Classified catalyst group for HMF synthesis from hexose sugar molecule (reproduced from Ref. [68])

Catalyst group	Example
Organic acids	Carboxylic acids, lactic acid, oxalic acid, levulinic acid, maleic acid, <i>p</i> -toluenesulfonic acid, boric acid
Inorganic acids	Sulfuric acid, phosphoric acid, hydrochloric acid, iodine or hydroiodic acid generated in situ
Slats	MgCl ₂ , (NH ₄) ₂ SO ₄ /SO ₃ , pyridine/PO ₄ ³⁻ , pyridine/HCl, aluminum salts, Th and Zr ions, zirconium phosphate ions: Cr, Al, Ti, Ca, In, ZrOCl ₂ , VO(SO ₄) ₂ , TiO ₂ , V-porphyrine, Zr-, Cr- and Ti-porphyrins, lanthanides (LaCl ₃ , NdCl ₃ , EuCl ₃ , DyCl ₃ and YbCl ₃)
Lewis acids	ZnCl ₂ , AlCl ₃ , BF ₃
Solid acids	Ion exchange resins, zeolites, supported acids, heteropoly compounds

(dimethyl acetamide), NMP (N-methyl pyrrolidinone), sulfolane etc. have been evaluated and consequently achieved higher HMF yields [70]. For instance, Qi and co-workers [60] successfully tested sulfated zirconia (SZ) for dehydration of fructose reactions achieving 72.8% HMF yield at 180 °C under microwave heating for 20 min in solvent mixture consisting of acetone–dimethylsulfoxide (DMSO) [60]. Recently, Moreno-Recio and co-workers achieved 42% HMF yield with 80% glucose conversion using HZSM-5 (Si/Al ratio of 18.9) in a biphasic system containing 20% NaCl and MIBK, within 30 min reaction at 195 °C [55]. Apprehensively, these processes increase the overall cost economics owing to complex recovery itinerary of such high boiling point solvents. Another advancement in this field is the use of bi-functional heterogeneous catalysts presenting both acidic and basic catalytic sites. In accordance with the literature reports that heterogeneous catalysts have shown superior catalytic activity over homogeneous catalysts in terms of product selectivity [26]. Table 3 lists various catalysts that have been reported for HMF synthesis under various reaction conditions.

With the continuous evaluation of various efficient catalysts for HMF synthesis, complete conversion of biomass derived sugars has been achieved, however, one-pot synthesis still remains a challenge owing to mass-transfer limitations. Due to this, commercialization of HMF from lignocellulosic biomass has not been realized. New heterogeneous catalysts, such as Metal Organic Frameworks (MOFs), Porous Organic Polymer (POP), Covalent Organic Frameworks (COFs) and Covalent Triazine Frameworks (CTFs) have emerged with excellent characteristics, suited the most pivotal being easy functionalization to facilitate direct valorization of lignocellulosic biomass. A recent example of use of such MOFs is hydrolysis of carboxymethylcellulose (CMC) to 5-HMF in aqueous phase at 200 °C for 4 h with aluminum based MIL-53(Al) and achieved a molar yield of 40.3% of 5-HMF [89].

Levulinic acid (LA): Another class platform molecule, which serve as precursor to numerous value-added chemicals production, and is generally prepared from lignocellulose via hydrolysis and dehydration/hydration reactions through intermediate HMF formation.

In popular, the well-established method for LA preparation from biomass is Biofine process, essentially a two-stage processing protocol. Briefly, in the first stage, a plug flow reactor is employed for initial biomass hydrolysis under elevated conditions (210–220 °C, 25 bar for 12 s) and subsequently, the slurry mixture is treated under relatively less severe conditions (190–200 °C, 14 bar and 20 min) at similar acid concentrations to yield ultimately a product mix consisting predominantly LA (50% by wt. of C6 sugar), furfural (50% by wt. of C5 sugar) and formic acid (20% by wt.) along with residual HMF concentrations. So far, variety of carbonaceous feedstocks (biomass) have been evaluated for LA preparation catalysed via both homogeneously and heterogeneously and could achieve up to 40–45% wt. under modest reaction conditions [61]. In a typical reaction setup, LA yields of about two thirds (or even less) than the theoretical value are attainable due to the formation of undesired black insoluble-materials called humins. Recent advancements in LA synthesis include use of SO_3^- functionalized ionic liquid, 1-(4-sulfonic acid) butyl-3-methylimidazolium hydrogen sulphate ([BSMim]HSO₄), giving the highest yield up to 40% wt. within 120 min in aqueous medium at 120 °C from cellulose [72]. Figure 9 illustrates various value-added commodities which are synthesized from biomass derived levulinic acid.

Sorbitol: A sugar alcohol, which is generally produced by the hydrogenation of glucose in the presence of suitable catalyst either homogenous or heterogeneous.

The earliest reports of sorbitol production from cellulose dates back to 1950 employing mineral acid and supported Ru catalysts under H₂ pressure (7 MPa) giving 99% recovery of sorbitol. Figure 10 summarizes use of sorbitol as potential platform molecule. Although literature cites on direct conversion of biomass

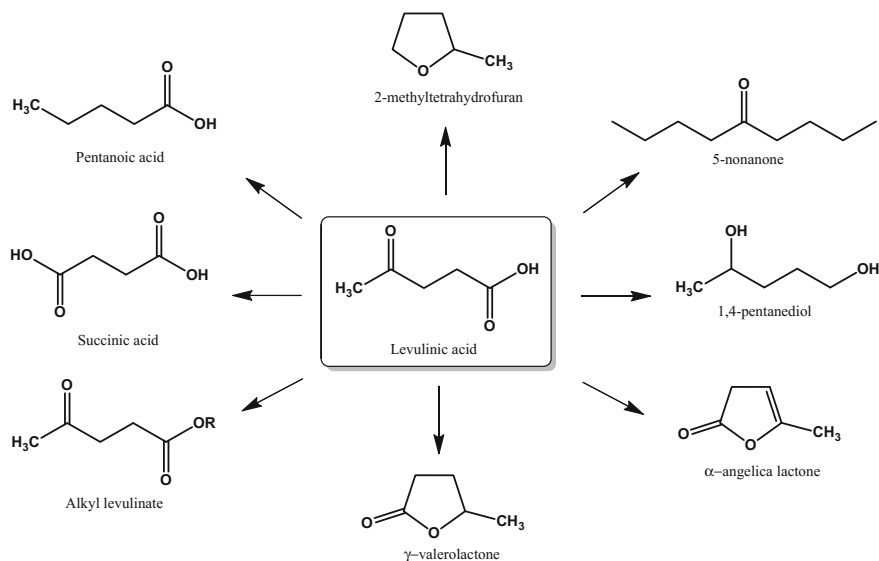


Fig. 9 Summary of end products derived from levulinic acid as building block [50]

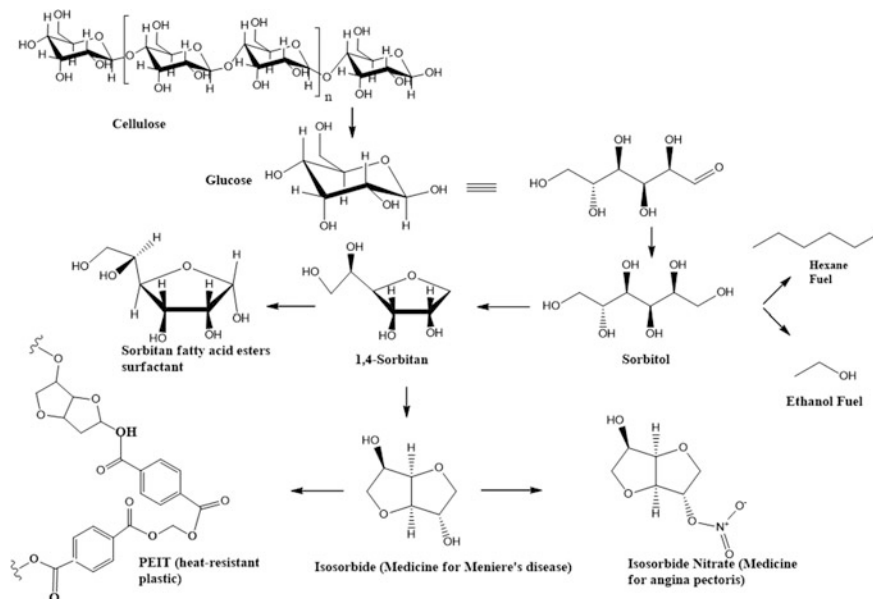


Fig. 10 Reaction scheme for sorbitol production from cellulose and its end-use [39]

substrates for sorbitol production is scarce, commercial D-glucose has been transformed into sorbitol by various researchers [13]. For instance, Kåldström and co-workers [37] employed hydrolytic hydrogenation of bleached birch kraft pulp in aqueous medium at 185 °C under 20 bar H_2 over H-MCM-48 and Pt/MCM-48 synthesis zeolite catalysts and identified that former was able to convert cellulosic and hemicellulosic fractions into variety of products include glucose, xylose, 5-HMF, furfural and furfuryl alcohol. The later catalyst was able to further transform the synthesized glucose and fructose molecules into sorbitol and xylitol products, respectively [37]. Subsequently, Kobayashi and co-workers [39] evaluated transformation of Avicel microcrystalline cellulose to sugar alcohols using γ - Al_2O_3 -supported Pt catalyst and $Pt(Cl)/\gamma$ - Al_2O_3 in the presence of H_2 pressure (5 MPa) at 190 °C for 24 h, resultantly achieved 25% wt. sorbitol along with considerable mannitol (6% wt.) as co-product [39]. Overall, reviews convey that cellulosic fraction of lignocellulosic biomass is an extensive source of platform compounds for production of value added chemicals. However, successful conversion of commercial cellulose appears to be promising technique.

Furfural: Furfural (2,5-furandicarboxyaldehyde) is the principal product of C5 sugar derived via dehydration reaction in the presence of mild acid under typical reaction conditions. It can be used as precursor for the production of wide range of high value chemicals and energy fuels, as depicted in Fig. 11. This value added product is exclusively produced from lignocellulose biomass even at commercial scale. The first known commercial production of furfural is accredited to the Quaker

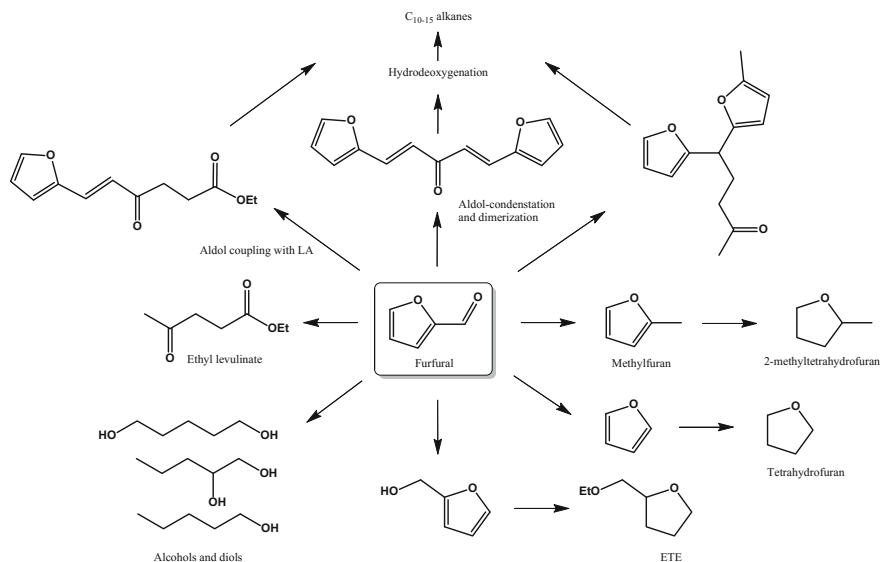


Fig. 11 Potential application of furfural as an industrial precursor

Oats technology established in 1921 and later, various modifications have been made to create new processes with improved furfural yields, recovery, and purity by groups like Westpro modified Huaxia Technology and Supra yield [38]. Despite commercialization of furfural, low yields are obtained which probably is due to the evolution of side reactions as well as cross-polymerization that involve sugars, furfural, and reaction intermediates in an acidic aqueous environment. Till date, varied furfural yields have been reported at bench scale level through employing variety of approaches, which are mainly governed by operating conditions. For instance, maximum up to 87% wt. furfural concentrations have been achieved in an integrated two stage processing i.e., hot water hydrolysis followed by homogenous catalysis (H_2SO_4), of various lignocellulosic biomass (hybrid poplar, miscanthus, switchgrass and corn stover) [51]. In another study, Lewis acid metal chloride catalysts ($CrCl_3$ and $CrCl_2$) have been employed as alternative to mineral acids for furfural production in a monophasic solvent system (N,N -dimethylacetamide/ $LiCl$) and reported maximum furfural yield (56% wt.) [2]. In another approach, use of microwave irradiation has been demonstrated to be effective in reducing the residence time without compromising overall yields [84]. Alternatively, solid catalysts have been employed for furfural synthesis and achieved remarkable yields and conversion performance. For instance, Lima and co-workers [48] employed microporous silicoaluminophosphates (SAPO-5, SAPO-11 and SAPO-40), as solid acid catalysts during dehydration of xylose into furfural under biphasic conditions, and obtained maximum furfural yield (65% wt.) at 170 °C in 24 h [48]. In a recent study, increased furfural yield (relatively 21% wt.) was obtained by Chen and

co-workers [9] in a process employing HZSM-5 with the addition of 4-Methoxyphenol, a polymerization inhibitor, due to less formation of humins [9]. Recent advancements in the area of utilization of biomass derived hemicellulosic fraction, including integrated two-stage strategies, application of microwave irradiation resulting in decreased residence time, addition of polymerization inhibitors for decreased humin formation have exerted the cumulative effect of increased furfural yield, resulting in improved economical aspect of industrial scale furfural production. Overall, it is therefore recommended to be carry forwarded towards application in biomass to value addition to realize the concept of biorefineries, in the context of substitute to petroleum derivatives.

5 Catalytic Valorization of Bio-derived Lignin

Lignin is the third most abundant natural polymer after cellulose and hemicellulose. It is composed of phenylpropane units which are bonded together by various C–C bonds such as aryl–aryl; aryl–aliphatic and aliphatic–aliphatic as well as ether and aryl ether C–O bonds. Various value added products that are synthesized from processing of lignin through hydrodeoxygenation, hydrolysis, oxidation, biotechnological conversions are represented in Fig. 12 [25].

Although lignin forms a large proportion of the non-food biomass eligible for production of renewable and carbon-neutral liquid fuels and chemical compounds, its separation from its covalently linked materials like cellulose and hemicellulose is one of many technical hurdles needed to be overcome for economical production of

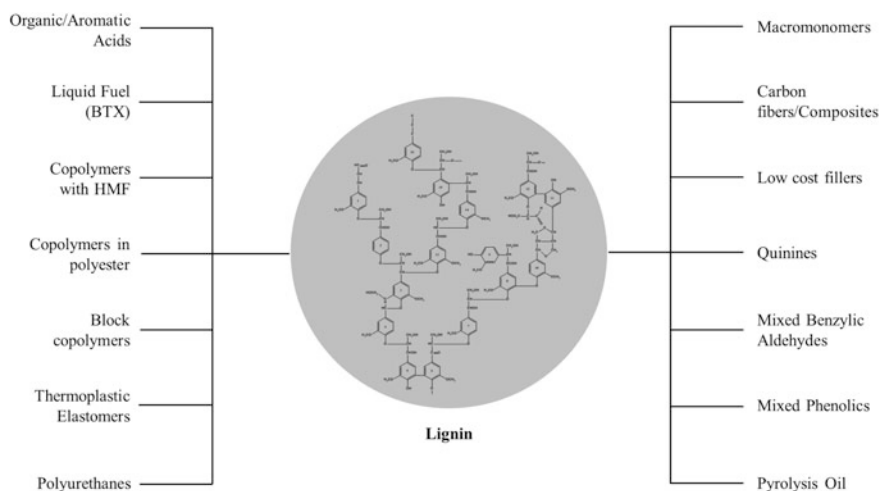


Fig. 12 Value added products from processing of bio-derived lignin through various conversion methodologies [25]

biofuels from cellulosic wastes. To realize this objective, various traditional lignin-isolation methods have been employed such as sulfite (SO_2 and alkali/acid), kraft or sulfate (Na_2S and NaOH) and soda (NaOH) processes. With time several non-conventional chemical methods, such as ammonia fiber expansion (AFEX), aqueous NH_3 , dilute and concentrated acids (e.g., H_2SO_4 , HCl , HNO_3 , H_3PO_4), alkaline (e.g., NaOH , KOH , $\text{Ca}(\text{OH})_2$), organic solvents (e.g., ethanol, formic acid, acetic acid, methanol), and ionic liquids have evolved, which offer the advantage of lignin production with little or no sulfur compounds and thus, increasing the applicability for manufacture of value-added products [17]. Although lignin obtained by organic solvents, called organosolv lignin, is beneficial over sulfonated and kraft lignins due to greater ability to be derivatised, lower ash content, higher purity (due to lower carbohydrate content), generally lower molecular weight and more hydrophobicity, it is not widely developed because of the lower quality of the pulp produced and extensive corrosion of the process equipment. Recent advancements in the area of lignin extraction and precipitation is employing of ionic liquids, where lignins can be recovered from IL by precipitation, allowing the IL to be recycled. Mostly alkylimidazolium based IL have been employed as biomass solvents for dissolution of cellulose. There are reports on use of N-methylimidazole indimethyl sulfoxide for lignin isolation from wood and later precipitation using dioxane/water mixture [22]. Recently, Tan and co-workers [78] utilized ionic liquid mixture consisting 1-ethyl-3-methylimidazolium cation and a mixture of alkylbenzene sulfonates with xylene sulfonate to extract lignin from sugarcane bagasse at elevated temperatures of 170–190 °C under atmospheric condition [78].

High energy content and presence of highly reactive functional groups represent lignin as a potential substrate for synthesis of wide range of renewable chemicals. Further lignin polymer is susceptible to a wide range of chemical transformations, principally cracking or hydrolysis reactions, catalytic reduction, and catalytic oxidation reactions to form valuable chemicals. Normally, lignin catalytic reduction reactions aim at removal of the extensive functionality of the lignin subunits to generate simpler monomeric compounds like phenols, benzene, toluene, or xylene, which can be then hydrogenated to alkanes (carbon atoms C7–C18) via coupling reactions or used as platform chemicals under appropriate reaction environment. Lignin valorisation is often realized through thermal hydrogenolysis (depolymerisation) which could be base-catalyzed, acid-catalyzed, metallic catalyzed and ionic liquids-assisted depolymerization for synthesis of various phenolics (Table 4). However, very meagre yields have been reported indicating pyrolysis to be better methodology for phenolics generation [1, 83].

Heterogeneous hydrogenation of lignin was reported in as early as 1938 when Harris and co-workers obtained monomeric propylcyclohexanols (substituted alkyl phenols) and methanol when lignin was reacted with hydrogen over copper-chromium oxide [28]. Later, many patented processes were reported, for example Noguchi process, which employed an Fe(II)-sulfide along with copper oxide as co-catalyst in phenol at 250–450 °C with an initial hydrogen pressure of 15.2–45.6 MPa and obtained 40% yield of C6–C9 mono phenols [57]. In another patented

Table 4 Production of aromatic phenolics from lignin through various catalytic reactions (reproduced from Ref. [80])

Lignin	Catalyst	Reaction conditions	Major products	Yields (%) wt.)	Ref.
Base-catalyzed					
Steam explosion hemp lignin	5% wt. NaOH	300–330 °C, 3.5 MPa	Guaiacol, Catechol Vanilin	0.9–2.8 0.8–3.0 0.5–0.8	[43]
Steam explosion softwood lignin			Guaiacol Catechol Vanilin	1.2–2.1 0.1–3.2 0.3–0.5	
Organosolv lignin	2% wt. NaOH	300 °C, 25 MPa	Syringol Hydroxyacetophenone Guaiacol	4.1 1.6 1.1	
Acid-catalyzed					
Wheat straw lignin	10% wt. formic acid 77% ethanol	360 °C, 25 MPa	Methoxyphenols Catechols Phenols	1.3 0.5 0.3	[24]
Wheat straw lignin	10% wt. formic acid 81% wt. ethanol	380 °C, 25 MPa	Methoxyphenols Catechols Phenols	2.9 1.5 2.0	[23]
Metallic-catalyzed					
Kraft lignin	Si–Al catalyst/ H ₂ O/butanol	200–350 °C, 1.1– 23 MPa	Phenols	6.5	[82]
Acidic hydrolysis spruce lignin	4.4% wt. formic acid 0.15% wt. Pd catalyst 0.94% wt. Nafion SAC-13	300 °C, 9.6 MPa	Guaiacol Pyrocatechol Resorcinol	2.0 1.8 0.5	[47]
(continued)					

(continued)

Table 4 (continued)

Lignin	Catalyst	Reaction conditions	Major products	Yields (%) wt.)	Ref.
Birch sawdust lignin	Ni/C	200 °C	Propenylguaiacol Propenylsyringol	12 36	[73]
<i>Ionic-liquid-catalysed</i>					
Organosolv beech lignin	[EMIM][CF ₃ SO ₃]/Mn(NO ₃) ₂	100 °C, 8.4 MPa	2,6-Dimethoxy-1,4-benzoquinone	11.5	[74]
Guaiacylglycerol-β-guaiacyl ether	[BdMIM]Cl/1,5,7-triazabicyclo [4.4.0]dec-5-ene	150 °C	Guaiacol	71.5	[34]

work, Inventa AG employed ferrous sulfate for the fragmentation of lignin into distillable products containing a substantial amount of monophenols [36]. Subsequently, Misson and co-workers [54] investigated catalytic pyrolysis of the pretreated empty palm fruit bunches using NaOH, H₂O₂, and Ca(OH)₂ and yielded up to 90 and 80% wt. phenolic monomers in the presence of AlMCM-41 and H-ZSM-5, respectively, when processed at 300 °C [54]. In recent work, Chan and co-workers [8] employed vanadium based catalysts for conversion of dioxasolv-lignin derived from *Miscanthus giganteus* (under 80 °C for 24 h in 10:1 acetonitrile/THF and 8:1 ethyl acetate/THF mixtures) and obtained a mixture of monophenolics, such as vanillin, syringic acid, syringaldehyde, 4-hydroxybenzaldehyde, vanillic acid, in major proportions [8]. However, utilization of lignin fraction of lignocellulosic biomass for value-added commodities synthesis has not been well established due to its heterogeneity nature.

Further improvements in the existing techniques along with development of novel protocols specifically heterogeneous based are emerging, which will enable the researchers to exploit the potential of lignin at industrial scale.

6 Summary and Perspectives

Lignocellulosic biomass is an abundant source of renewable energy with the potential to be successful alternative to petroleum-based economy. A large pool of value-added chemicals and fuel additives have been devised from cellulosic, hemicellulosic and lignin biogenic polymers and their scope as industrial commodities is revealed in this chapter. Considering the predicted opportunities of lignocellulosic biomass valorization, various catalytic processes that have been evolved for biomass processing, namely hydrolysis, liquefaction, gasification, pyrolysis and deoxygenation/hydrogenation have received increasing attention. However, irrespective of catalytic processes employed, present techniques have not yet offered complete commercialization barring only few bio-products. Although catalytic hydrolysis has evolved as simple process over present liquefaction, gasification and pyrolysis methods of lignocellulosic biomass processing, operational issues such as reactor corrosion, energy-intensive product separation and catalyst recycle remains a challenge in industrial scale production. Advent of heterogeneous as well as ionic liquid-mediated catalysis has emerged as acceptable alternatives, developments in the valorization of lignocellulose still remains a great challenge together with many opportunities. Nevertheless, efforts are being made to develop specific catalysts to overcome various limitations including mass-transfer and catalytic activity loss on reuse and certain novel candidates viz. MOF, POP, COF and CTFs, which finds considerable application in certain fields of biomass valorization. It is postulated that use of such tailored catalysts would bring remarkable improvements in process economics of biomass into biovalue. Commercial

considerations can be further improved through continued research and development and in support, recent trends suggest that chemical catalysis of lignocellulosic biomass will be a key player in establishing a worldwide bio-based economy to substitute conventional petroleum dependent industries.

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