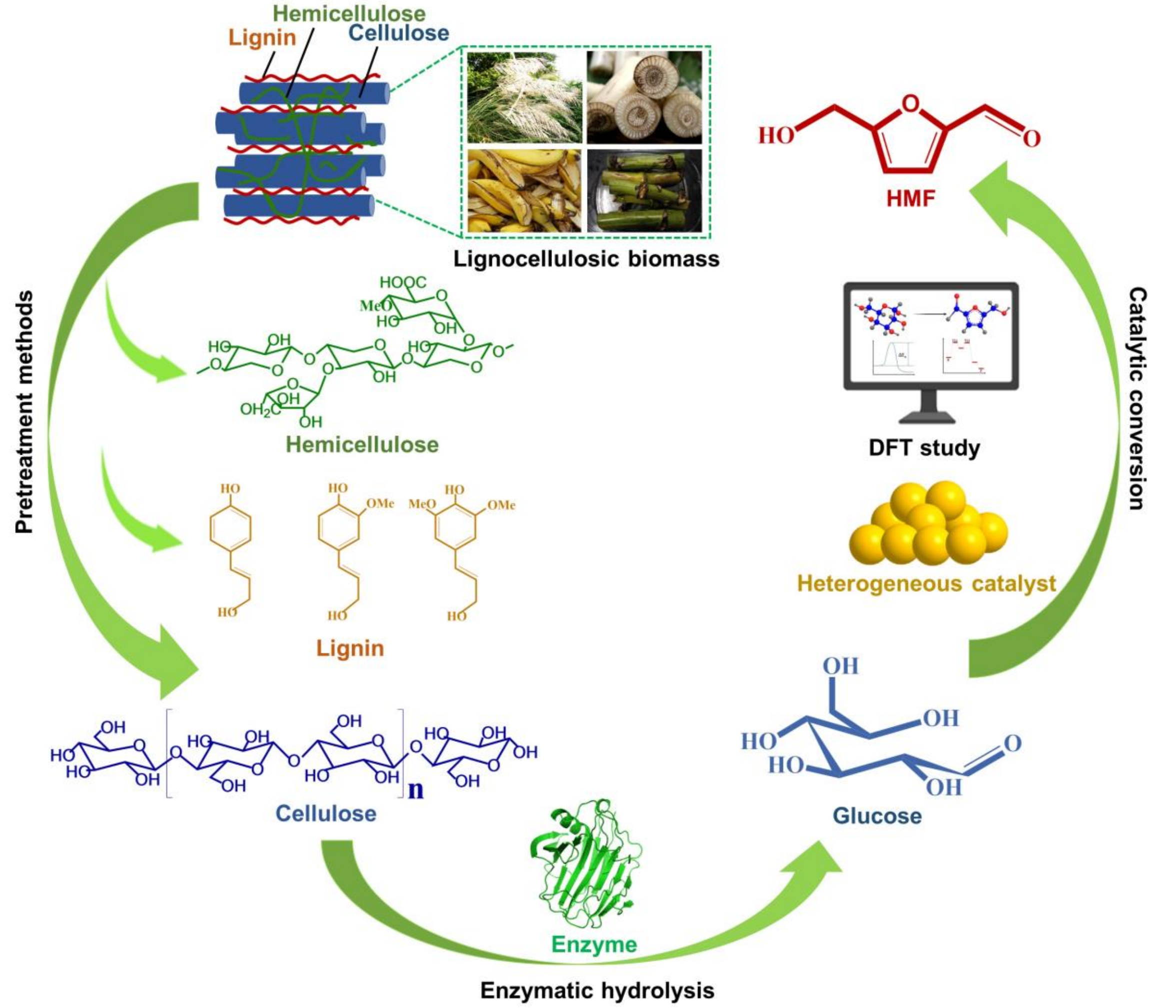
Chapter 2

Review of literature



2.1. Structure of lignocellulosic biomass (LCB) and its components

LCB primarily consist of three polymers: cellulose $(C_6H_{10}O_5)_n$, hemicellulose $(C_5H_8O_4)_m$, and lignin $[C_9H_{10}O_3(OCH_3)_{0.9\text{-}1.7}]_x$ in an intricate structure where the components are rigidly associated through non-covalent bonds and covalent cross-linkages as shown in Fig. 2.1 [1]. In general, the cellulose, hemicellulose, and lignin contents in a typical LCB fall within the range of 30-60%, 20-40% and 15-25% respectively [2]. However, the composition of these major components varies depending on the source. Cellulose is the main structural integral of LCB which is a linear polysaccharide that consists of D-glucose subunits linked by β-(1,4)-glycosidic bonds [3]. This polymer is insoluble in water unless at extremely low or high pH levels. However, it is soluble in solvents like ionic liquids (ILs) and N-methylmorpholine-N-oxide (NMMO) [4]. Cellulose possesses advantageous properties such as biocompatibility, stereoregularity, hydrophilicity, and reactive hydroxyl groups and serves as a versatile resource for derivatized materials such as fibers, films, composites as well as fuels and chemicals [5]. Hemicellulose is the second major component of LCB that consists of short chains of different polysaccharide molecules such as xylan, glucuronoxylan, galactomannan, glucomannan, arabinoxylan, and xyloglucan that are connected by β-(1,4)- and sometimes β-(1,3)-glycosidic bonds [6]. In contrast to cellulose polymers, hemicellulose is readily degradable into monosaccharides due to its low degree of polymerization and non-crystalline nature and thereby widely used in industrial applications such as drug carriers, hydrogels, and cosmetics [7]. Lignin forms a protecting boundary by covalently linking to the cellulose and hemicellulose which enhances the recalcitrance of the lignocellulose. It is a complex, three-dimensional cross-linked polymer that consists of phenyl propane structural units which vary depending on the substitute of the methoxyl groups present in the aromatic rings and are linked to each other by aryl ether linkages e.g., β-O-4, α-O-4 and carbon-carbon bonds e.g., 5-5, β-β. Three basic units that constitute the lignin polymer are p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) [8].

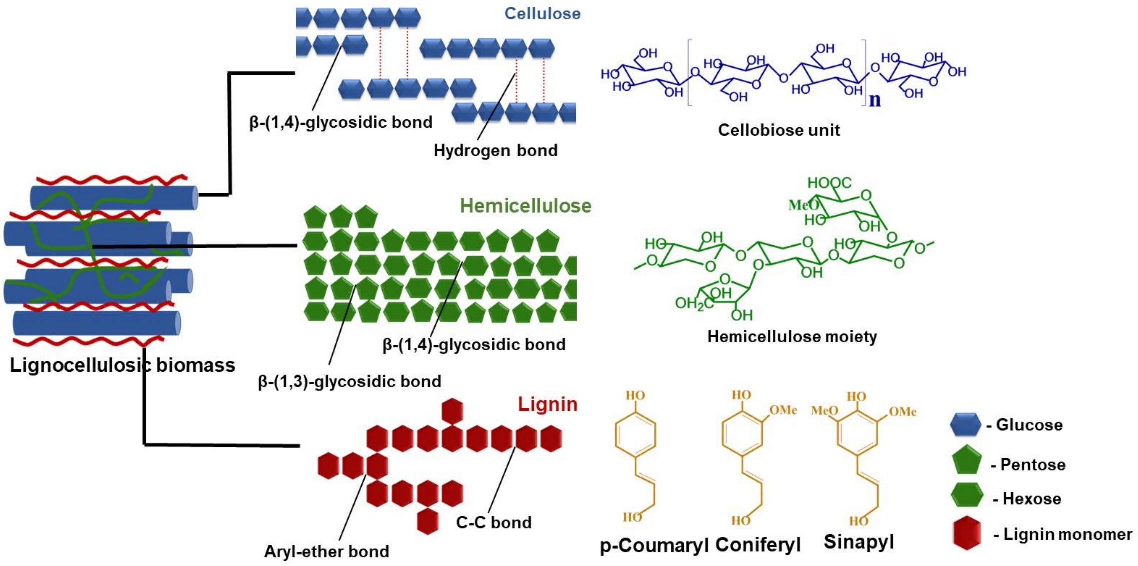


Fig. 2.1. *Schematic structure of lignocellulose [9].*

2.2. Pretreatment of LCB: necessity

LCBs are resistant to chemical and biological breakdown, known as biomass recalcitrance. Several factors such as the crystalline structure of cellulose, the degree of lignification and the structural heterogeneity and complexity of cell-wall constituents are responsible for the biomass recalcitrance that must be overcome for valuable utilization of lignocellulosic feedstocks [10]. In this context, pretreatment is a significant step in the biorefinery process. Throughout the pretreatment process, the recalcitrant structure of lignocellulose is disrupted resulting in breakage of lignin sheath, degradation of hemicellulose and reduction in crystallinity and degree of polymerization of cellulose [11]. A multitude of pretreatment techniques have been developed in the last few decades to improve the deconstruction of LCBs and can be categorized as shown in Fig. 2.2. Among the several pretreatments processes the preference of the convenient one depends on the type of LCBs used as the composition of cellulose, hemicellulose and lignin vary [2]. In the following sections, the major pretreatment techniques and their effects on the separation of the complex components of various lignocellulosic sources are discussed.

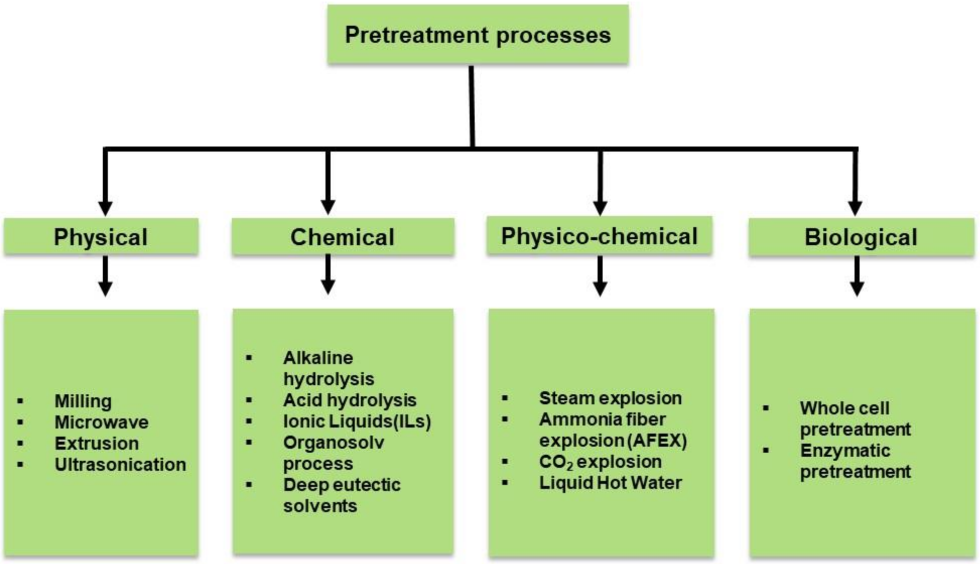


Fig. 2.2. *Flow chart diagram of pretreatment processes [9].*

2.2.1. Physical pretreatments

Physical pretreatments of LCB are a prerequisite before following any other pretreatment methods. It is primarily carried out to reduce the particle size, which results in an increased surface area, and a decrease in the degree of polymerization and crystallinity [12]. Consequently, the subsequent processes become more effective and easier [11]. These methods are eco-friendly and seldom produce any toxic material [13]. However, one major disadvantage of physical pretreatment is its high energy consumption. Generally, energy consumption depends on the type of LCB used. It was reported that size reduction of softwoods such as corn stover and switchgrass requires 11.0 and 27.6 kWh/metric ton respectively, while hardwoods such as pine and poplar chips require 85.4 and 118.5 kWh/metric ton respectively [12]. The commonly prevalent physical pretreatment methods include milling, extrusion, microwave treatment and ultrasonication. These approaches are described in greater detail in the following sections.

2.2.1.1. Milling

Milling is employed to reduce the crystallinity and particle size of LCB. Milling can reduce the particle size upto 0.2 mm. However, Chang et al. [14] unveiled that biomass particle of size less than 0.4 mm has no remarkable effect on the rate and yield of hydrolysis. Depending upon the type of motorized equipment operated the different milling methods are two-roll milling, ball milling, rod milling, hammer milling, vibratory milling, colloid milling, and wet disk milling. The reduction in particle size and crystallinity is determined by the type of milling method adopted, processing time and also the type of biomass used [15]. Bai et al. [16] studied the efficiency of pyrolysis using rod-milling and hammer-milling pretreatment in wheat straw wherein they have found significant size reduction and a decrease in crystallinity using rod-milling at an optimum duration of 60 min. The effective size reduction and the decrease in crystallinity lead to high surface contact and pore volume of wheat straw. Also, the kinetic analysis showed that wheat straw pretreated through rod milling has a lower thermal degradation temperature compared to the hammer-milled wheat straw which enhances the pyrolysis efficiency. However, one of the biggest shortcomings of milling pretreatment is its high-energy requirement and the capital cost of mechanical equipment.

Wet disk milling has been a well-known physical pretreatment owing to its low energy consumption. A study of combined pretreatment using hydrothermal and wet disk milling on oil palm mesocarp fiber (OPMF) demonstrated that hydrothermal pretreatment of OPMF followed by wet disk milling reduces the power consumption upto 9.6 MJ/kg with a more than 98% glucose yield [17]. Another combined pretreatment of hot compressed water (HCW) and wet disk milling on oil palm biomass produced 85.5% and 100% of total sugar yields from oil palm empty fruit branch and oil palm frond fiber, respectively [18]. Kim et al. [19] compared three different methods of milling; ball milling, attrition milling and planetary milling. It was found that attrition and planetary milling effectively reduced biomass particle size as compared to ball milling and the highest yield of glucose and galactose was obtained by planetary milling. Since milling pretreatment does not result in any toxic or inhibitory compounds it is a preferred preliminary pretreatment method for a wide variety of lignocellulosic feedstocks.

2.2.1.2. Microwave-assisted size reduction

Microwave irradiation is a non-conventional heating method that has long been used for the pretreatment of LCB under an applied electromagnetic field. The first study of microwave irradiation pretreatment was carried out by Ooshima et al. [20] and since then this method has been retained as a convenient strategy owing to its several advantages including easy operation, energy efficiency, minimum inhibitors formation, and high heating capacity within short time period [21]. In this method, the dielectric polarization causes molecular collisions and generates thermal energy that results in the disruption of the complex lignocellulosic structure [22]. Microwave irradiation was categorized into atmospheric and high-pressure treatment. High-pressure microwave pretreatments are operated in closed reactors within the temperature range from 150°C to 250°C [23]. A study on the microwave pretreatment of *Panicum spp.* and *Miscanthus spp.* showed 7-10% higher solubility of the materials in subcritical water as compared to the untreated materials. The samples were pretreated at different temperatures and the optimum conditions obtained are 60°C and 120°C for *Miscanthus spp.* and *Panicum spp.,* respectively at 1600 W treatment power [24]. In another study, the microwave pretreatment of *Hyacinthus spp.* was examined to enhance the methane production from anaerobic digestion and obtained the highest methane yield of 221 $mL \cdot g\text{-}sub^{-1}$ which was 38.3% higher than the substrate pretreated with water-heating [25]. In recent research, microwave pretreatment is often conjugated with other treatment methods as an upgraded attempt. Liu et al. [26] studied the effect of microwave irradiation during alkaline treatment for the separation of cellulose and hemicellulose from a delignified hardwood kraft pulp. They have found that under microwave treatment the complex fibre structure fractured effectively and the alkaline solution penetrated the inner fibre structure, resulting in the significant removal of hemicelluloses and a high cellulose yield of 93.05%. Microwave-assisted ionic liquid treatment of *Crotalaria juncea* fibres produced 78.7% glucose at 160°C in only 46 min processing time [27]. The studies of the microwave-assisted acid pretreatment of lignin and Moso bamboo sawdust have reported that microwave temperature is the most significant factor in determining the structure of the pretreated samples. The microwave temperature facilitated decarboxylation and dehydration during the process. Different analyses showed that the pretreated samples have lower O, H and ash contents and higher C contents, while in raw bamboo sawdust the C, H, and O are predominant [28]. The results established the microwave system as an assuring technique for fermentable sugar production from lignocellulosic materials.

2.2.1.3. Extrusion

Extrusion is one of the most commonly used physical pretreatment methods applied to LCBs. The action of one or two screws that spin into a tight barrel, which is furnished with temperature control forms the basis of this method [29]. The raw materials are passed through the barrel under high temperature (>300°C) where the recalcitrant structure of the lignocellulose disrupts due to the combined effects of high temperature and the shear forces caused by the rotating screw blades in the barrel [30]. Extrusion machines are mainly classified into single-screw extruders (made of one single solid piece) and twin-screw extruders (made of small pieces called screw elements arranged cylindrically). The screw configuration is an important factor affecting the decomposition of LCB. Wahid et al. [31] carried out a study on the effect of different screw configurations during extrusion pretreatment on wheat straw and deep litter to enhance biogas production. They analyzed pretreatment using five screw configurations namely, mild kneading, long kneading, reverse, kneading and reverse and kneading with reverse. The results showed effective sugar yield with each configuration that consequently led to significant methane production. However, high energy consumption (226-324 kWh t^{-1}) is the main bottleneck in this study that requires further investigation to make the pretreatment economical.

2.2.1.4. Ultrasonication

Ultrasonication pretreatment is based on the principle of cavitation by the employment of ultrasonic radiation. The cavitation generates shear forces that cleave the complex network structure of LCB and promotes the extraction of desired compounds such as cellulose, hemicellulose and/or lignin [32]. A study on the effects of ultrasound pretreatment on the structural changes of eucalyptus wood revealed that the crystallinity of the pretreated wood increased from 34.7% to 35.3% in the aqueous soda solution, 32.6% to 35.5% in distilled water and 33.4% to 35.5% in an aqueous acetic acid solvent. The increased crystallinity is due to the effective removal of the amorphous hemicellulose and lignin fractions that was established by the FTIR analysis [33]. It has been seen that the choice of solvents (dilute aqueous solutions of inorganic acids or alkalis, organic solvents, or ionic liquids) is critical in determining the optimum conditions for ultrasonication pretreatments [34]. Several factors influencing the sonication treatment include ultrasound frequency, sonication duration, sonication power and temperature Liyakathali et al. [35] have found that the enzymatic digestibility of energy cane bagasse increases with an increase in the sonication time and temperature while ultrasonic frequencies did not affect enzymatic digestibility. Cherpozat et al. [36] studied the use of ultrasonic pretreatment on wood chips for bio-oil production. The experiments were carried out at different conditions regarding frequency (40, 68 and 170 kHz), treatment time (0.5, 1 and 1.5 h) and applied power (125, 250, 500 and 1000 W). They found the combination of 170 kHz for 0.5 h and 40 kHz for 1.5 h and a power of 1000 W as adequate, resulting 12% increased yield of bio-oil as compared to untreated wood. However, ultrasonication for a prolonged period might cause adverse effects due to collision and aggregation between the particles [37]. The above studies clearly demonstrate that ultrasonication is a viable pretreatment technique owing to its potential to facilitate the disruption of various lignocellulosic materials. In fact, the use of ultrasound can scale down the hydrolysis time of biomass up to 80% aiding benefit for bio-fuel production [38]. However, the process is energy intensive and detailed investigations are necessary to optimize the process parameters for high-scale applications.

2.2.2. Chemical Pretreatments

2.2.2.1. Alkali pretreatment

Alkali pretreatment is a widely studied chemical pretreatment method which is based on the solubilization of lignin in the alkali solution. Various alkaline reagents used commonly for alkali pretreatment are the hydroxides of sodium, potassium, calcium, and ammonium. Among these sodium hydroxide was found to be the most effective [39]. A saponification reaction takes place throughout the alkali pretreatment process which causes cleavage of the intermolecular ester linkages between hemicelluloses and lignin. This results in the solubilisation of lignin and hemicellulose fragments in the alkali solution and brings the cellulose into the interaction of enzymes [40]. Also, alkali pretreatment changes the lignocellulosic structure via cellulose swelling that leads to a reduction in crystallinity and degree of polymerization thereby increasing internal surface area [41].

Various studies reflect many advantages of the alkali pretreatment technique. A study on the alkaline pretreatment of rice straw for biomethane production reported that 1% NaOH at room temperature for 3 h significantly reduces the hemicellulose and lignin contents while the cellulose content remains unaltered. This led to an increase in methane yield by more than 34% compared to untreated rice straw [42]. Likewise, Talha et al. [43] optimized the conditions of alkaline pretreatment of sugarcane bagasse and filter mud to enhance biomethanation. The results showed 86.27% lignin removal using 1% NaOH at 100°C for 3 h and an increase of 82.20% methane yield. Shen et al. [44] proved sodium hydroxide pretreatment as an effective method to enhance the process of anaerobic digestion. They optimized the pretreatment conditions on vinegar residue (VR) and found an increased methane yield of 205.86 mL g^{-1} VR at 3% NaOH concentration which was 53.99% higher than the untreated VR. Alkaline pretreatment using calcium hydroxide (also called lime) has also been studied and found simple and effective since $Ca(OH)_2$ is very inexpensive and safe to handle. A study on the lime pretreatment of corn cob residue to enhance biogas production revealed that the pretreatment accelerates the digestion process by removing lignin and obtained biogas 2 times higher than untreated corn cob [45]. Rabelo et al. [46] compared the effect of alkali pretreatment on sugarcane bagasse with lime and alkaline peroxide and found a maximum glucose yield of 200 mg g^{-1} on lime loading of 0.04 g g^{-1} at 70°C for 37 h. However, lime pretreatment takes a long residence time and high temperature compared to peroxide pretreatment. Ghorbani et al. [47] investigated the lime pretreatment effects on date palm leaves under aerated and non-aerated conditions and found oxidative treatment at 40°C with 0.2 g g^{-1} $Ca(OH)_2$ loading more suitable for delignification than the non-oxidative treatment. Extensive research works have also been conducted on ammonia-based alkali pretreatment because of its non-corrosivity, non-toxicity and easy recovery of ammonia. Sakuragi et al. [48] studied the effects of ammonia pretreatment on six different hardwood species and reported that species with high xylan and low lignin contents promotes enzymatic hydrolysis more effectively.

From the above studies, we can summarize that the alkali pretreatment is an effective technique in removing lignin and makes carbohydrates more exposed to use for the downstream processes. However, a major disadvantage of the technique is the recovery of the added alkalis which requires further investigations. Furthermore, alkali pretreatment is more favourable for low lignin content biomass such as herbaceous crops and agricultural residues and less productive for hardwoods.

2.2.2.2. Acid pretreatment

Acid pretreatment of LCBs is based on the susceptibility of the glycosidic bonds between hemicellulose and cellulose to acid. Hydronium ions which originate from the acid catalyst cause breakdown of the long cellulose and hemicellulose chains into sugar monomers [49]. Both, inorganic acids such as sulfuric acid [50], phosphoric acid [51], nitric acid [52] and hydrochloric acid [53] and organic acids such as formic acid [54], maleic acid [55] and oxalic acid [56] are used. Acid pretreatment can be used either as concentrated acids (30-70%) at low temperature (<100°C) or as dilute acids (0.1-10%) at high temperatures (100-250°C). Although, concentrated acid pretreatment can highly accelerate the sugar conversion rate (higher than 90%), most of the concentrated acids are very toxic and corrosive and hence require high operational and maintenance costs. Moreover, they cause undesired cellulose degradation leading to the generation of inhibitory compounds viz. furfurals, 5-hydroxymethyl furfural, phenolic acids, and aldehydes. Studies reveal that among the acids, dilute sulphuric acid (H_2SO_4) is the most extensively used to pretreat LCBs. Sahoo et al. [57] compared the effect of dilute acid and alkali pretreatment on wild rice grass (*Zizania latifolia*) for enzymatic hydrolysis. Results showed that 0.4% H_2SO_4 with 10% biomass loading releases 163 mg sugar g^{-1} biomass, while only 92 mg sugar g^{-1}

biomass was obtained when treated with 1 % NaOH. This proves that dilute acid pretreatment to be a more feasible method for this grass compared to alkali pretreatment. Sindhu et al. [58] studied dilute acid pretreatment of Indian bamboo (*Bambusa spp.)* varieties for bioethanol production. The pretreatment process with various mineral and organic acids revealed H_2SO_4 as the best pretreatment agent. Experiments were carried out with different biomass loadings, acid concentrations and pretreatment time. An optimized condition of 15% (w/w) biomass loading, 5% acid concentration and 30 min pretreatment time yielded 0.319 g/g of reducing sugar which produced 1.76% (v/v) ethanol on subsequent enzymatic saccharification and fermentation.

Amnuaycheewa et al. [59] investigated rice straw pretreatment with organic acids for the improvement of enzymatic hydrolysis and biogas production. Using a response surface method, they optimized the pretreatment conditions with acetic acid ($C_2H_4O_2$), citric acid ($C_6H_8O_7$), oxalic acid ($C_2H_2O_4$) and hydrochloric acid (HCl) and compared their effects. Results showed that oxalic acid pretreatment under optimal conditions of 5%, 135.91°C and 30.86 min led to the highest sugar production of 213.4 mg/ 500 mg of pretreated sample on enzymatic saccharification. Organic acids such as maleic acid and formic acid are also more efficient than dilute mineral acid for LCB pretreatment [60]. In addition, organic acids catalyze negligible sugar degradation. However, a study on the comparative effect of citric acid ($C_6H_8O_7$) pretreated rice husk and inorganic acids (HCl, H_2SO_4 and HNO_3) pretreated rice husk on the adsorption of phenol from wastewater showed less adsorption by the citric acid treated rice husk **[61]**. Therefore, further research into the benefits of organic acids over mineral acids for the processing of LCBs is required.

2.2.2.3. Ionic Liquids

Swatloski et al. [62] put forward the use of ionic liquids (ILs) as cellulose solvent and ever since pretreatment of LCB by ILs has become a promising prospect. ILs are relatively new class of solvents with a melting point of <100°C which are comprised of cations and anions. The cations, in general, are organic viz. imidazolium, pyridinium, aliphatic ammonium, alkylated phosphonium and sulfonium ions, while the anions include both organic and inorganic ions [63]. During the pretreatment process both the cations and anions play a significant role in solubilizing the cellulose and lignin. Fig. 2.3. represents the interruption of the intra- and intermolecular hydrogen bonding in cellulose by IL ions. Also, the cellulose dissolution increases in presence of electron-withdrawing groups in the alkyl chains of IL cations [63]. Most of the ILs are recoverable and reusable. They possess the striking advantages of negligible vapour pressure, non-volatility, non-toxicity, large thermal and chemical stability and most importantly the adjustable nature of their cations and anions on which the properties of the ILs depend [64]. These are the reasons why ILs have often been described as green solvents. Several types of ILs include imidazolium-based ($[(C_3N_2)X_n]^+$), pyridinium based ($[(C_5N)X_n]^+$), pyrrolidinium-based ($[C_4N)X_n]^+$, ammonium-based $[NX_4]^+$, phosphonium-based $[PX_4]^+$, sulfonium-based $[SO_3]^+$ and others such as cholin. Among these, imidazolium salts are the most commonly used ILs [65].

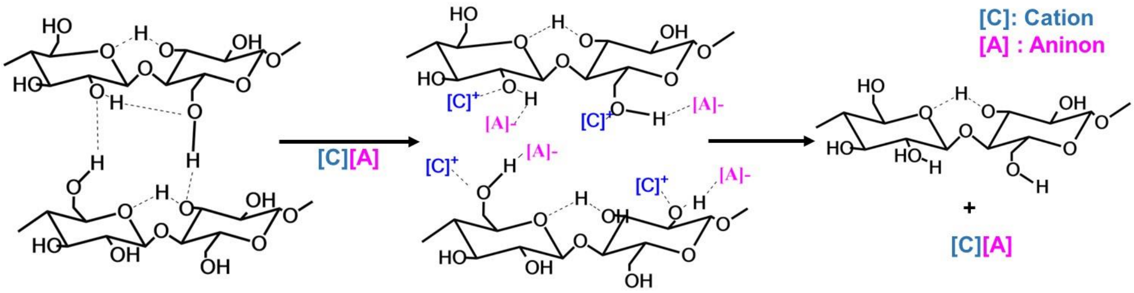


Fig. 2.3. *Interruption of intra- and intermolecular H-bonding in cellulose by ILs [9].*

Raj et al. [66] investigated the effect of various imidazolium-based ILs pretreatment on enzymatic hydrolysis of mustard stalk. It was found that ILs containing acetate ion enhanced specific surface area and porosity accessible for enzymes and improved the yield of reducing sugar significantly. The effect of pretreatment temperature on acetate ion based ILs was also studied. Differential scanning calorimetry analysis showed an increased porosity (108.9 mg/g) at 130°C/2h compared to 100°C/5h (107.8 mg/g) and produced 97.7% and 78.7% glucose, respectively, on subsequent hydrolysis. Stanton et al. [67] also studied the effect of different imidazolium-based ILs on the structure and properties of microcrystalline cellulose and silk blended biocomposite films. The results revealed that the intermolecular interactions in the films are directly correlated to the anion structure of the ILs.

Regardless of their distinctive chemical properties, ILs present the major shortcomings of being expensive and toxic to microorganisms and enzymes. Brandt-Talbot et al. [68] investigated for the first time the application of the low-cost IL triethylammonium hydrogen sulfate for the pretreatment of *Miscanthus x giganteus* grass. They found up to 75% lignin and 100% hemicellulose solubilization in the IL solution and a yield of 77% glucose by enzymatic saccharification. Also, the IL was reused four times with 99% recovery at each time. Nevertheless, further studies on these aspects with low-cost recovery technology and its toxicity to enzymes are still needed for economically-viable large-scale applications.

2.2.2.4. Organosolv process

In this process, LCBs are pretreated with organic solvents or their aqueous solutions that causes break down of the internal bonds between lignin and hemicellulose thereby leaving a relatively pure cellulose residue. During the process delignification and solubilization of hemicellulose lead to an increase of pore volume and surface area of cellulose and enhances the accessibility of enzymatic hydrolysis and saccharification [69]. A wide range of organic solvents such as, ethanol, methanol, acetone, organic acid, organic peracid and ethylene glycol or their mixture with water have been employed to pretreat various LCBs. The process is often accompanied by the addition of a catalyst to either lower the pretreatment temperature or improve the delignification rate. Usually mineral acids (hydrochloric acid, sulfuric acid, phosphoric acid), bases (lime, sodium hydroxide, ammonia) and some salts are used as catalysts [70].

Organosolv presents itself as an emerging pretreatment process owing to its inherent advantages such as, easy recovery of the solvents by distillation, recycles the solvents back to pretreatment and utilization of high-quality lignin isolated from this process as value-added byproducts for industrial applications. However, there also lies a few major disadvantages of organosolv pretreatment. Most of the organic solvents are too expensive and need to be recovered as much as possible which is an energy-intensive process. In addition, the high flammability and volatility of the organic solvents make the pretreatment to be carried out under especially controlled conditions [70].

2.2.2.5. Deep eutectic solvents

Pretreatment of LCB using deep eutectic solvents (DES) has attracted much interest in recent years. DESs are a new generation of ionic fluids comprising two or three components, often interlinked through hydrogen bonding and form a eutectic mixture with a lower melting point than each individual component. They are usually liquids at a temperature <100°C. DESs and ILs are much alike in terms of their physicochemical properties but their low-cost synthetic technology and biodegradability make them versatile alternatives to ILs [71]. DESs are mostly derived by mixing a quaternary ammonium salt with a metal salt or hydrogen bond donor (HBD) which is capable of forming a complex with the halide ion of the quaternary ammonium salt [72]. The decrease in melting point of the eutectic mixture is ascribed to the charge delocalization occurring between the halide ion and the hydrogen-donor moiety [73].

DESs can be represented by the general formula

$$Cat^{+}X^{-}zY$$

where Cat^+ is basically any ammonium, phosphonium or sulfonium cation, X^- is a Lewis base, commonly a halide anion, Y is Lewis or Brønsted acid, and z is the number of Y molecules that interact with the anion. The complexation between X^- and Y forms different anionic species [72]. Being a biodegradable, non-toxic and cheap organic salt, cholin chloride (ChCl) is used in most of the DESs in combination with the low-risk HBDs like, urea, glycerol, carboxylic acids, and polyols [71]. A study on the corn stover pretreatment by different DESs having the same halide salt i.e., ChCl found ChCl: Formic acid to be the ideal mixture for butanol fermentation. The findings implied that DES with acidic hydrogen donors could enhance the removal of lignin and hemicellulose more efficiently and are superior to ILs [74]. The results are further proved by Zhang and co-workers who investigated the pretreatment of corn cob by using three DESs; monocarboxylic acid: ChCl, dicarboxylic acid: ChCl and polyalcohol: ChCl. They found that delignification and cellulose accessibility greatly depends on the strength and amount of acid and the nature of hydrogen bond acceptors. The free hydroxyl groups of polyalcohol interact with the free and etherified hydroxyl groups of lignin thereby making the polyalcohol: ChCl to be an adequate mixture for pretreatment [75].

2.2.3. Physicochemical pretreatments

2.2.3.1. Steam explosion

Steam explosion is the most commonly employed and effective pretreatment method, which is typically a combination of both mechanical forces and chemical effects applied to LCBs. In this technique, the biomass is subjected to high-pressure saturated steam (0.69 – 4.83 MPa) at a temperature of 160-260°C to let water molecules penetrate the substrate structure. The pressure is then suddenly reduced to let the water molecules escape explosively. This rapid release of pressure causes an explosion of the bulk LCB into splitted fibers. Besides, high temperature and pressure enhances the breakdown of the glycosidic bonds in cellulose and hemicellulose and the cleavage of hemicellulose-lignin bonds [76]. During this treatment, the hydrolysis of hemicellulose into glucose and xylose monomers liberates acetic acid which catalyzes the further hydrolysis of hemicelluloses, and; hence the process is also termed autohydrolysis [77].

The steam explosion has several advantages such as low environmental effect, limited chemicals use, high energy efficiency, no recycling costs and total sugar recovery compared with other pretreatment methods [78]. Steam explosion can be employed directly to milled LCB without employing any chemicals. Vivekanand et al. [79] pretreated birch samples with steam at 170-230°C to investigate their enzymatic hydrolysis performance. Results showed that steam explosion at 220°C for 10 min generates the maximum enzymatic hydrolysis yield. However, under harsh steam explosion conditions, the production of inhibitors such as aromatic compounds and dehydration byproducts (weak acids and furan derivatives) influenced the subsequent hydrolysis process [79]. Similar results were also observed when corn stover was pretreated with steam explosion at 140-220°C for biogas production. Pretreatment at 160°C for 2 min increased the methane yield by 22% while harsh pretreatment conditions led to the formation of inhibitors [80]. Besides, many phenolic compounds are produced when lignin is broken down. Therefore, some detoxification methods are required to reduce the hindrances caused by these compounds for the benefit of the downstream processes.

2.2.3.2. Ammonia fiber explosion (AFEX)

In AFEX process, the LCB is heated with liquid ammonia (in 1:1 ratio) in a closed vessel at temperature around 60-100°C under high pressure for 5-30 min, and then the pressure is suddenly released [13]. The high pressure and given temperature causes swelling of lignocellulose and the rapid release of pressure disrupts the fibrous structure of biomass, reduces the crystallinity of cellulose and thereby improves the accessibility of enzyme. Optimization of AFEX pretreatment can be done by varying the four parameters including temperature, blowdown pressure, water loading and ammonia loading [81]. Silvergrass (*Miscanthus spp.)* when presoaked in water prior to AFEX pretreatment showed up to 10% increase in glucan conversion indicating that moisture content plays a major role in AFEX [82]. AFEX pretreatment partly removes the lignin and hemicellulose from lignocellulosic materials, but shows better enzymatic hydrolysis results at low enzyme loadings compared to other pretreatment processes. When oil palm empty fruit bunch fibre was pretreated with AFEX at 135°C for 45 min, the lignin-carbohydrate linkages changed along with some relocalization of lignin and resulted in 90% glucan conversion at a lower enzyme loading of 13.8 FPUg^{-1} glucans as compared to 25.5% conversion for untreated biomass

[83]. Therefore, AFEX pretreatment is more suitable for low lignin-content lignocellulosic biomass such as agricultural wastes and herbaceous plants like switch grass, rice straw, corn stover etc. Several investigations have been carried out to determine the optimal AFEX conditions for different LCBs. Zhao et al. [84] reported ammonia to biomass loading of 5:1, 70% moisture content and 170°C as optimal for enhanced enzymatic digestibility of corn stover. They further demonstrated that pre-soaking of corn stover prior to AFEX pretreatment enhances the delignification of corn stover from 15.74-24.07% and thereby increases glucan digestibility from 82.13-87.78%. Mathew et al. [85] when compared the effect of AFEX and dilute acid pretreatment on corn stover, found that AFEX treated hydrolysate of corn stover was superior to dilute acid treated hydrolysate for ethanol production.

The main advantage of AFEX lies in the negligible formation of inhibitors as compared to other pretreatment methods. Nonetheless, ammonia should be recovered and recycled due to its high cost and volatility to reduce the overall operating cost and minimize environmental damage.

2.2.3.3. CO_2 Explosion pretreatment

A key drawback in the application of steam explosion pretreatment lies in its use of high thermal energy which is essential for the decomposition of LCB. The AFEX pretreatments on the other hand use ammonia, which is highly corrosive with detrimental environmental effects, thereby limiting its scope. In this context, supercritical CO_2 explosion appears to be a viable alternative owing to its lower energy requirements and use of the greener alternative compared to ammonia [86]. Because of its characteristics of mass transfer of a "gaslike" with a "liquidlike" solvating power, supercritical CO_2 can diffuse through interspaces like gas and dissolve materials like liquid [87]. Under high pressure the CO_2 molecules penetrate into the biomass and shattered the higher level of structures comprising hemicellulose and lignin. Once dissolved in water, CO_2 will form carbonic acid, which catalyzes the hydrolysis of hemicellulose. This is the reason why this pretreatment process is not satisfactory to biomass with no moisture content. On the other hand, when the pressurized gas is released, it breaks the compact matrix structure of biomass thereby improving the accessibility of cellulose fibers [88]. Benazzi et al. [89] reported a single-step process for the hydrolysis of sugarcane bagasse using supercritical CO_2 and obtained a 60% yield of fermentable sugars. Soybean hull pretreated with supercritical CO_2 showed a high glucose yield of 97% after enzymatic hydrolysis. This high glucose yield was obtained under optimal conditions of 8 MPa pretreatment pressure and 130°C temperature for 30 min. Thus, the pretreatment pressure and temperature also plays a significant role in supercritical-CO_2 treatment [90]. Likewise, Narayanaswamy et al. [91] found that supercritical-CO_2 pretreatment of corn stover (75% moisture content) under optimal conditions of 24 MPa and 150°C for 60 min, increased the glucose yield by 2.5-fold compared with a native corn stove. A combined pretreatment of corn cob and corn stalk by supercritical CO_2 and ultrasonic pretreatment improved the enzymatic hydrolysis by 75% and 13.4%, respectively under optimal conditions of 20 MPa and 170°C [92].

Low cost of CO_2, low environmental impact, non-flammability, no toxins formation, and easy recovery make the employment of supercritical-CO_2 in the pretreatment of LCB an attractive approach. However, the economic input for the experimental set-up that can withstand high-pressure conditions of CO_2 pretreatment is significantly high and is a great obstacle in its application on industrial scale.

2.2.3.4. Liquid hot water (LHW)

LHW pretreatment is very much like the steam explosion but as the name suggests, LHW uses water at elevated temperature (170-230°C) and pressure (up to 5 MPa) in place of steam. Unlike steam explosion rapid release of pressure is not required in LHW and the application of pressure is only to prevent evaporation of water. LHW hydrolyzes hemicellulose by liberating its acetyl groups and removing lignin thereby making the cellulose fibres more exposable [93]. The detached hemicellulose remains in the liquid fraction of the pretreated slurry and the formation of monomeric sugars during the process is minimal. However, to avoid the sugar degradation and inhibitors formation, the LHW pretreatment is carried out at controlled pH between 4-7 [94]. It was reported that *Miscanthus X giganteus* pretreated with LHW under controlled pH at 200°C for 15 min showed high ethanol yield of 71.8% of theoretical fermentation [95]. Hongdan et al. [96] optimized the process variables (temperature and residence time) in LHW pretreatment of sugarcane bagasse and achieved 90% glucose recovery on enzymatic hydrolysis at 180°C for 30 min. LHW pretreatment of corn cobs at 160°C for 10 min provided maximum hemicellulose-derived sugar recovery of 58.8% and enzymatic hydrolysis yield of 73.1% with more than 60% lignin removal [97]. Furthermore, Imman et al. [98] investigated the effect of the alkaline catalyst on LHW pretreatment of rice straw and demonstrated that rice straw pretreated with LHW in presence of NaOH showed remarkably higher glucose yield compared with LHW pretreatment in the absence of NaOH. Likewise, another study on the effects of acid and alkali promoters during LHW pretreatment of rice straw revealed that the presence of such promoters changes the physical structure of the pretreated biomass and thus lowered the required LHW temperature and improving the enzymatic digestibility [99].

LHW pretreatment possesses several advantages as it does not require any catalyst or chemicals, the formation of toxic materials is almost absent and has a low-cost solvent for large-scale applications. Furthermore, biomass size does not influence since the particles are broken down during the treatment which makes the process more striking on large scale [100]. However, the process is very energy intensive due to the large amount of water involved.

2.2.4. Biological pretreatment

Biological pretreatment is a low cost and eco-friendly technique to treat LCB prior to enzymatic saccharification. This technique is promising as there is no inhibitor formation during the process, requires lesser energy consumption and is eco-friendly [101, 102]. Through this method, lignin-degrading bacteria or fungi, as whole cell or enzymes, are used to pretreat LCB. The enzymes used in the degradation of lignin are laccases, lignin peroxidase, manganese peroxidase and versatile peroxidase. Fungi are the best suited for such applications as they are capable of degrading cellulose, hemicelluloses, and lignin. Biological pretreatment is not only used for lignin removal, but also for the removal of specific components such as antimicrobial substances [103]. White-rot, brown-rot and soft-rot fungi are used for the degradation of lignin and hemicelluloses present in LCB [18]. However, mostly white-rot fungi are involved in biological pretreatment due to the high sugar yield associated with enzymatic saccharification [104]. Some white-rot fungi can simultaneously degrade lignin and polysaccharides, resulting in the loss of carbohydrates, while other white-rot fungi can selectively degrade lignin. There are two extracellular enzymatic systems involved in microorganisms, one hydrolytic and another ligninolytic system [105]. Hydrolytic system is responsible for the degradation of cellulose and hemicelluloses, while ligninolytic system depolymerizes the lignin. Lignin can be degraded by enzymes produced by various organisms, among which white-rot fungus has been found the most effective. Fungi are usually isolated from the soil, living plants or agricultural waste materials [106].

2.3. Glucose production from LCB

The first platform chemicals in a biorefinery could be the sugar molecules obtained from LCB. Since the production of further degradation products depends on the efficient release of C5 and C6 sugars with lower energy consumption, this step has critical importance [107]. The first step in utilising cellulose is depolymerizing it into soluble oligosaccharides and glucose. However, the natural polymer forms a robust crystal structure with high chemical stability consisting of numerous glucose units that are linked together by β-1,4-glycosidic linkages thus making the depolymerization processes more difficult. The hydrolysis of cellulose polymers occurs when acids break the β-1,4-glycosidic linkages, resulting in the sugar molecule glucose. Usually, hydrolysis of cellulose has been reported using mineral acids such as HCl and H_2SO_4. However, product separation, reactor corrosion, limited catalyst recyclability, and the necessity for waste effluent treatment are the major problems associated with acid hydrolysis. Enzymatic hydrolysis, on the other hand, is the most promising alternative to acid hydrolysis on account of the relatively mild reaction conditions, since it avoids the use of hazardous and corrosive chemicals.

2.4. HMF synthesis: An overview

HMF has been evaluated to be one of the "Top 10 + 4" bio-based chemicals from carbohydrate biomass as additions to the original list from U.S. Department of Energy (DOE) [108]. The first publication on the synthesis of HMF was reported by Dull [109] and Kiermayer [110] in 1895. Since then, there has been a growing interest in furan derivatives, possessing great potential in the production of bulk chemicals and fuels. In the last three decades, there has been a rapidly increasing interest in HMF chemistry. Since, it can be used to make a wide range of value-added furan-type compounds, polymers, and alkane molecules, HMF is now regarded as a resourceful intermediate linking biomass-based carbohydrate chemistry with the petroleum-based chemical industry [111]. It can be converted into a variety of versatile compounds currently derived from petroleum through a variety of reactions such as oxidations to form 2,5-diformylfuran [112] and 2,5-furandicarboxylic acid [113], selective hydrogenations to form 2,5-dimethylfuran [114] and 2,5-bishydroxymethylfuran [115], hydrolysis to form levulinic acid [116] and aldol condensation followed by hydrogenation to obtain C7–C15 liquid alkanes [117].

To date, significant progress has been made in the development of effective chemo-catalytic systems for converting glucose to HMF. For the conversion of glucose to HMF, two reaction mechanism has been proposed (Fig. 2.4) viz., (i) fructose mechanism (glucose isomerization to fructose and fructose dehydration to HMF) and (ii) 3-deoxyglucosone (3-DG) mechanism (direct dehydration of glucose to HMF through 3-DG intermediate) [118].

Extensive catalytic and kinetic studies have unravelled that the glucose-to-fructose isomerization is favoured by a Brønsted base or Lewis acid catalyst, whereas the succeeding fructose-to-HMF dehydration is favoured by both Lewis and Brønsted acid catalysts. As a result, for the glucose-to-HMF transformation, a Lewis acid or a combination of a base/Lewis acid and a Brønsted acid has demonstrated excellent catalytic performance [119]. For a long time, there has been significant interest in homogeneous acidic catalysts for glucose dehydration to produce HMF due to their high catalytic efficiency. However, poor separation, recyclability, waste treatment, and/or reactor corrosion have limited their practical applications [120]. Therefore, to overcome these limitations increasing attention has been focused on the dehydration of glucose to HMF using various types of heterogeneous acidic catalysts in a variety of solvent systems, and significant progress has been made on this exciting topic in recent years [121]. However, several side reactions such as rehydration of HMF to formic acid and levulinic acid [122], degradation of glucose [123], and formation of humin or oligomers through self-polymerization of HMF or cross-polymerization between glucose and HMF [124] are likely to occur during the conversion reaction under acidic catalysts [125]. Therefore, concerted efforts are now directed towards the development of efficient catalytic systems for the conversion of glucose to HMF to reduce the occurrence of side reactions.

Although some evaluations on the transformation of carbohydrates to HMF have been published [126], the area of HMF synthesis from glucose is growing rapidly, with numerous new findings being produced all the time. As a result, a real-time and comprehensive study of heterogeneous glucose and cellulose conversion to HMF is still required. In this chapter, we attempt to provide both the general mechanistic aspects of the conversion reaction from the earlier literature and the recent progress in HMF synthesis. Special emphasis is placed on the use of various solvent systems (water, organic solvents, ionic liquids, biphasic solvents, mixed solvents), and on the different heterogenous acidic catalysts (metal oxides, zeolites, heteropolyacids, carbonaceous materials, silica-based, ionic resins/polymer-based, and other catalysts systems) reported in the past decade. Additionally, an outlook to highlight the challenges and opportunities associated with this intriguing and important route for HMF production has also been provided.

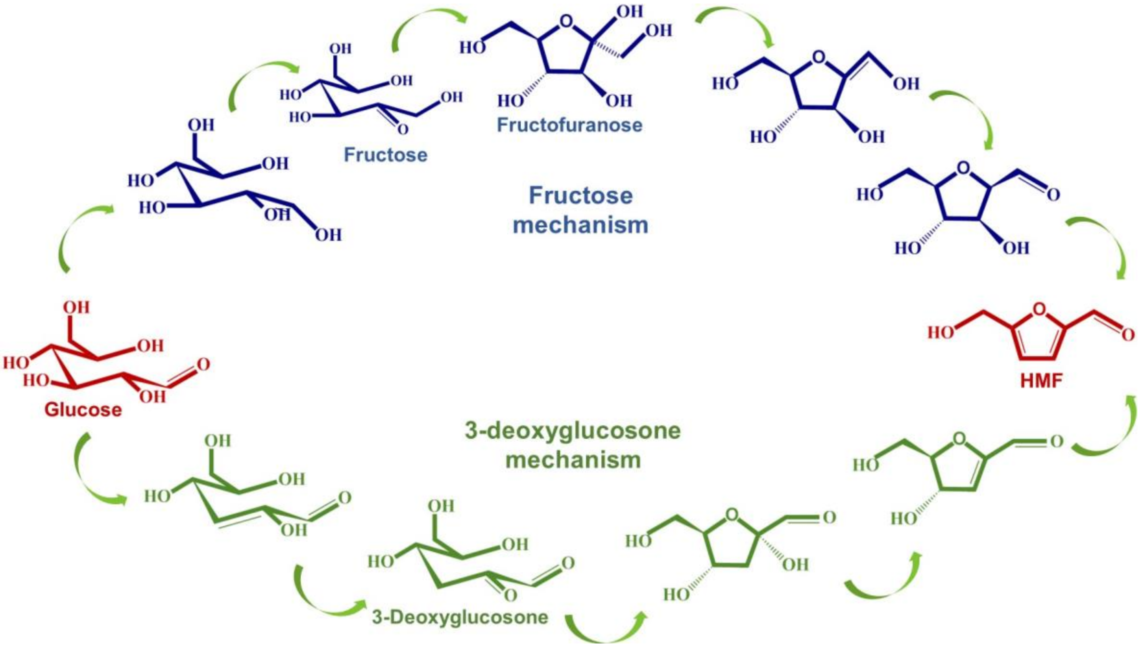


Fig. 2.4. *Two pathways postulated for the glucose-to-HMF conversion [118].*

2.5. Solvent effects towards glucose to HMF production

The solvent appears to have a strong influence on the course of a reaction. The primary function of solvent is to induce fluidity and allow reactant and catalyst to come into contact. If working in concentrated mixtures is preferred, good solvation properties for the solutes are required, and solute interactions leading to side reactions must be avoided. Therefore, a suitable solvent that not only prevents the formation of byproducts but also allows for easy extraction of HMF has piqued the interest of researchers in recent years. Many options were considered, but some of them stood out as particularly interesting because they promote the reaction while also being highly selective. Water, organic solvents, ionic liquids, biphasic solvents, and mixed solvents are among the most common ones covered in this section.

2.5.1. Water

Water is an ideal solvent in the context of green chemistry since it is inexpensive, non-toxic, and non-flammable. Although water can be used to efficiently conduct many types of reactions [127], the yields of HMF from heterogeneous dehydration of glucose are generally not satisfactory due to the unstable nature of HMF in water in the presence of acidic catalysts. There have been numerous effective examples of dehydration of glucose over heterogeneous acidic catalysts in water, but the yields are generally low because HMF is easily rehydrated in an aqueous solvent into levulinic and formic acids over acidic sites [122]. However, valuable insight has been obtained from HMF production in aqueous media, as well as some promising high-yielding HMF processes.

Theoretically, the hydrolysis and dehydration of carbohydrates in an aqueous solution do not require a catalyst because water can dissociate to produce H^+ and OH^- on its own. Ranoux et al. performed a dehydration reaction of 30 wt% concentrated fructose in water for 40 min at 190°C without a catalyst and obtained 43% yield of HMF. They assumed that the formic acid generated by HMF hydration aided in the autocatalytic dehydration of fructose [128]. Recently, Ke et al. investigated the effect of pressure during HMF production from glucose in an aqueous phase catalytic system. In this study, the reaction was carried out in a cylindrical stainless steel batch reactor at 190°C for 60 min while reducing the pressure by slightly opening the vent valve every 10 min while the reaction was running. This results in the increase of HMF yield from 9.3 to 35.2%. They attributed that the main reason for using pressure reduction is to promote the boiling of water. Boiling creates bubbles that disrupt the reaction system, allowing HMF to quickly desorb from the acid sites of the solid catalyst and glucose to adsorb to more acid sites, improving glucose conversion and HMF yield [129].

2.5.2. Organic solvents

Even though water has many advantages as a solvent, such as low toxicity, low cost, and environmental friendliness in the conversion of glucose to HMF, the yield is low due to the formation of side products (Fig. 2.5). Therefore, much research continues to focus on the use of organic solvents, which can greatly aid in the conversion process by inhibiting the side reactions to some extent [130]. For HMF production from glucose using heterogeneous catalysts, the effective organic solvents are generally the polar aprotic solvents such as Dimethyl sulfoxide (DMSO), Dimethylacetamide (DMA), Dimethylformamide (DMF), N-methyl pyrrolidone (NMP), Tetrahydrofuran (THF), γ-Velerolactone (GVL) and acetonitrile, etc.

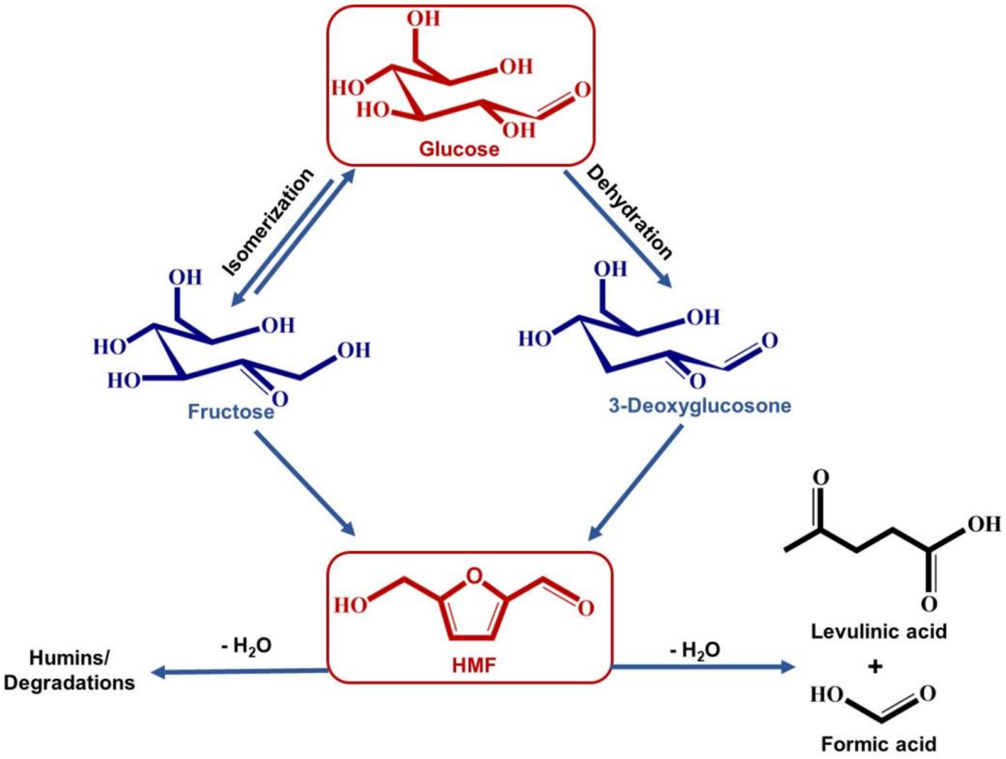


Fig. 2.5. *Routes to major side products after producing HMF from sugar dehydration [143].*

DMSO is one of the most effective organic solvents for furan production, and it has been extensively investigated in recent years. Aylak et al. compared the glucose conversion to 5-hydroxymethylfurfural with chromium exchanged bentonite and montmorillonite catalysts in 1-butyl-3-methylimidazolium chloride, DMA, NMP, DMF, and DMSO solvent systems, and DMSO was proven to offer the best catalytic efficiency as high as 94% [131]. Recently, Tudino et al. studied the influence of DMSO solvent in the fructose conversion to HMF using an acidic carbon as a catalyst. 5-HMF selectivities higher than 90% were found by proper control of DMSO catalytic activity in an inert atmosphere [132]. Likewise, the yield of HMF was found to be 40% in DMSO solvent compared to 14% in the aqueous solvent with zeolite catalyst, while glucose conversion in both cases was greater than 90%. The reason for this is that the accumulation of by-products, humins is higher in the aqueous environment thereby deactivating the zeolite catalysts [133]. In another study, HMF yield of 61.2% was obtained from glucose using Boehmite catalyst in DMSO solvent, while only 4.8% yield of HMF was obtained in DMF solvent [134]. The role of DMSO in the dehydration of carbohydrates to HMF in presence of Brønsted acid has been theoretically investigated by Ren et al. at G4 level in DMSO solution. According to their study, when Brønsted acid is present in the reaction system,

H^+ preferentially interacts with DMSO rather than fructose, resulting in $[DMSOH]^+$ as the catalytically active species. The valence unsaturation of both S and O atoms, as well as the unsaturated double bond of SO, accounts for the catalytic performance of DMSO in the dehydration of fructose to HMF. In addition, the catalytic role of $[DMSOH]^+$ is due to the H-mediated effect of SOH group as well as the valence unsaturation of both S and O atoms [135]. Interestingly, GVL is becoming another promising solvent in the biomass conversion route that can be directly produced from biomass. Li et al. used phosphate-doped SnO_2 to catalyze the conversion of glucose to HMF in a water-GVL solvent mixture resulting in a 46.4% yield of 5-HMF [136]. They reported in another study that the GVL could accelerate the reaction rate of carbohydrates by affecting the stabilization of acidic protons and lowering the activation energy compared to protonated transition states due to its polar aprotic solvent effect [137]. The study on GVL/water solvent to tune the glucose decomposition reaction reported that the activation energy of glucose decomposition in hot compressed GVL/water reduced slightly from 117 kJ/mol in water to 96 kJ/mol in 75% GVL. Therefore, with increasing the GVL concentration from 1 to 75%, the selectivities of dehydration reactions to 5-HMF at 175°C increase from 22% to 30% [138]. Comparative research on hexose decomposition pathways in an aprotic solvent (GVL, 1,4-dioxane, and acetone) and protic solvent (methanol and ethanol) demonstrated that HMF was the main product in an aprotic solvent, while it became a secondary product in the protic solvent. Furthermore, the protic solvent was able to lower the activation energy barrier for sugar decomposition while maintaining a higher reaction rate constant than the aprotic solvent [139].

2.5.3. Ionic Liquids (ILs)

ILs are a large and diverse class of salts that are liquid at or below 100°C and contain ions [140]. In recent years, ILs have drawn extensive attention because of their unusual properties such as hydrophobicity, polarity, and most importantly their tunable solvent capacity by combining or modifying the cations and anions. Moreover, the cations or anions in some ILs may also have catalytic effects thereby serving as both solvent and catalyst [141]. Over the last few years, a lot of works on the use of ILs for the conversion of glucose to HMF have been reported. Imidazole ILs, such as 1-ethyl-3-methylimidazolium chloride [EMIM]Cl, 1-ethyl-3-methylimidazolium bromide [EMIM]Br, 1-ethyl-3-methylimidazolium tetrafluoroborate $[EMIM]BF_4$, 1-Allyl-methylimidazolium chloride [AMIM]Cl, are the most commonly used IL medium [142].

A high concentration of glucose (up to 10%) was effectively converted into 49.7% yield of HMF by aluminum oxide in IL, EMIMBr [143]. After that, Bai et al. reported that the introduction of a small amount of Sn species into Al_2O_3 in IL, EMIMBr allows for efficient glucose (up to 35%) to HMF conversion up to 55.6% while minimizing HMF degradation [144]. In another study, high concentration glucose (10 wt%) was effectively and selectively converted into HMF by tin phosphate, yielding an HMF yield of 58.3%, in the IL, EMIMBr [145]. A recent study reported that the structural parameters of the ionic liquid used as a catalyst, as well as the presence or absence of Brønsted acid used as a co-catalyst, had a significant impact on glucose conversion. In this work, a high selectivity (>90%) of HMF from glucose was achieved in a catalytic system consisting of weak acidic hydrogen sulfate imidazolium ILs and strong protic Brønsted acid (H_2SO_4). This effect could be explained by the presence of a specific synergism between acidic IL and Brønsted acid [146]. A mechanistic understanding of humin formation is critical for humin minimization in cost-effective 5-HMF production. Keeping in this view, Xu et al. investigated the mechanism of humin formation in the conversion of glucose in [BMIM]Cl solvent with $CrCl_3$ catalyst through the characterization of solid humins prepared under intensified conditions. As the temperature and amount of water decreased, the yield of solid humins increased. They found no nitrogen in any of the solid humins, indicating that [BMIM]Cl did not play role in humin formation [147]. Pyridinium ILs have been proven to be superior to many reported expensive imidazolium ILs as high yields of HMF were achieved from fructose (> 99%) and glucose (82%) within a short reaction time [148]. Remarkable yields of 93% and 83% HMF yields were obtained with 1-Butylpyridinium chloride and 1-Butyl-3-methylpyridinium chloride at 80°C within 2 h when used for the conversion of fructose and glucose, respectively [149]. Likewise, highly efficient and selective dehydration of glucose to HMF was observed using a tri-cationic IL, glycerol-tri (3-methylimidazolium) trichloride. The synthesized tri-cationic IL was found to have Lewis's acid character that facilitates the high conversion process yielding 58% HMF from glucose with CC-SO_3H catalyst at 130–140°C in 2–5 h reaction time [150]. Besides, ILs have dielectric properties that make them ideal for rapid and efficient heating in microwave reactors. Therefore, microwave energy could be directly coupled with molecules of reactant, catalyst, and solvent, resulting in a short reaction time and low energy requirement for the entire reaction. In fact, using both ILs and microwave heating reduced the activation energy while increasing the reaction rate [151].

Even though higher yields can be obtained in ILs under mild conditions, IL synthesis is typically expensive, complex, and energy-intensive, with dehydration products that are difficult to separate. Furthermore, the reusability of solvent is difficult, which hinders its widespread use in industry.

2.5.4. Biphasic solvents

A biphasic solvent system consists of an aqueous phase which is the reaction phase and an organic phase which is the extraction phase (Fig. 2.6). Since the production of HMF in water is always low as stated earlier, due to the formation of by-products (fumaric acid, levulinic acid, and humins) hence to prevent the decomposition of HMF, organic solvents are often used as extracting agents [152]. Kinetic studies revealed that during the dehydration reactions of sugar, the side reactions occurred more readily in the aqueous solvent than in organic solvent, and therefore the furan formation in the organic phase could be greatly enhanced [153]. Roman-Leshkov et al. made significant contributions to the development of the biphasic system. They compared the effects of extracting agents such as alcohols and ketones with C3-C6 atoms, and also THF, and discovered that the organic phase with carbon number 4 had the best efficiency. The highest selectivity was achieved using THF as an extracting agent [154]. Xia et al. established a reaction model for HMF production from glucose in a biphasic solvent system (THF/H_2O), which included the mass transfer of HMF from water to the organic phase. The presence of the extraction phase was found to be very important in the system, as the HMF yield increased from 3% in a single-phase system to 61% in a biphasic system under the same conditions [155]. Candu et al. performed glucose dehydration with niobium-β-zeolites in H_2O/MIBK biphasic solvent, and a high HMF yield of 84.3% was obtained. The successful outcome was ascribed to the utilization of a biphasic solvent system [156]. It was reported that when an inorganic salt is added to a biphasic reaction system the salting-out effect remarkably improved the HMF partition coefficient [157]. The introduction of NaCl into the biphasic THF/H_2O solvent system resulted in intensified catalytic conversion of glucose into fructose by sulfonated oxidized activated carbon catalyst and thereby 93% yield of HMF production at 160°C in 3h [158].

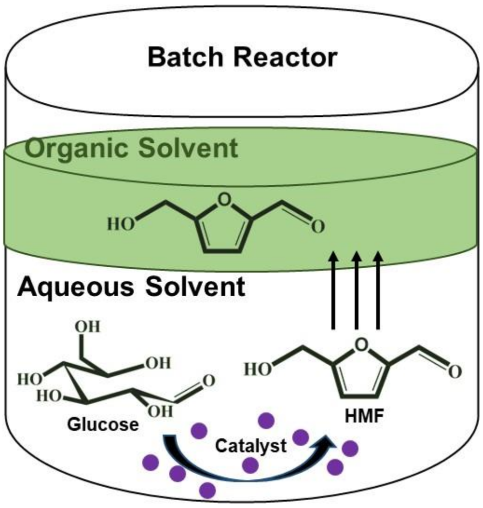


Fig. 2.6. *Biphasic solvent system for the dehydration of carbohydrates to HMF [122].*

The two phases of a biphasic solvent system can be separated by standing, which allows for the recycling and reuse of homogeneous catalysts in the aqueous phase. Guo et al. prepared $AlCl_3$/HCl mixture as the catalyst and H_2O/MIBK mixture as the biphasic solvent and achieved an HMF yield of 53% from glucose. The organic phase was able to extract over 66% of the total HMF from the aqueous phase but not the catalyst. As a result, the biphasic solvent system demonstrated satisfactory recyclability [159]. Chen et al. conducted acid-catalyzed dehydration of fructose to HMF using sulfonic derivatives as a catalyst in different biphasic systems consisting of different organic solvents. They found the highest HMF yield of 79.3% in H_2O−acetonitrile with CH_3SO_3H catalyst and 96.2% of HMF was extracted in the acetonitrile phase and 66.3% of CH_3SO_3H recycled in the aqueous phase. Thus, a biphasic system consisting of an aqueous phase and an organic solvent with a low boiling point significantly influences the fructose dehydration activity [160].

2.5.5. Mixed solvents

The properties of the solvent such as polarity, viscosity, solvent power, etc. can be controlled by combining two or more solvents useful in the design of efficient solvent systems to improve the efficiency of some chemical reactions. There are some such works reported for dehydration of glucose into HMF in mixed solvents using various heterogeneous catalysts. Heterogeneous catalysts usually performed well in mixed solvents of organic solvent and ILs. ILs containing chloride anions were most commonly used due to the enhancement effect of chloride ions on biomass conversion [161]. For example, ammonium aluminum carbonate hydroxide catalyst was prepared by Tang and

Su and was used for the conversion of glucose to HMF in [BMIM]Cl and DMSO mixed solvent. They found that the catalyst in [BMIM]Cl/DMSO mixed solvent provided a higher HMF yield of 52.17% than the reaction conducted in pure solvent DMSO and [BMIM]Cl resulting in 8.73% and 11.45% HMF, respectively [162]. In another study, Tang and Su synthesized boehmite (γ-AlOOH) catalyst for the production of HMF from different carbohydrates in [BMIM]Cl/DMSO mixed solvent, and the HMF yields obtained from glucose (61.2%) and cellulose (58.4%) were higher than that in [BMIM]Cl or DMSO alone [163]. Raines and Graham tested a variety of boronic acids as well as combinations of organic solvents and [BMIM]Cl for the dehydration of glucose. It was demonstrated that the addition of DMF, DMA, NMP, and DMSO as co-solvents resulted in a significant increase in HMF yields from glucose when using 2-carboxyphenylboronic acid in combination with [BMIM]Cl [164]. Liu et al. proposed a cleaner method of obtaining HMF from cornstalk raw material using tin and magnesium ion-loaded biochar as catalysts in different combinations of organic solvents and ILs. The maximum HMF yield of 63.57% was achieved in an [AMIM]Cl/isopropanol mixed solvent system at a low reaction temperature of 100℃ [165]. Additionally, inorganic molten salt hydrate (MSH, aqueous solution with high concentrations of inorganic salt) is also a type of special ionic liquid that has recently been investigated for use in biopolymer depolymerization. The molar ratio of water to salt in MSH is comparable to the coordination number of the salt cations and the access of the cations to anions is sheltered by a hydration shell. In the hydration shell, the water molecules interact with the ions and are polarized to form acidic protons, which are finally released by the anions of the salt [166]. This phenomenon was exhibited by Sadula et al. where highly efficient glucose dehydration was achieved resulting in >80% yield of HMF, after adding $AlCl_3$ and ethyl acetate as co-catalyst and extracting solvent [167].

2.6. Heterogeneous catalysts for the dehydration of carbohydrates into HMF

Although significant progress has been made to date in the production of HMF using homogeneous catalysts, the disadvantages of using a homogeneous catalyst are apparent, mostly serious reactor corrosion problems caused by high Brønsted acidity, particularly mineral acids; the relatively high difficulty of separating homogeneous catalysts from solvent; and the production of more toxic waste. To address such issues, much emphasis has been placed on the development of heterogeneous catalysts. Because of their distinct molecular architectures and porous structure, heterogeneous catalysts are both atom economical and chemoselective [121]. The exclusive properties such as recoverability, reusability, and stability in the conversion reactions of heterogeneous solid acid catalysts have been regarded to play important role in the development of greener catalytic procedures [168].

2.6.1. Metal oxides

Metal oxides, particularly early transition metal oxides (TiO_2, ZrO_2, NbO_2, etc.) have been widely used in the production of HMF due to their Lewis acidic properties, easy and low-cost preparation, and low toxicity [169]. However, the efficiency of using metal oxide directly to catalyze glucose dehydration was relatively low due to the lack of appropriate strength of Brønsted acidic sites in these materials. As a result, modified metal oxides in the form of mixed oxides, phosphated and sulfated oxides, nanoparticles, nanosheets, etc. were synthesized in a variety of ways to meet the reaction requirement of efficient glucose conversion to HMF [169]. In a typical reaction, ZrO_2 acts as a base to promote glucose to fructose isomerization, whereas anatase TiO_2 aids glucose isomerization in addition to enhanced HMF yield. Surprisingly, the combination of TiO_2 and ZrO_2 was able to effectively inhibit the rehydration of HMF into formic acid and levulinic acid, which occurs under similar conditions. For example, Silahua-Pavon et al. investigated the isomerization of glucose to fructose and subsequent dehydration to HMF using TiO_2-ZrO_2 catalyst and found a remarkable yield of 76% HMF in THF/H_2O biphasic system [170]. In another study, they evaluated the conversion reaction using Al_2O_3-TiO_2-ZrO_2 mixed oxides catalyst under similar reaction conditions and found an improved HMF yield of 78% [171]. Thus, ZrO_2 due to its bifunctionality behaviour proves to be an appealing catalyst for glucose conversion to HMF. Because metal oxides-containing systems lacked proper Brønsted acidity, Fang et al. directly added external $NaHSO_4$ to ZrO_2 catalyst in THF/H_2O biphasic system, where $NaHSO_4$ acted as a salting-out agent as well as provided H^+ ions. Only a trace amount of humins over ZrO_2 was detected and a high HMF yield of 86.5% was achieved at 190°C in 60 min [169]. Qu et al. successfully synthesized sulfated zirconia, SO_4^{2-}/ZrO_2 catalyst for dehydration of glucose to HMF and reported 61.84% HMF yield at 160°C for 2h in NaCl-THF/H_2O solvent mixture. Further investigations showed that calculated control sulfur loading content allows for precise tuning of the required acidity for glucose dehydration to HMF, affecting product distribution [158]. Recently, Tomer et al. employed sulfated titania, SO_4^{2-}/TiO_2 catalyst for the production of HMF from glucose and fructose in a water/DMSO biphasic solvent system. A maximum

HMF yield of 37% and 74.7% was achieved from glucose and fructose, respectively at 150°C within 2 h. The lower yield of 5-HMF from glucose was attributed to the β-1,4-glycosidic bond of glucose that is difficult to break due to the stable pyranoside ring structure [172]. They also found that the product yield was highly temperature-dependent and higher temperature (>150°C) aided the degradation of glucose and HMF to other soluble and insoluble organic byproducts.

Another important metal oxide is Nb_2O_5, which has a high surface acidity and hence favours sugar degradation reactions. It also has better thermal stability in an aqueous medium during acid-catalyzed reactions [173]. Different studies used Nb_2O_5 catalyst in different forms such as dispersed niobia phase in carbon-silica nanocomposite [174], ordered mesoporous carbon-niobium oxide composites [175], Nb_2O_5-mixed oxides [176] for HMF production. From the literature, it is observed that depending on the characteristics of catalysts the yield percentage of HMF varied from 6.7% to 58% during the conversion reactions. In addition, the impact of solvent is also substantial on the final product yield in presence of Nb_2O_5-based catalyst. For instance, Khumho et al. obtained 57.5% HMF yield through glucose dehydration at 190°C within 1 h using THF/H_2O biphasic solvent [174]. However, a much lower yield of only 6.7% HMF was observed under similar operating conditions in the presence of regenerated cellulose-supported Nb_2O_5 catalyst in an aqueous system [170]. In another study, 57% HMF yield was achieved in aqueous medium at 165°C after 3 h using pristine Nb_2O_5 catalyst [176]. Eblagon et al. studied the impact of thermal treatment of Nb_2O_5 on its performance in HMF production from glucose and found that treatment of niobic acid at 550 ◦C resulted in Nb_2O_5 catalysts with a high ratio of Lewis to Brønsted acid sites and poor total acidity. On the other hand, an adequate value of surface acidity was attained on treatment at 300°C, thereby accelerating the glucose conversion rate and low degradation of HMF to side products. Thus, it was evidenced that thermal treatment of niobic acid has a significant impact on the final product as well as on the stability of HMF in an aqueous medium [177]. After confirming the suitability of solid oxides for HMF synthesis, researchers looked into mixed oxides. Due to the increased number of acidic sites and/or the addition of both Lewis and Brønsted acidity, these characteristic solids have excellent catalytic properties. The link between acidity and catalytic activity has been proven in numerous studies [169]. Huang et al. synthesized heterojunction catalyst $TiO_2/Nb_2O_5{\cdot}nH2O$ with a distinct and high catalytic activity for the conversion of glucose into HMF in aqueous media with a yield of 42% HMF. This yield is higher than that obtained using only $Nb_2O_5{\cdot}nH_2O$ (12%

HMF) and could be attributed to a large number of Lewis acid and Brønsted acid sites on its surface [170]. Ramesh et al. attempted to exploit the Lewis and Brønsted acidity of Al_2O_3 by the addition of Ti species and subsequent sulfonation. They found that sulfonation of catalysts played an important role in catalytic conversion of glucose leading to 65% HMF in NaCl-THF/H_2O biphasic system at 170°C within 4h [178]. Briefly, metal oxides come in a variety of forms and have been successfully employed in the production of HMF. Metal oxide-mediated HMF synthesis has several advantages, including low cost and ease of modification. Furthermore, the effect of sulfonation in metal oxide has also been demonstrated. As a result, more metal oxide combinations and functional modifications, both in native and naturally occurring precursors, would result in a transition in HMF synthesis reactions.

2.6.2. Silica-based catalysts

Aluminosilicate-based catalysts viz., zeolites and montmorillonite have been extensively studied in the synthesis of furanic compounds due to their pore selective properties, open channel structure, high surface area, and tunable properties of acidic functional groups [179]. The properties such as pore structure, thermal stability, and/or acidity of aluminosilicates can be tuned through different approaches including metal insertion, adding inorganic acid radicals, sulfonation, etc. [180]. Thus, a multifunctional aluminosilicate-based catalyst with adjustable Brønsted and Lewis acidity can be easily synthesized. Recent studies indicated that when carbohydrates are dehydrated using micropore zeolites, the diffusion of carbohydrates is easily limited by the small pore size, resulting in undesirable results [181, 182]. Moreno-Recio et al. compared the catalytic efficiency of microporous zeolites (H-ZSM-5, H-Y) with mesoporous MCM-41 for the dehydration of glucose into HMF in a H_2O/MIBK biphasic solvent aided by a high concentration of NaCl. An acceptable HMF yield of 55.8% was achieved, at 195°C, after only 30 min, while a lower yield of 40% was obtained using MCM-41 under similar reaction conditions. Thus, it can be concluded that the textural properties of porous aluminosilicates play a vital role in glucose conversion reactions [183]. In a similar study, the influence of morphological structures of LTL-zeolites on the stability and catalytic performance of the conversion of glucose to HMF was investigated. They found that using needle and rod morphologies favours glucose molecule diffusion to the active sites present in LTL zeolites, with a maximum 5-HMF yield of 63.1% at 175°C after 90 min [184]. Velaga et al. synthesized mordenite zeolite with mesoporosity using a seed-assisted method that resulted in a unidirectional growth of zeolite crystals. At an optimum Lewis/Brønsted acidic sites ratio a high HMF yield of 66% was achieved from glucose [185]. Thus, mesoporosity and the optimal number of Lewis-Brønsted acid sites of the mordenite were critical in achieving the highest activity.

SiO_2, specifically mesoporous SiO_2 (such as SBA-15, KIT-6, MCM-41) with an ordered pore structure, high thermal stability, and high specific surface area, are satisfactory for use as a catalyst matrix to provide increased heterogeneity for doped acid species [186]. Until now, Brønsted/Lewis acidity has been developed by introducing heteroatoms through in situ addition during silica synthesis and/or organic functional groups via post-grafting. Jiang et al. synthesized in situ doped zirconium onto KIT-6 through a hydrothermal method, and Zr-KIT-6 exhibited comparatively good catalytic performance for HMF production (34.5%) in MIBK/H_2O biphasic system [187]. The results from analytical outcomes revealed that the structure of Zr-KIT-6, which has higher acid densities as a catalytic site and a larger specific surface area for proton transfusion, is primarily responsible for its superior catalytic performance in glucose hydrolysis. It was found that the Lewis acid site was discovered to promote glucose isomerization, whereas the Brønsted acid site not only inhibited effective glucose conversion but also promoted the aldol addition and condensation reaction of HMF. There is a strong linear correlation between the ratio of weak/total Lewis acid and HMF selectivity; weak Lewis acid sites promote the positive conversion of glucose to HMF, whereas medium-strong Lewis acid sites aggravate the unwanted side reactions, resulting in the formation of levulinic acid and humins [188]. Likewise, Zhu et al. introduced Ti during the synthesis of SBA-15, and an increased HMF yield of 82% was obtained from fructose using Ti-SBA-15 in DMSO solvent [189]. Thus, it could be concluded that characteristic silica, preferably metal-doped and functionalized silica have promising properties for heterogeneous catalysis of different sugars to produce HMF.

2.6.3. Heteropoly acids

Heteropoly acids (HPA) are acidic compounds comprising of hydrogen cations and polyoxometalate anions, holding significant characteristics such as high acidity, thermal stability, and oxidation capability that make it a catalyst of choice for dehydration of hexose-based sugars. The most widely accessible form of heteropoly acid class is 12-phosphotungstic acid ($H_3PW_{12}O_{40}$) [189]. However, the high solubility of heteropolyacids in aqueous and organic solvents makes it difficult to separate the catalyst from solvent thereby rendering HMF production [190]. Nonetheless, its inherent high acidity motivates researchers to investigate its potential application, particularly in dehydration reactions. Dual Brønsted-Lewis acidity is introduced into the heterogeneous heteropolyacids catalysts via reactions with different metal salts (Cr, Ag, Fe, Cu, Ce, and Cs) and ionic liquids [168]. Rahaman et al. studied $H_3PW_{12}O_{40}$ for HMF production after encapsulation into a metal-organic framework (MIL-101) and obtained a 58% yield of HMF from glucose at 120°C in 1-butyl-3-methylimidazolium chloride ionic liquid, $[C_4C_1im]Cl$ solvent. According to the analytical results, the MOF pores were uniformly dispersed with $H_3PW_{12}O_{40}$, which provided both Brønsted and Lewis acid sites for the conversion reaction [192]. The Brønsted-Lewis acid sites ratio of solid heteropolyacid catalysts can also be well regulated during the modification process. For example, Wang et al. evaluated the catalytic performance of Aluminium doped phosphotungstic acid (PWAl-200) synthesized by electric-flocculation method in the synthesis of HMF to glucose. The four-coordinated Al surrounded by tungsten species in PWAl-200 and the six-coordinated Al affected by terminal W=O bond in generated Lewis acid sites for the glucose isomerization reaction, while the H^+ acted as Brønsted acid sites for the dehydration reaction. Thus, PWAl-200 with the suitable Brønsted-Lewis acid sites ratio produced 61.7% of HMF at 170℃ DMSO/H_2O solvent [193].

2.6.4. Carbon-based solid acids

A solid catalyst with a carbon skeleton and acidic functional groups, such as sulfonic acid and metal species, is referred to as carbon-based solid acid (CSA). CSA catalysts have outstanding catalytic activity for acid-catalyzed reactions like hydrolysis, hydration, and esterification reactions [194]. CSA includes sulfonated activated carbons, polymer solid acid, and acidic ion exchange resin.

Carbonaceous materials such as amorphous activated carbon, graphene, and carbon nanotubes are attractive catalyst and/or catalysts support in biorefinery due to their excellent textural properties, electron conductivity, and chemical inertness [195]. Besides, the majority of the carbonaceous materials are derived from waste biomass making their preparation and applications much more cost-effective and environment-friendly [196]. To enhance the catalytic performance, the carbonaceous materials are often functionalized with organic groups such as sulfonic groups, carboxylic groups, hydroxyl groups, etc., and with metallic species (Al, Ni, Sn, Nb, etc.) [158]. Although carbonaceous materials alone have some inherent Lewis acid sites, they are not efficient enough for glucose isomerization leading to low HMF yields. Interestingly, a high HMF yield of 93% was achieved from glucose using sulfonated oxidized activated carbon as a catalyst in THF/H_2O-NaCl biphasic system [158]. The analytical results of the study confirmed that during the preparation of this catalyst, the sulfonation process leads to the formation of sulfonic acid groups (strong Brønsted acid) and consecutive oxidation leads to the formation of ketone and carbonyl groups (base sites). The synergistic effect of Brønsted acid-base sites accelerates the dehydration of glucose thereby enhancing HMF yield [158]. Similarly, in a recent study sulfonated chitosan-derived carbon-based catalyst was synthesized for the conversion of fructose to HMF that exhibited an excellent catalytic activity resulting in 80.9% HMF yield in 1, 4-dioxane solvent [197]. Besides, the use of Lewis acid functionalized carbon catalysts in the synthesis of HMF has also been reported. Wang et al. developed a bifunctional solid acid tin oxide/carbon catalyst by a hydrothermal-pyrolysis strategy and tuning the acid density by adjusting $SnCl_4$ dosage and pyrolysis temperature. At a suitable Brønsted to Lewis acid ratio, the catalyst showed superior activity and a high yield of 84.1% HMF was achieved from glucose in a THF/H_2O biphasic system [198]. From these studies, it can be inferred that HMF synthesis from hexose-based carbohydrates catalyst having dual Brønsted-Lewis acidity is challenging to reconcile the activity requirement of promoting isomerization and dehydration processes while suppressing undesirable side reactions.

As a result of its strong catalytic activity, ease of preparation, and sustainability, CSA is a high-potential solid acid catalyst. However, more research into improving catalytic stability and mechanical robustness is required. Furthermore, before this type of catalyst can be considered on an industrial scale, overall economic research and comparison with the typical solid acid catalyst are necessary.

2.6.5. Metal phosphates

Metal phosphates possess strong Brønsted-Lewis acid sites in addition to basic sites and are insoluble in aqueous or organic solvents, rendering them suitable catalysts for several acid-catalyzed reactions, preferably converting carbohydrates to HMF. Also, the acidity and pore structure of metal phosphates can be optimized by optimizing the metal-phosphorous dose ratio and chemical additives such as organic templates or by employing various synthesis techniques including hydrothermal, sol-gel method, etc [161]. Benvenuti et al. were the first to synthesize titanium and zirconium phosphates, as well as pyrophosphates, as heterogeneous catalysts for the synthesis of HMF [199].

In terms of catalytic activity and desired product selectivity, comparative experiments revealed that zirconium pyrophosphate and titanium phosphate performed best during HMF production. Metal phosphates performed differently for selective HMF synthesis due to inherent differences between metals. Ordomsky et al. previously reported on the Brønsted-Lewis acid species in AlPO, TiPO, ZrPO, and NbPO, as well as their catalytic actions on the conversion of glucose to HMF, and discovered that the activities of these phosphates declined in the following order: NbPO>ZrPO>TiPO>AlPO [199]. Furthermore, the addition of organic solvents limits HMF rehydration and deactivation of the catalyst in the aqueous phase, resulting in increased activity and stability of the catalyst. To summarise, phosphate-based catalysts are best suited for processes with moderate reaction conditions, however, they have lower HMF yields than other heterogeneous catalysts. Nonetheless, because of their enhanced selectivity and stable product formation, these catalysts are expected to be intensively investigated in the future for higher HMF yields.

2.7. Density functional theory (DFT) study of glucose dehydration to HMF

For producing HMF from glucose, a variety of catalysts have been designed. The mechanism of HMF dehydration from glucose produced by a heterogeneous catalyst in a solvent media, on the other hand, is less well understood. The mechanism of HMF synthesis from glucose by the application of a catalyst is extremely important to understand. DFT was used to investigate the effects of ionic liquid, 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) mixed with transition metal salts ([BMIM]/$MoCl_3$, [BMIM]/WCl_3, [BMIM]/$FeCl_3$) on glucose isomerization and fructose dehydration into HMF. The investigations have shown that the energy barrier and the stabilities of intermediates are susceptible to the metal centre at every reaction step during the isomerization of glucose [200]. They observed that the isomerization of glucose declined in the order WCl_3> $MoCl_3$> $CrCl_3$> $FeCl_3$ over various metal chloride catalysts. Likewise, using periodic DFT simulations, Li et al. investigated a new mechanism for glucose dehydration to HMF without isomerization to fructose for surface models of anatase TiO_2 [201]. TiO_2 activated the glucose at C3-OH site, initiating the process that resulted in adsorbed 3-deoxyglucosone. A comparison of several surface models reveals that the existence of tetrahedral Ti^{4+} species on a defective TiO_2 (101) anatase surface was critical for understanding the activity. To establish the direct conversion of glucose to HMF, a cooperation between a strong Lewis acidic Ti site and a vicinal basic oxygen site of a TiOH group was required. This study also indicates that a balanced Lewis and Brønsted acidity was preferable for dehydrating glucose to HMF. Yue et al. adjusted the amount of Nb introduced into the tungsten oxide to control its acidity [202]. They discovered that the process proceeded through isomerization to fructose and dehydration of fructose to a partially dehydrated intermediate in THF/water due to the strong Lewis acidity and weak Brønsted acidity. The DFT calculations were employed to show how the Lewis acidic W and Nb sites promote the isomerization of glucose. According to the calculations, the Lewis acid sites on the tungstite surface might isomerize glucose into fructose. The deprotonated glucose adsorbate has been stabilized by replacing W with Nb which could reduce the total activation barrier for glucose isomerization. Thus, DFT study could help researchers better understand the mechanisms involved in converting glucose to HMF, such as glucose isomerization, fructose dehydration, and catalyst activity sites.

To sum up, the high crystallinity of cellulose and its sheathing by hemicellulose-lignin matrix furnish the resilient structure of lignocellulosic biomass. Therefore, pretreatment is an extremely important step for the conversion of lignocellulosic biomass to sugars and further processing for industrially important bioproducts. Extensive investigations have been carried out on the effects of different pretreatment methods on lignocellulosic composition and sugar yield. Analysis of various methods brings us to the conclusion that each method has its pros and cons. Therefore, assessing these methods straight through the test data is not accurate. Until now, a cost-effective and environmentally benign pretreatment method with optimized process conditions that can completely delignify biomass is yet to be established. In addition, the lignocellulosic biomass properties and features greatly influence in choosing the correct pretreatment method. Hence, the challenges to pretreat biomass with high efficiency comprise of cost-effectivity, energy-effectivity, and environmental sustainability, which are the existing bottlenecks for its integration as feedstocks in biorefinery approaches. Secondly, significant progress has been made to date, in the conversion of glucose to HMF, with several types of heterogeneous catalysts developed and in a variety of solvent systems, including aqueous, organic, biphasic, mixed solvent; and ionic liquids. However, there are many challenges needed to be addressed to set new levels in HMF production. Since HMF is synthesized via isomerization and dehydration of glucose, therefore, multi-functional heterogeneous catalysts should be improved further for this tandem conversion reaction.

Catalysts with multi-catalytic sites may have higher activity and selectivity in this context, and as such, special consideration should be given to this aspect. Favourable studies revealed that reaction conditions (reaction temperature and time) also play a key role in the conversion reaction. Furthermore, the reaction mechanism during the reaction is still needed to investigate. The molecular interactions of the substrate, catalyst, and solvents will reveal their unique role in the dehydration of glucose to HMF, which will aid in the development of novel heterogeneous catalysts and solvent systems.

References

[1] Akhtar, N., Gupta, K., Goyal, D., and Goyal, A. Recent advances in pretreatment technologies for efficient hydrolysis of lignocellulosic biomass. *Environmental Progress & Sustainable Energy*, 35(2):489-511, 2016.

[2] Dahadha, S., Amin, Z., Bazyar Lakeh, A. A., and Elbeshbishy, E. Evaluation of Different Pretreatment Processes of Lignocellulosic Biomass for Enhanced Biomethane Production. *Energy Fuels*, 31:0335-10347, 2017.

[3] Tu, W. C., and Hallett, J. P. Recent advances in the pretreatment of lignocellulosic biomass. *Current Opinion in Green and Sustainable Chemistry*, 20:11-17, 2019.

[4] Liu, Y. R., Thomsen, K., Nie, Y., Zhang, S. J., and Meyer, A. S. Predictive screening of ionic liquids for dissolving cellulose and experimental verification. *Green Chemistry*, 18(23):6246-6254, 2016.

[5] Jedvert, K., & Heinze, T. Cellulose modification and shaping–a review. *Journal of Polymer Engineering*, 37(9):845-860, 2017.

[6] Zhou, X., Li, W., Mabon, R., and Broadbelt, L. J. A critical review on hemicellulose pyrolysis. *Energy Technology*, 5(1):52-79, 2017.

[7] Farhat, W., Venditti, R. A., Hubbe, M., Taha, M., Becquart, F., and Ayoub, A. A Review of Water-Resistant Hemicellulose-Based Materials: Processing and Applications. *ChemSusChem*, 10:305-323, 2017.

[8] Xu, C., and Ferdosian, F. *Conversion of lignin into bio-based chemicals and materials*. New York, NY, USA: Springer, 2017.

[9] Baruah, J., Nath, B. K., Sharma, R., Kumar, S., Deka, R. C., Baruah, D. C., and Kalita, E. Recent trends in the pretreatment of lignocellulosic biomass for value-added products. *Frontiers in Energy Research*, 6:141, 2018.

[10] Guerriero, G., Hausman, J. F., Strauss, J., Ertan, H., and Siddiqui, K. S. Lignocellulosic biomass: biosynthesis, degradation, and industrial utilization. *Engineering in Life Sciences*, 16(1):1-16, 2016.

[11] Chen, H., Liu, J., Chang, X., Chen, D., Xue, Y., Liu, P., Lin, H., and Han, S. A review on the pretreatment of lignocellulose for high-value chemicals. *Fuel Processing Technology*, 160:196-206, 2017.

[12] Rajendran, K., Drielak, E., Sudarshan Varma, V., Muthusamy, S., & Kumar, G. Updates on the pretreatment of lignocellulosic feedstocks for bioenergy production–a review. *Biomass Conversion and Biorefinery*, 8(2):471-483, 2018.

[13] Shirkavand, E., Baroutian, S., Gapes, D. J., and Young, B. R. Combination of fungal and physicochemical processes for lignocellulosic biomass pretreatment–A review. *Renewable and Sustainable Energy Reviews*, 54:217-234, 2016.

[14] Kumar, A. K., and Sharma, S. Recent updates on different methods of pretreatment of lignocellulosic feedstocks: a review. *Bioresources and Bioprocessing*, 4(1):1-19, 2017.

[15] Kumar, A. K., and Sharma, S. (2017). Recent updates on different methods of pretreatment of lignocellulosic feedstocks: a review. *Bioresources and Bioprocessing*, 4(1):1-19, 2017.

[16] Bai, X., Wang, G., Yu, Y., Wang, D., and Wang, Z. Changes in the physicochemical structure and pyrolysis characteristics of wheat straw after rod-milling pretreatment. *Bioresource Technology*, 250:770-776, 2018.

[17] Zakaria, M. R., Norrrahim, M. N. F., Hirata, S., and Hassan, M. A. Hydrothermal and wet disk milling pretreatment for high conversion of biosugars from oil palm mesocarp fiber. *Bioresource Technology*, 181:263-269, 2015.

[18] Zakaria, M. R., Hirata, S., Fujimoto, S., and Hassan, M. A. Combined pretreatment with hot compressed water and wet disk milling opened up oil palm biomass structure resulting in enhanced enzymatic digestibility. *Bioresource Technology*, 193:128-134, 2015.

[19] Kim, H. J., Lee, S., Kim, J., Mitchell, R. J., and Lee, J. H. Environmentally friendly pretreatment of plant biomass by planetary and attrition milling. *Bioresource Technology*, 144:50-56, 2013.

[20] Gao, Y., Ramón, J., and Matthau, A. S. Microwave-assisted hydrothermal treatments for biomass valorisation: a critical review. *Green Chemistry*, 23(10):3502-3525, 2021.

[21] Tayyab, M., Noman, A., Islam, W., Waheed, S., Arafat, Y., Ali, F., Zaynab, M., Lin, S., Zhang, H., and Lin, W. Bioethanol production from lignocellulosic biomass by environment-friendly pretreatment methods: A review. *Applied Ecology and Environmental Research*, 16(1):225-249, 2018.

[22] Aguilar-Reynosa, A., Romaní, A., Rodríguez-Jasso, R. M., Aguilar, C. N., Garrote, G., and Ruiz, H. A. Microwave heating processing as alternative of pretreatment in second-generation biorefinery: An overview. *Energy Conversion and Management*, 136:50-65, 2017.

[23] Li, H., Qu, Y., Yang, Y., Chang, S., and Xu, J. Microwave irradiation–A green and efficient way to pretreat biomass. *Bioresource Technology*, 199:34-41, 2016.

[24] Irmak, S., Meryemoglu, B., Sandip, A., Subbiah, J., Mitchell, R. B., and Sarath, G. Microwave pretreatment effects on switchgrass and miscanthus solubilization in subcritical water and hydrolysate utilization for hydrogen production. *Biomass and Bioenergy*, 108:48-54, 2018.

[25] Zhao, B. H., Chen, J., Yu, H. Q., Hu, Z. H., Yue, Z. B., and Li, J. Optimization of microwave pretreatment of lignocellulosic waste for enhancing methane production: Hyacinth as an example. *Frontiers of Environmental Science & Engineering*, 11(6):1-9, 2017.

[26] Liu, Y., Sun, B., Zheng, X., Yu, L., and Li, J. Integrated microwave and alkaline treatment for the separation between hemicelluloses and cellulose from cellulosic fibers. *Bioresource Technology,* 247:859-863, 2018.

[27] Paul, S., and Dutta, A. Challenges and opportunities of lignocellulosic biomass for anaerobic digestion. *Resources, Conservation and Recycling*, 130:164-174, 2018.

[28] Duan, D., Ruan, R., Wang, Y., Liu, Y., Dai, L., Zhao, Y., Zhou, Y., Wu, Q. Microwave-assisted acid pretreatment of alkali lignin: Effect on characteristics and pyrolysis behavior. *Bioresource Technology,* 251:57-62, 2018.

[29] Wang, Y., Duan, D., Liu, Y., Ruan, R., Fu, G., Dai, L., Zhou, Y., Yu, Z., Wu, Q., and Zeng, Z. Properties and pyrolysis behavior of moso bamboo sawdust after microwave-assisted acid pretreatment. *Journal of Analytical and Applied Pyrolysis*, 129:86-92, 2018.

[30] Duque, A., Manzanares, P., and Ballesteros, M. Extrusion as a pretreatment for lignocellulosic biomass: Fundamentals and applications. *Renewable Energy,* 114:1427-1441, 2017.

[31] Kumar, A. K., and Sharma, S. (2017). Recent updates on different methods of pretreatment of lignocellulosic feedstocks: a review. *Bioresources and Bioprocessing*, 4(1):1-19, 2017.

[32] Wahid, R., Hjorth, M., Kristensen, S., and Møller, H. B. Extrusion as pretreatment for boosting methane production: effect of screw configurations. *Energy & Fuels*, 29(7):4030-4037, 2015.

[33] Ravindran, R., and Jaiswal, A. K. A comprehensive review on pre-treatment strategy for lignocellulosic food industry waste: challenges and opportunities. *Bioresource Technology,* 199:92-102, 2016.

[34] He, Z., Wang, Z., Zhao, Z., Yi, S., Mu, J., and Wang, X. Influence of ultrasound pretreatment on wood physiochemical structure. *Ultrasonics Sonochemistry,* 34:136-141, 2017.

[35] Koutsianitis, D., Mitani, C., Giagli, K., Tsalagkas, D., Halász, K., Kolonics, O., Gallis, C., and Csóka, L. Properties of ultrasound extracted bicomponent lignocellulose thin films. *Ultrasonics Sonochemistry,* 23:148-155, 2015.

[36] Liyakathali, N. A. M., Muley, P. D., Aita, G., and Boldor, D. Effect of frequency and reaction time in focused ultrasonic pretreatment of energy cane bagasse for bioethanol production. *Bioresource Technology,* 200:262-271, 2016.

[37] Cherpozat, L., Loranger, E., and Daneault, C. (2017). Ultrasonic pretreatment effects on the bio-oil yield of a laboratory-scale slow wood pyrolysis. *Journal of Analytical and Applied Pyrolysis*. 126:31-38, 2017.

[38] Ivetić, D. Ž., Omorjan, R. P., Đorđević, T. R., and Antov, M. G. The impact of ultrasound pretreatment on the enzymatic hydrolysis of cellulose from sugar beet shreds: Modeling of the experimental results. *Environmental Progress and Sustainable Energy,* 36:1164-1172, 2017.

[39] Luo, J., Fang, Z., and Smith Jr, R. L. Ultrasound-enhanced conversion of biomass to biofuels. *Progress in Energy and Combustion Science*, 41:56-93, 2014.

[40] Kim, J. S., Lee, Y. Y., and Kim, T. H. A review on alkaline pretreatment technology for bioconversion of lignocellulosic biomass. *Bioresource Technology*, 199:42-48, 2016.

[41] Sun, S., Sun, S., Cao, X., and Sun, R. The role of pretreatment in improving the enzymatic hydrolysis of lignocellulosic materials. *Bioresource Technology*, 199:49-58, 2016.

[42] Behera, S., Arora, R., Nandhagopal, N., and Kumar, S. Importance of chemical pretreatment for bioconversion of lignocellulosic biomass. Renewable and Sustainable Energy Reviews, 36:91-106, 2014.

[43] Shetty, D. J., Kshirsagar, P., Tapadia-Maheshwari, S., Lanjekar, V., Singh, S. K., and Dhakephalkar, P. K. Alkali pretreatment at ambient temperature: A promising method to enhance biomethanation of rice straw. *Bioresource Technology*, 226:80-88, 2017.

[44] Talha, Z., Ding, W., Mehryar, E., Hassan, M., and Bi, J. Alkaline pretreatment of sugarcane bagasse and filter mud codigested to improve biomethane production. *BioMed Research International*, 2016, 2016.

[45] Shen, J., Zhao, C., Liu, G., and Chen, C. Enhancing the performance on anaerobic digestion of vinegar residue by sodium hydroxide pretreatment. *Waste Biomass Valorization*, 8:1119-1126, 2017.

[46] Shah, T. A., and Tabassum, R. Enhancing biogas production from lime-soaked corn cob residue. *International Journal of Renewable Energy Research*, 8(2):761-766, 2018.

[47] Rabelo, S. C., Fonseca, N. A., Andrade, R. R., Maciel Filho, R., and Costa, A. C. Ethanol production from enzymatic hydrolysis of sugarcane bagasse pretreated with lime and alkaline hydrogen peroxide. *Biomass and Bioenergy*, 35:2600-2607, 2011.

[48] Ghorbani, M., Ahmadi, F., Rad, A. R., Zamiri, M. J., Cone, J. W., and Polikarpov, I. The effect of lime pre-treatments of date palm leaves on delignification and in vitro rumen degradability. *The Journal of Agricultural Science*, 155(1):184-190, 2017.

[49] Sakuragi, K., Igarashi, K., and Samejima, M. Application of ammonia pretreatment to enable enzymatic hydrolysis of hardwood biomass. *Polymer Degradation and Stability*, 148:19-25, 2018.

[50] Kang, S., Fu, J., and Zhang, G. From lignocellulosic biomass to levulinic acid: A review on acid-catalyzed hydrolysis. *Renewable and Sustainable Energy Reviews*, 94:340-362, 2018.

[51] Kärcher, M. A., Iqbal, Y., Lewandowski, I., and Senn, T. Comparing the performance of *Miscanthus x giganteus* and wheat straw biomass in sulfuric acid-based pretreatment. *Bioresource Technology*, 180:360-364, 2015.

[52] Nair, R. B., Lundin, M., Brandberg, T., Lennartsson, P. R., and Taherzadeh, M. J. Dilute phosphoric acid pretreatment of wheat bran for enzymatic hydrolysis and subsequent ethanol production by edible fungi *Neurospora intermedia*. *Industrial Crops and Products*, 69:314-323, 2015.

[53] Kim, I., Seo, Y. H., Kim, G. Y., and Han, J. I. Co-production of bioethanol and biodiesel from corn stover pretreated with nitric acid. *Fuel*, 143:285-289, 2015.

[54] Zu, S., Li, W. Z., Zhang, M., Li, Z., Wang, Z., Jameel, H., and Chang, H. M. Pretreatment of corn stover for sugar production using dilute hydrochloric acid followed by lime. *Bioresource Technology*, 152:364-370, 2014.

[55] Du, H., Liu, C., Zhang, Y., Yu, G., Si, C., and Li, B. Preparation and characterization of functional cellulose nanofibrils via formic acid hydrolysis pretreatment and the followed high-pressure homogenization. *Industrial Crops and Products*, 94:736-745, 2016.

[56] Jung, Y. H., Park, H. M., and Kim, K. H. Whole slurry saccharification and fermentation of maleic acid-pretreated rice straw for ethanol production. *Bioprocess and Biosystems Engineering*, 38(9):1639-1644, 2015.

[57] Jeong, S. Y., and Lee, J. W. Optimization of pretreatment condition for ethanol production from oxalic acid pretreated biomass by response surface methodology. *Industrial Crops and Products*, 79:1-6, 2016.

[58] Sahoo, D., Ummalyma, S. B., Okram, A. K., Pandey, A., Sankar, M., and Sukumaran, R. K. Effect of dilute acid pretreatment of wild rice grass (*Zizania latifolia*) from Loktak Lake for enzymatic hydrolysis. *Bioresource Technology*, 253:252-255, 2018.

[59] Sindhu, R., Kuttiraja, M., Binod, P., Sukumaran, R. K., and Pandey, A. Bioethanol production from dilute acid pretreated Indian bamboo variety (*Dendrocalamus* sp.) by separate hydrolysis and fermentation. *Industrial Crops and Products*, 52:169-176, 2014.

[60] Amnuaycheewa, P., Hengaroonprasan, R., Rattanaporn, K., Kirdponpattara, S., Cheenkachorn, K., and Sriariyanun, M. Enhancing enzymatic hydrolysis and biogas production from rice straw by pretreatment with organic acids. *Industrial Crops and Products*, 87:247-254, 2016.

[61] Qing, Q., Huang, M., He, Y., Wang, L., and Zhang, Y. Dilute oxalic acid pretreatment for high total sugar recovery in pretreatment and subsequent enzymatic hydrolysis. *Applied Biochemistry and Biotechnology*, 177(7):1493-1507, 2015.

[62] Daffalla, S. B., Hilmi, M., and Maizatul, S. Effect of organic and inorganic acid pretreatment on structural properties of rice husk and adsorption mechanism of phenol. *International Journal of Chemical and Environmental Engineering*, 3(3), 2012.

[63] Singh, S. K., and Savoy, A. W. Ionic liquids synthesis and applications: An overview. *Journal of Molecular Liquids*, 297:112038, 2020.

[64] Yoo, C. G., Pu, Y., and Ragauskas, A. J. Ionic liquids: Promising green solvents for lignocellulosic biomass utilization. *Current Opinion in Green and Sustainable Chemistry*, 5:5-11, 2017.

[65] Chen, H., Liu, J., Chang, X., Chen, D., Xue, Y., Liu, P., Lin, H., and Han, S. A review on the pretreatment of lignocellulose for high-value chemicals. *Fuel Processing Technology*, 160:196-206, 2017.

[66] Zhang, Q., Hu, J., and Lee, D. J. Pretreatment of biomass using ionic liquids: research updates. *Renewable Energy*, 111:77-84, 2017.

[67] Raj, T., Gaur, R., Lamba, B. Y., Singh, N., Gupta, R. P., Kumar, R., Puri, S. K., and Ramakumar, S. S. V. Characterization of ionic liquid pretreated plant cell wall for improved enzymatic digestibility. *Bioresource Technology*, 249:139-145, 2018.

[68] Stanton, J., Xue, Y., Pandher, P., Malek, L., Brown, T., Hu, X., and Salas-de la Cruz, D. Impact of ionic liquid type on the structure, morphology and properties of silk-cellulose biocomposite materials. *International Journal of Biological Macromolecules*, 108:333-341, 2018.

[69] Brandt-Talbot, A., Gschwend, F. J., Fennell, P. S., Lammens, T. M., Tan, B., Weale, J., and Hallett, J. P. (2017). An economically viable ionic liquid for the fractionation of lignocellulosic biomass. *Green Chemistry*, 19(13):3078-3102, 2017.

[70] Zhang, K., Pei, Z., and Wang, D. Organic solvent pretreatment of lignocellulosic biomass for biofuels and biochemicals: A review. *Bioresource Technology*, 199:21-33, 2016.

[71] Borand, M. N., and Karaosmanoğlu, F. Effects of organosolv pretreatment conditions for lignocellulosic biomass in biorefinery applications: a review. *Journal of Renewable and Sustainable Energy*, 10(3):033104, 2018.

[72] Zdanowicz, M., Wilpiszewska, K., and Spychaj, T. Deep eutectic solvents for polysaccharides processing. A review. *Carbohydrate Polymers*, 200:361-380, 2018.

[73] Smith, E. L., Abbott, A. P., and Ryder, K. S. Deep eutectic solvents (DESs) and their applications. *Chemical Reviews*, 114(21):11060-11082, 2014.

[74] Wagle, D. V., Zhao, H., and Baker, G. A. Deep eutectic solvents: sustainable media for nanoscale and functional materials. *Accounts of Chemical Research*, 47(8):2299-2308, 2014.

[75] Xu, G. C., Ding, J. C., Han, R. Z., Dong, J. J., and Ni, Y. Enhancing cellulose accessibility of corn stover by deep eutectic solvent pretreatment for butanol fermentation. *Bioresource Technology*, 203:364-369, 2016.

[76] Zhang, C. W., Xia, S. Q., and Ma, P. S. Facile pretreatment of lignocellulosic biomass using deep eutectic solvents. *Bioresource Technology*, 219:1-5, 2016.

[77] Chen, H. Z., and Liu, Z. H. Steam explosion and its combinatorial pretreatment refining technology of plant biomass to bio-based products. *Biotechnology Journal*, 10(6):866-885, 2015.

[78] Singh, J., Suhag, M., and Dhaka, A. Augmented digestion of lignocellulose by steam explosion, acid and alkaline pretreatment methods: a review. *Carbohydrate Polymers*, 117:624-631, 2015.

[79] Pielhop, T., Amgarten, J., von Rohr, P. R., and Studer, M. H. Steam explosion pretreatment of softwood: the effect of the explosive decompression on enzymatic digestibility. *Biotechnology for Biofuels*, 9(1):1-13, 2016.

[80] Vivekanand, V., Olsen, E. F., Eijsink, V. G., and Horn, S. J. Effect of different steam explosion conditions on methane potential and enzymatic saccharification of birch. *Bioresource Technology*, 127:343-349, 2013.

[81] Lizasoain, J., Trulea, A., Gittinger, J., Kral, I., Piringer, G., Schedl, A., Nilsen, P. J., Potthast, A., Gronauer, A., and Bauer, A. Corn stover for biogas production: effect of steam explosion pretreatment on the gas yields and on the biodegradation kinetics of the primary structural compounds. *Bioresource Technology*, 244:949-956, 2017.

[82] El-Naggar, N. E., Deraz, S., and Khalil, A. Bioethanol production from lignocellulosic feedstocks based on enzymatic hydrolysis: Current status and recent developments. *Biotechnology*, 13:1-21, 2014.

[83] Lee, W. C., and Kuan, W. C. Miscanthus as cellulosic biomass for bioethanol production. *Biotechnology Journal*, 10(6):840-854, 2015.

[84] Abdul, P. M., Jahim, J. M., Harun, S., Markom, M., Lutpi, N. A., Hassan, O., Balan, V., Dale, B. E and Nor, M. T. M. Effects of changes in chemical and structural characteristic of ammonia fibre expansion (AFEX) pretreated oil palm empty fruit bunch fibre on enzymatic saccharification and fermentability for biohydrogen. *Bioresource Technology*, 211:200-208, 2016.

[85] Zhao, C., Ding, W., Chen, F., Cheng, C., and Shao, Q. Effects of compositional changes of AFEX-treated and H-AFEX-treated corn stover on enzymatic digestibility. *Bioresource Technology*, 155:34-40, 2014.

[86] Mathew, A. K., Parameshwaran, B., Sukumaran, R. K., and Pandey, A. An evaluation of dilute acid and ammonia fiber explosion pretreatment for cellulosic ethanol production. *Bioresource Technology*, 199:13-20, 2016.

[87] Bharathiraja, B., Jayamuthunagai, J., Chakravarthy, M., and Kumar, R. P. (2018). Bioprocessing of biofuels for green and clean environment. In *Bioprocess Engineering for a Green Environment,* pages 237-249. CRC Press, 2018.

[88] Rostagno, M. A., Prado, J. M., Mudhoo, A., Santos, D. T., Forster–Carneiro, T., and Meireles, M. A. A. Subcritical and supercritical technology for the production of second-generation bioethanol. *Critical Reviews in Biotechnology*, 35(3):302-312, 2015.

[89] Capolupo, L., and Faraco, V. Green methods of lignocellulose pretreatment for biorefinery development. *Applied Microbiology and Biotechnology*, 100(22):9451-9467, 2016.

[90] Benazzi, T., Calgaroto, S., Dalla Rosa, C., Vladimir Oliveira, J., and Mazutti, M. A. Hydrolysis of sugarcane bagasse using supercritical carbon dioxide to obtain fermentable sugars. *Journal of Chemical Technology & Biotechnology*, 88(9):1766-1768, 2013.

[91] Islam, S. M., Li, Q., Al Loman, A., and Ju, L. K. CO_2-H_2O based pretreatment and enzyme hydrolysis of soybean hulls. *Enzyme and Microbial Technology*, 106:18-27, 2017.

[92] Narayanaswamy, N., Faik, A., Goetz, D. J., and Gu, T. Supercritical carbon dioxide pretreatment of corn stover and switchgrass for lignocellulosic ethanol production. *Bioresource Technology*, 102(13):6995-7000, 2011.

[93] Yin, J., Hao, L., Yu, W., Wang, E., Zhao, M., Xu, Q., and Liu, Y. Enzymatic hydrolysis enhancement of corn lignocellulose by supercritical CO_2 combined with ultrasound pretreatment. *Chinese Journal of Catalysis*, 35(5):763-769, 2014.

[94] Zhuang, X., Wang, W., Yu, Q., Qi, W., Wang, Q., Tan, X., Zhou, G., and Yuan, Z. Liquid hot water pretreatment of lignocellulosic biomass for bioethanol production accompanying with high valuable products. *Bioresource Technology*, 199:68-75, 2016.

[95] Li, H. Q., Jiang, W., Jia, J. X., and Xu, J. pH pre-corrected liquid hot water pretreatment on corn stover with high hemicellulose recovery and low inhibitors formation. *Bioresource Technology*, 153:292-299, 2014.

[96] Boakye-Boaten, N. A., Xiu, S., Shahbazi, A., and Fabish, J. Liquid hot water pretreatment of Miscanthus x giganteus for the sustainable production of bioethanol. *Bioresources*, 10:5890-5905, 2015.

[97] Hongdan, Z., Shaohua, X., and Shubin, W. Enhancement of enzymatic saccharification of sugarcane bagasse by liquid hot water pretreatment. *Bioresource Technology*, 143:391-396, 2013.

[98] Imman, S., Laosiripojana, N., and Champreda, V. Effects of liquid hot water pretreatment on enzymatic hydrolysis and physicochemical changes of corncobs. *Applied Biochemistry and Biotechnology*, 184:432-443, 2018.

[99] Imman, S., Arnthong, J., Burapatana, V., Champreda, V., and Laosiripojana, N. Influence of alkaline catalyst addition on compressed liquid hot water pretreatment of rice straw. *Chemical Engineering Journal*, 278:85-91, 2015.

[100] Imman, S., Arnthong, J., Burapatana, V., Champreda, V., and Laosiripojana, N. Effects of acid and alkali promoters on compressed liquid hot water pretreatment of rice straw. *Bioresource Technology*, 171:29-36, 2014.

[101] Bhutto, A. W., Qureshi, K., Harijan, K., Abro, R., Abbas, T., Bazmi, A. A., Karim, S., and Yu, G. Insight into progress in pre-treatment of lignocellulosic biomass. *Energy*, 122:724-745, 2017.

[102] Sindhu, R., Binod, P., and Pandey, A. Biological pretreatment of lignocellulosic biomass–an overview. *Bioresource Technology*, 199:76-82, 2016.

[103] Bhatia, S. K., Kim, S. H., Yoon, J. J., and Yang, Y. H. Current status and strategies for second generation biofuel production using microbial systems. *Energy Conversion and Management*, 148:1142-1156, 2017.

[104] Wan, C., and Li, Y. Fungal pretreatment of lignocellulosic biomass. *Biotechnology Advances*, 30(6):1447-1457, 2012.

[105] Yesilada, O., Birhanli, E., and Geckil, H. Bioremediation and decolorization of textile dyes by white rot fungi and laccase enzymes. In *Mycoremediation and Environmental Sustainability*, pages 121-153. Springer, Cham, 2018.

[106] Wagner, A. O., Lackner, N., Mutschlechner, M., Prem, E. M., Markt, R., and Illmer, P. Biological pretreatment strategies for second-generation lignocellulosic resources to enhance biogas production. *Energies*, 11(7):1797, 2018.

[107] Vats, S., Maurya, D. P., Shaimoon, M., Agarwal, A., and Negi, S. Development of a microbial consortium for production of blend of enzymes for hydrolysis of agricultural wastes into sugars. *Journal of Scientific and Industrial Research*, 72:585-590, 2013.

[108] Kobayashi, H., and Fukuoka, A. Synthesis and utilisation of sugar compounds derived from lignocellulosic biomass. *Green Chemistry*, 15(7):1740-1763, 2013.

[109] Werpy, T. A., Holladay, J. E., & White, J. F. *Top value added chemicals from biomass: I. Results of screening for potential candidates from sugars and synthesis gas.* Technical report 14808, Pacific Northwest National Lab, Richland, WA (United States), 2004.

[110] Düll, G. Action of oxalic acid on inulin. *Chemiker Zeitung*, 19:216-220, 1895.

[111] Kiermayer, J. A derivative of furfuraldehyde from laevulose. *Chemiker Zeitung*, 19:1003-1006, 1895.

[112] Rosatella, A. A., Simeonov, S. P., Frade, R. F., and Afonso, C. A. 5-Hydroxymethylfurfural (HMF) as a building block platform: Biological properties, synthesis and synthetic applications. *Green Chemistry*, 13(4):754-793, 2011.

[113] Fang, R., Luque, R., and Li, Y. Selective aerobic oxidation of biomass-derived HMF to 2, 5-diformylfuran using a MOF-derived magnetic hollow Fe–Co nanocatalyst. *Green Chemistry*, 18(10):3152-3157, 2016.

[114] Han, X., Geng, L., Guo, Y., Jia, R., Liu, X., Zhang, Y., and Wang, Y. Base-free aerobic oxidation of 5-hydroxymethylfurfural to 2, 5-furandicarboxylic acid over a Pt/C–O–Mg catalyst. *Green Chemistry*, *18*(6), 1597-1604, 2016.

[115] Nishimura, S., Ikeda, N., and Ebitani, K. Selective hydrogenation of biomass-derived 5-hydroxymethylfurfural (HMF) to 2, 5-dimethylfuran (DMF) under atmospheric hydrogen pressure over carbon supported PdAu bimetallic catalyst. *Catalysis Today*, 232:89-98, 2014.

[116] Chen, J., Liu, R., Guo, Y., Chen, L., and Gao, H. Selective hydrogenation of biomass-based 5-hydroxymethylfurfural over catalyst of palladium immobilized on amine-functionalized metal–organic frameworks. *ACS Catalysis*, 5(2):722-733, 2015.

[117] Shen, Y., Sun, J. K., Yi, Y. X., Wang, B., Xu, F., and Sun, R. C. One-pot synthesis of levulinic acid from cellulose in ionic liquids. *Bioresource Technology*, 192:812-816, 2015.

[118] Xia, Q. N., Cuan, Q., Liu, X. H., Gong, X. Q., Lu, G. Z., and Wang, Y. Q. Pd/$NbOPO_4$ multifunctional catalyst for the direct production of liquid alkanes from aldol adducts of furans. *Angewandte Chemie*, 126(37):9913-9918, 2014.

[119] Jadhav, H., Pedersen, C. M., Sølling, T., and Bols, M. 3-Deoxy-glucosone is an Intermediate in the Formation of Furfurals from D-Glucose. *ChemSusChem*, 4(8):1049-1051, 2011.

[120] Tang, J., Zhu, L., Fu, X., Dai, J., Guo, X., and Hu, C. Insights into the kinetics and reaction network of aluminum chloride-catalyzed conversion of glucose in NaCl–H_2O/THF biphasic system. *ACS Catalysis*, 7(1):256-266, 2017.

[121] Zhao, Y., Lu, K., Xu, H., Zhu, L., and Wang, S. A critical review of recent advances in the production of furfural and 5-hydroxymethylfurfural from lignocellulosic biomass through homogeneous catalytic hydrothermal conversion. *Renewable and Sustainable Energy Reviews*, 139:110706, 2021.

[122] Xue, Z., Ma, M. G., Li, Z., and Mu, T. Advances in the conversion of glucose and cellulose to 5-hydroxymethylfurfural over heterogeneous catalysts. *RSC Advances*, 6(101):98874-98892, 2016.

[123] Jin, C., Yang, M., Shuang, E., Liu, J., Zhang, S., Zhang, X., Sheng, K., and Zhang, X. Corn stover valorization by one-step formic acid fractionation and formylation for 5-hydroxymethylfurfural and high guaiacyl lignin production. *Bioresource Technology*, 299:122586, 2020.

[124] Hou, Q., Zhen, M., Li, W., Liu, L., Liu, J., Zhang, S., Nie, Y., Bai, C., Bai, X., and Ju, M. Efficient catalytic conversion of glucose into 5-hydroxymethylfurfural by aluminum oxide in ionic liquid. *Applied Catalysis B: Environmental*, 253:1-10, 2019.

[125] Nitzsche, R., Köchermann, J., Gröngröft, A., and Kraume, M. Nanofiltration of Organosolv Hemicellulose Hydrolyzate: Influence of Hydrothermal Pretreatment and Membrane Characteristics on Filtration Performance and Fouling. *Industrial & Engineering Chemistry Research*, 60(2):916-930, 2021.

[126] Motagamwala, A. H., Huang, K., Maravelias, C. T., and Dumesic, J. A. Solvent system for effective near-term production of hydroxymethylfurfural (HMF) with potential for long-term process improvement. *Energy & Environmental Science*, 12(7):2212-2222, 2019.

[127] Zhu, L., Fu, X., Hu, Y., and Hu, C. Controlling the Reaction Networks for Efficient Conversion of Glucose into 5-Hydroxymethylfurfural. *ChemSusChem*, 13(18):4812-4832, 2020.

[128] Kitanosono, T., Masuda, K., Xu, P., and Kobayashi, S. Catalytic organic reactions in water toward sustainable society. *Chemical Reviews*, 118(2):679-746, 2018.

[129] Ranoux, A., Djanashvili, K., Arends, I. W., and Hanefeld, U. 5-Hydroxymethylfurfural synthesis from hexoses is autocatalytic. *ACS Catalysis*, 3(4):760-763, 2013.

[130] Ke, K., Ji, H., Shen, X., Kong, F., and Li, B. Pressure Reduction Enhancing the Production of 5-Hydroxymethylfurfural from Glucose in Aqueous Phase Catalysis System. *Polymers*, 13(13):2096, 2021.

[131] Kim, Y., Mittal, A., Robichaud, D. J., Pilath, H. M., Etz, B. D., St. John, P. C., Johnson, D. K., and Kim, S. Prediction of hydroxymethylfurfural yield in glucose conversion through investigation of Lewis acid and organic solvent effects. *ACS Catalysis*, 10(24):14707-14721, 2020.

[132] Aylak, A. R., Akmaz, S., and Koc, S. N. Glucose conversion to 5-hydroxymethylfurfural with chromium exchanged bentonite and montmorillonite catalysts in different solvents. *Chemical Engineering Communications*, 207(8):1103-1113, 2020.

[133] Tudino, T. C., Nunes, R. S., Mandelli, D., and Carvalho, W. A. Influence of dimethylsulfoxide and dioxygen in the fructose conversion to 5-hydroxymethylfurfural mediated by glycerol's acidic carbon. *Frontiers in Chemistry*, 8:263, 2020.

[134] Patrylak, L., Konovalov, S., Pertko, O., Yakovenko, A., Povazhnyi, V., and Melnychuk, O. Obtaining Glucose-Based 5-Hydroxymethylfurfural on Large-Pore Zeolites. *Eastern-European Journal of Enterprise Technologies*, 2(6), 110, 2021.

[135] Tang, Z., and Su, J. Direct Conversion of Glucose to 5-Hydroxymethyl-furfural (HMF) Using an Efficient and Inexpensive Boehmite Catalyst in Dimethyl Sulfoxide. *BioResources*, 14(3):5943-5963, 2019.

[136] Ren, L. K., Zhu, L. F., Qi, T., Tang, J. Q., Yang, H. Q., and Hu, C. W. Performance of dimethyl sulfoxide and Brønsted acid catalysts in fructose conversion to 5-hydroxymethylfurfural. *ACS Catalysis*, 7(3):2199-2212, 2017.

[137] Li, W., Yang, T., Su, M., and Liu, Y. Catalytic Conversion of Glucose to 5-Hydroxymethylfurfural and Furfural by a Phosphate-Doped SnO_2 Catalyst in γ-Valerolactone-Water System. *Catalysis Letters*, 150(11):3304-3313, 2020.

[138] Huang, F., Li, W., Liu, Q., Zhang, T., An, S., Li, D., and Zhu, X. Sulfonated tobacco stem carbon as efficient catalyst for dehydration of C6 carbohydrate to 5-hydroxymethylfurfural in γ-Valerolactone/water. *Fuel Processing Technology*, 181:294-303, 2018.

[139] Song, B., Yu, Y., and Wu, H. Tuning glucose decomposition in hot-compressed gamma-valerolactone/water mixtures: From isomerization to dehydration reactions. *Fuel*, 238:225-231, 2019.

[140] Song, B., Wu, Z., Yu, Y., and Wu, H. Hydrothermal Reactions of Biomass-Derived Platform Molecules: Distinct Effect of Aprotic and Protic Solvents on Primary Decomposition of Glucose and Fructose in Hot-Compressed Solvent/Water Mixtures. *Industrial & Engineering Chemistry Research*, 59(16):7336-7345, 2020.

[141] Naveed, A., Rasheed, T., Raza, B., Chen, J., Yang, J., Yanni, N., and Wang, J. Addressing thermodynamic Instability of Zn anode: classical and recent advancements. *Energy Storage Materials*, 44:206-230, 2022.

[142] Nie, Y., Hou, Q., Li, W., Bai, C., Bai, X., and Ju, M. (2019). Efficient synthesis of furfural from biomass using $SnCl_4$ as catalyst in ionic liquid. *Molecules*, 24(3):594, 2019.

[143] Wang, H., Zhu, C., Li, D., Liu, Q., Tan, J., Wang, C., Cai, C., and Ma, L. Recent advances in catalytic conversion of biomass to 5-hydroxymethylfurfural and 2, 5-dimethylfuran. *Renewable and Sustainable Energy Reviews*, 103:227-247, 2019.

[144] Hou, Q., Zhen, M., Li, W., Liu, L., Liu, J., Zhang, S., Nie, Y., Bai, C., Bai, X., and Ju, M. Efficient catalytic conversion of glucose into 5-hydroxymethylfurfural by aluminum oxide in ionic liquid. *Applied Catalysis B: Environmental*, 253:1-10, 2019.

[145] Bai, C., Hou, Q., Bai, X., Nie, Y., Qian, H., Zhen, M., and Ju, M. Conversion of Glucose to 5-Hydroxymethylfurfural at High Substrate Loading: Effect of Catalyst and Solvent on the Stability of 5-Hydroxymethylfurfural. *Energy & Fuels,* 34(12):16240-16249, 2020.

[146] Hou, Q., Zhen, M., Liu, L., Chen, Y., Huang, F., Zhang, S., Li, W., and Ju, M. Tin phosphate as a heterogeneous catalyst for efficient dehydration of glucose into 5-hydroxymethylfurfural in ionic liquid. *Applied Catalysis B: Environmental*, 224:183-193, 2018.

[147] Nowicki, J., and Stanek, N. Conversion of selected carbohydrates into furan aldehydes in aqueous media. Effect of cation structure of imidazolium ionic liquids on the selectivity phenomena. *Biomass and Bioenergy*, 154:106252, 2021.

[148] Xu, Z., Yang, Y., Yan, P., Xia, Z., Liu, X., and Zhang, Z. C. Mechanistic understanding of humin formation in the conversion of glucose and fructose to 5-hydroxymethylfurfural in [BMIM] Cl ionic liquid. *RSC Advances*, 10(57):34732-34737, 2020.

[149] Eminov, S., Wilton-Ely, J. D., and Hallett, J. P. Highly selective and near-quantitative conversion of fructose to 5-hydroxymethylfurfural using mildly acidic ionic liquids. *ACS Sustainable Chemistry & Engineering*, 2(4):978-981, 2014.

[150] Naz, S., Uroos, M., and Muhammad, N. One-pot production of 5-hydroxymethylfurfural and simultaneous lignin recovery from non-food lignocellulosic wastes using cost-effective ionic liquids. *Biomass Conversion and Biorefinery,* 1-12, 2022.

[151] Rathod, P. V., Mujmule, R. B., Chung, W. J., Jadhav, A. R., and Kim, H. Efficient dehydration of glucose, sucrose, and fructose to 5-hydroxymethylfurfural using tri-cationic ionic liquids. *Catalysis Letters*, 149(3):672-687, 2019.

[152] Delbecq, F., and Len, C. Recent advances in the microwave-assisted production of hydroxymethylfurfural by hydrolysis of cellulose derivatives—a review. *Molecules*, 23(8):1973, 2018.

[153] Sener, C., Motagamwala, A. H., Alonso, D. M., and Dumesic, J. A. Enhanced Furfural Yields from Xylose Dehydration in the γ-Valerolactone/Water Solvent System at Elevated Temperatures. *ChemSusChem*, 11(14):2321-2331, 2018.

[154] Zhao, Y., Xu, H., Lu, K., Qu, Y., Zhu, L., and Wang, S. Experimental and kinetic study of arabinose conversion to furfural in renewable butanone–water solvent mixture catalyzed by Lewis acidic ionic liquid catalyst. *Industrial & Engineering Chemistry Research*, 58(36):17088-17097, 2019.

[155] Jing, Y., Guo, Y., Xia, Q., Liu, X., and Wang, Y. Catalytic production of value-added chemicals and liquid fuels from lignocellulosic biomass. *Chem*, 5(10):2520-2546, 2019.

[156] Xia, H., Hu, H., Xu, S., Xiao, K., and Zuo, S. Catalytic conversion of glucose to 5-hydroxymethyfural over Fe/β zeolites with extra-framework isolated Fe species in a biphasic reaction system. *Biomass and Bioenergy*, 108:426-432, 2018.

[157] Candu, N., El Fergani, M., Verziu, M., Cojocaru, B., Jurca, B., Apostol, N., Teodorescu, C., Parvulescu, V. I., and Coman, S. M. Efficient glucose dehydration to HMF onto Nb-BEA catalysts. *Catalysis Today*, 325:109-116, 2019.

[158] Yang, L., Yan, X., Xu, S., Chen, H., Xia, H., and Zuo, S. One-pot synthesis of 5-hydroxymethylfurfural from carbohydrates using an inexpensive $FePO_4$ catalyst. *RSC Advances*, 5(26):19900-19906, 2015.

[159] Nahavandi, M., Kasanneni, T., Yuan, Z. S., Xu, C. C., and Rohani, S. Efficient conversion of glucose into 5-hydroxymethylfurfural using a sulfonated carbon-based solid acid catalyst: an experimental and numerical study. *ACS Sustainable Chemistry & Engineering*, 7(14):11970-11984, 2019.

[160] Guo, W., Heeres, H. J., and Yue, J. Continuous synthesis of 5-hydroxymethylfurfural from glucose using a combination of AlCl3 and HCl as catalyst in a biphasic slug flow capillary microreactor. *Chemical Engineering Journal*, 381:122754, 2020.

[161] Chen, G., Sun, Q., Xu, J., Zheng, L., Rong, J., and Zong, B. Sulfonic Derivatives as Recyclable Acid Catalysts in the Dehydration of Fructose to 5-Hydroxymethylfurfural in Biphasic Solvent Systems. *ACS omega*, 6(10):6798-6809, 2021.

[162] Zhang, T., Wei, H., Xiao, H., Li, W., Jin, Y., Wei, W., and Wu, S. Advance in constructing acid catalyst-solvent combinations for efficient transformation of glucose into 5-Hydroxymethylfurfural. *Molecular Catalysis,* 498:111254, 2020.

[163] Tang, Z., and Su, J. One step conversion of glucose into 5-hydroxymethylfurfural (HMF) via a basic catalyst in mixed solvent systems of ionic liquid-dimethyl sulfoxide. *Journal of Oleo Science*, ess18196, 2019.

[164] Tang, Z., & Su, J. Direct conversion of cellulose to 5-hydroxymethylfurfural (HMF) using an efficient and inexpensive boehmite catalyst. *Carbohydrate Research*, 481:52-59, 2019.

[165] Graham, B. J., and Raines, R. T. Efficient metal-free conversion of glucose to 5-hydroxymethylfurfural using a boronic acid. *Biomass Conversion and Biorefinery*, 9(2):471-477, 2019.

[166] Liu, L., Yang, X., Hou, Q., Zhang, S., and Ju, M. Corn stalk conversion into 5-hydroxymethylfurfural by modified biochar catalysis in a multi-functional solvent. *Journal of Cleaner Production*, 187:380-389, 2018.

[167] Rodriguez Quiroz, N., Norton, A. M., Nguyen, H., Vasileiadou, E., and Vlachos, D. G. Homogeneous metal salt solutions for biomass upgrading and other select organic reactions. *ACS Catalysis*, 9(11):9923-9952, 2019.

[168] Sadula, S., Oesterling, O., Nardone, A., Dinkelacker, B., and Saha, B. One-pot integrated processing of biopolymers to furfurals in molten salt hydrate: understanding synergy in acidity. *Green Chemistry*, 19(16):3888-3898, 2017.

[169] Doustkhah, E., Lin, J., Rostamnia, S., Len, C., Luque, R., Luo, X., Bando, Y., Wu, K. C. W., Kim, J., Yamauchi, Y., and Ide, Y. Development of sulfonic-acid-functionalized mesoporous materials: synthesis and catalytic applications. *Chemistry*, 25(7):1614-1635, 2019.

[170] Fang, X., Wang, Z., Yuan, B., Song, W., Li, S., and Lin, W. Efficient Conversion of Cellulose to 5-Hydroxymethylfurfural in $NaHSO_4/ZrO_2/H_2O$-THF Biphasic System. *ChemistrySelect*, 3(43):12243-12249, 2018.

[171] Cortez-Elizalde, J., Silahua-Pavón, A. A., Córdova-Pérez, G. E., Arévalo-Pérez, J. C., Guerra-Que, Z., Espinosa-González, C. G., Ortiz-Chi, F., Godavarthi, F., and Torres-Torres, J. G. Production of 5-Hydroxymethylfurfural from glucose using Al_2O_3-TiO_2-ZrO_2 ternary catalysts. *Catalysis Today,* 392:116-130, 2021.

[172] Tomer, R., and Biswas, P. Dehydration of glucose/fructose to 5-hydroxymethylfurfural (5-HMF) over an easily recyclable sulfated titania (SO_4^{2-}/TiO_2) catalyst. *New Journal of Chemistry*, 44(47):20734-20750, 2020.

[173] Zhao, Y., Eley, C., Hu, J., Foord, J. S., Ye, L., He, H., and Tsang, S. C. E. Shape-Dependent Acidity and Photocatalytic Activity of Nb_2O_5 Nanocrystals with an Active TT (001) Surface. *Angewandte Chemie*, 124(16):3912-3915, 2012.

[174] Khumho, R., Yousatit, S., and Ngamcharussrivichai, C. Glucose Conversion into 5-Hydroxymethylfurfural over Niobium Oxides Supported on Natural Rubber-Derived Carbon/Silica Nanocomposite. *Catalysts*, 11(8):887, 2021.

[175] Kang, S., Miao, R., Guo, J., and Fu, J. Sustainable production of fuels and chemicals from biomass over niobium-based catalysts: A review. *Catalysis Today*, 374:61-76, 2021.

[176] García-López, E. I., Pomilla, F. R., Megna, B., Testa, M. L., Liotta, L. F., and Marcì, G. (2021). Catalytic dehydration of fructose to 5-hydroxymethylfurfural in aqueous medium over Nb_2O_5-based catalysts. *Nanomaterials*, 11(7):1821, 2021.

[177] Morawa Eblagon, K., Malaika, A., Ptaszynska, K., Pereira, M. F. R., and Figueiredo, J. L. Impact of thermal treatment of Nb_2O_5 on its performance in glucose dehydration to 5-hydroxymethylfurfural in water. *Nanomaterials*, 10(9):1685, 2020.

[178] Ramesh, A., Rajesh, D., Shanthi, K., Bhargav, P. B., and Nguyen-Le, M. T. Catalytic conversion of glucose to 5-hydroxymethylfurfural productions over sulphated Ti-Al_2O_3 catalysts. *Biomass and Bioenergy*, 154:106261, 2021.

[179] Pattnaik, F., Tripathi, S., Patra, B. R., Nanda, S., Kumar, V., Dalai, A. K., and Naik, S. Catalytic conversion of lignocellulosic polysaccharides to commodity biochemicals: a review. *Environmental Chemistry Letters*, 19(6):4119-4136, 2021.

[180] Li, W., Sun, L., Xie, L., Deng, X., Guan, N., and Li, L. Coordinatively unsaturated sites in zeolite matrix: Construction and catalysis. *Chinese Journal of Catalysis*, 40(9):1255-1281, 2019.

[181] van der Graaff, W. N., Tempelman, C. H., Pidko, E. A., and Hensen, E. J. Influence of pore topology on synthesis and reactivity of Sn-modified zeolite catalysts for carbohydrate conversions. *Catalysis Science & Technology*, 7(14):3151-3162, 2017.

[182] Bayu, A., Abudula, A., and Guan, G. Reaction pathways and selectivity in chemo-catalytic conversion of biomass-derived carbohydrates to high-value chemicals: A review. *Fuel Processing Technology*, 196:106162, 2019.

[183] Moreno-Recio, M., Jiménez-Morales, I., Arias, P. L., Santamaría-González, J., and Maireles-Torres, P. The Key Role of Textural Properties of Aluminosilicates in the Acid-Catalysed Dehydration of Glucose into 5-Hydroxymethylfurfural. *ChemistrySelect*, 2(8):2444-2451, 2017.

[184] Ginés-Molina, M. J., Ahmad, N. H., Mérida-Morales, S., García-Sancho, C., Mintova, S., Eng-Poh, N., and Maireles-Torres, P. Selective conversion of glucose to 5-Hydroxymethylfurfural by using L-type zeolites with different morphologies. *Catalysts*, 9(12):1073, 2019.

[185] Velaga, B., and Peela, N. R. Seed-assisted and OSDA-free synthesis of H-mordenite zeolites for efficient production of 5-hydroxymethylfurfural from glucose. *Microporous and Mesoporous Materials*, 279:211-219, 2019.

[186] Manayil, J. C., Lee, A. F., and Wilson, K. Functionalized periodic mesoporous organosilicas: tunable hydrophobic solid acids for biomass conversion. *Molecules*, 24(2):239, 2019.

[187] Jiang, C., Zhu, J., Wang, B., Li, L., and Zhong, H. One-pot synthesis of 5-hydroxymethylfurfural from glucose over zirconium doped mesoporous KIT-6. *Chinese Journal of Chemical Engineering*, 26(6):1270-1277, 2018.

[188] Li, X., Peng, K., Liu, X., Xia, Q., and Wang, Y. Comprehensive Understanding of the Role of Brønsted and Lewis Acid Sites in Glucose Conversion into 5-Hydromethylfurfural. *ChemCatChem*, 9(14):2739-2746, 2017.

[189] Zhu, Y., Xu, X., He, J., Guo, J., and Song, K. Effective Dehydration of Fructose Over Stable Ti-Doped SBA-15 Catalysts. *Frontiers in Chemistry*, 9:817417, 2021.

[190] Gomes, F. N., Mendes, F. M., and Souza, M. M. Synthesis of 5-hydroxymethylfurfural from fructose catalyzed by phosphotungstic acid. *Catalysis Today*, 279:296-304, 2017.

[191] Lv, G., Deng, L., Lu, B., Li, J., Hou, X., and Yang, Y. Efficient dehydration of fructose into 5-hydroxymethylfurfural in aqueous medium over silica-included heteropolyacids. *Journal of Cleaner Production*, 142:2244-2251, 2017.

[192] Rahaman, M. S., Tulaphol, S., Hossain, M. A., Jasinski, J. B., Sun, N., George, A., Simmons, B. A., Maihom, T., Crocker, M., and Sathitsuksanoh, N. Cooperative Brønsted-Lewis acid sites created by phosphotungstic acid encapsulated metal–organic frameworks for selective glucose conversion to 5-hydroxymethylfurfural. *Fuel*, 310:122459, 2022.

[193] Wang, X., Lv, T., Wu, M., Sui, J., Liu, Q., Liu, H., Huang, J., and Jia, L. Aluminum doped solid acid with suitable ratio of Brønsted and Lewis acid sites synthesized by electric-flocculation of phosphotungstic acid via hydrothermal treatment for producing 5-hydroxymethylfurfural from glucose. *Applied Catalysis A: General*, 574:87-96, 2019.

[194] Mahajan, A., and Gupta, P. Carbon-based solid acids: a review. *Environmental Chemistry Letters*, 18(2):299-314, 2020.

[195] Konwar, L. J., Mäki-Arvela, P., and Mikkola, J. P. SO_3H-containing functional carbon materials: synthesis, structure, and acid catalysis. *Chemical Reviews*, 119(22):11576-11630, 2019.

[196] Clohessy, J., and Kwapinski, W. Carbon-based catalysts for biodiesel production—a review. *Applied Sciences*, 10(3):918, 2020.

[197] Zhang, T., Li, W., Jin, Y., and Ou, W. Synthesis of sulfonated chitosan-derived carbon-based catalysts and their applications in the production of 5-hydroxymethylfurfural. *International Journal of Biological Macromolecules*, 157:368-376, 2020.

[198] Wang, K., Rezayan, A., Si, L., Zhang, Y., Nie, R., Lu, T., Wang, J., and Xu, C. Highly Efficient 5-Hydroxymethylfurfural Production from Glucose over Bifunctional SnO_x/C catalyst. *ACS Sustainable Chemistry & Engineering*, 9(34):11351-11360, 2021.

[199] Kang, S., Fu, J., and Zhang, G. From lignocellulosic biomass to levulinic acid: A review on acid-catalyzed hydrolysis. *Renewable and Sustainable Energy Reviews*, 94:340-362, 2018.

[200] Guan, J., Cao, Q., Guo, X., and Mu, X. The mechanism of glucose conversion to 5-hydroxymethylfurfural catalyzed by metal chlorides in ionic liquid: A theoretical study. *Computational and Theoretical Chemistry*, 963(2-3):453-462, 2011.

[201] Li, G., Pidko, E. A., Hensen, E. J., and Nakajima, K. A density functional theory study of the mechanism of direct glucose dehydration to 5-hydroxymethylfurfural on anatase titania. *ChemCatChem*, 10(18):4084-4089, 2018.

[202] Yue, C., Li, G., Pidko, E. A., Wiesfeld, J. J., Rigutto, M., and Hensen, E. J. (2016). Dehydration of glucose to 5-hydroxymethylfurfural using Nb-doped tungstite. *ChemSusChem*, 9(17):2421-2429, 2016.