Integration of Deep Eutectic Solvents and Hydrotalcites for Biomass Conversion and Aldol Condensation: Toward Platform Chemicals and Jet Fuel Synthesis—A Review

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Abstract

The abundance and renewability of lignocellulosic biomass have made it a suitable alternative to fossil fuels in the reduction of global warming. The complex nature of the cellulose–hemicellulose–lignin bonds in the biomass makes it difficult to directly obtain platform chemicals. Pretreatment of the biomass has become a solution to remove lignin and obtain cellulose and or hemicellulose to produce platform chemicals. Platform chemicals such as hydroxymethylfurfural, furfural, and levulinic acid are viable feedstocks for aldol condensation to produce C_8–C_{15} fuels. This review reports on deep eutectic solvents and microwave-assisted pretreatment as green techniques for the delignification and platform chemicals production. Emphasis is placed on the use of hydrotalcites (HTs) as catalysts in platform chemicals production and aldol condensation for C_8–C_{15} alkane fuels. Additionally, the hydrogenation of furfural into cyclopentanone and successive conversion into C_{10} and C_{15} alkanes with HTs was reviewed.

Keywords: Aldol reaction, Biorefinery, Hydrogen bonds, Hydrotalcite, Platform chemicals

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1 Introduction

Global warming has become a universal problem, and the replacement of fossil fuels with biomass has been a means to curb it. The conversion of biomass into platform chemicals can serve as an alternative for the use of fossil fuels and as the precursor for about 90 % of commercial chemicals [1]. Biomass such as forestry waste, agricultural waste, and paper waste are renewable, abundant, and carbon-neutral in nature and therefore do not negatively affect the environment [2]. Forestry and agricultural waste are very predominant in the environment and generally used as manure or just burned to clear the land. About 27 % of municipal solid waste is also made up of paper waste [3]. However, the reuse of paper waste does not only add an economic value to the residue but also reduces paper waste by 82 %, air pollution and greenhouse gases by 30 % and 40 %, respectively, and the energy required for the production of the paper products by 40 % [3].

The global annual availability of lignocellulosic biomass (LCB) is approximately 170–200 billion tons [4]. The bio-based chemical industry targets the utilization of LCB to create products with properties equivalent to those produced from fossil sources with lower environmental footprints [5]. In 2020, the European Commission reported that bio-based chemicals constituted around 22 % of the year's chemical sales, a percentage anticipated to increase [6].

The diverse LCB feedstock exhibits varying compositions of its three major components: cellulose (30–60 %), hemicellulose (20–40 %), and lignin (15–25 %) [7]. Overcoming the recalcitrant nature of LCB to add value involves pretreatment, which deconstructs and separates its main constituents. Most biorefineries prioritize the separation of cellulose and hemicellulose from LCB to produce platform chemicals. Simultaneously, the isolated lignin is commonly utilized for energy production, contributing to the conversion of cellulose and hemicellulose into these platform chemicals. Additionally, the isolated lignin finds applications in the synthesis of carbon fibers, engineered plastics, thermoplastics, elastomers, polymeric foams, battery components, and various aromatic chemicals [1, 8].

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LCB conversion into platform chemicals involves a pretreatment to break down its structure, hydrolysis of the polysaccharide fraction into sugars, and catalytic conversion into platform chemicals [9]. These chemicals serve as basic building blocks for synthesizing high-value products like biojet fuel, resins, bioplastics, additives, and other bio-based materials for various applications [10–12]. The aviation industry has shown interest in biojet fuels as a sustainable alternative, with over 300 million liters produced globally in 2022 [13]. The European Union's push to increase biojet fuel use in the aviation industry by 6 % in 2030 has further fueled this interest.

Over the years, various pretreatment techniques based on chemical, physical, and biological processes have been developed to remove lignin from LCB, enhancing the accessibility of cellulose to biological and chemical treatments. Despite their merits, many pretreatment methods are environmentally unfriendly and energy-intensive, contributing up to 20 % of the total glucose production cost [14, 15]. Hence, there is a growing need for an energy-efficient treatment that is both economically and environmentally friendly. In response, novel green pretreatments such as pulsed electric field (PEF), inorganic salts, and deep eutectic solvents (DESs) pretreatments have emerged, offering fractionation effectiveness, potential for low cost, reduced chemical waste production, chemical recovery, and environmental friendliness [16, 17].

To harness the functionalized cellulose and hemicellulose obtained from LCB, treatment processes are essential for converting them into specialized products, including platform chemicals and alkane fuels [18]. Platform chemicals are chemicals that can be used as substrates to produce other high-values chemicals. The United States Department of Energy identified 12 potential platform chemicals that can be produced from LCB [19]. While various platform chemicals exist, studies have predominantly focused on the fermentation of cellulosic sugars to produce ethanol and lactic acid (LA) [20, 21]. Production of platform chemicals such as hydroxymethylfurfural (HMF), furfural, and levulinic acid (LevA) is still limited causing their price to double, compared to ethanol and LA [3]. Consequently, exploring pathways for the production of HMF, LevA, and furfural could offer enhanced benefits, and it is a priority for the development of a biogenic carbon-based chemical industry.

In platform chemical production, DES and microwave irradiation are employed for the hydrolysis of cellulose and hemicellulose, leading to the production of HMF, furfural, and LevA [22]. The effectiveness of these techniques hinges on substrate composition and treatment severity, with a higher severity needed for the production of platform chemicals like LevA, HMF, or furfural, compared to hemicellulose and cellulose pretreatments [23]. Optimization of process conditions is essential to achieve high selectivity for specific products.

Monomeric sugars derived from carbohydrate hydrolysis are used to produce platform chemicals like furfural, HMF, and LevA. Xylose dehydration yields furfural, while glucose dehydration produces HMF from cellulose and hemicellulose. LevA is then obtained through the rehydration of HMF. Catalysts can be employed to enhance reaction speed and overall production yield.

Catalysts have also gained an important place in this conversion process due to the ability to perform hydrolysis, hydration, and condensation reactions for these carbohydrates [2]. In comparison with traditional homogeneous catalysts, these heterogeneous catalysts present advantages such as ease of separation, reusability, improved selectivity, less equipment corrosivity, and improved process safety [2, 24]. Furthermore, they are industrially applicable in the above-mentioned treatment processes [25]. Among solid catalysts, hydrotalcites (HTs), which are solid basic catalysts have recently been reported [2]. HTs have also shown good functionality in the production of platform chemicals and aldol condensation for the production of fuel-grade alkanes [26, 27].

The application of techniques such as DES and microwave-irradiation and HT catalysts to produce platform chemicals and fuel alkanes offers economic and green sustainable methods that require more attention. Therefore, this review focuses on the fractionation of LCB into its polysaccharides using DES and microwave pretreatments. Furthermore, the current state of furfural, HMF, and LevA production from the obtained carbohydrates using microwave-assisted DES treatment or heterogeneous catalysts was also reviewed. As the catalyst of focus, the role of HTs in platform chemicals production and latter aldol condensation processes to produce fuel was also discussed.

2 LCB Pretreatment

The intricate structure and resistance of LCB is a challenge to efficiently convert polymeric sugars (cellulose and hemicellulose) into monomeric sugars. Pretreatment is essential to break down this complex structure (Fig. 1), making polymeric sugars accessible for further conversion while minimizing

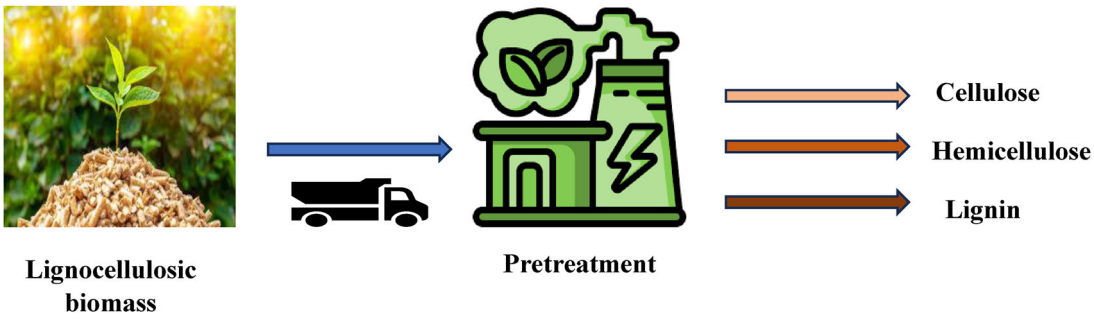

Figure 1. Pretreatment of lignocellulosic biomass to obtain cellulose, hemicellulose, and lignin.

constituent loss. Various pretreatment methods, including physical (e.g., ball milling, microwave, ultrasound, pyrolysis), chemical (e.g., acid, alkaline, organosolv, ozonolysis, etc.), physiochemical (e.g., ammonia fiber explosion, steam explosion, hot water), and biological (e.g., enzyme and microbial) approaches, have been developed. Despite achieving some success, these methods face challenges such as high energy consumption, excessive use of non-recyclable chemicals, specialized equipment requirements, low-solid loading, prolonged operating times, low polymeric sugar yields, or environmental concerns [28, 29]. In response to these issues, innovative green pretreatment techniques like inorganic salts, PEF, and DES pretreatment have been introduced.

2.1 PEF

One of the most recent and less studied pretreatment is the PEF. This treatment is an innovative method that enhances biomass porosity and permeability through short yet intense, high-voltage pulses (5.0–20.0 kV cm^{-1}) lasting from nano to milliseconds to cause significant electroporation without inducing substantial heating effects [30–32]. This treatment induces a rapid and uniform temperature increase in the biomass due to the Joule effect [31]. This disruption allows intracellular compounds to pass into the surrounding solution. PEF can cause either lethal damage to cells or induce sublethal stress by transiently permeabilizing cell membranes and facilitating the electrophoretic movement of charged species between cellular compartments [33].

The PEF technique is cost-efficient with low energy requirements, suitable for biorefinery conditions, and enhances cellulose hydrolysis efficiently [30]. PEF treatment allows compound extraction without altering biomass chemical composition [34]. PEFs break LCB cell walls without forming inhibitors. While simple, it is typically used on fresh LCB and needs modification for dry feedstock [30]. PEF application promotes delignification and surface porous formation in biomass [35]. Kumar et al. demonstrated that pretreating LCB with PEF (2000 pulses and 10 kV cm^{-1} field strength) enhanced biomass conversion into value-added products [36]. Despite the major successes in the extracting of polyphenols, proteins, and anthocyanins from LCB, very little research has been conducted in the field of carbohydrates extraction or lignin removal from biomass [37].

2.2 Inorganic Salts

Innovative pretreatment strategies involving inorganic salts either as an aqueous solution in an acid-free setting or as catalysts in acid pretreatment, often combined with methods like microwave irradiation or organosolv, have been recently studied [38]. Salts like NaCl, KCl, $CaCl_2$, $MgCl_2$, $Fe_2(SO_4)_3$, $FeCl_2$, $ZnCl_2$, $FeSO_4$, and $FeCl_3$ have been employed for pretreating various LCB, forming complexes with metal cations acting as Lewis acids to break hemicellulose glycosidic bonds, yielding xylose [32]. Metal salts assist in enhancing lignin removal, hemicellulose degradation, achieving complete biomass conversion, ensuring higher reaction rates, and offering a non-toxic, environmentally friendly process without the need for expensive corrosion-resistant reactors [32, 39, 40].

Comparing NaCl, NaOH, and hot water pretreatments, NaOH and NaCl exhibited similar delignification yield (28 % and 26 %, respectively), while hot water had the lowest lignin removal (5 %) [41]. In a microwave-assisted pretreatment using water, NaOH, H_2SO_4, and $FeCl_3$, the latter demonstrated the highest removal of hemicellulose (90 %), lignin (80 %), and cellulose (52 %) after 5 min [42]. $MgCl_2$ removed approximately 90 % hemicellulose and 10 % cellulose from eucalyptus at a severity of 4.5 [43]. Moodley and Kana explored NaCl, $ZnCl_2$, and $FeCl_3$ in microwave-assisted pretreatment of sugarcane leaf waste, observing increased effectiveness with the higher valence of metal cation ($Fe^{3+} > Zn^{2+} > Na^{+}$) [44]. The cellulose content was highest in microwave-assisted $FeCl_3$-treated biomass (62 % vs. 45 %), while hemicellulose was lowest (8% vs. 27%), compared to native biomass. Zhang et al. found $AlCl_3$ to outperform $FeCl_3$ in improving biomass for saccharification in a ball mill-assisted pretreatment [45]. In a study on the effect of two aluminum salts during microwave heating, $Al_2(SO4)_3$ removed more lignin (42 % vs. 33 %) than $AlK(SO_4)_2$ [46]. The main limitation of this pretreatment is the scarcity of research, hindering a comprehensive understanding of catalyst effects.

2.3 DESs

Chemical pretreatments are widely used for LCB fractionation, with DESs emerging as a more effective alternative. DES offers advantages such as cost-effectiveness, ease of preparation, lack of purification requirements, and biodegradability [47]. Notably, DES exhibits superior LCB dissolution, compared to traditional chemical pretreatments [48, 49]. DES is an eutectic mixture of two or more compounds composed of a hydrogen bond acceptor (HBA) and hydrogen bond donor (HBD). DES comprising an HBA and HBD, leverages electron acceptance and donation to dissolve polysaccharides [47]. However, the weak susceptibility of the hydrogen bond between the HBA and HBD in DES, compared to the cellulose chain hydrogen bond, leads to limited dissolution [50]. The release of H^+ from the DES HBD disrupts ester and ether bonds between lignin and hemicellulose, facilitating their dissolution [51]. Despite negligible cellulose dissolution, DES pretreatment enhances accessibility to cellulose for subsequent treatments by removing hemicellulose and lignin from LCB [52, 53].

Choosing an appropriate HBA is crucial for enhancing dissolution efficiency, with emphasis on selecting the right HBD (Tab. 1) [54]. Polyalcohol-based DES exhibits selective lignin extraction, with higher hydrophobicity enhancing LCB fractionation. Hou et al. found increased lignin removal in the order ethylene glycol < 1,2-propanediol < 1,3-propanediol using a DES formed from ChCl and polyalcohols [23]. Acidifying polyalcohol-based DES can improve efficiency, but it leads to a twofold increase in energy consumption during DES recycling at 20 % water content [55]. At 20 % water content in ChCl-ethylene glycol-acidified DES, delignification efficiency is not significantly affected, but maintaining water content at 10 % is recommended for maximum lignin and sugar yields [56].

Table 1. Deep eutectic solvent (DES) pretreatment of lignocellulosic biomass (LCB) and effects on cell wall composition.

LCB	DES	Molar ratio	Pretreatment conditions	Biopolymer composition in solid fraction [%]				Percent removal from biomass [%]			Reference
				C	H	L	SR	C	H	L	
Corn cob	BTMAC-LA	1:2	S/L = 1:20, 140 °C, 2 h	72.2	6.1	5.9	50.9	4.5	80.8	63.4	[68]
Wheat straw	BTEAC-LA	1:9	S/L = 1:15, 100 °C, 6 h	50	10	10	55	20	66	65	[69]
Corn stover	TMAC-LA	1:2	S/L = 1:10, 130 °C, 2 h				50.41	15.01	78.66	62.57	[70]
	ChCl-LA	1:2					48.83	17.3	77.61	61.93	
Oil palm empty fruit brunch	K_2CO_3-Gly	1:6	S/L = 1:10, 120 °C, 8 h	37.6	14.4	13.7	74.8	25	36	51	[57]
	ChCl-LA	1:5		71.4		4.7	53.1		100	88	
Switchgrass[a)]	ChCl-Gly	1:2	S/L = 1:10, 121 °C, 1 h	60.32	7.36	14.89	49.41	5.62	80.97	63.84	[55]
Switchgrass[b)]	ChCl-EG	1:2	S/L = 1:5, 121 °C, 1 h					2	75	78.9	[56]
Oil palm empty fruit brunch	ChCl-FA	1:1.5	S/L = 1:19, 100 °C, 2 h					6.6	83.8	0.98	[60]
Oil palm empty fruit brunch	ChCl-FA	1:2	S/L = 1:10, 120 °C, 8 h	85		7	50				[49]
Akebia herb residues	ChCl-FA	1:2	S/L = 1:10, 120 °C, 8 h					2.2	87	40.7	[48]
Corn cob	ChCl-OxA	1:1	S/L = 1:20, 90 °C, 24 h				53.1			98.5	[52]
Rice straw	ChCl-OxA	1:2	S/L = 1:20, 120 °C, 1 h	61.5	0.2	13.5	40.2	27.7	99.6	75.1	[23]
Rice straw	ChCl-OxA	1:1	S/L = 1:20, 120 °C, 3 h	54.3	1.1	33.4	58.4	10.7	96.9	9.3	[71]
	ChCl-LA			54.6	6.6	26.6	60.3	7.3	80.7	25.4	
Rice straw	ChCl-LA	1:5	S/L = 1:20, 60 °C, 12 h	46	24.6	3.8	95			6.8	[72]
Miscanthus[c)]	ChCl-LA	1:2	S/L = 1:10, 152 °C, 45 s	67.7	6.9	18.4	53.2	4	77.5	65.2	[17]
Switchgrass[c)]	ChCl-LA	1:2		64.5	7.2	11.5	50.5	8.1	83.7	72.2	
Corn stover[c)]	ChCl-LA	1:2		65.8	5	9.2	36.6	24.9	90.1	79.6	
Switchgrass	ChCl-LA	1:2	S/L = 3:17, 130 °C, 0.5 h	71.4	9.9	7.3	46.3	2.1	80.4	83.4	[73]
Bamboo residues	ChCl-LA	1:4	S/L = 1:15, 130 °C, 1.5 h				51.3	4.1	75.7	83.6	[59]
Willow	ChCl-LA	1:10	S/L = 1:30, 120 °C, 12 h					19.16	90.26	93.8	[74]

Where BTMAC is benzyltrimethylammonium chloride; BTEAC is benzyltriethylammonium chloride; K_2CO_3 is potassium carbonate; ChCl is choline chloride; LA is lactic acid; EG is ethylene glycol; Gly is glycerol; FA is formic acid; OxA is oxalic acid; S/L is solid to liquid ratio, C is cellulose; H is hemicellulose; L is lignin; SR is solid recovery. a) 20 wt % water and 0.9 % H_2SO_4 added to the DES during pretreatment; b) DES acidified by adding 1 % H_2SO_4; c) DES treatment performed with the assistance of a microwave at 800 W.

Acid-based DESs, extensively investigated, enhance both lignin and hemicellulose removal by approximately 30 %, compared to their respective organic acids [48, 49]. Acid-based DESs can remove around 100 % hemicellulose, 99 % lignin, and up to 14 % cellulose from LCB at temperatures above 100 °C [52, 57, 58]. Increasing the molar ratio from 1:1 to 1:4 in ChCl-LA DES improves lignin (25.5 % to 83.6 %) and xylan (56.1 % to 75.5 %) removal yields with minimal impact (>5 %) on glucan removal. Further increasing the molar ratio from 1:4 to 1:8 does not significantly alter lignin (84.1 %) and xylan (77.1 %) removals, highlighting the importance of selecting an adequate molar ratio [59].

While LA is the most commonly used acid-based DES, formic acid (FA) and oxalic acid (OxA) also demonstrate effective delignification [17, 49, 52, 57]. Zhang et al. found that, under similar treatment conditions, ChCl-OxA achieved 98.5 % delignification, compared to ChCl-LA with 64.7 % delignification [52]. However, ChCl-OxA, with high lignin removal, generated carbon dioxide and charred residues at elevated treatment temperatures, leading to a lower glucose yield. FA, a simple carboxylic acid with a shorter hydrocarbon chain and a simpler side chain (−H), exhibited higher LCB dissolution strength and delignification than LA, which has a longer hydrocarbon chain and a larger side chain [60]. Muley et al. conducted a study on the effects of LA, FA, and OxA-based DES in a microwave treatment of pinewood sawdust, finding that under optimal conditions, lignin removal followed the order ChCl-FA > ChCl-OxA > ChCl-LA, with FA consistently achieving lignin removal above 80 % at 150 °C [61].

The complex bonding in LCB necessitates elevated treatment temperatures and times for successful fractionation. However, extended conditions increase the risk of side reactions, reducing selectivity and yield [62]. Microwave-assisted pretreatment is an effective method to enhance heat transfer, prevent partial

overheating, accelerate reactions, break LCB bonds, and release constituents. Liu et al. demonstrated that combining ChCl-OxA with microwave-assisted pretreatment (80 °C and 800 W) achieved 80 % lignin removal in just 3 min, slightly lower than the 90 % obtained with traditional oil bath treatment at 110 °C for 9 h using the same DES [16]. Similar results were observed by Chen and Wan, where microwave-assisted treatment combined with ChCl-LA pretreatment resulted in 65–80 % lignin removal and 85–87 % purity within 45 s at 800 W and 152 °C [17]. Compared to other green pretreatments, such as ultrasonication-assisted pretreatment, microwave-assisted DES pretreatment demonstrated superior lignin removal from LCB [63], offering reduced treatment time and energy consumption while maintaining lignin quality comparable to conventional methods.

The exploration of DES began only a decade ago, and there is still much to investigate. Consensus on the most suitable DES for specific feedstocks remains elusive, requiring further research. Tailoring DES for selective biopolymer extraction without severe impact on others, alongside comparisons with commercially produced biopolymers, is an area that needs attention. Investigation into treatment conditions, including DES molar ratio, water content, solid-to-liquid ratio, temperature, and time, is essential for determining optimal conditions. Microwave-assisted DES treatment can further boost yields of platform chemicals like LevA, furfural, and HMF, with or without a catalyst [64, 65]. Moreover, a comprehensive examination of the efficiency and techno-economics of combining DES with other treatments, such as ultrasonication and microwave-assisted pretreatment, could enhance the overall process [66, 67]. However, scaling up of the ultrasonicated-assisted or microwave-assisted DES pretreatment remains a technological issue to address.

3 Furfural, HMF, and LevA Production

Furfural is a heterocyclic aldehyde compound that can undergo alkylation, hydrogenation, oxidation, halogenation, nitration, acetylation, and aldol condensation reactions [75]. Furfural is a platform chemical that can be obtained from xylan, a branched five-carbon (C-5) polysaccharide unit in LCB. The process involves dehydrating xylose, the monomeric sugar obtained from xylan, to release water. The hydration of xylose can occur in the presence of either a Brønsted acid catalyst or a combination of a Lewis acid/base catalyst. In the case of the combined catalyst, the Lewis acid/base first converts xylose to xylulose, which is then transformed into furfural by the Brønsted acid catalyst (Fig. 2). The synergistic action of both catalysts accelerates the conversion of xylose to furfural, resulting in higher yields, compared to using only the Brønsted acid [76]. This combined catalyst approach, coupled with the higher selectivity of furfural when using xylose as the substrate instead of xylan, establishes xylose as the preferred substrate for furfural production [77].

HMF is a hexose derivative with an aromatic aldehyde, aromatic alcohol, and a furan ring system [78]. It exhibits versatility by undergoing esterification, reduction, oxidation, halogenation, nitration, sulfonation, and dehydration reactions to yield various derivatives. The synthesis of HMF from cellulose involves three stages: hydrolysis, isomerization, and dehydration (Fig. 2). Initially, cellulose undergoes hydrolysis using a Brønsted acid catalyst to yield glucose. Subsequently, glucose is isomerized to fructose through enzymatic action, Lewis acids, or aqueous/solid base catalysts. Finally, fructose is dehydrated to form HMF, employing a Brønsted acid catalyst [2, 79]. HMF, being an unstable intermediate, is prone to rehydration, leading to the formation of LevA, FA, and humin [62].

LevA is a linear C5 carbon chain ($C_5H_8O_3$) keto acid, based on its functional groups with carboxylic acid and ketonic functional groups [80]. These functional groups render it suitable for reactions with other functional groups, facilitating the formation of derivatives. LevA can undergo organic reactions such as hydrocyclization, hydrogenation, dehydration, oxidation, reductive amination, halogenation, alkylation, and condensation [81]. Commercial production of LevA often involves petrochemicals like maleic anhydride or furfuryl alcohol, presenting environmental and cost concerns [82]. There is growing interest in utilizing alternative feedstocks such as LCB, starchy waste, polysaccharides, monosaccharides, furfural, and HMF to address these issues [65]. In the cellulose conversion process, HMF production and subsequent rehydration to generate LevA occur in an aqueous system, accompanied by the formation of an equimolar amount of FA [62]. For hemicellulose, the dehydration of pentose sugars leads to furfural, which can be further catalyzed into furfuryl alcohol through hydrogenation, followed by acid hydrolysis into LevA [83]. LevA yields of 5–55 % have been reported for varied LCB due to a difference in composition, treatment techniques, conditions, and chemicals, which is comparable to prime feedstocks such as sucrose (50 %) and starch (35 %) [80]. Theoretically, the maximum LevA yield achievable from pure cellulose is 71.6 wt %. Considering that cellulose content in LCB ranges from 10 % to 95% [84], the maximum obtainable LevA yields for LCB are within 7.2–67.7 wt %.

4 Conversion of Sugars to Platform Chemicals by Innovative Green Pretreatment Technique

4.1 DES for Furfural, HMF, and LevA Production

As a universal and environmentally friendly solvent, water was extensively investigated for platform chemical production. However, water promoted the generation of by-products, reducing the yield of the required products [85]. Due to this, other solvents such as organic solvents, biphasic solvents, ionic liquids (ILs), and DESs were investigated. Organic solvents such as dimethyl sulfoxide (DMSO) and tetrahydrofuran were found to suppress the formation of by-products, whereas biphasic solvents made up of both an aqueous and organic phases depress the formation of by-products while extracting the product from the aqueous phase into the organic phase [86]. ILs such as [BMIM]HSO_4, [BMIM]Cl, [BMIM]Br, and [DBDIM]I were also used to produce furfural, HMF, and LevA [87–90]. The

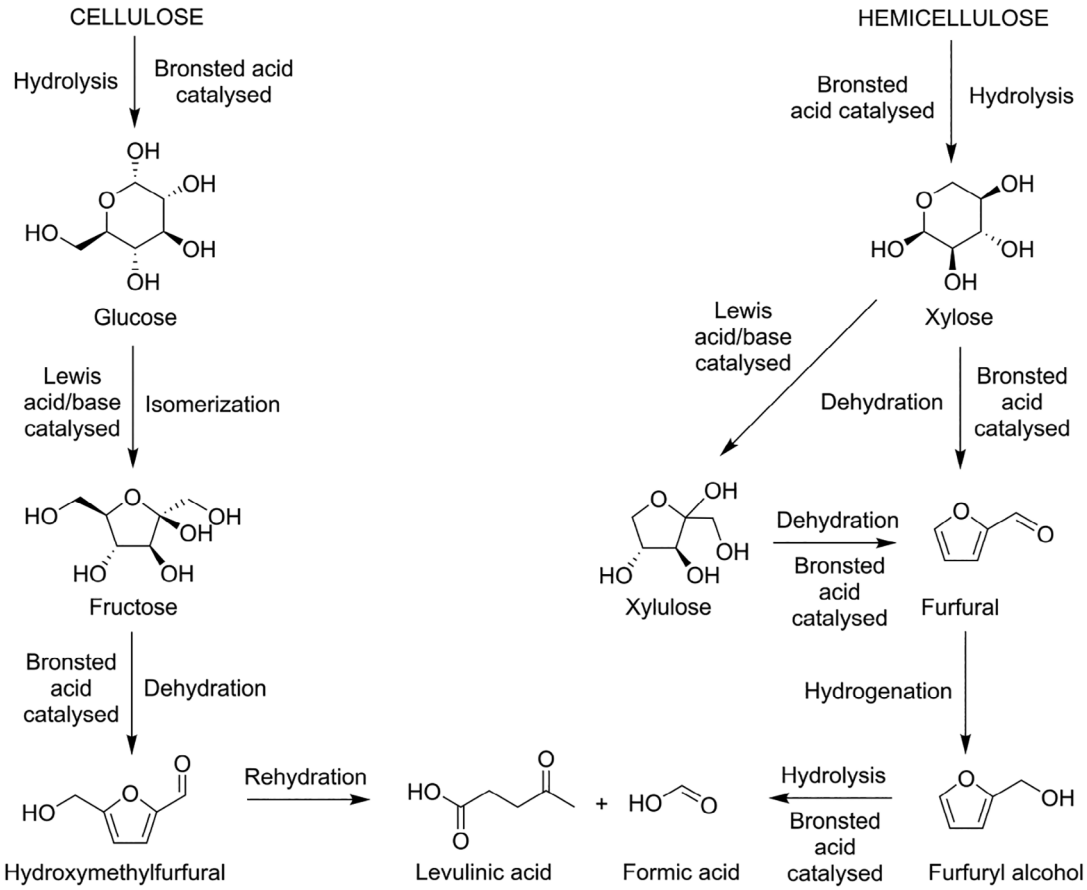

Figure 2. Reaction pathways for the conversion of cellulose and hemicellulose to HMF and furfural, respectively, with further conversion to levulinic acid.

main advantage of using ILs is that they function as both the reaction medium and catalyst improving the product yields. Nevertheless, the excessive cost and environmental issues associated with ILs have led to the use of the less costly and "greener" DES. Besides having similar characteristics as the ILs, sugars such as glucose and fructose were used as the HBD in the formation of DES to generate HMF with yields of up to 60.3 % and 92.3 %, respectively, with the assistance of catalysts such as heteropoly acids and HCl [91, 92].

In the production of platform chemicals, microwave treatment can be used to speed up the hydrolysis of LCB into intermediate products such as glucose and xylose or direct conversion into desired platform chemicals. Sangib et al. showed that microwave-assisted treatment had a positive impact on cellulose conversion, glucose yield, and glucose selectivity (12.3 %, 10.8 %, and 87.7 %, respectively) than traditional autoclave treatment (8.5 %, 4.1 %, and 55.5 %, respectively) performed at similar process conditions. An increase in treatment time could produce products such as HMF and LevA [93]. Maiti et al. compared the direct conversion of LCB into LevA, HMF, and furfural catalyzed by a Brønsted acid catalyst in both a microwave and an autoclave system at similar experimental conditions. Increments of 1.4–4.5, 1.1–4.2, and 2.2–2.7 fold for HMF, furfural, and LevA yields, respectively, were obtained for the microwave treatment in comparison with the autoclave treatment [65].

Arslano and Sert investigated the effect of temperature and time on the extraction of HMF, furfural, and LevA from sunflower cellulose using DES as a catalyst [94]. The results showed that beside furfural, both HMF and LevA were affected by temperature and time. An increase in temperature from 150, 160 to 170 °C resulted in yields of 0.58 %, 1.41 %, and 2.63 % for HMF and 5 %, 10 %, and 25% for LevA, respectively. An increase in time from 3.5, 5.0, to 7.5 min produced yields of 9.2 %, 25.2 %, and 25.5 % for LevA, respectively, and 0.5 %, 2.5 %, and 4.0 % for HMF, respectively. Therefore, after 5 min, the microwave treatment did not have any significant effect on LevA yield; however, it favored the FA formation and other products.

The higher yield and conversion of glucose into other products during microwave-assisted pretreatment can be explained based on the process kinetics. Mukherjee and Dumont performed a kinetic study on the production of LevA from starch using a microwave and an oil bath [95]. The dehydration of glucose to HMF was found to be the rate-determining step. From the study, microwave irradiation produced significantly lower activation energy (91–101 kJ mol^{-1}) in comparison with an oil bath (228–246 kJ mol^{-1}) for the dehydration of glucose to HMF. Therefore, at the same energy level, more HMF will be produced

from glucose, implying more HMF formation using a microwave than a conventional oil bath.

5 HTs

Basic solid catalysts unlike their acidic species are rarely used in the production of platform chemicals. Alkaline earth metal hydroxides, HTs, zeolites, and other compounds with active basic sites and high basicity can all be used as basic solid catalysts [25]. HTs are layered double hydroxides made up of dispersed mixed metals. They are excellent precursors or catalyst supports [96]. They have the general formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}[A^{n-}]_{x/n}\cdot yH_2O$ where M^{2+} and M^{3+} are divalent cations (e.g., Zn^{2+}, Ni^{2+}, Co^{2+}, Fe^{2+}, and Mg^{2+}) and trivalent cations (e.g., Al^{3+}, Fe^{3+}, and Co^{3+}), respectively, $[A^{n-}]$ is the anion and x is the surface charge determined by the molar ratio of the two metal cations ($x = M^{3+}/(M^{2+} + M^{3+})$). In an HT, the excess partial metal cation replacement positive charge is offset by the anion and water molecules existing in the inter-lamella layers [62, 96]. The anions also function as active sites for isomerization [62, 97]. Upon calcination, it transforms into a uniformly dispersed mixed metal oxide (e.g., Mg(Al)O) with a high surface area, strong Lewis base sites, and good thermal stability making it a favorable material for catalysis. The Lewis basicity is due to the presence of M^{2+} cations with O_2 species, whereas the Lewis acidity offered is due to the interaction between M^{3+} and O_2 species [98, 99]. Due to the presence of the acid-base pair in the mixed metal oxides, they have been applied in aldol condensations, Baeyer–Villiger oxidation of ketones, and alcohol hydrogen transfer reduction of aldehydes and ketones, among others [100, 101]. Mg-Al HT calcination at temperatures between 300 and 500 °C makes rehydration possible while increasing the basic strength [102, 103]. At 650 °C and above, the O_2 species decreases resulting in an almost negligible presence of basic hydroxyl groups giving rise to more Lewis acid sites of medium to high strength [100]. Interestingly, it is possible to reconstruct the calcined mixed metal oxides into their original double-layered HTs by rehydration in water at room temperature [104]. The rehydrated HTs possess strong Brønsted basic properties [104]. The rehydration process also produces HT layers with smaller crystallite size due to exfoliation and vertical breaking that enhances glucose isomerization into fructose and improves selectivity making it comparable to strong basic sites [2, 74, 105].

HTs can be used to produce furfural, HMF, and cyclopentanone (CP) as well as in aldol condensation reactions [104, 106–108]. The basic properties of HTs make them effective, especially in the isomerization reaction of glucose to fructose to produce platform chemicals such as HMF and LevA. HTs have high hydrothermal stability with negligible leaching in comparison with catalysts such as zeolite [2, 24]. However, the minimal leaching noticed is due to the solvent used. In the comparison of various solvents, water produced the highest Mg leaching (0.190 wt %) with HTs, whereas 2-butanol, ethanol, toluene, N,N-dimethylformamide (DMF), and gamma-valerolactone (GVL) produced negligible leaching (0.002–0.005 wt %), and 1-butanol did not produce any leaching [109].

The nature and strength of HTs are affected by the selected cations, the molar ratio of the cations, the anions selected, and calcination conditions such as temperature [96]. For instance, in comparing OH^- and CO_3^{2-}, the higher basicity of OH^- translated to a better catalytic activity in comparison with the latter [62]. However, the unstable nature of OH^- anions in the presence of air results in the formation of carbonate through CO_2 absorption [97]. The strength of basic catalysts in glucose isomerization into fructose is also directly proportional to the alumina content in alumina-based catalysts [110]. The introduction of alumina into the structure of MgO forming Mg(Al)O caused a decrease in the total number of basic sites; however, there is a simultaneous increase in the number of strong basic sites present in the catalyst [100]. Prinetto et al. showed that replacing Mg with Ni in Mg(Al)O caused a reduction in the strong basic O^{2-} sites of the catalyst, whereas both Ni^{2+} and Al^{3+} functioned as Lewis acid sites [111].

5.1 HTs as Catalysts for Glucose Isomerization into Fructose

Glucose isomerization into fructose is a vital step in the production of HMF and LevA. The abstraction of an α-hydrogen by the base in the process is referred to as the Lobry de Bruyn–Alberda van Ekenstein transformation [112]. Under basic conditions, glucose underwent deprotonation at the O-1 position, causing the sugar ring to open and transferring the charge to the O-5 position. Subsequently, a proton was extracted from the O-2 position, leading to the formation of the enediol anion. This electron pair movement through the carbon skeleton resulted in the formation of fructose [113].

Decades ago, this process was conducted with potassium hydroxide (KOH). A glucose conversion and fructose selectivity of 18 % and 61 %, respectively, were reported [114, 115]. The constraints of using homogeneous catalysts like KOH, NaOH, and Na_2CO_3 have recently led to the use of HTs as suitable alternatives and have proven to give higher glucose conversion, fructose selectivity, and yield [107]. An initial investigation into various solid base catalyst revealed that the HT ($Mg_6Al_2(OH)_{16}CO_3$) in a reaction media of DMF gave the 62 % glucose conversion and 38 % fructose yield at 100 °C for 3 h [116]. Glucose isomerization using HTs has been successful in reaction media such as 1-butanol, 2-butanol, 1-propanol, DMSO, DMF, ethanol, GVL, methanol, toluene, and water (Tab. 2). An et al. investigated the effect of various solvents on the basic properties of Mg-Al HTs used in glucose isomerization [117]. They observed that the yield of fructose during the isomerization process increased with the base strength of the catalyst. The basic properties of the HT are affected by the reaction solvent used, thereby having an influence of the fructose yield. For instance, in water, a glucose conversion, fructose yield, and selectivity of 58 %, 33 %, and 59 % were attained, respectively, when the Mg/Al ratio was 4.0. The highest was attained when the Mg/Al ratio was 1.5 in methanol (70 %, 50 %, and 72%, respectively), DMSO (61 %, 37 %, and 60 %, respectively), and DMF (69 %, 49 %, and 71 %, respectively).

Reaction time, temperature, and pH are the main factors influencing the effectiveness of HTs in the isomerization of glucose to fructose. At room temperature (25 °C), glucose cannot be totally converted to fructose due to the thermodynamic

Table 2. Glucose isomerization to fructose using hydrotalcites (HTs).

Reaction media	Reaction temperature [°C]	Reaction time [min]	HT molar ratio [Mg/Al]	Mass catalyst/Mass glucose	Glucose conversion [wt %]	Fructose selectivity [%]	Fructose yield [%]	Reference
1-Butanol	100	300	2	0.5	62	82	51	[109]
1-Propanol	90	120	3	1.0	56	86	48	[118]
Ethanol	90	120	3	1.0	61	83	50	
DMF	80	180	3	1.0	47	85	40	[26]
DMF	100	180	3	0.3	38	66	25	[119]
DMF[a)]	100	180	3	0.3	42	88	37	[120]
DMF	100	180		1.0	62		38	[116]
DMF	100	300	3	0.3	40	74	30	[121]
DMF	100	300	3	0.3	48	80	34	[122]
DMF	100	300	3	0.3	50	69	35	[123]
Water[b)]	90	40	3	0.2	50	48	24	[124]
Water[c)]	90	40	3	0.5	45	54	25	
Water	90	60	4.5	0.2	27	78	22	[102]
Water	90	120	3	0.3	41	75	31	[125]
Water	95		3	0.2	42	60	25	[24]
Water	100	300	3		18	78	14	[103]
Water	110	120	3	0.2	29	89	25	[97]
Water	120	60		1.0	43	64	27	[126]
Water	120	240	3		36	75	27	[127]
Water[d)]	120	5 MW	2	0.4	40		25	[128]

DMF, N,N-dimethylformamide.

a) 10 min assisted sonication rehydration of HT; b) Treatment performed at pH 7; c) Treatment performed at pH 2; d) After co-precipitation of the HT, it was subsequently treated in acetone before used in the isomerization reaction.

equilibrium ratio favoring glucose formation (54:46). However, the weak standard reaction enthalpy (2.8 kJ mol^{-1}) of the reaction makes it possible to improve glucose conversion into fructose by increasing the reaction temperature above 25 °C [129]. In water, there was no significant change in the yield of fructose after exceeding 100 °C [103]. In another study, conducted in water, it was found that an increase in temperature above 25 °C improved glucose conversion (from 16 % to 35 %), while selectivity reduced (from 87 % to 65 %) [130]. The authors reported a temperature of 45 °C as the optimal temperature when water is used as a solvent. At this temperature, glucose conversion, fructose selectivity, and fructose yield of 24 %, 85 %, and 21 % were achieved. A temperature increase from 100 °C to 120 °C was beneficial to glucose conversion (62 % to 81 %) but detrimental to fructose selectivity (62 % to 40 %) and yield (38 % to 32 %) with DMF as solvent [26]. Exceeding optimal temperature increases humin production by the condensation of glucose and fructose, causing a reduction in selectivity [26, 103, 131]. Increasing treatment time from 2 to 24 h improved both glucose conversion and fructose yield with a steep selectivity decline due to by-product formation [125]. Most isomerization reactions with HTs are performed at an almost neutral pH or slightly alkaline pH (8–9); however, using acidic pH results in a considerable reduction in fructose yield and glucose conversion [124]. To obtain comparable results to the neutral pH, there was a need to use more than twice the initial catalyst loading. Nevertheless, at a nearly neutral pH, significant leaching of magnesium was observed, whereas at slightly alkaline conditions (pH ∼ 9), leaching was reduced significantly [125].

5.2 HTs as Catalysts for Production of Furfural and HMF

The acidic sites on the surface of HTs can also be exploited for acid-catalyzed reactions, such as the dehydration of pentoses and hexoses to furfural and HMF. As outlined in Sect. 3, HMF and furfural production involves dehydrating various substrates with acids. The acidity of the HTs can be altered by tuning the metal cations in the lamellar layer and the anions in the interlayer [113]. However, the major challenge in the dehydration step is the occurrence of undesired side reactions and the formation of insoluble polymers (humins) [19]. This is primarily due to the higher activation energy required for HMF or furfural production, compared to the side reactions. It is therefore important to determine the metal cations and the amount required to effectively tune the HT for a successful dehydration process.

Yan et al. studied the effects of various HTs on HMF synthesis from D-fructose by varying the M^{2+} cations (Co^{2+}, Zn^{2+}, and Ni^{2+}) in a pure ethanol reaction media at 180 °C for 1 h [106]. At the same M^{2+} to Al^{3+} ratio (2:1), Co/Al-HT afforded the highest conversion and HMF yield of 93 % and 22 %, respectively. Co/Al-HT possessed both weak and medium acid sites contributed by both Co^{2+} and Al^{3+} that were able to hydrate the fructose into HMF. Furthermore, an increase in the Co/Al ratio to 3:1 caused an increase in fructose conversion (99 %) with a reduction in HMF yield (15 %). An increase in temperature from 100 °C to 210 °C favored fructose conversion (from 46 % to 99 %, respectively) with a maximum HMF yield of 22 % at 180 °C, while a further increase in temperature to 210 °C reduced yield to 13 %. The HT was recyclable and reusable with no activity loss even after three cycles.

HTs were also used in the synthesis of HMF and furfural [26, 107, 116]. A combination of HT with Amberlyst-15 in DMF gave HMF conversion and selectivity of 64 % and 38 %, respectively [116]. Increase in treatment time (up to 9 h) was beneficial to glucose conversion and HMF yield, while selectivity declined within the first 4 h of treatment before staying constant. Glucose conversion and HMF selectivity further increased to 73 % and 58 %, respectively, when HT loading was doubled at 9 h, whereas at 4.5 h, they were 60 % and 76 %, respectively. HMF was also produced using a similar catalyst combination from sucrose and cellobiose suppressing anhydroglucose production [26].

In the presence of xylose, Takagaki et al. used the same HT-Amberlyst-15 catalysts to produce furfural at similar conditions [107]. The xylose conversion, furfural yield, and selectivity obtained were 72 %, 37 %, and 51 %, respectively, using DMF as the reaction media. The furfural synthesis underwent the xylose–xylulose reaction pathway before dehydration to furfural. They went further to combine glucose and xylose in a one-pot system using the same catalysts, reaction media, and process conditions to produce both HMF and furfural. In the one-pot system, HMF and furfural yields of 48 % and 41 %, respectively, were obtained [107].

5.3 HTs as Catalysts for Aldol Condensation of Furfural or HMF with Acetone

Aldol condensation is an addition reaction that involves two carbonyl-containing molecules coming together to form C-C bonds [10]. This reaction is an essential intermediate step in the production of larger alkanes (C_7 to C_{15}) used as biojet and diesel fuel through subsequent hydrogenation and aqueous phase dehydration [104]. Aldol condensation is vital in the biomass upgrading industry where biomass-derived oxygenates are dehydrated removing oxygen thereby increasing the carbon-to-oxygen ratio to form α,β-unsaturated aldehyde [132]. Biomass dehydration products such as HMF and furfural that contain carbonyl groups are prime targets for aldol condensation to form larger organic molecules [133]. However, due to the absence of α-H atom necessary for aldol condensation, they can only undergo aldol condensation when their aldehyde groups are attacked by enolate ions in compounds such as acetone, dihydroxyacetone, or glyceraldehyde [27, 134]. Conversely, HMF and furfural can be selectively hydrogenated to produce 1,5-bis[(5-hydroxymethyl)-2-furanyl]-1,4-pentadien-3-one and tetrahydrofurfural, respectively, which can undergo self-condensation [134]. These large organic molecules produced from the condensation reactions can then be converted to liquid alkanes (C_8 to C_{15}). The reaction pathway is depicted in Fig. 3.

Aldol condensations occur in the presence of a basic catalyst under mild conditions [135]. Industrially, strong homogeneous basic catalysts such as caustic soda and NaOH are used in this process [104]. However, using these strong bases causes equipment corrosion and increases wastewater treatment cost. HTs as basic solid materials are suitable catalysts for aldol condensations [136]. In particular, rehydrated HTs in an organic solvent were reported to be effective and stable catalysts for this reaction [137]. The aldol condensation reactions are rarely conducted in water with HTs due to their poor stability under hydrothermal conditions, which causes the leaching of the catalyst constituents into the aqueous phase [134].

A comparison of Mg/Al, Zn/Al, and Zn/Mg/Al mixed oxides operated under identical conditions (50 °C, acetone to furfural ratio of 10:1, catalyst M^{2+}/Al^{3+} molar ratio of 2:1) showed that Mg/Al had the highest furfural conversion (100 %) after 4 h [138]. The high furfural conversion was attributed to an increase in specific surface area and total basic sites and a reduction in acid sites of the catalysts. At 40 % furfural conversion and ~50 % C_8 alcohol selectivity for all the catalysts, different orders of catalyst selectivity were observed for the first aldol product (FAc) and second aldol product (F_2Ac). The FAc selectivity increased in the order Mg/Al < Zn/Mg/Al < Zn/Al, whereas F_2Ac increased in the order Zn/Al < Zn/Mg/Al < Mg/Al. The presence of a small amount of strong acid sites in Zn/Al and Zn/Mg/Al that aided the dehydration of C_8 alcohol to FAc was accredited for the FAc selectivity, whereas the higher amount of basic sites of Mg/Al necessary for F_2Ac formation was also accredited for the F_2Ac selectivity [138]. Cueto et al. also reported that Mg/Zr performed better as a catalyst than Mg/Al, especially in the production of the second adduct product (C_{15}) due to its medium-strength acid/base active sites [139]. Furthermore, while Mg/Al experienced total activity loss after the third cycle, Mg/Zr maintained over 60 % of its initial activity after the third cycle without any prior treatment. The addition of rare earth elements such as lanthanum (La) and yttrium (Y) to Mg/Al HT could also serve as a possible means to improve the specific surface area and the number of medium and strong basic sites of the catalyst [140].

The acidic nature of furan feedstocks such as HMF and furfural with respect to the basic nature of HT shows that there is a probability of neutralization of the catalyst thereby preventing effective aldol-condensation and conversion of the feedstock. Kikhtyanin et al. conducted a study into the effects of the acidity of furfural to the aldol condensation process catalyzed by Mg/Al mixed oxide [137]. It was noticed that the higher the acidity of furfural, the lower the furfural conversion of the catalyst. Similarly, the higher the concentration of the medium and high basic sites of the catalyst the higher the furfural conversion. Furthermore, due to the catalyst being spent on neutralizing the acidity of furfural, below a catalyst dosage equal to the concentration of the acidity of furfural, no aldol condensation occurred. The neutralization was attributed to furfural autooxidation and formed furoic acid through the Cannizzaro reaction

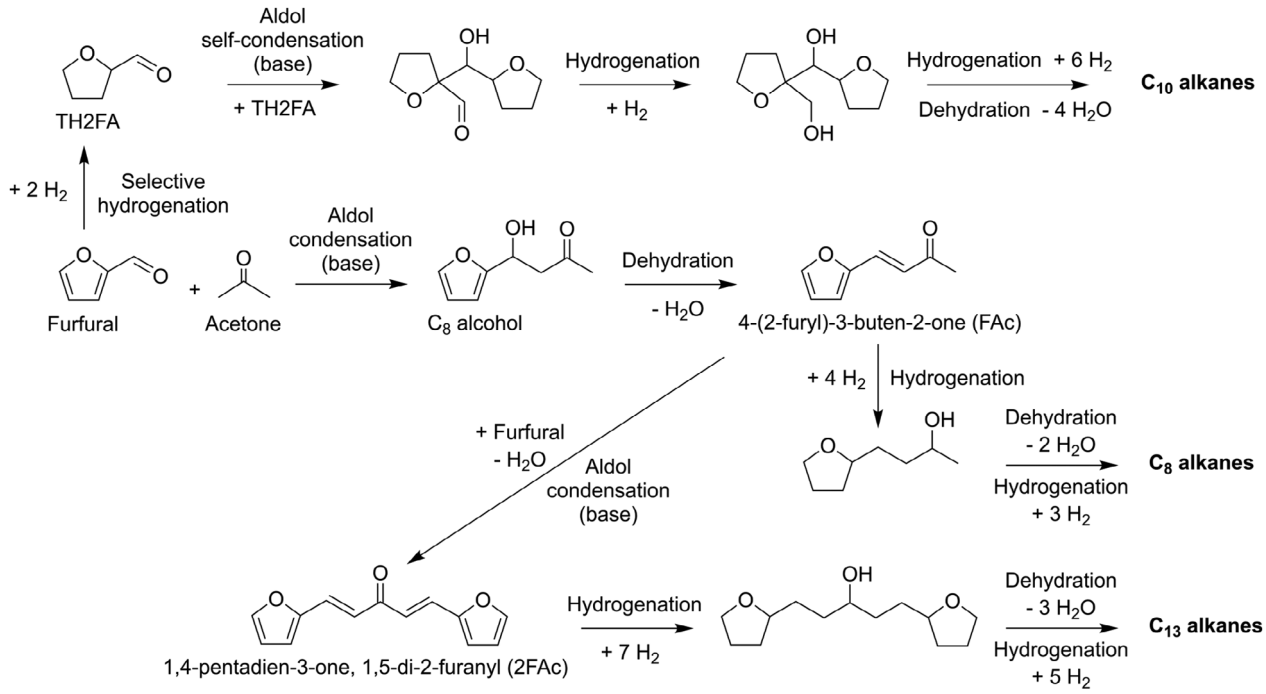

Figure 3. Conversion of furfural to liquid alkanes. A similar reaction pathway can be made for the conversion of hydroxymethylfurfural from C_{12}, C_9, and C_{15} alkanes.

attacking the basic sites and being adsorbed on the catalyst surface. To effectively resolve this challenge, using freshly distilled furfural and calcination of the HT helped to reduce the feedstock acidity and remove the adsorbed acids from the catalyst, respectively [137].

A prior study by Chheda and Dumesic found that the stability of Mg/Al mixed oxide, despite being the best-performing base catalyst for the aldol condensation of both HMF and furfural, decreased with successive recycling runs [134], a 79 % and 96 % reduction in the initial catalytic activity of the catalyst after the second and third recycle runs, respectively. Additionally, these reductions persisted even after the calcination of catalysts after each run. Tampieri et al. noticed that although Mg/Al mixed oxide gave a higher catalyst basic concentration than both the HT and rehydrated HT, the aldol condensation conversion for HMF (22 %) and combined selectivity (79 %) for C_9 and C_{15} were less than that for HT (71 % and 92 %, respectively) and rehydrated HT (96 % and 89 %, respectively) in a microwave-assisted treatment [104]. Similar to earlier studies, there was a reduction in catalyst activity after the catalyst was reused. After calcination and regeneration of catalysts of all three forms of the HT after the first run, the rehydrated HT produced results comparable to the fresh catalyst, while HT and the mixed oxide performed lower than the fresh catalyst. Interestingly, during the third run, the HMF conversion for the rehydrated catalyst was found to reduce from 94 % to 86 %, while the combined selectivity increased from 92 % to 99 %. Although the authors proposed it to be due to a probably irreversible structural change in the rehydrated catalyst, they observed that the rehydrated HT still possessed its original HT structure [104].

The higher performance of rehydrated HT in comparison with Mg/Al mixed oxides was similarly observed in the aldol condensation of furfural and acetone [141]. Additionally, the authors reported the need for water in proximity with both the reactants and rehydrated HT catalyst active sites for an effective aldol condensation. A study conducted to determine the influence of water on the aldol condensation of furfural and water over Mg/Al mixed oxide showed that the water content of the reaction medium had an effect on both conversion and selectivity [142]. The authors reported that with a 5 % water addition, a 100 % furfural conversion with a 10 % increase in FAc selectivity and an 8 % reduction in F_2Ac was observed in comparison to a reaction without water. With toluene as a secondary organic reaction medium, a 35.0 % furfural conversion with a 42.5 % FAc selectivity and 57.6 % F_2Ac selectivity was observed [143]. However, as the water content increased from 0 % to 50 %, an increase in furfural conversion and FAc selectivity of 80.4 % and 88.1 % were observed, respectively, whereas F_2Ac selectivity was reduced to 11.9 %. In this case, the high conversion was attributed to water weakening the double bond of the furfural carbonyl group, thereby making it more reactive, whereas the hydrophilic nature of the catalyst implied that its active sites favored interaction in water than toluene. The biphasic nature of the reaction medium could have contributed to the higher selectivity of FAc in comparison to F_2Ac by transferring the generated FAc into the organic phase, thereby reducing the reaction with furfural to undergo the second aldol condensation to produce F_2Ac [143]. A similar observation was made when HMF and acetone were treated with CO_2 as the catalyst in a water–toluene mixture [144]. Beyond a 1:20 water/acetone content ratio, both the HMF conversion and first aldol condensation product yield

Table 3. Aldol condensation of furfural or hydroxymethylfurfural (HMF) with acetone over HTs in the production of long-chain hydrocarbons.

Reactants	Acetone to furfural or HMF molar ratio	Reaction temperature [°C]	Reaction time [h]	HT molar ratio [Mg/Al]	HT to furfural or HMF ratio	Furfural or HMF conversion, [wt %]	1st product selectivity [%]	2nd product selectivity [%]	Reference
Acetone/Furfural	10:1	55	3	3[b)]	0.03	100	50	38	[137]
Acetone/Furfural	10:1	50	6	1.9[b),d)]	0.31	80	65	25	[136]
Acetone/Furfural	10:1	100	2	3[b)]	0.31	98	70.6	22.5	[27]
Acetone/Furfural	5 mL:0.1 g	100	0.5[a)]	2[c)]	0.5	100	95	4	[146]
Acetone/Furfural	2:1	100	3	2[b)]	400 mg catalyst	35	42.5	57.6	[143]
Acetone/Furfural	10:1	50	6	2[b)]	0.31	100	60	38	[138]
Acetone/HMF	10:1	25	0.67	2[b)]		100			[134]
Acetone/HMF	5 mL:0.1 g		0.17[a)]	2[c]	0.2	96	64	25	[104]
Acetone/HMF	1:1	50	24	4[b),e)]	0.5 g catalyst	68	20.7	2.9	[139]

a) Microwave-assisted process at 300 W; b) Calcined HT; c) Rehydrated HT; d) Zn/Al; e) Mg/Zr.

were reduced even in the absence of toluene. Thus, it can be inferred that the selectivity in an aldol reaction can be influenced by the choice and composition of the reaction medium.

Generally, the selectivity of the second adduct product is known to increase with increased furfural or HMF to acetone ratio (Tab. 3); however, the reaction temperature can also influence the conversion and product selectivity [145]. Hora et al. reported that an increase in temperature from 25 to 56 °C caused an increase in both furfural conversion and selectivity of FAc and F_2Ac [27]. Increasing the temperature to 100 °C for 2 h at an Mg/Al ratio of 3:1 in water, they achieved a 98.0 % conversion with a selectivity of 70.6 % and 22.5 % for FAc and F_2Ac, respectively. Thus, it was inferred that as the reaction temperature increased, the initial intermediate condensation product formed, and the C_8 alcohol was dehydrated into the first condensation product (FAc), which successively reacted with furfural again to produce the second condensation product (F_2Ac) [27]. However, Parejas et al. later showed some differing results [143]. They similarly reported an increase in furfural conversion from 3.8 % to 35.0 % when the temperature was increased from 60 to 100 °C at 3 h with an Mg/Al ratio of 2 in toluene. Additionally, an increase in temperature from 60 to 80 °C led to an increase in selectivity from 45.5 % to 50.3 % for FAc, while F_2Ac selectivity reduced from 54.4 % to 49.7 %. On the other hand, a further increase in temperature from 80 to 100 °C, resulted in a reduction in FAc selectivity (to 42.5 %), whereas F_2Ac selectivity increased to 57.6 % [143]. The difference seen could be attributed to a difference in catalyst characteristics and reaction media used.

5.4 HTs as Catalysts for Selective Hydrogenation of Furfural and Self-Aldol Condensation of CP

CP is a selective hydrogenation product of furfural that is known to be a chemical intermediate that is used in the synthesis of medicine, fungicides, perfumes, rubber chemicals, and fuels [10, 147]. CP is a versatile compound that can be used in the synthesis of long-chain alkanes by condensation and hydrogenation (Fig. 4) [147]. The hydrogenation reaction of furfural to produce CP can be conducted with a HT-like material such as Cu/Zn/Al and Cu/Ni/Al [108, 148].

At 150 °C, 4 MPa hydrogen pressure, 10 h with 2 wt % Cu/Zn/Al ratio of 6:9:5 calcined at 500 °C, it is possible to achieve approximately 100 % furfural conversion and 58 % CP yield [148]. Guo et al. also reported a 97.9 % furfural conversion and 60.3 % CP yield at 150 °C, 4 MPa hydrogen pressure, 6 h with 0.2 g of a catalyst obtained by calcination at 500 °C of an HT precursor with a Cu/Zn/Al ratio of 3:6:1, with cyclopentanol as the main by-product (2.5 % yield) [147]. Exceeding the operated reaction pressure and time resulted in a decrease in the yield of CP and an increase in the yield of cyclopentanol, whereas exceeding the temperature only resulted in a reduction in CP yields with no significant change in cyclopentanol. However, there was no significant effect on the furfural conversion when any of the reaction parameters were exceeded. Although the catalytic activity of the catalyst was slightly reduced after five cycles, furfural conversion only decreased to 90 %, whereas the CP yield reduced to 53.3 %. On the other hand, Zhu et al. reported a 95.8 % CP yield with similar furfural conversion when Cu/Ni/Al (1:14:5) HT calcined at 500 °C for 4 h was used [108]. Increasing the Cu content led to a lower dispersion of the metals and a lower surface area, thus promoting the production of by-products such as cyclopentanol from further hydrogenation of CP. Optimal reaction conditions of 140 °C, 4 MPa, 8 h, and 1.5 g catalyst dosage were reported. Exceeding the optimal reaction temperature and catalysts dosages did not alter the CP yield significantly, whereas exceeding the optimal reaction pressure and time resulted in a sharp decline in CP yield with a corresponding increase in cyclopentanol. In addition, the catalytic activity was found to gradually decrease after each catalyst recycle and reuse [108].

Due to the ability to produce cyclic hydrocarbons from CP with a higher density and heating value in comparison

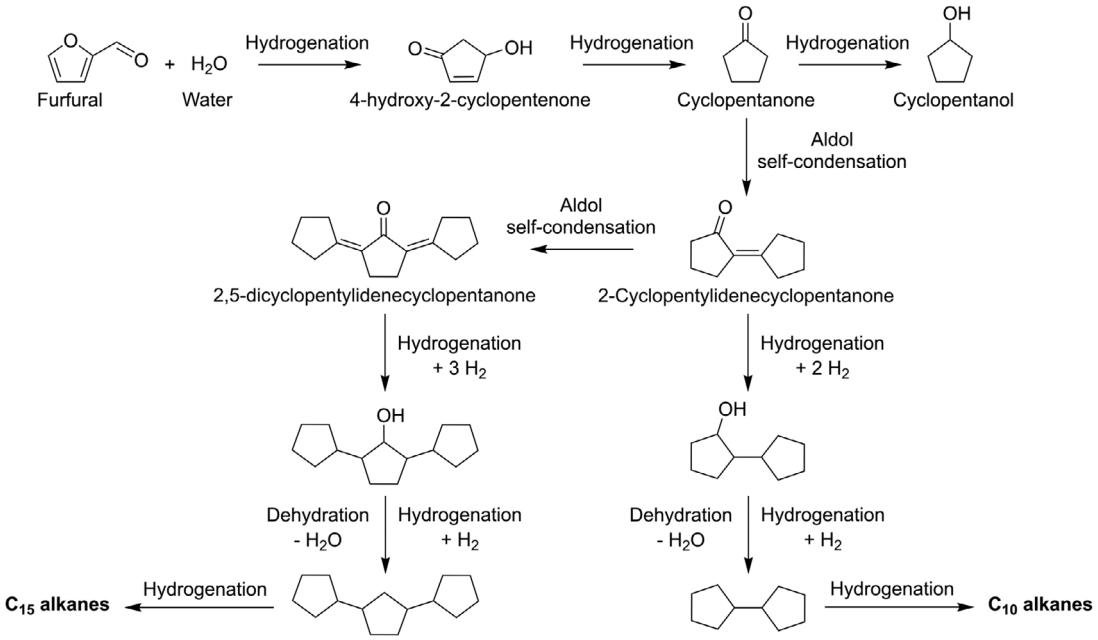

Figure 4. Conversion of furfural to cyclopentanone and subsequent aldol condensation and hydrodeoxygenation to C_{10} and C_{15} alkanes.

with linear alkanes, CP has become an attractive precursor in the production of synthetic aviation fuel [10]. In the production of the cyclic hydrocarbons, CP undergoes self-condensation and dehydration to produce a bicyclic C_{10} product, 2-cyclopentylidenecyclopentanone (CCP), that can further react with another molecule of CP to produce a tricyclic C_{15} product, 2,5-dicyclopentylidenecyclopentanone (DCCP) (Fig. 4). Although both CCP and DCCP can be obtained from the self-condensation of CP, CCP is preferred for aviation fuels [10].

A solvent-free self-aldol condensation was conducted with various solid basic catalysts on CP at 150 °C for 8 h at a substrate-to-catalyst ratio of 10:1 [149]. Among the various solid basic catalysts investigated, Li/Al HT and Mg/Al HT gave the highest conversion of CP and yield of CCP with the latter performing slightly better than the former (Tab. 3). At the treatment conditions, an 86 % yield of CCP and about a 90 % conversion of CP were obtained using Mg/Al HT (3:1) as the catalyst. The higher performance of the HT in comparison with the other basic catalysts was attributed to its higher content of basic and acid sites. Furthermore, it was suggested that there was a synergetic effect of the high basic and acid sites that promoted the self-aldol condensation of CP.

Shao et al. went further to determine suitable treatment parameters for the self-aldol condensation of CP using Mg/Al HT. An Mg/Al ratio of 3:1 gave the highest amount of weak and medium basic sites that ensured the highest CP conversion (80 %) and total product yield (77 %) at 170 °C for 9 h [150]. Furthermore, at Mg-Al ratios above 3:1, a 58 % and 38 % product selectivity were obtained for CCP and DCCP, respectively, while at a ratio of 1:1, ~90 % selectivity was obtained for CCP with less than 10 % selectivity for DCCP. An investigation into the effect of temperature showed that increasing temperature from 150 to 170 °C had a corresponding positive effect on CP conversion, total product yield, and DCCP selectivity, while CCP selectivity remained almost constant at 60 %. A further increase in temperature to 180 °C had no significant effect on both CP conversion, total product yield, and CCP selectivity, whereas the DCCP selectivity was reduced due to degradation. In terms of treatment time, there was a sharp increase in CP conversion, CCP, and DCCP yield and selectivity in the first 4 h of treatment, while after 7 h of treatment, the observed responses did not experience any notable change. Furthermore, a 51 % CP conversion was reached after just 3 h of treatment. Finally, the addition of ≤8 % water had negligible effect on improving the self-condensation of CP, whereas >8 % water reduced the alkalinity of the weak and medium basic sites of the catalysts impairing the catalytic process.

6 Summary and Outlook

LCB as an abundant feedstock is suitable for most industrial applications through suitable treatment processes. Major components of LCB such as cellulose and hemicellulose require adequate pretreatment techniques to extract them without presenting adverse effects both environmentally and economically. Innovative pretreatment methods such as PEF, inorganic salts, and DES can effectively achieve the required positive effects. Furthermore, the application of inorganic salts or DES with a microwave reactor serves to reduce the extensive reaction time while achieving better fractionation yields. The microwave-assisted DES treatment process can also convert the polymeric sugars into monomeric or platform chemicals after pretreatment. This process is essential, particularly as industrial applications aim to streamline operations into a single-step system,

thereby minimizing process steps and the need for additional equipment or reactors. It is therefore paramount to find a means to make this process economically feasible and sustainable on a scaled-up basis.

HTs are solid basic catalysts that are rarely used in the production of platform chemicals unlike their acidic counterparts. Although research in their use for platform chemical production is lacking, it does not void their ability to be applied in the production of platform chemicals. The use of a combination of a Lewis base/acid catalyst and a Brønsted acid catalyst results in higher yields and faster platform chemicals production. This gives much more reason to combine a HT with a Brønsted acid solid catalyst to improve both the reaction and yields obtained. Additionally, given that the few studies conducted using this combination were only conducted using monomeric sugars, there is a lack in understanding its effects on polymeric sugars. Also, DES, which could function as both a Brønsted acid catalyst and the reaction medium, could be used as a replacement for the Brønsted acid solid catalyst. However, there is a need to factor the techno-economics of the process given that more HTs will be required to offset the effects of the reaction medium.

Aldol condensation is an important process to increase the C-C bonds of chemicals in the production of biojet and diesel fuel alkanes. HMF or furfural reacted with acetone can achieve this aldol condensation process to produce C_8–C_{15} alkanes in the presence of a base catalyst. HTs have recently been used as the base catalysts in this reaction. However, a major challenge for this process has been the ability to control the selectivity of the aldol condensation product. In this regard, certain conclusions have been drawn that could potentially help in addressing this issue: (i) Mg in the HTs makes it more selective toward the F_2Ac, whereas Zn makes it more selective toward the FAc; (ii) the presence of some strong acid sites in the HTs could improve the selectivity of the FAc; (iii) the higher the number of the medium-strong basic sites in the HTs, the more selective it is for the F_2Ac; (iv) selectivity toward the FAc increases with the addition of water to the system or with the use of the biphasic reaction medium; and (v) based on the working reaction temperature, the reaction can be more selective toward a particular product. There is therefore a critical need to develop and tune the characteristics and composition of HTs to produce specific aldol condensation products while deciding suitable treatment conditions to achieve the best results.

Current industrial processes focus on green techniques, minimizing reaction conditions, waste generation, and enhancing process economics. Microwave-assisted DES can achieve these goals, whether applied solely for pretreatment or in platform chemical production. Utilizing HTs as heterogeneous, tuneable, and basic catalysts is another option for platform chemical production and aldol condensation processes. Combining these treatment techniques during the platform chemical production stage could yield significant improvements in both the process and yields, thereby improving the aldol production process in turn. To ensure that this process is industrially feasible and sustainable, there is a need for future studies to conduct a full techno-economic and life cycle analysis on a scale-up basis.

Conflicts of Interest

The authors declare no conflict of interest.

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