BioEnergy Research (2020) 13:693–736
https://doi.org/10.1007/s12155-020-10125-8

Catalytic Conversion of Carbohydrate Biomass in Ionic Liquids to 5-Hydroxymethyl Furfural and Levulinic Acid: A Review

Nur Aainaa Syahirah Ramli[1] · Nor Aishah Saidina Amin[2]

Abstract

The projections of ionic liquids as green solvents in chemical processes have increased in recent years. Ionic liquid is a versatile chemical with various applications. The aim of this review is to present a comprehensive perspective of ionic liquid for processing carbohydrate biomass by considering the recent progress in this field. Special attention is given to the application of ionic liquids for the production of 5-hydroxymethyl furfural (5-HMF) and levulinic acid (LA). Factors affecting the catalytic conversion of carbohydrate biomass in ionic liquid and the mechanisms of 5-HMF and LA production are also presented. In addition, the recyclability of the ionic liquid for carbohydrate biomass processing is discussed. The viewpoint for the application of functionalized ionic liquid as potential green solvent and catalyst is also highlighted. Future studies pertinent to carbohydrate biomass conversion in ionic liquids to 5-HMF and LA could use this review for selecting the appropriate reaction conditions required to achieve their specific goals. Besides, combination of technologies from ionic liquids and biomass processing strategies for the production of various fuels and value-added chemicals can be comprehended for applications in a lignocellulosic biorefinery.

Keywords Ionic liquid · 5-Hydroxymethylfurfural · Levulinic acid · Biomass conversion · Acid hydrolysis

Introduction

Over the past decades, fossil fuels have been the main sources for chemicals and energy production. Due to the rapid consumption in various sectors, concerns towards depletion of fossil fuel resources are increasing. Energy production from lignocellulosic biomass has several advantages compared with the conventional energy from fossil fuels such as its availability, renewable sources and carbon dioxide cycle from biomass that produce greener energy. Lignocellulosic biomass is typically composed of cellulose, hemicellulose and lignin [1]. The above-mentioned lignocellulosic biomass components can be converted into many building block chemicals have great market potential. These building blocks are useful to be converted into new bio-based chemicals with various applications including biofuels, medicinal and other high value-added compounds. In a report reviewed by US Department of Energy, several chemical compounds have been screened out as the top building blocks [2]. The compounds listed include succinic acid, fumaric acid, malic acid, 2,5-furandicarboxylic acid, 3-hydroxypropionic acid, aspartic acid, glucaric acid, glutamic acid, itaconic acid, levulinic acid, 3-hydroxybutyrolactone, glycerol, sorbitol and xylitol. Besides, the recently added to the list are para-xylene, propylene glycol, 1,3-propanediol, lactic acid, isoprene, glycerol, furfural, fatty alcohols, 1,3-butadiene, 1,4-butanediol and ethyl lactate [2, 3].

Lignocellulosic biomass can be converted to bio-based chemicals using organic and inorganic compounds as catalyst, solvent and extracting agent. Such compounds are excessively available at reasonable prices; however, the concern about their toxicity and risk of environmental pollution is of high concern. Therefore, the search for alternative compounds is steadily growing. Ionic liquids, composed of different cations and anions provide the alternatives for green catalysis and separation, due to their distinctive characteristics such as negligible vapour pressure and good solubility in both organic and inorganic materials. There has been increasing tendency for usage of ionic liquid in bio-based chemical production as catalyst or solvent. The number of published works in year 2010 to 2019 (Scopus search) involving application of ionic

---

✉ Nor Aishah Saidina Amin
noraishah@cheme.utm.my

[1] Advanced Oleochemical Technology Division, 6, Persiaran Institusi, Malaysian Palm Oil Board, Bandar Baru Bangi, 43000 Kajang, Selangor, Malaysia

[2] Chemical Reaction Engineering Group (CREG), School of Chemical and Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, 81310 Johor Bahru, Johor, Malaysia

liquids and carbohydrate biomass processing for 5-HMF and LA productions are depicted in Fig. 1 [4]. The trend indicates that the research area has attracted significant attention from researchers globally. Even though the productions of biomass-derived building block chemicals (5-HMF and LA) in different solvents including ionic liquid, have been previously reviewed [5–8], there must be aspects in the published works that can be addressed and further described, which subsequently can contribute to literature.

Therefore, the objective of this review is to highlight the ongoing research related to catalytic conversion of carbohydrate biomass to 5-HMF and LA in ionic liquids. The overview of the functionalized ionic liquid as potential green solvent and catalyst is addressed. This review elaborates the factors affecting the 5-HMF and LA productions in ionic liquid which are (1) reaction temperature and time, (2) types of heating, (3) catalyst properties / types of catalyst, (4) catalyst loading, (5) types of feedstocks, (6) feedstock loading, (7) types of ionic liquid (8) ionic liquid loading, (9) reaction media and solvent/co-solvent and (10) water content. The mechanisms proposed for carbohydrate biomass conversion to 5-HMF and LA in ionic liquid are described, and the differences between the proposed mechanisms, taken into account the role of ionic liquid and/or catalyst towards the mechanism, are also discussed. The recyclability and reusability of ionic liquid and kinetics on carbohydrate biomass conversion to 5-HMF and LA in ionic liquid are also presented.

Biomass-Derived Platform Chemicals—5-HMF, LA and Derivatives

Platform chemicals such as 5-HMF and LA have been widely studied over the years owing to their convertibility into a large number of chemicals with applications in various areas. 5-HMF contains hydroxyl and aldehyde functional groups, while LA contains carbonyl and carboxyl group. The presence of several functional groups provides functionalities and reactivities of 5-HMF and LA which make various chemical reactions possible. The overview of 5-HMF and LA markets has been reviewed [7, 8]. 5-HMF and LA can be synthesized from hexoses, where the simplified reaction pathway is described as follows: isomerization of glucose to fructose, dehydration of fructose to 5-HMF by elimination of three water molecules, then rehydration of 5-HMF to LA, and formic acid as by-product. Alongside formic acid, small amount of acetic acid was also produced. Humins, the insoluble carbonaceous residue, can also be formed due to the polymerization and decomposition of glucose and decomposition of 5-HMF and LA [9, 10]. In addition, other valuable chemical such as lactic acid can also be produced from carbohydrate biomass conversion. Nevertheless, this review focuses on 5-HMF and LA, as the production of these two products is interrelated which is through acid-catalysed reaction, whereas the commercial production route of other product is fairly different, i.e. lactic acid is produced by microbial fermentation of carbohydrates [3].

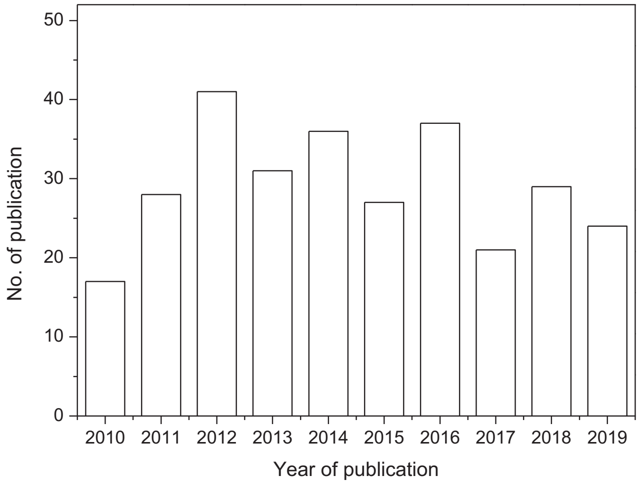


Fig. 1 Histogram of published works involving ionic liquids and biomass processing by year

5-HMF and LA are practically synthesized from monosaccharides, disaccharides and polysaccharides, as well as lignocellulosic biomass. The direct use of lignocellulosic biomass for 5-HMF and LA production looks more promising from the commercial point of view. In 5-HMF synthesis, the utilization of solvents could suppress unwanted side reactions and simultaneously extract more 5-HMF in order to increase the product yield [6]. The aqueous processes are preferred from an ecological and economical point of view, but unfortunately, the 5-HMF production in water is usually low. Instead, water has been regularly employed as solvent for catalytic production of LA as the presence of water will promote the rehydration of 5-HMF into LA. As reviewed elsewhere, other technologies have also been implemented for 5-HMF and LA productions, such as biphasic media, supercritical fluids and ionic liquids [6]. The application of ionic liquid for converting carbohydrate biomass to 5-HMF and LA is discussed in this review.

Various catalytic routes are applied to obtain different 5-HMF and LA derivatives with various applications. One of the 5-HMF derivatives is LA. Other 5-HMF derivatives such as 2,5-bis(hydroxymethyl)-furan can be obtained from hydrogenation of 5-HMF, which is used in the manufacturing of polyurethane foams. 2,5-dimethylfuran has gained attention as due to its superior energy density, high research octane number and ideal boiling point [11], while 2,5-furandicarboxylic acid can be used in the production of polyesters polyethylene terephthalate [12]. The LA derivatives such as δ-aminolevulinate acid is a biodegradable herbicide. LA can undergo reduction reaction to give 1,4-pentanediol, which could be used for the production of new bio polyesters. Esterification of LA with alcohols produces levulinic esters such as alkyl levulinates [13–15]. Alkyl levulinates show the similar properties as biodiesel and possess high potential as additives for transportation fuels. For example, ethyl levulinate is synthesized by esterification of LA with ethanol and can be used directly in a regular diesel car engine up to 5 wt% as diesel miscible biofuel [15]. Besides, LA can undergo hydrogenation to produce γ-valerolactone, which can be used as a fuel additive and solvent, and serve as a precursor of polymers [15].

Ionic Liquids for Biomass Processing

Lignocellulosic biomass is known as a potential source to produce biofuels and other bioproducts. The complex matrix of lignocellulosic biomass unfavourably obstructs its effective conversion into valuable chemical products. Thus, initial dissolution of biomass through pretreatment is an important tool for biomass conversion processes before it can be further converted to other products. The pretreatment process is to reduce the cellulose crystallinity and increase the surface area of cellulose available for the reaction, which could facilitate the conversion reaction [16, 17]. In order to be considered as an effective biomass pretreatment method, several properties should be complied: nontoxic, easy process, cost effective, low temperature process and chemically stable. A prolonged pre-treatment time could increase the possibility of the release of hazardous and toxic compounds during the process. The available pretreatment methods can be classified into physical (grinding, milling, microwave, extrusion, etc.), chemical (acid, alkaline, organic solvent), physochemical (steam explosion, liquid hot water, CO_2 explosion, etc.) and biological (microorganisms) methods [1]. The review of literatures found that conventional pretreatment methods displayed several limitations such as environmental concerns, limited application ranges, and can form inhibitory products during pretreatment process which suppress further hydrolysis steps [1, 18].

In recent years, ionic liquid has been discovered and widely used for biomass pretreatment. Ionic liquids are prepared from combination of different cations and anions. The ionic liquid properties can be altered by appropriate changes of the ionic liquid structure, where it can be done by a proper selection of the cation and anion [18]. Compared with other conventional pretreatment methods, ionic liquids have high potential for energy efficient biomass pretreatment due to their tuneable properties. In addition, as cellulose is reported to be poorly soluble in conventional solvents due to its intermolecular hydrogen bonds, ionic liquids have been found to be capable of disrupting the hydrogen bonds, and making the carbohydrates more susceptible to hydrolysis [18]. Comprehensive reviews on lignocellulosic biomass pretreatment involving ionic liquid have been reported elsewhere [1, 18]. Ionic liquid can play dual-role as a solvent and catalyst for the given reaction [7]; thus, direct hydrolysis of lignocellulosic biomass incorporating ionic liquid is considered to be a promising alternative route for the production of platform chemicals such as 5-HMF and LA. However, pretreatment and hydrolysis processes incorporating ionic liquid face some constraints such as the large amount needed and exorbitantly priced ionic liquid. Since the price of ionic liquid may be an issue, practicability of ionic liquid recycling to reduce the quantity of ionic liquid used is essential. The ionic liquid recycling process for carbohydrate biomass conversion to 5-HMF and LA is elucidated in the next subtopics. The reusability is one of the main advantages of ionic liquid. It is perceivable that this recyclable property will promote the industrial application of ionic liquid.

Catalytic Processes in Ionic Liquid for 5-HMF and LA Production

In the past years, studies have been conducted on conversions of carbohydrate biomass in ionic liquids. Most of the literatures related to conversions of monosaccharides, disaccharides, polysaccharides and lignocellulosic biomass in ionic liquid have focused more on the production of 5-HMF with increasing number of studies on the production of LA.

Conversion of Monosaccharides, Disaccharides and Polysaccharides

The summary on catalytic conversions of monosaccharides, disaccharides and polysaccharides to 5-HMF and LA is given in Table 1, where ionic liquid is employed as solvent and/or catalyst with or without the presence of co-catalyst and co-solvent. Monosaccharides such as glucose and fructose are the most extensively used feedstocks for 5-HMF and LA production in ionic liquids. Disaccharides, sucrose, maltose and cellobiose, consist of two monosaccharides linked by glycoside bond, have been widely employed in the hydrolysis process containing ionic liquid. This indicates dissolution ability of ionic liquid towards disaccharides for generation of 5-HMF and LA. Hydrolysis of polysaccharides such as cellulose, inulin and starch have also been carried out in ionic liquids. Along with the presence of catalyst, ionic liquid has the ability to cleave the hydrogen bonding in polysaccharide. The bond between linkage of polysaccharide and ionic liquid was stronger than the bond between polysaccharide chain with solvent such as water and methanol [19, 21]. This stronger bond has enhanced the dissolution of lignocellulosic biomass in ionic liquid, thus boosting the catalytic processes. In addition, electron donating anion from ionic liquid could distort the hydrogen bond in the crystalline cellulose [49]. The distortion changes the cellulose structure from crystalline to amorphous, and enhancing the overall hydrolysis process. Further discussion on the effect of different types of feedstocks is given in the next section.

In order to obtain an optimum yield, the optimum reaction condition for different substrates is different. For example,

Table 1 5-HMF and LA productions from catalytic conversion of monosaccharides, disaccharides and polysaccharides in ionic liquids

Feedstocks	Ionic liquid	Catalyst/solvent	Reaction condition		5-HMF yield (LA yield) (%)	Ref.
			Temperature (°C)	Time (min)		
Fructose	[BMIM][Cl]	$GeCl_4$	100.0	5.0	92.1	[19]
Fructose	[BMIM][Cl]	SBA 15-SO_3H	120.0	60.0	81.0	[20]
Fructose	[BMIM][Cl]	$IrCl_3$	120.0	30.0	89.0	[21]
Fructose	[EMIM][BF_4]	$SnCl_4$	100.0	180.0	61.0	[22]
Fructose	[BMIM][Cl]	SO_4^{2-}/ZrO_2	180.0	120.0	82.0	[23]
Fructose	[BMIM][Cl]	HCl	80.0	5.0	97.0	[24]
Fructose	[AMIM][Cl]	DMF	100.0	45.0	84.9	[25]
Fructose	[BMIM][Cl]	Cellulose carbonaceous catalyst	160.0	15.0	81.4	[26]
Fructose	[BMIM][Cl]	Lignosulfonic acid	100.0	10.0	93.4	[27]
Fructose	[BMIM][Cl]	$H_3PW_{12}O_{40}$ or $H_4SiW_{12}O_{40}$	80.0	5.0	99.0	[28]
Fructose	[BMIM][Cl]	Lignin-derived catalyst-DMSO	110.0[a]	10.0	84.0	[29]
Fructose	[BMIM][Cl]	$ZrCl_4$	400.0[a]	2.0	92.9	[30]
Fructose	[BMIM][Cl]	$ScCl_3$	400.0[a]	2.0	94.7	[31]
Fructose	[BMIM][Br]	KL zeolite	120.0	30.0	99.1	[32]
Fructose	[EMIM][Br]	Tyrosine	160.0	240.0	72.1	[33]
Fructose	[EMIM][Br]	2,5-Furandicarboxylic acid	100.0	240.0	91.7	[34]
Fructose	[BMIM][Br]	0.06-CuAPO-5	110.0	15.0	93.8	[35]
Glucose	[EMIM][Cl]	$B(OH)_3$	120.0	180.0	42.0	[36]
Glucose	[BMIM][Cl]	$AlEt_3$	120.0	360.0	51.0	[37]
Glucose	[BMIM][Cl]	TPA/$B(OH)_3$	140.0	40.0	51.9	[38]
Glucose	[BMIM][Cl]	$Yb(OTf)_3$	140.0	360.0	24.0	[39]
Glucose	[BMIM][Cl]	$CrCl_3$	130.0	40.0	62.9	[40]
Glucose	[BMIM][Cl]	$CrCl_3.6H_2O/B(OH)_3$	120.0	30.0	78.8	[41]
Glucose	[EMIM][Br]	Al_2O_3-b-0.05	140.0	180.0	49.7	[42]
Glucose	[BMIM][Cl]	$CrCl_3$	125.0	120.0	61.8	[43]
Glucose	[BMIM][Cl]	Bentonite-Cr	150.0	10.0	62.6	[44]
Glucose	[BMIM][Cl]	Cr-beta zeolite	130.0	60.0	58.8	[45]
Glucose	[BMIM][Br]	Modified mordenite	100.0	360.0	64.0	[46]
Glucose	[EMIM][Br]	SnPO	120.0	180.0	58.3	[47]
Sucrose	[BMIM][Cl]	Hβ zeolite	150.0	50.0	67.6	[48]
Sucrose	[EMIM][Cl]	$B(OH)_3$	120.0	180.0	66.0	[36]
Sucrose	[BMIM][Cl]	$ScCl_3$	400.0[a]	2.5	73.4	[31]
Sucrose	[AMIM][Cl]	DMF	100.0	60.0	40.3	[25]
Sucrose	[Et_3NH][HSO_4]	$IrCl_3$	100.0	180.0	33.2	[21]
Sucrose	[BMIM][Cl]	CM-SO_3H	80.0	30.0	44.8	[10]
Maltose	[BMIM][Cl]	$GeCl_4$	120.0	180.0	27.0	[19]
Maltose	[BMIM][Cl]	Hβ zeolite	150.0	50.0	47.8	[48]
Cellobiose	[BMIM][Cl]	$GeCl_4$	120.0	180.0	41.0	[19]
Cellobiose	[BMIM][Cl]	Hβ zeolite	150.0	50.0	49.3	[48]
Cellulose	[EMIM][Cl]	Cr-HY zeolite	176.5	140.0	(46.0)	[49]
Cellulose	[BMIM][Cl]	$AlCl_3$-DMSO	150.0	540.0	54.9	[50]
Cellulose	[BMIM][Cl]	$CrCl_3$	120.0	180.0	54.0	[51]
Cellulose	[BMIM][Cl]	$FeCl_3$	130.0	240.0	67.0	[52]
Cellulose	[BMIM][Cl]	γ-AlOOH-DMSO-H_2O	160.0	120.0	58.4	[53]
Cellulose	[BMIM][Cl]	CNTs-SO_3HNH_2-Cr(III)	130.0	180.0	40.2	[54]
Cellulose	[EMIM][Cl]	Mesoporous zirconia nanoparticle-H_2O	120.0	180.0	29.2	[55]
Starch	[BMIM][Cl]	$AlCl_3$-DMSO-H_2O	150.0[a]	20.0	59.8	[56]
Inulin	[BMIM][Cl]	CM-SO_3H	80.0	60.0	59.2	[10]
Inulin	[EMIM][BF_4]	$SnCl_4$	100.0	180.0	40.0	[22]

[a] Microwave irradiation

glucose needed longer reaction time and higher reaction temperature to generate similar yield as fructose. This is due to the stable glucose structure and glucose need to be isomerised into fructose before it can be dehydrated into 5-HMF. Discussion on the effect of reaction temperature and reaction time are elaborated in the next section. The selection of ionic liquid for 5-HMF and LA is normally based on the types of cation and anion. For instance, ionic liquid with imidazolium cation gives a good 5-HMF yield while other cations generated less, while halide anion such as Cl^- and Br^- not only act as a nucleophile, but also as a base mediator that promote the conversion of glucose into 5-HMF [38, 48]. In addition, the poor catalytic activity of ionic liquid was attributed to the strong basicity and nucleophilicity of the anion, such as Oac^- [38, 48, 57]. Several trends were observed on the effect of alkyl chain length towards 5-HMF production. Few studies suggested that increasing in alkyl chain length was not favourable for high 5-HMF yield in imidazolium-based ionic liquid with boric acid and germanium(IV) chloride as catalysts [19, 36]. On the contrary, alkyl chain length of imidazolium increased the 5-HMF yield using lanthanide as catalyst. The effect of different types of ionic liquids are further discussed in the next section.

Transition-metals have been known as favourable catalysts for 5-HMF and LA productions. Since they are able to prompt high yields of 5-HMF and LA under short reaction time, many studies have incorporated metal salts with ionic liquid (Table 1). Different metal salts may give different effect on the reaction, probably due to the anion effect. For instance, metal salts with larger size of the anion presenting more steric hindrance for the coordination between glucose and the catalyst [19]. An anion with more nucleophilic characteristic led to a stronger interaction between the ions which could inhibit the interaction between glucose and the catalyst, thus less competent for 5-HMF production [19]. Chromium chlorides were found to be an effective catalyst for the conversion of glucose, which might be attributed to the strong Lewis acidity of chromium. Details on the effect of chromium chlorides and other metal halides on conversion of carbohydrate biomass in ionic liquids are given in the next section. Normally, ionic liquid used for catalytic conversion of carbohydrates to 5-HMF and LA is a room temperature ionic liquid. The ionic liquid is in the liquid form during the reaction. To date, solid acid catalysts based ionic liquid have been synthesized by combination of ionic liquid with other materials for 5-HMF and LA productions [58–60]. For example, heteropolyacid-ionic liquid catalysts showed good performance for LA production from conversions of glucose, cellulose and starch [58, 59]. In other study, 5-HMF was obtained from fructose conversion in DMSO catalysed by heteropolyacid immobilized ionic liquid catalyst [60]. The catalyst contained Brønsted acidity from the heteropolyacid part, which favours dehydration of cellulose [60]. Further study on heteropolyacid-ionic liquid catalyst is recommended by introducing Lewis acid, in order to promote isomerization of glucose to fructose before dehydration reaction to produce 5-HMF and LA. Other types of solid acid catalyst and their effect on carbohydrate biomass conversion to 5-HMF and LA in ionic liquid are further emphasized in the next section. The discussion includes the effect of types of acidity as well as the effect of catalyst mesoporosity.

Reaction media also played roles in conversion of carbohydrate biomass to 5-HMF and LA in ionic liquid. As water is one of the products from 5-HMF formation that could promote rehydration reaction to produce LA, some compounds were used to restrain the rehydration reaction and emphasis on 5-HMF formation. For example, co-solvents such as DMSO and MIBK were added in the reaction system to increase 5-HMF yield and selectivity as well as inhibited the formation of LA and humins [21, 29, 61, 62]. Since water has a negative effect on 5-HMF production, studies have been conducted to study the effect of water content in the reaction [63–66]. A detailed discussion on the effect of co-solvent and water content on conversion of carbohydrate biomass in ionic liquid is given in the next section.

Hydrolysis of Lignocellulosic Biomass

Table 2 summarizes the hydrolysis of lignocellulosic biomass to 5-HMF and LA in ionic liquids, where several studies reported the potential of metal halides as catalyst in ionic liquid system for the conversion of lignocellulosic biomass as the combination of metal halides with ionic liquid show good performance for the reaction. In the lignocellulosic biomass conversion, ionic liquid is required for the initial fractionation process of the biomass structure, and as a source of active site for transformation of sugars to 5-HMF and LA. The effect HCl in [OMIM][Cl] for 5-HMF production from raw acorn biomass and chicory root has been explored [67, 68], where the good activity of HCl is due to proton from the HCl acted as a mediator and attacking the glycosidic oxygen in the cellulose compound. The interaction between H^+ and cation and anion of ionic liquid would assist the hydrolysis reaction and consequently promote the 5-HMF production [67, 68]. The effect of several chromium halides on 5-HMF production was investigated for acorn biomass conversion in [OMIM][Cl] [67]. It was confirmed that the difference in the catalytic activity of chromium halides may resulted from the different coordination ability of the halogen groups with the Cr centre. More discussion on the effect of different metal halides are given in the next section.

The effect of $CrCl_2$ has been reported for conversions of girasol tuber, potato tuber and chicory root in [OMIM][Cl] [68, 69]. The 5-HMF yield from conversion of potato tuber increased with the presence of $CrCl_2$. However, $CrCl_2$ did not act as a superior catalyst for 5-HMF production from chicory root [68]. It is presumed that the action of $CrCl_2$ on 5-HMF production may be reliant on the types of feedstocks involved. The similar process was conducted for conversions of switchgrass and comfrey in [BMIM][Cl] and [EMIM][Cl], in the presence $CrCl_3$ and $CuCl_2$ as catalysts [72]. The conversions of pine wood, rice straw, castor leaves and wheat straw in ionic liquid have been conducted under conventional heating and microwave irradiation [71]. Direct conversion of biomass in ionic liquid with the presence of metal halide under microwave irradiation has improved the 5-HMF yield and reduced the reaction time [71]. The use of microwave irradiation was also reported for the conversion of castor leaves and wheat straw to 5-HMF in ionic liquid [73, 74]. Besides, probe sonication assisted [BMIM][Cl] catalysed by $CrCl_3$ for 5-HMF production from bamboo has been reported [17]. The effect of heating methods including conventional heating and

Table 2 5-HMF and LA productions from catalytic hydrolysis of lignocellulosic biomass in ionic liquid

Biomass feedstocks	Ionic liquid	Catalyst/solvent	Reaction condition		5-HMF yield (LA yield) (%)	Ref.
			Temperature (°C)	Time (min)		
Acorn	[OMIM][Cl]	HCl-ethyl acetate	200.0	90.0	28.0	[67]
Acorn	[OMIM][Cl]	HCl, $CrCl_2$-ethyl acetate	200.0	90.0	52.8	[67]
Chicory root	[OMIM][Cl]	HCl-ethyl acetate	120.0	60.0	50.9	[68]
Chicory root	[OMIM][Cl]	HCl, $CrCl_2$-ethyl acetate	120.0	60.0	45.0	[68]
Girasol tuber	[OMIM][Cl]	HCl-ethyl acetate	120.0	60.0	58.2	[69]
Girasol tuber	[OMIM][Cl]	$CrCl_2$, HCl-ethyl acetate	120.0	60.0	55.0	[69]
Potato tuber	[OMIM][Cl]	$CrCl_2$, HCl-ethyl acetate	120.0	60.0	54.4	[69]
Potato tuber	[OMIM][Cl]	HCl-ethyl acetate	120.0	60.0	32.0	[69]
Corn stalk	[AMIM][Cl]	Biochar-Mg-Sn-isopropanol	100.0	180.0	63.6	[70]
Rice straw	[BMIM][Cl]	$CrCl_3.6H_2O$	400.0^a	3.0	47.0	[71]
Pine wood	[BMIM][Cl]	$CrCl_3.6H_2O$	400.0^a	3.0	52.0	[71]
Pine wood	[BMIM][Cl]	$CrCl_3.6H_2O$	200.0	6.0	35.0	[71]
Switchgrass	[EMIM][Cl]	$CrCl_3.6H_2O/CuCl_2$	140.0	30.0	18.0	[72]
Comfey	[BMIM][Cl]	$CrCl_3.6H_2O/CuCl_2$	140.0	15.0	6.0	[72]
Castor leaves	[BMIM][Cl]	$CuCl_2$-H_2O	190.0^a	15.0	6.0	[73]
Wheat straw	[BMIM][Cl]	$CrCl_3$, LiCl	160.0^a	15.0	61.4	[74]
Bamboo	[BMIM][Cl]	$CrCl_3$	140.0^b	3.0	13.0	[17]
Sunn hemp fibres	[BMIM][Cl]	$CuCl_2$-H_2O	200.0^a	46.0	(44.9)	[75]
Empty fruit bunch	[EMIM][Cl]	Cr/HY zeolite	176.5	140.0	(20.0)	[49]
Kenaf	[EMIM][Cl]	Cr/HY zeolite	176.5	140.0	(17.0)	[49]
Oil palm fronds	[BMIM][Br]	Fe/HY zeolite	153.0	354.0	(24.7)	[76]
Hardwood pulp	[BMIM][Cl]	$Fe_2(SO_4)_3$-MIBK	200.0	60.0	26.7	[77]
Softwood pulp	[BMIM][Cl]	$Fe_2(SO_4)_3$-MIBK	200.0	90.0	29.3	[77]

[a] Under microwave irradiation, Watt

[b] Ultrasonic treatment

microwave irradiation, as well as the principle behind the sonication process on 5-HMF production in ionic liquid is further discussed in the next subtopic.

The catalytic production of LA in ionic liquids from lignocellulosic biomass has also been reported, where the reactions were catalysed by the presence of metal halides modified HY zeolite in [EMIM][Cl] and [BMIM][Br] [49, 76]. Ionic liquid media have disrupted the covalent linkages in biomass feedstocks and dissolved the holocellulose. The dissolved holocellulose is accessible for the chemical transformation to produce LA in the presence of catalyst [49]. For lignocellulosic biomass conversion to 5-HMF and LA, untreated and treated lignocellulosic biomass were introduced in the ionic liquid reaction systems. Some of the biomass were extracted using HCl before being converted to 5-HMF [68, 69], and some were subjected to ball mill [17]. The increasing trend in the 5-HMF yield from the pre-treated biomass is possibly contributed by the size reduction and decrease in crystallinity of feedstocks which facilitate the conversion reaction.

The application of co-solvent has been reported for the conversion of biomass to 5-HMF and LA in ionic liquids [67–70, 73, 75, 77]. The presence of co-solvent such as isopropanol, ethyl acetate and MIBK is believed to promote 5-HMF production and inhibit other side reactions, while the presence of co-solvent such as water is to promote the rehydration for LA production. Further explanation on the effect of co-solvent on conversion of carbohydrate biomass in ionic liquid is given in the next section. Several studies also provide a simple practice for the hydrolysis of lignocellulosic biomass to produce monosaccharides for further applications. These biomasses contain a large amount of holocellulose which can be fractionated to release sugars. After completion of biomass dissolution in ionic liquid, the β-1,4-glycosidic bonds of cellulose dissolved in the ionic liquid can be easily attacked by the active sites of the catalyst present in the system, which promotes the hydrolysis process. The main product from the hydrolysis of lignocellulosic biomass, i.e. reducing sugar, can be further converted into a wide range of important chemicals including 5-HMF and LA [72, 78, 79].

Functionalized Ionic Liquid for Carbohydrate Biomass Conversion to 5-HMF and LA

It is a fact that ionic liquids are attracting extensive attention due to their possibility to be modified based on the requirements of a particular application. To date, functionalized ionic liquids, prepared through the inclusion of different types of functional groups on the cation and anion, show enormous potential in various processes. Commonly, functionalized ionic liquid is synthesized to give an ionic liquid with acid site. The example of ionic liquids with this property include sulfonic acid (SO_3H) and hydrogen sulfate (HSO_4) functionalized ionic liquids. Over the years, functionalized ionic liquids have been employed in various applications including in the catalytic conversion of carbohydrate biomass to 5-HMF and LA (Table 3). Alkyl methylimidazolium-based ionic liquids containing SO_3H group on the cation and HSO_4 group on the anion have been widely applied for carbohydrate biomass conversions.

The good performance of functionalized ionic liquid due to its high acidity were reported by various studies on 5-HMF and LA productions [9, 90, 104, 115–118]. Acidic ionic liquids with functional groups, $–SO_3H$, –COOH and –OH, gave better performance in glucose conversion to LA as compared with the non-functionalized ionic liquids such as [BMIM][Cl] and [BMIM][BF_4] [117]. The same trend on comparison with [BMIM][Cl] was obtained from fructose conversion to 5-HMF in ionic liquids with 1-methyl-3-(3-sulfopropyl)-imidazolium cation and different anions: 4-methylbenzenesulfonate, hydrogen sulfate and chloride [118]. A study explored the use of protic ionic liquid, triethylammmonium hydrogen sulfate, towards biomass conversion to LA [109]. A comparison on the effectiveness of protic and aprotic ionic liquid, [BMIM][Cl] was performed for cellulosic biomass conversion [113]. In contrast to [BMIM][Cl], the hydrogen sulfate-based protic ionic liquid, [Et_3NH][HSO_4], showed better activity for 5-HMF and LA productions [113]. Cellulose conversion to LA under microwave assisted reaction using 1-methyl-3-(3-sulfopropyl) imidazolium based ionic liquids ([C_3SO_3Hmim]) with different anions (HSO_4, CH_3SO_3, H_2PO_4) was explored [119]. The highest LA yield was obtained using ionic liquid with HSO_4 anion due to its high acidity. The activity of $–SO_3H$ functionalized Brønsted acidic ionic liquids with different anions and cations were studied for mushroom conversion to 5-HMF [120]. It was found that the main factors affecting the catalytic activity of the ionic liquids include their proton donating ability and acidity [120]. Liu et al. [107] have employed [C_3SO_3Hmim]HSO_4 for LA production from rice straw, where similar interpretation was disclosed on relationship between acidity of the ionic liquid and the hydrogen bonding ability of anions towards LA production. In cellulose decomposition using [C_3SO_3Hmim]-based ionic liquids, the highest LA yield was achieved in the presence of [C_3SO_3Hmim]Cl even though its acidity is lower than [C_3SO_3Hmim]HSO_4 [66]. The same trend was also reported in other study [90].

Eminov et al. [85] conducted a study on conversion of fructose to 5-HMF using a combination of $CrCl_3.6H_2O$ and [BMIM][HSO_4]. The mildly acidic proton located at anion of the ionic liquid is suitable for dehydration of fructose to 5-HMF, where it is likely to act as co-catalyst and solvent for the reaction. As reported by Zhou et al. [112], the same ionic liquid was employed for conversion of bamboo shoot shell to LA. The activity of 1-(4-sulfonic acid)butyl-3-methyl imidazolium hydrogen sulfate ([BSMim]HSO_4) was examined for cellulose hydrolysis in MIBK in the presence of metal chlorides as co-catalyst, where 5-HMF was obtained as main product [62, 78, 103]. The presence of metal chlorides acted as Lewis acid sites promote the dehydration reaction for 5-HMF production, while the SO_3H functionalized ionic liquid played a role as Brønsted acid sites for dissolution of cellulose. Shen et al. [104] investigated the role of [BSMim]HSO_4 for one-pot synthesis of LA from cellulose. The combination of $InCl_3$ with [BSMim]HSO_4 showed lower activity for LA production. The opposite trend of results with other studies suggested that the metal chlorides promote the dehydration of sugars to 5-HMF, but not for rehydration of 5-HMF to LA [104]. Liu et al. [101] have reported the application of various acidic ionic liquids combined with different metal salts to catalyse cellobiose conversion to LA in one pot reaction. The study disclosed that catalytic activity of the ionic liquid was originated from its double acid sites: Brønsted and Lewis.

A mixture of LA and ethyl levulinate were produced from cellulose conversion in aqueous ethanol medium catalysed by a Brønsted acidic functionalized ionic liquid: 1-(1-propylsulfonic)-3-methylimidazolium chloride [65]. The reaction was conducted under aqueous medium due to the important role of water in cellulose hydrolysis and for subsequent LA production. Meanwhile, ethanol acted as solvent as well as reactant for LA esterification to ethyl levulinate. Besides, oil palm empty fruit bunch and mesocarp fibre biomass were employed for LA and ethyl levulinate productions via two-steps sequential one-pot reaction, which are depolymerization and esterification in water and ethanol medium, respectively [110, 121]. The reactions were performed in the presence of Brønsted-Lewis acidic ionic liquid, $InCl_3$-[HMIM][HSO_4],

Table 3 5-HMF and LA production from carbohydrate biomass in acidic / functionalized ionic liquid

Feedstock	Ionic liquid	Co-catalyst/co-solvent	Reaction condition		5-HMF yield (LA yield) (%)	Ref.
			Temperature (°C)	Time (min)		
Fructose	[MMBIM]HSO_4 or [PSMBIM]HSO_4	DMSO	80.0	60.0	71.0–73.0	[9]
Fructose	[CMIM][Cl]	$ZrOCl_2$-DMSO	120.0	120.0	95.7	[80]
Fructose	[BMIM][HSO_4]	H_3BO_3-SiO_2	120.0	90.0	88.0	[81]
Fructose	[HO_2CMMIM][Cl]	Isopropanol	110.0	30.0	91.0	[82]
Fructose	[C_2OHMIM][BF_4]	DMSO	160.0	120.0	96.0	[61]
Fructose	[BSO_3HMIM][OTf]	DMSO	140.0	50.0	59.8	[83]
Fructose	[BMIM][Otf]	HCl-H_2O	100.0	10.0	80.8	[84]
Fructose	[BMIM][HSO_4]	$CrCl_3.6H_2O$	100.0	180.0	96.0	[85]
Fructose	[HNMP][CH_3SO_3]	[BMIM][Cl]	25.0	300.0	88.0	[86]
Fructose	Cr(Salen)-IM-HSO_4-MCM-41	DMSO	120.0	180.0	84.0	[87]
Fructose	Proline chlorate or proline bisulfate	H_2O	90.0	50.0	74.0	[88]
Fructose	Cr_3-SO_3H-polymeric ionic liquid	DMSO	120.0	60.0	91.0	[89]
Fructose	[C_3SO_3Hmim]HSO_4	H_2O	170.0	300.0	(77.0)	[66]
Fructose	[$PrSO_3$HMIM]Cl	H_2O	180.0	180.0	(79.0)	[90]
Fructose	[BMIM-SO_3H]HSO_4	H_2O	95.0	60.0	(70.0)	[91]
Fructose	[$C_6(Mpy)_2$][$NiCl_4$]$^{2-}$	DMSO	110.0	60.0	95.0	[92]
Fructose	$[3.2H]_3[PW_{12}O_{40}]_2$	DMSO	100.0	60.0	92.0	[93]
Fructose	[HMIM]HSO_4	n.a.	180.0	30.0	77.3	[94]
Fructose	PW_{12}-Ils-C_4-HNS	DMSO	100.0	120.0	93.7	[60]
Fructose	[GLY$(mim)_3$][Cl]$_3$	CC-SO_3H	130.0	180.0	96.0	[95]
Glucose	[SMIM][$FeCl_4$]	H_2O	150.0	240.0	(68.0)	[64]
Glucose	P[BVIM]Cl[$CrCl_2$]	DMF	120.0	180.0	66.0	[96]
Glucose	$[BMIM]_3[Pmo_{12}O_{40}]$	H_2O	170.0	180.0	6.0 (22.0)	[59]
Glucose	[HO_2CMMIm]Cl	$ZrOCl_2$-isopropanol	150.0	180.0	43.1	[97]
Sucrose	[HNMP][CH_3SO_3]	[BMIM][Cl]-ethanol	25.0	360.0	40.3	[98]
Sucrose	[AEMIM]BF_4	DMSO	160.0	480.0	68.7	[99]
Sucrose	[SO_3H-BMIM][Cl]/$AlCl_3$	Butanone-H_2O	170.0^{a}	1.0	65.1	[100]
Cellobiose	[HSO_3-$(CH_2)_3$-mim]Cl-$FeCl_3$	H_2O	180.0	600.0	(67.5)	[101]
Cellulose	Cr([PSMIM]HSO_4)$_3$	[BMIM][Cl]	120.0	300.0	53.0	[102]
Cellulose	[C_3SO_3HMIM][HSO_4]	$InCl_3$-DMSO	160.0	300.0	45.0	[103]
Cellulose	[C_3SO_3HMIM]Cl	H_2O	170.0	300.0	(66.0)	[66]
Cellulose	[BSMIM]HSO_4	H_2O	120.0	120.0	(39.0)	[104]
Cellulose	[MIMPS]$H_2PW_{12}O_{40}$	MIBK	140.0	720.0	(63.0)	[58]
Cellulose	[BMIM][Cl]-[$MIMC_4SO_3H$][HSO_4]	$CrCl_3$	130.0	240.0	50.0	[52]
Chitosan	[MIM][HSO_4]	H_2O	180.0	300.0	29.5	[105]
Chitosan	[HMIM][HSO_4]-$FeCl_2$	H_2O	180.0	240.0	44.0	[106]
Rice straw	[C_3SO_3Hmim]HSO_4	H_2O	180.0	90.0	(21.6)	[107]
Oil palm fronds	[SMIM][$FeCl_4$]	H_2O	155.0	222.0	(25.0)	[108]
Corn husk and cob	Triethylammmonium hydrogen sulfate	n.a.	120.0	120.0	(81.1), (93.1)^{b}	[109]
Palm biomass	$InCl_3$-[HMIM][HSO_4]	H_2O	177.0	288.0	(17.7)	[110]
Bamboo	[$C_4(Mim)_2$][2(HSO_4)(H_2SO_4)$_2$]	H_2O	100.0	60.0	(47.5)	[111]
Bamboo	[C_4MIM][HSO_4]	H_2O	145.0	104.0	(18.0)	[112]
June grass	[Et_3NH][HSO_4]	n.a.	180.0^{a}	41.0	34.8 (13.7)	[113]
Rice husk	[$C_4(Mim)_2$][2HSO_4]	n.a.	100.0^{c}	70.0	(40)	[114]

[a] Microwave irradiation

[b] based on amount of solubilized cellulose

[c] Ultrasonic treatment

which made up of $InCl_3$ and 1-methylimidazolium hydrogen sulfate. In other study, *N*-methyl-2-pyrrolidonium methyl sulfonate ([HNMP][CH_3SO_3]) was combined with [BMIM][Cl] for fructose conversion in ethanol [98], with 5-HMF as the major product produced. Besides, binary mixture containing [HNMP][CH_3SO_3] and [BMIM][Cl] was explored for fructose conversion to 5-HMF [86].

Most of studies reported on 5-HMF and LA productions from carbohydrate biomass featured monocationic ionic liquids, while the use of dicationic/tricationic ionic liquid was less explored [92, 111, 114, 122–127]. Several types of polyethylene glycol bridged geminal dicationic ionic liquids based on diphenylammonium/imidazolium cations were synthesized and were employed in fructose dehydration to 5-HMF [126]. Khan et al. [124] have introduced dicationic ionic liquids containing 1,1-Bis(3-methylimidazolium-1-yl) butylene ([$C_4(Mim)_2$]) cation for cellulose conversion to LA. Among the synthesized ionic liquid, [$C_4(Mim)_2$][2(HSO_4)(H_2SO_4)$_2$]

gave the highest LA yield due to its higher acidity coming from the anion. The same ionic liquid was also applied for bamboo biomass conversion to LA [111]. In other study, monocationic and dicationic ionic liquids with HSO_4^- anion were synthesized and compared for rice husk conversion to LA in probe sonication system [114]. Recently, tricationic ionic liquid, glycerol-tri (3-methylimidazolium) trimesylate ($[GLY(mim)_3][OMs]_3$), was introduced for dehydration of fructose, sucrose and glucose [95]. It was presumed that the hydrogen bond formed between mesylate anion and nitrogen-containing tri(imidazolium) cation is beneficial to sugar dissolution for 5-HMF production.

The incorporation of transition metals into functionalized ionic liquids have been introduced for 5-HMF and LA productions. The immobilization of Cr^{3+} with SO_3H-polymeric functionalized ionic liquid effectively catalyse 5-HMF production in DMSO [89], while lower 5-HMF yield was obtained when $CrCl_3.6H_2O$ was used as catalyst under the same catalytic process. In another study, the polymeric ionic liquid-supported metals were applied for glucose conversion to 5-HMF [96]. Among the ionic liquids investigated, poly(3-butyl-1-vinylimidazolium chloride), P[BVIM][Cl], was found to be the most effective. By combining with $CrCl_2$ and Et_2AlCl, the metallate complexes $P[BVIM]Cl[CrCl_2]$ and $P[BVIM]Cl[Et_2AlCl]$ were formed, respectively, and tested for selective cellulose conversion to 5-HMF [96]. The pyridinium-based dicationic ionic liquid with tetrachloronickelate (II) anion, $[C_6(Mpy)_2][NiCl_4]^{2-}$, reported high 5-HMF production from fructose dehydration in DMSO [92]. In addition, $[SMIM][FeCl_4]$ was synthesized by immobilizing $FeCl_3$ into 1-sulfonic acid-3-methyl imidazolium chloride ([SMIM][Cl]) for glucose and oil palm fronds conversions to LA [64, 108]. $CrCl_3$ was added to 1-(3-sulfonic acid) propane-3-methylimidazole hydrosulfate to form $Cr([PSMIM]HSO_4)_3$ for degradation of cellulose in [BMIM][Cl] [102]. In other study, $[SO_3H\text{-}BMIM]Cl/AlCl_3$ was employed for 5-HMF production from disaccharides and polysaccharides conversions [100]. From the studies, the presence of both Lewis and Brønsted acid sites from the metal chlorides and SO_3H functional groups have promoted the 5-HMF and LA productions [100, 102].

The hydroxy-functionalized ionic liquid, 1-hydroxyethyl-3-methyl imidazolium tetrafluoroborate ($[C_2OHMIM][BF_4]$), exhibited excellence activity for fructose conversion to 5-HMF in DMSO [61], suggested the presence of BF_4^- and hydroxy substituents in the imidazole ring promoted the dehydration reaction. The same ionic liquid was used for sucrose and cellobiose conversions to 5-HMF in DMSO [99]. Functionalized ionic liquids with different anion, $[C_2OHMIM][Cl]$, and different cation, $[EMIM][BF_4]$, were applied for glucose dehydration but resulted in very low 5-HMF yield. It is presumed that both hydroxy and BF_4^- groups play important roles in the reaction. The Lewis acid site from BF_4^- is known to promote the isomerization of glucose to fructose, while the basic character of hydroxy group could enhance the transformation between glucose and fructose [61]. Meanwhile, carboxy-functionalized ionic liquid, 1-carboxymethyl-3-methyl imidazolium chloride ($[HO_2CMMIM][Cl]$), was introduced for efficient 5-HMF production from fructose [82]. Later, a study was conducted on glucose conversion to 5-HMF in heterogeneous catalytic system consisting of $[HO_2CMMIm]Cl$ and $ZrOCl_2$ [97]. Li et al. [88] have synthesized proline functionalized ionic liquids: proline chlorate and proline bisulfate for catalytic conversion of fructose to 5-HMF in water reaction system. The proline functionalized ionic liquids were effective for fructose conversion to 5-HMF due to the presence of carboxylic group in the ionic liquid structure [88].

Other functionalized ionic liquids prepared to catalyse 5-HMF and LA productions include heteropolyacid-based ionic liquids [58–60, 93], metal chlorides-silica–immobilized ionic liquids [87, 128] and biochar sulfonic acid-derived ionic liquid [129]. The heteropolyacid-based functionalized ionic liquids were synthesized by combining ionic liquid with different heteropolyacid. The performance of heteropolyacid-based functionalized ionic liquids for carbohydrate biomass conversion was much better compared with the heteropolyacids, since the presence of Brønsted acidity, which originated from the heteropolyacid favours the dehydration reaction, while the ionic liquid promoted the dissolution of feedstock [58–60, 93]. The homogeneous metal chloride/ionic liquid was immobilized to silica composite, MCM-41 and SBA-15, to give heterogeneous catalysts for 5-HMF production [87, 128]. Meanwhile, study by Zhang et al. [129] disclosed the synthesis of fluorine-anion containing biochar sulfonic acid-derived ionic liquids. The biochar contributed to the acid sites of the ionic liquid, while the fluorine-anion containing ionic liquid improved the stability of SO_3H groups.

The effectiveness of functionalized ionic liquids for carbohydrate biomass conversion to 5-HMF and LA is subjected to several factors such as the ionic liquids' structure which is the types of anions and cations, the Brønsted and Lewis acids amount and strength, as well as the coordination of the ions with substrates during the reactions. The ionic liquid with bifunctional properties is imperative specifically for cellulose degradation to 5-HMF and LA, where the bifunctional refers to the ability of the ionic liquid to dissolve the cellulose structure and promoting the glucose dehydration to 5-HMF and subsequent rehydration of 5-HMF to LA. Generally, the effect of reaction conditions on 5-HMF and LA production using functionalized ionic liquids was also studied. The varied reaction parameters include reaction temperature, reaction time, ionic liquid loading, feedstock loading, as well as water content. The effect of these parameters on 5-HMF and LA production using the functionalized ionic liquid rendered the same trend as non-functionalized ionic liquids. Detailed on the effect of reaction conditions as well as the types of ionic liquids towards the reaction processes is discussed in the later subtopic.

Factors Affecting the Catalytic Processes in Ionic Liquid

Reaction Temperature and Time

Reaction temperature and time are two important factors affecting the carbohydrate biomass conversion to 5-HMF and LA. These two factors also affect kinetics, selectivity and activity of catalyst. The application of ionic liquid reduces the temperature required for dehydration of monosaccharides compared with aqueous and other organic solvents [122, 130]. Generally, reaction involving heterogenous catalyst in ionic liquid require higher temperature and longer time compared with homogeneous catalyst. This is because reactants must come to the surface of catalyst and react with the catalytic sites, and resulting products must diffuse away from the catalyst [55]. A sufficient reaction time is critical for achieving adequate mass transportation in the heterogeneous reactions. For better discussion in this review, reaction temperatures are categorized into several groups: room temperature, low (below 100 °C), medium (100 to 150 °C) and high temperature (above 150 °C). The circumstances of the effect of reaction temperature and time can be deduced as follows: at higher temperature and prolonged time, the initially produced 5-HMF is not stable which caused self- or cross-polymerization of 5-HMF and leads to formation of insoluble humins, as well as conversion of 5-HMF to LA and formic acid [9, 10, 80, 89, 92, 123, 131]. The presence of humins in the reaction mixture is difficult to be identified and quantified. Nevertheless, these could be confirmed by the colour change of reaction-ended mixture from orange to brown, even to black [132].

The dehydration of fructose was carried out at room temperature in [BMIM][Cl] catalysed by $GeCl_4$ [133]. The reaction proceeded smoothly, with 70% 5-HMF yield obtained at prolonged time of 12 h. Other employed ionic liquids include [BMIM][Oac] and [BMIM][BF_6]. Fructose conversion at room temperature was also investigated using binary mixture of [HNMP][CH_3SO_3] and [BMIM][Cl], with 5-HMF yield up to 88% in 5 h [86]. Besides, binary mixture was applied for 5-HMF production from fructose in ethanol solvent [98]. The 5-HMF yield obtained from the reaction was up to 89% in 6 h. The reaction rate at room temperature was slower than that at higher temperature; thus, a long reaction time was necessary to obtain high 5-HMF yield. Nevertheless, shorter times were reported for fructose, glucose and sucrose conversions at room temperature in ionic liquid mixtures catalysed by solid acid catalysts [134, 135]. The mixture of [BMIM][Cl]/[BMIM][BF_4] yielded high 5-HMF yield up to 56% in 3 h [135].

Low temperature was generally employed for fructose conversion since no crucial step like isomerization is needed. Studies reported the optimum temperature of 70–75 °C for fructose conversion to 5-HMF in unsymmetrical dicationic ionic liquid [136] and in [BMIM][Cl] catalysed by acidic ion exchange resin [57]; optimum temperature of 80 °C for fructose conversion to 5-HMF in [BMIM][Cl] catalysed by HCl [24], in [BMIM][Cl] catalysed by heteropolyacid [28], in [BMIM][Cl] catalysed by yeast derived carbonaceous catalyst [10] and in [PSMBIM][HSO_4]-DMSO [9]; and optimum temperature of 90 °C for fructose conversion to 5-HMF in proline-derived ionic liquid-water [88]. In addition, higher temperature of 95 °C was reported to obtain the optimum LA yield from fructose conversion in [BMIM-SO_3H]HSO_4 aqueous mixture [91]. It is suggested that as fructose conversion performed at low temperature (80 °C), the 5-HMF produced is stable; thus, the reaction could be sustained for a longer period, providing an opportunity to employ high fructose loading [24]. At higher reaction temperature (100 °C), the 5-HMF yield started to decrease [57, 136] and colour of the reaction mixture turned darker [136]. On the other hand, 5-HMF yield significantly increased at elevated temperature up to 100 °C as compared with reaction conducted at 60–80 °C [27, 63]. Several studies demonstrated 100 °C as the optimum temperature for fructose conversion to 5-HMF in ionic liquid systems such as [AMIM][Cl]-DMF [25], [ClC2MIM][Cl]-water [63], ionic liquid-based polyoxometalate salt-DMSO [93], [BMIM][HSO_4] catalysed by $CrCl_3$ [85] and [BMIM][Cl] catalysed by lignosulfonic acid [27]. The formation of by-products from fructose dehydration performed at relatively low temperature was observed but negligible [25, 130, 136]. The 5-HMF yield kept increasing with prolonged time, as the reaction proceeded at low temperature of 70 °C [88, 136]. Higher temperature ~ 100 °C was beneficial for fructose conversion to 5-HMF at shorter time [27, 57, 85, 88, 93]. Increasing reaction temperature not only accelerates the dehydration reaction but also speeds up the side reactions such as polycondensation of 5-HMF. This can be verified as the 5-HMF yield decreases faster at 100 °C than that at 75 °C with prolonging time [57].

The low feedstock conversion at low temperature indicates insufficient activation energy for the reaction to proceed. Generally, conversions of carbohydrate biomass in ionic liquid were conducted at medium temperature range (100–150 °C). The reported optimum temperature for fructose conversion in ionic liquid was in the range of 110 to 120 °C as in several studies involving reaction systems [HO_2CMMIm][Cl]-isopropanol [82], [BMIM][Cl] catalysed by sulfated zirconia [137], [BMIM][Cl] catalysed by solid base catalyst [138], polyethylene glycol functionalized dicationic acidic ionic liquid-DMSO [123], [BMIM][Cl] catalysed by $IrCl_3$ [21], [BMIM][Cl[catalysed by SBA-15-SO_3H [20], [CMIM][Cl]-DMSO [80], Cr^{3+} immobilized SO_3H functionalized solid polymeric ionic liquid [89] and pyridinium-based dicationic ionic-DMSO [92]. The selectivity and 5-HMF yield were reported to continuously decrease as reaction time becomes longer [21, 92]. Other than significant degradation of 5-HMF at higher temperature and longer time, the loss of active compounds and destroy of catalysts could occur over high temperature. This condition is anticipated for fructose conversion in [BMIM][Cl] catalysed by acidic ion exchange resin and SBA-15-SO_3H [20, 57].

Increasing temperature not only increase the product yield, but also shorten the time needed to reach the optimum yield. This trend has been acquired for glucose conversions at medium temperature range in [BMIM][Cl] catalysed by Cr^{3+} modified ion exchange resin [131], in [BMIM][Cl] catalysed by 12-tungstophosphoric acid/boric acid [38], in [BMIM][C] catalysed by $GeCl_4$ [19], in [BMIM][Cl catalysed by $CrCl_3$/boric acid [41] and in [BMIM][Cl]–DMSO catalysed by bentonite-Cr [132]. The similar trend was also observed for sucrose conversions to 5-HMF in pyridinium-based dicationic ionic liquid catalysed by $CrCl_2$ [122], and cellulose conversion catalysed by ionic liquid-heteropoly acid catalyst in MIBK-water [58]. In cellulose conversion reaction, the limit of 5-HMF production at medium temperature (~ 120 °C) was due to slow reaction rate, caused by low solubility and breakdown of the polysaccharide in the ionic liquid [51]. Meanwhile, at higher temperature (~ 170 °C), high 5-HMF yield was attained at much shorter time. Nevertheless, the formation of humins was very high and unavoidable, which caused 5-HMF yield dropped significantly after only a short period [51]. The optimum conversion of glucose to LA using [SMIM][$FeCl_4$] was attained at temperature of 150 °C [64]. Low glucose conversion rate was observed at low temperature compared with the conversion at higher temperature, which deduced that at elevated temperature, atoms donate or receive electrons more easily thus increasing the chemical reaction rate [64]. Increasing temperature can decrease viscosity of reaction system and subsequently accelerate the mass transfer rate which facilitated the cellulose degradation [102, 104, 139, 140]. A range of low to medium temperatures from 80 to 120 °C were tested for cellulose and bamboo biomass conversions to LA catalysed by Brønsted acidic dicationic ionic liquid [111, 124]. The results demonstrated that the LA yield from cellulose increased when temperature increased from 80 to 100 °C, then decreased when the temperature was over 100 °C. It is suggested that LA is unstable at high temperature in the acidic condition, thus caused the decreased in LA yield.

Reactions conducted at high temperature (above 150 °C) were reported for conversions of monosaccharides, disaccharides and polysaccharides. Conversion of fructose in [BMIM][OH]-DMSO required high temperature of 160 °C and prolonged time of 8 h [141]. The demanded high temperature and prolonged time was possibly due to the application of alkaline ionic liquid [BMIM][OH]. The effect of types of ionic liquid is discussed in the following section. When the temperature was elevated to 160 °C for glucose conversion catalysed by carbonaceous catalyst in [BMIM][Cl], the optimum 5-HMF yield was achieved at only 15 min as compared with 140 min at 120 °C [26]. The same trend was reported for cellulose hydrolysis in [BMIM][Cl]-DMSO catalysed by $AlCl_3$ and γ-AlOOH [50, 53]. By further increasing the temperature to 180 °C, the reaction only required 3 h to obtain the maximum 5-HMF yield compared with 9 h at 150 °C [50]. In other study on glucose dehydration catalysed by silica-supported ionic liquid layer in water, glucose conversion at 150 °C continuously increasing after 2 h reaction while the 5-HMF yield remained constant [128]. The maximum 5-HMF yield was achieved at 160 °C from sucrose conversion in [EMIM][Br] catalysed by tyrosine then the 5-HMF yield significantly declined at 180 °C [33]. For the conversion of chitosan, the optimum temperature of 180 °C was chosen when the reaction conducted in [MIM][HSO_4] aqueous solution [105] and [HMIM][HSO_4]–$FeCl_2$ aqueous solution [106]. The decrease of 5-HMF yield as reaction temperature vary from 130 to 140 to 200–220 °C was likely due to rehydration reaction in aqueous systems occurring at higher temperature [105, 106].

In LA production from glucose in [BSO_3HMIm][HSO_4]-water, increased in reaction temperature and time has increased the rate of glucose conversion and product yield [90]. The same trend was observed for cellulose and chitosan conversions to LA, when temperature ranging from 140 to 180 °C and reaction time from 30 to 210 min in [BSO_3HMIm][HSO_4]-water system [90], and when temperature ranging from 160 to 180 °C and reaction time from 30 to 180 min in [C_3SO_3Hmim]HSO_4-water system [142]. In SO_3H functionalized ionic liquid system, the maximum glucose conversion and LA yield was achieved at 155 °C and 5 h [117]. At temperatures > 165 °C and > 180 °C for glucose and chitosan conversion, respectively, LA yield further decreased due the formation of humins [117, 142]. Ren et al. [66] suggested that cellulose conversion in [C_3SO_3HMIM][HSO_4]-water for LA formation was favoured at higher temperature during short time or prolonged time at lower temperature [66]. At temperatures 130–150 °C, LA yield was low for cellulose conversion catalysed by 1-(1-propylsulfonic)-3-methylimidazolium chloride in water-ethanol medium [65]. Gradual increase in temperature resulted in increase of LA yield, with the optimum temperature of 170 °C, while 5-HMF yield decreased at temperature beyond 150 °C. In cellobiose conversion catalysed by [HSO_3-$(CH_2)_3$-mim]Cl-$FeCl_3$, with increasing temperature from 160 to 180 °C, the LA yield increased, while glucose and 5-HMF yield decreased [101]. Higher temperature was beneficial for LA production due to decreased of viscosity and increased of reaction rate.

Types of Heating

The types of heating methods applied for the preparation of 5-HMF and LA include convective-conductive heating and microwave irradiation, either in the presence of ionic liquids or not. The microwave heating has gained more attention in organic synthesis due to its main advantages: high heating efficiency and shorter reaction time [71]. 'Energy efficiency' is one of the principles of green chemistry. This principle needs to be applied to save time and reduce energy consumption. A significant energy saving can be anticipated by the use of microwave energy compared with the conventional heating mode. Microwave-assisted reaction containing ionic liquid can be heated up more rapidly and effectively than other heating methods as ionic liquid consisted of anions and cations which has excellent microwave irradiation conductivity [74]. The microwave-assisted reaction avoided the drawbacks resulted from conventional oil bath heating such as partly overheating [31, 71]. It is suggested that microwave-assisted reaction decrease the activation energy or increase in the pre-exponential factor in the Arrhenius [71, 73, 143, 144].

There were extensive studies on the carbohydrate biomass conversion in ionic liquid using microwave heating system. In general, the studies revealed that microwave irradiation provides a more effective conversion for 5-HMF production than a conventional oil bath and electrical heating. Under microwave irradiation, conversion of fructose in [BMIM][Cl] afforded 5-HMF yield up to 97% within 3 min in the absence of catalyst [143]. Glucose conversion catalysed by $ClCl_3$ in [BMIM][Cl] gave 71% 5-HMF yield in 30 s, which is ~48% higher than oil-bath heating [144]. In addition, higher 5-HMF yield (47.8%) was obtained from glucose conversion in [BMIM][Cl] using $ZrCl_4$ under microwave irradiation in 3.5 min, compared with oil bath heating reaction; 12.4% 5-HMF yield at 220 °C for 3.5 min [30]. Under microwave irradiation, several studies have reported on hydrolysis of cellulose to 5-HMF in [BMIM][Cl] catalysed by different catalysts such as $CrCl_3$/LiCl, $CrCl_3$ $AlCl_3$ and $ZrCl_4$ [30, 56, 74, 144]. Besides, the combination of SO_3H-functionalized ionic liquid and microwave irradiation provides efficient approach for cellulose conversion to LA under aqueous condition [119]. Conversion of lignocellulosic biomass to 5-HMF in ionic liquid under microwave irradiation have been previously conducted. They include conversion of castor leaves catalysed by $CuCl_2$ in [BMIM][Cl], conversion of untreated wheat straw catalysed by $CrCl_3$/LiCl in [BMIM][Cl] and conversion of corn stalk, rice straw and pipe wood catalysed by $CrCl_3$ in [BMIM][Cl] [71, 73].

The combination of [BMIM][Cl], catalyst and microwave irradiation generated synergistic effect for efficient conversion of carbohydrate biomass to 5-HMF [29, 56, 74, 75, 144]. The presence of [BMIM][Cl] provides complete dissolution of polysaccharide and disaccharides, thus leaves the saccharides chains accessible to chemical transformation. It is implied that [BMIM][Cl] has excellent dielectric property for transforming microwave into heat [31, 71, 143]. Under microwave irradiation, alternating electric field promote the vibrational motion of ions and leads to the internal heating [71]. Due to the microwave effect, as reaction in ionic liquid had almost pure ionic condition, the reaction is heated up quickly, volumetrically and simultaneously. By this, the synergistic effect of ionic liquid and microwave irradiation circumvented partly overheating resulted from conventional heating [71, 143]. Other than convective–conductive heating and microwave irradiation heating system, probe sonication has been previously applied for carbohydrate biomass conversions to 5-HMF and LA. For instance, conversions of glucose, cellulose, bamboo, rice husk to 5-HMF catalysed by $CrCl_3$ in [BMIM][Cl], and to LA in a dicationic ionic liquid [17, 114], and conversions of fructose, glucose and sucrose to 5-HMF catalysed by solid catalysts such as zeolites and acidic resins in ionic liquid mixtures [134, 135]. Compared with the conventional heating technique, the use of ultrasonic irradiation probe reduced the reaction time from hours to minutes. Within less than 10 min, 43%, 31% and 13% of 5-HMF yields were obtained from glucose, cellulose and bamboo, respectively [17]. In addition, a good increase in 5-HMF yield was obtained at a significantly lower reaction temperature of 25 °C in contrast to 90 °C for conventional heating [135].

Catalyst Properties/Types of Catalyst

It is apparent that different catalysts have diverse effects on conversion of carbohydrate biomass to 5-HMF and LA in ionic liquids. The trend of feedstock conversion and products yield and selectivity are interrelated to the catalyst properties. In conversion of carbohydrate biomass, acidic sites, Brønsted and Lewis, are required and played different roles in 5-HMF and LA productions. The hydrolysis of cellulose to glucose was mainly due to the Brønsted acid sites and dehydration of fructose to 5-HMF [145]. The Lewis acid sites favour the isomerization of glucose into fructose, whereas the combination of Brønsted and Lewis acidity favour the dehydration-rehydration reaction [101, 145]. Nevertheless, Lewis acid sites can also decrease the LA production by catalysing the decomposition of glucose and reaction between glucose and furfural to form humins [146]. Several homogeneous catalysts which are strong mineral acids, HCl, HNO_3 and H_2SO_4, were equally effective for 5-HMF production from fructose conversion in [BMIM][Cl] [24]. Besides, organic acids such as maleic acid and acetic acid also catalysed the reaction effectively.

Metal halides, acted as Lewis acid, have been extensively used for productions of 5-HMF and LA in ionic liquids. The most common metal halides used were chromium chlorides: $CrCl_3$ and $CrCl_2$. Other than $CrCl_3$ and $CrCl_2$, $CrBr_3$ and CrF_3 were also employed to scrutinize their effect on 5-HMF production from acorn biomass conversion in [OMIM][Cl] [67]. Among them, $CrCl_2$ was the most effective for 5-HMF production, whereas CrF_3 gave the lowest 5-HMF yield. The results suggested that the catalytic activity was varied with the type of halide. The promotion effect was higher in chlorohalide groups than in other halides groups, which might be resulted from stronger coordination ability of chloro-group with chromium centre compared with bromo and fluoro-groups [67]. Other studies which have employed $CrCl_3$ and $CrCl_2$ include glucose conversion in [BMIM][Cl] [40], sucrose conversion in pyridinium based-dicationic ionic liquid, $[C_{10}(Epy)_2]2Br^-$ [122] and cellulose conversion in [BMIM][Cl] and [BMIM][Cl]/toluene [52, 139, 140, 147]. For cellulose conversion in [BMIM][Cl], other metal chlorides were also tested such as $CuCl_2$, $SnCl_4$, WCl_6, $FeCl_3$, $TiOSO_4$, $ZnCl_2$ and $MgCl_2$ [52, 139, 147]. The results showed that both $CuCl_2$ and WCl_6 have good ability to degrade cellulose, but the degradation products are unstable [139]. Meanwhile, $SnCl_4$ showed poor performance possibly because $SnCl_4$ is easily converted into $Sn(OH)_4$ in the reaction [139]. However, in other study, $SnCl_4$ showed good performance as high 5-HMF yield was attained from monosaccharides and disaccharides conversion [148]. Other metal halides were opted for 5-HMF production in ionic liquid due to their advantages compared with $CrCl_2$ or $CrCl_3$, which were reported to possess toxicity and polluting characteristics [103]. In search of a possibly more environmentally feasible process, conversion of glucose in [BMIM][Cl] and [EMIM][Cl] using $ZrCl_4$ and $Yb(Otf)_3$ as catalysts were explored [30, 39]. Besides, $InCl_3$ was used for cellulose conversion in $[C_3SO_3HMIM][HSO_4]$ and biomass conversion in $[HMIM][HSO_4]$, due to its properties such as low toxicity, air and water compatibility, operational simplicity and ability to suppress side reactions in acid-sensitive substrates [103, 110, 121]. In addition, Lewis acid $Fe_2(SO_4)_3$ is considered as a non-toxic and inexpensive catalyst, and has been incorporated for 5-HMF production in [BMIM][Cl] from hardwood and softwood pulp conversions [77].

It was reported that trivalent metal chlorides showed higher activity than divalent metal chlorides on glucose conversion in [BMIM][Cl]-DMSO [50]. The 5-HMF yield decreased as different metal chlorides used in the following order $AlCl_3 > CrCl_3 > FeCl_3 > ZnCl_2 > MnCl_2 > CuCl_2$. In addition, $AlCl_3$ was used as catalyst for conversion of starch to 5-HMF in [BMIM][Cl]-DMSO under microwave-assisted reaction [56]. In [BMIM][Cl], fructose conversion was conducted in the presence of various metal halides including $ScCl_3$, $IrCl_3$ and $AuCl_3$ [21, 31]. Several germanium salts, $GeCl_4$, $Ge(Oet)_4$ and $GeBr_2$, were tested for glucose conversion in [BMIM][Cl] [19]. $Ge(Oet)_4$ was less competent for 5-HMF production, which may be explained by the anion effect. Besides, the preliminary testing indicated that $GeCl_4$ was a superior catalyst compared with other metal halides. Metal salts such as iron salts, cobalt salts and manganese salts have been employed for conversion of cellulose to 5-HMF in 1-(4-sulfonic acid) butyl-3-methylimidazolium hydrogen sulfate [62, 78, 149]. Among the metal salts used, the promoting effect on 5-HMF yield was remarkable for $FeSO_4$ and $FeCl_2$, $CoSO_4$, $Co_2(SO_4)_3$ and $CoCl_2$ and $MnSO_4$ and $MnCl_2$. The similar trend between iron, cobalt and manganese salts was reported, where $Fe(NO_3)_3$, $Co(NO_3)_2$ and $Mn(NO_3)_2$ caused decreased in the conversion, suggested that nitrate anion is most unfavourable to the reaction. This can be explained as NO_3^- cannot directly act as single-ligand to form stable coordination compounds; thus, the formation of metal nitrate complex was difficult compared with others [62, 78, 149].

The performance of SO_3H functionalized ionic liquid with different metal chlorides, $FeCl_3$, $CoCl_2$, $NiCl_2$, $CuCl_2$ and $ZnCl_2$, have been examined for glucose conversion to LA [117]. Higher activity was obtained in the presence of $NiCl_2$ compared with sole SO_3H reaction system. The effect of metal sulfates and metal nitrates was also investigated. Among the metal sulfates, the $NiSO_4{\cdot}6H_2O$-SO_3H-functionalized ionic liquid system showed the highest synergistic effect on LA yield. The study showed that metal sulfates were more predominant in the reaction as compared with metal chlorides [117]. The results indicated that the Brønsted acidity of the ionic liquid is not the sole factor affecting the glucose conversion to LA. Nevertheless, different trend of results was obtained in other study on the addition of metal nitrates [62, 78, 149]. The addition of metal nitrates with SO_3H functionalized ionic liquid resulted in a negative effect on LA yield. Nitrates possess strong oxidizing property and can oxidize glucose to other insoluble products [117]. A series of metal phosphates were tested for glucose conversion to 5-HMF in [EMIM][Br] [47], which SnPO exhibited high glucose conversion and 5-HMF yield. Even though previous studies showed high activity of chromium-based catalysts, CrPO showed poor performance. From the analysis, synergistic effect of SnPO and [EMIM][Br] leads to the excellent catalytic performance, where the tetra-coordinated Sn^{4+} sites from the catalyst were identified as the active species for isomerization of glucose into fructose [47].

A more efficient catalytic process could be achieved by pairing the catalysts, which may be due to synergetic effects between the catalyst. Studies on pairing different metal salts have been conducted for cellulose and biomass conversions in ionic liquids [67, 74]. It was found that adding metal halides to [BMIM][Cl]-$CrCl_3$ could promote the 5-HMF yield from cellulose conversion compared with single $CrCl_3$ as catalyst [74]. Among the paired catalyst, $CrCl_3$/LiCl exhibited better catalytic activity than $CrCl_3$/$LaCl_3$ and $CrCl_3$/LiBr. The different trend of activity possibly due to the different size of cation anion radius of the metal salts [74]. Combination of different metal chlorides with Brønsted acidic ionic liquid was examined for cellulose conversion to LA [101]. The ionic liquid system was affected by the metal chloride, and their acidity increased in the following order: $CrCl_3 < ZnCl_2 < FeCl_3$. Even though $CrCl_3$ generally resulted in high 5-HMF production, the cellobiose conversion in the presence of $CrCl_3$ combined with Brønsted acidic ionic liquid showed poor catalytic effect [101]. It was reported that boric acid could promote formation of 5-HMF from glucose in [EMIM][Cl] [36]. The combination of boric acid with other catalysts has been applied for 5-HMF production in ionic liquids. The paired heteropolyacid and boric acid gave higher 5-HMF yield from glucose dehydration in [BMIM][Cl] compared with a single heteropolyacid or single boric acid catalyst [38]. When boric acid was paired with different heteropolyacids, $H_3PW_{12}O_{40}$, $H_3SiW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$, $H_3PW_{12}O_{40}$/boric acid exhibited better catalytic activity for 5-HMF production [38]. In other study through combination of boric acid with $CrCl_3$ for glucose conversion to 5-HMF in [BMIM][Cl], it was revealed that boric acid exhibited obvious promotion activity [41].

Several studies have reported the use of heteropolyacid-based catalyst for 5-HMF production in ionic liquid. Various heteropolyacids were applied for fructose conversion to 5-HMF in [BMIM][Cl] [28]. The reactions showed that feedstock conversion decreased in the order of the decreasing acidity of the heteropoly acid. Furthermore, all the used heteropolyacids exhibited comparable catalytic activity to H_2SO_4 and HCl. Ionic liquid-based polyoxometalate salts, prepared from the combination of ionic liquid with heteropolyacids were employed for fructose conversion to 5-HMF [93]. It was revealed that as using the same ionic liquid, the catalytic activity of the catalysts were in accordance with the Brønsted acidity of the heteropolyacids [93]. The similar trend was obtained using solid catalyst fabricated based on heteropolyacid immobilized ionic liquid–modified organosilica hollow nanospheres tested for fructose conversion to 5-HMF [60]. The catalyst prepared using heteropolyacid with strongest Brønsted acid strength promote the release of proton during fructose dehydration. Furthermore, the catalyst showed better performance for 5-HMF production without promoting side-reactions compared with its parent heteropolyacid catalyst [60]. Ionic liquid-based polyoxometalate catalysts prepared using molybdenum and tungsten oxides were also tested for cellulose conversion to 5-HMF [147]. The catalysts showed good activity for cellulose degradation, however, the 5-HMF yield attained was much lower than the yield obtained using $CrCl_3$ catalyst [147].

Catalyst with large surface area could increase the catalytic activity since catalytic performance takes place on the catalyst surface. Several studies have reported that the pore size distribution of catalyst has significant influence on glucose and fructose dehydration reactions [35, 146]. Both catalyst mesoporosity and microporosity have affected the carbohydrate conversion to 5-HMF and LA. For instance, in aqueous solution, catalyst with a large mesopore size would promote the side reactions including fragmentation and polymerization, thus decreasing the LA yield [150]. Mesoporosity may enhance the diffusion of 5-HMF away from the active sites and lead to the formation of coke, thus resulted in low LA production. It is suggested that dehydration of glucose to 5-HMF and LA requires a catalyst with appropriate mesopore and micropore sizes. The sizes of relevant molecules in the production of 5-HMF and LA are presented in Fig. 2. The trend of molecule diffusion can be envisaged by comparing the catalyst pore size and the sizes of feedstock and product. For instance, the size of feedstock, such as glucose with 0.9 nm, and pore sizes of the catalysts indicated whether the conversion process happened on the outer surface or in the pore of the respective catalysts [48]. Both Lewis and Brønsted acids played roles for conversion of carbohydrate biomass to 5-HMF and LA, and a good balance between the acid site density and the acid site strength is an important factor [48, 151]. Therefore, catalyst mesoporosity and ratio of Lewis and Brønsted acid sites must be scrutinized in order to maximize the 5-HMF and LA production. The acidity of catalysts can be determined by temperature-programmed desorption of ammonia (NH_3-TPD). The acid sites based on desorption temperature can be classified as weak acid (< 250 °C), medium acid (250–350 °C) and strong acid (> 350 °C). The NH_3-TPD provides general information on the amount and strength distribution of acid sites, while FTIR spectroscopy of pyridine adsorption elucidated the nature of acid sites: Brønsted or Lewis type.

The activity of several zeolite and modified zeolite catalysts was examined for 5-HMF production in ionic liquids [32, 40, 45, 46, 48]. It was depicted that glucose conversion to 5-HMF was greatly influenced by the Si/Al ratio, which affected the acid site density and strength of the catalyst. Zeolite with higher Si/Al ratio demonstrated less acid site density and stronger acid site strength. A good balance

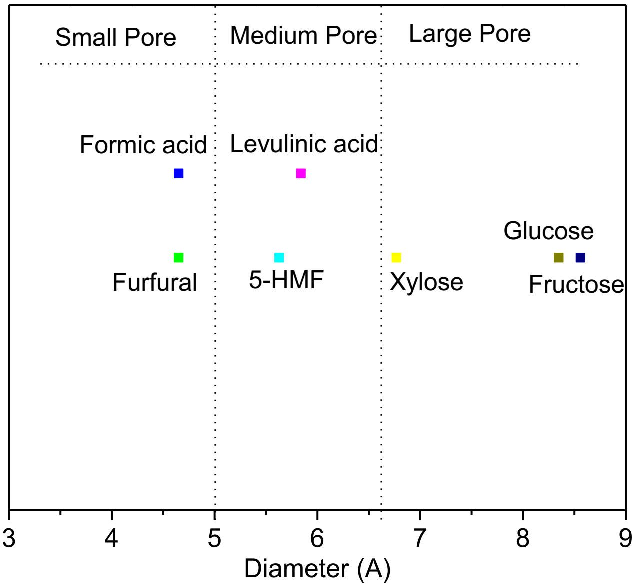


Fig. 2 Comparison of molecular dimensions of typical feedstock and product involved in 5-HMF and LA production. Adapted with permission from [150]

between the acid site density and the acid site strength is necessary for 5-HMF production [32, 45, 48]. In another study, chromium-loaded zeolite showed better 5-HMF production from glucose in [BMIM][Cl], compared with bare zeolites, USY, Beta and ZSM-5 zeolite [45]. This is due to USY zeolite possessed higher Si/Al ratio than Cr-USY zeolite, thus showed less 5-HMF yield [45]. In addition, modified mordenite and modified KL zeolite were used for glucose and fructose conversions in [BMIM][Br], respectively [32, 46]. The modified catalyst with moderate Si/Al ratio and high Brønsted acid sites possessed high catalytic activity in the ionic liquid reaction system. The study suggested the quick adsorption and strong interaction of ionic liquid with zeolite [46]. This condition hindered the diffusion of the products thus enhanced the role of zeolite mesoporosity on the catalytic activity when the reaction was carried out in ionic liquid solution.

It was found that acidity and pore structure of ion exchange resins showed prominent effect on fructose conversion to 5-HMF in [BMIM][Cl] [57, 131]. It was interpreted that the catalyst with large surface area applies more active sites, while large pore diameter allows the quick access of sugars molecule to the inner of the particular catalysts. A catalyst with strong adsorptive property is suitable for 5-HMF production since the adsorption of water produced from the dehydration of sugars can be done in order to avoid the further rehydration of 5-HMF to LA [57]. Besides, according to the characteristics of the catalysts, resins with sulfonic acid group possessed stronger acidity than resins with carboxyl group, thus showed better catalytic performance for fructose conversion to 5-HMF [57]. This statement was supported by study on conversion of glucose to 5-HMF in [BMIM][Cl] catalysed by ion-exchanged resin modified by $CrCl_3$ [131]. Macroporous strong-acidic ion exchanged resin exhibits better catalytic activity due to the larger surface area, stronger acidity and large number of macrospores [131]. The same rules of acid site density and strength and pore structure also applied for other solid catalysts such as mesoporous SBA-15-based catalysts, modified activated carbon, mesoporous titania and zirconia nanoparticles for 5-HMF production in ionic liquid [20, 55, 128, 152, 153]. The 5-HMF yield from fructose conversion in [BMIM][Cl] using SBA-15-SO_3H as catalyst (SBA-15 functionalized with propylsulfonic acid) was comparable with 5-HMF yield using H_2SO_4 as catalyst [20]. From the findings, the catalytic performance of SBA-15-SO_3H depended on both sulfonic group content and mesoporous structure.

In a study on cellulose conversion in [BMIM][Cl] catalysed by modified activated carbon, the results indicate that the presence of functional group attached on the catalyst increases the pore size thus increasing the number of active sites which helps in fast cellulose hydrolysis to 5-HMF [153]. In heterogeneous catalytic reactions, reactants must come to the surface of the catalyst and react with the catalytic sites, and the resulting products must diffuse away from the catalyst for the next reactant. Mesoporous titania and zirconia nanoparticles (MTN and MZrN) were prepared as catalyst for cellulose conversion in [EMIM][Cl] [55]. The difference in catalytic activity for 5-HMF production of these two catalysts was suggested due to their specific surface area and acidic properties, since the pore size and particle size of the catalysts were similar [55]. The MZrN-based catalyst exhibited three different acidic strengths, according to NH_3-TPD profile, while MTN-based catalyst exhibited only one acidic strength. Therefore, it was concluded that the higher production of 5-HMF using MZrN-based catalyst was attributed to the stronger acid strength [55].

As many studies reported on the use of metal salts for 5-HMF production in ionic liquids, studies have been conducted on the synthesis of metal salts exchanged catalyst to give a heterogeneous catalyst for the respective reaction. For instance, fructose conversion to 5-HMF catalysed by pyridinium based dicationic ionic liquids as catalyst [92]. It was implied that the reaction system would be more preferable than many other Lewis acid catalysed system as the ionic liquid contained transition metal complexes [92]. Metal salt-bentonite–exchanged catalysts were prepared and used for glucose conversion to 5-HMF in [BMIM][Cl]-DMSO [132]. Due to the high Lewis acidity of Cr^{3+}, the catalytic activity of Bentonite-Cr increased significantly. Furthermore, the 5-HMF yield using Bentonite-Cr was comparable than that of the homogenous catalyst $CrCl_3$, with added advantages of easy separation and recycling [132]. In addition, bentonite-Cr and montmorillonite-Cr were prepared and employed as catalyst for fructose conversion in [BMIM][Cl] [44]. Shorter reaction time was recorded to give highest 5-HMF yield in the presence of bentonite-Cr catalyst for [BMIM][Cl] reaction system [44] compared with the [BMIM][Cl]-DMSO as reported in different study [132].

The effect of different metal ions, including Cu^{2+}, Mo^{5+}, Fe^{3+}, Mg^{2+}, Al^{3+}, Cr^{2+} and Cr^{3+} used for modification of ion exchanged resin catalyst, was investigated for glucose conversion to 5-HMF in [BMIM][Cl] [131]. More than 60% 5-HMF yield was achieved in the presence of ion-exchanged resins modified with Cr^{2+} and Cr^{3+}, whereas less than 20% 5-HMF yield was obtained using other ions modified catalyst. The result was in agreement with previous study which found that chromic salts can promote the isomerization of glucose to fructose, whereas other metal salts can only improve the mutarotation of a-glucopyranose anomer to b-glucopyranose anomer [131]. A series of metal (Cu) substituted aluminophosphate molecular sieves displayed excellent performance as catalyst for fructose conversion to 5-HMF in [BMIM][Br] [35]. The catalyst with higher surface area, pore volume, and stronger acidity gave higher 5-HMF yield, highlighted the effect of acidity and porosity towards the reaction [35]. Heterogeneous catalysts were prepared by immobilizing homogeneous metal chloride/[EMIM][Cl] to mesoporous structure SBA-15 [128], and immobilizing Cr^{3+} to SO_3H-functionalized solid polymeric ionic liquid [89] for 5-HMF production from glucose and fructose, respectively. Several metal chlorides were used which $CrCl_2$/[EMIM][Cl] immobilized on SBA-15 showed the highest activity [128]. In addition, the strong acid sites of SO_3H groups together with $CrCl_3$ in the bulk of functionalized solid polymeric ionic liquid played the roles as active centers for the dehydration reaction [89]. The activity of Brønsted and Lewis acid polymeric catalysts was tested for cellulose conversion in [BMIM][Cl] [145]. The Brønsted acid sites were obtained by ion-exchanged while the Lewis acid sites were obtained through adsorption of Cr^{3+} [145]. The results of this study signified that the Brønsted acidic sites to be more effective in hydrolysis of cellulose to glucose and dehydration of fructose to 5-HMF, whereas Lewis acidic sites to be more effective in glucose-to-fructose isomerization [145].

Aluminium-containing catalyst with high Lewis acidity and low Brønsted acidity was employed to convert glucose to 5-HMF in [EMIM][Br] [42]. The oxide catalyst, Al_2O_3-b-0.05, was prepared by alkaline and acid treatments, which led to the increase of pore volume and average pore size, and slight decrease of specific surface area. The NH_3-TPD indicated that the number of acidic sites decreased after the treatments. In addition, the combined NH_3-TPD and pyridine adsorption revealed that the mild alkaline treatment is effective to block most Brønsted acid sites and weak Lewis acid sites, thus leading to the high Lewis acidity and low Brønsted acidity of the catalyst. As compared with [EMIM][Br]/Al_2O_3-b-0.05 heterogeneous system, the activity of homogeneous $AlCl_3$ in [EMIM][Br] was also investigated for glucose conversion to 5-HMF. From the analysis, the optimum 5-HMF yield of the homogeneous [EMIM][Br]/$AlCl_3$ was apparently lower than the heterogeneous [EMIM][Br]/Al_2O_3-b-0.05 owing to the severe side-reactions in the homogeneous system [42]. The hydrothermal stability of Al_2O_3 was reported to be low; thus, one of its precursor, boehmite (γ-AlOOH) with high hydrothermal stability, was prepared and employed for cellulose conversion in [BMIM][Cl]-DMSO [53]. The γ-AlOOH acted as a Lewis acid catalyst with existence of mesopores and relatively uniform distribution of pore size, exhibited excellent catalytic effects in the degradation of cellulose to 5-HMF [53].

The role of Brønsted and Lewis acid sites on conversion of polysaccharides to 5-HMF was examined on conversion of chitosan by various Brønsted-Lewis acidic ionic liquids [106]. The study was conducted using ionic liquids with different metal salts as the Lewis acid component, where ionic liquid with $FeCl_2$ showed the best performance. Acid–chromic chloride bi-functionalized catalysts were employed in conversion of cellulose to 5-HMF in ionic liquids such as [EMIM][Cl] and [BMIM][Cl] [54, 154]. The catalysts were prepared by grafting SO_3H and Cr(III) onto the surface of treated attapulgite (ATP) and halloysite nanotubes (HNTs). The grafting of SO_3H and Cr(III) can be assigned to Brønsted and Lewis acidic sites of the catalyst, respectively [154]. The HNTs–SO_3H–Cr(III) catalyst contained larger amounts of SO_3H and Cr(III) compared with ATP–SO_3H–Cr(III) catalyst, which results in better catalytic performance. The acidic features of the catalysts determined by NH_3–TPD were categorized into weak, medium and strong acid. Meanwhile, an acid base catalyst was fabricated by grafting acid and base, i.e. –SO_3H and –NH_2 groups on carbon nanotubes and further functionalized with Cr(III) species for further enhancement of acidity. Co-existed base and Lewis acid sites were found to promote glucose isomerization to fructose, and Brønsted acid sites direct the dehydration of fructose to 5-HMF [54].

Biomass-derived carbonaceous catalysts have been extensively studied. They were typically prepared by carbonisation and sulfonation process. Lignin-derived acid catalysts were used for fructose and glucose conversion to 5-HMF in [BMIM][Cl] and [BMIM][Cl]-DMSO [27, 29]. The full solubilization of the sulfonated lignin in [BMIM][Cl] results in an acidic solution, which was suitable as reaction media for 5-HMF production. The NH_3-TPD desorption profile of the catalyst showed a major peak at around 100 °C, which assigned to Brønsted acid sites from the sulfonic acid [29]. Other than lignin, solid acid catalysts containing –SO_3H, –COOH and phenolic –OH groups were prepared from cellulose, glucose or starch, for glucose conversion to 5-HMF in [BMIM][Cl] [26]. The study showed the synergic effect of –SO_3H, –COOH and phenolic –OH groups for glucose conversion to 5-HMF in [BMIM][Cl][26]. In addition, carbonaceous catalyst was also prepared from carbonisation and sulfonation of yeast cells for 5-HMF production in [BMIM][Cl]. The obtained carbonaceous catalyst exhibited high catalytic activity suggesting that –SO_3H groups served as active sites [10]. Besides, biochar modified catalyst was prepared through pyrolysis of corn stalk, and subsequently employed for 5-HMF production in [AMIM][Cl]-isopropanol reaction system [70]. The biochar modified catalyst possess appropriate components to effectively promote the degradation of lignocellulosic content [70].

It was known glucose conversion to 5-HMF reaction process consisted of isomerization and dehydration steps, which acid catalyst, Brønsted and Lewis, was generally employed. Alkaline/base catalysts have also been employed for glucose conversion to 5-HMF. It was found that the increase of the alkalinity of catalyst or catalytic system would effectively improve the isomerization of glucose into fructose [54, 138, 155]. A study was conducted on glucose conversion to 5-HMF in [BMIM][Cl]-DMSO catalysed by a simple base catalyst, ammonium aluminium carbonate hydroxide ($NH_4Al(OH_2)CO_3$) [138]. The study indicated the catalytic activity primarily arise from the catalyst, while [BMIM][Cl] and DMSO were acted as the solvent to dissolve glucose and products [138]. Furthermore, the use of basic bone char and acidic ionic liquid [C_3SO_3HMIM][HSO_4] combination shows a synergistic effect on increasing 5-HMF selectivity from glucose conversion [155]. The mesoporous bone char catalyst was synthesized using cattle bone powder and its basicity was examined by CO_2-TPD, which exhibits medium and strong basic sites [155].

Catalyst Loading

Other than ionic liquids, various types of catalysts have been applied for conversion of carbohydrate biomass to 5-HMF and LA. The effect of catalyst loading on the feedstock conversion and product yield have been evaluated accordingly to select the appropriate catalyst loading. For instance, the effect of heteropolyacid acid catalyst (i.e. tungstophosphoric acid, silicotungstic acid) loading was investigated as the catalyst was combined with boric acid or used as sole catalyst for fructose conversions in [BMIM][Cl] [28, 38]. Further increase in the catalyst loading, the 5-HMF yield increase accordingly. Metal halides have been extensively studied as catalyst for conversion of carbohydrate biomass in ionic liquid. The influence of chromium chlorides (i.e. $CrCl_2$, $CrCl_3$) loading has been investigated for conversions of glucose, sucrose and cellulose in different types of ionic liquids [17, 122, 139, 140, 144]. The use of chromium chloride leads to a remarkable increase in feedstock conversion and 5-HMF yield at the beginning of the reaction, but then the 5-HMF yield reaches a plateau. Results from several studies implied that ~ 2 mol% of the chromium catalyst was sufficient for the catalytic systems of glucose conversion in [BMIM][Cl] [17] and sucrose conversion in pyridinium-based dicationic ionic liquid [122]. The destruction of cellulose glycosidic bonds in [BMIM][Cl]/toluene reaction system increased as $CrCl_3$ loading increased, thus significantly weakened the degree of cellulose intramolecular and intermolecular hydrogen bonds [140]. Nevertheless, further increased of $CrCl_3$ loading led to 5-HMF decomposition due to excessively high reaction system acidity [140]. Other than chromium chlorides, the effect of different metal halides loading was evaluated including $GeCl_4$, $AlCl_3$, $InCl_3$ and $IrCl_3$. The optimum 5-HMF yield was achieved from reaction conducted in [BMIM][Cl] with catalyst loading up to 10 mol% for fructose conversion catalysed by $IrCl_3$ [21], glucose conversion catalysed by $GeCl_4$ [19] and cellulose conversion catalysed by $AlCl_3$ [50]. Meanwhile, an optimum catalyst loading of 0.2 mmol $IrCl_3$ and 0.15 g $AlCl_3$ were reported for cellulose conversion in [(C_3SO_3H)mim][HSO_4]-DMSO and starch conversion in [BMIM][Cl]-DMSO, respectively [56, 103]. By further increased of the amount of catalyst, the 5-HMF yields dropped due to the overactivity of the catalyst that not only accelerated the substrate conversion to 5-HMF but also promoted additional side reactions.

Various heterogeneous catalysts were developed and employed for the conversion of carbohydrate biomass to 5-HMF and LA, and the effect of catalyst loading was studied accordingly. Different loading of carbonaceous catalysts was employed for conversions of various carbohydrate biomass in [BMIM][Cl] [10, 26, 27, 29]. The catalysts which having acidic SO_3H groups deduced different optimal catalyst loading. Fructose conversion catalysed by lignin derived carbonaceous catalyst significantly improved the 5-HMF production using 5 wt% catalyst loading as compared with fructose dehydration in [BMIM][Cl]-DMSO in the absence of catalyst [29]. Only small increment in 5-HMF yield was observed when the catalyst loading increased further from 5 to 7 wt%. Meanwhile, favourable catalyst loading for satisfactory fructose conversion in [BMIM][Cl] was found at 25 wt% of lignosulfonic acid catalyst [27]. The optimum carbonaceous catalyst loading of 10, 20 and 20% is essential for optimum 5-HMF yield from fructose, sucrose and inulin conversions in [BMIM][Cl], respectively [10]. On the other hand, higher amount with optimal 40 wt% of cellulose derived carbonaceous catalyst loading is required as increasing amount of the catalyst from 20 to 40 wt% resulted in remarkable increased in glucose conversion and 5-HMF yield [26]. Insignificant increment of 5-HMF yield or decreased in the 5-HMF yield by further increasing of carbonaceous catalyst loading can be observed. This could be ascribed to more available acidic sites derived from the excessive catalyst, which facilitated the 5-HMF decomposition and polymerization of 5-HMF and glucose to humins [26].

Different loading of zirconia (ZrO_2)-based catalysts has been evaluated for 5-HMF production from various carbohydrate biomass conversions in ionic liquids [23, 55, 137]. In addition, fructose and glucose conversions in [BMIM][Cl] catalysed by different heterogeneous catalysts such as acidic ion exchange resin [57], chromium-modified ion exchange resin [131] and chromium exchanged bentonite [132] were explored and the effect of catalyst lading was investigated accordingly. The effect of catalyst loading on feedstock conversion and 5-HMF yield was also influenced by the catalyst properties such as acidity and mesoporosity. When too many catalysts were present in the reaction system, 5-HMF was further decomposed into other by-products. The addition of excess catalysts led to mass transfer limitations, thus limiting more feedstocks to join in reaction at the same time. This supported the fact that no more catalyst should be loaded once the amount of catalyst in the reaction system meets its necessity.

Types of Feedstocks

The ionic liquid system should be pertinent for the conversion of various carbohydrates into 5-HMF and LA. The suitability and activity of the reaction system containing ionic liquid were tested for the conversion of different types of carbohydrates including monosaccharides, disaccharides, polysaccharides and lignocellulosic biomass. The performance of the reaction system was significantly affected by the component units and structure of the feedstocks. To give a clear view of the effect, the component units and structure of each saccharides are as follows: sucrose is a disaccharide with a β(1,2) glycosidic bond between a glucose and a fructose molecule, maltose is a disaccharide with two glucose molecules linked by a α(1,4) glycosidic bond, cellobiose is a disaccharide with two glucose molecules linked by a β(1,4) glycosidic bond, starch is a polymer of glucose units containing α(1,4) glycosidic bonds in a linear fashion and α(1,6) in a branched fashion, and cellulose is a polymer of glucose units linked by β(1,4) glycosidic bonds. Chitosan has structural similarities with cellulose, whereas the chemical difference lies in the functional group on the second carbon, which is hydroxyl group in cellulose and amino group in chitosan. In general, the more facile of the monosaccharide units degradation, the easier their corresponding disaccharides or polysaccharides conversion into 5-HMF and LA [53, 100, 156].

Fructose and glucose are the most common monosaccharide used for 5-HMF and LA productions. The performance of ionic liquid system on these two feedstocks were compared. Since glucose (monomer of cellulose) can be obtained by hydrolysis of cellulose, its conversion is more significant for the practical applications. In [EMIM][Br]-tyrosine catalyst reaction system, lower 5-HMF yield was obtained from glucose (38%) compared with 5-HMF yield produced from fructose (72%) [33]. This condition was due to the crucial step of glucose isomerization for 5-HMF production. The same trend was reported when the reactivity of fructose and glucose in [AMIM][Cl] [156]. Fructose can be efficiently converted into 5-HMF with high yield in [AMIM][Cl] without the addition of catalyst. Nevertheless, very poor performance was recorded for glucose dehydration (only 1% 5-HMF yield) in [AMIM][Cl]. On the other hand, in fructose and glucose conversions catalysed by lignin-based carbonaceous in DMSO-[BMIM][Cl] [29], different trend of 5-HMF yield from fructose and glucose were reported. The 5-HMF yield increased with time for glucose conversion but decreased for fructose conversion [29].

Conversion of disaccharides have been widely tested for 5-HMF production in ionic liquid systems including sucrose, maltose, lactose and cellobiose. The synthesis of 5-HMF from disaccharides was preceded in three steps: (i) hydrolysis of disaccharides into monosaccharide, (ii) isomerization of glucose to fructose and (iii) dehydration of fructose to 5-HMF. The degradation of sucrose to 5-HMF performed well in ionic liquids system such as [AMIM][Cl] and [BMIM][Cl] [156], [BMIM][Cl] catalysed by $GeCl_4$ [19], [BMIM][Cl] catalysed by yeast derived carbonaceous catalyst [10], [BMIM][Br] catalysed by tyrosine [33], [EMIM][BF_4] catalysed by $SnCl_4$ [22], [BMIM][Cl] catalysed by Hβ zeolite [48] and [EMIM][Br] catalysed by 2,5-furandicarboxylic acid [34]. The 5-HMF yield was low for the conversion of maltose and cellobiose (2 glucose units) compared with sucrose (glucose–fructose unit) [19, 22, 33, 36, 48, 100, 156]. This is because in maltose and cellobiose, the monosaccharide units are joined by 1,4-glycosidic bond, which make hydrolysis more difficult than that of 1,2-glycosidic bond for sucrose [33]. Other reason for low 5-HMF yield from maltose and cellobiose was the presence of glucose unit which is known to have a crucial step of glucose isomerization for 5-HMF production. In addition, it was implied that maltose and cellobiose tended to undergo retro aldolization reaction to produce oxygenated aliphatic [100]. Comparison of sucrose and cellobiose conversions in [EMIM][Br] catalysed by 2,5-furandicarboxylic acid showed lower 5-HMF yield from cellobiose than sucrose [34]. The similar trend was obtained from study on sucrose, maltose and cellobiose conversions in sulfonated ionic liquid, where the 5-HMF yield reported in the order of sucrose > cellobiose > maltose [100].

Comparison have been made between sucrose and its components: fructose and glucose. Several studies showed that 5-HMF yield obtained from sucrose was lower than that obtained from fructose but higher than obtained from glucose. This trend was reported for reactions in ionic liquid systems such as [CMIM][Cl] in DMSO catalysed by $ZrOCl_2$ [80], [$C_{10}(Epy)_2$]$2Br^-$ catalysed by $CrCl_2$, [122], [BMIM][Cl] catalysed by $IrCl_3$, [$GLY(mim)_3$][$Cl]_3$ catalysed by glucose-derived carbonaceous catalyst [95], and polyethylene glycol-400-functionalized dicationic acidic ionic liquid in DMSO [123]. The results revealed that the dehydration of glucose to 5-HMF was a bit difficult as compared with fructose, as the conversion of glucose involves isomerization of glucose followed by dehydration of fructose. In several studies, the 5-HMF yield obtained from sucrose was around half of the 5-HMF yield obtained from fructose. This trend has been reported for sucrose conversion in [BMIM][OH] [141], [BMIM][Cl] [10], [AMIM][Cl]/DMF-based system [25], protic ionic liquid [88] and ionic liquid-based polyoxometalate salts in DMSO system [93]. This trend was possibly due to the ionic liquid system which can hardly promote the isomerization of glucose into fructose. From the results, since sucrose is a disaccharide consisting of glucose and fructose, it can be suggested that only fructose moiety in sucrose was converted into 5-HMF. Most of the studies on sucrose conversion to 5-HMF reported that either glucose unit was a bit difficult to be converted to 5-HMF compared with fructose or 5-HMF was only produced from fructose moiety and the glucose moiety was wasted. Nevertheless, there were several works that revealed both glucose and fructose moiety could be converted into 5-HMF and most of the carbon in sucrose was utilized. The ionic liquid systems which afforded this trend include [EMIM][BF_4]/$SnCl_4$ [22], [BMIM][Cl]/$CrCl_3$ [144], [BMIM][Cl]/$ScCl_3$ [31] and [EMIM][Br]/tyrosine [33].

The conversion of polysaccharides to 5-HMF is substantially more challenging than the conversion of other simple sugars, as it combined the hydrolysis of the carbohydrates into the monosaccharides, which then undergo dehydration to 5-HMF. Nevertheless, the reaction system comprising of ionic liquid and catalyst could efficiently transform the polysaccharide to 5-HMF. In general, with the increasing degree of polymerization of the polysaccharides, the catalytic activity of the catalytic system gradually decreased. The direct transformations of the polysaccharides to 5-HMF frequently reported in literatures include inulin, cellulose, chitosan and starch. The conversion of inulin, the polymer of fructose, into 5-HMF comprised of two consecutive reactions. The first step is hydrolysis of the polymer into monosaccharide fructose and the second step is the dehydration of fructose to final product 5-HMF. On the other hand, the conversion of cellulose, the polymer of glucose into 5-HMF, involves three reactions, which are hydrolysis into monosaccharide glucose, followed by isomerisation from glucose to fructose and finally formation of 5-HMF from fructose. The addition of glucose isomerization step in cellulose conversion typically resulted in lower 5-HMF yield from cellulose compared with inulin [87, 100].

Many efficient ionic liquid reaction systems have been reported for inulin conversion to 5-HMF. They include [CMIM][Cl] in DMSO [80], [BMIM][Cl] catalysed by yeast derived carbonaceous catalyst [10], [BMIM][HSO_4] catalysed by silica-supported boric acid [81], and ionic liquid-based catalyst Cr(Salen)-IM-HSO_4-MCM-41 in DMSO [87]. The 5-HMF production from cellulose depends on the degree of polymerization of the feedstock, which the ionic liquid/catalyst systems were explored to reduce the degree of cellulose polymerization [139]. As comparison, degree of polymerization of inulin is 2 to 60, while degree of polymerization of microcrystalline cellulose is in the range of 200–350, which introduced difficulties in cellulose hydrolysis [100]. Both reaction rate and 5-HMF yield decreased with increasing of polymerization degree. Several effective ionic liquid systems for cellulose conversion are [BMIM][Cl] in DMSO catalysed by functional polymeric ionic liquid [89], [BMIM][HSO_4] catalysed by silica-supported boric acid [81], [BMIM][Cl] catalysed by $CrCl_3$ [139], [BMIMCl] catalysed by $GeCl_4$ [19] and [BMIM][Cl] catalysed by Hβ zeolite [48].

In a study by Hou et al. [142], it was highlighted that the hydrogen bonding ability of ionic liquid did not affect the conversion efficiency towards chitosan as notably as in cellulose conversion. With the presence of water in the reaction mixture, chitosan can be barely dissolved in [C_3SO_3Hmim]HSO_4 in contrast to [C_3SO_3Hmim]Cl. Even though the solvation ability of [C_3SO_3Hmim]Cl is better than [C_3SO_3Hmim]HSO_4 which due to stronger hydrogen bonding ability of Cl^-, the LA yield from [C_3SO_3Hmim]Cl is lower [142]. This can be explained by that the interactions between NH_2 groups of chitosan and acidic ionic liquid predominate over the hydrogen bonding interactions, given that amine group is more basic than hydroxyl group [142]. Several effective ionic liquid systems were reported for conversion of starch, include [C_2OHMIM][Cl] catalysed by $CrCl_2$ [16], [BMIM][Cl] catalysed by Hβ zeolite [48] and [BMIM][Cl] in DMSO catalysed by $AlCl_3$ [56]. The catalytic performance of [BMIM][Cl] in the presence of $CrCl_3$ modified ion exchange resin for cellulose and starch conversions were lower compared with glucose conversion [131]. This suggested that the ionic liquid system could not catalyse the complex hydrolysis of polysaccharides at short reaction time and low temperature. The maximum 5-HMF yield was obtained from prolonged reaction conducted at 8 and 24 h for cellulose and starch, respectively, using [BMIM][Cl]/boric acid system [36]. In addition, the waterless environment also resulted in poor catalytic performance of the ionic liquid system [131]. This can be supported by difficulty of hydrolysis of starch and cellulose to 5-HMF in the organic media using ionic liquid-based catalyst in DMSO [87].

In the catalytic conversion of lignocellulosic biomass, the product yield relied on the cellulose content in the biomass feedstock. Ya'aini et al. [157] has made a comparison of two different lignocellulosic biomass resources, empty fruit bunch and kenaf on LA production. Based on the findings, the LA yields depended on the biomass sources, where biomass with high C_6-sugar, cellulose content, produced higher yield. The similar trend was reported on the conversion of various biomass feedstocks for LA production using dicationic ionic liquid [111]. The 5-HMF and LA yield from biomass are generally lower compared with the yields from sugars and polysaccharides. This is due to the recalcitrance of the lignocellulosic biomass caused the difficulty of the catalytic reaction [111]. Even though the yields obtained from cellulose and biomass conversions were lower than that from monosaccharides, direct use of cellulose and biomass could avoid several steps such as tedious pretreatment, hydrolysis and separation processes. In ionic liquid system, the biomass can be dissolved and subsequently converted into 5-HMF and LA in one pot reaction. The biomass could undergo pretreatment process for size reduction and decrease in crystallinity [17]. The size reduction can increase the surface area available for the reaction and facilitate the conversion reaction, which later contribute to higher product yield. For example, the conversion of wheat straw (milled wheat straw) in [BMIM][Cl] catalysed by $CrCl_3$ and LiCl reached 5-HMF yield comparable with pure cellulose [74].

Feedstock Loading

In practical application, the use of high concentration of feedstock is necessary to obtain high concentration of product. The tolerance for the concentration of feedstock is an important aspect to evaluate a catalytic conversion process from an economical point of view. The process economics and environmental friendliness can be improved if higher feedstock loading is used with a constant amount of solvent and/or catalyst. In conversion of carbohydrate biomass in ionic liquids to 5-HMF and LA, attempts were made to study the effect of initial feedstock loading on the feedstock conversion, product yield and selectivity. In several studies, when the initial glucose/fructose loading increased from 5 to 10 wt%, the 5-HMF yield increased from 47.3 to 51.9%, 78.2 to 78.8% and 53 to 73% for reactions carried out in [BMIM][Cl] catalysed by 12-tungstophosphoric acid/boric acid, in [BMIM][Cl] catalysed by $CrCl_3.6H_2O$ and boric acid, and in Brønsted acidic ionic liquids, respectively [38, 41, 118]. The similar trend was also reported for the conversion of fructose in [BMIM][Cl] catalysed by acidic ion exchange resin (from 0.05 to 0.1 g with yield increase from 83.4 to 93%) [57]. Besides, the conversions of dried root and acorn to 5-HMF in [OMIM][Cl]-ethyl acetate showed increased in 5-HMF yield by 1.2 fold as the feedstock loading increased from 10 to 20% and 10 to 15%, respectively [67, 68]. Nevertheless, the 5-HMF yield started to decrease when the feedstock loading was further increased [38, 41, 57, 67, 68, 118]. For instance, when the glucose loading increased to 30 wt%, the 5-HMF yield decreased to 59.9% in contrast to 78.8% yield for 10 wt% glucose loading [41].

A gradual decrease in feedstock conversion and 5-HMF yield was observed as higher feedstock loading was applied in the reaction system. The decrease in glucose conversion catalysed by [SMIM][$FeCl_4$] from 97 to 91% was reported as glucose weight was increased from 0.2 to 0.3 g [64]. Similar pattern was observed for glucose conversion in [BMIM][Cl]/$CrCl_3$ system, as the conversion decreased from 97 to 73% when the feedstock loading increased up to 20 wt% [17]. It was presumed that the excess glucose does not participate in the reaction as the unreacted glucose was clearly visible after the reaction. The 5-HMF yield decreased from 92.7 to 73% as glucose loading increased from 5 to 50 wt% for reaction conducted in [BMIM][Cl] catalysed by lignosulfonic acid [27]. Other studies showed the same trend on 5-HMF yield as the initial feedstock loading increased. They include glucose conversions in [BMIM][Cl]-DMSO catalysed by lignin-derived solid acid catalyst [29], in [BMIM][Cl] catalysed by $CrCl_3$ [144], and in [BMIM][Cl] catalysed by $CrCl_3$-modified ion exchange resin [131]. Other ionic liquid reaction systems with decreased in 5-HMF yield as the initial loading increased include fructose, sucrose and chitosan conversions in [HO_2CMMIM][Cl]-isopropanol, pyridinium-based ionic liquid-$CrCl_2$ and [MIM][HSO_4], respectively [82, 105, 122].

The similar outcome was also obtained for LA yield. It was found that the LA yield from the conversions of glucose and cellulose in [BSO_3HMIm][HSO_4]-water decreased from 60.8 to 52.9% and 54.5 to 49%, respectively, as the feedstock to solvent ratio increased from 0.01 to 0.05 [90]. Besides, in [BMIM-SO_3H]HSO_4 aqueous mixture for fructose conversion, LA yield dropped from 70 to 44% when increasing fructose loading from 2.5 to 15 wt%, although fructose and 5-HMF were converted completely [91]. The low LA yield at increased fructose loading can be attributed to the higher rate of substrates participated in undesired side reactions. In addition to feedstock conversion and 5-HMF yield, 5-HMF selectivity was also addressed by examining the effect of initial feedstock loading. The low selectivity is considered as the main drawback from high initial feedstock loading. For reaction system containing 1-(4-sulfonic acid) butyl-3-methylimidazolium hydrogen sulfate in MIBK, the 5-HMF selectivity has increased as fructose loading increased from 0.3 to 1 g, then to 1.5 g [116]. Additional increase in the fructose loading up to 2 g led to lower 5-HMF selectivity. The same trend on 5-HMF selectivity has been reported in several studies [92, 130]. The effect of feedstock loading also correlated to other factors such as reaction time. It was reported that longer reaction time was needed when the initial feedstock loading was higher [24, 28, 118].

The decreased in products yield as the initial feedstocks loading increased was most likely due to several reasons. The feedstocks such as glucose and fructose could self-polymerize and cross-polymerize with 5-HMF to give other soluble by-products [38, 41, 57, 82, 116, 144]. The condition has been verified by examining the stability of 5-HMF in the reaction system by adding 5-HMF and $CrCl_3$ catalyst into [BMIM][Cl] in the absence of glucose [144]. After a certain reaction time, 96% of the 5-HMF could be recovered, suggesting that 5-HMF was stable under the predetermined reaction condition in the absence of glucose. This could be further indicated that the lower 5-HMF yields with increasing feedstock loading was attributed to the formation of by-products resulted from self-polymerization and co-polymerization of feedstock and 5-HMF. The cross-polymerization of feedstocks and 5-HMF as feedstock loading was increased also led to the generation of the insoluble by-products, humins, especially in an aqueous mixture system [27, 64, 66, 119].

The insufficient active catalyst site to accommodate the conversion of feedstock also contributed to lower feedstock conversion and product yield at higher initial feedstock loading [102, 118, 122, 131]. Meanwhile, at lower initial feedstock loading (5 wt%), lower 5-HMF selectivity was obtained from fructose conversion in Brønsted acidic ionic liquids. This was due to side reactions by the excess active catalyst sites of the ionic liquid [118]. For cellulose conversion reaction, it was observed that higher cellulose loading affected the reaction as the viscosity of reaction system increased and the amount of catalysts per molar of cellulose might reduce [102]. Similar result was obtained for biomass conversion in [OMIM][Cl]-ethyl acetate [68]. Higher initial feedstock loading of 30 and 40% showed highly viscous property that was difficult to handle and resulted in lower product formation. The limited solubility of cellulose at high loading in the ionic liquid would create a multiphase reaction system [51]. Besides, the decrease in 5-HMF yield from biomass conversion, was due to the combined effect of low dissolution of feedstock at higher concentrations, limitation in transport phenomena and decrease in hydrolysis rate to monosaccharides [120]. Nevertheless, it has also been reported that as the initial feedstock loading increased, the product yield and selectivity did not decrease significantly. This has been reported for fructose conversion to 5-HMF in [BMIM][Cl] catalysed by Amberlyst 15 and acidic ion exchange resins [57, 130] as well as for glucose conversion to 5-HMF and LA catalysed by functionalized ionic liquid [SMIM][$FeCl_4$] [64, 108]. For fructose conversion in [BMIM][Cl], it was perceived that ionic liquid can inhibit the formation of humins in contrast to aqueous or aqueous mixtures reaction system [57, 130]. Additionally, as the glucose loading increased, it was inferred that excess reactive sites were available for extra conversion of glucose under the applied reaction condition [64, 108].

High solubility of feedstock in reaction system is crucial for high efficiency of conversion particularly for reaction at high initial feedstock loading. For instance, water has been employed as co-solvent for fructose conversion. However, water also participates in the reversible equilibrium in the hydrolysis of 5-HMF, which resulted in poor results in contrast to results obtained in non-aqueous solution [143]. Thus, it is important to highlight the strong dissolving power of ionic liquid towards fructose, which could allow the use of high initial feedstock loading [143]. As deliberated in previous studies, the self- and co-polymerization from carbohydrate biomass conversions to 5-HMF could not be avoided, thus to obtain high 5-HMF yield from high initial feedstock loading remained a challenge. The main drawback from high initial feedstock loading is low product selectivity as well as problems in the physical handling. Nevertheless, few studies have reported satisfactory results obtained at high initial feedstock loading.

Fructose conversions to 5-HMF in [BMIM][Cl] with high initial fructose loading (≥30 wt%) have been conducted previously with the considerably high 5-HMF yield. They include reactions in the presence of SBA-15-SO_3H as catalyst with fructose loading up to 60 wt% and 60.5% 5-HMF yield [20], HCl as catalyst with fructose loading up to 67 wt% and 51% 5-HMF yield [24], and lignosulfonic acid as catalyst with fructose loading up to 50% and 73% 5-HMF yield [27]. Besides, initial loading up to 40% with 52% 5-HMF yield was reported for fructose conversion in Brønsted acidic ionic liquids [118]. Interestingly, very high sugar concentration (80 wt% with respect to the ionic liquid) has been employed in [EMIM][Br]/$SnCl_4$ reaction system with 5-HMF yield up to 66% from sucrose conversion [148]. In cellulose conversion catalysed by [C_3SO_3HMIM][HSO_4] and [BMIM][Cl] as solvent, high LA yield (~50%) was attained at high cellulose to ionic liquid ratio up to 220% [66, 119]. In addition, high initial loading was also reported for biomass conversions to 5-HMF. However, up to 40% and 50% loading of dried root and acorn biomass, respectively, reduced the relative productivity of 5-HMF [67, 68]. High biomass loading results in non-uniform mixing leading to limited interaction of catalyst and ionic liquid with biomass and hence decreases the product yield [79].

Types of Ionic Liquids

Ionic liquids are prepared from combinations of different cations and anions, and regarded as tunable solvents where their structures have a remarkable effect on the reaction. In 5-HMF and LA productions, the interactions among cation, anion and carbohydrates play important roles during the process. A comprehensive study was conducted on elucidating the structure-property relationship of ionic liquids towards hydrolysis of inulin [158]. The study focused on inulin hydrolysis for reducing sugar production where the effect of chemical structures of the ionic liquids on their acidity and catalytic properties was investigated. In this section, the relationship between the ionic liquid property and the catalytic activity is highlighted, where the effect of ionic liquid structure, different anions and cations, as well as acidity and basicity, on 5-HMF and LA productions is discussed, regardless of the ionic liquid was employed as solvent or catalyst.

Review of previous studies showed that anions-containing ionic liquid which have been employed in conversion of carbohydrate biomass include chloride (Cl^-), bromide (Br^-), fluorine (F^-), tetrafluoroborate (BF_4^-), hexafluorophosphate (PF_6^-), nitrate (NO_3^-), hydrogen sulfate (HSO_4^-), alkyl sulfate ($ROSO_3^-$), alkyl sulfonate (RSO_3^-), acetate (OAc), p-toluene sulfonate (PS^-), dihydrogen phosphate, (H_2PO4^-) and bistriflate imide (NTf_2^-). Among these anions, halides anion-containing ionic liquids were the most common ionic liquids reported. Halide anion-containing ionic liquids, such as [BMIM][Cl], [BMIM][Br], [Bpy][Cl] and [EMIM][Cl], gave reasonably high 5-HMF yields from fructose and glucose conversions, regardless of types of the cations [24, 37, 137, 143]. The solvation of fructose/glucose through hydrogen bonding between Cl^- in the liquid and carbohydrate hydroxy groups generate a profound influence for the enhancement of the dehydration reaction compared with other ionic liquids. In cellulose conversion, ionic liquid with stronger hydrogen bond acceptors could increase accessibility of the feedstock to the active sites, then promote the catalytic performance [66, 119]. The anion facilitates the breakage of hydrogen bonding network of cellulose and improve its dissolution. The hydrogen bonding effect between Cl^-containing ionic liquid and hydroxyl groups have been reported in several studies, such as conversion of fructose to 5-HMF and conversion of cellulose to LA [28, 57, 66, 119, 143].

The hydrogen bonding between the anion and the hydroxyl group of carbohydrate biomass was influenced by nature of the anion, which is the relative nucleophilicity and coordinating ability. Nucleophilicity of anion was required to obtain a high 5-HMF yield [39, 96, 133]. It was suggested that halide (Cl^-, Br^-, F^-) anion has better coordination ability compared with other anions such as PF_6^-, BF_4^- and NO_3^-. In several studies, [BMIM][PF_6] and [BMIM][BF_4] gave low 5-HMF yields from fructose conversion to 5-HMF [24, 28, 57, 133, 143, 159]. This phenomenon was due to poor coordinating ability of PF_6^- and BF_4^- and these anions were less competent than halides in providing a strong hydrogen-bonding for the dehydration reaction [24, 57, 143]. The presence of non-interacting hydrophobic cation in [BMIM][Cl] results in free chloro group, which was more reactive than BF_4^- and PF_6^- anions [117]. In addition, a study on corn stalk conversion to 5-HMF in different ionic liquids systems, [AMIM][Cl] and [AMIM][BF_4], signified that [AMIM][BF_4] contained very large anion and presented greater steric hindrance, which resulted in lower solubility of cellulose in [AMIM][BF_4] [70]. As reported by Zhang et al. [133], [BMIM][PF_6] did not improve the 5-HMF yield from fructose conversion in DMSO catalysed by $GeCl_4$, compared with [BMIM][Cl]. This is because [BMIM][PF_6] is not stable in the presence of water, which produced during the dehydration of fructose [133]. This would result in the decomposition of [BMIM][PF_6], where the decomposition product might lead to further conversion of 5-HMF into unwanted by-products. Besides, nucleophilicity of PF_6^- is weak and it could not promote fructose dehydration compared with Cl^-, leading to lower 5-HMF yield. Several different anions containing 3-(2-chloroethyl)-1-imidazolium [ClEMIM]$^+$ ionic liquid, range from small hydrogen bond donor (Cl^-) to larger non-coordinating anions, BF_4^- and NO_3^-, were examined. Due to the low coordinating ability, far lower 5-HMF yield was obtained from [ClEMIM][BF_4] and only trace of 5-HMF was attained from [ClEMIM][NO_3] [63]. The synergistic effect of Cl^- in both anion and cation of [ClEMIM][Cl], which acted as both H bond donor and nucleophile, causing efficient dehydration of fructose to 5-HMF.

Several studies reported that BF_4^- containing ionic liquid did not exhibited good performance in 5-HMF production, due to poor coordination ability of BF_4^-. However, in chitosan conversion in aqueous [BMIM][BF_4], comparable 5-HMF yield was obtained with [MIM][Cl] [105]. It was presumed that both Cl^- and BF_4^- have strong hydrogen bond accepting abilities, which can break the intramolecular hydrogen bonds in chitosan for 5-HMF production. Meanwhile, [BMIM][BF_4] gave considerable 5-HMF yield for fructose conversion using $SnCl_4$ as catalyst, compared with other anions with good coordination ability such as Cl^-, Tf_2N^-, TFA^-, $Trif^-$, $Sacc^-$ [22]. It was understood that these strong coordination ability anions would have stronger interactions with the Sn atom, which competed with the interaction between glucose and Sn atom and inhibited the formation of 5-HMF. It was also suggested that BF_4^- has low coordination ability to $SnCl_4$ but high coordination ability with catalyst such as $GeCl_4$ and HPW [19, 28]. Other than Cl^-, Br^- and F^- containing ionic liquids possess good effect on 5-HMF production. Br^- has been considered to be better nucleophile than Cl^-, as slightly higher 5-HMF yield was produced from fructose conversion using [BMIM][Br] compared with [BMIM][Cl] [159]. The similar trend was obtained from studies by Hou et al., where 5-HMF yield and selectivity from glucose conversion using [EMIM][Br] were remarkably higher than that obtained with [EMIM][Cl] [42, 47]. From these studies, it can be concluded that both Cl^- and Br^- have similar nucleophilicity when similar cation-containing ionic liquid was used. Meanwhile, Br^-containing pyridinium based dicationic ionic liquids gave good 5-HMF yield from glucose [122]. The Br^-containing ionic liquid offers the optimal balance between coordination ability and nucleophilicity. In addition, F^- anion-containing ionic liquids-functionalized biochar sulfonic acids possessed an excellent activity for cellulose hydrolysis to 5-HMF [129]. This is due to good affinity of the ionic liquid-based catalyst with the glycosidic bonds of oligosaccharides.

The non-halide anions containing ionic liquids, such as $ROSO_3^-$, HSO_4^-, $H_2PO_4^-$, RSO_3^- were also employed for 5-HMF and LA productions. In glucose conversion catalysed by boric acid, 5-HMF formation was observed albeit in small amount compared with [EMIM][Cl] when ethyl sulfate and methyl sulfate-containing ionic liquids were involved [36]. The low 5-HMF formation possibly due to the acidity of the ionic liquid which lead to rehydration of 5-HMF to LA. This can be supported by the use of HSO_4^- and RSO_3^- containing ionic liquids for conversion of cellulose and biomass to LA [66, 112, 119]. Meanwhile, $H_2PO_4^-$ containing ionic liquid showed moderate effect on LA production from cellulose [66, 119]. Eminov et al. [51] suggested that [HSO_4]$^-$ anion inhibited the isomerization of glucose to fructose, as the presence of [BMIM][HSO_4] was found to lower the conversion of cellulose to 5-HMF, in comparison with [BMIM][Cl]. This condition validated their finding from previous study on glucose conversion to 5-HMF in [BMIM][HSO_4] [85]. Several anions which reported to give low 5-HMF yield include OAc^-, NTf_2^- and PS^- [19, 37, 133, 159]. In fructose and glucose conversions, OAc^- containing ionic liquid was among the worst ionic liquid for 5-HMF production [19, 37, 133, 159]. The low performance of the ionic liquid may be due to the basicity of the anion [19, 37, 133]. In addition, the use of hydrophobic ionic liquid [BMIM][NTf_2] caused low conversion and yield from $GeCl_4$-catalysed 5-HMF production from glucose [19]. On the other hand, hydrophobic ionic liquid, 1-decyl-3-methylimidazolium trifluoromethanesulfonate

($C_{10}MI·CF_3SO_3$), associated with HCl, is highly effective for 5-HMF production from sugars [160]. The good performance of the reaction system was also assisted by the presence of HCl as catalyst.

Different types of cations were employed for ionic liquid in carbohydrate biomass conversion to 5-HMF and LA. They include imidazolium, pyridinium, morpholinium, triphenylphosphonium and triethylammonium, with different functional groups attached such as hydroxyl, sulfonic acid and carboxylic. In imidazolium ionic liquid, the hydroxyl group in 1-hydroxyethyl-3-methylimidazolium chloride ([E(OH)MIM][Cl]) formed a strong hydrogen bond with glucose for 5-HFM production using $CrCl_2$ catalyst [16]. The hydrogen bond thus weakens the C–O bond and lower the activation energy of the dehydration reaction. The hydroxyl group in [E(OH)MIM][Cl] also provided good effect on 5-HMF production as reported for fructose to 5-HMF in HPW catalyst, which was comparable with [BMIM][Cl] [28]. However, different trend has been observed for fructose conversion to 5-HMF in water, as [E(OH)MIM][Cl] acted as both solvent and catalyst [63]. No 5-HMF was produced from the reaction. This was probably due to the absence of catalyst and the presence of water in the reaction system. The effect of sulfonic acid group attached to imidazolium ionic liquid has been examined for cellulose conversion to 5-HMF and LA [16, 66, 119]. The acidity resulted from the sulfonic acid-based ionic liquid facilitated the cleavage of glycosidic bonds in cellulose. Li et al. [88] reported the enhanced effect of carboxylic groups (–COOH) of proline-derived ionic liquids for fructose conversion to 5-HMF. This demonstrated that as proline-derived ionic liquids were much more efficient for 5-HMF production than other cation-based ionic liquids such as imidazolium-based and boron core based protic ionic liquid.

In a study on cellobiose conversion to LA, for ionic liquids with the same chloride anion, the acidity of the ionic liquids are in the order of imidazolium > pyridinium > triethylamine [101]. The ionic liquid with higher acidity showed good performance for LA production. In other study on fructose conversion catalysed by HCl, comparable performance was recorded from imidazolium ionic liquid, [BMIM][Cl], and pyridinium-based ionic liquid, [Bpy][Cl] [24]. The similar trend was reported for Ghatta et al. [84], where no significant effect of the cations on 5-HMF yield was observed between [BMIM][Otf], [EMIM][Otf], and [BMPyr][Otf] for fructose conversion catalysed by HCl. Besides, no substantial difference in activity was obtained from cellulose conversion to LA in the presence of different cations-ionic liquid, imidazolium, pyridinium, triphenylphosphonium and triethylammonium [66, 119]. Among imidazolium, pyridinium and morpholinium cations, imidazolium-based ionic liquid was found to be the best solvent for sucrose conversion to 5-HMF catalysed by tyrosine [33]. In the reaction, pyridinium and morpholinium cation ionic liquids were unfavourable for 5-HMF production. This was possibly due to their low decomposition temperature, as the reaction was conducted at high temperature, 160 °C. The pyridinium-based dicationic ionic liquid, $[C_{10}(Epy)_2]2Br^-$, was employed in sucrose conversion to 5-HMF catalysed by $CrCl_2$ [122]. It was suggested that the dicationic ionic liquid offered several advantages over monocationic ionic liquid such as high thermal stability, better solubility for many compounds and high miscibility in water.

The chain length of alkyl group in the cation showed different effects on carbohydrate biomass conversion to 5-HMF and LA. There were studies reported that longer alkyl chain resulted in decreased performance of the reaction, while some studies reported otherwise. The general relationship between the chain length of the alkyl group and reaction performance was not clear, as other parameters should also be taken into consideration. In $GeCl_4$-promoted 5-HMF production from glucose, 5-HMF yield decreased when the alkyl group was changed from butyl ([BMIM][Cl]) to decyl ([DMIM][Cl]) [19]. Besides, for sucrose conversion using tyrosine as catalyst, much lower 5-HMF yield was obtained in [BMIM][Br] compared with [EMIM][Br] [33]. It was implied that shorter chain cations possess larger dissolving ability than those with longer chain cations when their anions are identical. Lower 5-HMF yield obtained using longer carbon chain of cation ionic liquid has also been observed for fructose conversion using acidic ion exchange resin as catalyst [57]. Li et al. [57] have suggested two reasons behind this phenomenon, which were the aggregation ability of the cation, and the hydrophilic and hydrophobic properties of the ionic liquids. The aggregations led to nonuniform and coadjacent structure of ionic liquids in which the aggregation became stronger with the increasing carbon chains. The transfer of electrons and protons in the molecular interior was hindered, thus impeding the reaction. Besides, long carbon and highly branch chain resulted in weak hydrophilicity of ionic liquids. It was observed that fructose was partly dissolved in ionic liquid with weak hydrophilicity, which would prevent fructose from contacting with the catalyst [57].

In contrast, higher 5-HMF yields were attained with the increase of alkyl chain length of the cation. With the increase of alkyl chain length from ethyl ([EMIM][Cl]) to butyl ([BMIM][Cl]), and hexyl ([HMIM][Cl]) to octyl ([OMIM][Cl]), 5-HMF yield increased for glucose conversion catalysed by $YbCl_3$ [39]. The same trend was observed from ethyl ([EMIM][Cl]) to hexyl ([HMIM][Cl]) for fructose conversion to 5-HMF catalysed by SO_4^{2-}/ZrO_2 [137]. The improved performance with increased in alkyl chain length of the ionic liquid clearly suggested the different interactions of the catalyst with ionic liquid [39]. Longer alkyl chain length on the imidazolium ring increased the hydrophobicity of the ionic liquid. Other study has reported on the application of a series of hydrophobic ionic liquids for conversion of corncob to 5-HMF [161]. As suggested by Stahlberg et al. [39], cations with more hydrophobic character are expected to have a weaker association with the chloride ion, which in turn would become more reactive. Higher reaction rate would be attained from stronger hydrophobic ionic liquids.

Fructose conversion to 5-HMF catalysed by phosphotungstic acid showed no clear trend from the alkyl chain length of ionic liquids tested: [BMIM][Cl], [OMIM][Cl], [OMIM][PF_6], [BMIM][BF_4], [BMIM][PF_6] and [OMIM][BF_4] [28]. This implied that the reaction was more affected by the anion rather than the alkyl chain on the cation. Among the ionic liquids with the same chloride anion for glucose conversion, no specific trend was reported on the 5-HMF yield [37]. Ionic liquid with shorter chain in the cation (H, methyl) gave low 5-HMF yield. Nevertheless, [BMIM][Cl] gave lower 5-HMF yield than [EMIM][Cl]. 1-methyl imidazolium chloride gave the lowest 5-HMF yield since it is a protic ionic liquid, which could inhibit the formation of more stable fructose-catalyst complexes for 5-HMF formation. The similar trend has been reported for glucose conversion catalysed by boric acid [36]. In addition, dimethyl imidazolium ionic liquids, 1-R-3-methylimidazolium chloride and 1-R-2,3-dimethylimidazolium chloride, where R is butyl, hexyl or octyl, were employed for fructose conversion in DMSO [159], showed that alkyl chain length and the additional alkyl group did not affected the 5-HMF yield. Elongating the alkyl chain linked with the sulfonic acid-based ionic liquid from propyl to butyl, and hydrogen sulfate-based ionic liquid from ethyl to octyl also caused negligible effect to LA production from cellulose and bamboo shoot shell, respectively [66, 112, 119].

The introduction of appropriate functional groups into the anion and cation can generate acidic sites on the ionic liquid, for example carboxyl (COOH) and sulfonic acid (SO_3H) on the cation, and hydrogen sulfate (HSO_4) on the anion. Ionic liquids functionalized with SO_3H group have shown to be more efficient solvents for the dissolution and hydrolysis of cellulose compared with simple inorganic acids [16]. In conversion of cellulose, the acidic ionic liquid was believed to have double functions, not only to dissolve cellulose like other ionic liquids but also its acidity can weaken the glycosidic bonds and subsequently promote the hydrolysis of cellulose effectively. Conversions of cellulose, inulin and chitosan to 5-HMF and LA were facilitated by the use of ionic liquids containing SO_3H and HSO_4 such as 1-(4-sulfonic acid) butyl-3-methylimidazolium hydrogen sulfate [62, 78, 90, 103, 104, 149]. The presence of catalyst promoted the cellulose hydrolysis efficiently, which suggested the synergistic interaction between the ionic liquid and catalyst.

Ionic liquids with acidic anion ([BMIM][HSO_4], [MIM][HSO_4]) and acidic cation ([IMIM-COOH][Cl]) showed better performance than neutral ionic liquids ([BMIM][Cl], [BMIM][Br], [BMIM][BF_4]) for conversion of chitosan to 5-HMF [105]. Neutral ([BMIM][Cl], [EMIM][Cl], [HMIM][Cl]) and Brønsted acidic ([EMIM][HSO_4] [BMIM][HSO_4]) ionic liquids were also compared for fructose conversion to 5-HMF catalysed by SO_4^{2-}/ZrO_2 [137]. The neutral ionic liquids were very efficient for both conversion and product yield, while Brønsted acidic ionic liquids only favourable for fructose conversion with low product yield. For fructose conversion reaction, the use of acidic ionic liquid in the presence of acidic catalyst promoted side reactions such as rehydration of 5-HMF to LA, and decomposition of 5-HMF to humins. The same trend on low 5-HMF yield in the presence of acidic ionic liquid and catalyst have been reported for fructose conversion catalysed by HCl using 1-(4-sulfobutyl)-3-methylimidazolium bisulfate ([SBMIM][HSO_4]) [24], and fructose conversion catalysed by $IrCl_3$ using triethylamine hydrogen sulfate ([Et_3NH][HSO_4]) [21]. The low 5-HMF yield by the presence of SO_3H and HSO_4 functionalized ionic liquids was due to the rehydration of 5-HMF to LA. This can be supported by LA production from good performance of [BMIM-SO_3H]HSO_4 aqueous mixture in fructose conversion [91]. Besides, a comparison with other ionic liquid has been performed, where [EMIM][HSO_4] with weaker acidity, resulted 5-HMF as the main product [91].

The effect of different anions on the ionic liquid acidity was reported on conversion of mushroom to 5-HMF [120]. A slight difference in the activity of [BBIM-SO_3][Otf] and [BBIM-SO_3][NTf_2] was found, which was likely due to the higher acidity of the NTf_2 anion, thus resulted in higher 5-HMF yield. The order of catalytic activity of the ionic liquids tested in the study are in the following order: [BBIM-SO_3][NTf_2] > [DMA][CH_3SO_3] > [BBIM-SO_3][Otf] > [NMP][CH_3SO_3] [120]. Other than acidity, the trend of catalytic activity of the ionic liquids can be explained by their proton donating ability. The imidazolium based sulfonic acid ionic liquid containing two trifluoro methane sulfonate groups perhaps accounts for better proton donating ability for [BBIM-SO_3][NTf_2]. A study by Li et al. [162] presented a theoretical elucidation on the conversion of 5-HMF to LA catalysed by SO_3H functionalized imidazolium based ionic liquid. They reported the density functional theory (DFT) study on molecular mechanism of 5-HMF to LA. It was emphasized that the catalytic performance of the ionic liquid depended on acidity and nucleophilicity of its constituent ion [162]. The study on calculations of DFT was also explored on fructose conversion in other imidazolium based ionic liquids [163, 164] and chlorometallate ionic liquids [165]. The theoretical study confirms that glucose isomerization to fructose catalysed by Lewis acids is the rate determining step in the glucose conversion reaction.

Determination of the amount of Brønsted acid in the ionic liquid was conducted based on Hammett acidity function (H_0), where lower H_0 value corresponds to greater acid strength. From the results of several studies, it was proposed that 5-HMF and LA productions from carbohydrate biomass increased with the increasing of acidity (H_0). Symmetrical and unsymmetrical Brønsted acidic ionic liquids tested on fructose conversion show that the trend of 5-HMF yield was in agreement with the Hammett acidity order of the ionic liquids [9]. The activity of several Brønsted acidic ionic liquids were compared with neutral ionic liquid [BMIM][Cl] [118]. The acidic ionic liquids showed higher 5-HMF yield from fructose compared with the neutral ionic liquid, which was consistent with the acidity amount based on Hammett acidity. Results obtained from fructose conversion to 5-HMF catalysed by polyethylene glycol functionalized dicationic acidic ionic liquids were also consistent with the Hammett acidity function of the ionic liquids [123]. The conversion of mushroom showed that [DMA][CH_3SO_3] with slightly higher acidity than that of [NMP][CH_3SO_3], as determined by Hammett acidity method, gave higher 5-HMF yield [120]. Brønsted acid functionalized ionic liquids with different functional groups on the cation were employed for glucose conversion to LA [117]. The order of the ionic liquids' activity was observed to be SO_3H > COOH > OH. The SO_3H functionalized ionic liquid showed a maximum conversion which due to its highest acidity as obtained from the Hammett function. The similar trend on the ionic liquid acidity was observed for LA productions from cellobiose, cellulose, and chitosan conversions catalysed by acidic ionic liquids [101, 124, 142]. In addition, from the comparison between monocationic and dicationic ionic liquids using Hammett test, it was found that dicationic ionic liquid is more acidic and showed better performance for risk husk biomass conversion to LA [114]. Furthermore, dicationic ionic liquids differ in ortho, meta and para positions revealed that the position influence the acidity of the ionic liquids [127]. The H_0 values indicates that the acidity of ionic liquid with ortho-position was the strongest among all the tested ionic liquids, subsequently showed the best performance for fructose conversion to 5-HMF.

Other than Hammett acidity function, the acidic types (Brønsted and Lewis) of the ionic liquid were determined by FTIR using pyridine as a probe [64, 115]. Pyridine can react separately with Brønsted and Lewis acids in the ionic liquid. Brønsted acid site was observed at the absorption peak near 1540 cm^{-1} in the FTIR spectra, whereas the absorption peak of Lewis acid site was detected close to 1450 cm^{-1}. High 5-HMF yield was recorded when Brønsted acidic anion (HSO_4^-)-containing ionic liquid was employed for fructose conversion [136]. Nevertheless, Lewis acidic anion ($CH_3SO_3^-$)-containing ionic liquid also showed adequate 5-HMF production at longer reaction time. In other study, high conversion of glucose to 5-HMF and LA was attributed to the medium-strong acid sites of SO_3H^+ groups together with $FeCl_4^-$ in [SMIM][$FeCl_4$] ionic liquid. The presence of $FeCl_4$ group contributed to the Lewis acid sites. It is suggested that Lewis acid sites which was characterized using the pyridine test also play role in the overall dehydration reaction [64]. The poor performance of [SMIM][Cl] in contrast to [SMIM][$FeCl_4$] for the conversion of glucose was probably due to the absence of Lewis acid sites in [SMIM][Cl] [64]. Thus, glucose conversion using [SMIM][Cl] was only attributed by the Brønsted acid sites. The remaining 5-HMF in the product was low since the produced 5-HMF rehydrated to LA in the presence of Brønsted acid sites. Meanwhile, high activity demonstrated by [SMIM][$FeCl_4$] was most likely because of its high acidity comprised of both Lewis and Brønsted acid sites. Based on the results of these studies, the mechanism underlying the different performances between the Brønsted and Lewis acidic ionic liquids is not yet clear. It is implied that the differences in the type of acidity might result in different kinds of intermediates.

Alkaline ionic liquids are generally recognized by the presence of functional groups such as acetate (Ac) and hydroxyl (OH) [19, 36, 37, 61, 133, 137, 141]. Few studies have reported the good performance of alkaline ionic liquids on carbohydrate biomass conversion to 5-HMF and LA. For instance, [BMIM][OH] and [EMIM][OH] gave high 5-HMF yields from fructose conversion [61]. Besides, compared with [BMIM][Br], higher 5-HMF yield was obtained from fructose conversion in DMSO using alkaline [BMIM]-based ionic liquid [141]. The 5-HMF yield increased with increasing alkalinity of the ionic liquid in the following order: [BMIM][OH] > $[BMIM]_2[CO_3]$ > [BMIM][PhCOO] > [BMIM][Br]. However, there were studies that showed the opposite trend of catalytic activity using alkaline ionic liquids. The use of [BMIM][OAc] for fructose and glucose conversions catalysed by $GeCl_4$ gave low 5-HMF selectivity even at high conversions rate [19, 133]. This was probably due to the side reactions between glucose and the imidazolium ring induced by the strong basic acetate group. In addition, it seems that the basic ionic liquid [BMIM][OAc] inhibited the formation of 5-HMF from fructose in the presence of acid catalyst [137]. This condition was probably due to the neutralization of catalyst acid sites by the basic ionic liquid. No 5-HMF was produced from glucose conversions using alkyl aluminoxanes and boric acid catalysts in [EMIM][OAc] [36, 37]. The basic ionic liquid [EMIM][OAc] could rapidly degrade 5-HMF even at moderate temperature of 100 °C [37, 39].

Ionic Liquid Loading

The effect of ionic liquid loading was studied either the ionic liquid was acted as solvent or catalyst. The amount of [BMIM][Cl] played a positive effect on conversions of fructose catalysed by $H_3PW_{12}O_{40}$ [28]. The 5-HMF yield improved with increasing amount of [BMIM][Cl], then with further increased of [BMIM][Cl], both 5-HMF yield and selectivity remain the same. In a study on cellulose conversion to 5-HMF catalysed by $CrCl_3$ in [BMIM][Cl]/toluene, the reaction system became diluted when the [BMIM][Cl] loading was excessive, and the acidity of the reaction system decreased. This condition resulted in difficulty of cellulose and glucose conversions to 5-HMF [140]. As compared with DMSO as the sole solvent, the addition of [BMIM][Cl] into the reaction in the presence of chromium-exchanged bentonite catalyst resulted in sharp increase in feedstock conversion and 5-HMF yield [132]. The 5-HMF yield increased with the increase of amount of [BMIM][Cl]. Nevertheless, as the [BMIM][Cl] loading was more than 50 wt%, the condition did not improve the 5-HMF production, which might be ascribed to the high viscosity of [BMIM][Cl] [132]. The same trend has been reported for [BMIM][Cl]-DMSO reaction medium in fructose conversion catalysed by $GeCl_4$ [133] and cellulose conversion catalysed by $AlCl_3$ [50].

The increasing loading of four different ionic liquids containing the OH^- anion, [EMIM][OH], [BMIM][OH], [HMIM][OH] and [OMIM][OH], show different trends on 5-HMF yields from fructose. The different trend was possibly related to the effect of alkyl chain of the cation of the ionic liquid [141]. Increasing [CMIm][Cl] loading resulted in increasing fructose dehydration rate [80], suggested that the acidity of the carboxylic group of [CMIm][Cl] played a key role in the reaction [80]. Higher fructose conversion and 5-HMF yield with increasing dosage of ionic liquid could be attributed to an increase in the availability and number of catalytically active sites, as reported on study involving ionic liquid based polyoxometalate salt: $[3.2H]_3[PW_{12}O_{40}]_2$ [93]. However, the 5-HMF yield did not increase with further increment of ionic liquid loading. Besides, high dosage of ionic liquid above the optimum loading showed decomposition of 5-HMF and formation of humins [82, 92, 136]. In fructose conversion involving acidic ionic liquids such as $[PSMBIM]HSO_4$ and 1-(4-sulfonic acid) butyl-3-methylimidazolium hydrogen sulfate, decrease in 5-HMF yield with increasing ionic liquid loading might be due to the increased availability of acidic sites, favouring rehydration of 5-HMF [9, 116].

Similar to fructose conversion reactions, the same trend was observed from studies on the effect of different ionic liquid loading for conversions of glucose, cellulose and chitosan to 5-HMF. As observed for glucose conversion in DMSO catalysed by acidic ionic liquid immobilized on mesoporous silica, the availability of more active sites with increasing ionic liquid loading led to an increase in 5-HMF yield [87]. After it reached the optimum loading, the excessive ionic liquid loading did not facilitate the 5-HMF production but into undesired products. In glucose conversion in DMSO catalysed by $[C_2OHMIM][BF_4]$, on increasing the amount of ionic liquid, the corresponding increase in the number of hydroxyl groups in the cations seems to favour the reaction for 5-HMF production [61]. Besides, it was reported that low ionic liquid loading is not sufficient to fully degrade chitosan, while high loading not only accelerate the conversion of chitosan to 5-HMF but also promote other side reactions [105, 106]. The effect of ionic liquid loading were also studied for glucose conversion to LA using water as solvent catalysed by acidic ionic liquids such as $[SMIM][FeCl_4]$ and $[BSO_3HMIm]HSO_4$ [64, 90]. Upon increasing the amount of ionic liquid, the corresponding increase in the number of acidic sites seems to favour the overall reactions. The subsequent increase of the ionic liquid loading appears no significant impact on the LA yield [64, 90]. This may be attributed to more viscous mixture which hamper the glucose conversion and induced the humins formation. This condition was also reported for reactions catalysed by heteropolyacid ionic liquid in MIBK-water [58], SO_3H-functionalized ionic liquids in water [104, 119], Brønsted-Lewis acidic ionic liquid in water [101], and Brønsted acidic dicationic ionic liquid in water [124]. The LA yield increased then levelled off when more ionic liquid was added. Notably, the presence of water conceivably play a key role for the LA production.

Ionic liquids generally have very high viscosity, which may hinder access to the active sites and it is not facile for the mass transfer between catalyst and feedstocks. Solvents was commonly added to reduce the viscosity of the reaction mixture. Several attempts have been made to lower the viscosity of halide based ionic liquids by using mixtures of ionic liquids for carbohydrate biomass conversions. For this purpose, ionic liquid mixtures differing in size, shape and coordination ability of the anion and differing in cation, aromatic and aliphatic, were tested for 5-HMF productions in the presence of solid acid catalysts [134, 135]. It was found that equimolar mixture of the ionic liquids has been able to give the best 5-HMF yields under mild conditions. For instance, equimolar mixture of $[BMIM][BF_4]/[BMIM][Cl]$ led to higher 5-HMF yield, while low 5-HMF yields was detected in pure $[BMIM][BF_4]$ or in mixtures richer in this component which possibly due to the lower ability of $[BF_4^-]$ in catalysed the dissolution of sugar [135].

Reaction Media and Solvent/Co-Solvent

Ionic liquid is relatively expensive compared with other conventional solvents. The introduction of co-solvent to partially replace ionic liquid is essential, as it is not economical to use large amount of ionic liquid. Besides, ionic liquids generally have very high viscosity. In conversion of carbohydrate biomass, the high viscosity mixture may hinder access to the active sites of ionic liquid. In some cases, ionic liquids play a dual solvent-catalyst role for carbohydrate biomass conversion. In other cases, such as for catalytic conversion in the presence of functionalized/polymeric-based ionic liquids, solvents are needed in the reaction systems. Different solvents were employed, include polar protic solvents such as methanol, ethanol, iso-propanol, butanol, acetic acid and water, polar aprotic solvents such as dimethyl sulfoxide (DMSO), methyl isobutyl ketone (MIBK), dimethyl formamide (DMF), dimethyl acetamide (DMA), N-methyl pyrrolidone (NMP), glycol dimethyl ether (GDE), dimethyl carbonate (DMC), acetone, ethyl acetate and acetonitrile, and non-polar aprotic solvent such as toluene. Each solvent gave different effect on the conversion of carbohydrate biomass depending on the reaction system, ionic liquid, catalyst and other operating conditions.

DMSO appeared to be the preferred solvent/co-solvent in ionic liquid-mediated conversion of carbohydrate biomass due to its ability to prevent the formation of by-products thus improved the 5-HMF yield to a certain degree [9, 56, 87, 103]. The trend has been observed in DMSO-[BMIM][Cl] mixtures for cellulose conversion catalysed by $AlCl_3$, glucose conversion catalysed by bentonite-Cr, glucose conversion catalysed by solid base catalyst, and fructose conversion catalysed by $GeCl_4$ [50, 132, 133, 138]. Lower 5-HMF yield was recorded in pure [BMIM][Cl], probably due to very high viscosity of reaction media, which was not facile for the mass transfer between the catalyst and feedstock. DMSO has different effect on different ionic liquid systems. For instance, highly efficient dehydration of fructose to 5-HMF was achieved in DMSO using $[C_6(Mpy)_2][NiCl_4]^{2-}$ while $[C_{10}(Epy)_2]2Br^-$ gave highly efficient 5-HMF production without the presence of DMSO [92]. The different trend was probably due to the different interaction effect of the ionic liquid and DMSO. Besides, it was observed that DMSO was the most efficient solvent due to DMSO being an electron acceptor to improve the dehydration of fructose to 5-HMF [123]. DMSO with a high boiling point (189 °C) was selected as co-solvent in the conversion of cellulose to 5-HMF in $[(C_3SO_3H)MIM][HSO_4]$ [103]. However, Liu and team [123] reported that the use of DMSO might cause difficulty in separation of 5-HMF using distillation due to high boiling point of DMSO.

Several polar aprotic solvents (DMSO, MIBK, NMP) and polar protic solvents (n-butanol, sec-butanol, isopropanol) were employed for fructose dehydration in [BMIM][OH] [141]. From the observation, DMSO demonstrated much higher 5-HMF yield compared with other solvents. In other study, polar solvents (DMSO, NMP, DMA, DMF, ethanol) were incorporated in fructose conversion to 5-HMF using [CMIm][Cl] [80]. The same trend was recorded, where high 5-HMF yield was obtained using DMSO. Nevertheless, good 5-HMF yields were also obtained using NMP, DMF and DMA as solvents. Low 5-HMF yield was obtained when ethanol was used as solvent even though the fructose conversion was fairly high. It is suggested that by-product such as ethyl fructoside, was produced from fructose conversion using ethanol as solvent [80]. In a study by Qu et al. [99] on cellobiose conversion in 1-hydroxyethyl-3-methylimidazolium tetrafluoroborate, the stability of 5-HMF produced in different solvents were suggested to be in the following order: DMSO > DMF > DMAc > NMP > MIBK > 2-butanol.

High 5-HMF yield was achieved using DMSO for glucose conversion in the presence of ionic liquid-based catalyst: Cr(Salen)-IM-HSO_4-MCM-41 [87]. Meanwhile, less effective reaction was observed using DMA, DMF and NMP. The activity of the catalyst was also investigated by introducing water as co-solvent, giving DMSO-water and DMA-water systems. From the tests, comparable 5-HMF yield was obtained when DMA-water and DMA were used as solvent, while lower 5-HMF yield was obtained from DMSO-water compared with DMSO as solvent [87]. The opposite trend was recorded for reaction system containing DMSO-water for conversion of corn starch to 5-HMF catalysed by $AlCl_3$ in [BMIM][Cl]. The different trend was due to the different effect of the ionic liquids and catalysts employed towards the feedstock conversion. Besides, the study specified that the system was tolerant to optimal water loading, where the presence of water influence the product distribution [56]. The biphasic system (organic solvent-water) has also been explored by Liu et al. [123] for fructose conversion to 5-HMF using functionalized ionic liquid $[4.2H][HSO_4]_2$. The biphasic systems include MIBK-water and acetone-water, which gave fairly high yields.

The applications of DMSO, DMF and DMA as solvents exhibited good outcome on 5-HMF production from glucose in $[C_2OHMIM][BF_4]$ [61]. On the other hand, very low 5-HMF yields were obtained as MIBK, n-butanol and sec-butanol were employed as solvent. However, n-butanol and sec-butanol demonstrated favourable role in fructose conversion catalysed by functionalized ionic liquid $[MIMPS]_3PW_{12}O_{40}$ [166]. There were a few studies reported on favourable role of alcohols as solvent for 5-HMF production [70, 82, 167]. Ionic liquid [HNMP][Cl]-catalysed dehydration of fructose was conducted in deep eutectic solvents, which was formed by combination of [EMIM][Cl] with different alcohols [167]. Different alcohols gave different effects on fructose dehydration, which possibly resulted from the viscosity and polarity of the deep eutectic media. The 5-HMF yields increased with the increase of the alkyl chain length of the alcohol, while branched chain alcohols led to higher 5-HMF yields. The addition of t-butanol was tested as isomerization promoter for conversion of glucose in mixture of DMSO and 1-sulfobutyl-3-methylimidazolium trifluoromethane sulfate, ($[BSO_3HMIM][OTF]$) [83]. Small dosage of t-butanol improved the 5-HMF selectivity by inhibiting polymerization of glucose with 5-HMF. Meanwhile, addition of methanol into binary mixture of ionic liquids for fructose conversion resulted in lower 5-HMF production compared with the addition of DMSO [86]. It was presumed that there is a dilution effect in the presence of methanol, which caused lower performance. Reaction system containing ethanol-water was employed for cellulose conversion in Brønsted acidic ionic liquid 1-(1-propylsulfonic)-3-methylimidazolium chloride [65], where both water and ethanol acted as solvents in production of LA through dehydration/rehydration and production of ethyl levulinate through in situ esterification.

The application of MIBK as solvent in the conversion of carbohydrate biomass to 5-HMF is usually described as phase modifier to continuously extract product from the aqueous phase. As 5-HMF is continuously extracted, it could minimize degradation of the remaining 5-HMF in the reactive aqueous phase and more efficient recovery of 5-HMF in the subsequent isolation step could be achieved. The studies involved the use of MIBK in cellulose conversion catalysed by $CoSO_4$ and $MnCl_2$ in 1-(4-sulfonic acid) butyl-3-methylimidazolium hydrogen sulfate [62, 149]. Besides, MIBK-water biphasic system was also employed for fructose conversion to 5-HMF [116] and cellulose conversion to glucose and LA [58]. In a study on conversion of high glucose concentration to 5-HMF, several biphasic systems were tested through combination of [EMIM][Br] with organic solvents such as MIBK, GDE, DMC and THF [148]. All solvents can form two phases with [EMIM][Br] and partially extract 5-HMF during the reaction. The 5-HMF yield varies depending on the organic solvents used. From the study, it was found that the maximal 5-HMF were achieved from the GDE/[EMIM][Br] and [DMC]/[EMIM][Br] system [148]. The efficiency of different extracting agents such as toluene, ethyl acetate, acetone, MIBK and methanol was inspected for cellulose conversion to 5-HMF in [BMIM][Cl] catalysed by $CrCl_3$ [168]. From the analysis, toluene was selected as the preferred solvent for the reaction [168]. However, with addition of toluene for glucose conversion catalysed by $AlEt_3$ in [EMIM][Cl], no positive change was observed on 5-HMF yield [37]. As reported in a study, due to the small value of dielectric constant of toluene, toluene can be used to construct a biphasic reaction system with an ionic liquid for glucose conversion to 5-HMF [140]. 5-HMF was continuously extracted from the organic solvent layer, thereby reducing the formation of by-products, increasing the selectivity of reaction and accelerating the reaction rate. Toluene and other organic solvents can also reduce the viscosity of ionic liquids to a certain extent and facilitate the movement of ions, which implied that the organic solvents are conducive to the mass transfer process [140].

Studies have showed significant effect of DMF as solvent in 5-HMF production. 5-HMF yield improved with the addition of DMF for fructose conversion in [AMIM][Cl] [25]. However, 5-HMF yield was substantially reduced when DMF was employed [37]. In other study, the presence of DMF substantially reduced the viscosity of [AMIM][Cl] and enhancing the heat transfer effect. The use of polymeric ionic liquid, P[BVIM]Cl and $CrCl_2$ for glucose conversion to 5-HMF requires a polar co-solvent, which could make a homogenous mixture containing glucose, ionic liquid and catalyst [96]. DMF is the most effective solvent among the other tested solvents: DMSO and DMA. Even so, by using the molecular and monomeric ionic liquids [EMIM][Cl] and [BVIM][Cl], DMA is the most effective solvent for 5-HMF production. DMA is a common industrial solvent and has been used as solvent/co-solvent for 5-HMF production in ionic liquid [61, 80, 87, 96, 123]. Meanwhile, the application of acetonitrile as solvent seems to give insignificant effect on fructose conversion to 5-HMF in [BMIM][HSO_4] [85]. Acetonitrile acted as a diluent and reduced the viscosity of the solution, thus enabled faster mass transport. Nevertheless, without the presence of acetonitrile, the 5-HMF yield obtained was equally high [85].

Water Content

The aqueous reaction systems are preferred from an ecological and economical point of view, but unfortunately, 5-HMF production in water was usually low and formation of LA and formic acid were enhanced compared with reaction in an organic media. Though, small amount of water could help the reaction, probably because water not only reduced the viscosity of the solvent, which is beneficial to mass transfer, but also increased the solubility of feedstock and catalyst [38, 53, 153]. Water has been regularly employed as solvent for catalytic production of LA, as the presence of water will promote the rehydration of 5-HMF into LA. The effect of water content was examined since studies involving catalytic conversion for 5-HMF production were usually carried out in a non-aqueous environment. Given the high cost of ionic liquid, the addition of water may offset the quantity of ionic liquid used. Table 4 shows the effect of water content in ionic liquid on 5-HMF yield.

Several trends were reported for fructose conversion to 5-HMF in ionic liquid. For instance, low water content (below 5–8%) had a small effect on 5-HMF production from fructose in [BMIM][Cl] catalysed by Amberlyst ion exchange resin and HCl [24, 130]. When the water content was above 5–8%, the 5-HMF yield decreased significantly. Meanwhile, higher water content (up to 25%) did not gave substantial effect on fructose conversion to 5-HMF in [ClC2MIM][Cl] [63]. In contrast, no positive effect on 5-HMF production was observed even at very low water content [21, 25, 80]. The presence of water in binary [AMIM][Cl]/DMF system resulted in sharp decreased of 5-HMF yield. This was probably due to reduction of dissolution capacity of [AMIM][Cl] in the presence of water, which subsequently caused reduction in catalytic activity [25]. As reported for fructose conversion in different functionalized ionic liquids, [BMIM][HSO_4], [BMIM][Otf], [ClC2MIM][Cl], 1-(4-sulfonic acid) butyl-3-methylimidazolium hydrogen sulfate, and proline-derived ionic liquid, the 5-HMF yields improved with increased water content up to the optimum amount [84, 85, 88, 116]. For proline chlorate (ProCl)-catalysed fructose conversion, the significant decreased of 5-HMF yield as water content was above 10% might be attributed to the generation of hydrated chloride ions that are unable to participate in the reaction [88]. However, for proline bisulfate ($ProHSO_4$), very negative effect of water content (> 5%) on fructose conversion to 5-HMF was observed. It was suggested that the presence of water and free HSO_4^- in $ProHSO_4$ with high acid strength facilitated the degradation of 5-HMF [88]. Increasing water content in [BMIM][Otf] led to poor 5-HMF yield, which may be due to the overly aggressive activity of the H^+ ions, leading to side reactions [84].

Different amounts of water were added into ionic liquid to study the effect of water content on the conversion of glucose to 5-HMF. Glucose conversion in reaction medium of [BMIM][Cl] catalysed by Hβ-zeolite gave improved 5-HMF yield as the amount of water increased from 1 to 5%, compared with in the absence of water [48]. The presence of small amount of water could reduce the viscosity of [BMIM][Cl], which is beneficial for mass transfer, and promote the glucose dissolution [48]. The similar trend was observed for glucose conversion in $[HO_2CMMIm]Cl-ZrOCl_2$-isopropanol [97]. Nonetheless, large amount of water resulted in the rehydration of 5-HMF into LA, as well as deactivation of acid sites on Hβ-zeolite catalyst [48]. In addition, Hu and team [38, 41] have examined the effect of water content for glucose conversion to 5-HMF in [BMIM][Cl] using $CrCl_3$/boric acid and 12-tungstophosphoric acid/boric acid catalysts. Remarkable decreased in 5-HMF yields were observed when the initial water concentration was further increased to 30%. A large amount of water resulted in a significant decreased in 5-HMF yield from glucose conversion in ionic liquid, which was in agreement with the results of other studies [19, 36, 38, 41, 48]. Thus, anhydrous or near anhydrous condition was essential for the conversion of glucose to 5-HMF in ionic liquid medium.

A small amount of water showed positive effect on cellulose conversion to 5-HMF catalysed by $Cr([PSMIM]HSO_4)_3$ in [BMIM][Cl] [102]. In the conversion of cellulose to 5-HMF in [BMIM][Cl] catalysed by $CrCl_3$, the product yield decreased with increasing water content [51, 139]. The decreased in 5-HMF yield was attributed to the conversion of 5-HMF to LA and formic acid, and reduction of cellulose solubility in [BMIM][Cl] [139]. The addition of water does not affect the conversion of inulin to 5-HMF in [BMIM][Cl], where comparable yields were obtained when no external water was added [27]. Since inulin is an oligosaccharide consisting of fructose, it was suggested that the three molecules of water produced from dehydration of one molecule of fructose was sufficient for the hydrolysis of inulin into fructose and 5-HMF. Positive effect of water content was achieved in the conversion of chitosan to 5HMF in $[MIM][HSO_4]$ [105]. It can be concluded that the presence of water in the reaction system is beneficial particularly for conversion of cellulose. However, with the increased of water content, the 5-HMF yield decreased, which can be attributed to the conversion of 5-HMF to LA and formic acid. Thus, water content should be carefully controlled to obtain optimum 5-HMF yield.

The effect of water content was also investigated in the LA production from glucose and cellulose in the presence of acidic ionic liquids [64–66]. A complete conversion of glucose catalysed by $[SMIM][FeCl_4]$ was consistently reported regardless of the amount of water loaded in the reaction system [64]. It appears that the presence of water only affects the products yield. The increased in water content resulted in progressive rehydration of 5-HMF to LA. At low water content, the high viscosity of $[SMIM][FeCl_4]$ caused low mass transfer rate and affected the occurrence of dehydration / rehydration reaction. One-pot conversion of cellulose catalysed by 1-(1-propylsulfonic)-3-methylimidazolium chloride in ethanol and water gave LA and ethyl levulinate as the main products [65]. The LA yields continued to increase with increasing water content up to ~ 54%. The reaction carried out without the presence of water (pure ethanol) showed very low conversion to LA and ethyl levulinate. Besides, most of the unreacted cellulose was recovered. This corroborated the importance of water for the initial hydrolysis of cellulose to glucose. The similar trend was reported for conversion of chitosan to LA in $[C_3SO_3Hmim]HSO_4$, as only 2.1% of LA was obtained in the absence of water [142]. It was observed that the increasing amount of water suppressed the formation of humins, dark-coloured solid by-products [66, 142], which suggesting dilution effect promotes the target reaction towards LA. The high amount of water content was necessary for initial dissolution of cellulose. However, higher reaction temperature was needed to give comparable LA yield when larger amount of water was introduced [66].

Ionic Liquid Recyclability and Reusability

Factor which impedes the utilization of ionic liquid in a large-scale process is its price, which is relatively expensive in contrast to other conventional solvents, thus hindered its commercial viability [1]. An alternative to diminish this drawback is by recycling and reusing the ionic liquid. Reactants and products formed during the reaction need to be separated before ionic liquid/ionic liquid-catalyst can be reused for the next process. After the reaction was completed, water was added to decrease the viscosity of ionic liquid and facilitate the extraction of product. For lignocellulosic biomass conversion reaction, the remaining biomass feedstocks were filtered after the addition of water [108]. The residual feedstock could be first removed by centrifugation [103]. Then, extractive solvent was added several times, resulted in the formation of a two-layer solution: organic and aqueous phase. Several types of solvents have been applied in the extraction process such as

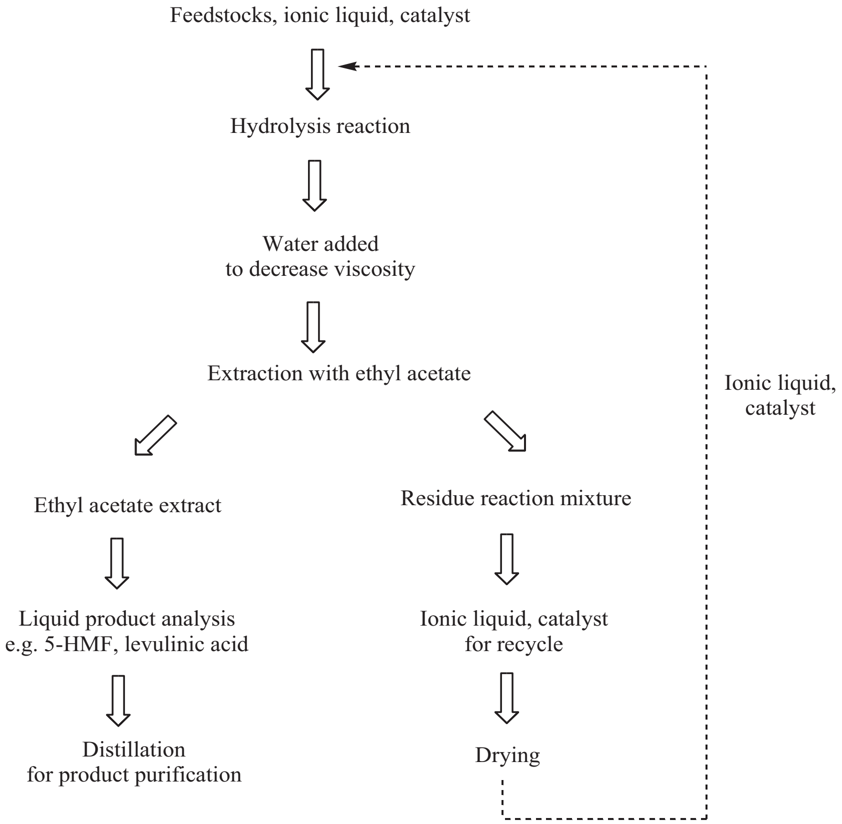
Table 4 Effect of water content in ionic liquid on carbohydrate biomass conversion to 5-HMF

Feedstock	Ionic liquid, catalyst	Water content (%)	5-HMF yield (%)	Reference
Fructose	[BMIM][Cl], Amberlyst 15	0 5 20	79 80 45	[130]
Fructose	[BMIM][Cl], HCl	0 31 47	92 72 28	[24]
Fructose	[AMIM][Cl]	0 5 20	85 68 25	[25]
Fructose	ProCl	5 10 20	68 73 32	[88]
Fructose	[C4C1im][HSO_4], $CrCl_3$	0 15 50	80 85 65	[85]
Glucose	[BMIM][Cl], Hβ zeolite	0 5 30	51 52 35	[48]
Glucose	[BMIM][Cl], $CrCl_3$/boric acid	0 5 30	52 48 22	[38]
Glucose	[BMIM][Cl], 12-tungstophosphoric acid/boric acid	0 5 30	79 76 68	[41]
Glucose	[BMIM][Cl], $GeCl_4$	0 5 10	34 29 20	[19]
Glucose	[HO_2CMMIm]Cl $ZrOCl_2$–isopropanol	0 3.1 20	29 35 26	[97]
Cellulose	[BMIM][Cl], $CrCl_3$	0 1.5 6.5	53 48 15	[139]

ethyl acetate [9, 17, 26, 38, 80, 95, 108], ethanol [119], tetrahydrofuran [136], MIBK [66, 101, 116, 142], diethyl ether [56, 88] and glycol dimethyl ether [42].

Feedstocks (fructose, glucose, etc.) and ionic liquid were found to be insoluble in solvent thus can be easily separated, while the hydrolysate product, i.e. 5-HMF was the sole product in solvent phase. The remaining ionic liquid and catalyst in the reaction mixture were dried before they are used for the next cycle with fresh feedstock. The general steps for ionic liquid-catalyst recycling process using ethyl acetate as extraction solvent is depicted in Fig. 3. In addition, for reaction involving water-insoluble ionic liquid, the 5-HMF was easily separated from the ionic liquid phase by water extraction, instead of the use of organic solvent to extract 5-HMF [160]. Afterwards, the aqueous phase containing the conversion products is removed through a simple decantation. In studies where the ionic liquid was in the form of heterogenous solid catalyst, the ionic liquid was recovered by filtration or centrifugation [60, 82, 89, 169]. For example, Cr_3-SO_3H-polymeric ionic liquid used as catalyst for fructose conversion in DMSO was recovered by centrifugation after adding a certain amount of ethanol used as precipitant. Then, the recovered ionic liquid was washed with acetone several times, and dried before directly used for the next run. In other study, [HO_2CMMIm]Cl was separated from the reaction medium by cooling down the solution thereby precipitating [HO_2CMMIm]Cl out from the solvent for subsequent reaction runs [82]. The separation and recyclability of ionic liquids was also performed using nanofiltration membrane [43]. Prior to separation, insoluble humins generated in the reaction system was removed. Humins was removed using microfiltration and retained as cake since the presence of humins could retards the

Fig. 3 General steps for ionic liquid-catalyst recycling process for carbohydrate biomass conversion to 5-HMF and LA



performance of the membranes. It was reported that insoluble by-product humins can be removed from the ionic liquid phase by the addition of ethanol [27]. This is because ionic liquid is soluble in ethanol but not for humins. The catalytic system proceeded to the next reaction after filtration of precipitated humins and removal of ethanol.

The capability to reuse ionic liquid is a good step towards reducing the overall cost for a reaction process involving ionic liquid. One of the important parameters of ionic liquid being used as catalyst is its catalytic activity. It is expected in every reaction that there is insignificant reduction in the activity of the recycled ionic liquid-catalyst after going through appropriate separation and purification routes. Table 5 summarizes the performance of reused ionic liquid/ionic liquid-catalyst in the carbohydrate biomass conversion processes. The ionic liquid-catalyst system is stable for at least three runs. In some cases, the product yield in the next few cycles was higher than the first recycle step, which can be attributed to the retention of product and unreacted feedstock [38, 57, 74, 102, 107]. The reduction in activity of ionic liquid system might be due to several factors. Incomplete extraction of by-products could inhibit further conversion of feedstock [27, 43, 108]. Besides, precipitation of humins in the reaction mixture and accumulation of humins on the catalyst surface probably caused the catalyst deactivation and consequently lower the catalytic activity of reaction system [27, 108]. In SO_3H functionalized ionic liquid, the decrease in glucose conversion and LA yield in further recycling experiments was attributed to the increasing water content [117]. Besides, the accumulation of side products in each reaction step required harsh recycling conditions [117]. In studies where the ionic liquids were prepared through immobilization of functional groups (i.e. SO_3H, $CrCl_3$), the reduced 5-HMF yield was possibly due to the leaching of the functional groups during repeated process [89]. The purified 5-HMF was obtained from distillation under reduced pressure [103, 105] and through silica gel eluting with ethyl acetate [30]. In addition, 5-HMF produced from fructose, glucose and cellulose in $[HMIM]HSO_4$ was continuously recovered using vacuum steam distillation technique [94].

Magnetic-based catalyst has attracted attention in carbohydrate biomass conversion into valuable chemicals due to their facile separation process [170]. The separation method is easy, economical and save time and energy. Studies on the application of magnetic catalyst for conversions of cellulose and biomass feedstocks in imidazolium based ionic liquids have been conducted [152, 161]. Combination of magnetic and functionalized ionic liquid is an attractive alternative for catalytic conversion of carbohydrate biomass to 5-HMF and LA. For instance, dual functional magnetic and acidic ionic liquids were prepared and introduced as catalyst for hydrolysis of cellulose and conversion of xylose [171, 172]. Interestingly, the catalyst was found to be very effective for conversion glucose and xylose to 5-HMF and furfural. More studies on the application of magnetic and functionalized ionic liquid for carbohydrate biomass conversion to 5-HMF and LA need to be explored.

Proposed Mechanisms of Carbohydrate Biomass Conversion to 5-HMF and LA in Ionic Liquid

A number of mechanisms have been proposed for the 5-HMF and LA productions from carbohydrate biomass. The proposed mechanisms are presented and briefly elucidated to give a better understanding on the reaction scheme. In addition, the role of ionic liquid in the reaction is also discussed. The overall reaction scheme of 5-HMF and LA productions from biomass comprised of several steps. The first step is dissolution process, which provided more accessibility for the biomass to be converted into the desired product. Cellulose was hydrolysed to give sugars, mainly glucose. Then, glucose was isomerized to fructose before the formation of 5-HMF. Theoretically, 5-HMF is produced by the loss of three molecules of water from hexose in acid-catalysed reaction, while LA is produced by the rehydration of 5-HMF. Besides, there are occurrence of side reactions such as polymerization of the reactants and products to produce insoluble humins. There are various proposed mechanisms can be found for glucose, fructose and cellulose conversions to 5-HMF in ionic liquids. Some of the mechanisms are described herein, and the differences among the proposed mechanism are highlighted. Table 6 summarizes the differences among the proposed mechanisms, taken into account the role of ionic liquid and/or catalyst towards the mechanism. All the proposed mechanisms still need further investigation in order to confirm the reaction pathway.

The mechanism for fructose dehydration to 5-HMF in 1-allyl-3-methyl imidazolium chloride showed that anion of the ionic liquid played a major role [25]. Initially, Cl^- of the ionic liquid attached to the OH group on C1 fructose, followed by dehydration reaction through elimination of water molecule resulting an enediol intermediate compound. The intermediate compound went through isomerization to form aldehyde isomers. Then, elimination of two water molecules from the isomers occur. Finally, 5-HMF was obtained as the ionic liquid dissociated from the compound. As proposed for fructose conversion in 1-allyl-3-methylimidazolium chloride, the anion part of the ionic liquid played a major role in the mechanism. Meanwhile, Ryu et al. described the mechanism of fructose conversion to 5-HMF in [BMIM][Cl] with the involvement of both ionic liquid's cation and anion [159]. Firstly, the $BMIM^+$ of the ionic liquid attacked the OH group on C1 fructose forming complex compound. Removal of OH from the complex compound resulted in the formation of intermediate compound, which spontaneously converted to fructofuranosyl oxocarbenium ions through elimination of water molecule. Afterwards, enol compound was formed through two possible pathways, nucleophile and base, both involving the Cl^- anion from the ionic liquid. In the nucleophile pathway, the Cl^- attacked the oxocarbenium to form an intermediate. Alternatively, the enol compound was formed as the Cl^- acted as base that deprotonates the C1 group. Finally, 5-HMF was formed through the elimination of two water molecules.

Similar to fructose conversion in [BMIM][Cl], both cation and anion of the ionic liquid were responsible for the mechanism of the reaction in the presence of Brønsted acidic ionic liquid [PSMBIM]HSO_4 [9], but in different manner. The sulfonic acid part of the cation acted as an electrophile, which activates the C–OH bond of the anomeric carbon of fructose. Meanwhile, the anion HSO_4^- of the ionic liquid acted as nucleophile that activates the C–H of the C1 of fructose via hydrogen bonding. This activation resulted in the removal of the first water molecule and the formation of an enol intermediate. The subsequent elimination of a second and third water molecules for 5-HMF production was driven by the anion HSO_4^- of the ionic liquid. In addition, a reaction path was proposed for condensation reactions of 5-HMF and furfural Brønsted acidic ionic liquid-acetone reaction system [173]. Even though the dehydration of glucose gives 5-HMF as the major product, furfural formation as a minor product appears to be common in acidic ionic liquids catalysed dehydrations.

Extensive works have been carried out to study the mechanism of carbohydrate biomass conversion to 5-HMF in the presence of Lewis acids. For example, the mechanism of cobalt salt ($CoSO_4$) promoting the conversion of glucose in 1-(4-sulfonic acid) butyl-3-methylimidazolium hydrogen sulfate has been proposed by Tao and co-workers [62]. The proposed mechanism is focusing on isomerization of glucose compound to fructose, which involving complexes $[Co(SO_4)_n]^{(2n-2)-}$ formed from the combination of $CoSO_4$ and ionic liquid. The complexes promoted the conversion of α-anomers glucose to β-anomers through the formation of hydrogen bonding between oxygen atom in SO_4^{2-} and hydroxyl groups in glucose. The β-anomers glucose was converted into open chain form, which then combined with the cobalt complexes to form enolate intermediate, followed by the release of complexes $[Co(SO_4)_n]^{(2n-2)-}$ to form fructose. The isomerisation was followed by the loss of three water molecules to produce 5-HMF. In addition, Tao et al. [78, 149] have described the putative mechanisms of glucose conversion to 5-HMF in 1-(4-sulfonic acid) butyl-3-methylimidazolium hydrogen sulfate promoted by other metal chlorides, include $MnCl_2$ and $FeCl_2$. The reaction mechanisms were the same as designated for $CoSO_4$ described herein.

As described above, the isomerization of glucose to fructose involving complexes formed from the combination of $CoSO_4$ and ionic liquid. Similar mechanism was proposed on glucose isomerization to fructose by $GeCl_4$ catalyst in [BMIM][Cl] [19, 133], however, no complexes was formed from the catalyst and ionic liquid. The sequential steps of glucose isomerization to fructose focused on the conversion

Table 5 Performance of recycled ionic liquid/catalyst-ionic liquid after subsequent runs

Catalyst–ionic liquid	Feedstocks	Number of runs	Conversion/yield (%)		Ref.
			Initial	Final	
$GeCl_4$–[BMIM][Cl]	Fructose	5	92 (Y)	88 (Y)	[19]
$IrCl_3$–[BMIM][Cl]	Fructose	5	99 (C)	95 (C)	[21]
[AMIM][Cl]–DMF	Fructose	5	85 (Y)	80 (Y)	[25]
[CMIM][Cl]	Fructose	6	95 (Y)	89 (Y)	[80]
SBA 15-SO_3H–[BMIM][Cl]	Fructose	4	81 (Y)	73 (Y)	[20]
D001-cc resin–[BMIM][Cl]	Fructose	7	93 (Y)	86 (Y)	[57]
Lignosulfonic acid–[BMIM][Cl]	Fructose	6	77 (Y)	63 (Y)	[27]
[PSMBIM]HSO_4	Fructose	5	73 (Y)	63 (Y)	[9]
SO_4^{2-}/ZrO_2–[BMIM][Cl]	Fructose	5	82 (Y)	65 (Y)	[23]
[HO_2CMMIM][Cl]	Fructose	5	82 (Y)	78 (Y)	[82]
[tetraEG(mim)(triethylamo)] [HSO_4]$_2$	Fructose	6	92 (Y)	82 (Y)	[136]
Cr_3-SO_3H-polymeric ionic liquid	Fructose	5	88 (Y)	77 (Y)	[89]
PW_{12}-Ils-C_4-HNS	Fructose	6	94 (Y)	91 (Y)	[60]
CM-SO_3H	Fructose	8	83 (Y)	80 (Y)	[10]
[GLY(mim)$_3$][Cl]$_3$–CC-SO_3H	Fructose	4	97 (Y)	84 (Y)	[95]
0.06-CuAPO-5–[BMIM][Br]	Fructose	5	84 (Y)	82 (Y)	[35]
[BMIM-SO_3H]HSO_4	Fructose	3	70 $(Y)^L$	70 $(Y)^L$	[91]
KL zeolite–[BMIM][Br]	Fructose	4	99 (Y)	96 (Y)	[32]
$C_{10}MI\cdot CF_3SO_3$	Fructose	3	90 (Y)	80 (Y)	[160]
TPA/B$(OH)_3$–[BMIM][Cl]	Glucose	5	49 (Y)	46 (Y)	[38]
[SMIM][$FeCl_4$]	Glucose	5	69 $(Y)^L$	60 $(Y)^L$	[108]
[C_2OHMIM][BF_4]	Glucose	6	67 (Y)	58 (Y)	[61]
$SnCl_4$–[BMIM][Br]	Glucose	5	59 (Y)	56 (Y)	[148]
$CrCl_3\cdot 6H_2O/B(OH)_3$–[BMIM][Cl]	Glucose	5	75 (Y)	71 (Y)	[41]
Hβ zeolite–[BMIM][Cl]	Glucose	7	49 (Y)	48 (Y)	[48]
SnPO–[EMIM][Br]	Glucose	5	58 (Y)	56 (Y)	[47]
H_3BO_3–SiO_2–[BMIM][HSO_4]	Glucose	4	81 (Y)	65 (Y)	[81]
Al_2O_3-b-0.05	Glucose	3	50 (Y)	49 (Y)	[42]
$ZrOCl_2$–[HO_2CMMIm]Cl	Glucose	5	43 (Y)	38 (Y)	[97]
1-(4-Sulfonic acid)butyl-3-methylimidazolium chloride	Glucose	4	47 $(Y)^L$	37 $(Y)^L$	[117]
Cellulose-derived carbonaceous catalyst–[BMIM][Cl]	Glucose	4	44 (Y)	37 (Y)	[26]
Cr-USY–[BMIM][Cl]	Glucose	5	55 (Y)	28 (Y)	[45]
[SO_3H-BMIM]Cl/$AlCl_3$	Sucrose	3	65 (Y)	56 (Y)	[100]
$CoSO_4$–[(SO_3H)BMIM][HSO_4]	Cellulose	5	24 (Y)	18 (Y)	[62]
$AlCl_3$–[BMIM][Cl]	Cellulose	5	55 (Y)	46 (Y)	[50]
$InCl_3$–[C_3SO_3HMIM][HSO_4]	Cellulose	5	45 (Y)	32 (Y)	[103]
$ZrCl_4$–[BMIM][Cl]	Cellulose	6	51 (Y)	47 (Y)	[30]
[C_3SO_3HMIM][HSO_4]	Cellulose	5	59 $(Y)^L$	66 $(Y)^L$	[66]
γ-AlOOH–[BMIM][Cl]	Cellulose	5	58 (Y)	48 (Y)	[53]
[MIMC_4SO_3H][HSO_4]–[BMIM][Cl]	Cellulose	8	39 (Y)	20 (Y)	[52]
[HSO_3-$(CH_2)_3$-mim]Cl-$FeCl_3$	Cellobiose	5	67 $(Y)^L$	62 $(Y)^L$	[101]
$AlCl_3\cdot 6H_2O$–[BMIM][Cl]	Starch	5	60 (Y)	48 (Y)	[56]
[MIM][HSO_4]	Chitosan	5	30 (Y)	25 (Y)	[105]
[HMIM][HSO_4]–$FeCl_2$	Chitosan	4	44 (Y)	30 (Y)	[106]
[C_3SO_3Hmim]HSO_4	Chitosan	5	49 $(Y)^L$	6 $(Y)^L$	[142]
[BBIM-SO_3][NTf_2]	Mushroom	3	45 (Y)	40 (Y)	[120]
[$C_4(Mim)_2$][2(HSO_4)(H_2SO_4)$_2$]	Bamboo	4	48 $(Y)^L$	47 $(Y)^L$	[111]
$CrCl_3$, LiCl–[BMIM][Cl]	Wheat straw	3	61 (Y)	62 (Y)	[74]

(C) is value for conversion, (Y) is value for 5-HMF yield, $(Y)^L$ is value for LA yield

of α-anomers glucose to straight chain intermediate through ring opening step and hydrogen transfer. Then, enolate was formed, followed by the released of $GeCl_4$ to give fructose. Fructose was then dehydrated by the loss of one water molecule to form furanosyloxocarbenium ion, followed by deprotonation of the ion to form enol. As described in the previous mechanism of fructose conversion in [BMIM][Cl], a similar mechanism was proposed. There were two pathways for enol formation: nucleophilic and base. Nucleophile pathway involved the formation of intermediate from the attacked of oxorcabenium ion by the Cl − anion from the ionic liquid. The intermediate lost HCl to form an enol. Meanwhile for base pathway, enol formation occurred by deprotonation of furanosyloxocarbenium ion with Cl − anion from the ionic liquid acted as base. Then, the loss of two water molecules resulted in the formation of 5-HMF.

Table 6 Role of ionic liquid and/or catalyst from the proposed mechanisms of carbohydrate biomass conversion to 5-HMF

Reaction process	Role of ionic liquid/catalyst	Description	Ref.
Fructose to 5-HMF	Anion of the ionic liquid (i.e. Cl^{-})	• Cl− attached to OH group of C1 fructose before elimination of water molecule to form enediol • Enediol intermediate go through isomerization and elimination of two water molecules • 5-HMF obtained through dissociation of ionic liquid	[25]
Fructose to HMF	Cation of the ionic liquid (i.e. $BMIM^{+}$)	• [BMIM] + attacked the OH group of C1 fructose • Elimination of water molecule resulting in fructofuranosyl oxocarbenium ion	[159]
	Anion of the ionic liquid (i.e. Cl^{-})	• Formation of enol compound through nucleophile or base pathway • Nucleophile: Cl^{-} attacked oxocarbenium ion. Base: Cl^{-} acted as base that deprotonates C1 group • 5-HMF obtained through elimination of two water molecules	[19, 26, 133, 159]
Fructose to HMF	Cation of the ionic liquid (i.e. sulfonic acid)	• Cation acted as nucleophile and activates C-OH bond of fructose anomeric carbon for elimination of one water molecule and formation of enol intermediate	[9]
	Anion of the ionic liquid (i.e. HSO_4^{-})	• HSO_4^{-} acted as nucleophile that activates C-H of C1 fructose via hydrogen bonding • Elimination of two water molecules for 5-HMF formation driven by anion HSO_4^{-}	[9]
Glucose to fructose	Catalyst (i.e. $CoSO_4$, $MnCl_2$, $FeCl_2$) and ionic liquid	• Complexes formed from combination of catalyst with ionic liquid, promoted conversion of α-anomers glucose to open chain glucose • Complexes combined with glucose to form enolate intermediate • Enolate converted to fructose by the release of catalyst-ionic liquid complexes	[62, 78, 149]
Glucose to fructose	Catalyst (i.e. $GeCl_4$)	• Conversion of α-anomers glucose and to open chain glucose through ring opening step and hydrogen transfer • $GeCl_4$ combined with glucose to form enolate intermediate • Enolate converted to fructose by the release of $GeCl_4$	[19, 133]
Degradation of cellulose	Catalyst (i.e. $CrCl_3$, $FeCl_2$, $InCl_3$) and ionic liquid	• Complexes formed from combination of catalyst with ionic liquid • Catalyst part from complexes attacked the β-1,4-glycosidic bond • Ionic liquid part from complexes form hydrogen bond with the hydroxyl groups of cellulose • Glucose generated from the breakage of β-1,4-glycosidic bonds	[102, 103, 106, 139]

A mechanism of cellulose degradation to 5-HMF in [BMIM][Cl] with $CrCl_3$ catalyst was proposed by Zhou and team [139]. The mechanism described the involvement of $CrCl_3$-Im formed through coordination of $CrCl_3$ with [BMIM][Cl], and the mechanism emphasized on the cellulose degradation to glucose and subsequent isomerization to fructose. The β-1,4-glycosidic bond in cellulose was attacked by Cr part from $CrCl_3$-Im while [BMIM][Cl] part from $CrCl_3$-Im formed hydrogen bond with the hydroxyl groups of cellulose to enhance the breaking of the glycosidic bond. Then, glucose was generated from the breakage of β-1,4-glycosidic bonds. The isomerization of glucose to fructose follows the similar steps as previously proposed mechanism involving catalyst in ionic liquid. The α-glucopyranose was isomerized into β-glucosepyranose through coordination with $CrCl_3$-Im. The enolate intermediate was formed through the interaction of $CrCl_3$-Im with the hemiacetal portion of β-glucopyranose. Then, the released of $CrCl_3$-IM from the enolate gave fructose. The 5-HMF is then produced by the removal of three molecules of water from fructose. Generally, the mechanism of 5-HMF production from cellulose and other polysaccharide degradations catalysed by other metal salts followed similar pathways. This can be found in the proposed mechanisms for cellulose and chitosan degradations promoted by different metal salts, such as $FeCl_2$ and $InCl_3$ and in different ionic liquids [102, 103, 106].

Other than metal salts, the mechanisms of carbohydrate biomass conversion in [BMIM][Cl] with the presence of acid catalyst have been proposed. The acid catalysts include cellulose-derived carbonaceous catalyst (CCC) and 12-tungstophosphoric acid-boric acid (12-TPA/$B(OH)_3$) [26, 38]. In the solid catalyst CCC-catalysed polysaccharides and disaccharides conversions to 5-HMF, the substrate was first adsorbed onto the surface of CCC by –COOH and –OH groups. The H^+ released from the SO_3H groups of CCC promoted the hydrolysis of substrates to glucose. Then, glucose was isomerized to fructose before dehydrated to 5-HMF. The proposed mechanism of 12-TPA/$B(OH)_3$-catalysed glucose conversion to 5-HMF consisted of formation of 1,2-enediol intermediate from the enolization of glucose, which promoted by the synergistic effect of catalysts: 12-TPA and $B(OH)_3$. Then, 5-HMF was produced from the 1,2-enediol through two possible pathways. The first pathway was direct dehydration of enediol to 5-HMF by 12-TPA. The other pathway was indirect dehydration by 12-TPA and $B(OH)_3$ which isomerization of 1,2-enediol to fructose, then dehydration of fructose to 5-HMF. In the proposed mechanisms, it seemed that 5-HMF production was mainly attributed by the presence of catalyst. Nonetheless, [BMIM][Cl] also played an important role in the mechanism [26]. [BMIM][Cl] could dissolve the carbohydrates to generate homogeneous solutions, making the catalyst more accessible to the carbohydrate. Besides, the isomerization of glucose into fructose was also promoted by the presence of Cl^- of the ionic liquid, which acted as both base and nucleophile [26].

Kinetics of Carbohydrate Biomass Conversion to 5-HMF and LA in Ionic Liquid

One of the important aspects in a chemical reaction is related to reaction kinetics. An enormous interest in 5-HMF and LA applications has led to numerous kinetic studies on the decomposition of carbohydrates to produce 5-HMF and LA. Kinetic studies are not only important to find out the mechanism for 5-HMF and LA formation on a molecular level but also for process development studies to identify optimum reactor configurations and process conditions for the highest product yields. There were several factors affected the kinetics and led to the variation in the activation energy such as types of catalyst and solvent, heating method and temperature range. The kinetics data from glucose conversion reaction showed that a higher temperature accelerated the intermediate species dehydration reaction rate [97]. It was reported that the activation energies for the degradation of cellulose and reducing sugar decrease from with the addition of catalyst [174]. Besides, microware irradiation can improve the dissolution of carbohydrate substrates and the combination of ionic liquid with microwave irradiation could lower the reaction's activation energy.

The kinetic models of 5-HMF and LA productions from carbohydrate biomass feedstocks were developed based on several individual reaction schemes, while some of the models did not considered the individual reaction of each products. The parallel reactions of humins formation from glucose and 5-HMF have been proposed and integrated in the kinetic models. The experimental data for glucose decomposition reaction were best described using a first-order kinetic model [43, 61, 89, 175, 176]. There have been increasing numbers of kinetic studies on carbohydrate biomass conversion to 5-HMF and LA. Table 7 summarizes some selected kinetic studies on 5-HMF and LA production in ionic liquids. A wide range of activation energy for glucose conversion to 5-HMF have been reported, which the lowest activation energy was reported for the dehydration of glucose using a functionalized solid polymeric ionic liquid [89]. The activation energy for 5-HMF conversion to LA was reported for reaction involving acidic functionalized ionic liquid, [SMIM][$FeCl_4$]. The activation energies for humins formations from glucose and 5-HMF were also reported [66, 90]. In addition, a kinetic model of glucose decomposition was developed by considering only decomposition of glucose to LA and humins, without including the formation of 5-HMF [66, 90]. The application of microwave irradiation resulted in slight reduction in activation energy for glucose conversion to 5-HMF catalysed by $CrCl_3$ in [BMIM][Cl] [43, 144, 177].

Similar to glucose, the kinetic model of fructose conversion was best described using a first order [82, 141]. The lowest activation energy of fructose decomposition to 5-HMF has been reported, which suggested a synergetic effect between [BMIM][Cl]-heteropolyacid catalyst and fructose for 5-HMF production under mild process conditions [28]. 5-HMF is an intermediate in the proposed reaction scheme of carbohydrates conversion to LA. For LA production, the undesired reaction of 5-HMF to humins should be suppressed. The reactivity of 5-HMF could also be investigated from the decomposition of glucose, where the formation and decomposition of 5-HMF are integrated in the kinetic model [178, 179]. Qu et al. [99] have studied the kinetics of fructose conversion using acidic and alkaline ionic liquids. The kinetic models followed first-order reaction, which proposed to include two steps reactions: decomposition of fructose to 5-HMF and by-products and decomposition of 5-HMF to by-products. The activation energy of 5-HMF decomposition using alkaline ionic liquid was lower compared with acidic ionic liquid, revealed that 5-HMF was degraded into by-products such as LA, and formic acid at much faster rate [99].

As major sugars are available in polymers such as cellulose, it is appropriate to emphasize the process and its kinetic study. Pseudo homogeneous first-order model was used to describe the kinetic of cellulose decomposition reactions [90, 115]. In a studies on hydrothermal decomposition of carbohydrates to LA in the presence of acidic ionic liquid, two different kinetic models were proposed: decomposition of glucose as well as decomposition of cellulose to LA [90]. In the kinetic study of cellulose decomposition, the reaction scheme includes decomposition of cellulose to glucose and the subsequent conversion of glucose to LA and humins [66]. The activation energy obtained from the decomposition of cellulose was higher than the activation energy of glucose conversion to LA. The higher activation energy explained the need of higher temperature for the initial depolymerization and hydrolysis of cellulose. Besides, the higher molecular weight and the cellulose crystallinity might resulted in the higher activation energy value [90]. On the other hand, the simplified kinetic model of cellulose decomposition to LA only involved reaction rate of cellulose decomposition, without considering the subsequent conversion of glucose to LA and humins [124].

Zhang et al. [140, 180] have investigated the kinetic study of cellulose decomposition in [BMIM][Cl]. As $CrCl_3$ was used as catalyst, the simplified model of cellulose degradation includes degradation of cellulose, degradation of 5-HMF and degradation of glucose to 5-HMF [180]. It was indicated that the decomposition reactions of cellulose, 5-HMF and glucose

Table 7 Kinetic studies of carbohydrate biomass conversion to 5-HMF and LA in ionic liquid

Proposed model	Reaction conditions	Ea ($kJ.mol^{-1}$)	References
$\text{Glucose} \xrightarrow{1} \text{5-HMF}$	140 – 180 °C $[C_2OHMIM][BF_4]$ in DMSO	$Ea_1 = 56$	[29]
$\text{Glucose} \xrightarrow{1} \text{5-HMF}$	140 – 160 °C $[HO_2CMMIm]Cl – ZrOCl_2$ in isopropanol	$Ea_1 = 48$	[116]
$\text{Glucose} \xrightarrow{1} \text{5-HMF}$	110 – 170 °C Cr_3-SO_3H- polymeric ionic liquid in DMSO	$Ea_1 = 22$	[109]
$\text{Glucose} \xrightarrow{1} \text{5-HMF}$	90 – 120 °C $CrCl_3$ in [BMIM][Cl] or [AMIM][Cl]	$Ea_1 = 120.0 – 134.9$	[55,177] [175]
$\begin{tikzcd} \text{Glucose} \arrow[r, "1"] \arrow[d, "2"] & \text{5-HMF} \arrow[d, "3"] \\ \text{Degradation products} & \text{} \end{tikzcd}$	140 – 160 °C Zeolite – $CrCl_3$ in [BMIM][Cl]	$Ea_1 = 104.7$ $Ea_2 = 88.8$ $Ea_3 = 83.8$	[178]
$\begin{tikzcd} \text{Glucose} \arrow[r, "1"] \arrow[d, "2"] & \text{5-HMF} \arrow[r, "3"] \arrow[d, "4"] & \text{LA} \\ \text{Humins} & \text{Humins} & \end{tikzcd}$	110 – 170 °C $[SMIM][FeCl_4]$ in H_2O	$Ea_1 = 37$ $Ea_2 = 41$ $Ea_3 = 30$ $Ea_4 = 43$	[179]
$\text{Fructose} \xrightarrow{1} \text{5-HMF}$	120 – 180 °C [BMIM]OH in DMSO	$Ea_1 = 99$	[141]
$\text{Fructose} \xrightarrow{1} \text{5-HMF}$	90 – 110 °C $[HO_2CMMIm]Cl$ in isopropanol	$Ea_1 = 62.1$	[115]
$\text{Fructose} \xrightarrow{1} \text{5-HMF}$	60 – 90 °C [BMIM][TSO]	$Ea_1 = 51.5$	[124]
$\text{Fructose} \xrightarrow{1} \text{5-HMF}$	50 – 80 °C $H_3PW_{12}O_{40}$ in [BMIM][Cl]	$Ea_1 = 32$	[43]
$\begin{tikzcd} \text{Fructose} \arrow[r, "1"] \arrow[d, "2"] & \text{5-HMF} \\ \text{Humins} & \end{tikzcd}$	80 – 100 °C $IrCl_3$ in [BMIM]Cl	$Ea_1 = 165$ $Ea_2 = 124$	[19]
$\begin{tikzcd} \text{Cellulose} \arrow[r, "1"] & \text{Glucose} \arrow[r, "2"] \arrow[d, "3"] & \text{LA} \\ & \text{Humins} & \end{tikzcd}$	160 – 180 °C $[C_3SO_3HMIM][HSO_4]$ in H_2O	$Ea_1 = 122$ $Ea_2 = 203$ $Ea_3 = 167$	[35]
$\begin{tikzcd} \text{Cellulose} \arrow[r, "1"] & \text{Glucose} \arrow[r, "2"] \arrow[d, "3"] & \text{LA} \\ & \text{Humins} & \end{tikzcd}$	140 – 180 °C $[BSO_3HMIm]HSO_4$	$Ea_1 = 187$ $Ea_2 = 114$ $Ea_3 = 148$	[83]
$\text{Cellulose} \xrightarrow{1} \text{LA}$	80 – 100 °C $[C_4(Mim)_2][2(HSO_4)(HSO_4)_2]$	$Ea_1 = 40.4$	[101]
$\text{Cellulose} \xrightarrow{1} \text{Glucose} \xrightarrow{2} \text{5-HMF}$	80 – 120 °C $[C_4SO_3HMIM]Cl$	$Ea_1 = 114$ $Ea_2 = 95$	[80]
$\begin{tikzcd} \text{Cellulose} \arrow[r, "1"] & \text{Glucose} \arrow[r, "2"] \arrow[d] & \text{5-HMF} \arrow[r, "3"] & \text{Decomposition product} \\ & \text{By-products} & & \end{tikzcd}$	140 – 170 °C $CrCl_3$ in [BMIM][Cl]	$Ea_1 = 61$ $Ea_2 = 48.6$ $Ea_3 = 37.6$	[180]

were all first-order reaction. The kinetics of cellulose decomposition was also studied in the presence of $CrCl_3$ using ionic liquid/organic solvent [140]. Similar to previous, the reaction rates include the degradation rate constants of cellulose, degradation rate constants of 5-HMF, degradation rate constant of glucose to 5-HMF. Besides, the kinetic model also includes reaction rate for 5-HMF diffusion coefficient). The decomposition rate constants of cellulose, glucose and 5-HMF, along with the diffusion coefficient of 5-HMF, in the biphasic system were obtained using the first-order reaction model. The reaction rate of 5-HMF diffusion coefficient was mainly affected by the temperature.

Conclusions and Future Perspective

Production of chemicals from biomass offers a promising opportunity to reduce dependence on fossil fuels and to expand the sustainability of biorefinery. 5-HMF and LA are potential chemicals from biomass that can be transformed into numerous value-added products. Various attempts have been carried out to develop efficient process for 5-HMF and LA productions from biomass, which include ionic liquid system. Over the years, the high number of studies related to 5-HMF and LA productions from carbohydrate biomass in ionic liquids indicate that the research area is relevant and has attracted significant attention from researchers worldwide. Therefore, in-depth review on this subject has been carried out, and conclusions that can be elucidated from this review are as follows:

1. Direct one-pot conversion of biomass to 5-HMF and LA in ionic liquid offers promising benefit compared with the sequential steps. Ionic liquid with the ability to dissolve the cellulose structure and promote glucose dehydration to 5-HMF and subsequent rehydration of 5-HMF to LA is imperative.
2. Functionalized ionic liquids, prepared through the inclusion of different types of functional groups on cations and anions, have been widely applied for 5-HMF and LA productions. Generally, the functionalized ionic liquid is synthesized to give an ionic liquid with Brønsted and/or Lewis acid sites. The ionic liquid can act as solvent, catalyst or as both solvent and catalyst. Other than monocationic ionic liquid, dicationic and tricationic ionic liquids are also introduced. Besides, functionalized ionic liquids employed are prepared through different methods such as incorporation of transition metals, inclusion of heteropolyacid, polymeric ionic liquid, silica immobilized ionic liquids and biochar sulfonic acid-derived ionic liquid.
3. The activity of ionic liquid is attributed to several aspects such as the ionic liquid structure, which is the types of anions and cations, the amount and strength of Brønsted and Lewis acids, as well as the coordination of the ions with substrates during the reaction. For instance, good performance of high acidity ionic liquid has been reported by various studies on 5-HMF and LA productions. The aforementioned aspects are important in designing and fabricating ionic liquid with specific role in 5-HMF and LA productions.
4. The 5-HMF and LA productions in ionic liquid from carbohydrate biomass conversion are affected by various factors: reaction temperature and time, types of heating, catalyst properties/types of catalyst, catalyst loading, types of feedstocks, feedstock loading, ionic liquid loading, reaction media and solvent/co-solvent and water content. The presence of catalyst with appropriate mesoporosity, acidity and other properties are useful for the reaction. The optimization of these parameters is vital as it will affect the process efficiency, yield and selectivity of the targeted product, as well as the by-products.
5. The cost of ionic liquid has always been one of the important issues to be considered. The reusability of ionic liquid is essential for reducing the overall cost. The insignificant reduction in activity of the reused ionic liquid is the important parameter to be maintained.
6. Mechanism and kinetics of carbohydrate biomass conversion to 5-HMF and LA have been proposed to provide more insights on the significant role played by the ionic liquid.

With that notion, a successful lignocellulosic biorefinery can be built through a combination of different technology and biomass processing strategy for the production of value-added chemicals. Based on the current reviews, the future perspective for further research should focus on the development of better catalytic system, particularly ionic liquid. The following specific study should be carried out:

1. Design of ionic liquid with specific properties in order to improve and expand the area of ionic liquid applications. Ionic liquid with properties such as easy to recycle, high stability, can be tailored for one-pot conversion of biomass, with minimum by-product formation. The use of environmentally friendly ionic liquids allows the process to be considered as green and sustainable. The one-pot reaction can avoid the costly intermediate separation process.
2. An effective ionic liquid system should be further discovered such as through effective combination of tailor-made ionic liquid with high activity catalyst, solvent and microwave irradiation. Besides, in regard to reusability of ionic liquid, extensive studies on magnetic-based ionic liquids should be further explored. Magnetic-particle as catalyst support have attracted substantial attention in the past years due to its easy and economical separation method.

3. Other than focusing on optimizing the 5-HMF and LA yields, future studies should focus on isolation and purification techniques which can give high purity of the produced 5-HMF and LA. The technique developed should be economically feasible at industrial scale.
4. Present studies are mostly limited to individual experimental and kinetic studies, while multiscale reactor modelling to computationally describe the catalytic reactions are scarce. More attention to reaction mechanism and kinetics of carbohydrate biomass conversion to 5-HMF and LA, for example through study on density functional theory (DFT) should be performed.
5. Extensive investigation on direct conversion of lignocellulosic biomass to 5-HMF and LA in ionic liquid, to make the process feasible and industrially applicable. Some barriers need to be overcome for commercializing the conversion process using ionic liquid. The barriers include economic remuneration analysis, ionic liquid manufacturing, environment, safety and health, and the most important thing is the fundamental understanding of the compositional structure against its performance.

Conflict of interest The authors declare that they have no conflict of interest.

Authors Contributions All authors contributed to the design of the manuscript. The idea for the article comes from both authors. The literature search and data analysis were performed by Nur Aainaa Syahirah Ramli. The first draft of the manuscript was written by Nur Aainaa Syahirah Ramli and the corresponding author (Nor Aishah Saidina Amin) critically commented the work. All authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

Funding information The study is financially supported by Universiti Teknologi Malaysia under collaborative research grant (CRG) Vot 08G62 and Vot 08G63.

Compliance with Ethical Standards

Availability of Data and Material Not applicable.

Code Availability Not applicable

References

1. Halder P, Kundu S, Patel S, Setiawan A, Atkin R, Parthasarthy R, Paz-Ferreiro J, Surapaneni A, Shah K (2019) Progress on the pretreatment of lignocellulosic biomass employing ionic liquids. Renew Sust Energ Rev 105:268–292. https://doi.org/10.1016/j.rser.2019.01.052
2. Falarz LJ, Singer SD, Chen G (2018) Biomass-derived building block chemicals. In: Chen G, Weselake RJ, Singer SD (eds) Plant bioproducts. Springer New York, New York, pp 177–200
3. Biddy MJ, Scarlata C, Kinchin C (2016) Chemicals from biomass: a market assessment of bioproducts with near-term potential. National Renewable Energy Lab. (NREL), Golden
4. Scopus (2019) (search query: 'levulinic acid 5-hydroxymethyl furfural ionic liquid'). www.scopus.com. Accessed 5 Oct 2019
5. Chinnappan A, Baskar C, Kim H (2016) Biomass into chemicals: green chemical conversion of carbohydrates into 5-hydroxymethylfurfural in ionic liquids. RSC Adv 6(68):63991–64002. https://doi.org/10.1039/C6RA12021K
6. Zheng X, Gu X, Ren Y, Zhi Z, Lu X (2016) Production of 5-hydroxymethyl furfural and levulinic acid from lignocellulose in aqueous solution and different solvents. Biofuels Bioprod Biorefin 10(6):917–931. https://doi.org/10.1002/bbb.1720
7. Badgujar KC, Wilson LD, Bhanage BM (2019) Recent advances for sustainable production of levulinic acid in ionic liquids from biomass: current scenario, opportunities and challenges. Renew Sust Energ Rev 102:266–284. https://doi.org/10.1016/j.rser.2018.12.007
8. Mukherjee A, Dumont M-J, Raghavan V (2015) Review: sustainable production of hydroxymethylfurfural and levulinic acid: challenges and opportunities. Biomass Bioenergy 72:143–183. https://doi.org/10.1016/j.biombioe.2014.11.007
9. Kotadia DA, Soni SS (2013) Symmetrical and unsymmetrical Bronsted acidic ionic liquids for the effective conversion of fructose to 5-hydroxymethyl furfural. Cat Sci Technol 3(2):469–474. https://doi.org/10.1039/C2CY20493B
10. Li X, Wang Y, Xie X, Huang C, Yang S (2019) Dehydration of fructose, sucrose and inulin to 5-hydroxymethylfurfural over yeast-derived carbonaceous microspheres at low temperatures. RSC Adv 9(16):9041–9048. https://doi.org/10.1039/C8RA10465D
11. Nagpure AS, Venugopal AK, Lucas N, Manikandan M, Thirumalaiswamy R, Chilukuri S (2015) Renewable fuels from biomass-derived compounds: Ru-containing hydrotalcites as catalysts for conversion of HMF to 2,5-dimethylfuran. Cat Sci Technol 5(3):1463–1472. https://doi.org/10.1039/C4CY01376J
12. Yan D, Xin J, Zhao Q, Gao K, Lu X, Wang G, Zhang S (2018) Fe–Zr–O catalyzed base-free aerobic oxidation of 5-HMF to 2,5-FDCA as a bio-based polyester monomer. Cat Sci Technol 8(1):164–175. https://doi.org/10.1039/C7CY01704A
13. Zainol MM, Amin NAS, Asmadi M, Ramli NAS (2019) Esterification of levulinic acid to ethyl levulinate using liquefied oil palm frond-based carbon cryogel catalyst. BioEnergy Res 12(2):359–369. https://doi.org/10.1007/s12155-019-09977-6
14. Ramli NAS, Sivasubramaniam D, Amin NAS (2017) Esterification of levulinic acid using ZrO2-supported phosphotungstic acid catalyst for ethyl levulinate production. BioEnergy Res 10(4):1105–1116. https://doi.org/10.1007/s12155-017-9872-1
15. Démolis A, Essayem N, Rataboul F (2014) Synthesis and applications of alkyl levulinates. ACS Sustain Chem Eng 2(6):1338–1352. https://doi.org/10.1021/sc500082n
16. Siankevich S, Fei Z, Scopelliti R, Jessop PG, Zhang J, Yan N, Dyson PJ (2016) Direct conversion of mono- and polysaccharides into 5-hydroxymethylfurfural using ionic-liquid mixtures. ChemSusChem 9(16):2089–2096. https://doi.org/10.1002/cssc.201600313
17. Sarwono A, Man Z, Muhammad N, Khan AS, Hamzah WSW, Rahim AHA, Ullah Z, Wilfred CD (2017) A new approach of probe sonication assisted ionic liquid conversion of glucose, cellulose and biomass into 5-hydroxymethylfurfural. Ultrason Sonochem 37:310–319. https://doi.org/10.1016/j.ultsonch.2017.01.028
18. Tadesse H, Luque R (2011) Advances on biomass pretreatment using ionic liquids: an overview. Energy Environ Sci 4(10):3913–3929. https://doi.org/10.1039/C0EE00667J
19. Zhang Z, Wang Q, Xie H, Liu W, Zhao Z (2011) Catalytic conversion of carbohydrates into 5-hydroxymethylfurfural by

germanium(IV) chloride in ionic liquids. ChemSusChem 4(1): 131–138. https://doi.org/10.1002/cssc.201000279

20. Guo X, Cao Q, Jiang Y, Guan J, Wang X, Mu X (2012) Selective dehydration of fructose to 5-hydroxymethylfurfural catalyzed by mesoporous SBA-15-SO$_3$H in ionic liquid BmimCl. Carbohydr Res 351:35–41. https://doi.org/10.1016/j.carres.2012.01.003
21. Wei Z, Li Y, Thushara D, Liu Y, Ren Q (2011) Novel dehydration of carbohydrates to 5-hydroxymethylfurfural catalyzed by Ir and au chlorides in ionic liquids. J Taiwan Inst Chem Eng 42(2):363–370. https://doi.org/10.1016/j.jtice.2010.10.004
22. Hu S, Zhang Z, Song J, Zhou Y, Han B (2009) Efficient conversion of glucose into 5-hydroxymethylfurfural catalyzed by a common Lewis acid SnCl$_4$ in an ionic liquid. Green Chem 11(11): 1746–1749. https://doi.org/10.1039/B914601F
23. Mohammad BN, Helen CH, Julian RGE (2017) Preparation of 5-hydroxymethylfurfural from glucose and fructose in ionic liquids by reactive vacuum distillation over a solid catalyst. Curr Org Synth 14(4):596–603. https://doi.org/10.2174/1570179414666161115155958
24. Li C, Zhao ZK, Wang A, Zheng M, Zhang T (2010) Production of 5-hydroxymethylfurfural in ionic liquids under high fructose concentration conditions. Carbohydr Res 345(13):1846–1850. https://doi.org/10.1016/j.carres.2010.07.003
25. Shi J, Yang Y, Wang N, Song Z, Gao H, Xia Y, Li W, Wang H (2013) Catalytic conversion of fructose and sucrose to 5-hydroxymethylfurfural using simple ionic liquid/DMF binary reaction media. Catal Commun 42:89–92. https://doi.org/10.1016/j.catcom.2013.08.009
26. Hu L, Zhao G, Tang X, Wu Z, Xu J, Lin L, Liu S (2013) Catalytic conversion of carbohydrates into 5-hydroxymethylfurfural over cellulose-derived carbonaceous catalyst in ionic liquid. Bioresour Technol 148:501–507. https://doi.org/10.1016/j.biortech.2013.09.016
27. Xie H, Zhao ZK, Wang Q (2012) Catalytic conversion of inulin and fructose into 5-hydroxymethylfurfural by lignosulfonic acid in ionic liquids. ChemSusChem 5(5):901–905. https://doi.org/10.1002/cssc.201100588
28. Xiao Y, Song Y-F (2014) Efficient catalytic conversion of the fructose into 5-hydroxymethylfurfural by heteropolyacids in the ionic liquid of 1-butyl-3-methyl imidazolium chloride. Appl Catal A Gen 484:74–78. https://doi.org/10.1016/j.apcata.2014.07.014
29. Guo F, Fang Z, Zhou T-J (2012) Conversion of fructose and glucose into 5-hydroxymethylfurfural with lignin-derived carbonaceous catalyst under microwave irradiation in dimethyl sulfoxide–ionic liquid mixtures. Bioresour Technol 112:313–318. https://doi.org/10.1016/j.biortech.2012.02.108
30. Liu B, Zhang Z, Zhao ZK (2013) Microwave-assisted catalytic conversion of cellulose into 5-hydroxymethylfurfural in ionic liquids. Chem Eng J 215–216:517–521. https://doi.org/10.1016/j.cej.2012.11.019
31. Zhou X, Zhang Z, Liu B, Xu Z, Deng K (2013) Microwave-assisted rapid conversion of carbohydrates into 5-hydroxymethylfurfural by ScCl3 in ionic liquids. Carbohydr Res 375(supplement C):68–72. https://doi.org/10.1016/j.carres.2013.04.003
32. Ma Z, Hu H, Sun Z, Fang W, Zhang J, Yang L, Zhang Y, Wang L (2017) Acidic zeolite L as a highly efficient catalyst for dehydration of fructose to 5-hydroxymethylfurfural in ionic liquid. ChemSusChem 10(8):1669–1674. https://doi.org/10.1002/cssc.201700239
33. Su K, Liu X, Ding M, Yuan Q, Li Z, Cheng B (2013) Effective conversion sucrose into 5-hydroxymethylfurfural by tyrosine in [Emim]Br. J Mol Catal A Chem 379:350–354. https://doi.org/10.1016/j.molcata.2013.09.003
34. Wang Q, Su K, Li Z (2017) Performance of [Emim]Br, [Bmim]Br and 2,5-furandicarboxylic acid in fructose conversion to 5-hydroxymethyfurfural. Mol Catal 438:197–203. https://doi.org/10.1016/j.mcat.2017.06.004
35. Huang Y, Zhang P, Hu H, Hu D, Yang J, Zhang Y, Chen C, Yang Y, Zhang J, Wang L (2019) Efficient production of 5-hydroxymethylfurfural from fructose over CuAPO-5 molecular sieves synthesized using an ionothermal method. RSC Adv 9(56):32848–32853. https://doi.org/10.1039/C9RA07217A
36. Ståhlberg T, Rodriguez-Rodriguez S, Fristrup P, Riisager A (2011) Metal-free dehydration of glucose to 5-(hydroxymethyl)furfural in ionic liquids with boric acid as a promoter. Chem Eur J 17(5): 1369–1369. https://doi.org/10.1002/chem.201002171
37. Liu D, Chen EYX (2012) Ubiquitous aluminum alkyls and alkoxides as effective catalysts for glucose to HMF conversion in ionic liquids. Appl Catal A Gen 435–436:78–85. https://doi.org/10.1016/j.apcata.2012.05.035
38. Hu L, Sun Y, Lin L, Liu S (2012) 12-Tungstophosphoric acid/boric acid as synergetic catalysts for the conversion of glucose into 5-hydroxymethylfurfural in ionic liquid. Biomass Bioenergy 47:289–294. https://doi.org/10.1016/j.biombioe.2012.09.032
39. Stahlberg T, Sorensen MG, Riisager A (2010) Direct conversion of glucose to 5-(hydroxymethyl)furfural in ionic liquids with lanthanide catalysts. Green Chem 12(2):321–325. https://doi.org/10.1039/B916354A
40. Aylak AR, Akmaz S, Koc SN (2017) An efficient heterogeneous CrOx–Y zeolite catalyst for glucose to HMF conversion in ionic liquids. Part Sci Technol 35(4):490–493. https://doi.org/10.1080/02726351.2016.1168895
41. Hu L, Sun Y, Lin L, Liu S (2012) Catalytic conversion of glucose into 5-hydroxymethylfurfural using double catalysts in ionic liquid. J Taiwan Inst Chem Eng 43(5):718–723. https://doi.org/10.1016/j.jtice.2012.04.001
42. Hou Q, Zhen M, Li W, Liu L, Liu J, Zhang S, Nie Y, Bai C, Bai X, Ju M (2019) Efficient catalytic conversion of glucose into 5-hydroxymethylfurfural by aluminum oxide in ionic liquid. Appl Catal B Environ 253:1–10. https://doi.org/10.1016/j.apcatb.2019.04.003
43. Sarwono A, Man Z, Idris A, Khan AS, Muhammad N, Wilfred CD (2019) Optimization of ionic liquid assisted sugar conversion and nanofiltration membrane separation for 5-hydroxymethylfurfural. J Ind Eng Chem 69:171–178. https://doi.org/10.1016/j.jiec.2018.09.020
44. Aylak AR, Akmaz S, Koc SN (2019) Glucose conversion to 5-hydroxymethylfurfural with chromium exchanged bentonite and montmorillonite catalysts in different solvents. Chem Eng Commun 1–11. https://doi.org/10.1080/00986445.2019.1641489
45. Sezgin E, Esen Keçeci M, Akmaz S, Koc SN (2019) Heterogeneous Cr-zeolites (USY and Beta) for the conversion of glucose and cellulose to 5-hydroxymethylfurfural (HMF). Cellulose 26(17):9035–9043. https://doi.org/10.1007/s10570-019-02702-8
46. Mamo W, Chebude Y, Marquez-Alvarez C, Diaz I, Sastre E (2016) Comparison of glucose conversion to 5-HMF using different modified mordenites in ionic liquid and biphasic media. Cat Sci Technol 6(8):2766–2774. https://doi.org/10.1039/C5CY02070K
47. Hou Q, Zhen M, Liu L, Chen Y, Huang F, Zhang S, Li W, Ju M (2018) Tin phosphate as a heterogeneous catalyst for efficient dehydration of glucose into 5-hydroxymethylfurfural in ionic liquid. Appl Catal B Environ 224:183–193. https://doi.org/10.1016/j.apcatb.2017.09.049
48. Hu L, Wu Z, Xu J, Sun Y, Lin L, Liu S (2014) Zeolite-promoted transformation of glucose into 5-hydroxymethylfurfural in ionic liquid. Chem Eng J 244:137–144. https://doi.org/10.1016/j.cej.2014.01.057

49. Ya'aini N, Amin NAS (2013) Catalytic conversion of lignocellulosic biomass to levulinic acid in ionic liquid. Bioresources 8(4): 5761–5772. https://doi.org/10.15376/biores.8.4.5761-5772
50. Xiao S, Liu B, Wang Y, Fang Z, Zhang Z (2014) Efficient conversion of cellulose into biofuel precursor 5-hydroxymethylfurfural in dimethyl sulfoxide–ionic liquid mixtures. Bioresour Technol 151:361–366. https://doi.org/10.1016/j.biortech.2013.10.095
51. Eminov S, Filippousi P, Brandt A, Wilton-Ely JDET, Hallett JP (2016) Direct catalytic conversion of cellulose to 5-hydroxymethylfurfural using ionic liquids. Inorganics 4(4):32. https://doi.org/10.3390/inorganics4040032
52. Chiappe C, Rodriguez Douton MJ, Mezzetta A, Pomelli CS, Assanelli G, de Angelis AR (2017) Recycle and extraction: cornerstones for an efficient conversion of cellulose into 5-hydroxymethylfurfural in ionic liquids. ACS Sustain Chem Eng 5(6):5529–5536. https://doi.org/10.1021/acssuschemeng.7b00875
53. Tang Z, Su J (2019) Direct conversion of cellulose to 5-hydroxymethylfurfural (HMF) using an efficient and inexpensive boehmite catalyst. Carbohydr Res 481:52–59. https://doi.org/10.1016/j.carres.2019.06.010
54. Li F, Zhang G, Song Y (2018) Fabrication and evaluation of multi-walled carbon nanotubes supported novel catalyst for select conversion of cellulose to 5-hydroxymethylfurfural. Energy Technol 6(9):1633–1641. https://doi.org/10.1002/ente.201700800
55. Kuo IJ, Suzuki N, Yamauchi Y, Wu KCW (2013) Cellulose-to-HMF conversion using crystalline mesoporous titania and zirconia nanocatalysts in ionic liquid systems. RSC Adv 3(6):2028–2034. https://doi.org/10.1039/C2RA21805D
56. Roy Goswami S, Dumont M-J, Raghavan V (2016) Microwave assisted synthesis of 5-hydroxymethylfurfural from starch in $AlCl_3 \cdot 6H_2O$/DMSO/[BMIM]cl system. Ind Eng Chem Res 55(16):4473–4481. https://doi.org/10.1021/acs.iecr.6b00201
57. Li Y, Liu H, Song C, Gu X, Li H, Zhu W, Yin S, Han C (2013) The dehydration of fructose to 5-hydroxymethylfurfural efficiently catalyzed by acidic ion-exchange resin in ionic liquid. Bioresour Technol 133:347–353. https://doi.org/10.1016/j.biortech.2013.01.038
58. Sun Z, Cheng M, Li H, Shi T, Yuan M, Wang X, Jiang Z (2012) One-pot depolymerization of cellulose into glucose and levulinic acid by heteropolyacid ionic liquid catalysis. RSC Adv 2(24): 9058–9065. https://doi.org/10.1039/C2RA01328B
59. Ramli NAS, Amin NAS (2013) Ionic solid nanomaterials: synthesis, characterization and catalytic properties investigation. Adv Mater Res 699:155–160. https://doi.org/10.4028/www.scientific.net/AMR.699.155
60. An S, Wang Z, Zhang H, Miras HN, Song Y-F (2019) Self-organization of ionic liquid-modified organosilica hollow nanospheres and heteropolyacids: efficient preparation of 5-hmf under mild conditions. ChemCatChem 11(10):2526–2536. https://doi.org/10.1002/cctc.201900285
61. Qu Y, Huang C, Song Y, Zhang J, Chen B (2012) Efficient dehydration of glucose to 5-hydroxymethylfurfural catalyzed by the ionic liquid,1-hydroxyethyl-3-methylimidazolium tetrafluoroborate. Bioresour Technol 121:462–466. https://doi.org/10.1016/j.biortech.2012.06.081
62. Tao F, Song H, Chou L (2011) Catalytic conversion of cellulose to chemicals in ionic liquid. Carbohydr Res 346(1):58–63. https://doi.org/10.1016/j.carres.2010.10.022
63. Ma H, Zhou B, Li Y, Argyropoulos DS (2012) Conversion of fructose to 5-hydroxymethylfurfural with a functionalized ionic liquid. BioResources 7(1):533–544
64. Ramli NAS, Amin NAS (2015) A new functionalized ionic liquid for efficient glucose conversion to 5-hydroxymethyl furfural and levulinic acid. J Mol Catal A Chem 407:113–121. https://doi.org/10.1016/j.molcata.2015.06.030
65. Amarasekara A, Wiredu B (2014) Acidic ionic liquid catalyzed one-pot conversion of cellulose to ethyl levulinate and levulinic acid in ethanol-water solvent system. BioEnergy Res 7(4):1237–1243. https://doi.org/10.1007/s12155-014-9459-z
66. Ren H, Girisuta B, Zhou Y, Liu L (2015) Selective and recyclable depolymerization of cellulose to levulinic acid catalyzed by acidic ionic liquid. Carbohydr Polym 117:569–576. https://doi.org/10.1016/j.carbpol.2014.09.091
67. Lee J-W, Ha M-G, Yi Y-B, Chung C-H (2011) Chromium halides mediated production of hydroxymethylfurfural from starch-rich acorn biomass in an acidic ionic liquid. Carbohydr Res 346(2): 177–182. https://doi.org/10.1016/j.carres.2010.11.009
68. Yi Y-B, Lee J-W, Hong S-S, Choi Y-H, Chung C-H (2011) Acid-mediated production of hydroxymethylfurfural from raw plant biomass with high inulin in an ionic liquid. J Ind Eng Chem 17(1):6–9. https://doi.org/10.1016/j.jiec.2010.12.017
69. Yi Y-B, Lee J-W, Choi Y-H, Park S-M, Chung C-H (2012) Simple process for production of hydroxymethylfurfural from raw biomasses of girasol and potato tubers. Biomass Bioenergy 39:484–488. https://doi.org/10.1016/j.biombioe.2012.01.011
70. Liu L, Yang X, Hou Q, Zhang S, Ju M (2018) Corn stalk conversion into 5-hydroxymethylfurfural by modified biochar catalysis in a multi-functional solvent. J Clean Prod 187:380–389. https://doi.org/10.1016/j.jclepro.2018.03.234
71. Zhang Z, Zhao ZK (2010) Microwave-assisted conversion of lignocellulosic biomass into furans in ionic liquid. Bioresour Technol 101(3):1111–1114. https://doi.org/10.1016/j.biortech.2009.09.010
72. Martel AL, Montaut S, Ulíbarri G, Spiers GA (2018) Conversion of Symphytum officinale and Panicum virgatum plant extracts to 5-hydroxymethylfurfural catalysed by metal chlorides in ionic liquids. Can J Chem 96(8):815–820. https://doi.org/10.1139/cjc-2017-0663
73. Mathura D, Chakraborty S (2016) Kinetics of microwave-based ionic liquid-mediated catalytic conversion of Ricinus Communis to biofuel products. Chem Eng Trans 52:967–972. https://doi.org/10.3303/CET1652162
74. Wang P, Yu H, Zhan S, Wang S (2011) Catalytic hydrolysis of lignocellulosic biomass into 5-hydroxymethylfurfural in ionic liquid. Bioresour Technol 102(5):4179–4183. https://doi.org/10.1016/j.biortech.2010.12.073
75. Paul SK, Chakraborty S (2018) Microwave-assisted ionic liquid-mediated rapid catalytic conversion of non-edible lignocellulosic Sunn hemp fibres to biofuels. Bioresour Technol 253:85–93. https://doi.org/10.1016/j.biortech.2018.01.010
76. Ramli NAS, Amin NAS (2014) Catalytic conversion of oil palm fronds to levulinic acid in ionic liquid. Appl Mech Mater 625:361–365. https://doi.org/10.4028/www.scientific.net/AMM.625.361
77. Mukherjee A, Portillo-Perez G, Dumont M-J (2019) Synthesis of hydroxymethylfurfural and furfural from hardwood and softwood pulp using ferric sulphate as catalyst. Front Chem Sci Eng 13(3): 531–542. https://doi.org/10.1007/s11705-019-1814-3
78. Tao F, Song H, Chou L (2010) Hydrolysis of cellulose by using catalytic amounts of $FeCl_2$ in ionic liquids. ChemSusChem 3(11): 1298–1303. https://doi.org/10.1002/cssc.201000184
79. Tyagi U, Anand N, Kumar D (2019) Simultaneous pretreatment and hydrolysis of hardwood biomass species catalyzed by combination of modified activated carbon and ionic liquid in biphasic system. Bioresour Technol 289:121675. https://doi.org/10.1016/j.biortech.2019.121675
80. Hu Z, Liu B, Zhang Z, Chen L (2013) Conversion of carbohydrates into 5-hydroxymethylfurfural catalyzed by acidic ionic liquids in dimethyl sulfoxide. Ind Crop Prod 50:264–269. https://doi.org/10.1016/j.indcrop.2013.07.014

81. Walia M, Sharma U, Agnihotri VK, Singh B (2014) Silica-supported boric acid assisted conversion of mono- and poly-saccharides to 5-hydroxymethylfurfural in ionic liquid. RSC Adv 4(28):14414–14418. https://doi.org/10.1039/C4RA01771D
82. Ma Y, Qing S, Wang L, Islam N, Guan S, Gao Z, Mamat X, Li H, Eli W, Wang T (2015) Production of 5-hydroxymethylfurfural from fructose by a thermo-regulated and recyclable Bronsted acidic ionic liquid catalyst. RSC Adv 5(59):47377–47383. https://doi.org/10.1039/C5RA08107F
83. Guo X, Zhu C, Guo F (2016) Direct transformation of fructose and glucose to 5-hydroxymethylfurfural in ionic liquids under mild conditions. BioResources 11(1):13. https://doi.org/10.15376/biores.11.1.2457-2469
84. Ghatta AA, Wilton-Ely JDET, Hallett JP (2019) Rapid, high-yield fructose dehydration to 5-hydroxymethylfurfural in mixtures of water and the noncoordinating ionic liquid [bmim][OTf]. ChemSusChem 12(19):4452–4460. https://doi.org/10.1002/cssc.201901529
85. Eminov S, Wilton-Ely JDET, Hallett JP (2014) Highly selective and near-quantitative conversion of fructose to 5-hydroxymethylfurfural using mildly acidic ionic liquids. ACS Sustain Chem Eng 2(4):978–981. https://doi.org/10.1021/sc400553q
86. Xiao Y, Huang X (2018) The physicochemical properties of a room-temperature liquidus binary ionic liquid mixture of [HNMP][CH_3SO_3]/[Bmim]cl and its application for fructose conversion to 5-hydroxymethylfurfural. RSC Adv 8(34):18784–18791. https://doi.org/10.1039/C8RA03604G
87. Wang Y, Gu Z, Liu W, Yao Y, Wang H, Xia X-F, Li W (2015) Conversion of glucose into 5-hydroxymethylfurfural catalyzed by chromium(iii) Schiff base complexes and acidic ionic liquids immobilized on mesoporous silica. RSC Adv 5(75):60736–60744. https://doi.org/10.1039/C5RA08080K
88. Li H, Yang S (2014) Catalytic transformation of fructose and sucrose to HMF with proline-derived ionic liquids under mild conditions. Int J Chem Eng 2014:1–7. https://doi.org/10.1155/2014/978708
89. Li H, Zhang Q, Liu X, Chang F, Zhang Y, Xue W, Yang S (2013) Immobilizing Cr^{3+} with SO_3H-functionalized solid polymeric ionic liquids as efficient and reusable catalysts for selective transformation of carbohydrates into 5-hydroxymethylfurfural. Bioresour Technol 144:21–27. https://doi.org/10.1016/j.biortech.2013.06.063
90. Fu J, Xu X, Lu X, Lu X (2016) Hydrothermal decomposition of carbohydrates to levulinic acid with catalysis by ionic liquids. Ind Eng Chem Res 55(42):11044–11051. https://doi.org/10.1021/acs.iecr.6b02478
91. Alipour S, Omidvarborna H (2017) Enzymatic and catalytic hybrid method for levulinic acid synthesis from biomass sugars. J Clean Prod 143:490–496. https://doi.org/10.1016/j.jclepro.2016.12.086
92. Chinnappan A, Jadhav AH, Kim H, Chung W-J (2014) Ionic liquid with metal complexes: An efficient catalyst for selective dehydration of fructose to 5-hydroxymethylfurfural. Chem Eng J 237:95–100. https://doi.org/10.1016/j.cej.2013.09.106
93. Chen J, Zhao G, Chen L (2014) Efficient production of 5-hydroxymethylfurfural and alkyl levulinate from biomass carbohydrate using ionic liquid-based polyoxometalate salts. RSC Adv 4(8):4194–4202. https://doi.org/10.1039/C3RA45632C
94. Enomoto K, Hosoya T, Miyafuji H (2018) High-yield production of 5-hydroxymethylfurfural from d-fructose, d-glucose, and cellulose by its in situ removal from the reaction system. Cellulose 4:1–9. https://doi.org/10.1007/s10570-018-1717-3
95. Rathod PV, Mujmule RB, Chung W-J, Jadhav AR, Kim H (2019) Efficient dehydration of glucose, sucrose, and fructose to 5-hydroxymethylfurfural using tri-cationic ionic liquids. Catal Lett 149(3):672–687. https://doi.org/10.1007/s10562-019-02667-0
96. Liu D, Chen EYX (2013) Polymeric ionic liquid (PIL)-supported recyclable catalysts for biomass conversion into HMF. Biomass Bioenergy 48:181–190. https://doi.org/10.1016/j.biombioe.2012.11.020
97. Ma Y, Wang L, Li H, Wang T, Zhang R (2018) Selective dehydration of glucose into 5-hydroxymethylfurfural by ionic liquid-$ZrOCl_2$ in isopropanol. Catalysts 8(10):467. https://doi.org/10.3390/catal8100467
98. Zhang J, Yu X, Zou F, Zhong Y, Du N, Huang X (2015) Room-temperature ionic liquid system converting fructose into 5-hydroxymethylfurfural in high efficiency. ACS Sustain Chem Eng 3(12):3338–3345. https://doi.org/10.1021/acssuschemeng.5b01015
99. Qu Y, Li L, Wei Q, Huang C, Oleskowicz-Popiel P, Xu J (2016) One-pot conversion of disaccharide into 5-hydroxymethylfurfural catalyzed by imidazole ionic liquid. Sci Rep 6:26067. https://doi.org/10.1038/srep26067
100. Zhao Y, Lu K, Xu H, Qu Y, Zhu L, Wang S (2019) Comparative study on the dehydration of biomass-derived disaccharides and polysaccharides to 5-hydroxymethylfurfural. Energy Fuel 33(10):9985–9995. https://doi.org/10.1021/acs.energyfuels.9b02863
101. Liu S, Wang K, Yu H, Li B, Yu S (2019) Catalytic preparation of levulinic acid from cellobiose via Brønsted-Lewis acidic ionic liquids functional catalysts. Sci Rep 9(1):1810. https://doi.org/10.1038/s41598-018-38051-y
102. Zhou L, Liang R, Ma Z, Wu T, Wu Y (2013) Conversion of cellulose to HMF in ionic liquid catalyzed by bifunctional ionic liquids. Bioresour Technol 129:450–455. https://doi.org/10.1016/j.biortech.2012.11.015
103. Li H, Zhang Q, Liu X, Chang F, Hu D, Zhang Y, Xue W, Yang S (2013) $InCl_3$-ionic liquid catalytic system for efficient and selective conversion of cellulose into 5-hydroxymethylfurfural. RSC Adv 3(11):3648–3654. https://doi.org/10.1039/C3RA23387A
104. Shen Y, Sun J-K, Yi Y-X, Wang B, Xu F, Sun R-C (2015) One-pot synthesis of levulinic acid from cellulose in ionic liquids. Bioresour Technol 192:812–816. https://doi.org/10.1016/j.biortech.2015.05.080
105. Li M, Zang H, Feng J, Yan Q, Yu N, Shi X, Cheng B (2015) Efficient conversion of chitosan into 5-hydroxymethylfurfural via hydrothermal synthesis in ionic liquids aqueous solution. Polym Degrad Stab 121:331–339. https://doi.org/10.1016/j.polymdegradstab.2015.09.009
106. Jiang Y, Zang H, Han S, Yan B, Yu S, Cheng B (2016) Direct conversion of chitosan to 5-hydroxymethylfurfural in water using Bronsted-Lewis acidic ionic liquids as catalysts. RSC Adv 6(105):103774–103781. https://doi.org/10.1039/C6RA21289A
107. Liu L, Li Z, Hou W, Shen H (2018) Direct conversion of lignocellulose to levulinic acid catalyzed by ionic liquid. Carbohydr Polym 181:778–784. https://doi.org/10.1016/j.carbpol.2017.11.078
108. Ramli NAS, Amin NAS (2017) Optimization of biomass conversion to levulinic acid in acidic ionic liquid and upgrading of levulinic acid to ethyl levulinate. BioEnergy Res 10(1):50–63. https://doi.org/10.1007/s12155-016-9778-3
109. Semerci I, Guler F (2019) Pretreatment of crop wastes from edible biomass with a protic ionic liquid. Int J Renew Energy Res 9(1):1–7
110. Tiong YW, Yap CL, Gan S, Yap WSP (2019) Optimisation studies on the conversion of oil palm biomass to levulinic acid and ethyl levulinate via indium trichloride-ionic liquids: a response surface methodology approach. Ind Crop Prod 128:221–234. https://doi.org/10.1016/j.indcrop.2018.10.087

111. Khan AS, Man Z, Bustam MA, Nasrullah A, Ullah Z, Sarwono A, Shah FU, Muhammad N (2018) Efficient conversion of lignocellulosic biomass to levulinic acid using acidic ionic liquids. Carbohydr Polym 181:208–214. https://doi.org/10.1016/j.carbpol.2017.10.064

112. Zhou C, Yu X, Ma H, He R, Vittayapadung S (2013) Optimization on the conversion of bamboo shoot shell to levulinic acid with environmentally benign acidic ionic liquid and response surface analysis. Chin J Chem Eng 21(5):544–550. https://doi.org/10.1016/S1004-9541(13)60509-1

113. Roy S, Chakraborty S (2019) Comparative study of the effectiveness of protic and aprotic ionic liquids in microwave-irradiated catalytic conversion of lignocellulosic June grass to biofuel precursors. Bioresour Technol Rep 8:100338. https://doi.org/10.1016/j.biteb.2019.100338

114. Ullah Z, Man Z, Khan AS, Muhammad N, Mahmood H, Ben Ghanem O, Ahmad P, Hassan Shah M-U, Mamoon Ur R, Raheel M (2019) Extraction of valuable chemicals from sustainable rice husk waste using ultrasonic assisted ionic liquids technology. J Clean Prod 220:620–629. https://doi.org/10.1016/j.jclepro.2019.02.041

115. Jiang F, Zhu Q, Ma D, Liu X, Han X (2011) Direct conversion and NMR observation of cellulose to glucose and 5-hydroxymethylfurfural (HMF) catalyzed by the acidic ionic liquids. J Mol Catal A Chem 334(1–2):8–12. https://doi.org/10.1016/j.molcata.2010.10.006

116. Tao F, Song H, Chou L (2011) Dehydration of fructose into 5-hydroxymethylfurfural in acidic ionic liquids. RSC Adv 1(4):672–676. https://doi.org/10.1039/C1RA00088H

117. Kumar K, Parveen F, Patra T, Upadhyayula S (2018) Hydrothermal conversion of glucose to levulinic acid using multifunctional ionic liquids: effects of metal ion co-catalysts on the product yield. New J Chem 42(1):228–236. https://doi.org/10.1039/C7NJ03146G

118. Matsagar BM, Munshi MK, Kelkar AA, Dhepe PL (2015) Conversion of concentrated sugar solutions into 5-hydroxymethyl furfural and furfural using Bronsted acidic ionic liquids. Cat Sci Technol 5(12):5086–5090. https://doi.org/10.1039/C5CY00858A

119. Ren H, Zhou Y, Liu L (2013) Selective conversion of cellulose to levulinic acid via microwave-assisted synthesis in ionic liquids. Bioresour Technol 129:616–619. https://doi.org/10.1016/j.biortech.2012.12.132

120. Alam MI, De S, Khan TS, Haider MA, Saha B (2018) Acid functionalized ionic liquid catalyzed transformation of non-food biomass into platform chemical and fuel additive. Ind Crop Prod 123:629–637. https://doi.org/10.1016/j.indcrop.2018.07.036

121. Tiong YW, Yap CL, Gan S, Yap WSP (2017) One-pot conversion of oil palm empty fruit bunch and mesocarp fiber biomass to levulinic acid and upgrading to ethyl levulinate via indium trichloride-ionic liquids. J Clean Prod 168:1251–1261. https://doi.org/10.1016/j.jclepro.2017.09.050

122. Chinnappan A, Jadhav AH, Chung W-J, Kim H (2015) Conversion of sugars (sucrose and glucose) into 5-hydroxymethylfurfural in pyridinium based dicationic ionic liquid ([C$_{10}$(EPy)$_2$]2Br$^-$) with chromium chloride as a catalyst. Ind Crop Prod 76:12–17. https://doi.org/10.1016/j.indcrop.2015.05.085

123. Liu W, Wang Y, Li W, Yang Y, Wang N, Song Z, Xia X-F, Wang H (2015) Polyethylene glycol-400-functionalized dicationic acidic ionic liquids for highly efficient conversion of fructose into 5-hydroxymethylfurfural. Catal Lett 145(4):1080–1088. https://doi.org/10.1007/s10562-015-1485-8

124. Khan AS, Man Z, Bustam MA, Kait CF, Nasrullah A, Ullah Z, Sarwono A, Ahamd P, Muhammad N (2018) Dicationic ionic liquids as sustainable approach for direct conversion of cellulose to levulinic acid. J Clean Prod 170:591–600. https://doi.org/10.1016/j.jclepro.2017.09.103

125. Marullo S, Rizzo C, D'Anna F (2019) Task-specific organic salts and ionic liquids binary mixtures: a combination to obtain 5-hydroxymethylfurfural from carbohydrates. Front Chem 7(134). https://doi.org/10.3389/fchem.2019.00134

126. Gogoi P, Borah R (2018) Investigation of PEG-6000 bridged -N-SO$_3$H functionalized geminal dicationic ionic liquids for catalytic conversion of fructose to 5-hydroxymethylfurfural. J Chem Sci 130(12):1–11. https://doi.org/10.1007/s12039-018-1570-9

127. Yaman SM, Mohamad S, Manan NSA (2017) How do isomeric ortho, meta and paradicationic ionic liquids impact the production of 5-hydroxymethylfurfural? J Mol Liq 238:574–581. https://doi.org/10.1016/j.molliq.2017.02.076

128. Degirmenci V, Hensen EJM (2014) Development of a heterogeneous catalyst for lignocellulosic biomass conversion: glucose dehydration by metal chlorides in a silica-supported ionic liquid layer. Environ Prog Sustain Energy 33(2):657–662. https://doi.org/10.1002/ep.11830

129. Zhang C, Cheng Z, Fu Z, Liu Y, Yi X, Zheng A, Kirk SR, Yin D (2017) Effective transformation of cellulose to 5-hydroxymethylfurfural catalyzed by fluorine anion-containing ionic liquid modified biochar sulfonic acids in water. Cellulose 24(1):95–106. https://doi.org/10.1007/s10570-016-1118-4

130. Qi X, Watanabe M, Aida TM, Smith JRL (2009) Efficient process for conversion of fructose to 5-hydroxymethylfurfural with ionic liquids. Green Chem 11(9):1327–1331. https://doi.org/10.1039/B905975J

131. Liu H, Wang H, Li Y, Yang W, Song C, Li H, Zhu W, Jiang W (2015) Glucose dehydration to 5-hydroxymethylfurfural in ionic liquid over Cr3+−modified ion exchange resin. RSC Adv 5(12):9290–9297. https://doi.org/10.1039/C4RA09131K

132. Zhou J, Tang Z, Jiang X, Jiang R, Shao J, Han F, Xu Q (2016) Catalytic conversion of glucose into 5-hydroxymethyl-furfural over chromium-exchanged bentonite in ionic liquid-dimethyl sulfoxide mixtures. Waste Biomass Valoriz 7(6):1357–1368. https://doi.org/10.1007/s12649-016-9525-1

133. Zhang Z, Liu B, Zhao Z (2012) Conversion of fructose into 5-HMF catalyzed by GeCl$_4$ in DMSO and [Bmim]cl system at room temperature. Carbohydr Polym 88(3):891–895. https://doi.org/10.1016/j.carbpol.2012.01.032

134. Marullo S, Rizzo C, Meli A, D'Anna F (2019) Ionic liquid binary mixtures, zeolites, and ultrasound irradiation: a combination to promote carbohydrate conversion into 5-hydroxymethylfurfural. ACS Sustain Chem Eng 7(6):5818–5826. https://doi.org/10.1021/acssuschemeng.8b05584

135. D'Anna F, Marullo S, Vitale P, Rizzo C, Lo Meo P, Noto R (2014) Ionic liquid binary mixtures: promising reaction media for carbohydrate conversion into 5-hydroxymethylfurfural. Appl Catal A Gen 482:287–293. https://doi.org/10.1016/j.apcata.2014.05.039

136. Jadhav AH, Chinnappan A, Patil RH, Kostjuk SV, Kim H (2014) Green chemical conversion of fructose into 5-hydroxymethylfurfural (HMF) using unsymmetrical dicationic ionic liquids under mild reaction condition. Chem Eng J 243:92–98. https://doi.org/10.1016/j.cej.2013.12.054

137. Qi X, Guo H, Li L (2011) Efficient conversion of fructose to 5-hydroxymethylfurfural catalyzed by sulfated zirconia in ionic liquids. Ind Eng Chem Res 50(13):7985–7989. https://doi.org/10.1021/ie200488k

138. Tang Z, Su J (2019) One step conversion of glucose into 5-hydroxymethylfurfural (HMF) via a basic catalyst in mixed solvent systems of ionic liquid-dimethyl sulfoxide. J Oleo Sci 68(3):261–271. https://doi.org/10.5650/jos.ess18196

139. Zhou L, He Y, Ma Z, Liang R, Wu T, Wu Y (2015) One-step degradation of cellulose to 5-hydroxymethylfurfural in ionic

liquid under mild conditions. Carbohydr Polym 117:694–700. https://doi.org/10.1016/j.carbpol.2014.10.062
140. Zhang H, Wang Z, Yang H, Yang H (2018) Kinetic study on the decomposition of cellulose into 5-hydroxymethylfurfural in an ionic liquid/organic biphasic system. Nord Pulp Pap Res J 33(3): 375–384. https://doi.org/10.1515/npprj-2018-3053
141. Qu Y-S, Song Y-L, Huang C-P, Zhang J, Chen B-H (2012) Alkaline ionic liquids as catalysts: a novel and green process for the dehydration of carbohydrates to give 5-hydroxymethylfurfural. Ind Eng Chem Res 51(40):13008–13013. https://doi.org/10.1021/ie300140g
142. Hou W, Liu L, Shen H (2018) Selective conversion of chitosan to levulinic acid catalysed by acidic ionic liquid: intriguing NH2 effect in comparison with cellulose. Carbohydr Polym 195:267–274. https://doi.org/10.1016/j.carbpol.2018.04.099
143. Li C, Zhao ZK, Cai H, Wang A, Zhang T (2011) Microwave-promoted conversion of concentrated fructose into 5-hydroxymethylfurfural in ionic liquids in the absence of catalysts. Biomass Bioenergy 35(5):2013–2017. https://doi.org/10.1016/j.biombioe.2011.01.055
144. Qi X, Watanabe M, Aida TM, Smith RL (2010) Fast transformation of glucose and di-/polysaccharides into 5-hydroxymethylfurfural by microwave heating in an ionic liquid/catalyst system. ChemSusChem 3(9):1071–1077. https://doi.org/10.1002/cssc.201000124
145. Shen Y, Zhang Y, Chen Y, Yan Y, Pan J, Liu M, Shi W (2016) Combination of Brønsted and Lewis polymeric catalysts for efficient conversion of cellulose into 5-hydroxymethylfurfural (HMF) in IONIC LIQUIDS. Energy Technol 4(5):600–609. https://doi.org/10.1002/ente.201500415
146. Ramli NAS, Amin NAS (2015) Fe/HY zeolite as an effective catalyst for levulinic acid production from glucose: characterization and catalytic performance. Appl Catal B Environ 163:487–498. https://doi.org/10.1016/j.apcatb.2014.08.031
147. Aid T, Koel M, Lopp M, Vaher M (2018) Metal-catalyzed degradation of cellulose in ionic liquid media. Inorganics 6(3):78. https://doi.org/10.3390/inorganics6030078
148. Hou Q, Li W, Zhen M, Liu L, Chen Y, Yang Q, Huang F, Zhang S, Ju M (2017) An ionic liquid–organic solvent biphasic system for efficient production of 5-hydroxymethylfurfural from carbohydrates at high concentrations. RSC Adv 7(75):47288–47296. https://doi.org/10.1039/C7RA10237B
149. Tao F, Song H, Yang J, Chou L (2011) Catalytic hydrolysis of cellulose into furans in $MnCl_2$–ionic liquid system. Carbohydr Polym 85(2):363–368. https://doi.org/10.1016/j.carbpol.2011.02.040
150. Kruger JS, Nikolakis V, Vlachos DG (2012) Carbohydrate dehydration using porous catalysts. Curr Opin Chem Eng 1(3):312–320. https://doi.org/10.1016/j.coche.2012.06.003
151. Ramli NAS, Amin NAS (2015) Optimization of renewable levulinic acid production from glucose conversion catalyzed by Fe/HY zeolite catalyst in aqueous medium. Energy Convers Manag 95:10–19. https://doi.org/10.1016/j.enconman.2015.02.013
152. Nguyen T-D, Nguyen H-D, Nguyen P-T, Nguyen H-D (2015) Magnetic poly(vinylsulfonic-co-divinylbenzene) catalysts for direct conversion of cellulose into 5-hydroxymethylfurfural using ionic liquids. Mater Trans 56(9):1434–1440. https://doi.org/10.2320/matertrans.MA201539
153. Tyagi U, Anand N, Kumar D (2018) Synergistic effect of modified activated carbon and ionic liquid in the conversion of microcrystalline cellulose to 5-hydroxymethyl furfural. Bioresour Technol 267:326–332. https://doi.org/10.1016/j.biortech.2018.07.035
154. Zhang Y, Pan J, Gan M, Ou H, Yan Y, Shi W, Yu L (2014) Acid–chromic chloride functionalized natural clay-particles for enhanced conversion of one-pot cellulose to 5-hydroxymethylfurfural in ionic liquids. RSC Adv 4(23):11664–11672. https://doi.org/10.1039/C3RA46561F
155. Matsagar Babasaheb M, Van Nguyen C, Hossain MSA, Islam MT, Yamauchi Y, Dhepe PL, Wu KCW (2018) Glucose isomerization catalyzed by bone char and the selective production of 5-hydroxymethylfurfural in aqueous media. Sustain Energy Fuels 2(10):2148–2153. https://doi.org/10.1039/C8SE00339D
156. Shi J, Liu W, Wang N, Yang Y, Wang H (2014) Production of 5-hydroxymethylfurfural from mono- and disaccharides in the presence of ionic liquids. Catal Lett 144(2):252–260. https://doi.org/10.1007/s10562-013-1148-6
157. Ya'aini N, Amin NAS, Asmadi M (2012) Optimization of levulinic acid from lignocellulosic biomass using a new hybrid catalyst. Bioresour Technol 116:58–65. https://doi.org/10.1016/j.biortech.2012.03.097
158. Lu P, Zhao Z-P, Wang X-Y, Lan G-J, Wang X-L (2017) Understanding effect of molecular structure of imidazole-based ionic liquids on catalytic performance for biomass inulin hydrolysis. Mol Catal 435:24–32. https://doi.org/10.1016/j.mcat.2017.03.011
159. Ryu J, Choi J-W, Suh DJ, Ahn DJ, Suh Y-W (2012) Dual catalytic function of 1,3-dialkylimidzolium halide ionic liquid on the dehydration of fructose to 5-hydroxymethylfurfural. Catal Commun 24:11–15. https://doi.org/10.1016/j.catcom.2012.03.005
160. de Melo FC, Bariviera W, Zanchet L, de Souza RF, de Souza MO (2019) $C_{10}MI{\cdot}CF_3SO_3$: a hydrophobic ionic liquid medium for the production of HMF from sugars avoiding the use of organic solvent. Biomass Convers Bioref. https://doi.org/10.1007/s13399-019-00446-w
161. Yuan B, Guan J, Peng J, Zhu G-z, J-h J (2017) Green hydrolysis of corncob cellulose into 5-hydroxymethylfurfural using hydrophobic imidazole ionic liquids with a recyclable, magnetic metalloporphyrin catalyst. Chem Eng J 330:109–119. https://doi.org/10.1016/j.cej.2017.07.058
162. Li J, Jing Y, Liu C, Zhang D (2017) A theoretical elucidation: why does a SO_3H-functionalized imidazolium-based ionic liquid catalyze the conversion of 5-hydroxymethylfurfural to levulinic acid? New J Chem 41(17):8714–8720. https://doi.org/10.1039/C7NJ00878C
163. Li J, Li J, Zhang D, Liu C (2015) Theoretical elucidation of glucose dehydration to 5-hydroxymethylfurfural catalyzed by a So3H-functionalized ionic liquid. J Phys Chem B 119(42): 13398–13406. https://doi.org/10.1021/acs.jpcb.5b07773
164. Li J, Yang Y, Zhang D (2019) DFT study of fructose dehydration to 5-hydroxymethylfurfural catalyzed by imidazolium-based ionic liquid. Chem Phys Lett 723:175–181. https://doi.org/10.1016/j.cplett.2019.03.047
165. Parveen F, Patra T, Upadhyayula S (2018) A structure–activity relationship study using DFT analysis of Bronsted–Lewis acidic ionic liquids and synergistic effect of dual acidity in one-pot conversion of glucose to value-added chemicals. New J Chem 42(2): 1423–1430. https://doi.org/10.1039/C7NJ02364B
166. Qu Y, Huang C, Zhang J, Chen B (2012) Efficient dehydration of fructose to 5-hydroxymethylfurfural catalyzed by a recyclable sulfonated organic heteropolyacid salt. Bioresour Technol 106: 170–172. https://doi.org/10.1016/j.biortech.2011.11.069
167. Zhang J, Xiao Y, Zhong Y, Du N, Huang X (2016) Alcohol effect and the related mechanism on fructose dehydration into 5-hydroxymethylfurfural in the deep eutectic solvent of [Emim]cl/alcohol. ACS Sustain Chem Eng 4(7):3995–4002. https://doi.org/10.1021/acssuschemeng.6b00882
168. Zhang H, Li S, Song X, Li P, Li J (2016) Preparation of 5-(hydroxymethyl)furfural by the catalytic degradation of cellulose in an ionic liquid/organic biphasic system. Bioresources 11(2): 5190–5203. https://doi.org/10.15376/biores.11.2.5190-5203

169. Kuroda K, Miyamura K, Satria H, Takada K, Ninomiya K, Takahashi K (2016) Hydrolysis of cellulose using an acidic and hydrophobic ionic liquid and subsequent separation of glucose aqueous solution from the ionic liquid and 5-(hydroxymethyl)furfural. ACS Sustain Chem Eng 4(6):3352–3356. https://doi.org/10.1021/acssuschemeng.6b00420
170. Liu B, Zhang Z (2016) Catalytic conversion of biomass into chemicals and fuels over magnetic catalysts. ACS Catal 6(1): 326–338. https://doi.org/10.1021/acscatal.5b02094
171. Zhou C, Yu X, Ma H, Huang X, Zhang H, Jin J (2014) Properties and catalytic activity of magnetic and acidic ionic liquids: experimental and molecular simulation. Carbohydr Polym 105:300–307. https://doi.org/10.1016/j.carbpol.2014.01.071
172. Wu C, Yuan W, Huang Y, Xia Y, Yang H, Wang H, Liu X (2017) Conversion of xylose into furfural catalyzed by bifunctional acidic ionic liquid immobilized on the surface of magnetic γ-Al_2O_3. Catal Lett 147(4):953–963. https://doi.org/10.1007/s10562-017-1982-z
173. Amarasekara AS, Gutierrez Reyes CD (2019) Brønsted acidic ionic liquid catalyzed one-pot conversion of cellulose to furanic biocrude and identification of the products using LC-MS. Renew Energy 136:352–357. https://doi.org/10.1016/j.renene.2018.12.108
174. H-b M, X-p C, Liao X-y, Zhou T (2017) Sustainable synthesis of 5-hydroxymethylfurfural from waste cotton stalk catalyzed by solid superacid-SO_4^{2-}/ZrO_2. J Cent South Univ 24(8):1745–1753. https://doi.org/10.1007/s11771-017-3582-x
175. Zhang J, Cao Y, Li H, Ma X (2014) Kinetic studies on chromium-catalyzed conversion of glucose into 5-hydroxymethylfurfural in alkylimidazolium chloride ionic liquid. Chem Eng J 237:55–61. https://doi.org/10.1016/j.cej.2013.10.007
176. Weiqi W, Shubin W (2017) Experimental and kinetic study of glucose conversion to levulinic acid catalyzed by synergy of Lewis and Brønsted acids. Chem Eng J 307:389–398. https://doi.org/10.1016/j.cej.2016.08.099
177. Nguyen CV, Lewis D, Chen W-H, Huang H-W, Alothman ZA, Yamauchi Y, Wu KCW (2016) Combined treatments for producing 5-hydroxymethylfurfural (HMF) from lignocellulosic biomass. Catal Today 278:344–349. https://doi.org/10.1016/j.cattod.2016.03.022
178. Penín L, Peleteiro S, Yañez R, Parajó JC, Santos V (2017) Kinetics of 5-hydroxymethylfurfural production from monosaccharides in media containing an ionic liquid and a solid acid catalyst. BioResources 12(4):8402–8418. https://doi.org/10.15376/biores.12.4.8402-8418
179. Ramli NAS, Amin NAS (2018) Thermo-kinetic assessment of glucose decomposition to 5-hydroxymethyl furfural and levulinic acid over acidic functionalized ionic liquid. Chem Eng J 335:221–230. https://doi.org/10.1016/j.cej.2017.10.112
180. Zhang H, Li S, Xu L, Sun J, Li J (2016) Kinetic study of the decomposition of cellulose to 5-hydroxymethylfurfural in ionic liquid. BioResources 11(2):4268–4280. https://doi.org/10.15376/biores.11.2.4268-4280