Insights into HMF catalysis

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Abstract

In recent decades, the concept of biorefinery has gained considerable momentum as a promising approach to obtain energy commodity chemicals. 5-hydroxymethylfurfural (HMF) is one of the most promising building blocks for biobased chemicals and a strong candidate for large scale production. However, one of the main factors holding its transition is the need for green, sustainable, and financially feasible processes. This review provides a critical assessment of the progresses made towards catalytic and autocatalytic systems used for HMF production, as well as advancements in catalyst research, their mechanisms analyses, efficiency and sustainability. It also provides key information which can facilitate the selection and development of catalysts for HMF production.

Keywords: HMF; carbohydrate dehydration; homogeneous catalyst; heterogeneous catalyst; Lewis acids; Brønsted acids.

1. Introduction

The continuous and rapidly growing demand for energy derived from non-renewable resources has put a strain on the environment and the economy. The production of chemicals from fossil fuels such as crude oil or natural gas is an important contributor to this problem. According to the International Energy Agency (IEA), 13% of the global crude oil demand in 2016 arose from the petrochemical industry and the production of solvents and organic chemicals, and petrochemicals are expected to remain a key driver of the growth in oil demand at least until 2023 [1, 2]. To satisfy this demand, increasingly inaccessible sources of fossil fuels must be exploited (e.g. oil sands), raising the extraction and production costs, as well as contributing to the degradation of the environment. Accordingly, over the past two decades, a great deal of effort has been devoted to finding environmentally friendly ways to substitute gas and crude oil. In their influential 2004 report, the U.S. Department of Energy (DOE) identified 5-hydroxymethylfurfural (HMF) as one of several “building blocks” for bio-based chemicals [3]. A later revision of this report by Bozell and Petersen [4] placed HMF in their “Top 10 +4” revised list of platform chemicals, while highlighting some of the current issues, such as low production volumes and poor performance at the industrial scale. Development of an efficient and sustainable HMF production system would be a major milestone, as it could become a key compound in the emerging biorefinery industries.

The allure of HMF stems from its chemical structure, as it has various functionalities that arise from the presence of a furan ring coupled with the hydroxyl and aldehyde groups present at the exocyclic carbon atoms [5]. The alcohol group can undergo esterification, dehydration, oxidation and halogenation reactions while the aldehyde group can undergo reactions like reduction, decarbonylation and reductive amination. Further, the ring structure lends itself to reactions such as halogenation, nitration, sulphonation, Friedel-Crafts alkylation or acylation, and Diels-Alder cycloaddition [5]. This means that a variety of chemicals such as 5-hydroxymethyl-furoic acid, 2,5-dicarboxylic acid, 2,5-bis-hydroxymethylfuran, 2,5-furandicarboxylic acid, 2,5-furandicarboxyaldehyde, furfuryl alcohol, formic acid, and a range of pyridine, pyrrole, cyclopentenone and thiophene derivatives can be prepared using HMF as an intermediate [5, 6]. Some of these chemicals can, for instance, replace petroleum-derived compounds like adipic acid, alkyldiols or hexamethylenediamine in polymer production, while others find potential applications in markets ranging from solvents and biofuels to pharmaceuticals and textile [7-9].

Despite the above-mentioned potential, presently the production of HMF at an industrial scale is marginal [10, 11], with most of it being sold as specialty chemicals for laboratory and research purposes. This is because, while HMF can be produced from renewable sources with a high atom economy, its current production is not inherently sustainable. In order to adhere to the generally-held principles of green chemistry [12, 13] , the process should also be energy efficient, produce little to no waste, use safe solvents and auxiliaries, and catalysts which are as selective as possible.

There are several outstanding reviews on HMF covering its production, applications, and chemistry [8, 9, 14-22], but there is still a need for a thorough documentation of the different catalysts used until now. This review aims to fill in this gap by not only detailing the work done so far on catalytic and autocatalytic processes, but also revealing the most relevant insights obtained from these works. An emphasis is given to the mechanistic differences between Brønsted and Lewis acids in both homogeneous and heterogeneous systems, with several influential parameters being covered, such as acidity, steric effects, and cation-anion interplay to name a few. This work can thus potentially help in the selection and design of more efficient, selective, and sustainable catalysts, as a precursor to developing processes that are economically viable while satisfying green chemistry principles.

2. Autocatalytic systems

A reaction system in which one of the produced species functions as a catalyst is considered an autocatalytic system [23-26]. For example, the dehydration of hexoses can be catalyzed by organic acids, such as levulinic acid (LA) and formic acid (FA) [27-29], formed over the course of the reaction. Many other solvents have displayed catalytic activity for carbohydrate dehydration, and function as both solvent and catalyst. These reaction promoters work via different mechanisms, such as favoring a particular tautomer, having an increased solubility or by forming complexes with the solute [30, 31]. This section looks at reaction systems where HMF is formed without the initial addition of a catalyst [29].

2.1. Reactions in sub- and supercritical water

Water is the most readily available solvent, and it provides good sugar solubility at high concentrations, and therefore would be a clear choice to carry out the synthesis of HMF from sugar feedstocks. However, HMF is an intermediate product of the dehydration of hexoses to LA and FA, and in the presence of water, the reaction tends to be non-selective [32, 33]. Furthermore, even though water is a non-toxic solvent, it is not necessarily the most sustainable for chemical processes. Energy consumption considerations, waste water treatment and recyclability can sway the sustainability balance to other solvents, e.g. acetone, which can be more easily recovered and thus reduce considerably energy costs [34] or dimethyl sulfoxide (DMSO), that can more readily convert fructose to HMF [35]. Nevertheless, considerable insight has been gained from sugar dehydration in aqueous media, along with some promising high-yielding HMF processes. These advancements are thoroughly analyzed in the sections below.

2.1.1. Subcritical water

Sugar dehydration to produce 5-HMF has long been studied, with early results dating back to 1947 showing that the process tends to be autocatalytic in an aqueous environment [29, 32, 36]. It was observed that as the reaction progressed, the acidity of the system increased due to the formation of organic acids such as LA and FA. These organic acids seemed to work as catalysts for the dehydration reaction. However, when carefully analyzing their catalytic nature, it was shown that of the two, it was FA that played a more important role. This can be attributed to their different acidities (LA pKa 4.59; FA pKa 3.74), which suggests that FA is a key byproduct in the autocatalytic reaction [37]. This was backed up by a later study using inulin as feedstock [38].

Compared to catalytic processes, non-catalytic dehydration of sucrose and fructose in subcritical water has been proven to be slower and less selective towards HMF [39]. A thorough examination of the dehydration of fructose in subcritical water was performed by Asghari and Yoshida [40], where a fructose solution was subjected to temperatures ranging between 200-320 °C. A constant increase in HMF yield could be observed at temperatures up to 257 °C, after which the concentration started to decrease and the formation of organic acids, such as LA, FA, lactic acid, and acetic acid increased.

Previous experiments have shown that there is a correlation between the dehydration reaction rate and the temperature in hot compressed water, hinting at an optimal temperature range for autocatalytic processes [27, 41-43]. This was further expanded upon by Li et al. [44], who analyzed the fructose dehydration process at temperatures ranging from 180 to 220 °C and reaction times ranging from 10 to 80 minutes. The HMF yield did increase with longer reaction times, but seemed to decrease when the reaction temperature was set above 180 °C, due to the formation of acidic by-products. On the other hand, maximum fructose conversion was attained with higher temperatures and lower residence times.

Ranoux et al. [37] produced HMF using a more specific range of subcritical temperatures and reaction times, while also using solutions with a high sugar concentration (30 wt%). Their results were promising, obtaining up to 70% conversion rate and 61% selectivity using fructose, after 40 minutes at 190°C. However, they were not able to obtain similar results from glucose or sucrose solutions, since glucose does not isomerize appreciably to fructose in non-catalytic systems.

HMF production from raw biomass poses an additional challenge. In addition to dehydrating sugars, it is necessary to first obtain them from biomass by hydrolysis. This can be achieved by both sub- and supercritical conditions. For instance, Sasaki et al. [45, 46] used different temperature and pressure conditions to convert cellulose to HMF. Their results showed that under subcritical conditions, cellulose hydrolyzed slowly, while glucose underwent rapid conversion. The yields of HMF from cellulose were considerably lower than those obtained from glucose or fructose. Ehara and Saka showed that decreasing the temperature can lead to a higher glucose dehydration rate, producing more HMF from cellulose and yielding fewer hydrolysis products. An experiment performed using different combinations of sub- and supercritical conditions showed that hydrolysis is highly favored at supercritical values [47]. Experiments using starch showed a similar trend to cellulose, but an increase in reaction time led to higher HMF yields due to an increase in starch depolymerization [48]. The addition of NaCl enhances the generation of acidic products from cellulose and also increases cellulose surface acidity by pushing the generated protons to its surface. Moreover, the Cl^- ions assist cellulose depolymerization by disrupting its intermolecular bonding, with the combined effect being that cellulose can be autocatalytically hydrolyzed and converted to products like HMF [49].

More examples of autocatalytic dehydration can be found as control experiments for other catalysts using different starting materials [50-53]. From these experiments, it was observed that similar conversion of sugars can be achieved with and without catalyst. Nevertheless, catalysts help reduce unwanted side reactions, thereby increasing HMF yields, and enable operation at lower reaction temperatures and shortened processing times.

Temperature plays an important role in the dehydration reaction. In some early papers, it has been shown that the production of HMF from fructose was a first order reaction from fructose itself [54, 55]. In the past years, it has been established that an increase in temperature may inversely affect the reaction order. A change in temperature within the range of 175-400 °C can lower the order from 1 to 0.7. This change also determines the reaction pathway, such as dehydration, retro-aldol condensation, or condensation to form humins [37, 56, 57].

While the temperature at which the reactions are performed have a dramatic effect on the way they develop, initial sugar concentration also plays a role. Previous experiments have shown the effect of initial fructose concentration on HMF yield, showing that lower concentrations favored HMF formation reactions [58]. Nevertheless, when analyzing this effect, Yu and Wu [59] observed that glucose concentration values lower than 10 mg L^{-1} shifted the glucose decomposition pathway to retro-aldol condensation products due to the defining role $[OH^-]$ plays at these values. Higher initial glucose concentrations therefore favor dehydration and HMF production. It was also observed that the reaction rate constant is inversely proportional to the initial concentration. It is important to note the very low concentrations ($5.6x10^{-8}$ M - 0.0056 M) this experiment used when compared to most HMF production processes shown in Scheme 1.

It is clear from this section that, while initial feedstock concentration does play an important role in the reaction mechanism, temperature and reaction time have more pronounced effects on the conversion of sugars and on HMF yields. Figure 1 compares HMF yields from fructose dehydration *vs* reaction times at different temperature ranges. It can be clearly seen that lower temperatures require longer reaction times and vice versa. On the other hand, too high temperatures lead to low HMF yields, but reduce the reaction times considerably. An optimal point seems to be located in the temperature range of 170-220 °C and reaction times from 10 to 60 minutes.

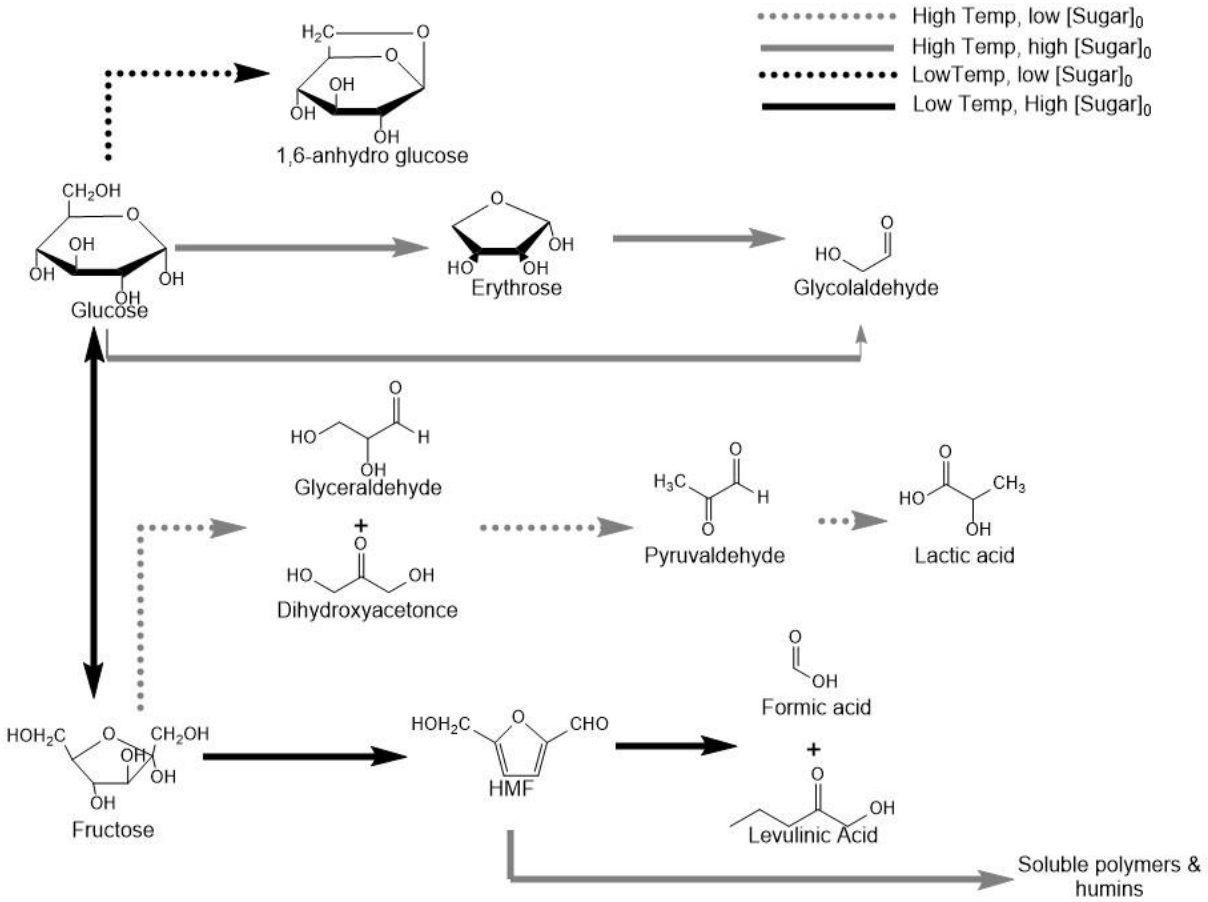
2.1.2. Supercritical Water

Supercritical fluids are compounds that are at or above their critical temperature and pressure. At this point, their properties are neither those of gas or liquid. Their density is higher than gases, but their viscosity is lower than at liquid phase. Additionally, they display a higher solubility than they otherwise would, and through the adjustment of the system’s pressure, they can be tuned to fit the desired process [60-62]. In this context, supercritical fluids, particularly supercritical water, offer a broad range of possibilities as green and inexpensive solvents.

Under supercritical conditions, cellulose undergoes hydrolysis to glucose. If the reaction time is prolonged, glucose will decompose to erythrose and glycolaldehyde, which demonstrates that continuing the reaction under these conditions leads to the formation of fragmentation products [41, 45, 47, 63]. Nevertheless, at higher pressures and lower temperatures, it is possible to obtain dehydration products. At lower temperatures the glucose decomposition rate is faster than the hydrolysis rate, which can be explained by the increased rate in glucose to fructose isomerization; at values over the critical point, the hydrolyzation rate is almost one order of magnitude higher [45, 64]. However, HMF yields are well below subcritical yield values. This was originally linked to higher water density [65], but later studies by Cantero et al. [66-68] showed that this effect was due to the change in $[H^+]$ and $[OH^-]$ ion concentrations in supercritical water, which are altered by several orders of magnitude depending on the medium's pressure.

Based on the results of Sinağ et al. [69] on the hydrolysis of glucose in supercritical water, Watanabe et al. [70] suggested that the heating rate influenced the yield of HMF, since some products formed during the heating process can determine the rate of later reactions. To test this, a glucose solution was examined at different temperatures (200-500 °C) and different temperature ramps. The fastest heating rate (12.5 °C/s) seemed to have favored the production of dehydration products.

Following this logic, microwave assisted organic synthesis would offer a way to accelerate the reactions rate. Microwave heating (MH) has been shown to result in better conversion rates and HMF yields for both fructose and glucose but shows no change in the distribution of the dehydration products [71, 72]. Sweygers et al. [73] performed a more thorough analysis of the effect of microwaves in the synthesis of HMF from cellulose. Their results showed that microwave radiation can increase the conversion of cellulose to glucose by a factor of 2.3 and glucose-fructose isomerization by 2.5. Additionally, MH can considerably reduce reaction times by shortening the heating period, which is advantageous when considering industrial-scale production systems where the production capacity can offset low yields.



Scheme 1: Glucose & fructose dehydration under hot compressed water and at different initial sugar concentration ([Sugar]$_0$).

A more detailed comparison between sub- and supercritical dehydration of different substrates is shown in Table 1. From Table 1, it can be noted that simple sugars conversion, e.g. fructose is possible in these systems. However, HMF synthesis from complex carbohydrates, such as cellulose, yields very little HMF. Unless otherwise stated, all conversion and HMF yields in this review are in mole %.

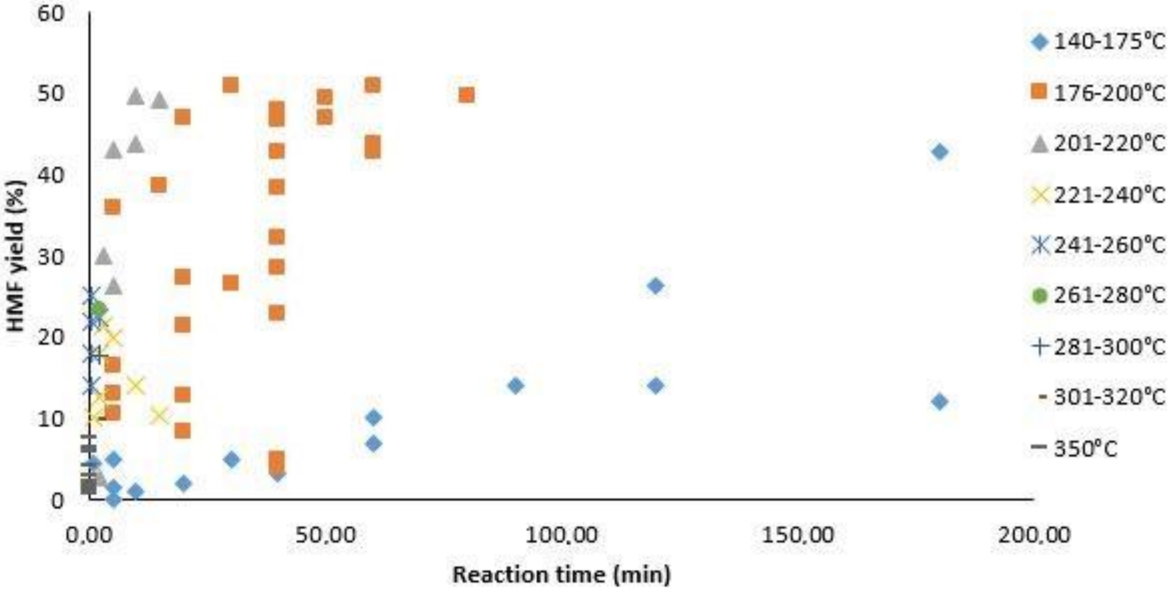


Figure 1: HMF yields from glucose at different reaction times and temperatures. Values collected from Table 1.

Table 1. HMF yields in sub- and supercritical water in literature

Material	Concentration	Temperature (°C)	MH (MW)	Pressure (MPa)	Reaction time	Conversion (%)	HMF Yield (%)	Reference
Cellulose	4 wt%	280		40	4 min	-	11.9	[47]
	10 wt%	350		25	8.8 sec	99.3	10.9	[46]
	4 wt%	280-400^{a}		40	45.1 sec	-	7.3	[47]
Fructose	0.3 M	140		1	1 hour	-	4.4	[50]
	30 wt%	170		6.9	3 hours	84.0	42.8	[37]
	0.25 M	175		5.06	2 hours	97.0	14.0	[29]
	27 wt%	190	300	-	5 min	57.3	35.8	[72]
	10.8 wt%	190		10	1 hour	90.7	50.9	[44]
	2 wt%	200	*	1.2	5 min	28.2	13.2	[71]
	30 wt%	200		14.53	1 hour	97.0	42.7	[37]
	0.1 M	250		24.5	32 sec	-	25.0	[39]
	0.05 M	250		3.9	2 min	75.8	22.4	[40]
	0.05 M	270		5.4	2 min	97.3	23.3	[40]
	0.05 M	350		100	0.6 sec	67.0	7.7	[42]
Galactose	0.3 M	140		1	1 hour	-	0.0	[50]
Glucose	0.3 M	140		1	1 hour	-	0.0	[50]
	9 wt%	200		2.5	5 min	22.0	3.5	[51]
	9 wt%	200		2.5	10 min	30.0	6.0	[51]
	1 M	350		40	1.02 sec	50.8	3.3	[65]
	9 wt%	350		2.5	1 min	98.8	16.2	[70]
Mannose	0.3 M	140		1	1 hour	-	0.0	[50]
Sorbose	1 M	150-153		-	2 hours	-	27.1	[36]
Starch	10 wt%	220		1	20 min	-	22.0	[48]
Sucrose	1 M	162-167		-	2 hours	-	21.6	[36]

a) Combined sub-/supercritical water. 45 seconds at 280 °C and 0.1 seconds at 400 °C

* Reaction was done using MH, but power (MW) was not reported

2.2. Solvents as reaction promoters

Carrying out the dehydration of sugars to HMF in an aqueous environment (catalytic or non-catalytic) leads to a non-selective process and to the rehydration of HMF to LA and FA. This reduces the total HMF yield considerably [32, 74]. For this reason, the search for an appropriate solvent that not only inhibits the formation of byproducts, but also allows the easy extraction of

HMF, has been of interest in the past years. Many options have been analyzed, but some of them have been especially attractive since they promote the reaction and they are highly selective. This section will cover the most prominent ones, such as ionic liquids (ILs), dimethyl sulfoxide (DMSO), and some deep eutectic solvents (DES).

2.2.1. Ionic liquids

ILs are a very diverse group of salts which are liquid at low temperatures. Originally it was considered that all ILs exhibited similar properties. However, per MacFarlane [75], the only properties they share are that they are liquid at or below a temperature of 100 °C, and that they contain ions. Nevertheless, generalities can be observed. As Clare et al. [76] pointed out, ILs' cations tend to be organic structures and usually contain nitrogen or phosphorous. Based on this, ILs can be classified into the following groups: 1) five-membered heterocyclic cations 2) six-membered and benzo-fused heterocyclic cations 3) ammonium, phosphonium and sulphonium based cations 4) functionalized imidazolium cations and 5) chiral cations. Sheldon [77] described ILs simply as "a fluid that is fluid at (or close to) ambient temperature, is colorless, has a low viscosity and is easily handled, i.e. a material with attractive properties for a solvent".

ILs have been considered as "green" solvents, due to their low vapor pressure, flammability, and toxicity, with several important reviews pointing to their advantages [78-80]. However, not all ILs share these properties. Additionally, other factors such as biodegradability and carbon footprint have been studied further, raising further questions about their environmentally friendly status [81-84]. Still, their use in a wide range of chemical reactions, both as solvent and catalyst, cannot be disputed [78, 85]. Cellulose and other carbohydrates can dissolve in high concentration in ILs [86-88].

The first mention of a molten salt being used in the conversion of carbohydrates to HMF dates from 1983, when Fayet and Gelas [89] used immonium salts (pyridinium chloride) to dehydrate fructose. Their experiments yielded 70% HMF after 30 minutes at 120 °C. Following this, Lansalot-Matras and Moreau [90] used a mixture of DMSO/1-butyl 3-methyl imidazolium tetrafluoroborate ($[BMIM^+][BF_4^-]$) and 1-butyl 3-methyl imidazolium hexafluorophosphate ($[BMIM^+][PF_6^-]$). In the blank experiment (only DMSO used), HMF was found only in traces, which contradicted other reports on fructose dehydration in DMSO [91, 92]. The lower temperature (80 ^oC) used in these runs may help explain this discrepancy. The use of $[BMIM^+][BF_4^-]$ enhanced the results to 36% yield HMF after 32 hours. It should be mentioned that fructose is not soluble in $[BMIM^+][PF_6^-]$. The use of 1-H-3-methyl imidazolium chloride $[HMIM^+][Cl^-]$ gave significantly better results. After 45 minutes at 90 °C, a 92% yield of HMF was obtained [93]. It was proposed that $[HMIM^+][Cl^-]$ lowered the activation energy barrier and led to the formation of an intermediate IL/sugar complex. Similar experiments using glucose yielded no HMF.

Zhao, et al. [94] used three ILs in the form of $[C_xMIM^+][Cl^-]$, where C_x is the alkyl group and the x denotes the chain length, in this case, octyl, butyl and ethyl. It was found that $[EMIM^+][Cl^-]$

was better suited as solvent. They tested the fructose conversion to HMF and obtained an average HMF yield of 73% at 120 °C and 3 hours using a 1:10 fructose/[EMIM$^+$][Cl$^-$] ratio and a 6 mol% loading of a metal halide catalyst. Once again, glucose showed lower reactivity in the IL, resulting in almost nonexistent conversion and HMF yield.

Li et al. [95] used [BMIM$^+$][Cl$^-$] with fructose as the substrate. At 80 ^{o}C and for a reaction time of 900 minutes, they obtained a 65% yield from the uncatalyzed dehydration. Using HCl catalyst increased the yield to 95% after only 8 minutes. Another very interesting finding of their research was that the ^{1}H NMR results confirmed that no byproduct was formed. This showed that the reaction was highly selective under these conditions. Moreover, no discernible carbonyl signal was detected. This was interpreted as the absence of acyclic forms of fructose present and thus, this supported the cyclic fructofuranosyl reaction pathway.

From the literature, it seems that [C$_x$MIM$^+$] ILs perform very differently. A more detailed study showed that the alkyl group had an effect on the ILs catalytic performance [96]. The authors tested different ILs, such as [BMIM$^+$][Cl$^-$], 1-hexyl-3-methyl imidazolium chloride ([HeMIM$^+$][Cl$^-$]), 1-benzil-3-methyl imidazolium chloride ([BeMIM$^+$][Cl$^-$]), 1-butyl-2,3-dimethyl imidazolium chloride ([BdMIM$^+$][Cl$^-$]), 1-octyl-3-methyl imidazolium chloride ([OMIM$^+$][Cl$^-$]), and 1-butyl-3-methyl imidazolium p-toluenesulfonate ([BMIM$^+$][PS$^-$]). It was found that only [BeMIM$^+$][Cl$^-$] and [BMIM$^+$][Cl$^-$] yielded a significant amount of HMF from fructose with yields of 17.7 and 63.1% respectively. Furthermore, it was suggested that the length of the alkyl chain was directly linked to the catalytic activity since longer chains resulted in lower Hammett acidities [97-99]. However, a more recent study from Ryu et al. [100] could not confirm this effect. It can be concluded from these results and the results from Binder and Raines, and Ståhlberg et al. [101, 102], that [Cl$^-$] anions, or any anions that can act as nucleophile, are well suited to promote the dehydration reaction of fructose.

Using a variety of [C$_4$MIM$^+$] and [C$_4$Py$^+$] ILs with different anions such as [Cl$^-$], [BF$_4^-$] and [PF$_6^-$], Li et al. [103] found that [BMIM$^+$][Cl$^-$] was most effective for the MH dehydration of fructose. From a 1:10 fructose/IL mixture, they obtained an HMF yield of 98% after 6 minutes at a reaction temperature of 80 °C. Increasing the radiation power resulted in similar yields in shorter reaction times. Raising the power beyond a certain point was detrimental to the process, as it promoted the formation of humins and lowered the HMF yield. When the authors compared MH to an oil bath heating system, MH drastically reduced the reaction time bringing higher or just as high yields. Given the dielectric properties of [BMIM$^+$][Cl$^-$], MH allowed to achieve rapid and homogeneous heating, which in turn prevented irregular overheating. The authors suggested that the MH effect of lowering the activation energy resulted in higher yields than with conventional heating. Similar [BMIM$^+$][Cl$^-$] experiments, but at lower reaction temperatures, showed lower or no HMF yield. A considerable increase in activity was observed at 120 °C [96, 104, 105].

ILs other than in the form of [C$_x$MIM$^+$] have also been studied for HMF production. Tong et al. [99] obtained good yields from fructose, glucose and sucrose using N,N-methylmorpholinium methylsulfonate ($[NMM^+][CH_3SO_3^-]$), 1-methyl imidazolium hydrogen sulfate ($[MIM^+][HSO_4^-]$), N-methyl 2-pyrrolidonium hydrogen sulfate ($[NMP^+][HSO_4^-]$), and N-methyl 2-pyrrolidonium methylsulfonate ($[NMP^+][CH_3SO_3^-]$) as catalysts in different solvents. Again, yields were higher for fructose than for the other sugars. Although the recovery of HMF and the recycling of ILs was possible, it proved to be highly energy demanding. Using 1-(4 sulfonic acid) butyl 3-methylimidazolium hydrogen sulfate ($[MIMC_4SO_3^+][HSO_4^-]$) to dehydrate fructose, Tao et al. [106] obtained moderate conversion rates and HMF yields. The addition of water to the system led to almost quantitative conversion and yields. The IL could be recycled via extraction with little loss in catalytic efficiency.

Although fructose can be dehydrated *via* halide-containing ILs, glucose remains seemingly inert, requiring the use of a catalyst to trigger the conversion [85, 93, 102, 107]. Nevertheless, dicationic ILs have proved to have aldose-dehydrating properties. Using di-, tri- and tetraethylene glycol-bis (3-methylimidazolium) dimesylate ($[DiEG(MIM)_2^+][Oms^-]_2$), $[TriEG(MIM)_2^+][Oms^-]_2$, and $[TetraEG(MIM)_2^+][Oms^-]_2$ respectively, Jahvad et al. [108] observed the dehydration of fructose and sucrose. They achieved yields up to 92% from fructose, using $[TetraEG(MIM)_2^+][Oms^-]_2$ at 120 °C. The process appeared to be extremely sensitive to the reaction temperature used, with a temperature of 100 °C resulting in a 54% yield only. The yield of HMF from sucrose at optimal conditions was 67%. Since sucrose is a glucose-fructose disaccharide, yield values above 50% indicated that glucose was also being dehydrated. Glucose dehydration gave a yield of 72%, which, until recently, was one of the best yields from glucose in ILs without the use of an additional catalyst. Using IL $[HMIM^+][HSO_4^-]$, Enoto et al. were able to obtain 77.3 % and 76.1% from fructose and glucose respectively. For this, the researcher devised a continuous steam distillation extraction system, where water would carry HMF out from the system and be immediately quenched in liquid N_2[109]. This process showcases the importance of HMF removal before further degradation. Qu et al. also examined the dehydration of sucrose with a range of different ILs and co-solvents, obtaining at 160 ^oC a highest HMF yield of 68.7% in a 1-hydroxyethyl-3-methylimidazolium tetrafluoroborate ($[AEMIM]BF_4$)/DMSO system, although the reaction time required was fairly long (480 minutes). A shorter reaction time (180 minutes) in the same system, however, also gave a respectable yield of 62.2 % [110].

Biomass hydrolysis has also been carried out in ionic liquids [86, 101]. $[C_xMIM^+][Cl^-]$ ILs can dissolve cellulose fairly well, up to 25 wt%. Several attempts have been made to obtain sugars and HMF from cellulose and starch in ILs, but they have always required a catalyst to obtain a significant amount of HMF [101, 111-113]. However, there are interesting articles dealing with the hydrolysis of inulin and cellulose, and the dehydration of fructose and glucose to yield HMF [87, 114, 115]. Inulin was hydrolyzed using Brønsted acidic ILs $[EMIM^+][HSO_4^-]$, $[BMIM^+][HSO_4^-]$ and $[HMIM^+][HSO_4^-]$ as catalyst in a $[BMIM^+][Cl^-]$ solution [114]. The use of an IL mixture successfully converted inulin into fructose and subsequently to HMF. Using only acidic ILs as both solvent and catalyst resulted in similar HMF yields, but $[EMIM^+][HSO_4^-]$ and $[BMIM^+][HSO_4^-]$ hydrolyzed inulin faster than the resulting fructose was dehydrated, producing high fructose concentrations. In a two-step process involving catalyst resin Amberlyst 15, the researchers obtained HMF yields of up to 80% at 80 ^{o}C and for a total reaction time of 65 minutes. Hsu et al. [116] performed a thorough experiment to find the optimal processing conditions using [$EMIM^+$][Cl^-], [$BMIM^+$][Cl^-] and 1-ethyl pyridinium chloride [$Epyr^+$][Cl^-]. The researchers observed that an optimal water/IL ratio was crucial for cellulose hydrolysis, since increasing the amount of water produced more sugars but inhibited HMF production. The authors found that the dissolution time played a critical part when using [$BMIM^+$][Cl^-], but not so much with other ILs. At optimal conditions (120 ^{o}C, 30 minutes of dissolution followed by 3 hours of reaction), [$EMIM^+$][Cl^-] delivered the best HMF yield (21%). [$Epyr^+$][Cl^-] brought only a 3% HMF yield, but converted cellulose to monosaccharides at a 32% yield. Jiang et al. [117] studied the capability of ILs to catalyze the reaction from cellulose, which involves breaking the β-1,4-glycosidic bonds. This yields mostly glucose and HMF. They also related the catalytic activity to the ILs' Brønsted acid strength. Their observations were in accordance with those of Swatloski et al. [87, 118], who described that the hydrolysis took place through the interactions between the hydroxyl group of cellulose and the [Cl^-] of the IL, and that the β-1,4-glycosidic oligomers presented a conformational behavior similar to the ones exhibited in water. Parveen et al. [119] studied the effect of three differently functionalized ILs as catalyst in a [$BMIM^+$][Cl^-]. The ILs were functionalized with sulfonic acid ([SO_3]), carboxylic acid ([COOH]), and hydroxyl ([OH]) groups. The ILs showed a Hammett acidity in the order of IL-SO_3>IL-COOH>IL-OH. IL-SO_3 had the highest hydrolysis yield, with 85% of sugars after 90 minutes at 100 °C.

Using a dicationic type of IL, Khan et al. [120] reported high yields of LA from cellulose, without the addition of any other catalyst. 1,1-bis(3-methylimidaziolium-1-y) butane [$C_4(MIM)_2$] was used as cation and [HSO_4^-], [$CH_3SO_3^-$], and [$CF_3SO_3^-$] were the selected anion. [$C_4(MIM)_2$] [($2HSO_4^-$)([$H_2SO_4^-$)$_2$] exhibited the highest Hammett acidity, and the highest LA yield (50%). The authors suggested that LA is formed through a glucose to fructose isomerization step, followed by dehydration to HMF, and later rehydration. However, no HMF values were reported.

More recently, Mingchuan et al. [121] also observed an increased HMF yield with higher acidity, when dehydrating chitosan in water and using catalytic amounts of benzimidazolium chloride [$Hbim^+$[Cl^-], obtaining 14.7% HMF yield at 180 °C after 3 hours. Under the same conditions, dehydration of chitosan in an aqueous HCl solution with a similar pH as [$Hbim^+$[Cl^-] resulted in only 9.9% HMF yield. When switching to a 10% DMSO-water mixture, the researcher obtained 35% HMF yield from chitosan.

Although there is a consensus on the correlation between the acidity and the catalytic efficiency of ILs, as well as in how the halide ions facilitate both the breakdown of cellulose and the dehydration of fructose, conflicting results from similar experimental conditions (Table 2) require further examination. The effect of water content on the effectiveness of ionic liquids also deserves further study [122]. Additionally, given the questionable sustainability of ionic liquids [81-84], a deeper analysis should be made on the environmental impact of using such solvents for HMF production. Ilgen et al. [123] made a thorough comparison on the toxicity and environmental impact of different solvents used in HMF production (Figure 2). Here it can be seen that water is considerably more benign for both humans and the environment than the rest of solvents, particularly ionic liquids.

2.2.2. Deep eutectic solvents

DESs have often been called ionic liquids in the literature. Even though they do share similarities, such as having low vapor pressure, they are not part of this group. DESs are a mixture of Lewis acids, Brønsted acids, and bases forming a eutectic system which is liquid at low temperatures. They are different from ILs since ILs are mostly formed from one cation and one anion in a single species, and DES can contain different species [124], i.e. quaternary salts with metal halides (type 1); quaternary salts and metal halides hydrates (type 2); or quaternary salt and a hydrogen-bond donor (type 3) [125].

Due to their association with ILs, and the fact that they also have low vapor pressure and flammability, DESs have inherited ILs’ status as “green” solvents. But as with ILs, this can be questioned. Since DESs are a combination of salts, some of them containing heavy metal salts, their toxicity is intrinsically tied to their composition. All metal-containing eutectic mixtures, viz. types 1 and 2 will inherit their metal salt’s toxicity. On the other hand, type 3 can include a variety of low-toxicity mixtures, e.g. urea, glycerol, and ethylene glycol.

Recent studies have shown that cellulose and starch are soluble in choline chloride (ChoCl) DESs, and that cellulose can be de-crystallized in this solvent [126, 127], making it interesting for HMF production. Even more interesting is the fact that carbohydrates can themselves form DESs at low temperatures, allowing for highly sugar-concentrated systems [123, 128, 129].

In order to find a clean and renewable solvent/catalyst system for fructose dehydration, Hu et al. [30] worked with different ILs and ChoCl-based DESs. Under similar experimental conditions, the use of ChoCl/metal chloride salts mixture was very inefficient in producing HMF, contrary to the effect previously reported with ILs [94]. Similarly, ChoCl/urea proved to be ineffective. Surprisingly, DESs prepared with organic renewable materials were very effective in transforming fructose to HMF. Particularly promising was the use of ChoCl/carboxylic acids, especially ChoCl/citric acid, both in the anhydrous and monohydrate forms, where HMF yields of over 70% were obtained at only 80 ^{o}C and for 1 hour of reaction. Malonic and oxalic acids also resulted in HMF yields over 40% and 60% respectively. While the anhydrous form of citric acid performed slightly better, it was noted that it increased the viscosity of the system and that its use was not energy efficient. To improve the results, the researchers used a biphasic system consisting of ethyl acetate (AcOEt) and ChoCl/citric acid, which increased the HMF yields to up to 86%. However, only 65% of HMF could be recovered from the system [30].

Hu et al. also studied the hydrolysis and later the dehydration of inulin in ChoCl/citric acid and ChoCl/oxalic acid. Inulin can be readily dissolved in both mixtures. In ChoCl/oxalic acid, fructose was very unstable and converted almost immediately to HMF, while with citric acid, a large fructose spike was detected, which was in turn transformed in HMF. It was also observed that higher temperatures were beneficial for HMF production, and lower temperatures promoted the conversion to fructose, especially with citric acid. Based on these results, a two-step method was developed, keeping the reaction at 50 °C to obtain fructose. Thereafter the mixture was heated to 80 °C to produce HMF [30]. This process improved HMF yields in citric acid, from 51 to 57%. The same process was not tested with oxalic acid [115]. Their results are summarized in Table 3.

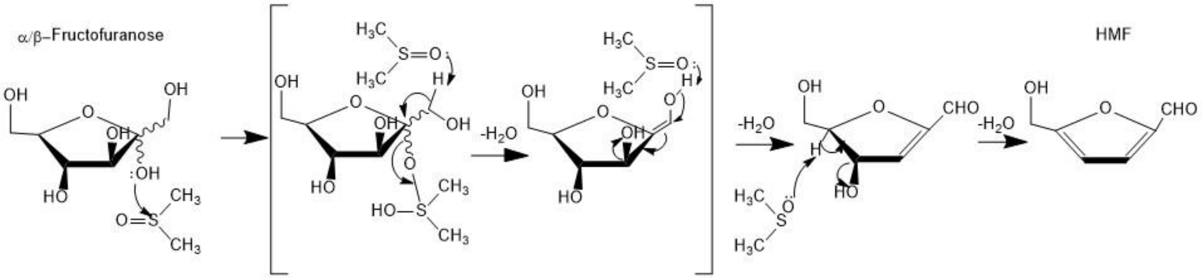
One of the main problems to overcome for scaling up HMF production is the use of low concentration solutions at the lab scale. A possible solution to this problem is presented in the form of carbohydrate DESs. Ilgen et al. [123] reported forming different DESs from d-fructose and N’-N’-dimethyl urea (DMU), N’-N’- tetramethyl urea (TMU), and choline chloride. Both DMU and TMU were deemed unsuitable for HMF synthesis as the former produced fructose-urea condensation products, while the acute toxicity of the latter as well as the energy-demanding separation process ruled it out. ChoCl/carbohydrate mixtures showed low melting points between 78-82 °C, as well as allowing a high ChoCl:sugar ratio (6:4). Liu et al. [130] were able to obtain HMF from a ChoCl/fructose with a fructose load of 100 wt%. However, the system wasn’t autocatalytic, requiring an additive - CO_2 - to carry out the reaction. Nevertheless, this process has been included in this section to keep continuity of the DESs narrative.

2.2.3 DMSO

DMSO has long been identified as a solvolytic medium. Its nucleophilic action via carbonium ions promotes the dehydration of 1,4-diketones in furanic compounds [131, 132]. These findings have recently been explained through data obtained by ^{1}H and ^{13}C NMR [31]. The results showed that at 150 °C, the β-pyranose form changes to α-furanose, which can be more readily transformed into HMF. While these results point to a cyclic route for the dehydration of fructose to HMF, it is important to note that this tautomerization process has exclusively been observed in DMSO. Computational data from Ren et al.[133] however, suggests that β-D-furanose is the most stable form in DMSO. It has also been shown that DMSO initiates HMF formation due to the arrangement of DMSO around the hydrogen atoms of the fructose molecule reducing the formation of reversion and polymerization products from fructose [35]. DMSO then binds to HMF more strongly than water does, and reduces its susceptibility to nucleophilic attack, thereby minimizing undesirable side reactions [134]. All these points mean that HMF yields from fructose in DMSO are often higher than in other solvents.

Early reports using DMSO as solvent showed that fructose could be fully converted to HMF after a reaction time of 16 hours and at a 100 °C reaction temperature [91]. A more recent study showed the formation of HMF in DMSO in high yields and considerably shorter reaction times [92]. Musau and Munavo [135] observed the facilitating properties of DMSO in the synthesis of tetrahydrofurans from 1,4-diols and that of dibenzyl ethers from benzylic alcohols. Based on this, they developed a non-catalytic method to produce HMF using DMSO as reaction promoter. The molar ratio proved to be an important factor in improving HMF yields, with a fructose:DMSO ratio of 1:8 giving a 92% yield at 150 ^{o}C for 2 hours. As the reaction progresses, DMSO associates with water, which in turn renders DMSO less available for the dehydration process. An excess of DMSO helps to alleviate this issue. Amarasekara et al. [31] proposed a mechanism for fructose dehydration in DMSO, involving a dihydrofuran-2-aldehyde intermediate (shown in Scheme 2). While these results showed promise in DMSO, there have been other authors reporting very low values for uncatalyzed reaction in DMSO [90, 97, 136-138]. It can be argued that neither the fructose:DMSO ratio, nor the reaction times were optimal since, as mentioned above, quantitative conversion can take up to 16 hours. Yet, these results are hard to reconcile, showing very short reaction times with high yields and vice versa. In a recent study by Svenningsen et al.it was observed that in a deaerated DMSO medium, no HMF could be produced at all, while in an aerated sample HMF was obtained at almost 80% yields. The authors credit the catalytic activity of DMSO to the formation of H2SO4 in the presence of oxygen at temperatures above 80°C [139]. A comparison of these experiments can be seen in Table 4.

Still, the main obstacle is not the difference in results, but the separation of HMF from the solvent. The distillation of DMSO is difficult and energy intensive, leading to carbonization of much of the HMF, while HMF’s affinity to DMSO makes the extraction *via* other solvents just as taxing a task [8, 91]. The high toxicity of DMSO also makes its use questionable at industrial scale.



Scheme 2 Proposed mechanism of fructose dehydration in DMSO [31][1]

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[1] "Reprinted from Carbohydrate Research, 343/18, Ananda S. Amarasekara, LaToya D. Williams, Chidinma C. Ebede, Mechanism of the dehydration of d-fructose to 5-hydroxymethylfurfural in dimethyl sulfoxide at 150°C: an NMR study, 3021-3024., Copyright 2008, with permission from Elsevier.

Solvent	Water	Dimethl formamide	Dimethyl Sulfoxide	Acetone	[C_2mim]Cl	[C_4mim]Cl	Ethyl Acetate	Choline Chloride	Citric acid
Environmental effects									
Mobility	░	░	░	▓	░	░	▒	░	░
Acute toxicity for humans	░	■	▒	▒	□	■	▒	▒	▒
Chronic Toxicity for humans	░	■	▒	░	□	□	░	░	░
Acute toxicity for aquatic	░	▒	▒	▒	□	█	▒	▒	▒
Persistency in environment	░	▒	▓	▒	■	■	░	▒	░
Bioaccumulation	░	░	░	░	░	░	░	░	░

Definition (qualitative)

No/low	░	Medium	▓	High	█
Low to medium	▒	Medium to high	■	Not enough data	□

Effect	Database
Mobility	Boiling point, temperature diff. Between boiling point and process temperature, vapor pressure
Acute toxicity for humans	EC classification (Xn, T, T+), GK, R-codes, LD50 (inhal., oral, dermal)
Chronic toxicity for humans	Carcinogenity, mutagenicity etc., R-codes, AGW, EC classification (Xn, T, T+)
Acute toxicity for aquatic organisms	WGK (German water hazard class), R-codes, EC50/LC50
Persistance in environment	OECD, EU classification (readily inherent, no)
Bioaccumulation	Log K_{ow} qualitative info

Figure 2 Qualitative solvent toxicity assessment, based on reference [123]

Table 2. HMF synthesis using different IL both as solvent and catalyst

Substrate type	Substrate	Solvent	Sugar/IL molar ratio	IL	Temperature (°C)	Reaction time	Conversion (%)	HMF Yield (%)	Reference
Fructose			1:9.55	[BdMIM][Cl]	140	50 min	67.5	0	[96]
			1:8.63	[BeMIM][Cl]	140	50 min	100	53.2	[96]
			1.0.06	[BMIM][Cl]	80	900 min		65	[95]
			1:10.31	[BMIM][Cl]	80	3 hours	3.85	0	[104]
			1:10.31	[BMIM][Cl]	100	3 hours	59.8	28.2	[104]
			1:20.63	[BMIM][Cl]	100	5 min	0	0	[105]
			1:10.31	[BMIM][Cl]	120	50 min	93.4	63.3	[96]
			1:10.31	[BMIM][Cl]	140	50 min	100	60.4	[96]
			1:10.43	[BMIM][Cl]	155[a]	1 min	99	98	[103]
			1:2.09	[BMIM][Cl]	175[a]	1.5 min	97	97	[103]
			1:0.26	[BMIM][Cl]	186[a]	1.5 min	65	62	[103]
			1:5.00	[BMIM][H_2SO_4]	80	1 hour	100	56.3	[30]
			1:5.80	[BMIM][PS]	140	50 min	49.9	0	[96]
			1:0.04	[C_3SO_3HMIM][HSO_4][b]	150	30 min	84	73	[140]
			1:1.00	[DiEG(mim)$_2$][OMs]$_2$	120	40 min	100	69.8	[108]
			1:12.29	[EMIM][Cl]	80	3 hours	9	1.5	[94]
			1:12.29	[EMIM][Cl]	100	3 hours	58	40	[94]
			1:12.29	[EMIM][Cl]	120	3 hours	100	73	[94]
			1:9.04	[Et_3NH][HSO_4]	100	3 hours	99.6	36.6	[104]
			1:5.00	[$EtNH_3$][NO_3]	80	1 hour	48.2	1.1	[30]
			1:5.00	[HMIM][Cl][c]	80	1 hour	96.5	69.7	[30]
	0.12 mol	0.6 ml	-	[HMIM][Cl][c]	90	45 min	99	92	[93]
	0.12 mol	0.6 ml	-	[HMIM][Cl][c]	90	10 min	75	62	[93]
			1:8.89	[HeMIM][Cl][d]	120	50 min	65.7	7.3	[96]
			1:8.89	[HeMIM][Cl][d]	140	50 min	85.1	21.9	[96]
			1:7.81	[OMIM][Cl]	120	50 min	42.5	0	[96]
			1:7.81	[OMIM][Cl]	140	50 min	79.6	8.6	[96]
			1:5.00	[Pyr][HCl]	80	1 hour	92	69	[30]
			1:0.15	[Pyr][HCl]	90-100	30 min		12	[89]
			1:1.00	[Pyr][HCl]	90-100	30 min		50	[89]
			1:1.00	[TetraEG(mim)$_2$][OMs]$_2$	120	40 min	100	92.3	[108]
			1:1.00	[TriEG(mim)$_2$][OMs]$_2$	120	40 min	100	77.2	[108]
			1:5.00	PyTSA	80	1 hour	52	7.8	[30]
			1:5.00	TMG LAC	80	1 hour	4.75	0.6	[30]
			1:5.00	TMG TFA	80	1 hour	1.34	0.4	[30]
Glucose			1:9.04	[Et_3NH][HSO_4]	100	3 hours	93.9	1.2	[104]
			1:9.04	[Et_3NH][HSO_4]	100	3 hours	92	0.88	[104]
			1:12.29	[EMIM][Cl]	180	3 hours	42	3	[94]
			1:10.94	[EMIM][Cl]/H_2O	180	3 hours	5.5	2.5	[94]
			1:10.31	[BMIM][Cl]	80	3 hours		0.065	[104]
			1:10.31	[BMIM][Cl]	150	3 hours		3	[104]
			1:10.31	[BMIM][Cl]	180	3 hours		2.4	[104]
Sucrose			1:2	[DiEG(MIM)$_2$][OMs]$_2$	120	150 min		52	[108]
			1:2	[TetraEG(MIM)$_2$][OMs]$_2$	120	150 min		63	[108]
			1:2	[TriEG(MIM)$_2$][OMs]$_2$	120	150 min		60	[108]
Maltose			1:19.48	[BMIM][Cl]	100	3 hours	2.5	0.28	[104]

Starch	1 g	4 g	-	[OMIM][Cl]	120	30 min		0	[113]
	1 g	4 g	-	[OMIM][Cl]	120	90 min		0	[113]
	1 g	4 g	-	[OMIM][Cl]	120	60 min		0	[113]
	1 g	4 g	-	[OMIM][Cl]	120	120 min		0	[113]
Cellulose	0.4 g	8 g	-	[BMIM][Cl]	100	1 hour		0	[117]
	0.1 g	2 g/0.2 g	-	[BMIM][Cl]/IL-SO_3	100	90 min	89	0	[119]

[a] Final temperature after MH at 400 MW

[b] 1-methyl-3-(3-sulfopropyl)-imidazolium hydrogen sulfate

[c] 1-H-3-methyl

[d] 1-hexyl-3-methyl

Table 3. HMF synthesis in ChoCl DESs from references [30, 115]

Material	Sugar/IL molar ratio	DES	Temperature (°C)	Reaction time	Conversion (%)	HMF Yield (%)
Fructose	1:5	ChoCl/Anhydrous citric acid	80	1 hour	99	79
	1:5	ChoCl/Citric acid	80	1 hour	91.7	76
	1:5	ChoCl/$CrCl_3$	80	1 hour	93.55	16.5
	1:5	ChoCl/Malonic acid	80	1 hour	91	40
	1:5	ChoCl/Oxalic acid	80	1 hour	100	62
	1:5	ChoCl/Urea	80	1 hour	0	0
	1:5	ChoCl/$ZnCl_2$	80	1 hour	27.6	1.8
Inulin	1:6	ChoCl/Citric acid	50	2 hours		3
	1:6	ChoCl/Oxalic acid	50	2 hours		19
	1:6	ChoCl/Oxalic acid	60	2 hours		28
	1:6	ChoCl/Oxalic acid	70	2 hours		45
	1:6	ChoCl/Citric acid	80	2 hours		51
	1:6	ChoCl/Oxalic acid	80	2 hours		56
	1:6	ChoCl/Oxalic acid	80	2 hours		64
	1:6	ChoCl/Oxalic acid	90	2 hours		55
	1:6	ChoCl/Citric acid	50/80	4 hours		57

Table 4. HMF synthesis using fructose in DMSO as both solvent and catalyst

Sugar/DMSO molar ratio	Temperature (°C)	Reaction time	Conversion (%)	HMF Yield (%)	Reference
1:10.56	80	44 hours	0	0	[90]
1:30.44	90	2 hours		2.4	[107]
1:44.8	100	16 hours	100	100	[91]
1:101	120	80 minutes	100	80	[92]
1:0.14	150	2 hours		1.8	[135]
1:6.2	150	2 hours		84	[135]
1:8.5	150	2 hours		92	[135]
1:12.4	150	2 hours		80	[135]
1:0.6	160	2 hours		22	[135]
1:20.77	q	4 min	100	92	[141]
1:20.77	150	300 min	100	90	[141]
1:7.2	150	30 min	100	78	[139]
1:7.2[b]	150	30 min	10	0	[139]

[a] MH (900 W)

[b] Deareated DMSO

3. Catalytic Systems

The catalytic dehydration of carbohydrates has been well known for over 120 years. The first experiments date back to 1895, when Düll and Kiermayer [142, 143] produced HMF from sucrose using oxalic acid to trigger the reaction. 50 years later, Haworth and Jones [144] picked up where they left off, and observed that only the fructose moiety of sucrose was actually dehydrated, and suggested that the dehydration proceeded via enediol. This finding suggested that the dehydration takes place through an acyclic intermediate. The lower glucose reactivity has been later explained by the low proportion of its acyclic form in water [58, 71]. Since then, considerable advancements have been done in the field of catalytic carbohydrate dehydration, and clear differences and uses between Brønsted and Lewis acidities have been identified.

3.1 Homogeneous catalysts

Homogeneous catalysts are those which are in the same phase as the reactants. Given that most reactions are conducted in a liquid phase, if both the reactant and the catalyst are soluble, a homogeneous catalysis takes place. Most of the early research performed on HMF used homogeneous liquid Brønsted catalysts such as HCl and H_2SO_4 [29, 36, 142, 145, 146]. In the past years, soluble Lewis acid salts became more widely used due to the ease of their recovery and recyclability [50, 94, 147]. Although Brønsted acids can generally hydrolyze cellulosic materials [146, 148], they are rarely selective towards HMF. On the other hand, Lewis catalysts have shown very promising results as the conversion of glucose and fructose resulted in high HMF selectivity [94, 112, 149].

3.1.1 Brønsted acids

Several experiments have been performed using a variety of Brønsted acids and bases, like HCl, H_2SO_4 and NaOH [29, 54, 150, 151], which showed that while these can easily convert fructose, they have very low selectivity towards HMF. Table 5 shows an extended list of these results. The use of strong bases and alkaline salts also revealed that glucose can be converted to the fructofuranose form in a basic medium [51, 71] and further dehydrated to HMF, hypothesizing that isomerization is an intermediate step in its dehydration [39, 150]. Although Kuster et al. [58] showed that the conversion rate is related to the medium’s acidity, according to later results, no clear correlation could be found between the Hammett acidity and the yields of HMF. It has also been observed that both HMF and other unwanted products require the same minimum Brønsted acidity [152][139].

Nevertheless, Bicker, Hirth and Vogel reported observing increasing HMF selectivity with higher H_2SO_4 concentrations in an acetone/water mixture [153]. However, the tautomeric equilibrium of fructose in acetone was also analyzed, showing that both α- and β-furanose forms are favored, which partly explains the high HMF selectivity [154]. Bao et al. [98] later observed that in a DMSO medium, the Hammett acidity of ILs 3-allyl-1-(4-sulfobutyl) imidazolium trifluoromethanesulfonate ($[ASBI^+][Tf^-]$) and 3-allyl-1-(4-sulfurylchloride butyl) imidazolium trifluoromethanesulfonate ($[ASCBI^+][Tf^-]$) was linearly correlated to fructose conversion and HMF yields. On the same issue, Tyrlik et al. [155] failed to obtain any HMF or LA using HNO_3. This, together with previous observations [29, 39, 54, 150], highlights the importance of the anion half of the Brønsted acids.

A more recent studied of fructose dehydration in DMSO, observed that, while acid concentration had a marked effect on conversion (100% at pH=1; 5% at pH=4.5), it impacted HMF selectivity very little (80-85%) [139]. By trying different mineral acids (HI, HBr, HCl, H_2SO_4), a slight change in conversion could be observed, but given the difference in magnitude between Ka values of the acids, suggested that this was not a rate-limiting step. The authors proposed that acid catalysts are responsible for the rate of fructose conversion but have little effect on HMF selectivity.

The solvent-catalyst interaction plays an important role in determining the activity of a catalyst. While in aqueous conditions, HCl and H_3PO_4 can catalyze HMF production from fructose, but when in $[BMIM^+][Cl^-]$ IL, these catalysts were practically inert [156]. On the other hand, H_2SO_4 produced HMF in yields of up to 70 mol% in the presence of $[BMIM^+][Cl^-]$. When HCl was used in a fructose solution with higher sugar concentration (10 wt%) and under similar experimental conditions (80 ^oC and 8 minutes), HMF was obtained in a 95% yield [95]. These results are hard to reconcile, given the resemblance of their parameters.

To explain the mechanism of fructose dehydration in the presence of halides, Binder and Raines [147] suggested that weakly paired anions favored the reaction. It was further proposed that a fructofuranosyl oxocarbenium ion is formed and deprotonated, and that the halide anion formed a 2-deoxy-2-halo intermediate, which in turn formed an enol, leading to HMF (Scheme 3). Hansen [157] and Ståhlberg [158] dehydrated fructose and glucose respectively using boric acid (H_3BO_3) in $[C_xMIM^+][Cl^-]$ ILs, and concluded that while acting as weak Lewis acid, H_3BO_3 could catalyze the dehydration reaction and produce HMF in yields of up to 52% for fructose after 45 min at 150°C; and 32% for glucose. It was further posited that H_3BO_3 promoted glucose isomerization and later formed a diborate compound with fructose, which was more stable than a monoborate specimen. This could explain the low HMF yields at high H_3BO_3 concentrations.

Asghari et al. [40] tested different kinds of acids, such as HCl, H_3PO_4, p-Toluenesulfonic acid (PTSA), oxalic acid and citric acid. H_3PO_4 and maleic acid exhibited similar behavior with HMF yield peaking at pH=2. Oxalic and citric acid had HMF yield peaking at pH=1.5. In all cases, lower pH values led to the rehydration of HMF to LA, FA or pyruvic acid. Higher pH values led to the formation of polymers. Aldohexoses, such as glucose and mannose, generated lower HMF yields, while ketoses like fructose and sorbose, produced it more readily. Of the two, fructose showed better selectivity to HMF, which the authors explained by the differences in their C3 and C4 hydroxyl configurations (C3OH and C4OH respectively). OH groups in positions 1 and 3 in fructose seemed to be involved in the dehydration reaction. However, a density functional theory (DFT) analysis by Yang et al. [159], showed that successful protonation of C2OH lead more often to HMF formation. It was also calculated that it is possible to obtain LA directly from fructose without HMF as an intermediate, but given the required free-energy, these pathways are thermodynamically unfavorable. Protonation of OH in position 2 is the preferred site for Brønsted acid-catalyzed reaction.

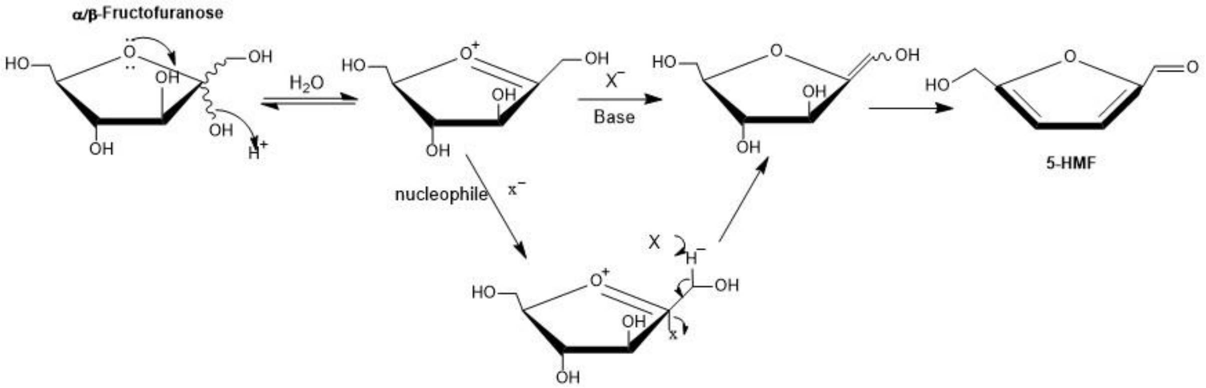
The initial carbohydrate concentration is another key aspect to consider in an acid-catalyzed dehydration reaction. Highly concentrated sugar solutions tend to generate humins and low HMF yields [40, 58, 59, 72, 160]. Such systems require highly concentrated acids to start the reaction at low temperatures. This complicates the use of biphasic systems since it makes them homogeneous. The formation of rehydration products is another major problem [161-164]. The use of metal salts acting as Lewis acids or acidic ILs can counter these side effects.

Antal et al. [39] proposed a glucose dehydration mechanism that did not require glucose isomerization to fructose, but instead involves 3-deox-d-erythro-hex-2-ulose (3-deoxyglucosone or 3-DG) as an intermediate. In this experiment, 3-DG was detected in low amounts under weak acidic conditions. More recently, it was shown that not only is 3-DG readily converted to HMF almost quantitatively, but also that this pathway is more energetically favorable, which suggests that this might be the main reaction route for glucose dehydration in Brønsted acidic media [165]. However, this pathway gives lower HMF yields than the fructose pathway. One reason for this is that the formation of 3-DG requires glucose to be present in the open-ring form. Although high temperatures and the presence of protic acids lead to an increase in the proportion of open-chain glucose present in aqueous solutions [166], this is nevertheless a bottleneck for HMF production from fructose, as are the numerous side reactions of 3-DG [167].

Through a DFT theoretical analysis of glucose dehydration, Qian [168] calculated that HMF formation can be obtained via a cyclic furan aldehyde intermediate. This process happens when protonation is started at C2OH of glucose. Alternatively, the same furan aldehyde intermediate can also lead to isomerization to fructose. These results differ from those of a similar study by Yang et al. [159], where the authors posited that the only energetically viable possibility to produce HMF from glucose is by the protonation of the O5, which leads to fructose isomerization. While C2OH protonation leads to a pathway that produces LA without an HMF intermediate. A more recent study has suggested that protonation of C2OH can also lead to the production of furfuryl alcohol, but the route to HMF is more thermodynamically favorable [169]. The model developed also shows the strong dependence of the reaction on temperature and pH. All three articles nevertheless coincide in that glucose condensation reaction takes place by protonation of C1OH. Scheme 4 shows a graphical representation of these reactions; reactions inside the bold line describe a cyclic and an acyclic route for HMF formation. Reactions inside the dash line are isomerization reactions to fructose. Grey solid lines are condensation reactions.

Both, cellulose hydrolysis and carbohydrate dehydration can be catalyzed via acids [146]. Using H_2SO_4 as catalyst, Mok et al. [148] were able to obtain, at 215 ^{o}C and for 120 minutes, up to 71% cellulose conversion to glucose. While this was their main goal, they also observed small amounts of HMF among the products. Using boric acid, Ståhlberg et al. [158] obtained close to 35% HMF yield after a long reaction time (8 hours) at 120 °C.

Another work by Wu et al. [170] used inulin as feedstock and CO_2 as acid catalyst in an aqueous media. Regulating pH via pressure, and adjusting the reaction times and temperatures accordingly, the researchers converted inulin at 100% and obtained HMF values as high as 50%. This yield is comparable to other more corrosive, and less environmentally friendly acids and solvents.



Scheme 3 Proposed mechanism for fructose dehydration in the presence of halides [147][2].

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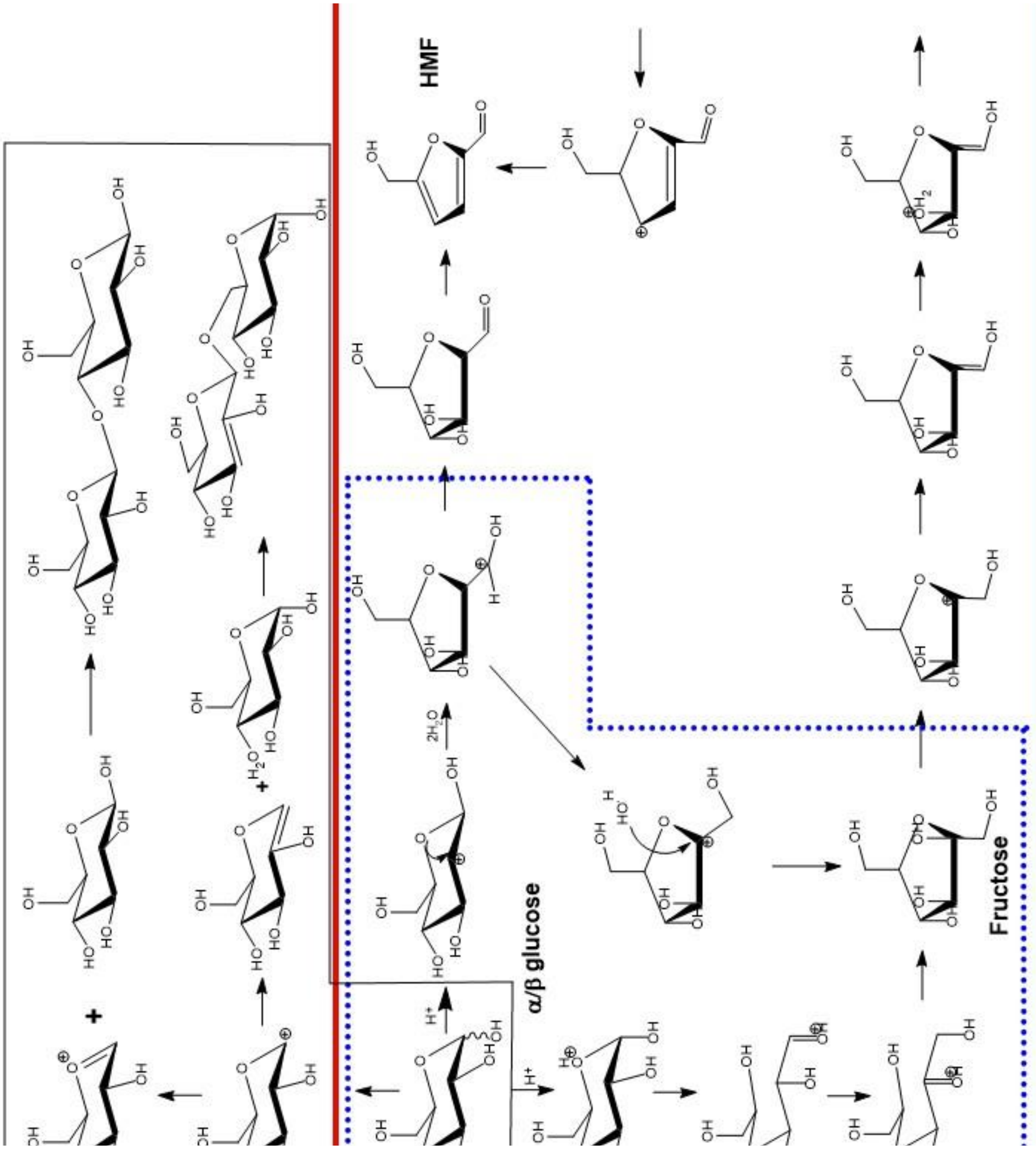
[2] Reprinted from Journal of the American Chemical Society, 131/5, Binder, Joseph, Raines, Ronald, Simple Chemical Transformation of Lignocellulosic Biomass into Furans for Fuels and Chemicals, 1979-1985, Copyright 2009, with permission from ACS.



Scheme 4 Possib
Based on referen

3.1.2 Lewis acids

Brønsted acids have been extensively tested and studied as catalysts. However, they are often corrosive and toxic in nature, and most of them are in the liquid form which makes their use at an industrial scale difficult. As an alternative, Lewis acids, particularly in the forms of salts, offer advantages such as an easier catalyst recovery, and less corrosiveness.

One of the early uses of Lewis acids describes the use of boron trifluoride etherate (BF_3•Et_2O) and halide salt $ZnCl_2$ in a DMSO solution for fructose and glucose dehydration, with BF_3 delivering HMF yields as high as 98.8% and 42.1% respectively [171]. Temperature was kept at 100°C for both samples, while reaction time was 45 minutes for fructose, but 48 hours for glucose. Since then, several other Lewis acids have been tested [50, 94, 147, 155, 172]. In their pivotal work, Zhao et al. [94] obtained very high HMF yields from fructose and glucose using metal chlorides coupled with different ILs, particularly from $CrCl_3$, since this salt promotes the glucose to fructose isomerization. They also presented their proposed mechanism for glucose dehydration in the presence of Lewis acidic metal halides, which suggested that the metal cation played a role in facilitating glucose mutarotation [94]. This was corroborated by later experiments, which detected 3-DG only in small amounts in a $CrCl_2$-[$BMIM^+$][Cl^-] system, suggesting that the glucose-to-fructose isomerization route is the main path for HMF formation from glucose in the presence of Lewis acid catalysts [173].

After the work of Zhao et al., several other authors have expanded this scheme for more specific cases such as $SnCl_4$ [174] or $CrCl_3$ [112]. A generalization of these mechanisms can be seen in Scheme 5. It was also observed that the coordination ability of the IL anion had an effect on the catalytic activity of the metal salt. Low coordinating anions, such as BF_4, have weak interactions with the metal cation, allowing it to react more readily with glucose. Similarly, Binder and Raines [147] used N,N dimethylacetamide (DMA) with LiCl as a solution to hydrolyze and dehydrate cellulose to HMF. When testing various metal halides, they observed that bromide and iodide salts were less strongly ion-paired, which gave good HMF yields. The good solubility of cellulose was due to the Li^+ tendency to form macrocations with DMA which allowed for high concentration of Cl anions, which were capable of interfering with hydrogen inter- and intramolecular bonds. This same effect was also observed by Chen et al. [175] when using caprolactam (CPL) containing LiCl in conjunction with various Cr and Sn halide salts, obtaining again best results with $CrCl_3$.

A more detailed study performed by Zhang et al. [176] on chromium catalysts revealed that the oxidation state didn't strongly affect the catalytic activity in [$EMIM^+$][Cl^-]. Comparing $CrCl_2$, $CrCl_3$ and $CrCl_3$•$6H_2O$, different catalytic activities were observed when dehydrating glucose. However, while all three catalysts achieved similar conversion and HMF yields, the reaction rates using $CrCl_3$•$6H_2O$ were considerably faster. $CrCl_2$ exhibited the highest concentration of fructose intermediate. This difference was due to the faster fructose dehydration rate using Cr(III) than Cr(II). On the other hand, anhydrous $CrCl_3$ slowly dissolved in [$EMIM^+$][Cl^-]. As a result, an induction period before the reaction started was observed.

Yong et al. [172] performed experiments using n-heterocyclic carbenes (NHC). They observed that when using Cr(II) and Cr(III) ligands in [$BMIM^+$][Cl^-] solution for fructose and glucose dehydration, the stereochemical properties of the molecules played an important role. Bulkier NHC provided better HMF yields, which the authors attributed to the bigger molecules protecting the Cr^+ center from reacting with the IL and forming Cl^- complexes.

Halides of rare earth metals can also convert glucose to HMF [50]. Ståhlberg et al. [102] used several lanthanide-IL combinations, and found that their catalytic effect varied depending on the IL used. In [EMIM$^+$][Cl$^-$], the reactivity decreased inversely with the molecular weight, with promethium chloride having the highest yield. The opposite was true in [BMIM$^+$][Cl$^-$], where ytterbium chloride, and particularly ytterbium triflate (Yb(OTf$_3$)), had the best yield and selectivity. CeCl had very little catalytic activity in both cases. Wang et al. [177] also experimented with a different set of rare earth metals triflates in DMSO, and found an inverse correlation between ionic radius and HMF yield, with scandium triflate (Sc(OTf)$_3$) having the highest yield value (83%). The same observation was later ratified by Beckerle and Okuda [178], who used rare earth metal chlorides in DMA to dehydrate cellobiose and glucose. Similarities between Sc and Cr(II) were observed, both having a coordination number of 6 and very close ionic radii (0.75 Å for Sc and 0.73 Å for Cr(II)). More recent results have also found correlations between glucose conversion and ionic radius, as wells as with the electronegativity and ionic charge of Cr(III) and Al(III) [179].

Pairing chlorinated ILs with metal halides has delivered good HMF yields when dehydrating polysaccharides. As mentioned in section 2.2.1, Cl$^-$ can promote the breaking of β-1,4-glycosidic bonds in cellulose to yield glucose. Cr halide salts, especially $CrCl_2$ and $CrCl_3$, can isomerize glucose to fructose and provide high HMF yields [113, 180, 181]. Su et al. [182] reported a method pairing $CuCl_2$ and $PdCl_2$ in [EMIM$^+$][Cl$^-$]. This method allowed for cellulose depolymerization at mild conditions (100 °C). However, HMF yields were comparatively low. Following this concept, Wang et al. [183] tested the dehydration of cellulose in [BMIM$^+$][Cl$^-$] with $CrCl_3$ as catalyst, and LiCl, LiBr and $LaCl_3$ as co-catalysts. The use of paired metal halides proved to be more efficient than the single $CrCl_3$. Of the aforementioned salts, LiCl was more effective in conjunction with $CrCl_3$, giving an HMF yield of 62% at 160 ^oC for 10 minutes. The addition of LiCl beyond 50% mol had a detrimental effect on HMF yields.

Other notable examples of polysaccharide dehydration via Lewis acids was demonstrated by Yu and collaborators [184-186], who obtained up to 30% yield of HMF from starch-based food waste (bread) using $SnCl_4$, $AlCl_3$ and $FeCl_3$. Also of interest is that even though $FeCl_3$ presented a higher Brønsted acidity (1.7-2.3) than $AlCl_3$ (2.3-3), it was in the presence of the latter that more humins were formed, suggesting that Lewis acidity played a more important role in the polymerization process.

Eminov et al. used $CrCl_3$•$6H_2O$ as catalyst in the presence of Lewis IL [BMIM$^+$][Cl$^-$] and Brønsted IL [BMIM$^+$][HSO$_4^-$]. The former can depolymerize cellulose while the latter dehydrates saccharides. They used this combination for cellulose and glucose dehydration, [160, 187]. Their previous work with fructose showed that [BMIM$^+$][HSO$_4^-$] could be a suitable co-catalyst to produce HMF [188], due to the anion being mildly acidic and abundant in the medium. This low acidity prevents the over-dehydration usually observed with stronger acids. However, the low yields obtained from glucose and cellulose with[BMIM$^+$][HSO$_4^-$] suggested that [HSO$_4^-$] prevents the isomerization of glucose to fructose, which tends to be base catalyzed.

A possible explanation is that, in the presence of $CrCl_3$, [Cl^-] leads to the formation of [$CrCl_4^-$], which catalyzes glucose-fructose isomerization. [HSO_4^-], on the other hand, appears to form a non-active complex with $CrCl_3$, which is preferred over [$CrCl_4^-$] [160, 187].A two-step process using NaOH to pretreat wood chips and $CrCl_3$•$6H_2O$ allowed Nguyen et al. [189] to obtain up to 79% HMF yield at low temperature (60 °C), albeit with long reaction times (24 h). These results highlight the need of an appropriate catalyst for the glucose to fructose isomerization step.

Given that Brønsted acids promote protonation and Lewis acids deprotonation, Fu et al. [190] researched if a synergistic effect could be observed when performing the dehydration reaction. They found that there was a strong synergetic effect between aluminum trifluoromethylsulfonate and oxalic acid. Brønsted-Lewis acidic functional ILs used with a metal halide anion exhibited the same synergic effect [191, 192]. Brønsted acidic 1-sulfonic acid-3-methylimidazolium chloride ([$SMIM^+$][Cl^-]) had very little selectivity towards HMF and a lower conversion of glucose, which was explained by the lack of Lewis acid sites. [$SMIM^+$][$FeCl_4^-$] and particularly [$BMIM^+$][$FeCl_4^-$] had a better catalytic activity and produced less LA due to their lack of Brønsted acid sites.

The salting-out effect, which improves the partition coefficient of a biphasic system, has been applied to HMF production [157, 193, 194]. It was found that using halide salts increased HMF yields [147, 195]. Testing several halide salts in conjunction with $CrCl_3$•$6H_2O$ in aqueous solution showed that different anions influenced the reaction differently, with halide ions having a positive effect in the order of Br>Cl>I>F [196]. Dehydrating glucose using KBr or NaCl caused lower fructose concentrations at all times, suggesting that the salts promoted fructose dehydration, which in turn helped shift the glucose isomerization equilibrium. When adding mineral Brønsted acids to the reaction, it was observed that both conversion and yield decreased, and LA as well as humins increased. Chromium forms acidic complexes in water, such as $[Cr(H_2O)_5OH]^{2+}$, as well as hydronium ions [197], causing the medium to act as a bifunctional Lewis-Brønsted acid system.. This acidity leads to dimerization of the complexes via olation, and further polymerization to trimers and tetramers, which then undergo oxolation, becoming more stable, and decelerate the isomerization step [196]. Despite this, a more recent study using NaCl aqueous solution, $AlCl_3$ and HCl to dehydrate simple and complex carbohydrates, presented a positive synergy of these components, reaching HMF yields up to 56% from simple carbohydrates and 42% from pretreated cellulose at 190 ^oC for 60 minutes [198].

From this section, a clear shift in trends can be witnessed. As research progressed, the understanding of the underlying mechanisms of carbohydrate dehydration and the impact of catalysts functionality improved. Studies shifted from focusing on liquid Brønsted acids (both organic and mineral), to using Lewis acid halide salts. More recently, researchers have been leaning towards a combined approach, which exploits both Brønsted acids' capabilities to promote hydrolysis and isomerization, and Lewis acids' capability to dehydrate hexoses.

As can be seen from Tables 5 to 10, several catalytic systems using Lewis acids that can reach almost quantitative yields have been developed. However, a thorough analysis of their environmental sustainability, as well as their economic feasibility needs to be performed.

Table 5. Fructose dehydration in the presence of homogeneous Brønsted catalysts

Solvent	Substrate Concentration (wt%)	Catalyst	Catalyst amount	Temperature (°C)	Reaction time	Conversion (%)	Yield (%)	Reference
DMSO	2.7	[ASBI][Tf]	1:1 Fru:Cat (w)	100^*	4 min	100	85	[98]
[BMIM][Cl]	9.1	[BIMIM][HSO_4]	0.17 mmol	80	30 min		80	[95]
[BMIM][Cl]	9.1	[SBMIM][HSO_4]	0.13 mmol	80	26 min		91	[95]
[BMIM][Cl]	9.1	CH_3COOH	0.17 mmol	80	720 min		78	[95]
Water	1.1	CH_2OH (FA)	0.23 mol %	220	4 min	99	55	[44]
[BMIM][Cl]	4.8	CH_3COOH	18 mol %	80	10 min	0	0	[156]
Water	1.1	CH_3COOH	0.18 mol %	220	4 min	97	58	[44]
Water	1.8	H_2SO_4	2 mmol	250	0.5 min		48	[39]
Water	9.1	H_2SO_4	1 M	200	5 min		23	[51]
Water/ (7:3 MIBK:2-butanol) 1:3	30	H_2SO_4	0.25 M	180	2.5 min	80	52.8	[199]
(8:2 Water:DMSO)/ (7:3 MIBK:2-butanol) 1:3	30	H_2SO_4	0.25 M	180	2.5 min	85	60.4	[199]
[BMIM][Cl]	4.8	H_2SO_4	0.75 mmol	120	30 min	100	97	[149]
[BMIM][Cl]	4.8	H_2SO_4	18 mol %	80	10 min	81	69	[156]
DMA-LiCl 10 wt%	10	H_2SO_4	6 mol %	80	4 hours		66	[147]
Water	2	H_2SO_4	2:1 Fru:Cat (w)	200	5 min	97.3	47	[71]
[BMIM][Cl]	9.1	H_2SO_4	0.1 mmol	80	3 min		91	[95]
[BMIM][Cl]	9.1	H_2SO_4	10 mol %	100	50 min	100	82.9	[96]
Water/ MIBK 1:4	30	H_3BO_3	3.2 M	150	45 min	58	28	[157]
Water-NaCl/ MIBK (1.2 M NaCl) 1:4	30	H_3BO_3	1.6 M	150	45 min	70	46	[72]
Water/ (7:3 MIBK:2-butanol) 1:3	30	H_3PO_4	0.25 M	180	2.5 min	65	42.3	[199]
(8:2 Water:DMSO)/ (7:3 MIBK:2-butanol) 1:3	30	H_3PO_4	0.25 M	180	2.5 min	51	38.8	[199]
Water	1.8	H_3PO_4	pH_{sol}=2	240	2 min		65	[40]
[BMIM][Cl]	4.8	H_3PO_4	18 mol %	80	10 min	1	0	[156]
[BMIM][Cl]	9.1	H_3PO_4	0.09 mmol	80	720 min		67	[95]
Water	9.1	H_3PO_4	pH_{sol}=2	200	5 min	90	28	[151]i
Sulfolane	6.3	HBr	5 mol %	90	60 min		93	[200]
Water/ PG-600 3:2	8.3	HCl	1 M	95	15 min		45	[29]
Water	30	HCl	0.25 M	180	2.5 min	50	25.5	[199]
Water/ MIBK	30	HCl	0.25 M	180	2.5 min	91	54.6	[199]
Water/	30	HCl	0.25 M	180	2.5 min	75	54.7	[199]

MIBK								
Water/ (7:3 MIBK:2-butanol) 1:1	30	HCl	0.25 M	180	2.5 min	68	47.6	[199]
Water/ (7:3MIBK:2-butanol) 1:1	30	HCl	0.25 M	180	2.5 min	86	68.8	[199]
(8:2 Water:DMSO)/ MIBK 1:1	30	HCl	0.25 M	180	2.5 min	94	63	[199]
(8:2 Water:DMSO)/ (7:3 MIBK:2-butanol) 1:1	30	HCl	0.25 M	180	2.5 min	80	60	[199]
(8:2 Water:DMSO)/ (7:3 MIBK:2-butanol) 1:3	30	HCl	0.25 M	180	2.5 min	87	71.3	[199]
(7:3 Water:PVP)/ MIBK 1:1	30	HCl	0.25 M	180	2.5 min	74	48.8	[199]
(7:3 Water:PVP)/ (7:3 MIBK:2-butanol) 1:1	30	HCl	0.25 M	180	2.5 min	62	47.1	[199]
(7:3 Water:PVP)/ (7:3 MIBK:2-butanol) 1:3	30	HCl	0.25 M	180	2.5 min	79	64.7	[199]
[7:3(8:2 Water:DMSO):PVP] /MIBK 1:1	30	HCl	0.25 M	180	2.5 min	79	59.2	[199]
[7:3(8:2 Water:DMSO):PVP] /(7:3 MIBK:2-Butanol) 1:1	30	HCl	0.25 M	180	2.5 min	82	68.0	[199]
[7:3(8:2 Water:DMSO):PVP] /(7:3 MIBK-2-Butanol) 1:3	30	HCl	0.25 M	180	2.5 min	89	75.7	[199]
Water	5	HCl	pH$_{sol}$=1.8	240	5 sec		20	[163]
[BMIM][Cl]	4.8	HCl	18 mol %	80	10 min	3	2	[156]
Water	27	HCl	0.01 M	200^{**}	1 min	95	53	[72]
[BMIM][Cl]	9.1	HCl	0.2 mmol	80	8 min		97	[95]
[BMIM][Br]	9.1	HCl	0.2 mmol	80	11.5 min		95	[95]
[AMIM][Cl]	9.1	HCl	0.2 mmol	80	25 min		96	[95]
[EMIM][Br]	9.1	HCl	0.2 mmol	80	2 min		88	[95]
[HMIM][Cl][a]	9.1	HCl	0.2 mmol	80	360 min		85	[95]
[BMIM][BF$_4$]	9.1	HCl	0.2 mmol	80	60 min		5	[95]
[BMIM][PF$_6$]	9.1	HCl	0.2 mmol	80	60 min		8	[95]
[BMIM][Cl]	67	HCl	9 mol %	80	120 min	67	51	[95]
[BMIM][Cl]	33	HCl	9 mol %	80	35 min	90	82	[95]
Water	10	HCl	0.1 M	140	25 min	65	40	[197]
Water-KBr/ MeCN (0.1 M KBr) 1:2	10	HCl	0.1 M	160^{***}	1 min	99	85	[201]
[BMIM][Cl]	9.1	HNO$_3$	0.2 mmol	80	5 min		93	[95]
[BMIM][Cl]	9.1	Maleic Acid	0.17 mmol	80	50 min		88	[95]
Water	9.1	NaOH	1 M	200	5 min		12	[51]
Water	2	NaOH	2:1 Fru:Cat (w)	200	5 min	72.9	2.8	[71]
Water	9.1	NaOH	pH$_{sol}$=11	200	5 min	82	19	[151]
Water	0.4	PTSA	1 M	88	240 min	52	22	[58]
DMSO/	8.3	PTSA	0.04 mmol	80	32 hours		68	[90]

[BMIM][BF_4] 5:3								
DMSO/ [BMIM][BF_4] 5:3	8.3	PTSA	0.04 mmol	80	20 hours		75	[90]

[a] [HMIM][Cl]=1-hexyl 3-methyl chloride

*MH at 200 W, **at 300W, ***No specification on power

Table 6. Glucose dehydration in the presence of homogeneous Brønsted catalysts

Solvent	Substrate concentration (wt %)	Catalyst	Catalyst amount	Temperature (°C)	Reaction time	Conversion (%)	Yield (%)	Reference
Water	24	$(NH_4)_2SO_4$	0.1 N	180	20 min		22.5	[202]
[BMIM][Cl]	8.3	CF_3COOH	0.01 mmol	120	180 min	58	43,5	[203]
[BMIM][Cl]	8.3	CF_3SO_3H	0.01 mmol	120	180 min	87	46	[203]
[BMIM][Cl]	8.3	CH_3SO_3H	0.01 mmol	120	180 min	73	58	[203]
[BMIM][Cl]	4.8	H_2SO_4	0.75 mmol	120	120 min	100	15	[149]
[BMIM][Cl]	8.3	H_2SO_4	0.01 mmol	120	180 min	93	66	[203]
[EMIM][Cl]	9.1	H_2SO_4	6 mol %	80	180 hours	93.7	9.3	[94]
CPL/LiCl 3:1	10	H_2SO_4	6 mol %	100	180 min		12.6	[175]
Water	9.1	H_2SO_4	1 M	200	5 min		3	[51]
Water	2	H_2SO_4	2:1 S:C (wt)	200	5 min	10.6	2.4	[71]
[BMIM][Cl]	9.1	H_2SO_4	10 wt %	400*	1 min		49	[112]
[BMIM][Cl]	9.1	H_3BO_3	0.44 mmol	120	180 min	46.6	14	[158]
[EMIM][Cl]	9.1	H_3BO_3	0.44 mmol	120	180 min	95	41	[158]
[BMIM][Cl]	8.3	H_3PO_4	0.01 mmol	393	180 min	13	12	[203]
Water	20	H_3PO_4	0.015 mol	228	57 min		14.9	[150]
Water	1	H_3PO_4	0.04 mol/l	170	120 min	26	8	[204]
Water	9.1	H_3PO_4	$pH_{sol}=2$	200	5 min	42	4.1	[151]
[BMIM][Cl]	8.3	HCl	0.01 mmol	393	180 min	53	32,9	[203]
Water-NaCl / 1-Butanol 1:3 (0.35 g NaCl)	10	HCl	$pH_{sol}=1$	160	60 min	26	10,4	[205]
Water-NaCl/ CPME (1:0.4:1)**	10	HCl	$pH_{sol}=2.5$	175	20 min	15.5	4.5	[198]
[BMIM][Cl]	8.3	HNO_3	0.01 mmol	120	180 min	56	43,1	[203]
Water	9.1	NaOH	1 M	200	5 min		2	[51]
Water	2	NaOH	2:1 S:C (wt)	200	5 min	46.6	4.93	[71]
Water	9.1	NaOH	$pH_{sol}=11$	200	5 min	40	4	[151]

* MH in (W), no temperature specified

** CPME = cyclopentyl methyl ether

Table 7. Fructose dehydration in the presence of homogeneous Lewis catalysts

Solvent	Substrate Concentration (wt %)	Catalyst	Catalyst amount	Temperature (°C)	Reaction time	Conversion (%)	Yield (%)	Reference
DMSO	3.1	[ASCBI][Tf]	1:1 Fru:Cat molar ratio	100	4 min	100	88	[98]

DMSO/Water 1:1	5	$AlCl_3$	55.5 mmol	140	20 min		23	[184]
[BMIM][Cl]	4.8	$BiCl_3$	10 mol %	100	5 min		8.1	[105]
[BMIM][Cl]	4.8	$CeCl_3$	10 mol %	100	5 min		0.9	[105]
ChoCl	40	$CrCl_2$	10 mol %	100	30 min		40	[123]
ChoCl	40	$CrCl_3$	10 mol %	100	30 min		60	[123]
[BMIM][Cl]	9.1	$CrCl_3*6H_2O$	10 mol %	100	120 min	100	75.3	[96]
[BMIM][HSO_4]	-	$CrCl_3*6H_2O$	7 mol %	80	24 hours		85	[188]
[BMIM][HSO_4]	-	$CrCl_3*6H_2O$	7 mol %	100	3 hours		96	[188]
DMSO/Water 1:1		$CrCl_3*6H_2O$	55.5 mmol	140	20 min		35	[184]
Water	10	$CrCl_3*6H_2O$	100:3 Fru:Cat molar	150	60 min	85	20	[197]
DMA-LiCl (10 wt%)	10	CuCl	6 mol %	80	5 hours		62	[147]
[BMIM][Cl]	4.8	CuCl2	18 mol %	80	10 min	97	80	[156]
DMSO/Water 1:1		$CuCl_2$	55.5 mmol	140	20 min			[184]
NMP	9.1	$FeCl_2$	0.56 mmol	90	120 min		1	[206]
[BMIM][Cl]	3.5	$FeCl_3$	0.001 mmol	80	120 min		87.7	[207]
[BMIM][Cl]/ Ethanol 1:1	3.5	$FeCl_3$	0.001 mmol	80	120 min		83	[207]
ChoCl	40	$FeCl_3$	10 mol %	100	30 min		59	[123]
DMSO/Water 1:1		$FeCl_3$	55.5 mmol	140	20 min		69	[184]
NMP	9.1	$FeCl_3$	0.56 mmol	90	120 min	98	42	[206]
[BMIM][Cl]	4.8	$GeCl_4$	10 mol %	100	5 min		92.1	[105]
[BMIM][Cl]	4.8	$HfCl_4$	10 mol %	100	5 min		57.7	[105]
DMSO	2	$Ho(Otf)_3$	4 mg	120	120 min		78.1	[177]
DMSO/Water 1:1		$InCl_3$	55.5 mmol	140	20 min		7	[184]
[BMIM][Cl]	9.1	$IrCl_3$ (hydrated)	10 mol %	100	30 min	99	70.2	[104]
Sulfolane	6.3	LiBr	100 wt %	90	240 min		79	[200]
DMA	10	LiCl	10 wt %	120	2 hours		65	[147]
DMSO/Water 1:1		LiCl	55.5 mmol	140	20 min		1	[184]
Sulfolane	7.7	LiCl	6.3 wt%	90	120 min		67	[200]
Sulfolane	6.3	LiI	100 wt %	100	360 min		30	[200]
DMSO	2	$Nd(Otf)_3$	4 mg	120	120 min		63.5	[177]
ChoCl	40	pTSOH	10 mol %	100	30 min		67	[123]
ChoCl	40	$Sc(Otf)_3$	10 mol %	100	30 min		55	[123]
DMSO	2	$Sc(Otf)_3$	4 mg	120	120 min		83.3	[177]
[BMIM][Cl]	4.8	$ScCl_3*6H_2O$	10 mol %	100	5 min		4	[105]
DMSO	2	$Sm(Otf)_3$	4 mg	120	120 min		73	[177]
[BMIM][Cl]	4.8	$SnCl_4*4H_2O$	10 mol %	100	5 min		5.5	[105]
[EMIM][BF_4]	16.7	$SnCl_4*5H_2O$	10 mol %	100	180 min	100	62	[174]

DMSO/Water 1:1		$SnCl_4*5H_2O$	55.5 mmol	140	20 min		63	[184]
DMSO/Water 1:1		$YbCl_3*6H_2O$	55.5 mmol	140	20 min		27	[184]
DMSO	2	$Yb(Otf)_3$	4 mg	120	120 min		80.2	[177]
ChoCl	40	$ZnCl_2$	10 mol %	100	30 min		8	[123]
[BMIM][Cl]	4.8	$ZrCl_4$	10 mol %	220	2 min	98.9	92.9	[208]
[BMIM][Cl]	4.8	$ZrCl_4$	10 mol %	100	5 min		43.8	[105]

Table 8. Glucose dehydration in the presence of homogeneous Lewis catalysts

Solvent	Substrate concentration (wt %)	Catalyst	Catalyst amount	Temperature (°C)	Reaction time	Conversion (%)	Yield (%)	Reference
Water	1	[BMIM][$FeCl_4$]	10 g	130	5 hours	100	50	[192]
Water	1	[SMIM][Cl]	10 g	130	4 hours	95	32	[192]
Water	1	[SMIM][$FeCl_4$]	10 g	110	5 hours	50	13	[192]
Water-NaCl/ CPME (1:0.4:5)	10	$AlCl_3$	0.025 mmol	175	20 min	88	57	[198]
Water-NaCl/ CPME (1:0.4:1)	10	$AlCl_3$	0.025 mmol	175	20 min	92.5	46	[198]
Water/THF	2	$AlCl_3*6H_2O$	0.1 M	170	10 min		43	[209]
CPL/LiCl 3:1	10	$AlCl_3$	6 mol %	100	180 min		9.7	[175]
DMSO/Water 1:1	5	$AlCl_3*6H_2O$	55.5 mmol	140	20 min		25	[184]
[EMIM][Cl]	9.1	$AlCl_4$	6 mol %	80	180 min	97.3	10.5	[94]
[EMIM][Cl]	9.2	$CeCl_3$	0.056 mmol	140	360 min	75	3	[102]
[BMIM][Cl]	9.2	$CeCl_3$	0.056 mmol	140	360 min	100	3	[102]
[EMIM][Cl]	9.1	$CrCl_2$	2.6 mg	100	180 min	94	63	[176]
ChoCl	40	$CrCl_2$	10 mol %	100	30 min		45	[123]
Water	1	$CrCl_3$	0.04 mol/l	170	120 min	90	10	[204]
Water	1	$CrCl_3$	0.04 mol/l	170	120 min	62	8	[204]
Water	10	$CrCl_3*6H_2O$	Glu:cat 3:100 (w)	140	90 min	77	18	[197]
[EMIM][Cl]	9.1	$CrCl_3$	2.6 mg	100	180 min	94	63	[176]
ChoCl	40	$CrCl_3$	10 mol %	100	30 min		31	[123]
[EMIM][Cl]	9.1	$CrCl_3$	6 mol %	80	180 min	94.4	67.8	[94]
[BMIM][HSO_4]	12.5	$CrCl_3*6H_2O$	7 mol %	100	24 hours		33	[187]
[BMIM][Cl]	12.5	$CrCl_3*6H_2O$	7 mol %	120	15 min		65	[187]
Tetraethylammonium chloride	5	$CrCl_3*6H_2O$	10 mol %	130	10 min		71.5	[210]
[EMIM][Cl]	9.1	$CrCl_3*6H_2O$	2.6 mg	100	180 min	97	72	[176]
[BMIM][Cl]	4.8	$CrCl_3*6H_2O$	0.015 g	140^*	0.5 min	98	71	[211]
[BMIM][Cl]	4.8	$CrCl_3*6H_2O$	0.015 g	140	0.5 min		48	[211]
CPL/LiCl 3:1	10	$CrCl_3*6H_2O$	6 mol %	100	180 min		66.7	[175]

CPL/LiBr 3:1	10	$CrCl_3 * 6H_2O$	6 mol %	100	180 min		61.5	[175]
CPL/ZnCl2 4:1	10	$CrCl_3 * 6H_2O$	6 mol %	100	180 min		14.1	[175]
[BMIM][Cl]	9.1	$CrCl_3 * 6H_2O$	3.6 wt %	400^{**}	1 min		91	[112]
[BMIM][Cl]	9.1	$CrCl_3 * 6H_2O$	3.6 wt %	100	60 min		17	[112]
[BMIM][Cl]	9.1	$CrCl_3 * 6H_2O$	3.6 wt %	400^{**}	10 min		1	[112]
DMSO/Water 1:1	5	$CrCl_3 * 6H_2O$	55.5 mmol	140	20 min		21	[184]
[EMIM][Cl]	9.1	$CrCl_4$	6 mol %	80	180 min	71.6	43.9	[94]
ChoCl-Water/MIBK	20	$Cu(NTf_2)_2$	3 mol %	180^{*}	15 min	72	46	[212]
ChoCl-Water/MIBK	10	$Cu(NTf_2)_2$	3 mol %	150^{*}	15 min	90	70	[212]
CPL/LiCl 3:1	10	$CuCl_2$	6 mol %	100	180 min		7.3	[175]
[EMIM][Cl]	9.1	$CuCl_2$	6 mol %	80	180 min	0	0	[94]
DMSO/Water 1:1	5	$CuCl_2$	55.5 mmol	140	20 min		3	[184]
[EMIM][Cl]	9.1	$CuCl_3$	6 mol %	80	180 min	84.7	5.7	[94]
[EMIM][Cl]	9.1	$CuClBr_2$	6 mol %	80	180 min	40.1	3.9	[94]
[EMIM][Cl]	9.2	$DyCl_3$	0.056 mmol	140	360 min	43.5	10	[102]
[BMIM][Cl]	9.2	$DyCl_3$	0.056 mmol	140	360 min	52.6	10	[102]
ChoCl	40	$FeCl_3$	10 mol %	100	30 min		15	[123]
[EMIM][Cl]	9.1	$FeCl_3$	6 mol %	80	180 min	0	0	[94]
DMSO/Water 1:1	5	$FeCl_3$	55.5 mmol	140	20 min		4	[184]
[EMIM][Cl]	9.1	$FeCl_4$	6 mol %	80	180 min	47.4	5.7	[94]
DMSO/Water 1:1	5	$InCl_3$	55.5 mmol	140	20 min		5	[184]
[BMIM][Cl]	9.1	$IrCl_3$ (hydrated)	7 mol %	140	180 min	69.5	7.5	[104]
[EMIM][Cl]	9.1	$LaCl_3$	6 mol %	80	180 min	0	0	[94]
[EMIM][Cl]	9.1	LiCl	6 mol %	80	180 min	0	0	[94]
DMSO/Water 1:1	5	LiCl	55.5 mmol	140	20 min		0	[184]
[EMIM][Cl]	9.1	$MnCl_3$	6 mol %	80	180 min	0	0	[94]
[EMIM][Cl]	9.1	$MoCl_4$	6 mol %	80	180 min	46.3	6.3	[94]
[EMIM][Cl]	9.1	NaCl	6 mol %	80	180 min	0	0	[94]
[EMIM][Cl]	9.2	$NdCl_3$	0.056 mmol	140	360 min	34.8	8	[102]
[BMIM][Cl]	9.2	$NdCl_3$	0.056 mmol	140	360 min	50	12	[102]
[EMIM][Cl]	9.1	$PdCl_3$	6 mol %	80	180 min	19.6	1.2	[94]
[EMIM][Cl]	9.2	$PrCl_3$	0.056 mmol	140	360 min	31.8	7	[102]
[BMIM][Cl]	9.2	$PrCl_3$	0.056 mmol	140	360 min	48.1	13	[102]
[EMIM][Cl]	9.1	$PtCl_3$	6 mol %	80	180 min	64.8	6.8	[94]
[EMIM][Cl]	9.1	$PtCl_5$	6 mol %	80	180 min	87.6	12.1	[94]
ChoCl	40	pTSOH	10 mol %	100	30 min		15	[123]
[EMIM][Cl]	9.1	$RhCl_4$	6 mol %	80	180 min	54.7	3.4	[94]
[EMIM][Cl]	9.1	$RuCl_4$	6 mol %	80	180 min	65	6.6	[94]
ChoCl	40	$Sc(Otf)_3$	10 mol %	100	30 min		9	[123]
CPL/LiCl 3:1	10	$SnCl_4 * 5H_2O$	6 mol %	100	180 min		64.7	[175]
DMSO	9.2	$SnCl_4 * 5H_2O$	10 mol %	100	180 min	97	42	[174]
[BMIM][Cl]	9.2	$SnCl_4 * 5H_2O$	10 mol %	100	180 min	66	12	[174]

[BMIM][BF_4]	9.2	$SnCl_4$*5H_2O	10 mol %	100	180 min	86	32	[174]
[BMIM][PF_6]	9.2	$SnCl_4$*5H_2O	10 mol %	100	180 min	99	2	[174]
[BMIM][Tf_2N]	9.2	$SnCl_4$*5H_2O	10 mol %	100	180 min	100	1	[174]
[BMIM][TFA]	9.2	$SnCl_4$*5H_2O	10 mol %	100	180 min	71	7	[174]
[BMIM][Trif]	9.2	$SnCl_4$*5H_2O	10 mol %	100	180 min	100	2	[174]
[BMIM][Sacc]	9.2	$SnCl_4$*5H_2O	10 mol %	100	180 min	96	4	[174]
[Bpyr][BF_4]	9.2	$SnCl_4$*5H_2O	10 mol %	100	180 min	78	21	[174]
[EMIM][BF_4]	9.2	$SnCl_4$*5H_2O	10 mol %	100	180 min	97	57	[174]
DMSO/Water 1:1	5	$SnCl_4$*5H_2O	55.5 mmol	140	20 min		22	[184]
[EMIM][Cl]	9.1	VCl_4	6 mol %	80	180 min	61.8	7.2	[94]
[EMIM][Cl]	9.2	Yb(Otf)$_3$	0.056 mmol	140	360 min	65	24	[102]
[BMIM][Cl]	9.2	Yb(Otf)$_3$	0.056 mmol	140	360 min	62.5	10	[102]
[EMIM][Cl]	9.2	$YbCl_3$	0.056 mmol	140	360 min	80	12	[102]
[BMIM][Cl]	9.2	$YbCl_3$	0.056 mmol	140	360 min	71.4	5	[102]
DMSO/Water 1:1	5	$YbCl_3$*5H_2O	55.5 mmol	140	20 min		2	[184]
ChoCl	40	$ZnCl_2$	10 mol %	100	30 min		6	[123]
DMSO/Water 1:1	5	$ZnCl_2$	55.5 mmol	140	20 min		0.5	[184]
[BMIM][Cl]	4.8	$ZrCl_4$	10 mol %	220*	3.5 min	72.3	47.8	[208]

*MH, **MH in (W), no temperature specified

Table 9. HMF production from Polysaccharides in the presence of homogeneous catalysts

Substrate	Solvent	Substrate concentration (wt%)	Catalyst	Catalyst amount	Temperature (°C)	Reaction time	Conversion (%)	Yield (%)	Reference
Avicel	[BMIM][Cl]	4.8	$CrCl_3$*6H_2O	10 mg	400*	2 min		61	[112]
	[BMIM][Cl]	4.8	$CrCl_3$*6H_2O	10 mg	100	240 min		17	[112]
Cellobiose	DMA-LiCl/DMF^a	8.4	$LaCl_3$	10 wt %	145	300 min	85	18	[178]
	[EMIM][BF_4]	16.7	$SnCl_4$*5H_2O	10 mol %	100	180 min	100	57	[174]
Cellulose	Water	4.8	$CrCl_3$*6H_2O	10 mg	400**	2 min		62	[112]
	Water	9.1	H_3PO_4	pH_{sol}=2	230	5 min		7	[151]
	[BMIM][Cl]	12.5	$CrCl_3$*6H_2O	7 mol %	120	180 min		54	[160]
	[BMIM][Cl]/ MIBK	4.8	$GeCl_4$	10 mol %	120	30 min	95	35	[105]
	[BMIM][Cl]	4.8	$CrCl_3$*6H_2O	10 mg	400**	2.5 min		62	[181]
	IL-1/MIBK	20	$MnCl_2$*4H_2O	1 ml	180	300 min		38	[213]
	[BMIM][H_2PO_4] / MIBK	20	$MnCl_2$*4H_2O	1 ml	150	300 min	22.83	7.91	[213]
	IL-1/MIBK	20	$CoSO_4$	1 ml	150	300 min	84	24	[106]
Chitosan	Water	0.2	[HMIM][HSO_4] [$FeCl_3$]	1.25 wt %	180	4 hours		44.11	[214]
Inulin	Water	4.8	CO_2	6 Mpa‡	180	90 min		53	[170]
	Water	4.8	HCl	2 ml	180	90 min		53	[170]

	ChoCl	50	$FeCl_3$	10 mol %	90	60 min		55	[123]
	ChoCl	50	$ZnCl_2$	10 mol %	90	60 min		3	[123]
	ChoCl	50	$CrCl_2$	10 mol %	90	60 min		36	[123]
	ChoCl	50	$CrCl_3$	10 mol %	90	60 min		46	[123]
	ChoCl	50	pTSOH	10 mol %	90	60 min		57	[123]
	ChoCl	50	Sc(Otf)$_3$	10 mol %	90	60 min		44	[123]
	[EMIM][BF_4]	16.7	$SnCl_4*5H_2O$	10 mol %	100	180 min	100	40	[174]
Pine Wood	[BMIM][Cl]	4.8	HCl	0.66 g/l	100	60 min		2.1	[181]
	[BMIM][Cl]	4.8	$CrCl_3*6H_2O$	10 mg	400[**]	3 min		52	[181]
	[BMIM][Cl]	4.8	$CrCl_3*6H_2O$	10 mg	100	60 min		6.4	[181]
Sigmacell	[BMIM][Cl]	4.8	$CrCl_3*6H_2O$	10 mg	400[**]	2 min		55	[112]
Spruce	[BMIM][Cl]	4.8	$CrCl_3*6H_2O$	10 mg	400[**]	2 min		53	[112]
Starch	Water-[BMIM][Cl]/ MIBK 1:5	1	$AlCl_3*6H_2O$	150 mg	140[*]	20 min	96	56.4	[215]
	[OMIM][Cl]/ Ethyl acetate	20	HCl	5 ml	120	60 min		30.2	[113]
	[EMIM][BF_4]	9.1	$SnCl_4*5H_2O$	21.6 g	100	24 hours	100	47	[174]

[a] DMF = N,N'-dimethylformamide

[*]MH, [**]no temperature specified

[ǂ]Gaseous catalyst

Table 10. Carbohydrates dehydration using two homogeneous catalysts

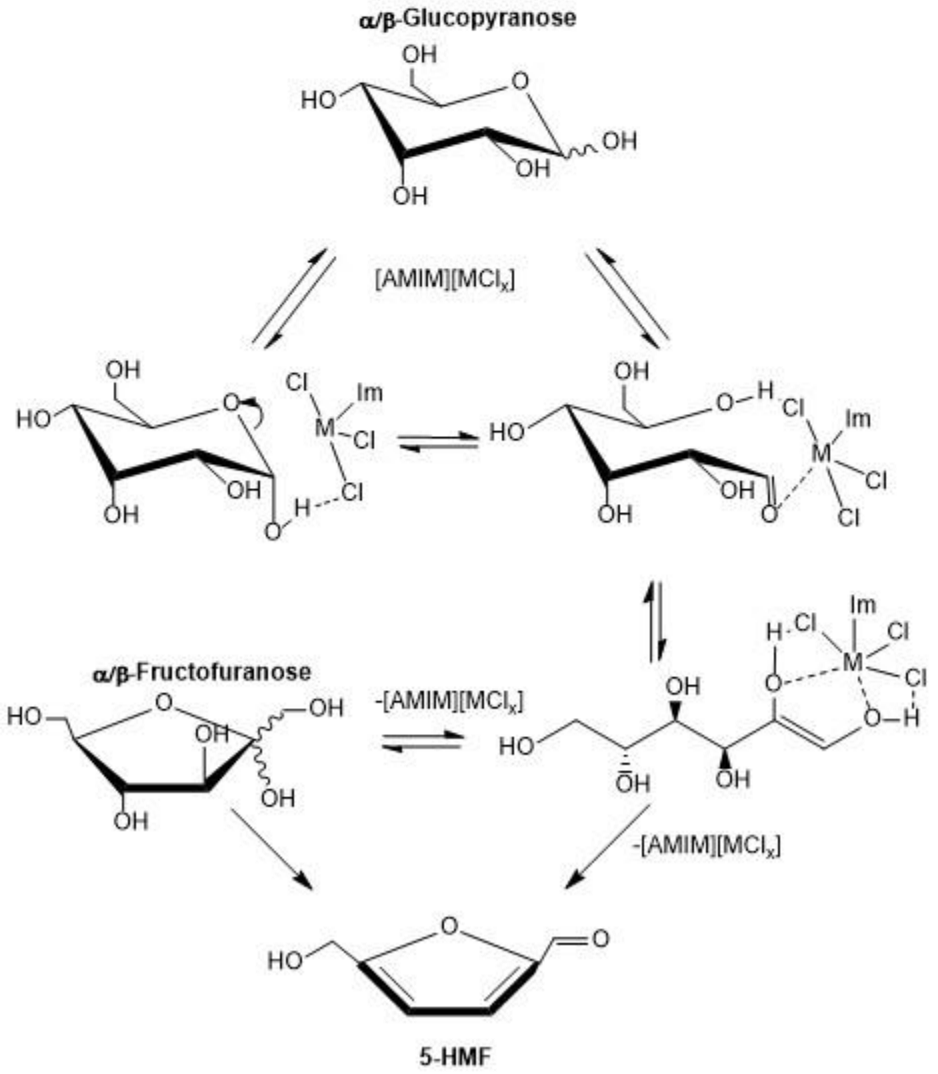
Substrate	Solvent	Substrate Concentration (wt %)	Catalyst	Catalysts amounts	Temperature (°C)	Reaction time	Conversion (%)	Yield (%)	Reference
Avicel	[BMIM][Cl]	4.8	$CrCl_3*6H_2O$/ 2,2'-bipyridine	10 mg/ 17.5 mg	400[**]	2 min		1.6	[112]
	[BMIM][Cl]	4.8	$CrCl_3*6H_2O$/ 2,2-bipyridine	10 mg/ 17.5 mg	100	240 min		2	[112]
Cellulose	[BMIM][Cl]/ Water	2.4	$CrCl_3$/ LiCl	0.155 mmol/ 0.155 mmol	140[*]	40 min		61.9	[183]
	[EMIM][Cl]	9.1	$CuCl_2$/ $PdCl_2$	13.5 µg/ 13.5 µg	120	30 min			[182]
Fructose	DMA-LiCl	10	CuCl/ [EMIM][Cl]	6 mol %/ 40 wt %	120	90 min		83	[147]
	DMA-LiCl	10	H_2SO_4/ [EMIM][Cl]	6 mol %/ 20 wt %	80	4 hours		78	[147]
	DMA-LiCl	10	H_2SO4/ [EtPy][Cl]	6 mol %/ 20 wt %	100	2 hours		81	[147]
	[BMIM][Cl]	9.1	HCl/ $AuCl_3$	7 mol %/ 7 mol %	120	180 min	98	47.8	[104]
	Water	10	HCl/ $CrCl_3$	0.1 M/ 100:3 Fr:Cat (w)	140	25 min	80	30	[197]

	NMP	9.1	$FeCl_3$/ Et_4NBr	0.56 mmol/ 1 mmol	90	120 min	100	86	[206]
Glucose	Water-NaCl/ CPME 1:1	10	HCl/ $AlCl_3$	pHsol=2.5 / 0.025 mmol	175	20 min	89.5	54.5	[198]
	Water	10	HCl/ $CrCl_3$	0.1 M/ 100:3 Fru:cat	140	50 min	55	13	[197]
	Water/ THF 1:2	10	HCl/ $CrCl_3$	0.1 M/ 100:3 Fru:cat	140	180 min	92	59	[197]
	Water	20	$(NH4)_2HPO_4$/ H_3PO_4	0.0076 mol/ 0.006 mol	180	57 min		23.2	[150]
	Water/ dioxane 1:1	20	Pyridine/ H_3PO_4	0.03 mol/ 0.018 mol	228	53 min		45	[150]
Sucrose	[MOIM][Cl][a]	10	HCl/ $CrCl_2$	0.5 M/ 0.2 g	120	60 min		78.5[ǂ]	[180]
	[MOIM][Cl]	50	HCl/ $CrCl_2$	0.3 M/ 0.2 g	120	60 min		61.6[ǂ]	[180]
	[MOIM][Cl]	10	HCl/ $ZnCl_2$	0.3 M/ 0.2 g	120	60 min		68.4[ǂ]	[180]
	[MOIM][Cl]	50	HCl/ $ZnCl_2$	0.3 M/ 0.2 g	120	60 min		42.2[ǂ]	[180]
Wheat Straw	[BMIM][Cl]	2.4	$CrCl_3$/ LiCl	0.155 mmol/ 0.155 mmol	160[*]	15 min		61.4	[183]
	Water/THF 1:3	10	$FePO_4$/ NaH_2PO_4	0.2 g /0.02 g	160	60 min		44	[216]

[a] [MOIM][Cl] = 1-methyl-3-octylimidazolium chloride

[ǂ] yields reported in wt %

[*] MH in W, [**]no temperature reported



Scheme 5. Glucose Isomerization and HMF formation mechanism in imidazolium ILs ([AMIM]) and metal chlorides [MCl$_x$]) [94, 174]

3.2 Heterogeneous Catalysts

Most of the early work on HMF synthesis was performed using homogeneous Brønsted acids, such as HCl and H_2SO_4. Lately however, catalytic HMF production has been predominantly performed through the development of heterogeneous catalytic systems. These systems are usually composed of a liquid phase, including the reactants and a solid catalyst. These solid materials have the advantage of being easily recyclable, having adjustable properties, and functioning as molecular sieves [217, 218]. However, though a strong case can be made for heterogeneous catalysts based on their recoverability and tuneability, many of them, particularly metal-based materials, can be costly, exhibit low HMF selectivity, and can’t really be considered “green” due to their manufacturing process [219].

The shift from liquid Brønsted acids to Lewis acids means that metal halides have been increasingly focused on. The use of these salts allowed for better yields as well as for better recyclability, which are crucial points when developing chemicals in a sustainable manner. Nowadays, there are an increasing number of articles investigating heterogeneous catalysis for the production of HMF. These catalysts are solids and include resins, zeolites, and other minerals (Tables 11 to 13). Solid catalysts are recyclable and versatile, which allow adjusting the acidic and basic active sites. Additionally, some of them, like zeolites, work like molecular sieves which can increase the selectivity of the reaction.

3.2.1. Zeolites

Zeolites are aluminum tectosilicates which can hold exchangeable cations in their three-dimensional framework [220]. They are frequently used in petrochemical and organic synthesis due to their high surface area, tailored active sites and adsorption properties [221]. These minerals can be both naturally occurring or be artificially synthesized. The synthesis of zeolite is not environmentally friendly, therefore considerable efforts have been devoted to improving the sustainability of the process [222].

The production of HMF using solid catalysts has only started a decade ago. An early paper described that the sieving properties of acidic HY-zeolites could dehydrate glucose [218]. It was suggested that given the pore size of the zeolite (0.75 nm), glucose couldn’t diffuse through the catalyst but 1,2-enediol could, and this eventually reacted with Brønsted acidic sites to form HMF. HMF, which has a size of 0.82 nm, remained trapped in the system and was further converted to FA and LA. Similarly, Moreau et al. [223] observed that fructose dehydration to HMF using H-mordenites (H-MOR), which has a low mesoporous volume, offered a high selectivity. They correlated this to the shape selectivity properties of the catalyst as well as to the Si/Al ratio, with optimal ratios between 6.8 and 18. Similar results were observed by Bhaumik et al. [224] when comparing H-MOR to silicoaluminophosphate (SAPO) catalysts. At 175 ^{o}C for 1 hour, they obtained an HMF yield of 63% with H-MOR versus 78% with the SAPO catalyst. Although SAPO catalyst contained the same total acid amount as H-MOR, it was suggested that H-MOR has more strong acid sites leading to further decomposition products, therefore reducing HMF yields.

Using H-beta (H-BEA) zeolite, Shimizu et al. [137] could reach a yield of about 60% HMF from fructose at 120 ^{o}C. Carrying out the reaction under a light vacuum (0.97×10^{5} Pa) improved this value to 97%. Given that the reaction took place in DMSO, it was suggested that the increased yield was due to the removal of water by evacuation. However, other experiments showed that using H-ZMS5 and H-BEA zeolite for glucose, xylose and fructose dehydration would lead to small amounts of HMF [225], or even no HMF and no sugar conversion [226]. The difference in these results is due to the utilization of different solvents. DMSO favors fructose in its acyclic form. An attempt to obtain 5-ethoxymethylfurfural at 70 °C using HY-zeolite was similarly unsuccessful [227]. This was ascribed to the weak acidity of the active sites.

Wang et al. [228] performed experiments using HZSM-5 and observed that Si/Al ratios are inversely correlated to the spatial proximity of the acid sites. A higher acid site density did change the dehydration reaction rate. Also, the HMF reaction activation energy reduced with the proximity of the Brønsted acid sites, which improved the results of the reaction.

The type of active centers in the zeolite can greatly affect the reaction. By incorporating Ti and Sn into large and medium pore zeolites (BEA, TS-1), it was observed that the larger pores of the BEA induced superior glucose conversion as compared to mesoporous TS-1, with the Sn active center showing better conversion. However, Ti displayed a higher selectivity towards fructose [229]. Bermejo et al. [230] suggested that the Sn centers of the zeolite behave as Lewis acids, which protonate C2OH to form enolate intermediates that lead to isomerization of glucose. Later papers described a combination of the Lewis acidic Sn-BEA and Brønsted acidic catalyst HCl, as well as Amberlyst 70 (Amb-70) [205, 231]. This allowed the dehydration of glucose to obtain high HMF yields. The stability of the zeolite at high temperatures and acid levels was also analyzed, showing that it did not suffer any structural changes, allowing for good recyclability. Impregnation of zeolites can also have a negative effect. Faba et al. [232] characterized beta zeolites after adding ruthenium to increase their active sites. However, the addition of the metal also led to a reduction in surface area as well as a decrease in pore volume.

Applying zeolites as hydrolyzing agents has also been studied. Chambon et al. [233] could not observe a catalytic effect from H-USY zeolite when used for cellulose hydrolysis. The authors posited that the low reactivity could be due to the leaching of Si under their hydrothermal conditions, which considerably decreased the Si/Al ratio of the zeolite. Lanzafame et al. suggested that given the size of cellulose, all catalytic activities took place on the surface of the zeolite, with little improvement from cellulose/zeolite ratios above 10 [234]. Nevertheless, glucose selectivity is negatively influenced at lower ratios, since glucose can interact with the internal crystal structure. Extended reaction times led to HMF formation when using H-mordenite (H-MOR) and H-BEA, with a positive correlation between acid sites and HMF formation. The use of IL [EMIM$^+$][Cl$^-$] allowed for cellulose dissolution and a better diffusion in H-form zeolites. Combining these with metal halides resulted in HMF yields of up to 40% [235]. The high HMF values are explained as a result of the formation of HCl from the zeolite's Brønsted acid sites, the halide group of the IL, and the metal salt [235, 236].

Through the deprotonation of Brønsted acidic sites or the dissolution of their Si groups, zeolites can act as homogenous catalysts since they reduce the pH of solutions [237, 238]. Si dissolution and dealumination of zeolites can also occur due to the acid products from HMF degradation, altering their catalytic activity. Si groups dissolution was shown to be limited by the solubility while dealumination was not, as it was mostly driven by low pH values. This effect led to a slow degradation of the zeolite (1-2 wt%). Nevertheless, calcinating beta zeolites also induced a cleavage of Si-O-Al groups, forming Al species. These increased the amount of active Lewis acid sites, increased the bifunctionality of the catalysts and improved its efficiency in dehydrating carbohydrates to HMF [239, 240].

Additionally, when using unpurified lignocellulosic materials, zeolites exhibited lowered catalytic activity after reuse [241]. Metal exchange on the Brønsted acid sites of the zeolite reduced their acidity. Nevertheless, this reduction was minuscule relative to the concentration of metal ions required for this degradation.

It is noticeable that, while zeolites have potential as recyclable catalysts, there are several variables determining their actual efficiency. Pore size, Si/Al ratio, strong/weak acid sites ratio, as well as their level of hydrophobicity play an important role. As described by Hu et al. [236], a high Si/Al ratio will generally lead to stronger acid sites, lower acid density, and vice versa. A proper balance of strong and weak acid sites is needed to prevent the formation of decomposition products. An ideal zeolite for cellulose dehydration will hydrolyze cellulose on its surface, while allowing glucose isomerization and further dehydration inside the crystalline structure. As for whether a zeolite can be considered as a “green” catalyst, this will depend greatly on its origin and reusability.

3.2.2. Functionalized silica materials

Several other solid inorganic materials can be used as solid catalysts, such as naturally occurring minerals (e.g. montmorillonite), synthetic frameworks (e.g. MCM-41), or simpler metal and metalloid oxides (e.g. Al_2O_3 and ZrO_2). As with zeolites, it is their crystalline structure with multiple active sites and ease of recovery that makes them very interesting as catalysts. Also, the same parameters must be considered (pore size, surface area, acidity, and active site types and distribution).

Mobil composition of matter (MCM) materials are some of the most popular solid catalysts used. They are mesostructured aluminosilicates with a larger pore size than zeolites and a hexagonal array of channels [218, 242]. However, these structures do not possess Brønsted acid sites and require some form of process to make them active. Lourvanij et al. used a HCl solution to increase the acidic activity of MCM-20 [218]. In their experiments, MCM-41 and MCM-20 exhibited a better HMF selectivity than HY-zeolite, but both MCM catalysts presented lower glucose conversion, resulting in similar HMF yields. Jimenez-Morales doped MCM-41 with aluminum, which effectively increased the Si/Al ratio as well as both Brønsted and Lewis acid sites. This resulted in higher conversion and HMF yields than their non-doped counterparts [243].

A similar mesoporous silica (SBA-15) has been used as support for solid catalysts. Crisci et al. [244, 245] modified SBA-15 grafting thiopropyl, propylsulfonic, and organosilane groups to generate bifunctional catalysts. The use of organosilane-grafted TESAS-SBA-15 to dehydrate fructose resulted in a 60% yield of HMF (130 ^{o}C, 141 min). When this type of ordered, functionalized catalysts were compared to similar nonordered silicas, the SBA-15-based catalysts showed a much higher selectivity (75% vs 20% of non-ordered). SBA-15 organosilicas were also more stable and less prone to hydrothermal degradation [246]. In a more recent experiment, Duo et al. [247] prepared a functionalized silica by using an ionic resin and tetraethyl orthosilicate (TEOS). Fluorinated Aquivion resin was used as both template and source of SO_3H active sites (Aquivion@silica). The catalyst was very effective in dehydrating fructose to HMF (85% at 90 °C and 2 h). The researcher also tested for leaching of active groups and observed that no SO3H could be found in the solution, suggesting that the slight decrease in activity (5% HMF yield drop after 4 runs) was due to fouling of the material.

3.2.3. Metal oxides and minerals

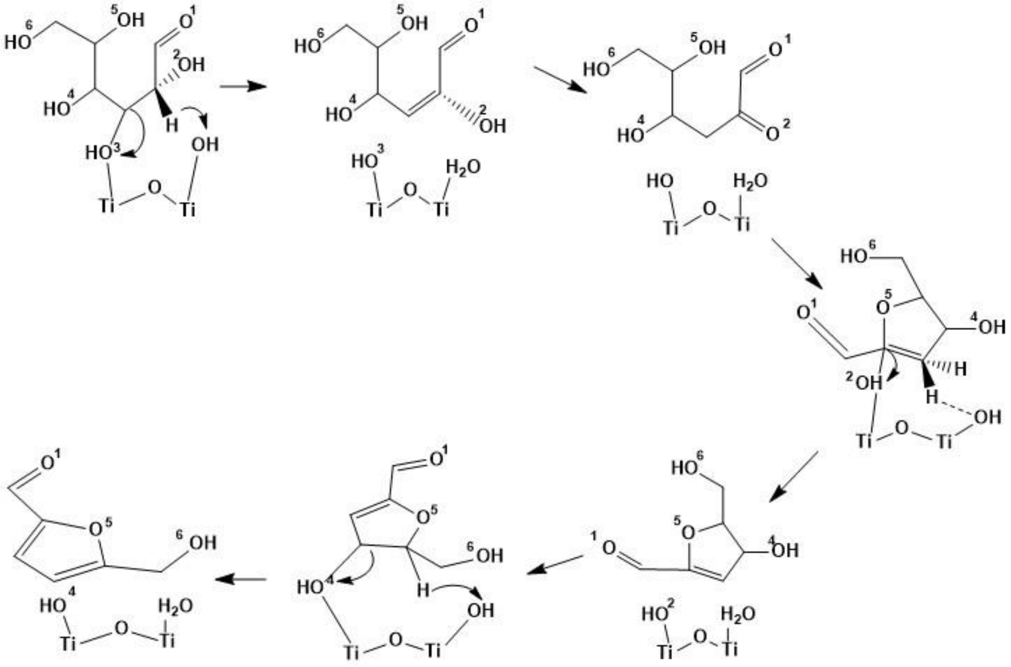
Metal oxides and phosphates have been widely used as heterogeneous catalysts. Particularly, niobium oxide (NbO) and phosphate (NbP) have often been used for HMF production due to their character as strong acid catalysts, their low cost, and low toxicity [248-252]. Both the oxide and the phosphate have a strong Brønsted acidity, with Hammett values of -5.6 and -8.2 respectively [249]. When used for fructose dehydration, niobium phosphate showed good conversion values at low reaction temperatures (100-110 °C), but the HMF yield was low (24 % after 30 minutes) [249]. It was also observed that when using NbO, no rehydration of HMF was observed and thus, no LA was formed. This suggested that for the water-fructose-NbO system, HMF is a final product whose yield increases with fructose conversion [250]. Pretreatment of NbO with phosphoric acid increases its surface area as well as the amount of strong acid sites [253]. This pretreated catalyst, when used for fructose and glucose dehydration, gave HMF yields of 89 and 49% respectively at 160 ^{o}C [254]. Similar results were obtained by Antonetti et al. [255] when using this and phosphate zirconium under microwave heating (ZrP). NbO could also hydrolyze Jerusalem artichoke but lower HMF yields were obtained (22%) [254]. Another pretreated niobium catalyst, sulfated niobium oxide (MNO-S), possesses a mesoporous structure and a surface area 50 times larger than NbO [256]. This catalyst proved to be more efficient than NbO, obtaining up to a 72% HMF yield from fructose.

Al_2O_3 is another popular choice for a solid catalyst, particularly in its γ and η forms since they have a larger surface area and pore size than the α form [257]. Pt/γ- Al_2O_3 has been reported to promote the hydrolysis of cellulose to glucose in a H_2 atmosphere [258]. It is suggested that the use of Pt splits H_2 or water and improves hydrolysis, while Al_2O_3 active sites further the catalytic activity of the system [259]. Cellulose conversion was also investigated by Chambon et al. [233, 260] using tungstated alumina (AlW), a Lewis acid which has a higher acid sites-density than Pt/γ- Al_2O_3, and tungstated zirconium (ZrW) which exhibits both Brønsted and Lewis acidities. Experimental runs using AlW and ZrW gave cellulose conversion values of 47 and 42% respectively. However, the dominant product in both cases was lactic acid. When Pt was supported in AlW, the conversion rate increased to 70%, but led to the formation of acetol and propylene glycol. The authors suggested that pyruvaldehyde was formed as an intermediate product, which depending on the catalyst undergoes different transformations.

ZrO_2 has been reported to act as a basic catalyst promoting glucose isomerization [51, 52], while sulfated zirconia has been successfully used for HMF formation from fructose [261]. Using SO_4^{2-}/ZrO_2-Al2O_3 (CZSA), Yang et al. [262] exploited the catalyst's bifunctionality to obtain up to 55% HMF yield from starch. These values were higher than other solid catalysts, like H- and BEA-zeolites, or ion-exchange resin Amberlyst 15. The researchers observed a better performance when the Zr/Al ratio was 1:1, while an excess of acid sites led to further decomposition products. Elsayed et al. [263] created a sulfonated Fe_3O_4 core shell magnetic catalyst (Fe_3O_4@SiO_2-SO_3H). The researchers were able to obtain an HMF yield as high as 70% from glucose. The authors attributed these yields to the isomerizing effect of Fe^{+3}, which acts as a Lewis acid.

Recently, Li et al. [264] performed a DFT study where it was calculated that anatase (TiO_2) activated glucose on C3OH. This either led to a furanose intermediate and a cyclic route, or an acyclic route through enol dehydration. Anatase presented both Lewis acidity and basicity, which allowed the catalyst to simultaneously activate with H and OH groups from glucose, leading to the direct formation of HMF without isomerization (scheme 6).

With a combination of ball-milling pretreatment and $Ca_3(PO_4)_2$, Mimura et al. [265] were able to obtain up to 35% HMF from cellulosic materials in water, albeit with high temperature and time values (200°C, 2 hours). Of interest was the use of cotton-based clothing waste as substrate, from which 30% HMF could be obtained.



Scheme 6 TiO_2 catalyzed glucose dehydration based on reference [264]

3.2.4. Heteropolyacids

Heteropolyacids (HPAs), particularly those of the Keggin type, are known to have a good catalytic activity. They have a very strong acidity, even stronger than usual mineral acids such as HCl. They have well defined structures, and their modifiable acidity makes them very interesting in the field of catalysis [266].

While HPAs can be soluble depending on the solvent, their salts can be used as heterogeneous catalysts. HPAs, such as 12-phosphomolybdic acid (12-MPA, $H_3PMo_{12}O_{40}$), 12-tungstophosphoric (12-TPA, $H_3PW_{12}O_{40}$), and 12-tungstosilicic acids (12-TSA, $H_4W_{12}SiO_{40}$), were tested for glucose dehydration in IL [$BMIM^+$][Cl^-] [267]. The protons of 12-TPA were substituted by Ag^+, resulting in the microporous $Ag_3PW_{12}O_{40}$ salt. The catalyst efficiently converted fructose and glucose to HMF in a 77.8% (120 ^oC, 90 minutes) and 76.3% (130 ^oC, 4 hours) yield respectively [268]. The HPA was shown to have both Brønsted and Lewis acidity and thus, was more effective than Lewis acid salt $AgNO_3$ or Cs-exchanged HPA $Cs_3PW_{12}O_{40}$. A similar experiment by Zhao et al. [269] who used $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ reported higher yields for this salt at similar experimental conditions, but with a higher feed fructose concentration (50%).

When 12-TPA was used in a DMSO solution, HMF was obtained at up to 92% yield (120 ^oC, 30 minutes). However, the catalyst was soluble in that system [92]. Protons were exchanged for Cs^+ to create a heterogeneous salt. While also effective in promoting HMF formation, the salt gave lower yields than the soluble acid, even lower than the DMSO alone, albeit with shorter reaction times. Comparable results were obtained when a MCM-41 silica was used as support. The authors attributed this effect to the strong adsorption of fructose to the surface of the catalysts, slowing down the HMF production. The lower yields could be offset by an improved handling and recovery of the heterogeneous catalysts. Similarly, He et al. [270] impregnated TiO_2-ZrO_2 mixed oxides with TPA to obtain a catalyst for glucose dehydration to HMF. After 4 hours at 160°C in a tetrahydrofuran (THF):water biphasic system the maximum HMF yield was 51.3%.

A ChoCl-HPA catalyst was synthesized from 12-TPA by Zhang et al. [271]. It was used to hydrolyze and dehydrate cellulose with noteworthy results. After a reaction time of 8 hours at a temperature of 140 °C, HMF was obtained in a yield of 75%. Results with the homogeneous 12-TPA showed that HMF formation was possible due to its strong acidity, but the selectivity was greatly improved by ChoCl.

3.2.5. Carbon-based catalysts

Carbonaceous catalysts have the potential to be very sustainable solid catalysts. Depending on their biomass source and preparation methods, carbon supports can be cheaper, sustainable and produce limited toxic waste. In contrast, popular metal catalysts, such as zinc, copper and chromium, can be expensive and are also subject to depletion [272-274]. The morphology of carbonaceous catalysts can vary greatly (shape, particle size and surface area), they offer good support for active sites, have a higher thermal stability than ion-exchange resins, such as Amberlyst and Dowex and can be produced from several types of biomass-derived waste materials [219, 275-277]. Using cheap waste biomass, such as agricultural and food waste, both costs and sustainability can be greatly improved. However, current processes rely on using H_2SO_4 or fuming H_2SO_4 for functionalization, which requires washing the material with large quantities of water and other solvents to remove free acid and organic compounds.

Several carbon-based catalysts have been developed recently and tested for HMF production. A glucose-based sulfonated carbon catalyst was created using PTSA and was tested for fructose dehydration in different solvents. It was found that almost quantitative yields were obtained in DMSO [275], despite the catalyst having a considerably smaller surface area than other solid catalysts. This good performance was ascribed to the presence of SO_3H groups, carboxylic acids and phenols [275, 278]. Also, DMSO helped the facile tautomerization of fructose to its fructofuranosyl form. Similarly, Guo, Fang and Zhou [279] tested different carbonaceous materials, like glucose, lignin, and bamboo to name a few, and observed a better catalytic activity with the sulfonated lignin catalyst (LCC). Using H_2SO_4-impregnated carbon, microwave heating, and a mixture of $[BMIM^+][Cl^-]$ and DMSO as solvents, the researchers obtained up to 84% HMF yield (110 ^oC, 10 minutes). When comparing the SO_3H content using the same supports, a positive correlation was observed between the acid sites and yields, but such a trend could not be observed among different materials [280].

Carbon catalysts have in general smaller surface areas than other solid catalysts. The activation of the carbons via pretreatment can increase their area. However, a study by Qi et al. [278] showed that while the activation did increase considerably the surface area of a cellulose-based catalyst (CSS), the amount of accessible acid sites in the activated version (a-CSS) diminished. At high carbonization temperatures, the structure of the catalyst changed considerably, forming large rigid carbon sheets. This made the access to the SO_3H groups difficult, rendering the catalyst less active [281]. The substitution of SO_3H by phosphorylation also led to catalytically active carbons [282]. The phosphorylated mesoporous carbons (P/N-0.25, P/N-0.5, P/N-75) showed good catalytic activity, but this could not be correlated to the acid sites or P group density on the surface. On the other hand, the selectivity towards HMF showed a positive correlation with the acid site density. Furthermore, it was suggested that the catalytic activity was dependent on the acid site accessibility. Deng et al. [283] showed that by using microporous carbonaceous material, steric hindrance may have helped prevent the formation of humins and oligomers, and therefore promoted HMF formation. A similar phosphorylated carbon (PC-4) was made by Yang et al. [284], who observed an increase in acid sites with higher acid concentrations, but this also lead to smaller surface areas. Further carbonization had an inverse effect, with acid sites diminishing and area increasing with higher temperatures. The highest HMF yield obtained from fructose was 80.4%, at 170°C.

It has recently been demonstrated that the functionalization of carbonaceous materials is not necessary to provide catalytic activity. Via hydrothermal carbonization of glucose, Qi, Liu and Lian [285] created a carbonaceous microsphere material containing -COOH and phenol groups. The material proved to be very effective in producing HMF from fructose. A proposed structure for sulfonated carbon catalysts and a suggested catalytic mechanism are shown in schemes 7 and 8.

Using wood biochar as support for a sulfonated catalyst (BSO_3), Xiong et al. [286] hydrolyzed a aqueous maltose solution (5% wt). The researchers obtained 85.4% glucose at 160°C after 40 minutes. Further conversion to HMF was not possible due to the low acidity of the material. It was also observed that higher temperatures were needed to obtain HMF from fructose (160-180°C). Throughout the entire temperature range tested, HMF yields reached a plateau of 42% after 60 minutes. Despite the aqueous medium, the low amounts of LA and FA present in the solution suggest that the low HMF selectivity is not due to rehydration, but to polymerization reactions.

Brønsted-Lewis acidic functionalization can also be achieved in carbonaceous supports. A Niobia/carbon (Nb/C-50) composite obtained from glucose, was effective in dehydrating hydrolyzing and dehydrating ball-milled cellulose to HMF with high yields (53.3%), after 8 h at 170 °C [287]. Functionalization of carbonaceous support with iron and H_2SO_4 can produce a magnetically recoverable material with Lewis acidic properties [288-290].

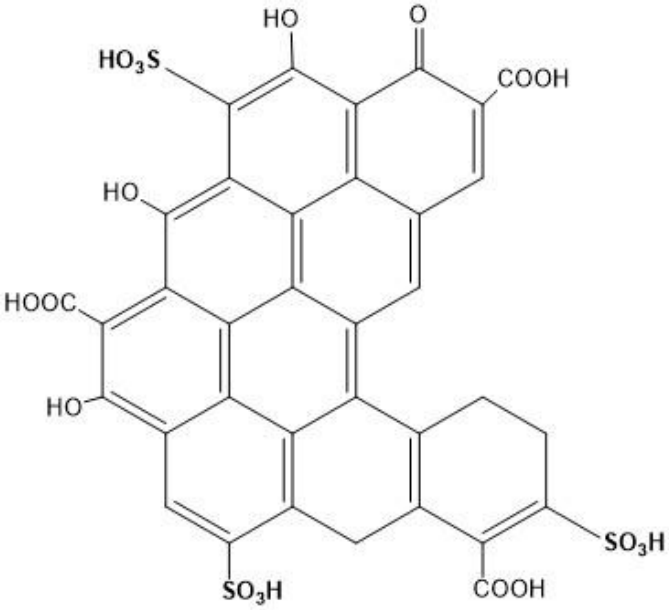
3.2.6 Organic catalysts

Ion exchange polymeric resins have also been extensively used in a broad variety of catalytic reactions. The most commonly used types are Amberlyst and Nafion. Amberlyst, is a polystyrene resin with sulfonic acid groups, while Nafion is a sulfonated tetrafluoroethylene perfluoro-2-(fluorosulfonylethoxy)propyl vinyl ether copolymer. Both resins have considerably smaller surface area as compared to mineral catalysts, or even carbonaceous catalysts. Surface areas can be increased by producing silica-resin composites, where the polymer particles act as the active sites [291].

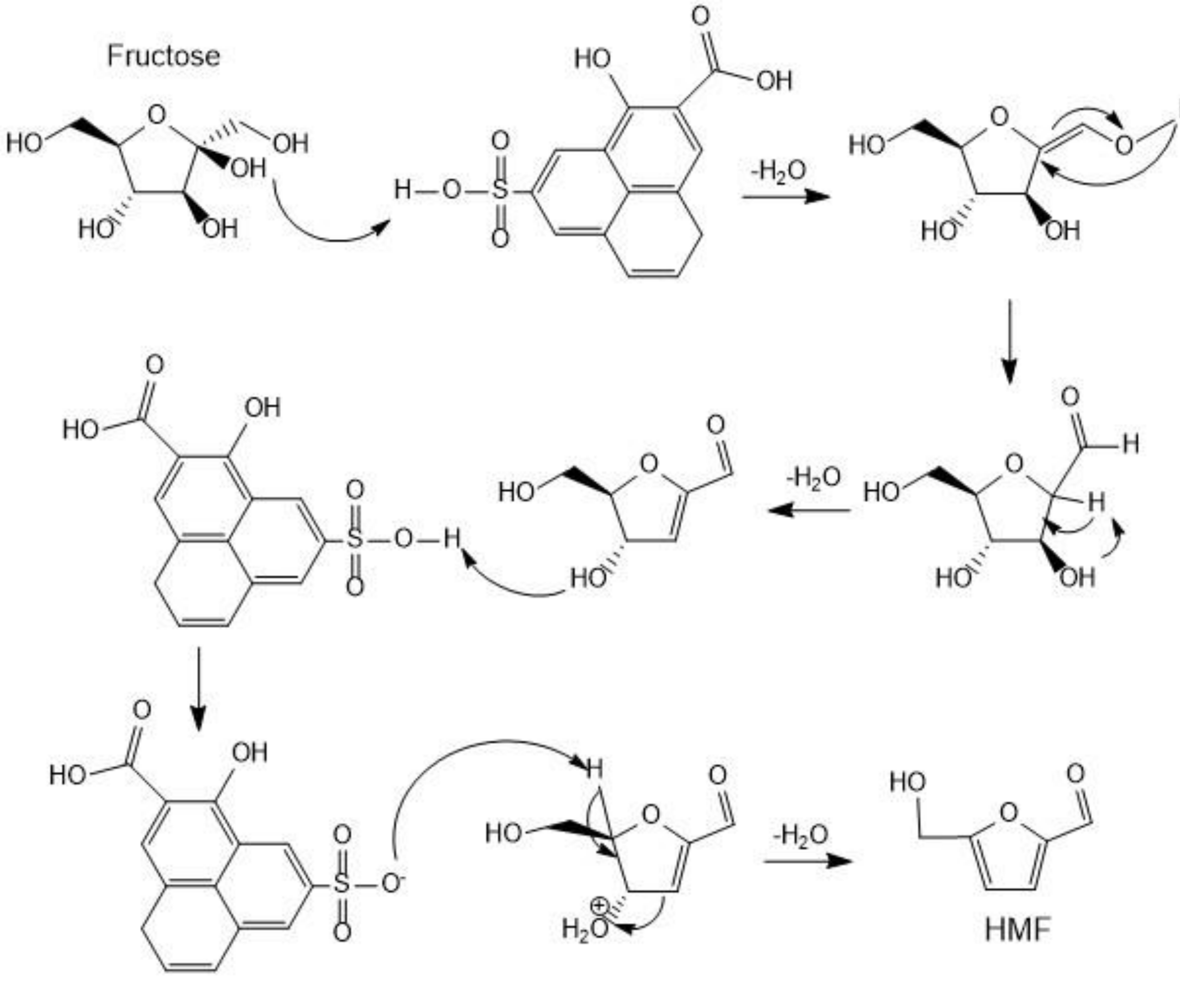
Amberlyst-15 has been known for quite some time as an effective catalyst for fructose dehydration [90, 91], but requires long reaction times. More recent experiments showed improved yields at higher temperatures (110-120 ^{o}C) and shorter times (< 2 hours), resulting in almost 100% HMF yield from fructose in DMSO at high fructose concentrations (50 wt%) [137, 292]. These results were attributable to its high concentration of sulfonic acid sites [293]. Nafion was equally effective as Amberlyst-15 at lower concentrations. However, when used for glucose dehydration, Amberlyst-15 produced anhydroglucose rather than HMF [226, 294]. A combination of hydrotalcite or zirconosilicates, which proved to be effective for glucose to fructose isomerization, and Amberlyst-15 was more effective to produce HMF from glucose, arabinose, raffinose and lactose, with a 42% yield [294-297]. The presence of water was detrimental to the catalytic activity of the resin [294]. When used in combination with ILs, it has been observed to hydrolyze cellulose in a very controlled fashion [234, 298, 299], possibly due to its Brønsted acidic properties. Recently, a CrCl3-coated Amberlyst-15 resin was observed to dehydrate glucose to HMF with a yield of 46.4% [300]. However, the recyclability of the material was low: HMF yields from fructose dropped from 90.6% to 63% after the fourth cycle, which is related to the reduction of both SO_3H and Cr active sites.

Ordomsky et al. [301] took a different approach by using a polypropylene-coated solid carbon foam as a support. They grafted it with sulfonated polystyrene (PS-PP/C-foam). Solid foams offered a higher surface area and an easier catalyst recovery. Similarly, Huang et al. [302] used mesocellular silica foams (MCF) impregnated with Nafion-15 resin (Nafion-15/MCF), and obtained high HMF yields in DMSO (89,3). This was explained by the synergic effect between the silanol groups on the surface of MCF and Nafion's strong attraction to electrons, weakening the hydroxyl bonds in fructose.

More recent attempts have been made to create specialized catalytic polymers. Tertiary amines have been observed to catalyze the isomerization of glucose to fructose [303, 304]. Zhu et al. [305] used polyaniline to develop a new catalyst by grafting formyl groups to the nitrogen atoms between the phenyl rings of the chain (FS-PAN), increasing its basicity. When the catalyst was used in conjunction with DMSO, it produced HMF from fructose at a 90% yield (140 ^{o}C, 4 hours). However, it performed poorly when used for glucose dehydration. Another catalyst, poly-divinylbenzene polymer grafted with Cr(III) and $SO_2NHSO_2C_4F_9$, was more successful in glucose dehydration which led to an HMF yield of 57% (140 ^{o}C, 30 minutes) [306]. The improvement in the HMF yield was attributed to the Cr(III) groups which isomerized the monosaccharide to fructose. This catalyst was also recyclable, giving stable HMF yields for 12 cycles. Although the polymeric catalyst could deliver good yields, the same functional groups supported in SiO_2 performed slightly better [306]. Carbon nanotubes (CNTs) were used to increase the microwave absorption of polyaniline by forming a shell around the CNTs. This catalyst (CP30) resulted in higher fructose dehydration rates and HMF yields with increasing microwave power [307].



Proposed structure of sulfonated carbon catalyst based on [281, 308, 309]



Scheme 7 Proposed catalytic pathway for the dehydration of fructose with sulfonated carbonaceous materials, based on reference [310]

3.2.7 Catalyst deactivation

Despite the advantages their solid-state offer, the aforementioned materials still suffer from a loss of catalytic activity over time. Catalyst deactivation can still be a driving factor on the price of HMF, depending on its frequency. Bartholomew [311, 312], classified this process in mechanical (fouling, attrition/crushing), thermal (degradation) and chemical (poisoning, phase reactions).

Most heterogeneous solid catalysts are susceptible to fouling due to possible accumulation of humins or even residual substrate. Washing and vacuum drying have been suitable methods for prolonging catalytic activity [267, 285, 313]. Calcination can also be used to remove blockage from active sites as well as adsorbed by-products [314], provided the material's thermal stability allows it.

Sulfonated ionic exchange resins, such as Amberlyst and Amberlite can also suffer from thermal degradation and therefore have a low maximum operational temperature (40-120°C) [315, 316]. Nevertheless, there are a few cases where Amberlyst has been successfully used at higher temperatures: Wrigsted et al. [201] and Herbst et al. [317] used Amberlyst-38 at 160°C (MH) and Amberlyst-15 at 130°C respectively, for fructose dehydration. Perfluorinated resins such as Nafion, have a higher thermal stability and can be used up to 280°C [291]. Similarly, the addition of fluorinated IL to sulfonated biochar increased its thermal stability, keeping HMF yields and turnover number constant after 6 runs [318].

Chemical deactivation can be observed in the form of leaching of active sites. Chambon et al. [233] observed leaching of different active sites in different catalysts. The experiment's hydrothermal conditions used to obtain HMF (190°C) lead to a reduction of 33% Si in H-USY zeolites, 43% of sulfur in sulfonated carbons, and 15% sulfur loss in ZrS. Li et al. [319] observed also leaching if aluminosilicates from zeolites, but the leached Al-O-Si composite was not catalytically active. A similar leaching effect has been observed in phosphorylated carbons, with a loss of over 80% of total acid sites after 4 cycles of use [284].

4. Insights on production rate of HMF

It is important to note that, while several articles report very high yields, their results are in the end impractical. By using the values of substrate concentration, reaction time and yield, it is possible to calculate the effective HMF output in g-min^{-1}. It is reported that about 13% of the total world oil demand arises from the chemical industry, equivalent to approximately 76,000 m^3/h of crude oil [1]. By comparison, one of the most efficient processes that uses cellulose as feedstock (86.2 % HMF yield) would require about 154 million m^3/h to produce the equivalent amount of HMF. Alternatively, a less efficient but much faster process (10.9% HMF yield) requires 867,000 m^3/h; almost 14 times the volume. These numbers highlight the importance of developing systems that are efficient, fast and can handle highly concentrated solutions.

HMF isolation and purification are extensive topics, and a detailed discussion is beyond the scope of this article. Nevertheless, it is clear that high in situ yields are of no use is not complemented by efficient extraction procedures. This is especially true if the solvent used is a high polarity, high boiling point solvent like DMSO, DMF, or an ammonium ionic liquid [320]. A combination of high vacuum and entrainers may, for instance, be required to separate HMF from an ionic liquid [321]. While hydrophobic zeolites can be used to selectively remove HMF from aqueous solutions [322], their efficacy is greatly reduced in ternary solutions also containing DMSO [323]. One alternative is to use a low-boiling extraction solvent like hexafluoroisopropanol (HFIP), which was a boiling point of around 58 ^{o}C, as compared to 189 ^{o}C for DMSO [324]. Another is to use methods that integrate HMF synthesis with its isolation. One such system was outlined by Simeonov, et al., and involved separation of the catalytic medium by crystallization followed by isolation of HMF by evaporation of the organic solvent. Using fructose as feedstock and tetraethylammonium bromide (TEAB) as solvent, they obtained, in a continuous process, isolated HMF yields of around 90% at purities of 91-97% [325]. A similar system using Cr^{3+} modified ion exchange resins as catalysts gave isolated yields of up to 70% from glucose [326]. A method utilizing NaOH neutralization to isolate HMF in high yields and with high purity from an autocatalytic system has also been demonstrated [327]. It is clear that more research is required in this area so as to develop efficient HMF isolation methods that can be scaled-up easily.

Currently, industrial scale synthesis of HMF is almost non-existent. The only publicly-listed facility currently in operation was developed by AVA Biochem BSL AG (Muttenz, Switzerland) [11, 328]. The plant was reported to produce 20 ton/year of HMF during its first phase of operation, with plans of increasing this value to 40 ton/year by the end of 2014 [329], but more recent numbers have not been published, Furthermore, it is stated that, while the site will be capable of processing waste biomass, as of 2014 it used fructose as feedstock. Novozymes A/S, a Denmark-based company, holds patents for the production of HMF since 2011 [330, 331], but there has been no mention of any plans to produce HMF at a large scale.

A techno-economic analysis of HMF and dimethylfuran production from fructose from 2010 arrived at an HMF minimum selling price (MSP) of 2.04 USD/kg [332]. A study by Kazi et al. [333] showed that a 20% increase in yield could reduce the MSP by 15.7%. The analysis also suggested a minimum selling price of 1.03 USD/kg (1.25 USD/kg) The study uses a highly concentrated fructose feed (26 wt%) and estimates 83% HMF yield. It is important to mention that in this study, the costs of utilities and waste management is calculated as purchased from a third party, and the cost of storage facilities for raw materials, products and waste are not calculated, which can considerably increase total installed equipment costs, legal fees, utilities, and construction expenses. Both of these studies used HCl as model catalyst, which might also lead to increased maintenance and waste management costs.

A more recent analysis that used a more conservative HMF yield (47%) and 20% substrate concentration, arrived at an MSP of 2.21 USD/kg, and also noted that fructose concentration was an important driver of the HMF price [34]. Additionally, it was observed that the use of acetone as solvent, while increasing solvent cost in respect to water, reduced the energy consumption considerably enough to offset its price. For this analysis, niobium phosphate was used as catalyst, which the authors calculate at 60 USD/kg. No mention of the recovery or regeneration process of the catalysts is mentioned. The results were not competitive when compared to p-xylene (0.84 USD/kg) [334], a compound which HMF could theoretically replace.

A study on the economic feasibility of a biorefinery showed that it is possible to produce HMF from sugarcane bagasse at costs as low as 0.35 USD/kg [335]. In this scenario, cellulosic biomass is used to produce ethanol, furfural and HMF, with the last two being used to obtain octane and nonane. This multiproduct biorefinery scheme allowed to distribute production costs through all products, effectively reducing HMF price. In a scenario where only HMF and furfural are produced, the price shoots up to 0.94 USD/kg. However, no mention is made as to the selected value for HMF or furfural yields.

These results highlight the importance of developing a process that can utilize cheap, sustainable feedstock and catalysts that can help reduce the production price of HMF and its derivate products. Further research into catalytic systems that can handle highly concentrated substrate solutions would greatly benefit the market viability of HMF as a platform chemical. Additional studies similar to the ones mentioned in this section are needed to assess the feasibility of catalytic systems.

Table 11. Fructose dehydration with heterogeneous catalysts

Solvent	Substrate Concentration (wt%)	Catalyst	Catalyst concentration	Temperature (°C)	Reaction time	Conversion (%)	Yield (%)	Reference
Water/MIBK 1:2.25	30	12-AgTPA	0.08 g	120	60 min	82.8	77.7	[268]
Water/MIBK 1:2.25	30	12-AgTPA	0.08 g	120	60 min	46	38	[268]
DMSO	2.5	12-CsTPA	10:1 Fru:Cat (w)	120	40 min	100	80	[92]
DMSO	2.5	12-TPA	10:1 Fru:Cat (w)	120	30 min	100	92	[92]
DMSO	2.5	12-TPA/MCM-41	10:1 Fru:Cat (w)	120	60 min	100	80	[92]
DMSO	3.2	Aquivion@silica	0,016 mmol H^+	90	2 hours	100	85	[247]
[BMIM][Cl]	9	a-CSS	2:1 Fru:Cat (w)	80	20 min		65	[278]
DMSO/[BMIM][BF4]	8	Amberlyst-15	70 mg	80	32 min		75	[90]
DMSO/[BMIM][BF4]	8	Amberlyst-15	143 mg	80	32 min		87	[90]
DMSO	3	Amberlyst-15	0.02 g	120	120 min	100	92	[137]
Water	4.8	Amberlyst-15	0.4 g	120	24 hours	57	15	[336]
DMSO	3	Amberlyst-15	0.06 mmol H^+	90	120 min	34.5	26.3	[302]
N,N-DMF	3.2	Amberlyst-15	0.1 g	100	3 hours	99	73	[226]
DMSO	3	Amberlyst-15-p^+	0.02 g	120	120 min	100	100	[137]
DMSO	7	Amberlyst-70	0.2 mmol H^+	140	60 min	100	93	[293]
DMSO	7	Ar-SBA-15	0.2 mmol H^+	140	60 min	100	79	[293]
DMSO	1	b-cyclodextrin-SO_3H	100 wt%	140	120 min		96	[337]
DMF	1	b-cyclodextrin-SO_3H	100 wt%	140	120 min		92	[337]
Isopropanol	1	b-cyclodextrin-SO_3H	100 wt%	100	120 min		63	[337]
Water	1	b-cyclodextrin-SO_3H	100 wt%	140	120 min		0	[337]
Water		BSO_3	1:10	160	15 min	60.4	42.3	[286]
Water/Ethanol 3:7	5.6	C/MCF	10 g	140	4 hours	93	39	[338]
Water/Ethanol 3:7	5.6	C/SBA(45)	10 g	140	6 hours	89	39	[338]
DMSO	5.7	Cellulose-Sulfuric acid	50 mg	100	45 min	100	93.6	[339]
DMA	5.7	Cellulose-Sulfuric acid	50 mg	100	45 min	97.8	90.5	[339]
NMO	5.7	Cellulose-Sulfuric acid	50 mg	100	45 min	96.7	87.2	[339]
DMF	5.7	Cellulose-Sulfuric acid	50 mg	100	45 min	98.3	85.5	[339]
Ethanol	5.7	Cellulose-Sulfuric acid	50 mg	100	45 min	27.8	8.7	[339]
Water	2.5	CP30	50 mg	160	30 min	80	58	[255]
DMSO	5	Carbon Sphere-2	0.1 g	160	90 min	100	74	[340]
Water/MIBK 1:5	30	$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	0.128 g	115	120 min	94	77.6	[269]
Water/MIBK 1:5	30	$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	0.128 g	115	60 min	85.6	74	[269]
[BMIM][Cl]	9	CSS	2:1 S:C w	80	20 min		76	[278]
[BMIM][Cl]	0.9	CSS	1:5 S:C w	80	10 min		83	[278]
Water	1.8	Ct1*	5 mg	170	4.5 hours	70.9	50.1	[283]
Water	7	Ct2*	5 mg	170	4.5 hours	100	59.9	[283]

Water	1.8	Ct3*	5 mg	170	4.5 hours	75,5	46,5	[283]
DMSO	4.3	FS-PAN	1.5:1 Fru:Cat (w)	140	4 hours	100	90.4	[305]
THF-Water 3:1	10	Ge_3N_4	10 wt%	150	100 min		39	[341]
THF	10	Ge_3N_4	10 wt%	150	100 min		37	[341]
DMF	10	Ge_3N_4	10 wt%	150	100 min		11	[341]
THF-Water 3:1	10	GeO_2	10 wt%	150	100 min		45	[341]
THF	10	GeO_2	10 wt%	150	100 min		40	[341]
DMF	10	GeO_2	10 wt%	150	100 min		12	[341]
DMF	7.7	Glu-TsOH	0.4 g	130	90 min	98.3	59.7	[275]
DMA	7.7	Glu-TsOH	0.4 g	130	90 min	97	60.4	[275]
N-MP	7.7	Glu-TsOH	0.4 g	130	90 min	97.9	85.8	[275]
DMSO	7.7	Glu-TsOH	0.4 g	130	90 min	99.9	91.2	[275]
Water	7.7	Glu-TsOH	0.4 g	130	90 min	67	8	[275]
DMSO	4.3	Graphene oxide	8 mg	120	6 hours	93	93	[275]
Water/MIBK (1:5)	9	H-mordenite	0.1 g	165	60 min	76	69	[223]
[BMIM][Cl]	4.8	HT carbonaceus material	10:1 Fru:Cat (w)	100	120 min		79.9	[285]
[BMIM][Cl]	4.8	HT carbonaceus material	1:1 Fru:Cat (w)	100	90 min		88.1	[285]
[BMIM][Cl]	10	HT carbonaceus material	2:1 Fru:Cat (w)	100	60 min		75.1	[285]
Water	16.6	LCC	1:1 Fru:Cat (w)	150‡	60 min		40	[342]
Water	16.6	LCC	0.5 Fru:Cat (w)	150	5 hours		17.5	[342]
[BMIM][Cl]	50	LCC	0.2 Fru:Cat (w)	110‡	10 min		70	[342]
[BMIM][Cl]/DMSO 6:4	5	LCC	0.1 Fru:Cat (w)	120‡	30 min	98	70	[342]
DMSO	2.5	MCM-41	10:1 Fru:Cat (w)	120	100 min	100	65	[92]
DMSO	3	Nafion	0.02 g	120	120 min	100	94	[137]
Water	4.8	Nafion NR50	0.4 g	120	24 hours	78	6	[336]
N,N-DMF	3.2	Nafion NR50	0.1 g	100	3 hours	99	45	[226]
DMSO	3	Nafion-15/MCF	0.06 mmol H^{+}	90	120 min	94	89.3	[302]
Water-NaCl (saturated)/ Sec-butyl phenol	5	Nb/CB-1-DP^{++}	0.1 g	170	120 min	34	18	[343]
Water-NaCl (saturated)/ Sec-butyl phenol	5	Nb/CB-2-DP^{++}	0.1 g	170	120 min	78	20	[343]
Water-NaCl (saturated)/ Sec-butyl phenol	5	Nb/CS-HT^{++}	0.1 g	170	120 min	34	11	[343]
DMA-NaBr	5	Nb-NTMPA^{+++}	2:1 Fru:Cat (w)	100	90 min	100	85.6	[344]
Water	5	NbO	4 g	100	44 min	40	8.8	[251]
N,N-DMF	3.2	NbO	0.1 g	100	3 hours	12	0	[226]
Water/2-butanol (2:3)	21	NbO	0.1 g	160	50 min	90	89	[254]
Water	5	NbP	4 g	110	33 min	74	25.9	[249]
Water	10	NbP	1:10 Fru:Cat (w)	180	10 min	86.5	33.9	[255]
Water	10	ZrP	1:7.5 Fru:Cat (w)	180	10 min	84.2	39.5	[255]
Water	5	P/N-0.25	2:1 Fru:Cat (w)	120	8 hours	48	33.6	[282]

Water	5	P/N-0.25	2:1 Fru:Cat (w)	120	8 hours	68	42.8	[282]
Water	5	P/N-0.25	2:1 Fru:Cat (w)	120	8 hours	78	41.3	[282]
Water	6	PC-4	6:1 Fru:Cat (w)	160	3 hours	96.3	74.9	[284]
DMSO	3.5	PDVB-TAEA-12-TPA	0.006 mmol	120	50 min	98	96	[345]
DMSO	3.5	PDVB-TAEA-12-TSA	0.006 mmol	120	50 min	97	95,6	[345]
Water/ Butanol 1:1.5	5.7	Phosphated tantalum hydroxide	0.1 g	160	100 min	94	90	[346]
DMSO	7	Pr-SBA-15	0.2 mmol H^+	140	60 min	100	85	[293]
Water/MIBK 1:3	20	PS-PP/C-foam-1	2 g	90	6 hours	29	23.2	[301]
Water-NaCl/ THF-NMP 1:4	5	P-TiO_2	4:1 Fru:Cat (w)	175	105 min	99.9	98.6	[347]
DMSO	3	SAC-13	0.06 mmol H^+	90	120 min	91	73.7	[302]
DMSO	7	SAC-13	0.2 mmol H^+	140	60 min	100	83	[293]
Water	4.8	SBA-SO3H	0.4 g	120	24 hours	84	20	[336]
[BMIM][Cl]	9	SCC[***]	29 wt%	160	15 min		81	[309]
DMSO	5	SGO-1[**]	10 mg	120	60 min	83	80	[348]
DMSO	5	SGO-2[**]	10 mg	120	60 min	76	72	[348]
DMSO	5	SGO-3[**]	10 mg	120	60 min	90	85	[348]
THF/DMSO 7:3	5	Sn-Mont	30 wt%	160	60 min	99	78.1	[349]
Water-NaCl/ THF	5	Sn-Mont	30 wt%	160	3 hours		69	[349]
DMSO	3	SO_4^{2-}/ZrO_2	0.06 mmol H^+	90	120 min	50	32.3	[302]
N,N-DMF	3.2	SO_4/ZrO_2	0.1 g	100	3 hours	99	21	[226]
Water	2	SO_4^{2-}/ZrO_2	10:2 Fru:Cat (w)	200ǂ	5 min	79.9	36	[261]
Acetone/DMSO 7:3	2	SO_4^{2-}/ZrO_2	10:2 Fru:Cat (w)	200ǂ	5 min	91.3	65.6	[261]
Water/ (MIBK:2-Butanol 7:3) 3:7	30	Taa-SBA-15	3 g	180	120 min	66	48.84	[244]
Water/ (MIBK:2-Butanol 7:3) 3:7	30	Taa-SBA-15	3 g	180	120 min	59	30.68	[244]
Water/ (MIBK:2-Butanol 7:3) 3:7	30	TESAS-SBA-15	50 mg	130	140 min	84	59.64	[244]
Water/ (MIBK:2-Butanol 7:3) 3:7	30	Tp-SBA-15	3 g	180	120 min	61	31.72	[245]
Water	2	ZrO_2	10:2 Fru:Cat (w)	200ǂ	5 min	59.3	20.7	[52]
Acetone/DMSO 7:3	2	ZrO_2	10:2 Fru:Cat (w)	200ǂ	5 min	71.3	40.8	[261]

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[*] Ct1, Ct2, Ct3= sulfonated lignin carbon catalyst, air atmosphere, air flow and N2 flow respectively

[**] SGO-1, SGO-2, SGO-3 sulfonated graphene via Tours method with $KMnO_4$= 9g; KMnO4=18 g; $KMnO_4$=18 g and NaNO3=1.5 g

[***] Starch-derived carbonaceous catalyst

[+] Amberlyst-p = powder with a diameter= 0.15-0.053 mm

[++] Niobia-Carbon Black, HT: hydrothermal, 1-DP and 2-Dp treated with nitric acid at 80and 120°C respectively

[+++] Nb-NTMPA= Niobium-nitrilotris(methylenephosphonic acid)

[‡] Microwave heated

Table 12. Glucose dehydration with heterogeneous catalysts

Solvent	Substrate Concentration (wt%)	Catalyst	Catalyst concentration	Temperature (°C)	Reaction time	Conversion (%)	Yield (%)	Reference
Water/MIBK 1:2.25	30	12-AgTPA	0.08 g	130	4 hours	87	76.3	[268]
Water/MIBK 1:2.25	30	12-CsTPA	0.08 g	130	4 hours	33	17	[268]
[BMIM][Cl]	10	12-MPA	20 wt%	120	60 min		19.7	[350]
[BMIM][Cl]	10	12-MPA/B(OH)$_3$	20 wt%/10%	120	60 min		26.7	[350]
[BMIM][Cl]	10	12-TPA	20 wt%	120	60 min		21.9	[350]
[BMIM][Cl]	10	12-TPA	10 wt%	140	40 min		23.5	[350]
[BMIM][Cl]	10	12-TPA/B(OH)$_3$	20 wt%/10%	120	60 min		40.9	[350]
[BMIM][Cl]	10	12-TPA/B(OH)$_3$	20 wt%/10%	140	40 min		51.9	[350]
[BMIM][Cl]	10	12-TSA	20 wt%	120	60 min		19.3	[350]
[BMIM][Cl]	10	12-TSA/B(OH)$_3$	20 wt%/10%	120	60 min		39.3	[350]
Water/MIBK	10	Al-MCM-41	50 mg	195	2.5 hours	85	35	[243]
Water/MIBK	10	Al-MCM-41	50 mg	195	2.5 hours	85	35	[243]
Water/MIBK (1:3) NaCl 20%	10	Al-MCM-41	50 mg	195	2.5 hours	96	65	[243]
THF/ Water-NaCl (saturated) 1:3	9	AlSiO-10	1:1 Glu:Cat (w)	160	90 min	98.8	47.9	[351]
THF/ Water-NaCl (saturated) 1:3	9	AlSiO-20	1:1 Glu:Cat (w)	160	90 min	91.7	63.1	[351]
THF/ Water-NaCl (saturated) 1:3	9	AlSiO-30	1:1 Glu:Cat (w)	160	90 min	67.2	37.8	[351]
THF/ Water-NaCl (saturated) 1:3	9	AlSiO-40	1:1 Glu:Cat (w)	160	90 min	58.7	25.3	[351]
DMF	3.33	Amberlyst-15	1:1 Glu:Cat (w)	100	120 min	100	88	[294]
N,N-DMF	3.2	Amberlyst-15	0.1 g	100	3 hours	69	0	[226]
ChoCl	20	Amberlyst-15-CrCl$_3$	40 wt%	140	2 hours		46.4	[300]
DMSO	7	Amberlyst-70	0.2 mmol H$^+$	140	60 min	97.5	63.7	[293]
DMSO	7	Ar-SBA-15	0.2 mmol H$^+$	140	60 min	97	47	[293]
DMSO	7	C-SO$_3$H	21 wt%	130	8 hours	73	10	[352]
DMSO	1	b-cyclodextrin-SO$_3$H	100 wt%	180	5 hours		47	[337]
DMF	1	b-cyclodextrin-SO$_3$H	100 wt%	180	5 hours		37	[337]
Sulpholane	1	b-cyclodextrin-SO$_3$H	100 wt%	180	5 hours		28	[337]
[BMIM][Cl]	1	b-cyclodextrin-SO$_3$H	100 wt%	180	5 hours		32	[337]
[BMIM][Cl]	9	CCC[†]	29 wt%	140	30 min	60.7	41.2	[309]
Water/MIBK	10	Fe$_3$O$_4$@SiO$_2$-SO$_3$H	40 wt%	140	24 hours	98	70	[263]
DMSO	4.3	FS-PAN	1.5:1 Glu:Cat (w)	140	4 hours	89.7	6.4	[305]

[BMIM][Cl]	9	GCC[††]	29 wt%	140	30 min	55.2	37.8	[309]
Water	15	HY-zeolite	0.033 g/ml	150	5 hours	75	13.3	[217]
Water	12	HY-zeolite	10 g	160	3 hours		9	[217]
[BMIM][Cl]	10	HZSM-5	20 wt%	120	60 min		3.1	[267]
Water	15	MCM-20	0.033 g/ml	150	23 hours	60	18.6	[218]
Water	15	MCM-41	0.033 g/ml	150	24 hours	87.5	15	[218]
THF/Water 39:1	5	MIL-SO$_3$H	0.5 g	130	25 min		29	[317]
Water	15	Montmorillonite	0.033 g/ml	150	5 hours	81.3	13	[218]
Water/THF 1:4	5	Mo-TiO$_2$	4:1 Glu:Cat (w)	175[*]	105 min	99.9	17	[353]
N,N-DMF	3.2	Nafion NR50	0.1 g	100	3 hours	34	0	[226]
N,N-DMF	3.2	NbO	0.1 g	100	3 hours	12	0	[226]
Water/2-butanol (2:3)	21	NbO	0.1 g	160	110 min	68	49	[346]
Water/ Butanol 1:1.5	5.7	Phosphated tantalum hydroxide	0.1 g	160	140 min	70	58	[346]
DMSO	7	Pr-SBA-15[+]	0.2 mmol H$^+$	140	60 min	98	46.5	[293]
Water/ THF 1:4	2	P-TiO$_2$	4:1 Glu:Cat (w)	175	105 min	93.6	83.4	[353]
Water/ THF 1:4	5	P-TiO$_2$	4:1 Glu:Cat (w)	175	105 min	96.5	62.8	[353]
Water-NaCl/ THF-NMP 1:4	5	P-TiO$_2$	4:1 Glu:Cat (w)	175	105 min	98.2	90.5	[353]
DMSO	7	SAC-13	0.2 mmol H$^+$	140	60 min	99	50	[293]
[BMIM][Cl]	10	SBA-15	20 wt%	120	60 min		1.2	[267]
[BMIM][Cl]	9	SCC	29 wt%	140	30 min	54.3	35.3	[309]
THF/DMSO 7:3	7	Sn-Mont	30 wt%	160	3 hours	98.6	48.2	[349]
THF/DMSO 7:3	10	Sn-Mont	30 wt%	160	3 hours	98.7	42.4	[349]
Water-NaCl/ THF	10	Sn-Mont	30 wt%	160	3 hours		79	[349]
N,N-DMF	3.2	SO$_4$/ZrO$_2$	0.1 g	100	3 hours	7	0	[226]
γ-GVL	7	SPTPA[**]	1.25:1 Glu:Cat (w)	175	20 min		59	[354]
Water/THF 1:4	2	TiO$_2$	4:1 Glu:Cat (w)	175	105 min	90.4	72.8	[353]
Water/THF 1:4	5	V-TiO$_2$	4:1 Glu:Cat (w)	175	105 min	99.9	35.5	[353]
Water/THF 1:4	5	W-TiO$_2$	4:1 Glu:Cat (w)	175	105 min	98.5	27.5	[353]
[HexilMIM][Cl]	5	ZrO$_2$	10:2 Glu:Cat (w)	200[*]	1 min	76	10	[355]
Water/[HexilMIM][Cl] 1:20	5	ZrO$_2$	10:2 Glu:Cat (w)	200	20 min	96	48	[355]

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[*] Microwave heating

[+] Propylsulfonic acid functionalized mesoporous silica

[**] Sulfonated Polytriphenylamine

[†] Cellulose-derived carbonaceous catalyst

[††] Glucose-derived carbonaceous catalyst

Table 13. Polysaccharide dehydration with heterogeneous catalysts

Solvent	Substrate	Substrate Concentration (wt%)	Catalyst	Catalyst concentration	Temperature (°C)	Reaction time	Conversion (%)	Yield (%)	Reference
Water/ MIBK 1:10	Cellobiose	17	12-TPA-ChoCl	0.11 mmol	130	3 hours	93	80	[271]
Water-NaCl/ THF-NMP 1:4		5	P-TiO$_2$	4:1 Sugar:Cat (w)	175	105 min	99.7	94.2	[347]
Water-NaCl/ THF		5	Sn-Mont	30 wt%	160	3 hours		40	[349]
Water/ MIBK 1:10	Cellulose	17	12-TPA	0.11 mmol	140	8 hours	89	57	[271]
Water/ MIBK 1:10		17	12-TPA-ChoCl	0.11 mmol	140	8 hours	87	75	[271]
Water		3.5	Amberlyst-15	0.2 g	190	5 hours		8	[234]
Water-NaCl/ THF-NMP 1:4		5	P-TiO$_2$	4:1 Sugar:Cat (w)	175	105 min	56.7	33	[347]
Water			HTC-220-6-SO$_3$H^a	5 wt%	180	5 min		1.6	[356]
Water/THF 3:1		5	Nb/C-50	1:1 Sugar:cat (w)	170	8 hours	99	53.3	[287]
[BMIM][Cl]		9	SCC	29 wt%	160	15 min		40.5	[309]
Water-NaCl/ THF		5	Sn-Mont	30 wt%	160	3 hours		40	[349]
Water-NaCl/ THF-NMP 1:4	Cellulose (pretreated)	5	P-TiO$_2$	4:1 Sugar:Cat (w)	175	105 min	99.9	86.2	[347]
[BMIM][Cl]	Corn Stalk	1	HCSS	0.05 g	150	30 min		45.1	[357]
[BMIM][Cl]		4.8	HCSS	0.05 g	150	30 min		44.1	[357]
[BMIM][Cl]		10	HCSS	0.05 g	150	60 min		32.9	[357]
DMSO	Fructose-glucose syrup	4	Amberlyst-36	1:1 Sugar:cat (m)	140$^\Upsilon$	40 min		71.3	[358]
Dioxane	HFCS	0.9	AC-SO$_3$H*	12 mol %	120	4 hours		60	[359]
Dimethoxyethane		0.9	AC-SO$_3$H*	12 mol %	120	4 hours		73	[359]
2-methoxyethyl ether		0.9	AC-SO$_3$H*	12 mol %	120	4 hours		75	[359]
Ttriethyleneglycol dymethyl ether		0.9	AC-SO$_3$H*	12 mol %	120	4 hours		56	[359]
Tetraethyleneglycol dymethyl ether		0.9	AC-SO$_3$H*	12 mol %	120	4 hours		57	[359]
Dioxane		0.9	Amberlyst-15	1:0.75 Sugar:Cat (w)	120	120 min	99	80	[359]
Dimethoxyethane		0.9	Amberlyst-15	1:0.75 Sugar:Cat (w)	120	120 min	99	81	[359]
2-methoxyethyl ether		0.9	Amberlyst-15	1:0.75 Sugar:Cat (w)	120	120 min	99	74	[359]

Triethyleneglycol dymethyl ether		0.9	Amberlyst-15	1:0.75 Sugar:Cat (w)	120	120 min	99	66	[359]
Tetraethyleneglycol dymethyl ether		0.9	Amberlyst-15	1:0.75 Sugar:Cat (w)	120	120 min	99	67	[359]
DMSO		15	Amberlyst-15	0.3 g	100	4 hours		80	[360]
Dioxane		15	Amberlyst-15	0.3 g	100	4 hours		80	[360]
Acetonitrile		15	Amberlyst-15	0.3 g	100	4 hours		45	[360]
DMSO		30	Amberlyst-15	0.3 g	100	4 hours		70	[360]
Dioxane		30	Amberlyst-15	0.3 g	100	4 hours		70	[360]
Acetonitrile		30	Amberlyst-15	0.3 g	100	4 hours		38	[360]
DMSO	Inulin	1	b-cyclodextrin-SO_3H	100 wt%	140	120 min		92	[337]
[AMIM][Cl]/water		4.5	D265-SO_3H^{***}	50 wt%	100	90 min		65	[280]
DMSO		4.3	FS-PAN	1.5:1 Sugar:Cat (w)	140	4 hours	100	52.3	[305]
[AMIM][Cl]/water		4.5	L225-SO_3H^{**}	50 wt%	100	60 min		65	[280]
Water/ 2-butanol (2:3)		21	NbO	0.1 g	160	140 min	54	86	[254]
Water/ Butanol 1:1.5		5.7	Phosphated tantalum hydroxide	0.1 g	160	150 min	95	87	[346]
Water-NaCl/ THF		5	Sn-Mont	30 wt%	160	3 hours		41	[349]
Water/ 2-butanol (2:3)	Jerusalem artichoke	6	NbO	0.1 g	160	40 min	46	22	[254]
Water/ Butanol 1:1.5		5.7	Phosphated tantalum hydroxide	0.1 g	160	2.5 hours	91	50	[346]
Water/ Butanol 1:1.5	Jerusalem artichoke (juice)	5.7	Phosphated tantalum hydroxide	0.1 g	160	120 min	91	79	[346]
Water/ MIBK 1:10	Starch	17	12-TPA-ChoCl	0.11 mmol	130	3 hours	92	78	[271]
DMSO		1	b-cyclodextrin-SO_3H	100 wt%	140	5 hours		10	[337]
Water-NaCl/ THF		5	Sn-Mont	30 wt%	160	3 hours		43	[349]
Water	Molasses	6.7	B-SO_3H^b	0.3 g	150^{Υ}	4		39.1	[361]
Water		6.7	M-SO_3H^c	0.3 g	150^{Υ}	3		34.2	[361]
Water-NaCl/ THF-NMP 1:4	Starch (potato)	5	P-TiO_2	4:1 Sugar:Cat (w)	175	105 min	99.8	84.6	[347]
Water-NaCl/ THF-NMP 1:4	Starch (rice)	5	P-TiO_2	4:1 Sugar:Cat (w)	175	105 min	99.7	80.7	[347]
Water/ MIBK 1:10	Sucrose	17	12-TPA-ChoCl	0.11 mmol	130	3 hours	90	78	[271]
DMSO		1	b-cyclodextrin-SO_3H	100 wt%	140	120 min		85	[337]
DMSO		4.3	FS-PAN	1.5:1 Sugar:Cat (w)	140	4 hours	100	42.9	[305]
THF/ Water 3:1		10	Ge_3N_4	10 wt%	150	100 min		19	[341]
THF		10	Ge_3N_4	10 wt%	150	100 min		16	[341]

THF/ Water 3:1	10	GeO_2	10 wt%	150	100 min		20	[341]
THF	10	GeO_2	10 wt%	150	100 min		18	[341]
Water-NaCl/ THF-NMP 1:4	5	P-TiO_2	4:1 Sugar:Cat (w)	175	105 min	99.8	98.2	[347]
Water-NaCl/ THF	5	Sn-Mont	30 wt%	160	3 hours		43	[349]

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[*] Sulfated wood powder
[**] Sulfated carbonized lignin at 225 °C
[***] Sulfated carbonized D-xylose at 265 °C
[a] Sulfonated glucose
[b] Sulfonated sugarcane bagasse
[c] Sulfonated sugarcane molasses
[ϒ] MH

Table 14. HMF production rate from biomass

Substrate	Solvent	Catalyst	Catalyst concentration	Temperature (°C)	HMF production rate (g/l*min)	Reference
Avicel	[BMIM][Cl]	$CrCl_3*6H_2O$	10 mg	400[**]	14.64	[112]
	[BMIM][Cl]	$CrCl_3*6H_2O$	10 mg	100	0.03	[112]
	[BMIM][Cl]	$CrCl_3*6H_2O$/2,2'-bipyridine	10 mg/17.5 mg	100	0.004	[112]
	[BMIM][Cl]	$CrCl_3*6H_2O$/2,2'-bipyridine	10 mg/17.5 mg	400[**]	0.38	[112]
Cellulose	Water/MIBK 1:10	12-TPA-ChoCl	0.11 mmol	140	15.94	[271]
	[BMIM][Cl]	$CrCl_3*6H_2O$	10 mg	400[**]	14.88	[112]
	[BMIM][Cl]	$CrCl_3*6H_2O$	10 mg	400[**]	11.90	[181]
	Water/MIBK 1:10	12-TPA	0.11 mmol	140	0.20	[271]
	[BMIM][Cl]	$CrCl_3*6H_2O$	7 mol %	120	0.38	[160]
	[BMIM][Cl]	SCC	29 wt%	160	2.43	[309]
	Water-NaCl/THF	Sn-Mont	30 wt%	160	0.11	[349]
	IL-1/MIBK	$MnCl_2*4H_2O$	1 ml	180	0.25	[213]
	[BMIM][Cl]/MIBK	$GeCl_4$	10 mol %	120	0.56	[105]
	Water-NaCl/ THF-NMP 1:4	P-TiO_2	4:1 Sugar:Cat (w)	175	0.16	[353]
	IL-1/MIBK	$CoSO_4$	1 ml	150	0.16	[106]
	Water	Pressure	40	280	1.19	[47]
	Water	Pressure	25	350	72.67	[46]
	Water	Amberlyst-15	0.2 g	190	0.01	[234]

	[BMIM][H$_2$PO$_4$]/MIBK	MnCl$_2$*4H$_2$O	1 ml	150	0.05	[213]
	Water	H$_3$PO$_4$	pH$_{sol}$=2	230	1.27	[151]
	[EMIM][Cl]	CuCl$_2$/PdCl2	13.5 µg/13.5 µg	120	0.19	[182]
	Water-NaCl/ THF-NMP 1:4	P-TiO$_2$	4:1 Sugar:Cat (w)	175	0.41^{c}	[353]
	[BMIM][Cl]/Water	CrCl$_3$/LiCl	0.155 mmol/0.155 mmol	140*	0.37	[183]
	Water	Pressure	40	400	3.89^{a}	[47]
Chitosan	Water	[HMIM][HSO$_4$] [FeCl$_3$]	1.25 wt %	180	0.00	[214]
Corn Stalk	[BMIM][Cl]	HCSS	0.05 g	150	0.15	[357]
	[BMIM][Cl]	HCSS	0.05 g	150	0.71	[357]
	[BMIM][Cl]	HCSS	0.05 g	150	0.55	[357]
Inulin	DMSO	b-cyclodextrin-SO$_3$H	100 wt%	140	0.08	[337]
	Water/ Butanol 1:1.5	Phosphated tantalum hydroxide	0.1 g	160	0.33	[346]
	[AMIM][Cl]/water	L225-SO$_3$H	50 wt%	100	0.49	[280]
	[AMIM][Cl]/water	D265-SO$_3$H	50 wt%	100	0.33	[280]
	ChoCl	pTSOH	10 mol %	90	4.75	[123]
	ChoCl	FeCl$_3$	10 mol %	90	4.58	[123]
	Water/ 2-butanol (2:3)	NbO	0.1 g	160	0.81	[254]
	Water	CO$_2$	6 Mpa$^{b)}$	180	0.28	[170]
	Water	HCl	2 ml	180	0.28	[170]
	DMSO	FS-PAN	1.5:1 Sugar:Cat (w)	140	0.09	[305]
	ChoCl	CrCl$_3$	10 mol %	90	3.83	[123]
	ChoCl	Sc(Otf)$_3$	10 mol %	90	3.67	[123]
	Water-NaCl/ THF	Sn-Mont	30 wt%	160	0.11	[349]
	[EMIM][BF$_4$]	SnCl$_4$*5H$_2$O	10 mol %	100	0.37	[174]
	ChoCl	CrCl$_2$	10 mol %	90	3.00	[123]
	ChoCl	ZnCl$_2$	10 mol %	90	0.25	[123]
Jerusalem artichoke	Water/Butanol 1:1.5	Phosphated tantalum hydroxide	0.1 g	160	0.19	[346]
	Water/2-butanol (2:3)	NbO	0.1 g	160	0.33	[254]
Jerusalem artichoke (juice)	Water/Butanol 1:1.5	Phosphated tantalum hydroxide	0.1 g	160	0.38	[346]

Pine Wood	[BMIM][Cl]	$CrCl_3*6H_2O$	10 mg	400^{**}	8.32	[181]
	[BMIM][Cl]	$CrCl_3*6H_2O$	10 mg	100	0.05	[181]
	[BMIM][Cl]	HCl	0.66 g/l	100	0.02	[181]
	[BMIM][Cl]	$CrCl_3*6H_2O$	10 mg	400^{**}	7.52	[181]
Sigmacell	[BMIM][Cl]	$CrCl_3*6H_2O$	10 mg	400^{**}	13.20	[112]
Spruce	[BMIM][Cl]	$CrCl_3*6H_2O$	10 mg	400^{**}	12.72	[112]
Starch	Water/MIBK 1:10	12-TPA-ChoCl	0.11 mmol	130	0.74	[271]
	[EMIM][BF_4]	$SnCl_4*5H_2O$	21.6 g	100	0.03	[172]
	Water-NaCl/THF	Sn-Mont	30 wt%	160	0.12	[349]
	[OMIM][Cl]/Ethyl acetate	HCl	5 ml	120	1.01	[174]
	Water	Pressure	1	220	1.10	[48]
	DMSO	b-cyclodextrin-SO_3H	100 wt%	140	0.00	[337]
	Water-NaCl/ THF-NMP 1:4	P-TiO_2	4:1 Sugar:Cat (w)	175	0.40^{+}	[353]
	Water-NaCl/ THF-NMP 1:4	P-TiO_2	4:1 Sugar:Cat (w)	175	0.38^{++}	[353]
	Water-[BMIM][Cl]/MIBK 1:5	$AlCl_3*6H_2O$	150 mg	140^{*}	0.28	[215]
Wheat Straw	Water/THF 1:3	$FePO_4$/NaH_2PO4	0.2 g/0.02 g	160	0.73	[216]
	[BMIM][Cl]	$CrCl_3$/LiCl	0.155 mmol/0.155 mmol	160^{*}	0.98	[183]

[a)] Combined sub-/supercritical water. 45 seconds at 280 °C and 0.1 seconds at 400 °C

[d)]Gaseous catalyst

[e)] pretreated cellulose

[*] MH in W, [**]no temperature reported
[+]potato starch, [++] rice starch

Table 15. Catalyst group properties

Catalyst type	Properties	Catalyst	Conversion			Research level
			Ketohexoses	Aldohexoses	Polysaccharides	
Homogeneous Brønsted	**Inorganic acids and bases** -Difficult to recover -Generally very corrosive -Low costs	HCl, H_2SO_4, H_3BO_3, H_3PO_4, HNO_3, HBr, NaOH ...	High conversion and high to moderate HMF yields depending on reaction conditions, short reaction times tend to be beneficial for HMF production	Bases can isomerize glucose to fructose, but don't catalyze dehydration. Low to moderate HMF yields	HCl can depolymerize cellulose and produce moderate HMF yields. In general, very low HMF values	Extensively researched. Several systems have been tested (see tables 5,6 and 10)
	Organic acids -Weak acids -Difficult to recover -Low costs	CH_3COOH, CH_2OH, CF_3COOH, PTSA...	Good conversion and low to moderate HMF yields.	Good glucose conversion, HMF yields are moderate to low.	Not efficient for complex polysaccharides	Very well researched (see tables 5.6 and 10).
Homogeneous Lewis	**Metal Salts** -Good system recoverability -Moderate corrosivity. -Can be expensive. -Limited sustainability	$AlCl_3$, CrCl3, CuCl2, MnCl3, Sc(Otf)3, ZnCl2 ZrCl4...	High conversion. Moderate to high HMF yield. Good solubility in solvent is required.	Good conversion, but moderate HMF yields.	Moderate HMF yield. Requires polysaccharide soluble in solvent.	Extensively researched. Several systems have been tested (see tables 7-10)
	Rare earth metals -Very abundant -Expensive	$CeCl_3$, DyCl3, Nd(Otf)3, YbCl3, NdCl3...	Low conversion and low HMF yields.	Moderate conversion and low HMF yields	Good conversion Low HMF values	Limited research possibly due to low catalytic activity (see tables 7-10)
Heterogeneous Mineral-based	**Zeolites** -Natural or artificial -Sieving properties - Very Low degradability	H-mordenite, HY-zeolite, HZSM-5, Sn-BEA...	Moderate HMF yields, which can be improved by tailoring adding acid sites.	Good conversion, low yields with pore size being an important factor for glucose difussion	Very low hydrolyzation, possibly related to pore size, leading to low acid site contact	Limited research, possibly due to low catalytic activities (see tables 10-13)
	-Heteropolyacid salts -Very strong acidity - Some tunability -Soluble in some systems	12-AgTPA, 12-CsTPA, 12-TSA, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ ...	High conversion and HMF yields at high substrate concentration. Yields can be adjusted depending on the metal cation.	Generally low HMF yields. Long reaction times (1-4 hours)	Low cellulose conversion in homogeneous form	Limited research. Potential for simple carbohydrates dehydration (see tables 10-13)
	Metal based/ Metal supported - Broad range of functionalizations -Good recoverability -Crystalline structure -Can be expensive	GeO_2, P-TiO_2, SO_4/ZrO_2, TiO_2, ZrO_2, MCM-41...	Generally low to moderate HMF yields, but some oxides (NbO, P-TiO2) can obtain high HMF values	High conversion can be achieved, but yields are mostly low or moderate, with a few exceptions (P-TiO2).	Generally low hydrolysing activity. Some exceptions (NbO, P-TiO2)	Some research exists, potential for further investigation (see tables 10-13)

	Synthesized polymers -Low thermal stability -Can be made to meet requirements - Good recoverability	Amberlys, Nafiont-15, FS-PAN, PS-PP/C-foam-1...	Good conversion and HMF yields from sulfonate resins (Amberlyst, Nafion). Water is detrimental for the system	Low to moderate conversion and yields. Potential increase of activity via funtionalization	Generally low hydrolysing activity. Low conversion for complex biomass.	Some research exists, potential for further investigation (see tables 10-13)
Heterogeneous Carbon-based	**Carbonized biomass** -Good functionalization - Potentially sustainable (sourcea and functionalization) -Cheap source -Low surface area	b-cyclodextrin-SO_3H, Graphene oxide, HT carbonaceus material...	Good conversion and yields due to Brønsted sites functionalization. Activity related to acid sites (SO3 groups)	Moderate conversion and yields. Potentially improved with further functionalization	Moderate HMF yields. Solubility and hydrolysis of complex biomass provided by solvent	Some research exists. Potential for further investigation (see tables 10-13)

4. Conclusion

As demonstrated in this review, multifarious advancements in catalysts and HMF production have been made in recent years. Early experimentation focused mainly on obtaining HMF from simple sugars using homogeneous Brønsted catalysts such as HCl and H_2SO_4. Later, interest in homogeneous Lewis acids increased, given their capability to dehydrate hexoses and improve HMF yields. Metal halides and halide-containing ILs are particularly attractive for dehydration of more complex carbohydrates. Lately, the use of heterogeneous catalysts, like resins, silica supported acids, or carbonaceous catalysts has become more prominent, and several new solid catalysts are being developed every year.

The use of liquid Brønsted acids, especially strong mineral acids, allows for hydrolysis of cellulose as well as dehydration of the resulting glucose units. However, this reaction is not selective and yields little HMF. The strong corrosive nature of these acids makes them very difficult to utilize beyond a lab-scale process. On the other hand, autocatalytic processes, while green in nature, require very high temperature and pressures. Such process conditions are quite costly, or even impractical to carry out at an industrial level. Additionally, they do not lead to high HMF yields on their own.

More promising are the metal halides, being less corrosive and more easily recycled than the liquid Brønsted acids. These salts have efficiently hydrolyzed cellulose in conjunction with ILs and do reach high HMF yields. Several metal halides have been tested with different combinations of ILs. However, high yields from complex lignocellulosic materials as well as the use of highly concentrated substrate are yet to be achieved. In this regard, DESs such as choline chloride may offer an alternative. DESs' capabilities of solubilizing highly concentrated carbohydrates can help offset low yields by increasing the production capacity.

As for solid catalysts, HMF yields from cellulose and lignocellulose are still very low, but given that the type and amount of acid sites as well as acid strength can be tuned, they have the potential to achieve the hydrolyzation and dehydration of lignocellulose. Bifunctional catalysts, with both Brønsted and Lewis acid sites in the right proportion, as well as an appropriate pore size that allows for glucose diffusion, can be developed to obtain high yields of HMF from more complex biomass. Their ease of recovery also makes them very interesting from a sustainable point of view.

It can be seen from the results in the different tables that quantitative HMF production can be obtained over several different catalytic processes and substrates. Nevertheless, the challenge remains in obtaining high yields from lignocellulosic biomass at both high concentrations and yields.

Finally, we present Table 15 as a guide to the different catalytic systems, listing their advantages and disadvantages for the different types of carbohydrates as well as the level of research done on them. While some areas have been extensively researched (e.g. Brønsted acids), others, like carbon-based catalysts, represent a vast field for potential research, thanks to their adjustable properties. It may be expected that future breakthroughs in catalytic HMF production would occur in these lesser-explored areas, thus paving the way for economically-feasible industrial-scale HMF production.

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