Solid catalysts synthesis, characterization, and their application for the production of HMF from carbohydrates

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Abstract

Depletion of fossil fuels and the impacts of their extraction and use on the environment have been a cause for concern since several decades, and yet the use of fossil oil-based chemicals has been consistently growing. Bio-derived alternatives to these commodities have been proposed in recent years. One such alternative, 5-hydroxymethylfurfural (HMF), has been highlighted as an important building block to produce fine chemicals, fuels, and polymers. HMF can be obtained from the dehydration of carbohydrates, such as agricultural, forestry, and food wastes. However, its large-scale production has been held back by its production cost, which is highly dependent on the substrate price.

While several catalytic processes to obtain HMF have been developed, many require the use of homogeneous catalytic systems, which can be difficult to recover and reuse, or require corrosive catalysts, such as HCl and H_2SO_4. Moreover, their efficiency for synthesizing HMF from aldohexoses, or more complex biomass has been limited. Thus, the focus of this project was to develop and characterize new, easily recoverable solid catalysts to implement a heterogeneous system to produce HMF.

Solid catalysts are a very attractive alternative for HMF synthesis. They are highly modifiable and easily recovered from the reaction medium. Still, they can be expensive, and tend to be less efficient in obtaining HMF than their homogeneous counterpart. An inexpensive material, such as hydrothermal carbon, can be functionalized to serve as an acid catalyst. The potential of softwood pulp-derived catalysts to produce HMF was investigated (Chapter 3). The material was characterized and tested on the dehydration of fructose in ionic liquid [BMIM][Cl] and MIBK in a biphasic system. The reaction was optimized by response surface methodology, obtaining quantitative yields of HMF from fructose. The material was recovered and recycled 4 times without considerable loss of efficiency.

Sulfonated materials, such as Amberlyst and Nafion, have been used as catalysts to produce HMF from fructose, albeit with long reaction times. These resins tend to be expensive, and hold limited thermal stability. Chapter 4 explored functionalization with sulfonic groups via polymer crosslinking. Using polyvinyl alcohol and sulfosuccinic acid (SSA) at varying concentrations, four resins were produced designated as PVA-10, PVA-20, PVA-30 and PVA-40, based on their crosslinker concentration. The method allowed for a controlled addition of functional groups to the material, as well as control of the physical and chemical properties. A possible structure and the degree of functionalization were determined. Quantitative yields could be obtained from fructose at very short reaction times (4 min) when the optimized catalyst PVA-40 was used. Glucose dehydration resulted in only 25 mol % HMF, while similar conditions using sucrose yielded 63.9 mol % HMF. The material could be reused up to 4 times without considerable loss of efficiency.

In Chapter 5, the most promising catalyst, PVA-40, was used in the valorization of fruit residues. Mango pulp was subjected to dehydration with the catalysts in an aqueous medium and compared to a more conventional homogeneous catalyst H_2SO_4. Mango pulp dehydration resulted in similar yields for both: 31.3% HMF yield with PVA-40 and 30.3% with H_2SO_4, making PVA-40 a more sustainable and competitive option for fruit waste dehydration.

Further exploring the potential of using SSA as an efficient source of sulfonic sites, the development of bifunctional metalorganic frameworks using Cr, Ti, and Zr as metal centers and SSA as the organic crosslinker is presented in Chapter 6. The characterization of the materials confirmed the presence of both sulfonic groups and metal centers. The resulting materials showed good isomerizing capabilities and HMF yields from glucose and fructose. A kinetic study suggested that the main pathway for HMF formation for Cr-SSA was not via glucose isomerization, but direct transformation into HMF.

Résumé

Depuis quelques années, des produits biosourcés sont proposés afin de diminuer la dépendance aux combustibles fossiles. L'une de ces alternatives, le 5-hydroxyméthylfurfural (HMF), est une molécule plateforme pouvant servir à la production de carburants, polymères, et de solvants. Le HMF peut être obtenu à partir de la déshydratation des glucides provenant de résidus de l'agriculture, la foresterie ainsi que des résidus alimentaires. Toutefois, sa production à grande échelle a été freinée par son coût de production, qui dépend fortement du prix du substrat.

Bien que plusieurs procédés catalytiques pour obtenir du HMF aient été mis au point, bon nombre nécessitent l'utilisation de systèmes homogènes, qui peuvent être difficiles à récupérer et réutiliser, ou peuvent être corrosifs (ex. HCl, H_2SO_4). Ainsi, l'objectif de ce projet était de développer de nouveaux catalyseurs solides facilement récupérables pour mettre en œuvre un système hétérogène de production du HMF.

Les catalyseurs solides sont une alternative très attrayante pour la synthèse du HMF puisqu'ils sont modifiables et peuvent être réutilisés mais, ils sont coûteux et ont tendance à être moins efficaces pour l'obtention du HMF que leurs homologues homogènes. Un matériau peu coûteux, comme le carbone hydrothermal, peut être fonctionnalisé pour servir de catalyseur acide. Le potentiel des catalyseurs dérivés de la pâte de résineux pour produire du HMF a été étudié (chapitre 3). Le matériau a été caractérisé et examiné pour la déshydratation du fructose dans un système biphasique. La réaction a été optimisée par la méthodologie de réponse de surface. Des rendements quantitatifs de HMF furent obtenus à partir du fructose. Le matériau a été récupéré et recyclé 4 fois sans perte d'efficacité considérable.

Les matériaux sulfonés, tels que Amberlyst et Nafion, peuvent être utilisés pour produire du HMF à partir de fructose, mais avec de longs temps de réaction. Ces résines sont coûteuses et détiennent une stabilité thermique limitée. La fonctionnalisation avec des groupes sulfoniques par réticulation de polymère a été explorée à l'aide d'alcool polyvinylique et d'acide sulfosuccinique (SSA) (chapitre 4). Quatre résines ont été produites en fonction de leur concentration en réticulation: PVA-10, PVA-20, PVA-30 et PVA-40. La méthode a permis un ajout contrôlé de groupes fonctionnels au matériau, ainsi qu'un contrôle des propriétés physiques et chimiques. Une structure

possible du catalyseur ainsi que le degré de fonctionnalisation ont été déterminés. Des rendements quantitatifs ont pu être obtenus à partir du fructose en 4 minutes lorsque le PVA-40 était utilisé. Par contre, un rendement de 25 mol % HMF fut obtenu avec le glucose, et de 63.9 mol% avec le saccharose. Le matériau pourrait être réutilisé jusqu'à 4 fois sans perte d'efficacité considérable.

Au chapitre 5, le catalyseur le plus prometteur, le PVA-40, a été utilisé pour obtenir du HMF à partir de résidus alimentaire (pulpe de mangue). Le rendement en HMF a été comparé à l'utilisation du H_2SO_4, un catalyseur homogène plus conventionnel. La déshydratation de la pulpe de mangue a donné des rendements similaires pour les deux catalyseurs : 31,3% de rendement en HMF avec PVA-40 et 30,3 % avec H_2SO_4, ce qui fait duPVA-40 une option plus durable et compétitive pour la déshydratation des résidus de fruits.

L'exploration du potentiel d'utilisation du SSA comme source efficace de sites sulfoniques a conduit au développement de cadres métallurgiques bifonctionnels en utilisant le Cr, Ti et Zr comme centres métalliques et le SSA comme agent de réticulation (chapitre 6). La caractérisation des matériaux a confirmé la présence des groupes sulfoniques et des centres en métal. Les matériaux résultants ont montré de bonnes capacités d'isomérisation, ainsi que de bons rendements en HMF à partir du glucose et du fructose. Une étude cinétique a suggéré que la voie principale pour la formation du HMF pour Cr-SSA n'ait pas été par l'intermédiaire de l'isomérisation du glucose, mais par transformation directe en HMF.

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List of Abbreviations

[MIMC$_4$SO$_3$][HSO$_4$]	*1-(4 sulfonic acid) butyl 3-methylimidazolium hydrogen sulfate*
[BeMIM][Cl]	*1-benzyl-3-methyl imidazolium chloride*
[BMIM][PF6]	*1-butyl 3-methyl imidazolium hexafluorophosphate*
[BMIM][BF4]	*1-butyl 3-methyl imidazolium tetrafluoroborate*
[BdMIM][Cl]	*1-butyl-2,3-dimethyl imidazolium chloride*
BMIM][PS]	*1-butyl-3-methyl imidazolium p-toluenesulfonate*
[BMIM][Cl]	*1-Butyl-3-methyl-imidazolium-chloride*
[EMIM][Cl]	*1-ethyl 3-methyl imidazolium tetrafluoroborate*
[Epyr][Cl]	*1-ethyl pyridinium chloride*
[HMIM][Cl]	*1-H-3-methyl imidazolium chloride*
[AEMIM][BF$_4$]	*1-hydroxyethyl-3-methylimidazolium tetrafluoroborate*
[MIM][HSO$_4$]	*1-methyl imidazolium hydrogen sulfate*
[MOIM][Cl]	*1-methyl-3-octylimidazolium chloride*
[OMIM][Cl]	*1-octyl-3-methyl imidazolium chloride*
[SMIM][Cl]	*1-sulfonic acid-3-methylimidazolium chloride*
HMF	*5-hydroxymethylfurfural*
[ASBI][Tf]	*3-allyl-1-(4-sulfobutyl) imidazolium trifluoromethanesulfonate*
[ASCBI][Tf]	*3-allyl-1-(4-sulfurylchloride butyl) imidazolium trifluoromethanesulfonate*
3-DG	*3-deoxyglucosone*
OBMF	*5,5’-oxy(bismethylene)-2-furaldehyde*
[AIMIM]	*Alkil methyl imidazolium*
BJH	*Barret-Joyner-Halenda*
[Hbim][Cl]	*Benzimidazolium chloride*
BF$_3$•Et$_2$O	*Boron trifluoride etherate*
BET	*Brunauer-Emmett-Teller*
CPL	*Caprolactam*
CNT	*Carbon nanotubes*
CCD	*Central composite design*

ChoCl	*Choline chloride*
DES	*Deep eutectic solvent*
DFT	*Density functional theory*
DOE	*Department of Energy*
$[DiEG(MIM)_2][Oms]_2$	*Diethylene glycol-bis (3-methylimidazolium) dimesylate*
DMF	*Dimethyl formamide*
DMSO	*Dimethyl sulfoxide*
FA	*Formic acid*
FTIR	*Fourier transform infrared spectroscopy*
HPA	*Heteropolyacid*
HFIP	*Hexafluoroisopropanol*
HPLC	*High pressure liquid chromatography*
H-MOR	*H-mordenite*
HTC	*Hydrothermal carbonization*
IEA	*International Energy Agency*
IL	*Ionic liquid*
LA	*Levulinic acid*
MCF	*Mesocellular silica foams*
MClx	*Metal chloride*
MOF	*Metalorganic framework*
MIBK	*Methyl isobutyl ketone*
MH	*Microwave heating*
MSP	*Minimum selling price*
DMA	*N,N dimethylacetamide*
$[NMM][CH_3SO_3]$	*N,N-methylmorpholinium methylsulfonate*
DMU	*N'-dimethyl urea*
TMU	*N'-N'- tetramethyl urea*
NHC	*N-heterocyclic carbenes*
$[NMP][CH_3SO_3]$	*N-methyl 2-pyrrolidonium methylsulfonate*
NMR	*Nuclear magnetic resonance*
PVA	*Polyvinyl alcohol*

PTSA	*p-toluene sulfonic acid*
$Sc(OTf)_3$	*Scandium triflate*
SEM	*Scanning electron microscope*
SP	*Side products*
SAPO	*Silicoaluminophosphate*
SSA	*Sulfosuccinic acid*
TEOS	*Tetraethyl orthosilicate*
TEAB	*Tetraethylammonium bromide*
$[TetraEG(MIM)_2][Oms]_2$	*Tetraethylene glycol-bis (3-methylimidazolium) dimesylate*
TGA	*Thermogravimetric analysis*
$[TriEG(MIM)_2][Oms]_2$	*Triethylene glycol-bis (3-methylimidazolium) dimesylate*
TPA	*Tungstophophoric acid*
TOF	*Turn over frequency*
USD	*United states dollars*
UQAM	*Université du Québec à Montreal*
XRD	*X-ray diffraction*
$Yb(OTf_3)$	*Ytterbium triflate*

Acknowledgements

"A journey of a thousand miles begins with one step".

Or so the famous proverb goes. This particular journey began back in 2016, when hesitantly I decided to quit what it would be considered by most a stable and comfortable life, for what I felt was my real wish. Almost 5 years later, I have finally reached my destination.

A journey of this magnitude is not possible without support. Lots of it. Even before embarking on this voyage, I needed help to find the courage to take that proverbial first step. And I found it thanks to my now wife Stephanie Bohn, who supported me in pursuing my goals, despite this meaning uprooting our stable lives in Germany, to move halfway across the world to Montreal.

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I would like to finish with a phrase by Henry Miller I found most fitting for this journey called PhD:

'One's destination is never a place, but a new way of seeing things.'

Contribution of authors

This thesis is submitted in the form of original papers, accepted or to be submitted for publication in peer-reviewed scientific journals. The candidate, Guillermo Alberto Portillo Perez, was responsible for designing and carrying out the experiments, as well as performing all the data analysis, and writing manuscripts and thesis. Dr Marie-Josée Dumont, the candidate's supervisor, contributed to all aspects of research work, including planning, and guiding the research, reviewing, and correcting the manuscripts and thesis. Dr. Agneev Mukherjee assisted in writing and editing the review paper. Drs. Kayim Pineda Urbina, R. Muñiz-Valencia, and Silvia Ceballos-Magaña contributed as part of a collaboration project for fruit waste valorization, providing use of their laboratories and samples. The details of the papers are provided as follows:

1. G. Portillo Perez, A. Mukherjee, M.-J. Dumont, Insights into HMF catalysis, J Ind Eng Chem, 70 (2019) 1-34
2. G. Portillo Perez, M.-J. Dumont, Production of HMF in high yield using a low cost and recyclable carbonaceous catalyst, Chem Eng J, 382 (2020) 122766.
3. G.A.P. Perez, M.-J. Dumont, Polyvinyl sulfonated catalyst and the effect of sulfonic sites on the dehydration of carbohydrates, Chem Eng J, 419 (2021) 129573.
4. G. Portillo-Pérez, M.-J. Dumont, K. Pineda-Urbina, R. Muñiz-Valencia, S.G. Ceballos-Magaña, Sustainable HMF production from mango pulp using a sulfonated PVA resin, submitted for publication.
5. G. Portillo Perez, M.-J. Dumont, Sulfosuccinic acid-based metal-organic framework for the synthesis of HMF from carbohydrates, submitted for publication.

1 Introduction

1.1 General introduction

In the past decades, it has become clear that the exhaustive use of fossil fuels and other non-renewables, such as minerals, have taken a toll on the planet, and this has translated to both an environmental and financial crisis. Society has been forced to look for increasingly difficult sources of fossil fuels to extract (e.g., oil sands). This drain of the planet's resources has had a harsh impact on the environment. The growing concern for the environment has led to look for substitutes for non-renewable products. Fossil gas and oil have found applications beyond their roles as fuels; they have become such a basic part of society that, according to the latest International Energy Agency's (IEA) oil market report, 9% of the crude oil is committed to the petrochemical industry and the production of solvents and organic chemicals [1, 2]. It is for this reason that research has been focusing in finding environmentally friendlier alternatives for these derivate oil fractions. One such replacement is 5-hydroxymethylfurfural (HMF), which was identified by the U.S Department of Energy (DOE) [3] as one of several "building blocks" for bio-based chemicals, while Bozell and Petersen [4] placed HMF in their "Top 10 +4". However, low production volumes and poor performing industrial scale-up are the main issues for its mainstream adoption. 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. A holistic approach to sustainable production has to consider several criteria like sustainable substrates, energy efficiency, waste generation, and highly-selective catalysts [5].

Homogeneous liquid Brønsted catalysts such as HCl and H_2SO_4 [6-10], have been widely used to produce HMF. Several experiments were performed using a variety of Brønsted acids and bases, like HCl, H_2SO_4 and NaOH [10-13], which showed that, while these can easily convert fructose, they have very low selectivity towards HMF. Brønsted acids can generally hydrolyze cellulosic materials [9, 14], but are rarely HMF-selective, generally leading to rehydration of the compound. The use of alkali media for glucose isomerization has been further explored [15-17], showing the importance of glucose isomerization for HMF synthesis.

Lewis acid salts helped reducing some of the main issues faced when using Brønsted acids. They have better recyclability and are less corrosive [18-20]. While Lewis acid salts have resulted in better selectivity from fructose and glucose, they tend to be soluble in the reaction system requiring the recyclability of the entire reaction system, i.e., catalyst and solvent [18, 21, 22].

Research on heterogeneous catalysis of HMF has been growing in popularity in recent years. These systems can be easily recyclable and have highly adjustable properties [23, 24]. While solid catalysts are more sustainable than soluble salts or liquid acids, they tend to be costly, and return low HMF yields from aldohexoses.

Carbonaceous catalysts can provide an ecofriendly solid support for catalysts. 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 despite having a considerably smaller surface area than other solid catalysts [25]. This good performance was ascribed to the presence of SO_3H groups, carboxylic acids, and phenols [25, 26]. Similarly, Guo, Fang and Zhou [27] tested different carbonaceous materials, like glucose, lignin, and bamboo to name a few, and observed a better catalytic activity with the sulfonated versions of the catalyst.

Ion exchange polymeric resins, such as Amberlyst and Nafion, have also been extensively used in a broad variety of catalytic reactions. Amberlyst is a polystyrene resin with sulfonic acid groups, while Nafion is a sulfonated and fluorinated vinyl ether copolymer. Both have been shown to work as catalysts for fructose dehydration [28, 29], albeit requiring long reaction times. More recent experiments showed improved yields at higher temperatures and shorter times, resulting in almost 100% HMF yield from fructose in DMSO at high fructose concentrations (50 wt%) [30, 31]. These results were attributable to its high concentration in sulfonic acid sites. However, when used for glucose dehydration, Amberlyst-15 produced anhydroglucose rather than HMF [32, 33]. Furthermore, the use of DMSO complicated separating the effects of the catalyst and the solvent, since DMSO has been known to act as a dehydration reaction promoter[34, 35].

Metal oxides, such as niobium, titanium and zirconium oxide, have often been used for HMF production due to their character as Lewis acid catalyst, isomerizing properties, and low toxicity [36-40]. Pretreatment of NbO with phosphoric acid increased its surface area as well as the amount of strong acid sites [41]. This pretreated catalyst, when used for fructose and glucose dehydration, gave HMF yields of 89 and 49%, respectively [42]. Similar results were obtained by Antonetti et al. [43] when using niobium phosphate and phosphate zirconium under microwave heating (ZrP).

Metalorganic frameworks (MOFs), organic-inorganic structured materials, are produced by forming arrays of metal centers crosslinked with organic molecules. The presence of the metal center and organic molecules with functional groups makes them attractive materials for catalysis [44-47]. Despite this, research on their application for carbohydrate dehydration has been limited. Zhang et al. used MIL-101 to encapsulate phosphotungstic acid to obtain HMF from sugars but failed in transforming glucose to HMF [48]. Herbts et al. developed a sulfonated version of MIL-101, obtaining yields of up to 50% molar yield of HMF from glucose [49]. Chen et al. observed a correlation between sulfonic sites density and HMF selectivity when using MIL-101 as catalyst [50].

Despite their numerous advantages (e.g. recyclability and tunability), few solid catalysts have been successfully applied in the conversion of complex biomass to HMF. Chambon et al. [51] could not observe a catalytic effect from H-USY zeolite when used for cellulose hydrolysis. Lanzafame et al. [52] suggested that given the size of cellulose, all catalytic activities took place on the surface of zeolites, with little improvement from cellulose/zeolite mass ratios above 10. Experimental runs using AlW and ZrW using tungstated alumina (AlW), a Lewis acid with high acid sites density, and tungstated zirconium (ZrW) which exhibits both Brønsted and Lewis acidities, gave cellulose conversion values of 47 and 42% respectively [51, 53]. Zhao et al. developed a Hafnium-functionalized version of MOF UiO-66, supported in a sulfonic polymer which was capable of reaching 49.6% HMF yield from cellulose [54].

While there is great potential in heterogenous systems for carbohydrate dehydration, research is still needed to improve selectivity from complex biomass, such as lignocellulosic wastes. The existing results show that bifunctional catalysts can produce HMF from aldohexoses, albeit with varying degrees of efficiency.

1.1. Hypothesis

1. Using non-expensive substrates, it is possible to develop an acid-functionalized, solid catalyst via sulfonation capable of dehydrating carbohydrates into HMF.

2. Controlled crosslinking of polyvinyl alcohol using sulfosuccinic acid as agent can provide sulfonic functional groups and can affect the physical properties to produce a solid catalyst resin for dehydration of carbohydrates into HMF.

3. It is possible to create a bifunctional catalyst in the form of a metalorganic framework, using sulfosuccinic acid as the crosslinker and known metal catalysts. Said material can convert aldohexoses into HMF.

4. Using a sulfonic catalyst, it is possible to valorize fruit waste, into HMF in a one-pot reaction.

1.2. Study Objectives

The objective of this work was to develop solid catalysts capable of transforming carbohydrates into HMF. Furthermore, the materials were characterized to determine functional groups, chemical composition, and thermal stability. Optimization via response surface methodology was used to find optimal conditions, and kinetic models provided insight into the reaction pathways of the different catalysts. More specifically, the objectives are described as follows:

Objective 1 (Chapter 2)

a) To review the current body of research on HMF synthesis, with a focus on understanding the catalytic processes, catalysts' properties, and identify potential lacks and trends in the literature.

Objective 2 (Chapter 3)

a) To develop a solid, recoverable catalyst, using an inexpensive softwood pulp and H_2SO_4 via hydrothermal carbonization and sulfonation.
b) To characterize said material to determine chemical composition and thermal stability.
c) To apply said material as a catalyst in the dehydration of fructose to obtain HMF
d) To optimize the reaction using response surface methodology, to maximize HMF yield

Objective 3 (Chapter 4)

a) To develop a polymeric sulfonic catalyst by using controlled addition of sulfosuccinic acid as crosslinking molecule providing both structure and functional sites.
b) To characterize chemically and physically the resulting materials.
c) To test the catalytic properties of the catalysts in the dehydration of sugars to HMF.
d) To optimize the reaction system to increase HMF yields via response surface methodology.
e) To develop a kinetic model fitting the experimental data to increase understanding of the reaction system.

Objective 4 (Chapter 5)

a) To apply the most promising PVA-SSA catalyst for the valorization of fruit residues to produce HMF.
b) To monitor sugar conversion via HPLC to understand the effects of the catalysts on the different substrates.

Objective 5 (Chapter 6)

a) To develop a bifunctional catalyst using sulfosuccinic acid as a crosslinking organic molecule, and known catalysts Cr, Ti, and Zr as metal centers of a novel metalorganic framework.
b) To characterize chemically and physically all three resulting materials.
c) To test the catalytic properties of the materials in the dehydration of sugars to HMF.
d) To develop kinetic models fitting the experimental data, to increase the understanding of the different pathways followed by the catalysts.

2 Literature review - Insights into HMF catalysis

2.1 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.

2.2 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 [2, 55]. 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 [56]. 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 [56]. 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 [56, 57]. 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 [58-60].

Despite the above mentioned potential, presently the production of HMF at an industrial scale is marginal [61, 62], 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 [5, 63] , 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 [59, 60, 64-72], 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.

2.3 Autocatalytic systems

A reaction system in which one of the produced species functions as a catalyst is considered an autocatalytic system [73-76]. For example, the dehydration of hexoses can be catalyzed by organic acids, such as levulinic acid (LA) and formic acid (FA) [10, 77, 78], 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 [34, 79]. This section looks at reaction systems where HMF is formed without the initial addition of a catalyst.

2.3.1 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 [80, 81]. 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 [82] or dimethyl sulfoxide (DMSO), that can more readily convert fructose to HMF[83]. 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.

2.3.1.1 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 [8, 10, 80]. 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 [84]. This was backed up by a later study using inulin as feedstock [85].

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 [86]. A thorough examination of the dehydration of fructose in subcritical water was performed by Asghari and Yoshida [87], 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 [77, 88-90]. This was further expanded upon by Li et al. [91], 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. [84] 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. [92, 93] 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 [94]. 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 [95]. 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 [96].

More examples of autocatalytic dehydration can be found as control experiments for other catalysts using different starting materials [15, 16, 19, 97]. 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 [12, 98]. 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 [84, 99, 100].

While the temperatures 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 [101]. Nevertheless, when analyzing this effect, Yu and Wu [102] 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 2.1.

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. Fig. 2.1 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.

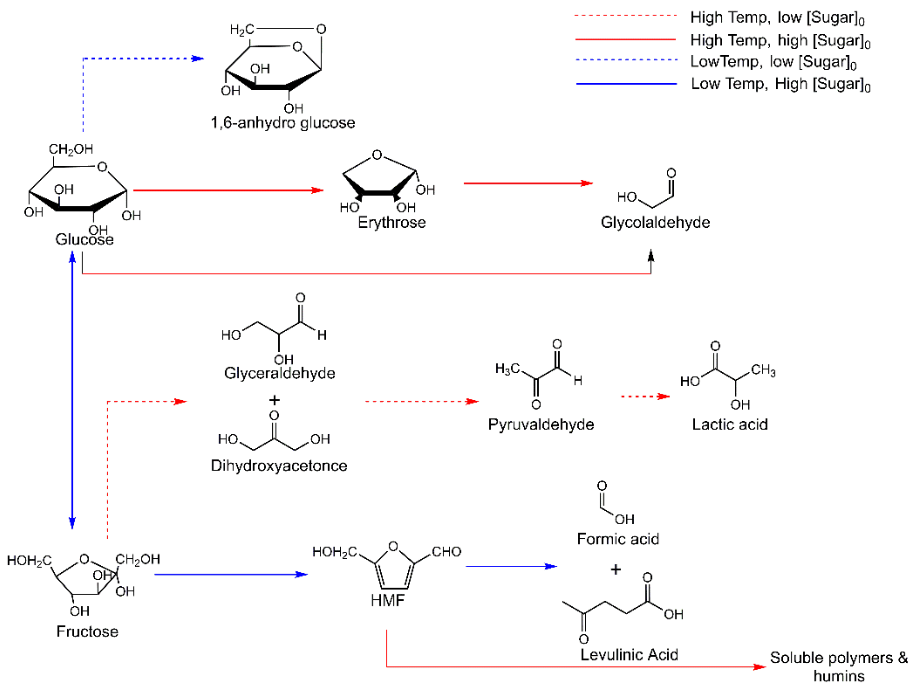
2.3.1.2 Supercritical Water

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 [103-105]. 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 [88, 92, 94, 106]. 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 [92, 107]. However, HMF yields are well below subcritical yield values. This was originally linked to higher water density [108], but later studies by Cantero et al. [109-111] 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. [112] on the hydrolysis of glucose in supercritical water, Watanabe et al. [113] 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 [17, 114]. Sweygers et al. [115] 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 2.1: 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 2.1. From Table 2.1, 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 %.

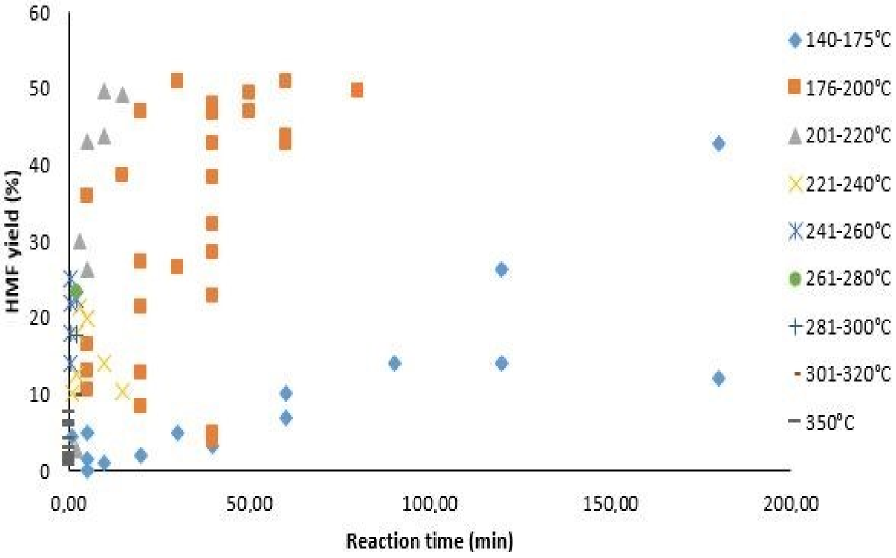


Figure 2.1: HMF yields from glucose at different reaction times and temperatures. Values collected from Table 2.1.

Table 2.1 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	[94]
	10 wt%	350		25	8.8 sec	99.3	10.9	[93]
	4 wt%	280-400^a		40	45.1 sec	-	7.3	[94]
Fructose	0.3 M	140		1	1 hour	-	4.4	[19]
	30 wt%	170		6.9	3 hours	84.0	42.8	[84]
	0.25 M	175		5.06	2 hours	97.0	14.0	[10]
	27 wt%	190	300	-	5 min	57.3	35.8	[114]
	10.8 wt%	190		10	1 hour	90.7	50.9	[91]
	2 wt%	200	*	1.2	5 min	28.2	13.2	[17]

	30 wt%	200	14.53	1 hour	97.0	42.7	[84]
	0.1 M	250	24.5	32 sec	-	25.0	[86]
	0.05 M	250	3.9	2 min	75.8	22.4	[87]
	0.05 M	270	5.4	2 min	97.3	23.3	[87]
	0.05 M	350	100	0.6 sec	67.0	7.7	[89]
Galactose	0.3 M	140	1	1 hour	-	0.0	[19]
Glucose	0.3 M	140	1	1 hour	-	0.0	[19]
	9 wt%	200	2.5	5 min	22.0	3.5	[15]
	9 wt%	200	2.5	10 min	30.0	6.0	[15]
	1 M	350	40	1.02 sec	50.8	3.3	[108]
	9 wt%	350	2.5	1 min	98.8	16.2	[113]
Mannose	0.3 M	140	1	1 hour	-	0.0	[19]
Sorbose	1 M	150-153	-	2 hours	-	27.1	[8]
Starch	10 wt%	220	1	20 min	-	22.0	[95]
Sucrose	1 M	162-167	-	2 hours	-	21.6	[8]

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

2.3.2 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 [80, 116]. 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).

2.3.2.1 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 [117], 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. [118] 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 [119] 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 [120-122]. 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 [123-126]. Still, their use in a wide range of chemical reactions, both as solvent and catalyst, cannot be disputed [120, 127]. Cellulose and other carbohydrates can dissolve in high concentration in ILs [128-130].

The first mention of a molten salt being used in the conversion of carbohydrates to HMF dates from 1983, when Fayet and Gelas [131] 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 [29] 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 [28, 132]. 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 [133]. 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. [18] 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 a 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. [134] used [$BMIM^+$][Cl^-] with fructose as the substrate. At 80 ºC 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 ^1H 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_xMIM^+] ILs perform very differently. A more detailed study showed that the alkyl group had an effect on the ILs catalytic performance [135]. The authors tested different ILs, such as [$BMIM^+$][Cl^-], 1-hexyl-3-methyl imidazolium chloride ([$HeMIM^+$][Cl^-]), 1-benzyl-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 [136-138]. However, a more recent study from Ryu et al. [139] could not confirm this effect. It can be concluded from these results and the results from Binder and Raines, and Ståhlberg et al. [140, 141], 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_4MIM^+] and [C_4Py^+] ILs with different anions such as [Cl^-], [BF_4^-] and [PF_6^-], Li et al. [142] 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 [135, 143, 144].

ILs other than in the form of [C_xMIM^+] have also been studied for HMF production. Tong et al. [138] 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. [145] 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 [127, 133, 141, 146]. 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. [147] 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[148]. 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 % [149].

Biomass hydrolysis has also been carried out in ionic liquids [128, 140]. [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 [21, 140, 150, 151]. However, there are interesting articles dealing with the hydrolysis of inulin and cellulose, and the dehydration of fructose and glucose to yield HMF [129, 152, 153]. Inulin was hydrolyzed using Brønsted acidic ILs [$EMIM^+$][HSO_4^-], [$BMIM^+$][HSO_4^-] and [$HMIM^+$][HSO_4^-] as catalyst in a [$BMIM^+$][Cl^-] solution [152]. 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 ºC and for a total reaction time of 65 minutes. Hsu et al. [154] 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 ºC, 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. [155] 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. [129, 156], 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.[157] 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 of the three, with 85% of sugars after 90 minutes at 100 °C.

Using a dicationic type of IL, Khan et al. [158] 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. [$C_4(MIM)_2$] [($2HSO_4^-$)([$H_2SO_4^-$]$)_2$] exhibit 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. [159] 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 2.2) require further examination. The effect of water content on the effectiveness of ionic liquids also deserves further study [160]. Additionally, given the questionable sustainability of ionic liquids [123-126], a deeper analysis should be made on the environmental impact of using such solvents for HMF production. Ilgen et al.[161] made a thorough comparison on the toxicity and environmental impact of different solvents used in HMF production (Fig. 2.2). 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.

2.3.2.2 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 [162], 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) [163].

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 [164, 165], 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 [161, 166, 167].

In order to find a clean and renewable solvent/catalyst system for fructose dehydration, Hu et al. [79] 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 [18]. 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 ºC 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 [79].

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 [79]. This process improved HMF yields in citric acid, from 51 to 57%. The same process was not tested with oxalic acid [153]. Their results are summarized in Table 2.3.

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. [161] 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. [168] 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.

2.3.2.3 DMSO

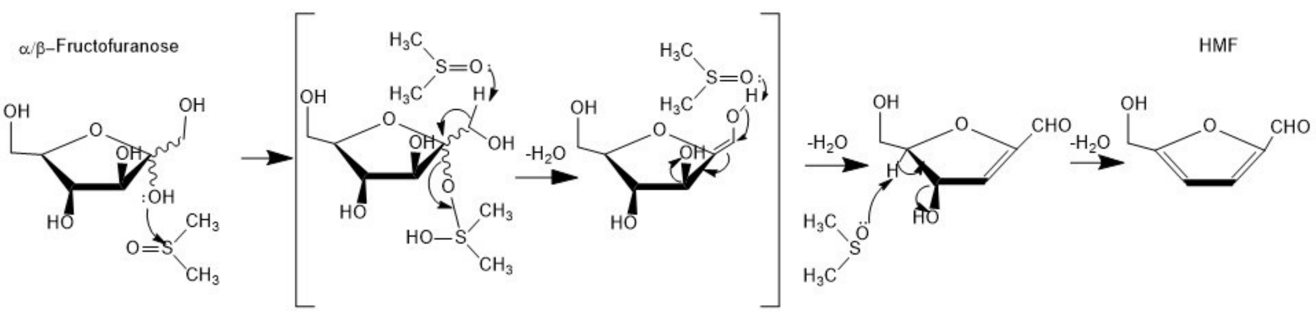
DMSO has long been identified as a solvolytic medium. Its nucleophilic action via carbonium ions promotes the dehydration of 1,4-diketones in furanic compounds [169, 170]. These findings have recently been explained through data obtained by ^{1}H and ^{13}C NMR [34]. The results showed that at 150 °C, 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.[171] 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 [83]. DMSO then binds to HMF more strongly than water does, and reduces its susceptibility to nucleophilic attack, thereby minimizing undesirable side reactions [172]. All these points mean that HMF yields from fructose in DMSO are often higher than in other solvents.

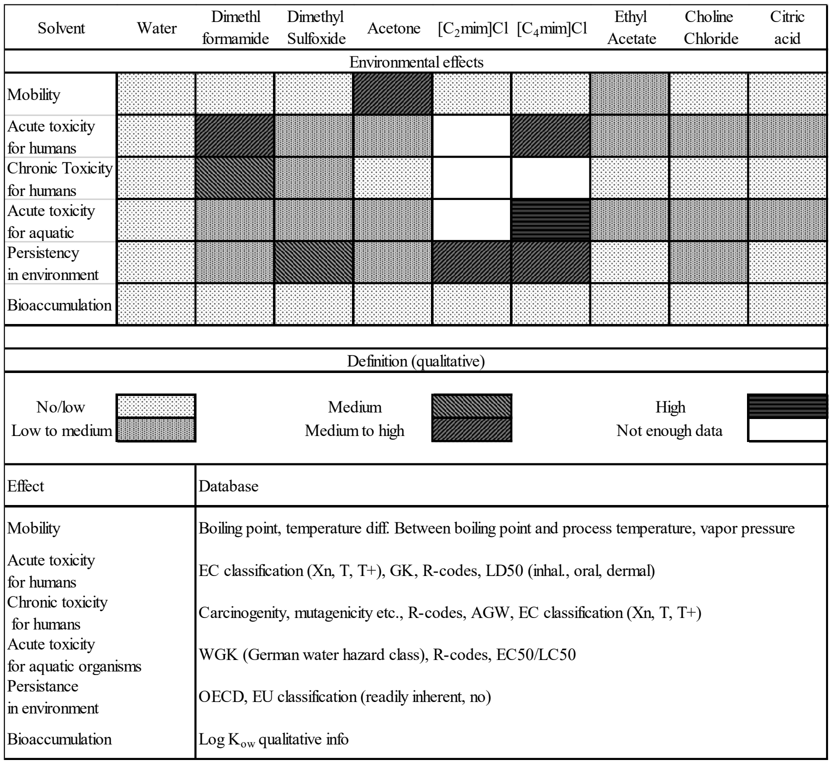
Early reports using DMSO as solvent showed that fructose could be fully converted to HMF after a reaction time of 16 hours and at a 100 °C reaction temperature [28]. A more recent study showed the formation of HMF in DMSO in high yields and considerably shorter reaction times [132]. Musau and Munavo [173] 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 ºC 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. [34] proposed a mechanism for fructose dehydration in DMSO, involving a dihydrofuran-2-aldehyde intermediate (shown in Scheme 2.2). While these results showed promise in DMSO, there have been other authors reporting very low values for uncatalyzed reaction in DMSO [29, 30, 136, 174, 175]. 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 H_2SO_4 in the presence of oxygen at temperatures above 80°C [35]. A comparison of these experiments can be seen in Table 2.4.

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 [28, 59]. The high toxicity of DMSO also makes its use questionable at industrial scale.



Scheme 2.2 Proposed mechanism of fructose dehydration in DMSO [34][1]



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 2.2 Qualitative solvent toxicity assessment, based on reference [161]

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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.

Table 2.2 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	[135]
			1:8.63	[BeMIM][Cl]	140	50 min	100	53.2	[135]
			1.0.06	[BMIM][Cl]	80	900 min		65	[134]
			1:10.31	[BMIM][Cl]	80	3 hours	3.85	0	[143]
			1:10.31	[BMIM][Cl]	100	3 hours	59.8	28.2	[143]
			1:20.63	[BMIM][Cl]	100	5 min	0	0	[144]
			1:10.31	[BMIM][Cl]	120	50 min	93.4	63.3	[135]
			1:10.31	[BMIM][Cl]	140	50 min	100	60.4	[135]
			1:10.43	[BMIM][Cl]	155[a]	1 min	99	98	[142]
			1:2.09	[BMIM][Cl]	175[a]	1.5 min	97	97	[142]
			1:0.26	[BMIM][Cl]	186[a]	1.5 min	65	62	[142]
			1:5.00	[BMIM][H_2SO_4]	80	1 hour	100	56.3	[79]
			1:5.80	[BMIM][PS]	140	50 min	49.9	0	[135]
			1:0.04	[C_3SO_3HMIM][HSO_4][b]	150	30 min	84	73	[176]
			1:1.00	[DiEG($mim)_2$][OMs]$_2$	120	40 min	100	69.8	[147]
			1:12.29	[EMIM][Cl]	80	3 hours	9	1.5	[18]
			1:12.29	[EMIM][Cl]	100	3 hours	58	40	[18]
			1:12.29	[EMIM][Cl]	120	3 hours	100	73	[18]
			1:9.04	[Et_3NH][HSO_4]	100	3 hours	99.6	36.6	[143]
			1:5.00	[$EtNH_3$][NO_3]	80	1 hour	48.2	1.1	[79]
			1:5.00	[HMIM][Cl][c]	80	1 hour	96.5	69.7	[79]
	0.12 mol	0.6 ml	-	[HMIM][Cl][c]	90	45 min	99	92	[133]
	0.12 mol	0.6 ml	-	[HMIM][Cl][c]	90	10 min	75	62	[133]
			1:8.89	[HeMIM][Cl][d]	120	50 min	65.7	7.3	[135]
			1:8.89	[HeMIM][Cl][d]	140	50 min	85.1	21.9	[135]
			1:7.81	[OMIM][Cl]	120	50 min	42.5	0	[135]
			1:7.81	[OMIM][Cl]	140	50 min	79.6	8.6	[135]
			1:5.00	[Pyr][HCl]	80	1 hour	92	69	[79]
			1:0.15	[Pyr][HCl]	90-100	30 min		12	[131]
			1:1.00	[Pyr][HCl]	90-100	30 min		50	[131]
			1:1.00	[TetraEG($mim)_2$][OMs]$_2$	120	40 min	100	92.3	[147]
			1:1.00	[TriEG($mim)_2$][OMs]$_2$	120	40 min	100	77.2	[147]
			1:5.00	PyTSA	80	1 hour	52	7.8	[79]
			1:5.00	TMG LAC	80	1 hour	4.75	0.6	[79]
			1:5.00	TMG TFA	80	1 hour	1.34	0.4	[79]
Glucose			1:9.04	[Et_3NH][HSO_4]	100	3 hours	93.9	1.2	[143]
			1:9.04	[Et_3NH][HSO_4]	100	3 hours	92	0.88	[143]

			1:12.29	[EMIM][Cl]	180	3 hours	42	3	[18]
			1:10.94	[EMIM][Cl]/H_2O	180	3 hours	5.5	2.5	[18]
			1:10.31	[BMIM][Cl]	80	3 hours		0.065	[143]
			1:10.31	[BMIM][Cl]	150	3 hours		3	[143]
			1:10.31	[BMIM][Cl]	180	3 hours		2.4	[143]
Sucrose			1:2	[DiEG(MIM)$_2$][OMs]$_2$	120	150 min		52	[147]
			1:2	[TetraEG(MIM)$_2$][OMs]$_2$	120	150 min		63	[147]
			1:2	[TriEG(MIM)$_2$][OMs]$_2$	120	150 min		60	[147]
Maltose			1:19.48	[BMIM][Cl]	100	3 hours	2.5	0.28	[143]
Starch	1 g	4 g	-	[OMIM][Cl]	120	30 min		0	[151]
	1 g	4 g	-	[OMIM][Cl]	120	90 min		0	[151]
	1 g	4 g	-	[OMIM][Cl]	120	60 min		0	[151]
	1 g	4 g	-	[OMIM][Cl]	120	120 min		0	[151]
Cellulose	0.4 g	8 g	-	[BMIM][Cl]	100	1 hour		0	[155]
	0.1 g	2 g/0.2 g	-	[BMIM][Cl]/IL-SO_3	100	90 min	89	0	[157]

[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 2.3 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 2.4 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	[29]
1:30.44	90	2 hours		2.4	[146]
1:44.8	100	16 hours	100	100	[28]
1:101	120	80 minutes	100	80	[132]
1:0.14	150	2 hours		1.8	[173]
1:6.2	150	2 hours		84	[173]
1:8.5	150	2 hours		92	[173]
1:12.4	150	2 hours		80	[173]
1:0.6	160	2 hours		22	[173]
1:20.77	q	4 min	100	92	[177]
1:20.77	150	300 min	100	90	[177]
1:7.2	150	30 min	100	78	[35]
1:7.2^b	150	30 min	10	0	[35]

^{a} MH (900 W)

^{b}Deareated DMSO

2.4 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 [6, 178] produced HMF from sucrose using oxalic acid to trigger the reaction. 50 years later, Haworth and Jones [179] 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 [17, 101]. 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.

2.4.1 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 [6-10]. In the past years, soluble Lewis acid salts became more widely used due to the ease of their recovery and recyclability [18-20]. Although Brønsted acids can generally hydrolyze cellulosic materials [9, 14], they are rarely selective towards HMF. On the other hand, Lewis acid catalysts have shown very promising results as the conversion of glucose and fructose resulted in high HMF selectivity [18, 21, 22].

2.4.1.1 Brønsted acids

Several experiments have been performed using a variety of Brønsted acids and bases, like HCl, H_2SO_4 and NaOH [10-13], which showed that while these can easily convert fructose, they have very low selectivity towards HMF. Table 2.5 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 [15, 17] and further dehydrated to HMF, hypothesizing that isomerization is an intermediate step in its dehydration [11, 86]. Although Kuster et al. [101] 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 [35, 180].

Nevertheless, Bicker, Hirth and Vogel reported observing increasing HMF selectivity with higher H_2SO_4 concentrations in an acetone/water mixture [181]. 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 [182]. Bao et al. [137] 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. [183] failed to obtain any HMF or LA using HNO_3. This, together with previous observations [10-12, 86], highlights the importance of the anion half of the Brønsted acids.

A more recent study 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%) [35]. 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 propose 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 [184]. 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 [134]. 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 [20] 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 2.3). Hansen [185] and Ståhlberg [186] dehydrated fructose and glucose respectively using boric acid (H_3BO_3) in [C$_x$MIM$^+$][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. [87] 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. [187], showed that successful protonation of C2OH will 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 [87, 101, 102, 114, 188]. 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 [189-192]. The use of metal salts acting as Lewis acids or acidic ILs can counter these side effects.

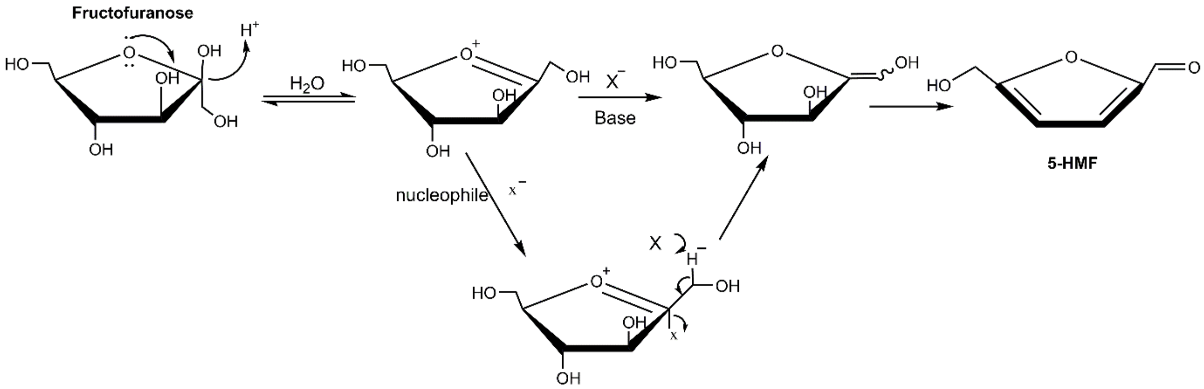
Antal et al. [86] proposed a glucose dehydration mechanism that did not require glucose isomerization to fructose, but instead involves 3-deox-d-erythro-hex-2-ulose (3-deoxyglucosone or 3-DG) as an intermediate. In this experiment, 3-DG was detected in low amounts under weak acidic conditions. More recently, 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 [193]. 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 [194], this is nevertheless a bottleneck for HMF production from fructose, as are the numerous side reactions of 3-DG [195].

Through a DFT theoretical analysis of glucose dehydration, Qian [196] 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. [187], 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 [197]. 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 2.4

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 [9]. Using H_2SO_4 as catalyst, Mok et al. [14] were able to obtain, at 215 °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. [186] obtained close to 35% HMF yield after a long reaction time (8 hours) at 120 °C.

Another work by Wu et al. [198] 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 2.3 Proposed mechanism for fructose dehydration in the presence of halides[20][2].

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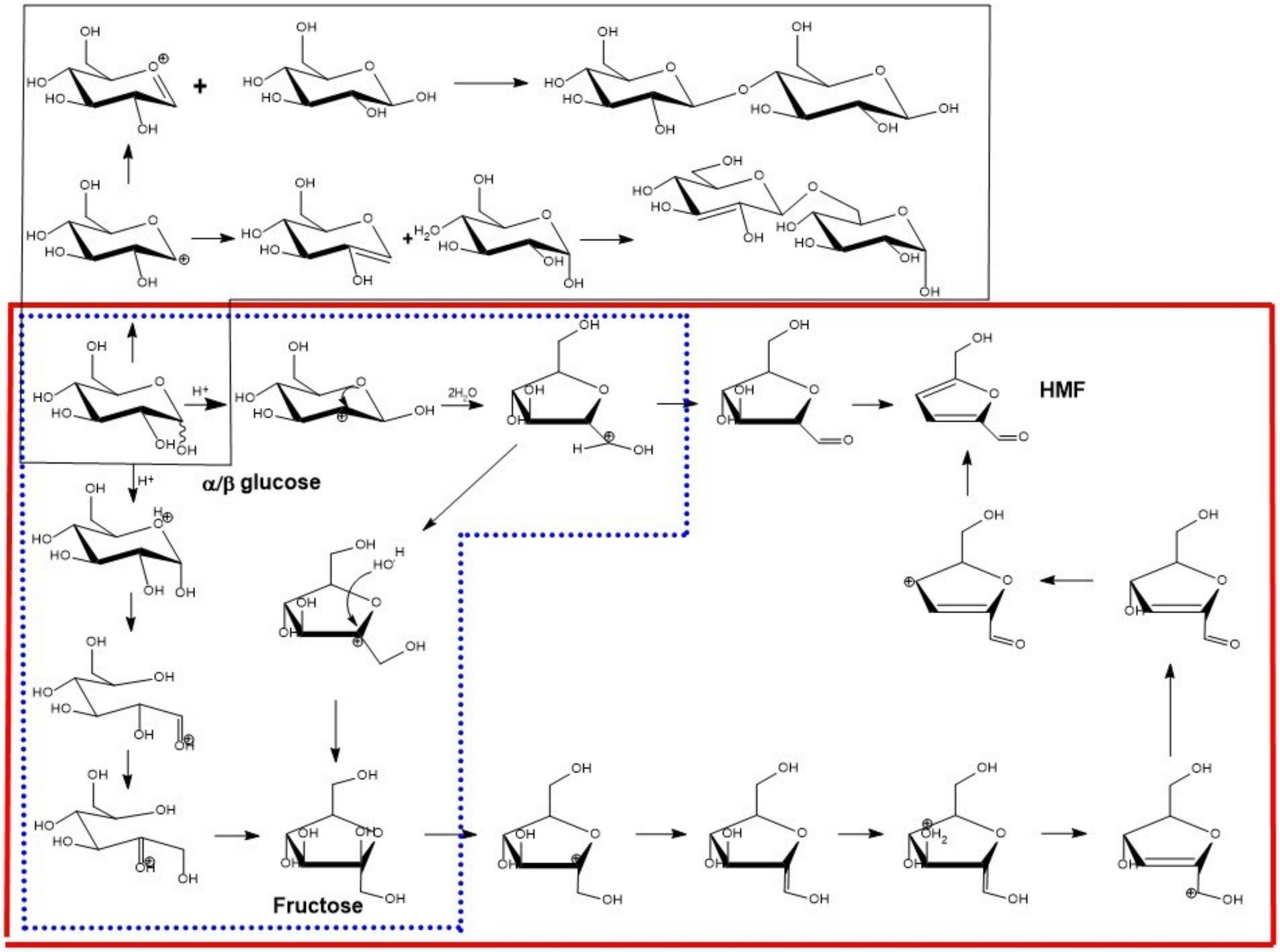
[2] Reprinted from Journal of the American Chemical Society, 131/5, Binder, Joseph, Raines, Ronald, Simple Chemical Transformation of Lignocellulosic Biomass into Furans for Fuels and Chemicals, 1979-1985, Copyright 2009, with permission from ACS.



Scheme 2.4 Possible catalytic pathways for glucose dehydration in the presence of Brønsted acids. Based on references [187, 196, 197].

2.4.1.2 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 [199]. 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 [18-20, 183, 200]. In their pivotal work, Zhao et al. [18] 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 [18]. 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 [201].

After the work of Zhao et al., several other authors have expanded this scheme for more specific cases such as $SnCl_4$ [202] or $CrCl_3$ [21]. A generalization of these mechanisms can be seen in Scheme 2.5. 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 [20] 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. [203] 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. [204] 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. [200] 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 [19]. Ståhlberg et al. [141] 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. [205] 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 [206], 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) [207].

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 [151, 208, 209]. Su et al. [210] 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. [211] 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 °C 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 [212-214], 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, [188, 215]. Their previous work with fructose showed that $[BMIM^+][HSO_4^-]$ could be a suitable co-catalyst to produce HMF [216], 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 $[CrCl_4^-]$ [188, 215].A two-step process using NaOH to pretreat wood chips and $CrCl_3•6H_2O$ allowed Nguyen et al. [217] 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. [218] 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 [219, 220]. 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 [185, 221, 222]. It was found that using halide salts increased HMF yields [20, 223]. 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 [224]. 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 [225], 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 decelerating the isomerization step [224]. 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 [226].

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 2.5 to 2.10, 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 2.5 Fructose dehydration in the presence of homogeneous Brønsted acid 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	[137]
[BMIM][Cl]	9.1	[BIMIM][HSO_4]	0.17 mmol	80	30 min		80	[134]
[BMIM][Cl]	9.1	[SBMIM][HSO_4]	0.13 mmol	80	26 min		91	[134]
[BMIM][Cl]	9.1	CH_3COOH	0.17 mmol	80	720 min		78	[134]
Water	1.1	CH_2OH (FA)	0.23 mol %	220	4 min	99	55	[91]

[BMIM][Cl]	4.8	CH_3COOH	18 mol %	80	10 min	0	0	[184]
Water	1.1	CH_3COOH	0.18 mol %	220	4 min	97	58	[91]
Water	1.8	H_2SO_4	2 mmol	250	0.5 min		48	[86]
Water	9.1	H_2SO_4	1 M	200	5 min		23	[15]
Water/ (7:3 MIBK:2-butanol) 1:3	30	H_2SO_4	0.25 M	180	2.5 min	80	52.8	[227]
(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	[227]
[BMIM][Cl]	4.8	H_2SO_4	0.75 mmol	120	30 min	100	97	[22]
[BMIM][Cl]	4.8	H_2SO_4	18 mol %	80	10 min	81	69	[184]
DMA-LiCl 10 wt%	10	H_2SO_4	6 mol %	80	4 hours		66	[20]
Water	2	H_2SO_4	2:1 Fru:Cat (w)	200	5 min	97.3	47	[17]
[BMIM][Cl]	9.1	H_2SO_4	0.1 mmol	80	3 min		91	[134]
[BMIM][Cl]	9.1	H_2SO_4	10 mol %	100	50 min	100	82.9	[135]
Water/ MIBK 1:4	30	H_3BO_3	3.2 M	150	45 min	58	28	[185]
Water-NaCl/ MIBK (1.2 M NaCl) 1:4	30	H_3BO_3	1.6 M	150	45 min	70	46	[114]
Water/ (7:3 MIBK:2-butanol) 1:3	30	H_3PO_4	0.25 M	180	2.5 min	65	42.3	[227]
(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	[227]
Water	1.8	H_3PO_4	$pH_{sol}=2$	240	2 min		65	[87]
[BMIM][Cl]	4.8	H_3PO_4	18 mol %	80	10 min	1	0	[184]
[BMIM][Cl]	9.1	H_3PO_4	0.09 mmol	80	720 min		67	[134]
Water	9.1	H_3PO_4	$pH_{sol}=2$	200	5 min	90	28	[13]i
Sulfolane	6.3	HBr	5 mol %	90	60 min		93	[228]
Water/ PG-600 3:2	8.3	HCl	1 M	95	15 min		45	
Water	30	HCl	0.25 M	180	2.5 min	50	25.5	[227]

Water/ MIBK	30	HCl	0.25 M	180	2.5 min	91	54.6	[227]
Water/ MIBK	30	HCl	0.25 M	180	2.5 min	75	54.7	[227]
Water/ (7:3 MIBK:2-butanol) 1:1	30	HCl	0.25 M	180	2.5 min	68	47.6	[227]
Water/ (7:3MIBK:2-butanol) 1:1	30	HCl	0.25 M	180	2.5 min	86	68.8	[227]
(8:2 Water:DMSO)/ MIBK 1:1	30	HCl	0.25 M	180	2.5 min	94	63	[227]
(8:2 Water:DMSO)/ (7:3 MIBK:2-butanol) 1:1	30	HCl	0.25 M	180	2.5 min	80	60	[227]
(8:2 Water:DMSO)/ (7:3 MIBK:2-butanol) 1:3	30	HCl	0.25 M	180	2.5 min	87	71.3	[227]
(7:3 Water:PVP)/ MIBK 1:1	30	HCl	0.25 M	180	2.5 min	74	48.8	[227]
(7:3 Water:PVP)/ (7:3 MIBK:2-butanol) 1:1	30	HCl	0.25 M	180	2.5 min	62	47.1	[227]
(7:3 Water:PVP)/ (7:3 MIBK:2-butanol) 1:3	30	HCl	0.25 M	180	2.5 min	79	64.7	[227]
[7:3(8:2 Water:DMSO):PVP] /MIBK 1:1	30	HCl	0.25 M	180	2.5 min	79	59.2	[227]
[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	[227]
[7:3(8:2 Water:DMSO):PVP]	30	HCl	0.25 M	180	2.5 min	89	75.7	[227]

/(7:3 MIBK-2-Butanol) 1:3								
Water	5	HCl	pH_{sol}=1.8	240	5 sec		20	[191]
[BMIM][Cl]	4.8	HCl	18 mol %	80	10 min	3	2	[184]
Water	27	HCl	0.01 M	200**	1 min	95	53	[114]
[BMIM][Cl]	9.1	HCl	0.2 mmol	80	8 min		97	[134]
[BMIM][Br]	9.1	HCl	0.2 mmol	80	11.5 min		95	[134]
[AMIM][Cl]	9.1	HCl	0.2 mmol	80	25 min		96	[134]
[EMIM][Br]	9.1	HCl	0.2 mmol	80	2 min		88	[134]
[HMIM][Cl][a]	9.1	HCl	0.2 mmol	80	360 min		85	[134]
$[BMIM][BF_4]$	9.1	HCl	0.2 mmol	80	60 min		5	[134]
$[BMIM][PF_6]$	9.1	HCl	0.2 mmol	80	60 min		8	[134]
[BMIM][Cl]	67	HCl	9 mol %	80	120 min	67	51	[134]
[BMIM][Cl]	33	HCl	9 mol %	80	35 min	90	82	[134]
Water	10	HCl	0.1 M	140	25 min	65	40	[225]
Water-KBr/ MeCN (0.1 M KBr) 1:2	10	HCl	0.1 M	160***	1 min	99	85	[229]
[BMIM][Cl]	9.1	HNO_3	0.2 mmol	80	5 min		93	[134]
[BMIM][Cl]	9.1	Maleic Acid	0.17 mmol	80	50 min		88	[134]
Water	9.1	NaOH	1 M	200	5 min		12	[15]
Water	2	NaOH	2:1 Fru:Cat (w)	200	5 min	72.9	2.8	[17]
Water	9.1	NaOH	pH_{sol}=11	200	5 min	82	19	[13]
Water	0.4	PTSA	1 M	88	240 min	52	22	[101]
DMSO/ $[BMIM][BF_4]$ 5:3	8.3	PTSA	0.04 mmol	80	32 hours		68	[29]
DMSO/ $[BMIM][BF_4]$ 5:3	8.3	PTSA	0.04 mmol	80	20 hours		75	[29]

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

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

Table 2.6 Glucose dehydration in the presence of homogeneous Brønsted acid 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	[230]
[BMIM][Cl]	8.3	CF_3COOH	0.01 mmol	120	180 min	58	43,5	[231]
[BMIM][Cl]	8.3	CF_3SO_3H	0.01 mmol	120	180 min	87	46	[231]
[BMIM][Cl]	8.3	CH_3SO_3H	0.01 mmol	120	180 min	73	58	[231]
[BMIM][Cl]	4.8	H_2SO_4	0.75 mmol	120	120 min	100	15	[22]
[BMIM][Cl]	8.3	H_2SO_4	0.01 mmol	120	180 min	93	66	[231]
[EMIM][Cl]	9.1	H_2SO_4	6 mol %	80	180 hours	93.7	9.3	[18]
CPL/LiCl 3:1	10	H_2SO_4	6 mol %	100	180 min		12.6	[203]
Water	9.1	H_2SO_4	1 M	200	5 min		3	[15]
Water	2	H_2SO_4	2:1 S:C (wt)	200	5 min	10.6	2.4	[17]
[BMIM][Cl]	9.1	H_2SO_4	10 wt %	400*	1 min		49	[21]
[BMIM][Cl]	9.1	H_3BO_3	0.44 mmol	120	180 min	46.6	14	[186]
[EMIM][Cl]	9.1	H_3BO_3	0.44 mmol	120	180 min	95	41	[186]
[BMIM][Cl]	8.3	H_3PO_4	0.01 mmol	393	180 min	13	12	[231]
Water	20	H_3PO_4	0.015 mol	228	57 min		14.9	[11]
Water	1	H_3PO_4	0.04 mol/l	170	120 min	26	8	[232]
Water	9.1	H_3PO_4	$pH_{sol}=2$	200	5 min	42	4.1	[13]
[BMIM][Cl]	8.3	HCl	0.01 mmol	393	180 min	53	32,9	[231]
Water-NaCl / 1-Butanol 1:3 (0.35 g NaCl)	10	HCl	$pH_{sol}=1$	160	60 min	26	10,4	[233]
Water-NaCl/ CPME (1:0.4:1)**	10	HCl	$pH_{sol}=2.5$	175	20 min	15.5	4.5	[226]
[BMIM][Cl]	8.3	HNO_3	0.01 mmol	120	180 min	56	43,1	[231]
Water	9.1	NaOH	1 M	200	5 min		2	[15]
Water	2	NaOH	2:1 S:C (wt)	200	5 min	46.6	4.93	[17]
Water	9.1	NaOH	$pH_{sol}=11$	200	5 min	40	4	[13]

* MH in (W), no temperature specified

** CPME = cyclopentyl methyl ether

Table 2.7 Fructose dehydration in the presence of homogeneous Lewis acid 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	[137]
DMSO/Water 1:1	5	$AlCl_3$	55.5 mmol	140	20 min		23	[212]
[BMIM][Cl]	4.8	$BiCl_3$	10 mol %	100	5 min		8.1	[144]
[BMIM][Cl]	4.8	$CeCl_3$	10 mol %	100	5 min		0.9	[144]
ChoCl	40	$CrCl_2$	10 mol %	100	30 min		40	[161]
ChoCl	40	$CrCl_3$	10 mol %	100	30 min		60	[161]
[BMIM][Cl]	9.1	$CrCl_3*6H_2O$	10 mol %	100	120 min	100	75.3	[135]
[BMIM][HSO_4]	-	$CrCl_3*6H_2O$	7 mol %	80	24 hours		85	[216]
[BMIM][HSO_4]	-	$CrCl_3*6H_2O$	7 mol %	100	3 hours		96	[216]
DMSO/Water 1:1		$CrCl_3*6H_2O$	55.5 mmol	140	20 min		35	[212]
Water	10	$CrCl_3*6H_2O$	100:3 Fru:Cat molar	150	60 min	85	20	[225]
DMA-LiCl (10 wt%)	10	CuCl	6 mol %	80	5 hours		62	[20]
[BMIM][Cl]	4.8	CuCl2	18 mol %	80	10 min	97	80	[184]
DMSO/Water 1:1		$CuCl_2$	55.5 mmol	140	20 min			[212]
NMP	9.1	$FeCl_2$	0.56 mmol	90	120 min		1	[234]
[BMIM][Cl]	3.5	$FeCl_3$	0.001 mmol	80	120 min		87.7	[235]
[BMIM][Cl]/ Ethanol 1:1	3.5	$FeCl_3$	0.001 mmol	80	120 min		83	[235]
ChoCl	40	$FeCl_3$	10 mol %	100	30 min		59	[161]
DMSO/Water 1:1		$FeCl_3$	55.5 mmol	140	20 min		69	[212]
NMP	9.1	$FeCl_3$	0.56 mmol	90	120 min	98	42	[234]
[BMIM][Cl]	4.8	$GeCl_4$	10 mol %	100	5 min		92.1	[144]
[BMIM][Cl]	4.8	$HfCl_4$	10 mol %	100	5 min		57.7	[144]
DMSO	2	$Ho(Otf)_3$	4 mg	120	120 min		78.1	[205]
DMSO/Water 1:1		$InCl_3$	55.5 mmol	140	20 min		7	[212]
[BMIM][Cl]	9.1	$IrCl_3$ (hydrated)	10 mol %	100	30 min	99	70.2	[143]
Sulfolane	6.3	LiBr	100 wt %	90	240 min		79	[228]
DMA	10	LiCl	10 wt %	120	2 hours		65	[20]

DMSO/Water 1:1		LiCl	55.5 mmol	140	20 min		1	[212]
Sulfolane	7.7	LiCl	6.3 wt%	90	120 min		67	[228]
Sulfolane	6.3	LiI	100 wt %	100	360 min		30	[228]
DMSO	2	$Nd(Otf)_3$	4 mg	120	120 min		63.5	[205]
ChoCl	40	pTSOH	10 mol %	100	30 min		67	[161]
ChoCl	40	$Sc(Otf)_3$	10 mol %	100	30 min		55	[161]
DMSO	2	$Sc(Otf)_3$	4 mg	120	120 min		83.3	[205]
[BMIM][Cl]	4.8	$ScCl_3*6H_2O$	10 mol %	100	5 min		4	[144]
DMSO	2	$Sm(Otf)_3$	4 mg	120	120 min		73	[205]
[BMIM][Cl]	4.8	$SnCl_4*4H_2O$	10 mol %	100	5 min		5.5	[144]
[EMIM][BF_4]	16.7	$SnCl_4*5H_2O$	10 mol %	100	180 min	100	62	[202]
DMSO/Water 1:1		$SnCl_4*5H_2O$	55.5 mmol	140	20 min		63	[212]
DMSO/Water 1:1		$YbCl_3*6H_2O$	55.5 mmol	140	20 min		27	[212]
DMSO	2	$Yb(Otf)_3$	4 mg	120	120 min		80.2	[205]
ChoCl	40	$ZnCl_2$	10 mol %	100	30 min		8	[161]
[BMIM][Cl]	4.8	$ZrCl_4$	10 mol %	220	2 min	98.9	92.9	[236]
[BMIM][Cl]	4.8	$ZrCl_4$	10 mol %	100	5 min		43.8	[144]

Table 2.8 Glucose dehydration in the presence of homogeneous Lewis acid 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	[220]
Water	1	[SMIM][Cl]	10 g	130	4 hours	95	32	[220]
Water	1	[SMIM][$FeCl_4$]	10 g	110	5 hours	50	13	[220]
Water-NaCl/ CPME (1:0.4:5)	10	$AlCl_3$	0.025 mmol	175	20 min	88	57	[226]
Water-NaCl/ CPME (1:0.4:1)	10	$AlCl_3$	0.025 mmol	175	20 min	92.5	46	[226]
Water/THF	2	$AlCl_3*6H_2O$	0.1 M	170	10 min		43	[237]
CPL/LiCl 3:1	10	$AlCl_3$	6 mol %	100	180 min		9.7	[203]
DMSO/Water 1:1	5	$AlCl_3*6H_2O$	55.5 mmol	140	20 min		25	[212]
[EMIM][Cl]	9.1	$AlCl_4$	6 mol %	80	180 min	97.3	10.5	[18]
[EMIM][Cl]	9.2	$CeCl_3$	0.056 mmol	140	360 min	75	3	[141]
[BMIM][Cl]	9.2	$CeCl_3$	0.056 mmol	140	360 min	100	3	[141]
[EMIM][Cl]	9.1	$CrCl_2$	2.6 mg	100	180 min	94	63	[204]
ChoCl	40	$CrCl_2$	10 mol %	100	30 min		45	[161]
Water	1	$CrCl_3$	0.04 mol/l	170	120 min	90	10	[232]
Water	1	$CrCl_3$	0.04 mol/l	170	120 min	62	8	[232]
Water	10	$CrCl_3*6H_2O$	Glu:cat 3:100 (w)	140	90 min	77	18	[225]
[EMIM][Cl]	9.1	$CrCl_3$	2.6 mg	100	180 min	94	63	[204]
ChoCl	40	$CrCl_3$	10 mol %	100	30 min		31	[161]
[EMIM][Cl]	9.1	$CrCl_3$	6 mol %	80	180 min	94.4	67.8	[18]
[BMIM][HSO_4]	12.5	$CrCl_3*6H_2O$	7 mol %	100	24 hours		33	[215]
[BMIM][Cl]	12.5	$CrCl_3*6H_2O$	7 mol %	120	15 min		65	[215]
Tetraethylammonium chloride	5	$CrCl_3*6H_2O$	10 mol %	130	10 min		71.5	[238]
[EMIM][Cl]	9.1	$CrCl_3*6H_2O$	2.6 mg	100	180 min	97	72	[204]
[BMIM][Cl]	4.8	$CrCl_3*6H_2O$	0.015 g	140^{*}	0.5 min	98	71	[239]
[BMIM][Cl]	4.8	$CrCl_3*6H_2O$	0.015 g	140	0.5 min		48	[239]
CPL/LiCl 3:1	10	$CrCl_3*6H_2O$	6 mol %	100	180 min		66.7	[203]
CPL/LiBr 3:1	10	$CrCl_3*6H_2O$	6 mol %	100	180 min		61.5	[203]
CPL/ZnCl2 4:1	10	$CrCl_3*6H_2O$	6 mol %	100	180 min		14.1	[203]
[BMIM][Cl]	9.1	$CrCl_3*6H_2O$	3.6 wt %	400^{**}	1 min		91	[21]
[BMIM][Cl]	9.1	$CrCl_3*6H_2O$	3.6 wt %	100	60 min		17	[21]
[BMIM][Cl]	9.1	$CrCl_3*6H_2O$	3.6 wt %	400^{**}	10 min		1	[21]

DMSO/ Water 1:1	5	$CrCl_3*6H_2O$	55.5 mmol	140	20 min		21	[212]
[EMIM][Cl]	9.1	$CrCl_4$	6 mol %	80	180 min	71.6	43.9	[18]
ChoCl-Water/MIBK	20	$Cu(NTf_2)_2$	3 mol %	180^*	15 min	72	46	[240]
ChoCl-Water/MIBK	10	$Cu(NTf_2)_2$	3 mol %	150^*	15 min	90	70	[240]
CPL/LiCl 3:1	10	$CuCl_2$	6 mol %	100	180 min		7.3	[203]
[EMIM][Cl]	9.1	$CuCl_2$	6 mol %	80	180 min	0	0	[18]
DMSO/Water 1:1	5	$CuCl_2$	55.5 mmol	140	20 min		3	[212]
[EMIM][Cl]	9.1	$CuCl_3$	6 mol %	80	180 min	84.7	5.7	[18]
[EMIM][Cl]	9.1	$CuClBr_2$	6 mol %	80	180 min	40.1	3.9	[18]
[EMIM][Cl]	9.2	$DyCl_3$	0.056 mmol	140	360 min	43.5	10	[141]
[BMIM][Cl]	9.2	$DyCl_3$	0.056 mmol	140	360 min	52.6	10	[141]
ChoCl	40	$FeCl_3$	10 mol %	100	30 min		15	[161]
[EMIM][Cl]	9.1	$FeCl_3$	6 mol %	80	180 min	0	0	[18]
DMSO/Water 1:1	5	$FeCl_3$	55.5 mmol	140	20 min		4	[212]
[EMIM][Cl]	9.1	$FeCl_4$	6 mol %	80	180 min	47.4	5.7	[18]
DMSO/Water 1:1	5	$InCl_3$	55.5 mmol	140	20 min		5	[212]
[BMIM][Cl]	9.1	$IrCl_3$ (hydrated)	7 mol %	140	180 min	69.5	7.5	[143]
[EMIM][Cl]	9.1	$LaCl_3$	6 mol %	80	180 min	0	0	[18]
[EMIM][Cl]	9.1	LiCl	6 mol %	80	180 min	0	0	[18]
DMSO/Water 1:1	5	LiCl	55.5 mmol	140	20 min		0	[212]
[EMIM][Cl]	9.1	$MnCl_3$	6 mol %	80	180 min	0	0	[18]
[EMIM][Cl]	9.1	$MoCl_4$	6 mol %	80	180 min	46.3	6.3	[18]
[EMIM][Cl]	9.1	NaCl	6 mol %	80	180 min	0	0	[18]
[EMIM][Cl]	9.2	$NdCl_3$	0.056 mmol	140	360 min	34.8	8	[141]
[BMIM][Cl]	9.2	$NdCl_3$	0.056 mmol	140	360 min	50	12	[141]
[EMIM][Cl]	9.1	$PdCl_3$	6 mol %	80	180 min	19.6	1.2	[18]
[EMIM][Cl]	9.2	$PrCl_3$	0.056 mmol	140	360 min	31.8	7	[141]
[BMIM][Cl]	9.2	$PrCl_3$	0.056 mmol	140	360 min	48.1	13	[141]
[EMIM][Cl]	9.1	$PtCl_3$	6 mol %	80	180 min	64.8	6.8	[18]
[EMIM][Cl]	9.1	$PtCl_5$	6 mol %	80	180 min	87.6	12.1	[18]
ChoCl	40	pTSOH	10 mol %	100	30 min		15	[161]
[EMIM][Cl]	9.1	$RhCl_4$	6 mol %	80	180 min	54.7	3.4	[18]
[EMIM][Cl]	9.1	$RuCl_4$	6 mol %	80	180 min	65	6.6	[18]
ChoCl	40	$Sc(Otf)_3$	10 mol %	100	30 min		9	[161]
CPL/LiCl 3:1	10	$SnCl_4*5H_2O$	6 mol %	100	180 min		64.7	[203]
DMSO	9.2	$SnCl_4*5H_2O$	10 mol %	100	180 min	97	42	[202]
[BMIM][Cl]	9.2	$SnCl_4*5H_2O$	10 mol %	100	180 min	66	12	[202]
[BMIM][BF_4]	9.2	$SnCl_4*5H_2O$	10 mol %	100	180 min	86	32	[202]
[BMIM][PF_6]	9.2	$SnCl_4*5H_2O$	10 mol %	100	180 min	99	2	[202]
[BMIM][Tf_2N]	9.2	$SnCl_4*5H_2O$	10 mol %	100	180 min	100	1	[202]

[BMIM][TFA]	9.2	$SnCl_4$*5H_2O	10 mol %	100	180 min	71	7	[202]
[BMIM][Trif]	9.2	$SnCl_4$*5H_2O	10 mol %	100	180 min	100	2	[202]
[BMIM][Sacc]	9.2	$SnCl_4$*5H_2O	10 mol %	100	180 min	96	4	[202]
[Bpyr][BF_4]	9.2	$SnCl_4$*5H_2O	10 mol %	100	180 min	78	21	[202]
[EMIM][BF_4]	9.2	$SnCl_4$*5H_2O	10 mol %	100	180 min	97	57	[202]
DMSO/Water 1:1	5	$SnCl_4$*5H_2O	55.5 mmol	140	20 min		22	[212]
[EMIM][Cl]	9.1	VCl_4	6 mol %	80	180 min	61.8	7.2	[18]
[EMIM][Cl]	9.2	Yb(Otf)$_3$	0.056 mmol	140	360 min	65	24	[141]
[BMIM][Cl]	9.2	Yb(Otf)$_3$	0.056 mmol	140	360 min	62.5	10	[141]
[EMIM][Cl]	9.2	$YbCl_3$	0.056 mmol	140	360 min	80	12	[141]
[BMIM][Cl]	9.2	$YbCl_3$	0.056 mmol	140	360 min	71.4	5	[141]
DMSO/Water 1:1	5	$YbCl_3$*5H_2O	55.5 mmol	140	20 min		2	[212]
ChoCl	40	$ZnCl_2$	10 mol %	100	30 min		6	[161]
DMSO/Water 1:1	5	$ZnCl_2$	55.5 mmol	140	20 min		0.5	[212]
[BMIM][Cl]	4.8	$ZrCl_4$	10 mol %	220[*]	3.5 min	72.3	47.8	[236]

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

Table 2.9 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	[21]
	[BMIM][Cl]	4.8	$CrCl_3*6H_2O$	10 mg	100	240 min		17	[21]
Cellobiose	DMA-LiCl/DMF ^{a}	8.4	$LaCl_3$	10 wt %	145	300 min	85	18	[206]
	[EMIM][BF_4]	16.7	$SnCl_4*5H_2O$	10 mol %	100	180 min	100	57	[202]
Cellulose	Water	4.8	$CrCl_3*6H_2O$	10 mg	400^{**}	2 min		62	[21]
	Water	9.1	H_3PO_4	$pH_{sol}=2$	230	5 min		7	[13]
	[BMIM][Cl]	12.5	$CrCl_3*6H_2O$	7 mol %	120	180 min		54	[188]
	[BMIM][Cl]/ MIBK	4.8	$GeCl_4$	10 mol %	120	30 min	95	35	[144]
	[BMIM][Cl]	4.8	$CrCl_3*6H_2O$	10 mg	400^{**}	2.5 min		62	[209]
	IL-1/MIBK	20	$MnCl_2*4H_2O$	1 ml	180	300 min		38	[241]
	[BMIM][H_2PO_4]/ MIBK	20	$MnCl_2*4H_2O$	1 ml	150	300 min	22.83	7.91	[241]
	IL-1/MIBK	20	$CoSO_4$	1 ml	150	300 min	84	24	[145]
Chitosan	Water	0.2	[HMIM][HSO_4] [$FeCl_3$]	1.25 wt %	180	4 hours		44.11	[242]
Inulin	Water	4.8	CO_2	6 Mpa‡	180	90 min		53	[198]
	Water	4.8	HCl	2 ml	180	90 min		53	[198]
	ChoCl	50	$FeCl_3$	10 mol %	90	60 min		55	[161]
	ChoCl	50	$ZnCl_2$	10 mol %	90	60 min		3	[161]
	ChoCl	50	$CrCl_2$	10 mol %	90	60 min		36	[161]
	ChoCl	50	$CrCl_3$	10 mol %	90	60 min		46	[161]
	ChoCl	50	pTSOH	10 mol %	90	60 min		57	[161]

	ChoCl	50	$Sc(Otf)_3$	10 mol %	90	60 min		44	[161]
	[EMIM][BF$_4$]	16.7	$SnCl_4*5H_2O$	10 mol %	100	180 min	100	40	[202]
Pine Wood	[BMIM][Cl]	4.8	HCl	0.66 g/l	100	60 min		2.1	[209]
	[BMIM][Cl]	4.8	$CrCl_3*6H_2O$	10 mg	400^{**}	3 min		52	[209]
	[BMIM][Cl]	4.8	$CrCl_3*6H_2O$	10 mg	100	60 min		6.4	[209]
Sigmacell	[BMIM][Cl]	4.8	$CrCl_3*6H_2O$	10 mg	400^{**}	2 min		55	[21]
Spruce	[BMIM][Cl]	4.8	$CrCl_3*6H_2O$	10 mg	400^{**}	2 min		53	[21]
Starch	Water-[BMIM][Cl]/ MIBK 1:5	1	$AlCl_3*6H_2O$	150 mg	140^{*}	20 min	96	56.4	[243]
	[OMIM][Cl]/ Ethyl acetate	20	HCl	5 ml	120	60 min		30.2	[151]
	[EMIM][BF$_4$]	9.1	$SnCl_4*5H_2O$	21.6 g	100	24 hours	100	47	[202]

[a] DMF = N,N'-dimethylformamide

*MH, **no temperature specified

‡Gaseous catalyst

Table 2.10 Carbohydrates dehydration using two homogeneous catalysts

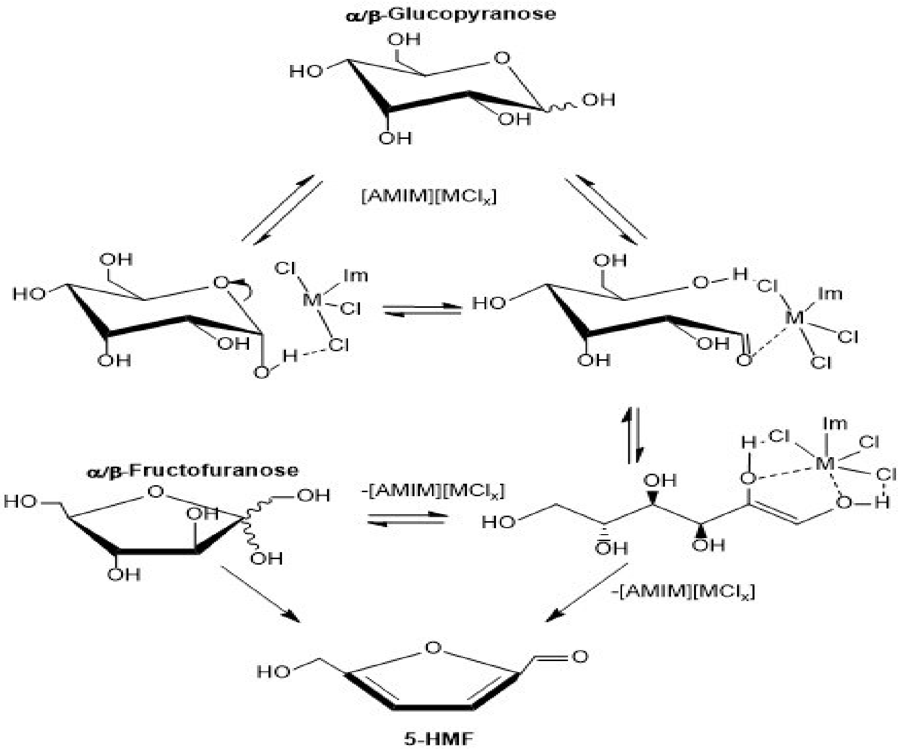
Substrate	Solvent	Substrate Concentration (wt %)	Catalyst	Catalysts amounts	Temperature (°C)	Reaction time	Conversion (%)	Yield (%)	Reference
Avicel	[BMIM][Cl]	4.8	$CrCl_3*6H_2O$/ 2,2'-bipyridine	10 mg/ 17.5 mg	400^{**}	2 min		1.6	[21]
	[BMIM][Cl]	4.8	$CrCl_3*6H_2O$/ 2,2-bipyridine	10 mg/ 17.5 mg	100	240 min		2	[21]
Cellulose	[BMIM][Cl]/ Water	2.4	$CrCl_3$/ LiCl	0.155 mmol/ 0.155 mmol	140^{*}	40 min		61.9	[211]
	[EMIM][Cl]	9.1	$CuCl_2$/ $PdCl_2$	13.5 µg/ 13.5 µg	120	30 min			[210]
Fructose	DMA-LiCl	10	CuCl/ [EMIM][Cl]	6 mol %/ 40 wt %	120	90 min		83	[20]
	DMA-LiCl	10	H_2SO_4/ [EMIM][Cl]	6 mol %/ 20 wt %	80	4 hours		78	[20]
	DMA-LiCl	10	H_2SO4/ [EtPy][Cl]	6 mol %/ 20 wt %	100	2 hours		81	[20]
	[BMIM][Cl]	9.1	HCl/ $AuCl_3$	7 mol %/ 7 mol %	120	180 min	98	47.8	[143]
	Water	10	HCl/ $CrCl_3$	0.1 M/ 100:3 Fr:Cat (w)	140	25 min	80	30	[225]
	NMP	9.1	$FeCl_3$/ Et_4NBr	0.56 mmol/ 1 mmol	90	120 min	100	86	[234]
Glucose	Water-NaCl/ CPME 1:1	10	HCl/ $AlCl_3$	pHsol=2.5 / 0.025 mmol	175	20 min	89.5	54.5	[226]
	Water	10	HCl/ $CrCl_3$	0.1 M/ 100:3 Fru:cat	140	50 min	55	13	[225]
	Water/ THF 1:2	10	HCl/ $CrCl_3$	0.1 M/ 100:3 Fru:cat	140	180 min	92	59	[225]

	Water	20	$(NH4)_2HPO_4$/ H_3PO_4	0.0076 mol/ 0.006 mol	180	57 min	23.2	[11]
	Water/ dioxane 1:1	20	Pyridine/ H_3PO_4	0.03 mol/ 0.018 mol	228	53 min	45	[11]
Sucrose	[MOIM][Cl][a]	10	HCl/ $CrCl_2$	0.5 M/ 0.2 g	120	60 min	78.5[ǂ]	[208]
	[MOIM][Cl]	50	HCl/ $CrCl_2$	0.3 M/ 0.2 g	120	60 min	61.6[ǂ]	[208]
	[MOIM][Cl]	10	HCl/ $ZnCl_2$	0.3 M/ 0.2 g	120	60 min	68.4[ǂ]	[208]
	[MOIM][Cl]	50	HCl/ $ZnCl_2$	0.3 M/ 0.2 g	120	60 min	42.2[ǂ]	[208]
Wheat Straw	[BMIM][Cl]	2.4	$CrCl_3$/ LiCl	0.155 mmol/ 0.155 mmol	160[*]	15 min	61.4	[211]
	Water/THF 1:3	10	$FePO_4$/ NaH_2PO_4	0.2 g /0.02 g	160	60 min	44	[244]

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

[ǂ] yields reported in wt %

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



Scheme 2.5. Glucose Isomerization and HMF formation mechanism in imidazolium ILs ([AMIM]) and metal chlorides [MCl$_x$]) [18, 202]

2.4.2 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 [23, 24]. 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 [245].

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 2.11 to 2.13). 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.

2.4.2.1 Zeolites

Zeolites are aluminum tectosilicates which can hold exchangeable cations in their three-dimensional framework [246]. They are frequently used in petrochemical and organic synthesis due to their high surface area, tailored active sites and adsorption properties [247]. 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 [248].

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 [24]. 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. [249] 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. [250] when comparing H-MOR to silicoaluminophosphate (SAPO) catalysts. At 175 ºC 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. [30] could reach a yield of about 60% HMF from fructose at 120 ºC. Carrying out the reaction under a light vacuum ($0.97\text{x}10^5$ 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 [251], or even no HMF and no sugar conversion [32]. 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 [252]. This was ascribed to the weak acidity of the active sites.

Wang et al. [253] 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 [254]. Bermejo et al. [255] suggested that the Sn centers of the zeolite behave as Lewis acids that 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) [233, 256]. 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. [257] 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. [51] 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 [52]. 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% [258]. 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 [258, 259].

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 [260, 261]. 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 [262, 263].

Additionally, when using unpurified lignocellulosic materials, zeolites exhibited lowered catalytic activity after reuse [264]. 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. [259], 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.

2.4.2.2 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 [24, 265]. 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 [24]. 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 [266].

A similar mesoporous silica (SBA-15) has been used as support for solid catalysts. Crisci et al. [267, 268] 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 ºC, 141 min). When these types 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 [269]. In a more recent experiment, Duo et al. [270]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 SO_3H 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.

2.4.2.3 Metal oxides and minerals

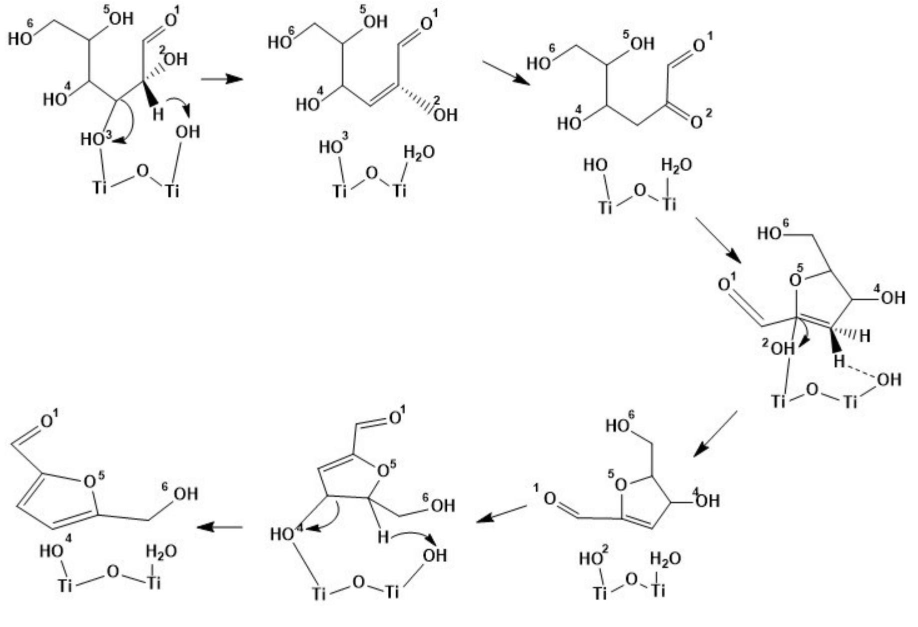
Metal oxides and phosphates have been widely used as heterogeneous catalysts. Particularly, niobium oxide (NbO) and phosphate (NbP) have often been used for HMF production due to their character as strong acid catalysts, their low cost, and low toxicity [36, 37, 271-273]. Both the oxide and the phosphate have a strong Brønsted acidity, with Hammett values of -5.6 and -8.2 respectively [271]. 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) [271]. 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 [272]. Pretreatment of NbO with phosphoric acid increases its surface area as well as the amount of strong acid sites [41]. This pretreated catalyst, when used for fructose and glucose dehydration, gave HMF yields of 89 and 49% respectively at 160 ºC [42]. Similar results were obtained by Antonetti et al.[43] when using this and phosphate zirconium under microwave heating (ZrP). NbO could also hydrolyze Jerusalem artichoke but lower HMF yields were obtained (22%)[42]. Another pretreated niobium catalyst, sulfated niobium oxide (MNO-S), possesses a mesoporous structure and a surface area 50 times larger than NbO [274]. 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 [275]. Pt/γ- Al_2O_3 has been reported to promote the hydrolysis of cellulose to glucose in a H_2 atmosphere [276]. 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 [277]. Cellulose conversion was also investigated by Chambon et al. [51, 53] 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 [15, 16], while sulfated zirconia has been successfully used for HMF formation from fructose [278]. Using SO_4^{2-}/ZrO_2-Al2O_3 (CZSA), Yang et al. [279] 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. [280] 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 attribute their yields to the isomerizing effect of Fe^{+3}, which acts as a Lewis acid.

Recently, Li et al. [281] 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 2.6).

With a combination of ball-milling pretreatment and $Ca_3(PO_4)_2$, Mimura et al. [282] 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 2.6 TiO_2 catalyzed glucose dehydration based on reference [281]

2.4.2.4 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 [283].

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^-] [284]. 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 [285]. 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. [286] 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 [132]. 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. [38] 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. [287]. 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.

2.4.2.5 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 [288-290]. 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 [25, 245, 291, 292]. 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 [25], 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 [25, 26]. Also, DMSO helped the facile tautomerization of fructose to its fructofuranosyl form. Similarly, Guo, Fang and Zhou [27] 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 [293].

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. [26] 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 [294]. The substitution of SO_3H by phosphorylation also led to catalytically active carbons [295]. 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. [296] 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.[297], 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 [298] 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 2.7 and 2.8.

Using wood biochar as support for a sulfonated catalyst (BSO_3), Xiong et al.[299] 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 inhydrolyzing and dehydrating ball-milled cellulose to HMF with high yields (53.3%), after 8 h at 170 °C [300]. Functionalization of carbonaceous support with iron and H_2SO_4 can produce a magnetically recoverable material with Lewis acidic properties [301-303].

2.4.2.6 Organic catalysts

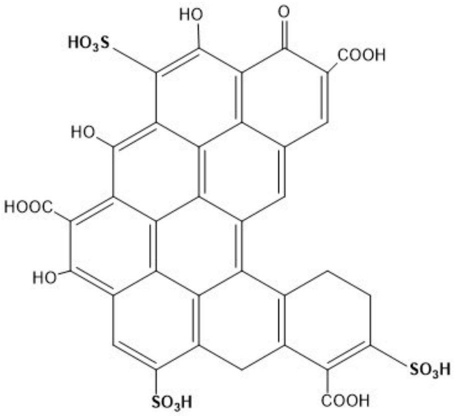
Ion exchange polymeric resins have also been extensively used in a broad variety of catalytic reactions. The most commonly used types are Amberlyst and Nafion. Amberlyst, is a polystyrene resin with sulfonic acid groups, while Nafion is a sulfonated tetrafluoroethylene perfluoro-2-

(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 [304].

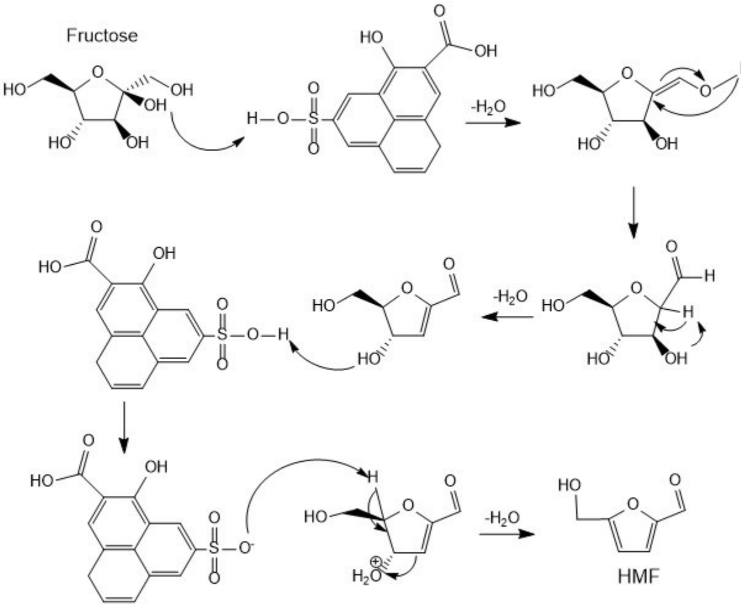
Amberlyst-15 has been known for quite some time as an effective catalyst for fructose dehydration [28, 29], but requires long reaction times. More recent experiments showed improved yields at higher temperatures (110-120 ºC) and shorter times (< 2 hours), resulting in almost 100% HMF yield from fructose in DMSO at high fructose concentrations (50 wt%) [30, 31]. These results were attributable to its high concentration of sulfonic acid sites [305]. Nafion was equally effective as Amberlyst-15 at lower concentrations. However, when used for glucose dehydration, Amberlyst-15 produced anhydroglucose rather than HMF [32, 33]. 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 [33, 306-308]. The presence of water was detrimental to the catalytic activity of the resin [33]. When used in combination with ILs, it has been observed to hydrolyze cellulose in a very controlled fashion [52, 309, 310], 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% [311]. 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. [312] 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. [313] 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 [314, 315]. Zhu et al. [316] 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 with 90% yield (140 ºC, 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 ºC, 30 minutes) [317]. 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 [317]. 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 [318].



Scheme 2.7 Proposed structure of sulfonated carbon catalyst based on [294, 319, 320]



Scheme 2.8 Proposed catalytic pathway for the dehydration of fructose with sulfonated carbonaceous materials, based on reference [321]

2.4.2.7 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 [322, 323], classified this process as 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 [284, 298, 324]. Calcination can also be used to remove blockage from active sites as well as adsorbed by-products [325], 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) [326, 327]. Nevertheless, there are a few cases where Amberlyst has been successfully used at higher temperatures: Wrigsted et al. [229] and Herbst et al. [49] 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 [304]. Similarly, the addition of fluorinated IL to sulfonated biochar increased its thermal stability, keeping HMF yields and turnover number constant after 6 runs [328].

Chemical deactivation can be observed in the form of leaching of active sites. Chambon et al. [51] 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. [329] observed also leaching in 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 [297].

2.5 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 due to the use of low substrate concentrations, unrecoverable catalysts, or difficulty to separate solvents. 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 [55]. 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 if 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 [330]. A combination of high vacuum and entrainers may, for instance, be required to separate HMF from an ionic liquid [331]. While hydrophobic zeolites can be used to selectively remove HMF from aqueous solutions [332], their efficacy is greatly reduced in ternary solutions also containing DMSO [333]. One alternative is to use a low-boiling extraction solvent like hexafluoroisopropanol (HFIP), which has a boiling point of around 58 ºC, as compared to 189 ºC for DMSO [334]. 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% [335]. A similar system using Cr^{3+} modified ion exchange resins as catalysts gave isolated yields of up to 70% from glucose [336]. A method utilizing NaOH neutralization to isolate HMF in high yields and with high purity from an autocatalytic system has also been demonstrated [337]. 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) [62, 338]. 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 [339], 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 [340, 341], 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 [342]. A study by Kazi et al. [343] 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 CAD/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 [82]. 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 made. The results were not competitive when compared to p-xylene (0.84 USD/kg) [344], 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 [345]. 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 2.11 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	[285]
Water/MIBK 1:2.25	30	12-AgTPA	0.08 g	120	60 min	46	38	[285]
DMSO	2.5	12-CsTPA	10:1 Fru:Cat (w)	120	40 min	100	80	[132]
DMSO	2.5	12-TPA	10:1 Fru:Cat (w)	120	30 min	100	92	[132]
DMSO	2.5	12-TPA/MCM-41	10:1 Fru:Cat (w)	120	60 min	100	80	[132]
DMSO	3.2	Aquivion@silica	0,016 mmol H^+	90	2 hours	100	85	[270]
[BMIM][Cl]	9	a-CSS	2:1 Fru:Cat (w)	80	20 min		65	[26]
DMSO/[BMIM][BF4]	8	Amberlyst-15	70 mg	80	32 min		75	[29]
DMSO/[BMIM][BF4]	8	Amberlyst-15	143 mg	80	32 min		87	[29]
DMSO	3	Amberlyst-15	0.02 g	120	120 min	100	92	[30]
Water	4.8	Amberlyst-15	0.4 g	120	24 hours	57	15	[346]
DMSO	3	Amberlyst-15	0.06 mmol H^+	90	120 min	34.5	26.3	[313]
N,N-DMF	3.2	Amberlyst-15	0.1 g	100	3 hours	99	73	[32]
DMSO	3	Amberlyst-15-p^+	0.02 g	120	120 min	100	100	[30]
DMSO	7	Amberlyst-70	0.2 mmol H^+	140	60 min	100	93	[305]
DMSO	7	Ar-SBA-15	0.2 mmol H^+	140	60 min	100	79	[305]
DMSO	1	b-cyclodextrin-SO_3H	100 wt%	140	120 min		96	[347]
DMF	1	b-cyclodextrin-SO_3H	100 wt%	140	120 min		92	[347]
Isopropanol	1	b-cyclodextrin-SO_3H	100 wt%	100	120 min		63	[347]
Water	1	b-cyclodextrin-SO_3H	100 wt%	140	120 min		0	[347]
Water		BSO_3	1:10	160	15 min	60.4	42.3	[299]
Water/Ethanol 3:7	5.6	C/MCF	10 g	140	4 hours	93	39	[348]
Water/Ethanol 3:7	5.6	C/SBA(45)	10 g	140	6 hours	89	39	[348]
DMSO	5.7	Cellulose-Sulfuric acid	50 mg	100	45 min	100	93.6	[349]
DMA	5.7	Cellulose-Sulfuric acid	50 mg	100	45 min	97.8	90.5	[349]
NMO	5.7	Cellulose-Sulfuric acid	50 mg	100	45 min	96.7	87.2	[349]
DMF	5.7	Cellulose-Sulfuric acid	50 mg	100	45 min	98.3	85.5	[349]
Ethanol	5.7	Cellulose-Sulfuric acid	50 mg	100	45 min	27.8	8.7	[349]
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	[350]
Water/MIBK 1:5	30	$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	0.128 g	115	120 min	94	77.6	[286]
Water/MIBK 1:5	30	$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	0.128 g	115	60 min	85.6	74	[286]

[BMIM][Cl]	9	CSS	2:1 S:C w	80	20 min		76	[26]
[BMIM][Cl]	0.9	CSS	1:5 S:C w	80	10 min		83	[26]
Water	1.8	Ct1*	5 mg	170	4.5 hours	70.9	50.1	[296]
Water	7	Ct2*	5 mg	170	4.5 hours	100	59.9	[296]
Water	1.8	Ct3*	5 mg	170	4.5 hours	75,5	46,5	[296]
DMSO	4.3	FS-PAN	1.5:1 Fru:Cat (w)	140	4 hours	100	90.4	[316]
THF-Water 3:1	10	Ge$_3$N$_4$	10 wt%	150	100 min		39	[351]
THF	10	Ge$_3$N$_4$	10 wt%	150	100 min		37	[351]
DMF	10	Ge$_3$N$_4$	10 wt%	150	100 min		11	[351]
THF-Water 3:1	10	GeO$_2$	10 wt%	150	100 min		45	[351]
THF	10	GeO$_2$	10 wt%	150	100 min		40	[351]
DMF	10	GeO$_2$	10 wt%	150	100 min		12	[351]
DMF	7.7	Glu-TsOH	0.4 g	130	90 min	98.3	59.7	[25]
DMA	7.7	Glu-TsOH	0.4 g	130	90 min	97	60.4	[25]
N-MP	7.7	Glu-TsOH	0.4 g	130	90 min	97.9	85.8	[25]
DMSO	7.7	Glu-TsOH	0.4 g	130	90 min	99.9	91.2	[25]
Water	7.7	Glu-TsOH	0.4 g	130	90 min	67	8	[25]
DMSO	4.3	Graphene oxide	8 mg	120	6 hours	93	93	[25]
Water/MIBK (1:5)	9	H-mordenite	0.1 g	165	60 min	76	69	[249]
[BMIM][Cl]	4.8	HT carbonaceus material	10:1 Fru:Cat (w)	100	120 min		79.9	[298]
[BMIM][Cl]	4.8	HT carbonaceus material	1:1 Fru:Cat (w)	100	90 min		88.1	[298]
[BMIM][Cl]	10	HT carbonaceus material	2:1 Fru:Cat (w)	100	60 min		75.1	[298]
Water	16.6	LCC	1:1 Fru:Cat (w)	150^{ǂ}	60 min		40	[352]
Water	16.6	LCC	0.5 Fru:Cat (w)	150	5 hours		17.5	[352]
[BMIM][Cl]	50	LCC	0.2 Fru:Cat (w)	110^{ǂ}	10 min		70	[352]
[BMIM][Cl]/DMSO 6:4	5	LCC	0.1 Fru:Cat (w)	120^{ǂ}	30 min	98	70	[352]
DMSO	2.5	MCM-41	10:1 Fru:Cat (w)	120	100 min	100	65	[132]
DMSO	3	Nafion	0.02 g	120	120 min	100	94	[30]
Water	4.8	Nafion NR50	0.4 g	120	24 hours	78	6	[346]
N,N-DMF	3.2	Nafion NR50	0.1 g	100	3 hours	99	45	[32]
DMSO	3	Nafion-15/MCF	0.06 mmol H^{+}	90	120 min	94	89.3	[313]
Water-NaCl (saturated)/ Sec-butyl phenol	5	Nb/CB-1-DP^{++}	0.1 g	170	120 min	34	18	[353]

Water-NaCl (saturated)/ Sec-butyl phenol	5	Nb/CB-2-DP++	0.1 g	170	120 min	78	20	[353]
Water-NaCl (saturated)/ Sec-butyl phenol	5	Nb/CS-HT++	0.1 g	170	120 min	34	11	[353]
DMA-NaBr	5	Nb-NTMPA+++	2:1 Fru:Cat (w)	100	90 min	100	85.6	[354]
Water	5	NbO	4 g	100	44 min	40	8.8	[37]
N,N-DMF	3.2	NbO	0.1 g	100	3 hours	12	0	[32]
Water/2-butanol (2:3)	21	NbO	0.1 g	160	50 min	90	89	[42]
Water	5	NbP	4 g	110	33 min	74	25.9	[271]
Water	10	NbP	1:10 Fru:Cat (w)	180	10 min	86.5	33.9	[43]
Water	10	ZrP	1:7.5 Fru:Cat (w)	180	10 min	84.2	39.5	[43]
Water	5	P/N-0.25	2:1 Fru:Cat (w)	120	8 hours	48	33.6	[295]
Water	5	P/N-0.25	2:1 Fru:Cat (w)	120	8 hours	68	42.8	[295]
Water	5	P/N-0.25	2:1 Fru:Cat (w)	120	8 hours	78	41.3	[295]
Water	6	PC-4	6:1 Fru:Cat (w)	160	3 hours	96.3	74.9	[297]
DMSO	3.5	PDVB-TAEA-12-TPA	0.006 mmol	120	50 min	98	96	[355]
DMSO	3.5	PDVB-TAEA-12-TSA	0.006 mmol	120	50 min	97	95,6	[355]
Water/ Butanol 1:1.5	5.7	Phosphated tantalum hydroxide	0.1 g	160	100 min	94	90	[356]
DMSO	7	Pr-SBA-15	0.2 mmol H^+	140	60 min	100	85	[305]
Water/MIBK 1:3	20	PS-PP/C-foam-1	2 g	90	6 hours	29	23.2	[312]
Water-NaCl/ THF-NMP 1:4	5	P-TiO_2	4:1 Fru:Cat (w)	175	105 min	99.9	98.6	[357]
DMSO	3	SAC-13	0.06 mmol H^+	90	120 min	91	73.7	[313]
DMSO	7	SAC-13	0.2 mmol H^+	140	60 min	100	83	[305]
Water	4.8	SBA-SO3H	0.4 g	120	24 hours	84	20	[346]
[BMIM][Cl]	9	SCC***	29 wt%	160	15 min		81	[320]
DMSO	5	SGO-1**	10 mg	120	60 min	83	80	[358]
DMSO	5	SGO-2**	10 mg	120	60 min	76	72	[358]
DMSO	5	SGO-3**	10 mg	120	60 min	90	85	[358]
THF/DMSO 7:3	5	Sn-Mont	30 wt%	160	60 min	99	78.1	[359]
Water-NaCl/ THF	5	Sn-Mont	30 wt%	160	3 hours		69	[359]
DMSO	3	SO_4^{2-}/ZrO_2	0.06 mmol H^+	90	120 min	50	32.3	[313]
N,N-DMF	3.2	SO_4/ZrO_2	0.1 g	100	3 hours	99	21	[32]
Water	2	SO_4^{2-}/ZrO_2	10:2 Fru:Cat (w)	200ǂ	5 min	79.9	36	[278]
Acetone/DMSO 7:3	2	SO_4^{2-}/ZrO_2	10:2 Fru:Cat (w)	200ǂ	5 min	91.3	65.6	[278]

Water/ (MIBK:2-Butanol 7:3) 3:7	30	Taa-SBA-15	3 g	180	120 min	66	48.84	[267]
Water/ (MIBK:2-Butanol 7:3) 3:7	30	Taa-SBA-15	3 g	180	120 min	59	30.68	[267]
Water/ (MIBK:2-Butanol 7:3) 3:7	30	TESAS-SBA-15	50 mg	130	140 min	84	59.64	[267]
Water/ (MIBK:2-Butanol 7:3) 3:7	30	Tp-SBA-15	3 g	180	120 min	61	31.72	[268]
Water	2	ZrO$_2$	10:2 Fru:Cat (w)	200ǂ	5 min	59.3	20.7	[16]
Acetone/DMSO 7:3	2	ZrO$_2$	10:2 Fru:Cat (w)	200ǂ	5 min	71.3	40.8	[278]

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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)

ǂMicrowave heated

Table 2.12 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	[285]
Water/MIBK 1:2.25	30	12-CsTPA	0.08 g	130	4 hours	33	17	[285]
[BMIM][Cl]	10	12-MPA	20 wt%	120	60 min		19.7	[360]
[BMIM][Cl]	10	12-MPA/B(OH)$_3$	20 wt%/10%	120	60 min		26.7	[360]
[BMIM][Cl]	10	12-TPA	20 wt%	120	60 min		21.9	[360]
[BMIM][Cl]	10	12-TPA	10 wt%	140	40 min		23.5	[360]
[BMIM][Cl]	10	12-TPA/B(OH)$_3$	20 wt%/10%	120	60 min		40.9	[360]
[BMIM][Cl]	10	12-TPA/B(OH)$_3$	20 wt%/10%	140	40 min		51.9	[360]
[BMIM][Cl]	10	12-TSA	20 wt%	120	60 min		19.3	[360]
[BMIM][Cl]	10	12-TSA/B(OH)$_3$	20 wt%/10%	120	60 min		39.3	[360]
Water/MIBK	10	Al-MCM-41	50 mg	195	2.5 hours	85	35	[266]
Water/MIBK	10	Al-MCM-41	50 mg	195	2.5 hours	85	35	[266]
Water/MIBK (1:3) NaCl 20%	10	Al-MCM-41	50 mg	195	2.5 hours	96	65	[266]
THF/ Water-NaCl (saturated) 1:3	9	AlSiO-10	1:1 Glu:Cat (w)	160	90 min	98.8	47.9	[361]
THF/ Water-NaCl (saturated) 1:3	9	AlSiO-20	1:1 Glu:Cat (w)	160	90 min	91.7	63.1	[361]
THF/ Water-NaCl (saturated) 1:3	9	AlSiO-30	1:1 Glu:Cat (w)	160	90 min	67.2	37.8	[361]
THF/ Water-NaCl (saturated) 1:3	9	AlSiO-40	1:1 Glu:Cat (w)	160	90 min	58.7	25.3	[361]
DMF	3.33	Amberlyst-15	1:1 Glu:Cat (w)	100	120 min	100	88	[33]
N,N-DMF	3.2	Amberlyst-15	0.1 g	100	3 hours	69	0	[32]
ChoCl	20	Amberlyst-15-CrCl$_3$	40 wt%	140	2 hours		46.4	[311]
DMSO	7	Amberlyst-70	0.2 mmol H$^+$	140	60 min	97.5	63.7	[305]
DMSO	7	Ar-SBA-15	0.2 mmol H$^+$	140	60 min	97	47	[305]
DMSO	7	C-SO$_3$H	21 wt%	130	8 hours	73	10	[362]
DMSO	1	b-cyclodextrin-SO$_3$H	100 wt%	180	5 hours		47	[347]

DMF	1	b-cyclodextrin-SO_3H	100 wt%	180	5 hours		37	[347]
Sulpholane	1	b-cyclodextrin-SO_3H	100 wt%	180	5 hours		28	[347]
[BMIM][Cl]	1	b-cyclodextrin-SO_3H	100 wt%	180	5 hours		32	[347]
[BMIM][Cl]	9	CCC†	29 wt%	140	30 min	60.7	41.2	[320]
Water/MIBK	10	$Fe_3O_4@SiO_2$-SO_3H	40 wt%	140	24 hours	98	70	[280]
DMSO	4.3	FS-PAN	1.5:1 Glu:Cat (w)	140	4 hours	89.7	6.4	[316]
[BMIM][Cl]	9	GCC††	29 wt%	140	30 min	55.2	37.8	[320]
Water	15	HY-zeolite	0.033 g/ml	150	5 hours	75	13.3	[23]
Water	12	HY-zeolite	10 g	160	3 hours		9	[23]
[BMIM][Cl]	10	HZSM-5	20 wt%	120	60 min		3.1	[284]
Water	15	MCM-20	0.033 g/ml	150	23 hours	60	18.6	[24]
Water	15	MCM-41	0.033 g/ml	150	24 hours	87.5	15	[24]
THF/Water 39:1	5	MIL-SO_3H	0.5 g	130	25 min		29	[49]
Water	15	Montmorillonite	0.033 g/ml	150	5 hours	81.3	13	[24]
Water/THF 1:4	5	Mo-TiO_2	4:1 Glu:Cat (w)	175	105 min	99.9	17	[363]
N,N-DMF	3.2	Nafion NR50	0.1 g	100	3 hours	34	0	[32]
N,N-DMF	3.2	NbO	0.1 g	100	3 hours	12	0	[32]
Water/2-butanol (2:3)	21	NbO	0.1 g	160	110 min	68	49	[356]
Water/ Butanol 1:1.5	5.7	Phosphated tantalum hydroxide	0.1 g	160	140 min	70	58	[356]
DMSO	7	Pr-SBA-15^{+}	0.2 mmol H^+	140	60 min	98	46.5	[305]
Water/ THF 1:4	2	P-TiO_2	4:1 Glu:Cat (w)	175	105 min	93.6	83.4	[363]
Water/ THF 1:4	5	P-TiO_2	4:1 Glu:Cat (w)	175	105 min	96.5	62.8	[363]
Water-NaCl/ THF-NMP 1:4	5	P-TiO_2	4:1 Glu:Cat (w)	175	105 min	98.2	90.5	[363]
DMSO	7	SAC-13	0.2 mmol H^+	140	60 min	99	50	[305]
[BMIM][Cl]	10	SBA-15	20 wt%	120	60 min		1.2	[284]
[BMIM][Cl]	9	SCC	29 wt%	140	30 min	54.3	35.3	[320]
THF/DMSO 7:3	7	Sn-Mont	30 wt%	160	3 hours	98.6	48.2	[359]
THF/DMSO 7:3	10	Sn-Mont	30 wt%	160	3 hours	98.7	42.4	[359]
Water-NaCl/ THF	10	Sn-Mont	30 wt%	160	3 hours		79	[359]

N,N-DMF	3.2	SO_4/ZrO_2	0.1 g	100	3 hours	7	0	[32]
γ-GVL	7	SPTPA**	1.25:1 Glu:Cat (w)	175	20 min		59	[364]
Water/THF 1:4	2	TiO_2	4:1 Glu:Cat (w)	175	105 min	90.4	72.8	[363]
Water/THF 1:4	5	V-TiO_2	4:1 Glu:Cat (w)	175	105 min	99.9	35.5	[363]
Water/THF 1:4	5	W-TiO_2	4:1 Glu:Cat (w)	175	105 min	98.5	27.5	[363]
[HexilMIM][Cl]	5	ZrO_2	10:2 Glu:Cat (w)	200*	1 min	76	10	[365]
Water/[HexilMIM][Cl] 1:20	5	ZrO_2	10:2 Glu:Cat (w)	200	20 min	96	48	[365]

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*Microwave heating

+Propylsulfonic acid functionalized mesoporous silica

**Sulfonated Polytriphenylamine

† Cellulose-derived carbonaceous catalyst

†† Glucose-derived carbonaceous catalyst

Table 2.13 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	[287]
Water-NaCl/ THF-NMP 1:4		5	P-TiO_2	4:1 Sugar:Cat (w)	175	105 min	99.7	94.2	[357]
Water-NaCl/ THF		5	Sn-Mont	30 wt%	160	3 hours		40	[359]
Water/ MIBK 1:10	Cellulose	17	12-TPA	0.11 mmol	140	8 hours	89	57	[287]
Water/ MIBK 1:10		17	12-TPA-ChoCl	0.11 mmol	140	8 hours	87	75	[287]
Water		3.5	Amberlyst-15	0.2 g	190	5 hours		8	[52]
Water-NaCl/ THF-NMP 1:4		5	P-TiO_2	4:1 Sugar:Cat (w)	175	105 min	56.7	33	[357]
Water			HTC-220-6-SO_3H^a	5 wt%	180	5 min		1.6	[366]
Water/THF 3:1		5	Nb/C-50	1:1 Sugar:cat (w)	170	8 hours	99	53.3	[300]
[BMIM][Cl]		9	SCC	29 wt%	160	15 min		40.5	[320]
Water-NaCl/ THF		5	Sn-Mont	30 wt%	160	3 hours		40	[359]
Water-NaCl/ THF-NMP 1:4	Cellulose (pretreated)	5	P-TiO_2	4:1 Sugar:Cat (w)	175	105 min	99.9	86.2	[357]
[BMIM][Cl]	Corn Stalk	1	HCSS	0.05 g	150	30 min		45.1	[367]
[BMIM][Cl]		4.8	HCSS	0.05 g	150	30 min		44.1	[367]
[BMIM][Cl]		10	HCSS	0.05 g	150	60 min		32.9	[367]
DMSO	Fructose-glucose syrup	4	Amberlyst-36	1:1 Sugar:cat (m)	140^{Υ}	40 min		71.3	[368]
Dioxane	HFCS	0.9	AC-SO_3H^*	12 mol %	120	4 hours		60	[369]
Dimethoxyethane		0.9	AC-SO_3H^*	12 mol %	120	4 hours		73	[369]
2-methoxyethyl ether		0.9	AC-SO_3H^*	12 mol %	120	4 hours		75	[369]
Ttriethyleneglycol dymethyl ether		0.9	AC-SO_3H^*	12 mol %	120	4 hours		56	[369]
Tetraethyleneglycol dymethyl ether		0.9	AC-SO_3H^*	12 mol %	120	4 hours		57	[369]
Dioxane		0.9	Amberlyst-15	1:0.75 Sugar:Cat (w)	120	120 min	99	80	[369]

Dimethoxyethane		0.9	Amberlyst-15	1:0.75 Sugar:Cat (w)	120	120 min	99	81	[369]
2-methoxyethyl ether		0.9	Amberlyst-15	1:0.75 Sugar:Cat (w)	120	120 min	99	74	[369]
Triethyleneglycol dymethyl ether		0.9	Amberlyst-15	1:0.75 Sugar:Cat (w)	120	120 min	99	66	[369]
Tetraethyleneglycol dymethyl ether		0.9	Amberlyst-15	1:0.75 Sugar:Cat (w)	120	120 min	99	67	[369]
DMSO		15	Amberlyst-15	0.3 g	100	4 hours		80	[370]
Dioxane		15	Amberlyst-15	0.3 g	100	4 hours		80	[370]
Acetonitrile		15	Amberlyst-15	0.3 g	100	4 hours		45	[370]
DMSO		30	Amberlyst-15	0.3 g	100	4 hours		70	[370]
Dioxane		30	Amberlyst-15	0.3 g	100	4 hours		70	[370]
Acetonitrile		30	Amberlyst-15	0.3 g	100	4 hours		38	[370]
DMSO	Inulin	1	b-cyclodextrin-SO$_3$H	100 wt%	140	120 min		92	[347]
[AMIM][Cl]/water		4.5	D265-SO$_3$H***	50 wt%	100	90 min		65	[293]
DMSO		4.3	FS-PAN	1.5:1 Sugar:Cat (w)	140	4 hours	100	52.3	[316]
[AMIM][Cl]/water		4.5	L225-SO$_3$H**	50 wt%	100	60 min		65	[293]
Water/ 2-butanol (2:3)		21	NbO	0.1 g	160	140 min	54	86	[42]
Water/ Butanol 1:1.5		5.7	Phosphated tantalum hydroxide	0.1 g	160	150 min	95	87	[356]
Water-NaCl/ THF		5	Sn-Mont	30 wt%	160	3 hours		41	[359]
Water/ 2-butanol (2:3)	Jerusalem artichoke	6	NbO	0.1 g	160	40 min	46	22	[42]
Water/ Butanol 1:1.5		5.7	Phosphated tantalum hydroxide	0.1 g	160	2.5 hours	91	50	[356]
Water/ Butanol 1:1.5	Jerusalem artichoke (juice)	5.7	Phosphated tantalum hydroxide	0.1 g	160	120 min	91	79	[356]
Water/ MIBK 1:10	Starch	17	12-TPA-ChoCl	0.11 mmol	130	3 hours	92	78	[287]
DMSO		1	b-cyclodextrin-SO$_3$H	100 wt%	140	5 hours		10	[347]
Water-NaCl/ THF		5	Sn-Mont	30 wt%	160	3 hours		43	[359]
Water	Molasses	6.7	B-SO$_3$H^b	0.3 g	150^{Υ}	4		39.1	[371]
Water		6.7	M-SO$_3$H^c	0.3 g	150^{Υ}	3		34.2	[371]

Water-NaCl/ THF-NMP 1:4	Starch (potato)	5	P-TiO_2	4:1 Sugar:Cat (w)	175	105 min	99.8	84.6	[357]
Water-NaCl/ THF-NMP 1:4	Starch (rice)	5	P-TiO_2	4:1 Sugar:Cat (w)	175	105 min	99.7	80.7	[357]
Water/ MIBK 1:10	Sucrose	17	12-TPA-ChoCl	0.11 mmol	130	3 hours	90	78	[287]
DMSO		1	b-cyclodextrin-SO_3H	100 wt%	140	120 min		85	[347]
DMSO		4.3	FS-PAN	1.5:1 Sugar:Cat (w)	140	4 hours	100	42.9	[316]
THF/ Water 3:1		10	Ge_3N_4	10 wt%	150	100 min		19	[351]
THF		10	Ge_3N_4	10 wt%	150	100 min		16	[351]
THF/ Water 3:1		10	GeO_2	10 wt%	150	100 min		20	[351]
THF		10	GeO_2	10 wt%	150	100 min		18	[351]
Water-NaCl/ THF-NMP 1:4		5	P-TiO_2	4:1 Sugar:Cat (w)	175	105 min	99.8	98.2	[357]
Water-NaCl/ THF		5	Sn-Mont	30 wt%	160	3 hours		43	[359]

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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 2.14 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	[21]
	[BMIM][Cl]	$CrCl_3*6H_2O$	10 mg	100	0.03	[21]
	[BMIM][Cl]	$CrCl_3*6H_2O$/2,2'-bipyridine	10 mg/17.5 mg	100	0.004	[21]
	[BMIM][Cl]	$CrCl_3*6H_2O$/2,2'-bipyridine	10 mg/17.5 mg	400^{**}	0.38	[21]
Cellulose	Water/MIBK 1:10	12-TPA-ChoCl	0.11 mmol	140	15.94	[287]
	[BMIM][Cl]	$CrCl_3*6H_2O$	10 mg	400^{**}	14.88	[21]
	[BMIM][Cl]	$CrCl_3*6H_2O$	10 mg	400^{**}	11.90	[209]
	Water/MIBK 1:10	12-TPA	0.11 mmol	140	0.20	[287]
	[BMIM][Cl]	$CrCl_3*6H_2O$	7 mol %	120	0.38	[188]
	[BMIM][Cl]	SCC	29 wt%	160	2.43	[320]
	Water-NaCl/THF	Sn-Mont	30 wt%	160	0.11	[359]
	IL-1/MIBK	$MnCl_2*4H_2O$	1 ml	180	0.25	[241]
	[BMIM][Cl]/MIBK	$GeCl_4$	10 mol %	120	0.56	[144]
	Water-NaCl/ THF-NMP 1:4	P-TiO_2	4:1 Sugar:Cat (w)	175	0.16	[363]
	IL-1/MIBK	$CoSO_4$	1 ml	150	0.16	[145]
	Water	Pressure	40	280	1.19	[94]
	Water	Pressure	25	350	72.67	[93]
	Water	Amberlyst-15	0.2 g	190	0.01	[52]
	[BMIM][H_2PO_4]/MIBK	$MnCl_2*4H_2O$	1 ml	150	0.05	[241]
	Water	H_3PO_4	pH_{sol}=2	230	1.27	[13]
	[EMIM][Cl]	$CuCl_2$/PdCl2	13.5 µg/13.5 µg	120	0.19	[210]
	Water-NaCl/ THF-NMP 1:4	P-TiO_2	4:1 Sugar:Cat (w)	175	0.41^{c}	[363]
	[BMIM][Cl]/Water	$CrCl_3$/LiCl	0.155 mmol/0.155 mmol	140^{*}	0.37	[211]

	Water	Pressure	40	400	3.89 ^{a}	[94]
Chitosan	Water	[HMIM][HSO_4] [$FeCl_3$]	1.25 wt %	180	0.00	[242]
Corn Stalk	[BMIM][Cl]	HCSS	0.05 g	150	0.15	[367]
	[BMIM][Cl]	HCSS	0.05 g	150	0.71	[367]
	[BMIM][Cl]	HCSS	0.05 g	150	0.55	[367]
Inulin	DMSO	b-cyclodextrin-SO_3H	100 wt%	140	0.08	[347]
	Water/ Butanol 1:1.5	Phosphated tantalum hydroxide	0.1 g	160	0.33	[356]
	[AMIM][Cl]/water	L225-SO_3H	50 wt%	100	0.49	[293]
	[AMIM][Cl]/water	D265-SO_3H	50 wt%	100	0.33	[293]
	ChoCl	pTSOH	10 mol %	90	4.75	[161]
	ChoCl	$FeCl_3$	10 mol %	90	4.58	[161]
	Water/ 2-butanol (2:3)	NbO	0.1 g	160	0.81	[42]
	Water	CO_2	6 Mpa$^{b)}$	180	0.28	[198]
	Water	HCl	2 ml	180	0.28	[198]
	DMSO	FS-PAN	1.5:1 Sugar:Cat (w)	140	0.09	[316]
	ChoCl	$CrCl_3$	10 mol %	90	3.83	[161]
	ChoCl	Sc(Otf)$_3$	10 mol %	90	3.67	[161]
	Water-NaCl/ THF	Sn-Mont	30 wt%	160	0.11	[359]
	[EMIM][BF_4]	$SnCl_4*5H_2O$	10 mol %	100	0.37	[202]
	ChoCl	$CrCl_2$	10 mol %	90	3.00	[161]
	ChoCl	$ZnCl_2$	10 mol %	90	0.25	[161]
Jerusalem artichoke	Water/Butanol 1:1.5	Phosphated tantalum hydroxide	0.1 g	160	0.19	[356]
	Water/2-butanol (2:3)	NbO	0.1 g	160	0.33	[42]
Jerusalem artichoke (juice)	Water/Butanol 1:1.5	Phosphated tantalum hydroxide	0.1 g	160	0.38	[356]
Pine Wood	[BMIM][Cl]	$CrCl_3*6H_2O$	10 mg	400**	8.32	[209]
	[BMIM][Cl]	$CrCl_3*6H_2O$	10 mg	100	0.05	[209]
	[BMIM][Cl]	HCl	0.66 g/l	100	0.02	[209]
	[BMIM][Cl]	$CrCl_3*6H_2O$	10 mg	400**	7.52	[209]
Sigmacell	[BMIM][Cl]	$CrCl_3*6H_2O$	10 mg	400**	13.20	[21]

Spruce	[BMIM][Cl]	$CrCl_3*6H_2O$	10 mg	400^{**}	12.72	[21]
Starch	Water/MIBK 1:10	12-TPA-ChoCl	0.11 mmol	130	0.74	[287]
	[EMIM][BF_4]	$SnCl_4*5H_2O$	21.6 g	100	0.03	[200]
	Water-NaCl/THF	Sn-Mont	30 wt%	160	0.12	[359]
	[OMIM][Cl]/Ethyl acetate	HCl	5 ml	120	1.01	[202]
	Water	Pressure	1	220	1.10	[95]
	DMSO	b-cyclodextrin-SO_3H	100 wt%	140	0.00	[347]
	Water-NaCl/ THF-NMP 1:4	P-TiO_2	4:1 Sugar:Cat (w)	175	0.40^{+}	[363]
	Water-NaCl/ THF-NMP 1:4	P-TiO_2	4:1 Sugar:Cat (w)	175	0.38^{++}	[363]
	Water-[BMIM][Cl]/MIBK 1:5	$AlCl_3*6H_2O$	150 mg	140^{*}	0.28	[243]
Wheat Straw	Water/THF 1:3	$FePO_4/NaH_2PO4$	0.2 g/0.02 g	160	0.73	[244]
	[BMIM][Cl]	$CrCl_3/LiCl$	0.155 mmol/0.155 mmol	160^{*}	0.98	[211]

[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 2.15 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 2.5,2.6 and 2.10)
	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 2.5.2.6 and 2.10).
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 2.7-2.10)
	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 2.7-2.10)
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 2.10-2.13)

	-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 2.10-2.13)
	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 2.10-2.13)
Heterogeneous Carbon-based	**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 2.10-2.13)
	Carbonized biomass -Good functionalization - Potentially sustainable (sourcea and functionalization) -Cheap source -Low surface area	b-cyclodextrin-SO_3H, Graphene oxide, HT carbonaceous 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 2.10-2.13)

2.6 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 acid 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, such as polysaccharides from cellulosic materials. 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 2.15 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.

Connecting Statement 1

Chapter 2 provided a categorical summary of the current HMF research, with a focus on the catalysts and their reaction systems. It was observed that research has moved from homogeneous systems in favor of heterogeneous ones, due to their ease of reuse and recovery, as well as their potential of being highly modifiable. However, solid catalysts have had limited success in transforming simple sugars to HMF. Moreover, emphasis has moved on from synthesizing HMF from fructose, to glucose, to more complex biomass, such as forestry, food, or agricultural wastes and by-products, which present additional challenges in their processing and valorization.

The following chapter presents the development, characterization, and efficiency of functionalized carbonaceous material as potential catalysts for HMF synthesis. Softwood pulp was used as a substrate to produce a sulfonated carbon, which was characterized by FTIR, TGA, elemental analysis, BET analysis and XRD. Fructose was the selected substrate for testing the catalytic properties of the materials. The reactions were carried in both single phase and biphasic systems and optimized to obtain quantitative HMF yields using a response surface methodology. This chapter is based on an article reproduced from Chemical Engineering Journal 2020, 382, 122766 with permission from Elsevier. The article was co-authored by Dr. Marie-Josée Dumont.

3 Production of HMF in high yield using a low cost and recyclable carbonaceous catalyst

3.1 Abstract

In this study, sulfonated wood pulp catalysts were produced by hydrothermal carbonization of softwood pulp and functionalized using H_2SO_4. These newly synthesized catalysts were used in a one-pot reaction system where ionic liquid [$BMIM^+$][Cl^-] acted as a solvent and MIBK acted as the organic phase in the conversion of fructose to HMF. Using response surface methodology, molar yields as high as 98.6 % were obtained at mild conditions of 112 °C and 24 minutes with a catalyst load of 5% weight. The catalyst was easily recovered by filtration and used four times with minor loss in catalytic activity. XRD patterns showed that the material remained stable through the reaction conditions.

Keywords: Sulfonated catalyst; stirred reaction; HMF; heterogeneous catalysis.

3.2 Introduction

The extensive use of fossil fuels as source of energy and chemical products is leading to a fast depletion of these resources. Their scarcity has led to the extraction of costly and environmentally questionable sources (e.g. oil sands). A promising substitute can be found in the form of biomass, such as forestry, or agricultural wastes. 5-hydroxymethylfurfural (HMF) has been identified in the U.S. Department of Energy's report as a building block for biochemicals [4]. HMF is synthesized by the dehydration of carbohydrates and has found use in the production of several polymers, fuels, and base chemicals [59, 60, 372]. While there are several processes capable of obtaining quantitative HMF yields from fructose [30, 144, 216, 236, 305, 347, 373, 374], there are still considerable obstacles to overcome before it can be produced in a sustainable and cost-effective fashion. High HMF yields are still to be obtained from lignocellulosic materials and highly concentrated carbohydrate mixtures. Additionally, according to the principles of green chemistry established by Anastas and Eghbali [5], the process should also use environmentally friendly solvents and catalysts. Several existing processes rely on a homogeneous catalyst, such as mineral acids and salts, which can be hard to recover or require auxiliary chemicals for their treatment, while others use metals that are rapidly depleting, as well as requiring environmentally unfriendly mining technics [288-290].

Recently, solid catalysts have been favored to produce HMF from renewable sources [375]. Given their ease of recovery and reuse, they are more sustainable and environmentally friendly than traditional homogeneous acid catalysts. Zeolites and other mineral solid catalysts have been extensively explored for HMF synthesis [36, 249, 256-258, 267, 271]. However, quantitative HMF yields have not been reached by the use of mineral solid catalysts when aldohexoses or complex carbohydrates are used as feedstocks. Sulfonated organic resins such as Amberlyst and Nafion have also been tested for HMF production [28, 29], with Amberlyst achieving excellent HMF yields from fructose [30, 31]. Nonetheless, both catalysts have been ineffective in converting glucose to HMF [32, 33]. Furthermore, these resins can be costly and have low thermal stability. Hara et al. synthesized a novel type of carbon-based catalyst obtained from the incomplete carbonization of naphthalene in the presence of sulfuric acid [319]. This material's structure was composed of sulfonated aromatic carbon sheets and active groups such as carboxyl and phenolics. The catalyst showed high acid activity and had a good thermal stability up to 247 °C. While not entirely "green" due to the use of large quantities of sulfuric acid, this material was prepared easily and at low cost. More recently, several papers have reported on the synthesis and use of these catalysts using different carbon sources as a base, ranging from simple sugars such as glucose or fructose [25, 294, 298, 350] to lignocellulosic materials [27, 293, 301, 320, 369] or more complex polymeric materials [376]. These catalysts have been successful in obtaining good HMF (72-82 mol %) yields from fructose and moderate values from glucose (27-48 mol %) [27, 320, 347]. The catalyst and reaction system proposed in this study resulted in almost quantitative yields of HMF, while using small substrate:catalyst ratios. The reaction conditions were also some of the mildest reported for this type of material.

Several methods for the preparation of sulfonated carbon catalysts have been reviewed [291, 377]. One of the most reported methods consists of a two-step process, where high temperature (400-500 °C) is used for the carbonization step followed by the addition of acidic sites via a sulfonating agent [27, 301, 319]. A second method consists of a one-pot reaction process, where the carbon source and the acid are mixed and reacted together at low temperatures (150-180 °C) [25, 347, 378]. From the literature, a decrease in acid sites and surface area can be observed with increasing reaction temperatures when glucose is used as carbon source [294, 320, 350, 378, 379]. Additionally, neither changes in total acid sites density, nor surface area appeared to influence HMF yields. It has also been observed that the use of concentrated acids is favored over diluted solutions, yielding more SO_3H active sites, albeit at the expense of a reduction in total acid sites [380].

The global pulp and paper production has been estimated to be 400 million tons worldwide [381]. Canada has the world's largest trade balance in the world for forestry product, with pulp and paper industry accounting for 36% of the total trade. However, due to recent changes in the market, Canadian softwood exports have declined, mainly due to the use of digital media [382, 383]. This has led to a transformation of the pulp and paper industry in different ways, one of them being the production of innovative products, such as bio-based chemicals and materials. In this work, a method to synthesize a sulfonated catalyst via carbonization and subsequent sulfonation using softwood pulp is presented. Softwood pulp has been selected as a feedstock due to its homogeneous composition and pre-existing infrastructure to provide standard starting material. The catalytic activity was tested for the dehydration of sugars, and the process was optimized to obtain quantitative yields from fructose using small catalytic loads and mild reaction conditions. The recyclability of the material was assessed, and the effects of the reaction on its physical properties have been established. Based on the authors' knowledge, this is the first time softwood pulp has been used as raw material for the synthesis of carbonaceous catalysts. The catalyst converted fructose to HMF more efficiently than commercially available acidic resins, such as Nafion and Amberlyst, which have been shown to require higher catalytic loads and longer reaction times to obtain lower HMF yields (73% and 89 mol % respectively) [32, 313]. Furthermore, the combination of high HMF yields, mild reaction conditions, and low catalytic loads is a step closer to the large-scale production of this platform chemical.

3.3 Experimental

3.3.1 Materials and reagents

D-glucose (99.5%), 5-hydroxymethylfurfural (99%, food grade), methyl iso-butyl ketone (MIBK) (99%), butyl methyl imidazolium chloride $[BMIM^+][Cl^-]$ (99.9%, HPLC grade), sulfuric acid (95-

98% ACS reagent), DMSO (99.9%, ACS reagent), and D_6 DMSO (99.9 atom % D) were purchased from Sigma-Aldrich (Canada). D-fructose (99.9%) was obtained from Alfa Aesar (USA). Bleached softwood pulp (glucan 84.8%, xylan 7.7%, mannan 5.6%) was provided by FP innovations (Point-Claire, Canada).

3.3.2 Catalyst preparation

The catalysts were prepared by a two-step process consisting of a hydrothermal carbonization step followed by a sulfonation step. The softwood pulp was freeze dried for 72 hours beforehand. 1 g of the dried pulp and 30 ml of deionized water were loaded in a high pressure stirred tank reactor (Anton Parr, Germany), and heated to a temperature range of 200-240 °C for periods of 12-24 h at autogenous pressure (Table 3.1). Once the reaction was completed, the material was recovered by filtration using filter paper (Fisherbrand, P2 1-5 µm) and washed using ethanol and distilled water to remove any soluble compounds from the solid material. The recovered material was oven-dried at 85 °C for 24 hours. The carbonaceous material was weighed, and the yield was reported as mass percentage. The full set of experimental conditions for this experiment are listed on Table 3.2.

Table 3.1 Factors and their corresponding levels for catalyst preparation

Levels / **Factors**	**-1**	**0**	**1**
(A) Time (hours)	12	18	24
(B) Temperature (°C)	200	220	240

The dried carbonaceous material was mixed in a round-bottom flask with concentrated H_2SO_4 in a 1:10 ratio of carbon to acid, at 140°C for 24 hours. The material was then recovered by filtration (Fisherbrand, P2 1-5 µm) and thoroughly washed with deionized water until no acid ions were detected by pH meter (VWR, symphony SB70P). The material was oven-dried at 85 °C for 24 h.

3.3.3 Characterization of the material

FTIR analysis was performed using a Nicolet IS10 (Thermofisher, MA, USA) with a diamond ATR crystal to determine the functional groups on the carbonaceous catalyst. The spectra were recorded at 32 scans, the range used was 400-4000 cm^{-1} and the resolution was 4 cm^{-1}. Elemental analysis for the determination of sulfur in the samples was performed at the Université du Québec à Montreal (UQAM) at the GEOTOP laboratory. Thermogravimetric analysis was used to determine the thermal stability of the catalyst. The equipment used was a TGA Q50 (TA Instruments, DE, USA). The samples were stabilized at 25 °C and heated up to 800 °C at a rate of 10 °C/min under a stream of 60 ml/min of N_2. N_2 adsorption-desorption was performed on a Micromeritics Tristar 3000 analyzer (Micromeritics, GA, USA) at -196 °C to determine the total surface area, pore volume, and pore size. The samples were degassed for 24 hours before the analysis.

X-Ray diffraction (XRD) analysis was performed on a Bruker D8 Advance diffractometer (Bruker AXS, WI, USA) for determination of the carbon sheet structure. Samples were smeared directly onto the silicon wafer of a proprietary low-background sample holder. Data were collected between 5-90° with increment of 0.02° using a continuous coupled $\theta/2\theta$ scan with Ni-filtered CuKα radiation operated at 40 kV and 40 mA.

3.3.4 Catalytic test

The experimental conditions for the conversion of sugars to HMF were determined by a central composite experimental design (CCD) and are available in Table 3.2. The results were modeled using a response surface analysis performed using JMP software. The best fitting model was used for optimizing the process. The factors studied were the reaction time, temperature, and catalyst load. The reactions were carried out in 5 ml glass tubes using 1 g of ionic liquid $[BMIM^+][Cl^-]$. as solvent and 0.1 g of either fructose or glucose. A biphasic system and a single-phase system were used for the catalytic tests. The biphasic media consisted of the ionic liquid $[BMIM^+][Cl^-]$ as the solvent and (MIBK) as the extracting solvent. The tubes were then placed in a pre-heated oil bath at a set temperature and for a predetermined reaction time (Table 3.2). The reaction was quenched by submerging the tubes in cold water. The reaction products were then diluted with water, and the organic layer was separated from the ionic liquid/water solution. Both phases were filtered through a syringe filter (Whatman RC 30, 0.2 μm) before analysis by liquid chromatography

(HPLC Agilent 1260, Zorbax Eclipse plus C18, 3.5 µm, 4.6x100 mm) at a wavelength of 280 nm and a column temperature of 30 °C. The mobile phase used was methanol:water (20 % w methanol) at a rate of 0.6 ml/min.

Table 3.2 Parameter values for the catalytic test CCD

	Temp (°C)	Time (min)	Catalyst (g)
Coordinate	X1	X2	X3
0	110	50	0.03
1	125	70	0.04
-1	95	30	0.02
1.68	135.2	83.6	0.0468
-1.68	84.8	16.4	0.0132

Additional experiments were carried out using a stirred reactor (Table 3.3). A 50 ml reactor with magnetic stirring was selected for this purpose. As with the previous catalytic experiments, the reaction conditions were determined using a CCD with temperature and reaction time as factors. Catalyst amount was set to a 20:1 sugar:catalyst mass ratio.

Table 3.3 Parameter values for the stirred reaction test CCD

	Temp (°C)	Time (min)
Coordinate	X1	X2
0	116	11.3
1	132	15
-1	100	7.5
1.41	138.6	16.6
-1.41	93.4	6

3.4 Results and discussion

3.4.1 Softwood pulp hydrothermal carbonization

The response surface analysis of the experimental data suggested a linear model, with a P=0.0015, demonstrating a good fit with the predicted data. Model predictions showed that the yield could increase using lower temperatures and shorter reaction times. However, after experimentation, it was observed that no carbonaceous material was obtained below the lowest set of condition (200 °C and 12 hours) (Fig. 3.1). Under these conditions, a maximum yield of 32 mass % was obtained.

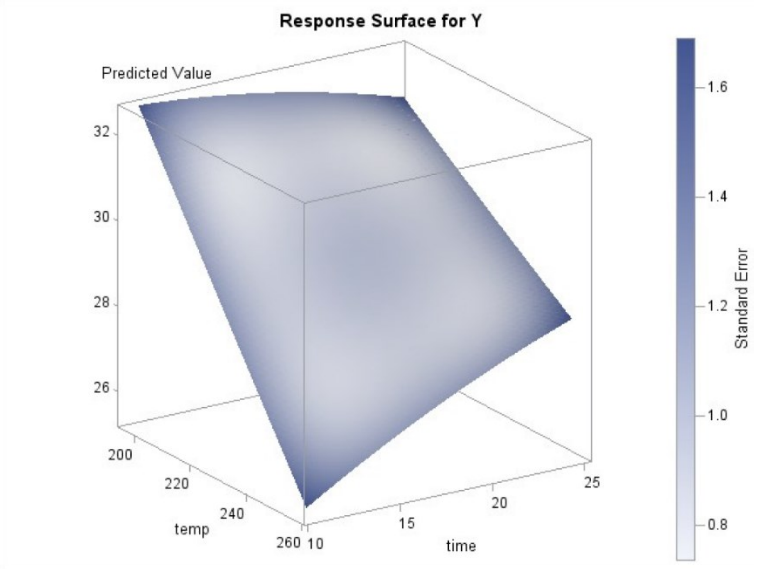


Figure 3.1 Response surface plot for the hydrothermal carbonization of softwood pulp. The predicted value represents mass % yield. Temperature is given in °C and time in hours.

The FTIR analysis of the carbonaceous samples showed that all carbons exhibited similar functional groups in all ranges of reaction times (Fig. 3.2). The FTIR spectrum showed a broad peak at 3410 cm^{-1}, typically associated with alcohol groups (-OH). The low intensity peak at 2910 cm^{-1} can be attributed to aliphatic –CH- stretching. The peak at 1680 cm^{-1} is related to the -C=O groups. These three peaks suggest the presence of carboxylic acids. The peak at 1584 cm^{-1} is attributed to C=C stretching. Peaks at 1280 cm^{-1} are attributed to aromatic esters. The treatment at the lowest temperature exhibited a sharper peak at 3337 cm^{-1}, suggesting the presence of OH groups, and a larger peak 1057 cm^{-1} associated with C-O stretching (Fig. 3.3). The peaks found in the 850-750 represent aromatic CH- bending. The appearances of these peaks, as well as the reduction in alcoholic -OH groups at higher temperatures, are a confirmation of the aromatization process during carbonization. This is in accordance to the mechanisms proposed in the literature, where dehydration products undergo aromatization and polymerization [384-386]. The resulting materials are likely composed of polyfuranic chains and aromatic carbon sheets.

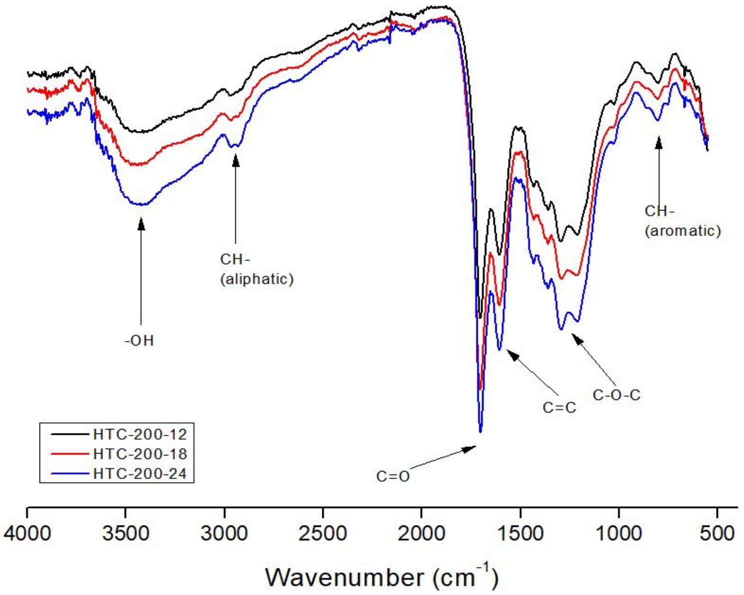


Figure 3.2 FTIR spectra of carbonaceous softwood pulp at different reaction times. Reaction temperature: 200 °C

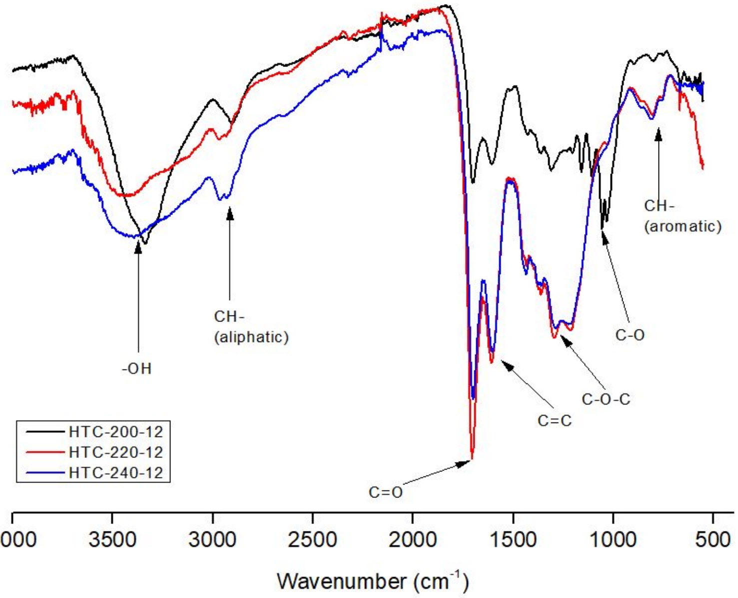


Figure 3.3 FTIR spectra of carbonaceous softwood pulp at different reaction temperatures. Reaction time: 12 h

3.4.2 Sulfonation and catalyst characterization.

FTIR spectra of the material can be seen in Fig. 3.4. Similar peaks to the carbonaceous softwood pulp can be observed, with the addition of a peak at 1036 cm^{-1}. This peak has been associated with sulfoxide groups (S=O). Additional sulfonic groups have been attributed to peaks found between 1370-1300 cm^{-1}. However, other functional groups, such as esters and ethers, can be found in this range, making it difficult to attribute these strong peaks solely to sulfonic sites. The bands found in the range of 1700-1600 cm^{-1} can be attributed to double bonds of aromatic structures, corroborated by the smaller peaks in the range of 700-800 cm^{-1}. Further confirmation of sulfonic groups present in the sample was obtained using elemental analysis (Table 3.4). The carbonization and sulfonation process are depicted in Scheme 3.1.

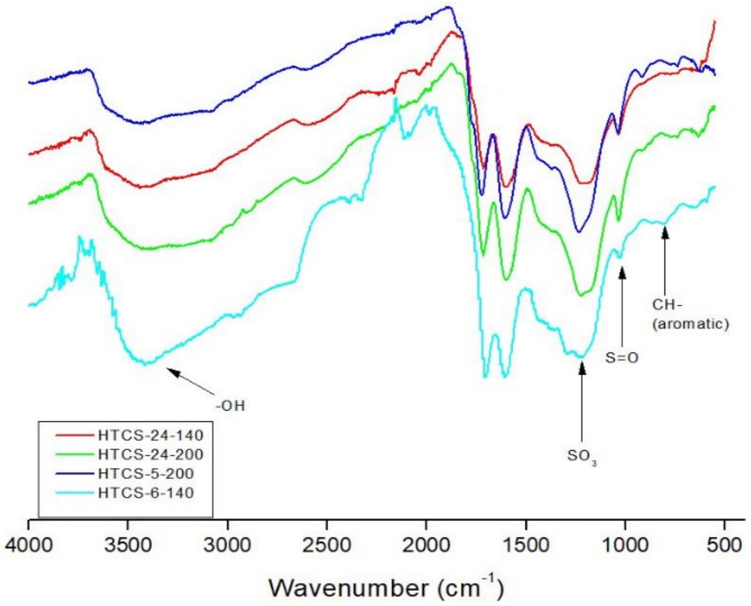
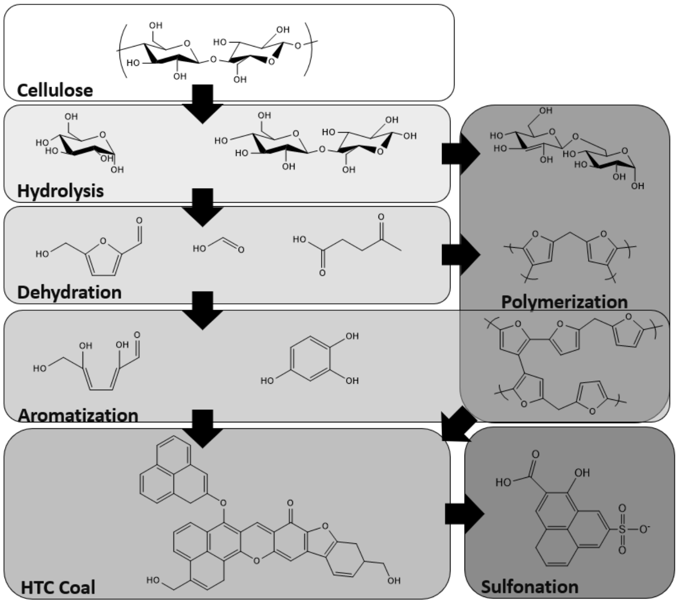


Figure 3.4 FTIR spectra of sulfonated carbonaceous catalyst at different reaction conditions

The carbonization process continues during sulfonation, increasing the degree of polymerization and aromatization, forming more carbon sheets. These sheets become larger, and the material exhibits a more organized structure. It has been suggested that at high treatment temperatures, the amount of acid sites is reduced, due to the fact that functional groups such as sulfonic and carboxylic can only exist on the edges of these sheets [293]. Smaller carbon sheets result in higher functional group densities.



Scheme 3.1 Hydrothermal carbonization and sulfonation of cellulose material

Elemental analysis confirmed that the sulfonation had been successful. Table 3.4 shows the sulfur content of the sulfonated material at different temperatures and reaction times. Samples are named following the structure HTCS-X-Y, where HTC stands for hydrothermal carbonization, X represents the reaction time, and Y the reaction temperature. A non-sulfonated carbon sample is also shown (HTC-0). Short reaction times did lead to a low degree of sulfonation, with 6 hours reaction time resulting in 1 wt% of sulfur content only. On the other hand, long reaction times and high temperatures reduced the mass yield of the catalyst by as much as 70%. At 24 h and 140 °C, a sulfur content of 2 % mass and a mass yield of 49 % were achieved.

Table 3.4 Sulfur content in carbonaceous catalyst determined by elemental analysis

Sample	%S	%SO_3	SO_3 (mmol/g)
HTCS-6-140	1.0	2.6	0.32
HTCS-24-140	2.0	5.0	0.62
HTCS-5-200	1.9	4.7	0.59
HTC-0	0.0	0.0	0.00

According to Shi et al. the following reactions take place during sulfonation of an aromatic ring [387]:

$$(1)\ H_2SO_4 \overset{H_2SO_4}{\Longleftrightarrow} SO_3 + H_2O$$

$$(2)\ C_6H_6 + SO_3 \overset{H_2SO_4}{\Longleftrightarrow} C_6H_5SO_3H$$

The species in (1) exist in equilibrium in sulfuric acid, where H_2SO_4 works as both the reactant and the catalyst. (2) is a trimolecular reaction involving a SO_3 functional group and H_2SO_4, where sulfuric acid acts as the receptor of a benzene hydrogen. This process is assumed to be the same taking place during sulfonation of the carbon catalysts.

The thermal stability of the material was analyzed by thermogravimetry analysis. Both the carbonaceous softwood pulp as well as the sulfonated carbonaceous catalyst showed a similar degradation profile (Fig. 3.5). These profiles were different from the dried softwood pulp. The decomposition shown by the softwood pulp at 300 °C is related to the pyrolysis of cellulose, while the later degradation stage at 380 °C is due to the decomposition of the remaining lignin in the pulp. For the carbonaceous materials as well as the sulfonated catalyst, the degradation starts at around 240 °C. From the literature, the mass losses are in the form of CO_2 attributed to the degradation of the carbon material, and loss of sulfonic groups from the catalyst in the form of SO_2 [299, 388]. The carbonaceous catalysts synthesized in this study have a similar thermodegradation pattern as perfluorinated resins such as Nafion, and better than sulfonic resin Amberlyst-15, common commercial resins used as catalysts in the dehydration of sugars to HMF [389, 390]. Moreover, the thermal degradation of Nafion has been identified as a source of persistent perfluorinated compounds, which can be damaging to the environment [391]. The slight difference in mass loss for the carbonaceous pulp and the sulfonated material near 200 °C can be attributed to the sulfonation process weakening the carbon structure.

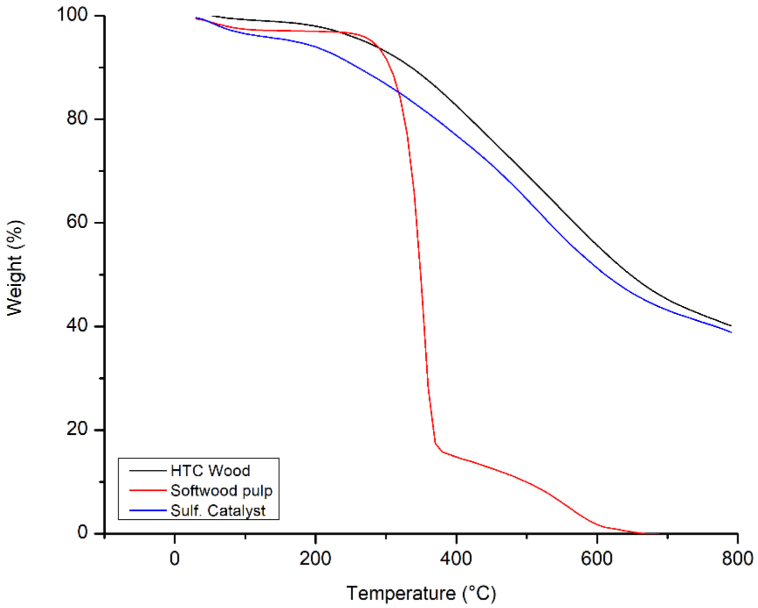


Figure 3.5 TGA plot of softwood pulp, HTC wood and sulfonated catalyst

3.4.3 Catalytic activity test

The sulfonated materials' efficiency as acidic catalyst was tested for the dehydration of sugars. The central point of the CCD experiment was at 110 °C, 50 min and 0.03 g of catalyst, and consisted of five replicates. The initial experiment with fructose showed that using a biphasic system, with MIBK as the extracting solvent increased the HMF molar yield up to 81.4 mol %, against a maximum of 52.1 mol % when not present (reaction conditions: 95 °C, 30 min, 0.02 g catalyst). Ketones have been shown to have a strong affinity for HMF, exhibiting a high partition coefficient. Continuous removal of HMF from the catalytic phase prevents further transformations of HMF into undesired products [221, 227]. A comparison of the results with and without MIBK is displayed in Table 3.5. No side product was detected when using the biphasic system. Therefore, all further experiments included MIBK.

Table 3.5 HMF yield comparison between reactions with and without MIBK as biphasic layer

Temperature (° C)	Time (min)	Catalyst (g)	Sugar:Catalyst ratio	Without MIBK (yields mol %)	With MIBK (yields mol %)
95	30	0.040	2.75:1	52.1 ± 2.4	71.3 ± 2.9
110	50	0.047	2.1:1	38.5 ± 3.2	71.1 ± 3.1
110	84	0.030	3.3:1	41.4 ± 2.0	70.7 ± 2.0
125	30	0.040	2.75:1	40.6 ± 2.4	81.4 ± 3.3

Table 3.6 shows a comparison of different reaction conditions and HMF yields, as well as a comparison to other similar catalysts. DMSO has been shown to help for the tautomerization of fructose from its pyranose to furanose form, as well as forming acidic species when oxygen is present, which facilitate the dehydration reaction [35, 173, 177]. This interaction could potentially mask the efficiency of the catalyst. When DMSO was tested as a blank and in combination with the catalyst, the reaction yielded several side products, showing that the process was not selective. Ionic liquids, such as [BMIM$^+$][Cl$^-$] have demonstrated to work as reaction promoters for HMF synthesis [18, 135, 142]. When tested under the experimental conditions of this study, blank fructose samples using [BMIM$^+$][Cl$^-$] as solvent resulted in negligible HMF yields. Therefore, [BMIM$^+$][Cl$^-$] was chosen for this experiment. The presence of the [Cl-] anion has been suggested to work as a nucleophile, while the shorter [CxMIM+] cation has a higher Hammett acidity, facilitating the dehydration reaction [140, 141].

Table 3.6 HMF production from fructose in a MIBK-[BMIM$^+$][Cl$^-$] biphasic media using carbonaceous sulfonated material as catalyst

Catalyst	Solvent	Temperature (°C)	Time (min)	Catalyst load (g)	Sugar: Catalyst ratio	HMF Yield (mol %)	Ref
HTC_24-140	[BMIM][Cl]	95	30	0.04	2.5:1	70.7 ± 2.9	This work
HTC_24-140	[BMIM][Cl]	95	70	0.04	2.5:1	82.8 ± 5.5	This work
HTC_24-140	[BMIM][Cl]	110	50	0.03	3.3:1	66.7 ± 7.1	This work
HTC_24-140	[BMIM][Cl]	95	30	0.02	5:1	87.3 ± 5.6	This work
HTC_24-140	[BMIM][Cl]	125	30	0.02	5:1	80.2 ± 3.9	This work
HTC_24-140	[BMIM][Cl]	132	81	0.01	10:1	96.1 ± 4.7	This work
HTC_24-140*	[BMIM][Cl]	112	24	0.005	20:1	98.6 ± 2.1	This work
Blank	[BMIM][Cl]	135	83	0	0	0.0	This work
Blank	[BMIM][Cl]	85	16	0	0	0.0	This work
Nafion(15)	DMSO	90	120	0.2	1.8:1	89.3	[313]
Amberlyst-15	N’N-DMF	120	120	0.02	1:1	73	[32]
CS-2^1	DMSO	140	30	0.1	5:1	78.0	[350]
SGO-3^2	DMSO	120	60	0.01	10:1	85.0	[358]
B-SO$_3$^{3}	DMSO	140	120	0.1	1:1	96.0	[347]

Carb-Sphere[4]	[BMIM][Cl]	100	90	0.05	1:5	88.1	[298]
Sulf. Char[5]	Water	180	15	0.25	2:1	42.3	[299]

*Reaction carried out in a stirred reactor

[1] Carbonized glucose spheres

[2] Sulfonated graphene oxide

[3] B-cyclodextrine-derived carbon

[4] Carbonaceous glucose microspheres

[5] Carbonized cellulose

A response surface analysis (Fig. 3.6 and 3.7) recommended a cubic model for the experimental data. Two modified versions were suggested: a hierarchical aliased model, and a modified cubic model. The hierarchical model had a P=0.007 and a lack of fit=0.05. With a P=0.0006 and a lack of fit=0.11 the modified cubic model was a good fit for the experimental area. Additionally, the model allowed calculating several optimal experimental conditions to obtain 100 mol % yield of HMF. These conditions were tested experimentally and returned a maximum value of 96.1% yield after 3 replicates (Table 3.6), further validating the model. The obtained model, in coded units, is as follows:

$$Yied = 69.06 + 0.18A - 0.22B - 0.65C + 3.03A^2 + 1.42B^2 + 2.43C^2 - 3.89ABC$$

Where A=Temperature, B=Time, and C=Catalyst load.

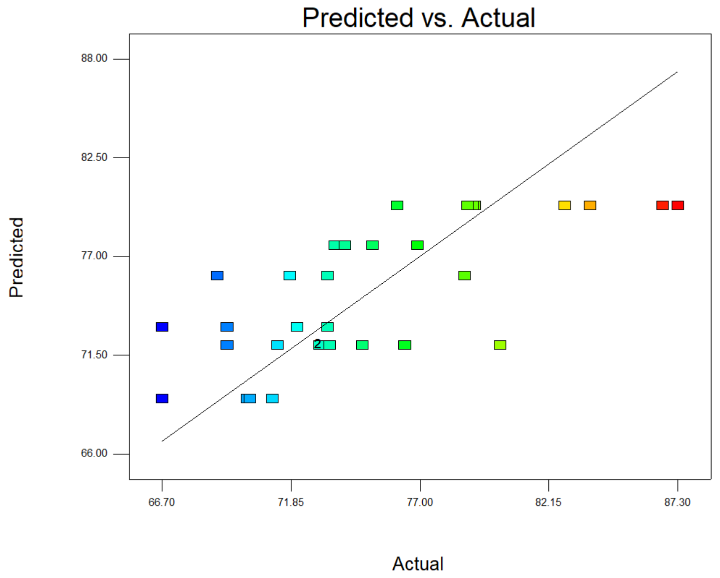


Figure 3.6 Experimental HMF values vs model-predicted values for fructose dehydration for a sugar:catalyst ratio of 10:1. Yields are given in mol %.

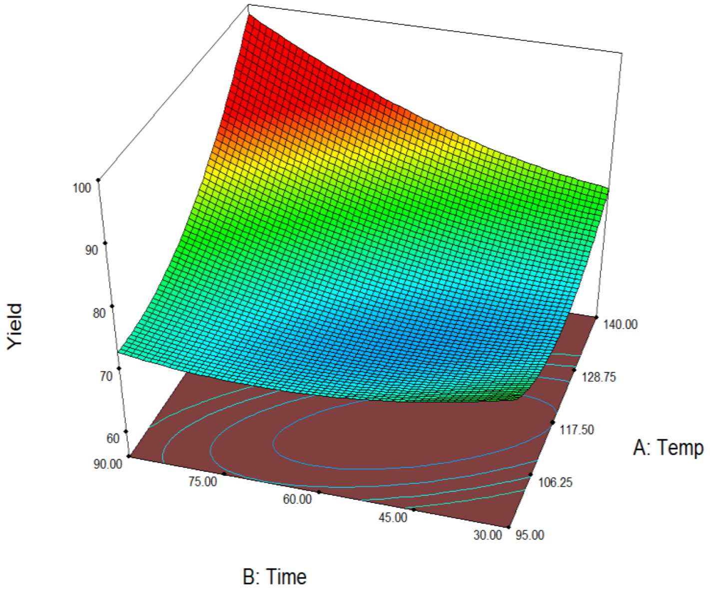


Figure 3.7 Response surface plot for the experimental data of fructose dehydration reaction for a sugar:catalyst ratio of 10:1. Yield is given in mol %.

Glucose was tested using similar experimental design and conditions as for the fructose experiments (Fig. 3.8 and 3.9). In this case, HMF was detected in lower amounts, with only 8% yield at 125 °C, 30 min and 0.02 g of catalyst. A response surface analysis suggested a cubic model with a P=0.0001, showing a good fit for the experimental data. As with the previous experiment, optimal conditions were obtained from the analysis, which predicted a maximum possible HMF yield of 42% at 152 °C and 150 min, for a sugar:catalyst ratio of 10:1. These conditions were tested and resulted in an HMF yield of 37% ± 2.3. The reduced efficiency of the catalyst on glucose dehydration can be attributed to a slower reaction rate of glucose to fructose isomerization in comparison to fructose dehydration. For this case, the resulting model can be expressed as:

$$Yield = 7.6 + 0.83A + 1.43B + 2.11\,C - 0.55AB - 0.33AC + 0.38BC - 1.99A^2 - 1.35B^2 - 1.19C^2 + 0.25ABC - 1.71A^2B - 2.22A^2C + 2AB^2$$

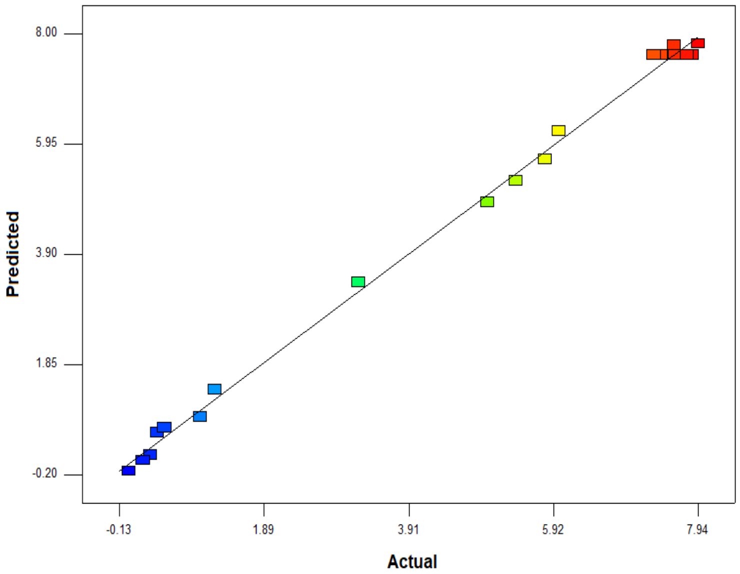


Figure 3.8 Experimental values vs model-predicted values for glucose dehydration

An additional set of experiments using a stirred reaction system was performed to verify the influence of the increased mass transfer on the reaction conditions. Initial screening experiments showed that it was possible to reduce the amount of catalyst from a 10:1 ratio to 20:1 under the optimized conditions for fructose dehydration. Encouraged by these results, a complete CCD analysis was used to determine the ideal reaction conditions under stirring. For this analysis, the sugar:catalyst ratio was fixed to 20:1, while the reaction temperature and time were variables determined by the experimental design. Within the conditions determined by the CCD, the maximum HMF yield obtained was 63.6 % at around 139 °C and 11 minutes. The response surface analysis suggested two models: a quadratic model with a P=0.0019, and a cubic model with a P=0.0009. While both models returned similar optimal conditions for the reaction, the cubic model exhibited a higher predicted R^2 value (cubic pred. R^2=0.79 vs quadratic pred. R^2=0.14), as well as a lack of fit=0.36. This coded model was described with the following equation:

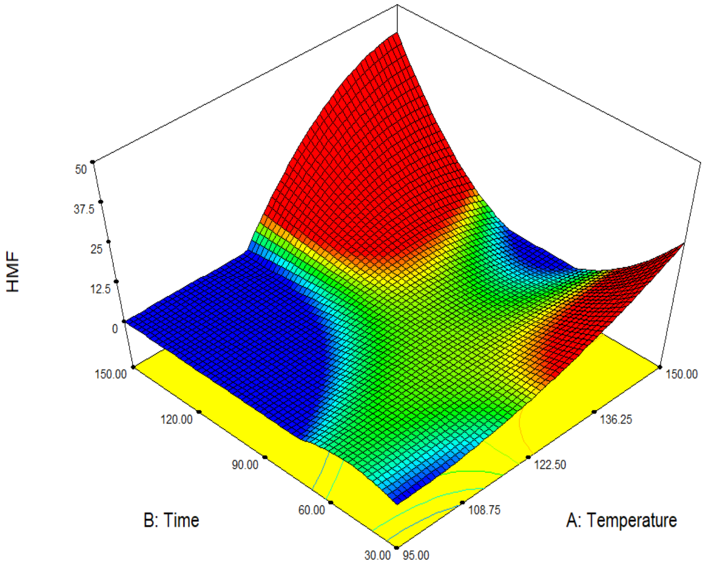


Figure 3.9 Response surface plot for the experimental data of glucose dehydration reaction using a sugar:catalyst ratio of 10:1

$$Yield = 56.1 + 0.67A + 14.64B - 1.65AB + 2.09A^2 - 6.23B^2 - 8.44A^2B + 3.58AB^2$$

The optimal parameters were tested at 112 °C and 24 minutes. These conditions were extrapolated from the cubic model and resulted in an HMF yield of 98.6 % (Table 3.6).

Not only the use of continuous stirring allowed a reduction in the amount of catalyst used, but also reduced the reaction time required to reach almost quantitative yields. This highlights the importance of good mass transfer when using heterogeneous catalysts. This reaction setup allowed to process fructose at high substrate concentrations (20 % mass), low temperature conditions, small catalytic loads (20:1 sugar:catalyst), and reduced reaction times. The reaction conditions used for this experiment were considerably milder than those of comparable catalysts (Table 3.6), with shorter reaction times, milder temperatures and lower catalyst ratios. The resulting response surface graphics for the dehydration of fructose under stirring are presented in Fig. 3.10 and Fig. 3.11.

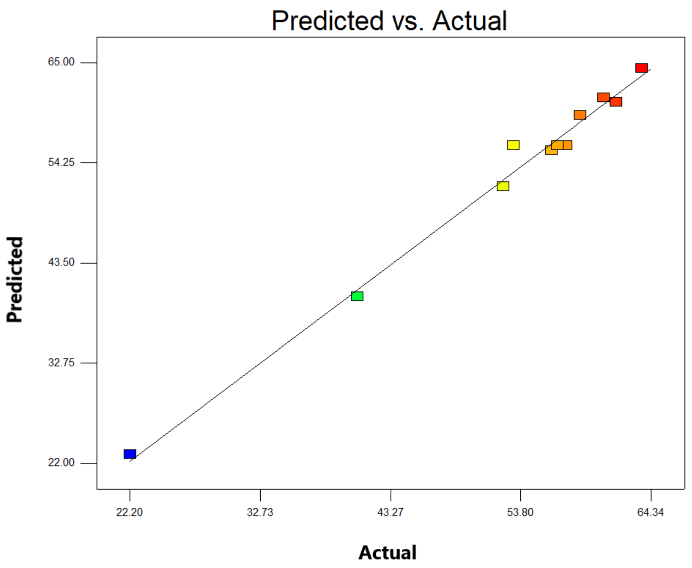


Figure 3.10 Experimental values vs model-predicted values for fructose dehydration under continuous stirring for a sugar:catalyst ratio of 20:1

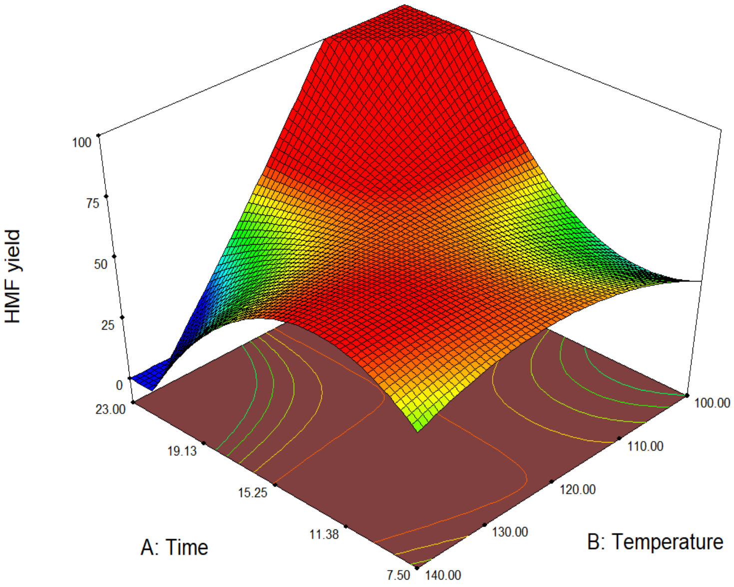


Figure 3.11 Response surface plot for the experimental data of fructose dehydration reaction under continuous stirring for a sugar:catalyst ratio of 20:1

3.4.4 Catalyst recycling

The recyclability of the catalyst was studied by recovering the used catalyst by filtration. The recovered material underwent several washing cycles using ethanol and water until the wash solvents were clear, and that HMF was not detected in the washed solvents by HPLC analysis. The recovered catalyst was then dried in an oven overnight at 85 °C, and reused for the dehydration of fructose under the same conditions as the optimized conditions for the non-stirred reactions (132 °C, 81 min and 0.01 g catalyst). These conditions were selected because of the higher temperature and longer reaction time than the optimal stirred reaction, putting the catalyst under harsher reaction conditions. The reaction using fresh catalyst returned 96.1 % HMF yield. After recycling, the efficiency of the catalyst dropped to 73.9 mol % yield. A second recycle reduced even further the efficiency to 66.1%. After the third run, the material was thoroughly washed using acetone in addition to water and ethanol. After washing with acetone, the HMF yield increased to 92.8% (Fig. 3.12). The drastic decrease in efficiency and its return to almost normal conditions suggest that a fouling effect was present where the porous structure was obstructed by humins.

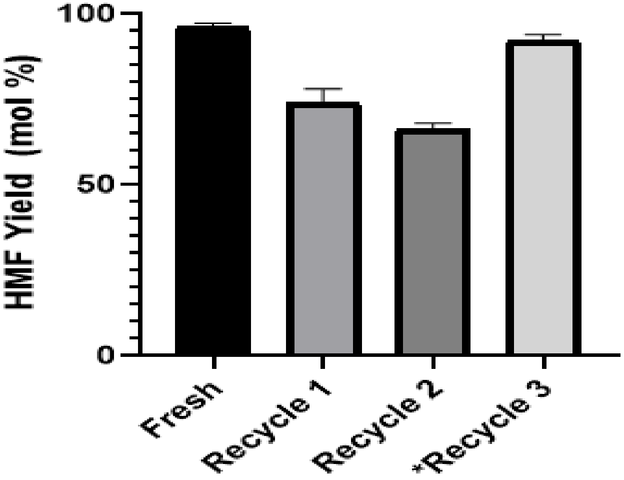


*Figure 3.12 Catalyst recyclability after fructose dehydration. *Additional washing with acetone*

Furthermore, the porosity and pore size of the materials were studied through N_2 adsorption/desorption. The analysis showed that sulfonation of the carbonaceous softwood pulp reduced its surface area and increased its pore size. The differences between surface areas before and after sulfonation can be related to their carbon structures. The HTC carbon exhibits an amorphous structure, while the sulfonated sample consists of unarranged aromatic carbon sheets in a turbostratic structure. A similar analysis of the recycled catalyst showed a further decrease in surface area and an increase in pore size after each run (Table 3.7). After one recycling step, the surface area dropped by half and the pores' size increased to 308 Å, with a second cycle further exacerbating this trend. This type of degradation can be attributed to attrition damage of the catalyst. Despite the considerable loss of surface area and increase in pore size, the catalytic activity remained high.

Table 3.7 Surface area and porosity of carbonaceous materials

Sample	**Surface area (m^2/g)**	**Surface area micropores (m^2/g)**	**Pore volume (cm^3/g)**	**Pore size (nm)**
HTC carbon	57	2.9	0.2	19.1
SO_3 catalyst	17	5.9	0.07	30.8
1st recycle	8	1.08	0.06	42.3
2nd recycle	2	0.62	0.04	97.4

The XRD pattern (Fig. 3.13) of the non-sulfonated material showed two weak peaks, one at θ=20-30° and another one at θ=45-50°. These two peaks have been often attributed to the planes (0 0 2) and (1 0 1) of amorphous carbon [294, 319]. After sulfonation, the peaks at 20-30° show a clear increase in intensity, suggesting that further carbonization led to a more organized structure. The structure appeared to be unchanged after being subjected to the dehydration reaction conditions, confirming the stability of the carbon sheets.

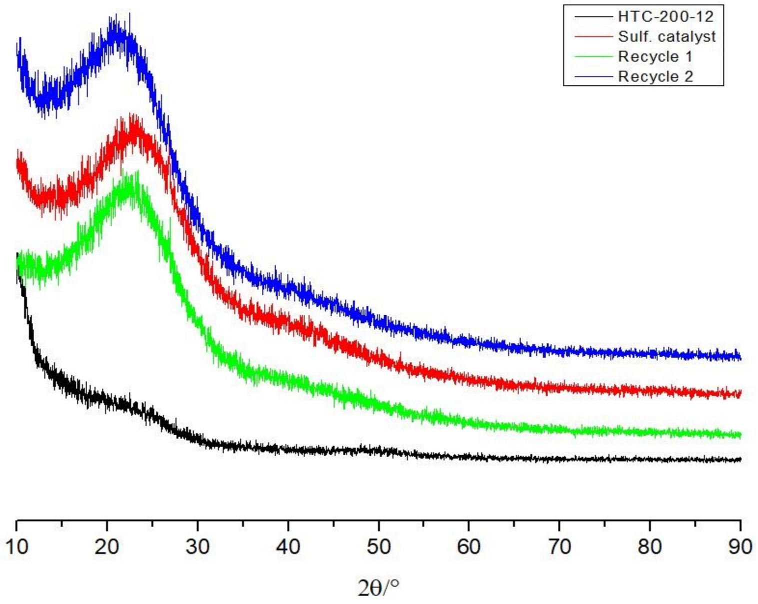


Figure 3.13 XRD pattern for carbon materials

3.5 Conclusion

A sulfonated carbonaceous catalyst was produced from softwood pulp using a two-step method of hydrothermal carbonization and sulfonation. Different reaction times for carbonization did not change the functional group distribution, while temperature reduced the amount of carboxylic acid groups and increased ester groups. Sulfonation was observed through FTIR and verified through elemental analysis. The catalytic tests showed that the acidic material effectively dehydrated fructose to HMF. The use of MIBK and continuous stirring conditions allowed a maximum HMF yield of 98.6 mol %, under mild reaction conditions (112 °C, 24 min) and low catalytic load (20:1 fructose:catalyst).

Recycling of the catalyst showed that the material can experience a fouling effect, which can be completely reversed by proper washing with acetone, thus restoring the catalyst to its normal efficiency. Additionally, N_2 adsorption analysis revealed signs of attrition on the catalyst, which reduced its surface area and increased the pore size with each recycle. Nonetheless, HMF yields of up to 92.8% were obtained.

Connecting Statement 2

The previous chapter highlighted the potential of functionalized carbonaceous materials as catalysts. The addition of sulfonic groups to the catalysts resulted in a highly efficient dehydration of fructose. The inclusion of a biphasic system further improved HMF yields, reaching up 98 mol %.

While the resulting catalyst was very efficient, the synthesis method required considerable amounts of H_2SO_4, a highly corrosive acid, as well as large amounts of water for washing. For these reasons, Chapter 4 explored the addition of sulfonic groups by using sulfosuccinic acid as the crosslinking molecule. A polyvinyl alcohol resin was functionalized this way to serve as catalyst for carbohydrate dehydration. Four different catalysts with varying amounts of sulfonic sites were developed, characterized, and tested in the dehydration of fructose. Characterization allowed to elucidate the possible structure of the materials, as well as their thermal stability and functional sites. The catalyst with the highest number of functional sites, denominated PVA-40, displayed the highest catalytic activity, effectively obtaining 100% HMF molar yield.

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4 Polyvinyl sulfonated catalyst and the effect of sulfonic sites on the dehydration of carbohydrates

4.1 Abstract

Several biobased platform chemicals have been identified as potential replacements of oil-based product, such as fuels and polymers. One of them, 5-hydroxymethylfurfural (HMF), has the potential to be transformed in a myriad of products, such as fungicides, fuels, and plastics. Environmentally and financially sustainable production of HMF has been one of the main bottlenecks for its commercialization at the industrial level. Here is presented a low-cost, tunable polyvinyl-based solid catalyst capable of efficiently transforming carbohydrates into HMF. The catalyst was produced using polyvinyl alcohol and sulfosuccinic acid (SSA) as the crosslinker. Adjusting crosslinking concentration had measurable effects on the physical properties and the efficiency of the catalyst. The crosslinking degree was observed to affect the thermal stability, the crystallinity, and the functional sites, providing an opportunity to fine tune the material to the reaction's needs. At the highest SSA concentration, SO_3H functional sites reached 1.7 mmol/g, and 3.6 mmol/g total acid sites. HMF synthesis was tested in ionic liquid [BMIM][Cl] and water. The use of ionic liquids reduced considerably the reaction temperature and time needed for quantitative yields from fructose. Optimal reaction conditions were found by response surface methodology, resulting in an HMF yield of 94.3% after 4 min at 125 °C from fructose. A kinetic model showed that HMF degradation proceeded via HMF self-condensation or self-etherification, and not through rehydration. The PVA-SSA catalyst was also tested on glucose and sucrose, with moderate yields (25% and 63.9% respectively) for both. The material shows promise as a highly tunable, recyclable catalyst.

Keywords: HMF, sulfosuccinic acid, heterogeneous catalysis, polymeric catalyst, kinetic study

4.2 Introduction

Production of 5-hydroxymethylfurfural (HMF) has been a topic of interest for the past decade. Ever since the publication of the Department of Energy's report on platform chemicals, and Bozell and Holladay's paper extension of this report [3, 4], interest ramped up in producing these molecules from renewable sources in more efficient, sustainable and financially feasible ways. HMF can be obtained from the dehydration of carbohydrates, and can be transformed into several other platform chemicals, such as levulinic acid, 2,5-furandicarboxylic acid or 2,5 dimethylfuran [59, 68, 392]. This versatility makes it a particularly interesting research topic, since HMF synthesis is the main bottleneck of many other platform chemicals.

Several catalytic processes have been developed over the years to produce HMF, with many of them reaching full conversion to HMF [70, 377]. Much of the early research on carbohydrate dehydration focused on homogeneous catalytic systems [70, 377]. While they could be catalytically efficient, they posed sustainability problems, such as catalysts recovery and regeneration, and use of auxiliary chemicals. More recently, heterogeneous catalytic systems have been favored [37, 266, 270, 280, 393-395], since they can be easily recovered, reused, and modified to better suit the needs of the reaction. Over the years, several solid catalysts have been tested to produce HMF. Some mineral catalysts, such as zeolites, have been routinely developed and showed some degree of success [32, 256-258, 278], with one recent example of Cr-loaded Beta zeolite resulting in 58% HMF yield from glucose [396]. Metal oxides and composites have also been tested, most commonly, Ti, Ni, Zr, and Ta, due to their capability for isomerizing glucose to fructose [39, 300, 356, 363, 397].While some of these metal-based heterogeneous catalysts show promising results, they can be costly, and are subject to depletion [245, 288-290].

The use of ion exchange resins as catalysts has been explored, with the most commonly used in carbohydrate dehydration being Amberlyst and Nafion [32, 33, 305, 311, 313]. Both commercial resins showed good results on fructose, albeit with long reaction times. Specialized catalytic resins have also been developed. Zhu et al. synthesized a formyl-modified polyaniline material that resulted in quantitative yields from fructose but was not effective at dehydrating glucose. Wang et al. used a Cr(III)-loaded polydivinylbenzene polymer to dehydrate glucose, obtaining up to 57 % HMF yield. Other types of catalytic resins have been developed and functionalized to provide interesting properties, such as localized heating through microwaves [318], and enzymes mimicry [398].

Polyvinyl alcohol (PVA) has been successfully used to produce membranes with different crosslinkers. The application of this resins are numerous, including proton exchange membranes [399], coating materials [400], adsorbing agents [401], and catalyst support [402]. Sulfosuccinic acid (SSA) has been used in the esterification of fatty acids for biodiesel production [403, 404]. SSA-crosslinked resins have been prepared for ion removal in water and fuel cell development [405-408], but their potential as catalysts in dehydration reactions remains unexplored. The presence of two dicarboxylic groups allows for the linking between two strands of PVA, while leaving the SO_3H group available for catalysis. Additionally, the use of SSA as a source of functional sulfonic groups, allows for a more efficient, controlled, and environmentally benign incorporation of the functional group, as compared to H_2SO_4.

In a previous study [409], we have shown that a sulfonated carbonaceous catalyst was very efficient in producing HMF from carbohydrates. Building up on this concept, an SSA-grafted polymer resins can work as a sulfonated catalyst that can be more finely tuned by controlling the crosslinker content. Herein, a biphasic heterogeneous catalytic system is presented. A low cost, recyclable sulfonated polyvinyl resin has been synthesized, characterized, and used as a catalyst in combination with ionic liquid 1-butyl-3-methylimidazolium chloride ([BMIM][Cl]), or water as solvents. The polyvinyl resin can be easily synthesized from polyvinyl alcohol and functionalized with SSA to produce a solid and recoverable catalyst. To the authors' knowledge, this is the first instance of PVA-SSA material designed for catalytic transformation of carbohydrates.

4.3 Materials & methods

4.3.1 Materials

Polyvinyl alcohol hydrolyzed (98-99%), and D-fructose (99.9%) were purchased from Alfa Aesar (USA). Sulfosuccinic acid (SSA) 70% in H_2O, methyl isobutyl ketone (99%), methanol (99.9% HPLC grade), acetonitrile (99.9% HPLC grade), D-glucose (99%), 5-hydroxymethylfurfural (99%, food grade), and 1-butyl-3-methylimidazolium chloride ([BMIM][Cl]) were purchased from Sigma-Aldrich (Canada).

4.3.2 4.3.2 Catalyst preparation

The catalyst was prepared following similar procedures from literature [406, 408]. PVA was given deionized water in a round bottom flask following a 1:10 PVA:H_2O ratio. The mixture was then heated in an oil bath at 90 °C under continuous stirring at 750 rpm for 6 h. After this period, different amounts of SSA were added to the solution to prepare the catalyst at five different SSA concentrations: 0, 10, 20, 30, 40 wt%. The solution was kept at 70 °C for 24 h under the same stirring conditions. Then, the resin was poured into Teflon molds and oven-dried at 60 °C for 24 h, followed by vacuum-drying at 110 °C for 2 h. The material was then rinsed with 500 ml of a 50% water:ethanol solution and left to dry at 60 °C for 24 h. The resulting film was then frozen using liquid nitrogen and ground in a mortar and passed through a 0.5 mm sieve to obtain a particle size of <0.5 mm.

4.3.3 Catalyst characterization

The PVA-SSA was analyzed by FTIR using a Nicolet IS10 (Thermofisher, MA, USA), equipped with a diamond ATR crystal. The obtained spectra were used to observe changes in functional groups on the PVA-SSA resins. The analyses were performed at 32 scans, in a range of 500-4000 cm^{-1}, and a resolution of 4 cm^{-1}.

Elemental analysis was used to determine the composition of the material and concentration of sulfonic sites present in the catalyst. The analyses were carried out at the Université de Sherbrooke (Sherbrooke, Canada) at the Laboratoire de Chimie Analytique using a Flash 2000 Organic Elemental Analyzer (Thermo Scientific, USA) according to ASTM D-5373-16.

Thermal stability of the materials was determined by thermogravimetric analysis, using a TGA Q50 (TA instruments, DE, USA). Samples were stabilized at 25 °C and heated up to 800 °C at a rate of 20 °C/min. An N_2 stream of 60 ml/min was used.

X-ray diffraction analysis was done on a Bruker D8 Advance diffractometer (Bruker AXS, WI, USA). Samples were smeared directly onto an aluminum plate holder. Data were collected between 5-90 ° with increment of 0.02 ° using a continuous coupled $\theta/2\theta$ scan with Ni-filtered CuKα radiation operated at 40 kV and 40 mA.

4.3.4 Catalytic test

The PVA-catalysts were tested in the conversion of carbohydrates to HMF. For the dehydration of simple carbohydrates, i.e. fructose, glucose and sucrose, a biphasic system under continuous stirring was used. The bottom phase consisted on either 500 mg of [BMIM][Cl] mixed with 100 mg of deionized water and 50 mg of a given sugar, or 600 mg of deionized water only with 50 mg of sugar. The top layer consisted of 3 ml of methyl isobutyl ketone (MIBK) as the extracting solvent. The reactions took place in an oil bath at various temperatures and reaction times. After the elapsed reaction time, the reactors were quenched in cold water to stop the reaction. The samples were then diluted with water, and HMF was further extracted using additional MIBK. Both phases were filtered using a syringe filter (Whatman RC 13, 0.2 µm) prior to liquid chromatography (HPLC Agilent 1260, Zorbax Eclipse Plus C18, 3.5 µm, 4.6x100 mm and Hi-Plex Ca (duo), 8 µm, 4x250 mm). The mobile phase consisted of methanol:water 20:80 v:v, and the data were collected at a wavelength of 280 nm, with a flow rate of 0.8 ml/min, and at a column temperature of 30 °C.

Screening runs were used as a basis to define the experimental area. To optimize the reaction, a rotatable central composite experimental design (CCD) with three factors was used. The three factors were time, temperature, and amount of catalyst. Conditions are determined by the distance of the center point, coded "0", at regular intervals of -1 to +1 and -α to +α. The value of α is calculated as $(2^k)^{1/4}$, where k = number of factors and represents the position of the axial points of the design. Table 4.1 shows the conditions of each factor at each coded value.

Table 4.1 Experimental conditions for CCD catalytic experiment

Coordinates	*-1*	*1*	*0*	*-α*	*α*
Time (min)	20	65	43	5	80
Temp (°C)	78	132	105	60	150
Catalyst (mg)	4.9	16	10.5	1	20

4.4 Results and discussion

4.4.1 Catalyst characterization

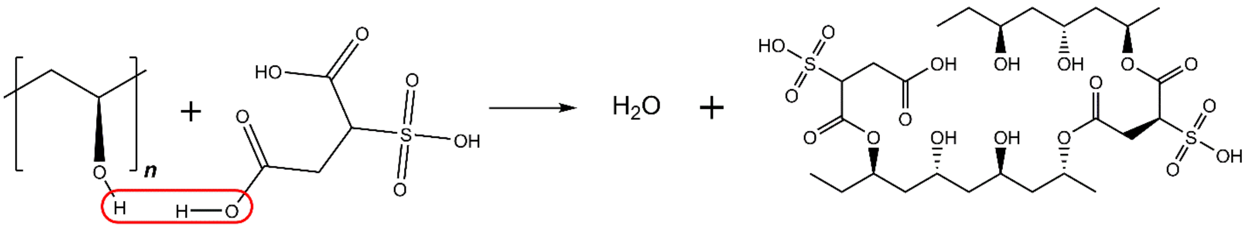
4.4.1.1 FTIR

FTIR analyses of PVA samples containing different concentrations of SSA showed clear changes within the PVA molecular structure (Fig. 4.1). The pure PVA sample shows a broad peak at around 3270 cm^{-1}, characteristic for the -OH stretch vibration, which can be assigned to PVA's hydroxyl groups (with contribution of inter- and intramolecular -OH bonds). This is accompanied by bands for the OH vibration at 1410 cm^{-1} (often observed as a doublet) and the alcohol's CO stretching mode at 1084 cm^{-1}. The bands at 2970 cm^{-1} represent the symmetric and asymmetric -CH stretching modes originating from the alkyl groups of the PVA chain. Addition of SSA led to other spectral features, with the most distinctive band appearing at 1707 cm^{-1}, representative of an ester functional group as well as other bands at 1258 cm^{-1} and 1084 cm^{-1} [378, 380, 402]. The FTIR spectra confirms the proposed condensation reaction between the alcohol groups in the PVA and the carboxylic acid groups in the SSA, which is occurring upon addition of SSA (see Scheme 4.1).

Consecutively increasing the concentration of SSA in the reaction results in an increase of the formed ester group at 1707 cm^{-1}, while the band intensities of the -OH stretching in the range of 3500-3000 cm-1 steadily decreases. These observations indicate a steady increase of SSA crosslinking within PVA with each concentration.

The peaks at 1258 cm^{-1} and 1084 cm^{-1} point to a carboxylate ester, which would result from the esterification of the -OH and -COOH groups of the PVA and SSA respectively. Sulfonic groups have also been related to the peak at 1084 cm^{-1} and 1258 cm^{-1} [378, 380, 402]. However, the overlap with the acyl group from the carboxylate ester makes it difficult to attribute this peak solely to SO_3. Nevertheless, the additional peak observed at 1032 cm^{-1} is associated with S=O stretching [378, 380]. This is a clearer indication of the presence of sulfonic groups in the catalyst.

The FTIR results confirmed that the crosslinking took place by condensation reaction between the carboxylic acid groups of SSA and the hydroxyl groups in the PVA chain. A reduction of the -OH stretch vibration with increasing SSA concentrations shows that the -OH groups are being replaced by ester bonds.



Scheme 4.1 PVA catalyst reaction and proposed structure

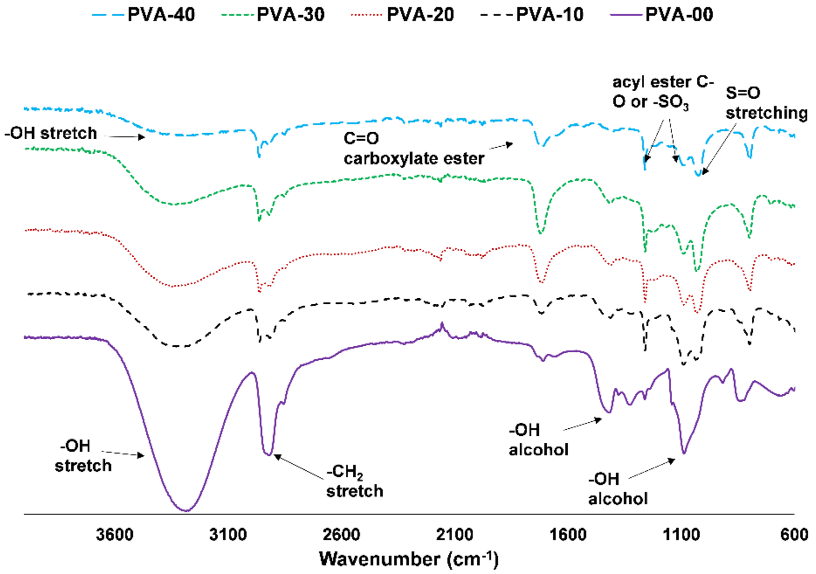


Figure 4.1 FTIR spectra of PVA-SSA catalysts. The number at the end of the name denotes the weight % of SSA in the mixture

4.4.1.2 X-Ray diffraction

X-ray diffraction was used to determine the crystallinity of the different PVA-SSA mixtures. From the X-ray spectra (Fig. 4.2) it can be observed that at $2\theta \approx 20°$ and $2\theta \approx 40°$, sharp peaks are observed in the less crosslinked samples. PVA is a semi-crystalline polymer, and these peaks are attributed to the (1 0 1) diffraction, due to intermolecular hydrogen bonding between PVA chains [410]. As the degree of crosslinking increases, the amount of intermolecular hydroxyl bonds reduces due to the presence of SSA. However, as more SSA molecules incorporate into the PVA chains, new phases can be observed, especially at $2\theta \approx 47°$ and $2\theta \approx 98°$ corresponding to phases (3 3 1) and (8 3 2).

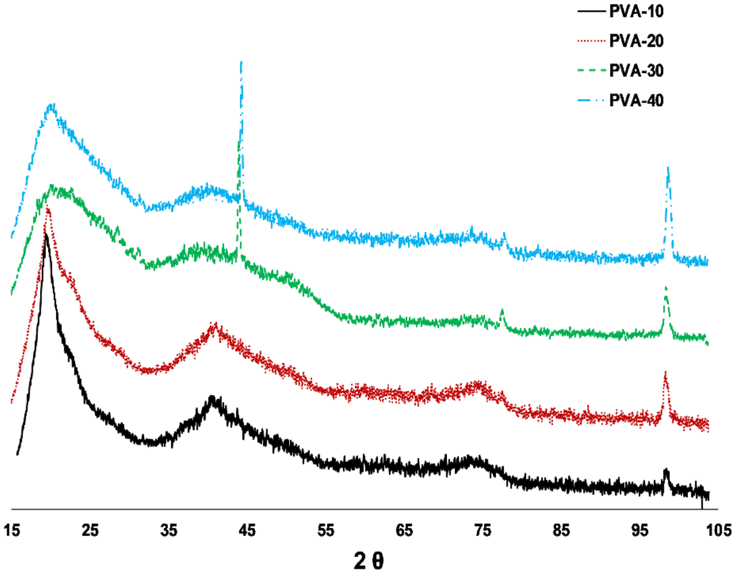


Figure 4.2 XRD pattern for PVA-SSA mixtures

4.4.1.3 TGA

Thermogravimetric analyses were performed on pure PVA and PVA-SSA mixture (Fig. 4.3). The pure PVA shows a slight loss of weight after 100 °C, attributable to the desorption of water molecules in the matrix. Additionally, it exhibits one degradation step starting at 274 °C and finishing at 472 °C, leaving no residue after this temperature. This step is due to the decomposition of the PVA polymeric chain. For the SSA-crosslinked catalysts, a larger weight loss can be observed after 100 °C. This loss has also been attributed to physically adsorbed water molecules, and it increases proportionally with the amount of crosslinker. This is in accordance with previous studies of similar materials [399, 411-413], which suggest that this proportionality is related to the degree of esterification of the film or to the hydrogen bonds formed between water molecules and -SO_3 groups. A second degradation step can be observed between 160 °C to 294 °C, which corresponds to the loss of sulfonic groups and the breaking of the crosslinked chains at the ester bonds. At ratios below 20%, SSA appeared to increase the thermal stability of the material. However, the effect is reversed at ratios above 30%, with PVA-40 having the lowest thermal stability (first degradation step at 147 °C). A possible explanation is that, due to the bulkiness of the SSA molecule, the chains become less structured, bending them away from each other, and reducing the amount of intermolecular hydrogen bonds between the chains and the SO_3 groups.

The interactions of hydrogen bonds between SO_3-OH, and OH-OH decrease in number, leaving more crosslinking units attached only to one side of the chain. This is congruent with the FTIR analysis.

Additionally, it has been noted that the presence of the acidic groups in the material catalyze the first degradation step , facilitating the elimination of functional groups [414]. Increasing the proportion of SSA would further affect the thermal stability, making the material unfit for the temperatures required for dehydration of carbohydrates. At 40% SSA, PVA-40 started to quickly lose functional groups at 147 °C, which is the lowest at which glucose and sucrose undergo dehydration.

A final decomposition step is observed at around 420 °C, as the main PVA chain begins to degrade. Pure PVA is almost completely degraded after this point, due to the breaking of the main chain into mostly water and gases, such as methane and ethylene. The residues for the sulfonic polymers are in the range of 21-32 wt%, probably due to some degree of aromatization of the residues, leading to more solid, and insoluble carbons, while degradation of PVA has been observed [413].

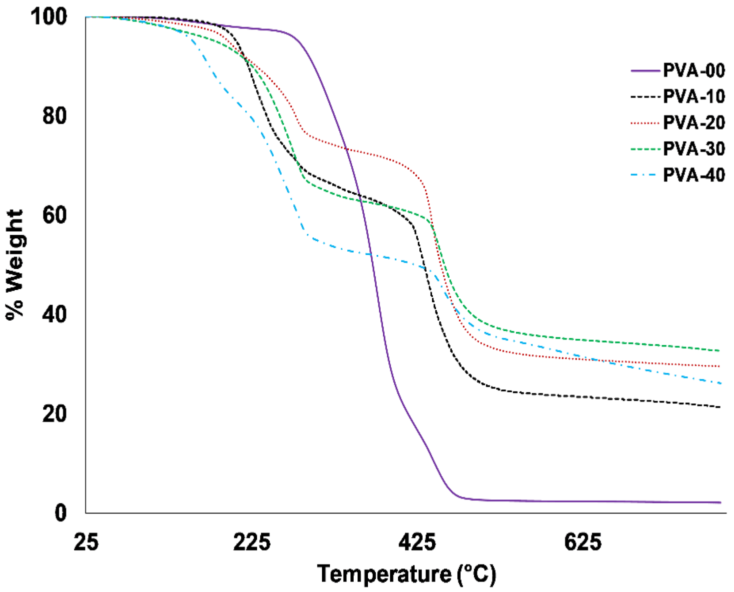


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Figure 4.3 Thermogravimetric analysis of different PVA-SSA mixtures.

4.4.1.4 Elemental Analysis

Elemental analysis further confirmed the different degrees of crosslinking at different SSA concentrations used. Furthermore, it allowed to recreate the structure of the different PVA catalysts. Table 4.2 shows the amount of C, H, O, and S in wt%, as well as the acid site concentration in mmol of SO_3H per gram of catalyst. Combining this information with that of the functional groups detected through FTIR, it was possible to elucidate the structure of the PVA resins. Since the only source of sulfur is the sulfonic group present in the crosslinker, this served as a marker of the amount of crosslinker present in the catalysts, with all the remaining C,H,O atoms belonging to the main PVA chain. Taking the basic PVA unit, C_2H_4O, it is possible to determine the number of blocks between linkers, as well as the remaining -OH groups. Table 4.3 presents the atomic ratios and the length of the PVA blocks between linker units (*n*).

Scheme 4.2 depicts the basic structure of PVA-SSA chain, ***n*** representing the length of the PVA block. From the data, the distance between linker units and acid sites does not correlate linearly to the percentage of SSA used. This suggest that there is a limit to the amount of crosslinking achievable. A possible reason for this is the non-flat structure of the SSA molecule, as well as the orientation of the -OH groups of the PVA, causing the molecules to twist and turn away from each other, increasing the space between two PVA chains.

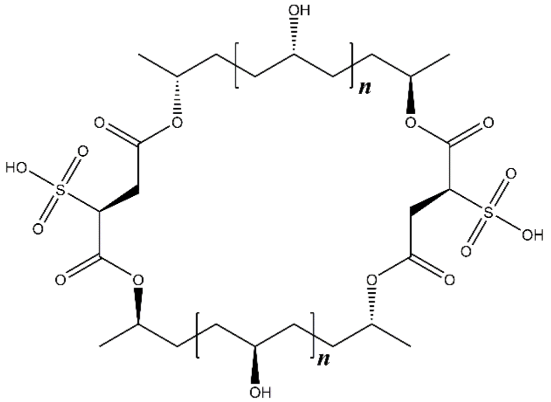
Table 4.2 C, H, S, and O weight %

	C	H	S	O	SO_3H mmol/g	OH groups mmol/g	Total acid groups
PVA	52.8 ±0.31	9.2 ±0.14	0.0	38.0 ±0.45	0.0	2.4	2.4
PVA-10	53.0 ±1.73	8.0 ±0.29	2.0 ±0.2	37.1 ±2.22	0.6	2.1	2.8
PVA-20	50.8 ±1.06	7.6 ±0.15	3.3 ±0.16	38.3 ±1.37	1.0	2.1	3.1
PVA-30	49.6 ±3.0	6.5 ±0.43	4.8 ±0.3	39.0 ±3.73	1.5	2.0	3.5
PVA-40	49.4 ±0.15	6.7 ±0.1	5.5 ±0.19	38.3 ±0.44	1.7	1.9	3.6

Table 4.3 PVA atomic ratios and chain length

	C	H	S	O	PVA chain length (***n***)
PVA*	1.9	3.9	0.0	1.0	-
PVA-10	69.2	124.9	1.0	36.3	30.0
PVA-20	40.8	72.9	1.0	23.1	16.0
PVA-30	27.4	43.3	1.0	16.1	9.0
PVA-40	23.8	38.6	1.0	13.8	7.3

***Ratio based on O**



Scheme 4.2 PVA-SSA structure. n represents the length of PVA blocks between crosslinked sections

4.4.2 Catalytic tests

4.4.2.1 Catalysts screening

The different PVA catalysts were screened for the dehydration of fructose in a stirred biphasic reaction system consisting of [BMIM][Cl], deionized water, and an MIBK organic phase. This setup was selected based on our successful previous results with a sulfonated carbonaceous catalyst [409]. The catalytic system proved to be very selective and efficient, with no side product being detected in neither the organic nor the aqueous phases. The lowest yield obtained was 86.9 mol %, using PVA-10 after 40 minutes, while both PVA-30 and PVA-40 attained 100% molar yields, albeit PVA-40 reached quantitative yields in half the time (20 min) (Fig. 4.4).

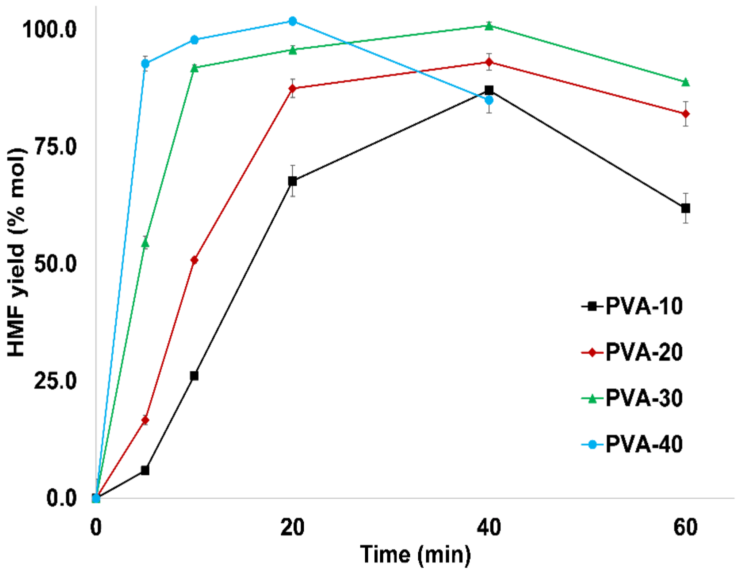


Figure 4.4 Fructose dehydration in [BMIM][Cl] using different PVA catalysts. Conditions: 50 mg fructose, 0.5 g [BMIM][Cl], 0.1 g water, 3 ml MIBK, and 10 mg catalyst. Reaction temperature 117 °C

A clear correlation can be observed between reaction rates, HMF yields and functional sites on PVA. Higher concentrations of SSA in the catalyst led to faster reaction rates and higher HMF yields. Degradation of HMF after achieving full conversion of fructose also increased with acid sites concentration. HMF yields started to decrease after 20 min, while it took over 40 min for PVA-30 and PVA-20. PVA-40 proved to be the most efficient catalyst, reaching 93% HMF yield within 5 min. After 20 minutes, quantitative HMF yields were obtained. This was followed by a reduction in HMF yield. It was also observed that the yields in the organic phase remained constant, while the yields in the ionic liquid reduced considerably. On average, 70.6% (+/-4.03%) of HMF was recovered in the organic phase, highlighting the importance of continuous removal of HMF from the catalytic system.

4.4.2.2 Fructose reaction optimization

The reaction system was further optimized using a CCD design for the use of PVA-40 as catalyst in combination with the biphasic system water, and MIBK. The highest obtainable yield within the experimental area was 81.2% HMF, using 4.9 mg of catalyst and 50 mg of fructose, at 132°C and 20 min reaction time (Table 4.4). The best fitting model for the design was a hierarchical cubic model. The statistical descriptors of the model are presented on Table 4.5. The plots of predicted vs. actual values as well as the response surface can be seen in Fig. 4.5 and 4.6. A $P_{value}<0.0001$ and a Lack of fit $P_{value}=0.8368$ indicate that the overall model is a good fit for the experimental data. The R^2 also shows that the variations of the response can be properly explained by the chosen factors, while the predicted R^2 shows that it is possible to use the statistical model to navigate beyond the experimental area.

Table 4.4 CCD results for the dehydration of fructose using PVA-40 in IL-water

Run No.	Time (min)	Temp (°C)	Catalyst (mg)	HMF yield (%)
1	20	78	4.9	4.3
2	65	78	4.9	6.2
3	20	132	4.9	81.2
4	65	132	4.9	57.2
5	20	78	16.1	6.7
6	65	78	16.1	15.4
7	20	132	16.1	77.2
8	65	132	16.1	57.4
9	5	105	10.5	10.2
10	80	105	10.5	78
11	43	60	10.5	0.03
12	43	150	10.5	55.3
13	43	105	1.0	22.2
14	43	105	20.0	70
15	43	105	10.5	70.5
16	43	105	10.5	68.9
17	43	105	10.5	58.2
18	43	105	10.5	71.8
19	43	105	10.5	69
20	43	105	10.5	75.9

Table 4.5 CCD Fructose model parameters

Model P_{value}	0.0001	*R-Squared*	0.9898
Std. Dev.	5.42	*Adj R-Squared*	0.9676
Mean	47.78	*Pred R-Squared*	0.9644
C.V. %	11.33	*Adequate Precision*	17.7616
Lack of fit P_{value}	0.8368		

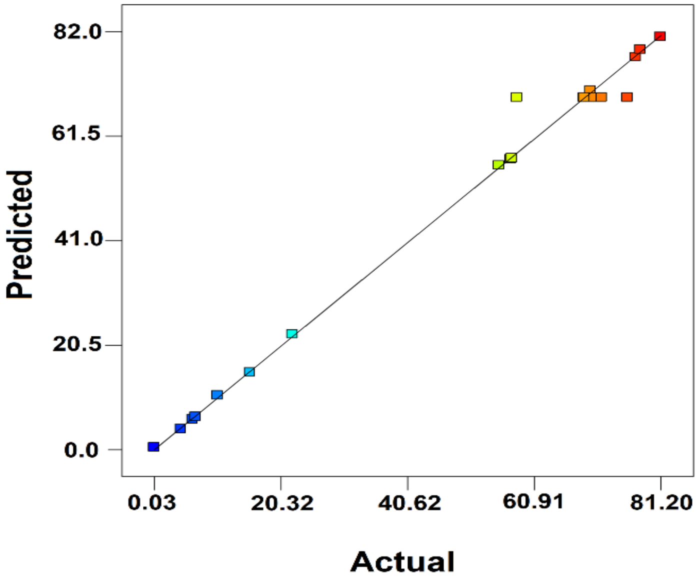


Figure 4.5 Model predicted vs. actual values of the CCD for fructose.

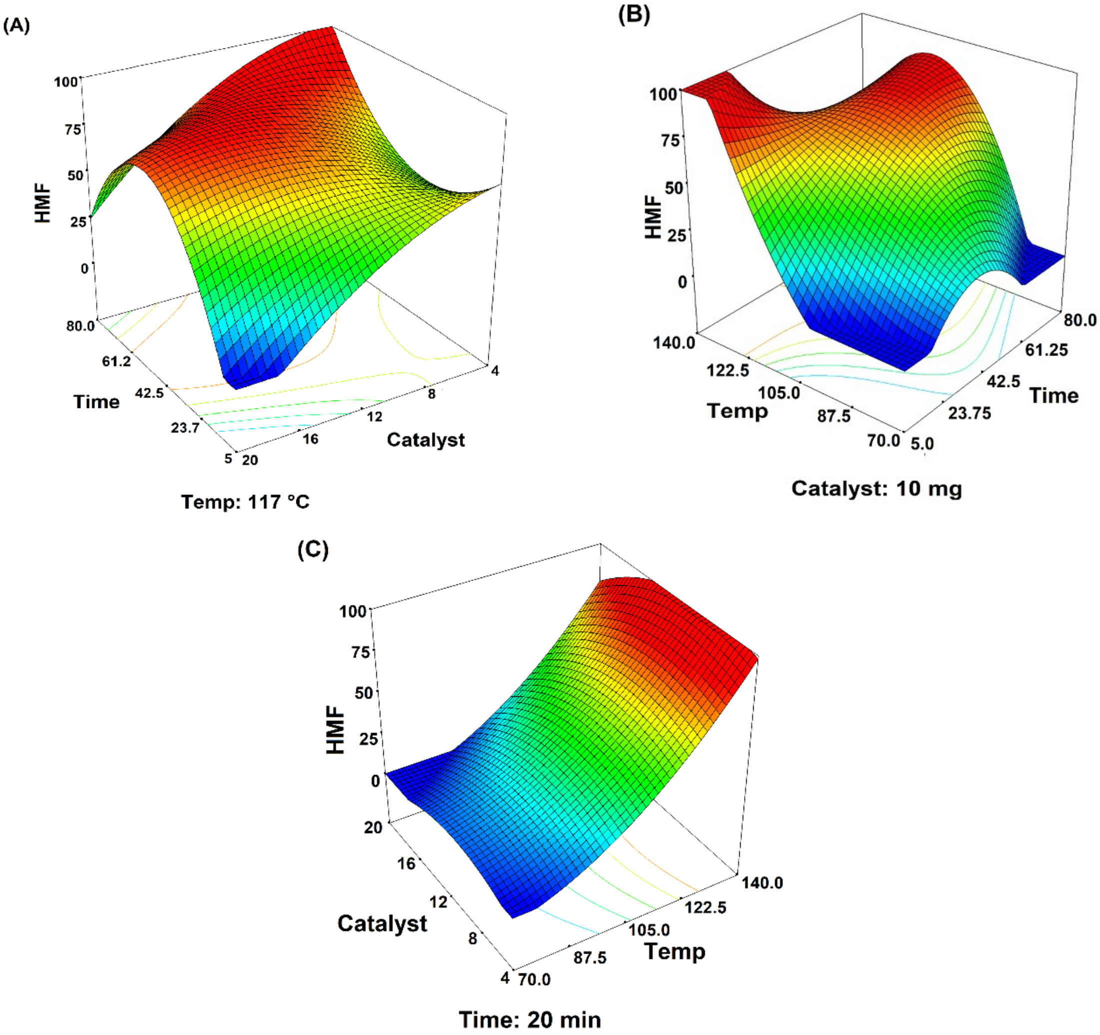
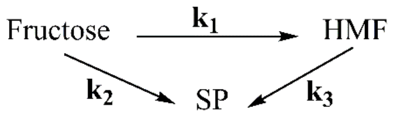


Figure 4.6 Response surface plots for fructose dehydrations. A) Time vs catalyst load, 117 °C. B) Temperature vs time, catalyst load: 10 mg. C) Catalyst load vs temperature, time 20 min.

The high prediction confidence of the statistical model allowed to calculate optimal conditions for the reaction system. All three factors proved significant and could be adjusted for optimization. The calculation suggested several ideal scenarios with almost quantitative HMF yields, that is, solutions exist where the amount of catalyst used is minimal, while the reaction time and temperature are increased, or reaction time can be shortened by increasing the catalyst amounts. To test the reliability of the optimization, one of these possible solutions was experimentally tested: a reaction temperatures of 125 °C, 10 mg catalyst, 50 mg fructose, and reaction time of 4 min. These conditions were calculated to result in 98.6 % HMF yield, which was very close to the experimental value obtained of 94.33 ± 2.22%.

4.4.2.3 Reaction kinetics

The experimental data allowed for the development of a kinetic model, which allows for a better understanding of the catalytic reaction. A first order reaction was used based on Fig. 4.7 and following the reaction system of Scheme 4.3, where fructose is converted to HMF and side products (SP), while HMF can also degrade to SP. The following catalytic reaction was considered:



Scheme 4.3 Fructose dehydration reaction pathway

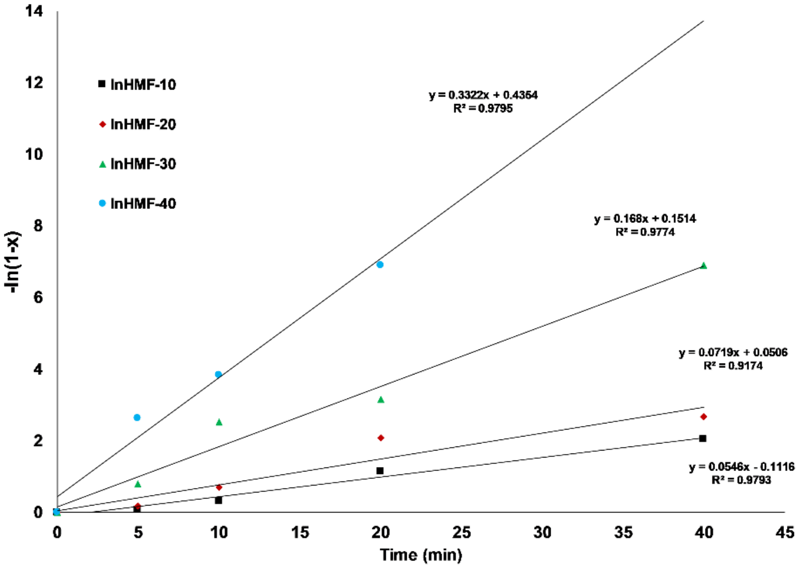


Figure 4.7 -ln(1-x) versus time where x=[fructose]

From which the following mathematical model was derived:

$$[F] \overset{k_1}{\rightarrow} [HMF] \qquad (1)$$

$$[F] \overset{k_2}{\rightarrow} [SP] \qquad (2)$$

$$[HMF] \overset{k_3}{\rightarrow} [SP] \qquad (3)$$

Where [*F*] is the amount of fructose, [*HMF*] is HMF concentration, and [SP] is the concentration of side products produced. From this model the derivative rate laws are as follow:

$$-\frac{d[F]}{dt} = \mathrm{k}_1[F] + \mathrm{k}_2[F] = \mathrm{k}_\mathrm{F}[F] \qquad (4)$$

$$\frac{d[HMF]}{dt} = \mathrm{k}_1[F] - \mathrm{k}_3[HMF] \qquad (5)$$

$$\frac{d[SP]}{dt} = \mathrm{k}_2[F] + \mathrm{k}_3[HMF] \qquad (6)$$

The integrated rate laws:

$$[F] = [\mathrm{F}]_0\mathrm{exp}^{-\mathrm{k}(t)} \qquad (7)$$

$$[HMF] = \frac{\mathrm{k}_1[\mathrm{F}]_0}{\mathrm{k}_3-\mathrm{k}_\mathrm{F}}\left(e^{-\mathrm{k}_\mathrm{F}(t)} - e^{-\mathrm{k}_3(t)}\right) \qquad (8)$$

The model was fitted, and the kinetic constants calculated using experimental data obtained at 117 °C, 10 mg catalyst, 50 mg of fructose and IL-water as solvent. The values obtained via graphical approach (Fig. 4.7) were congruent with those from the fitted data. Fructose conversion followed first order kinetics, while HMF formation also followed a similar order for most of the reaction. At long reaction times, there is a considerable degradation of HMF, leading to side products. The equation presented in (6) did not describe this process satisfactorily. A possible explanation for this is that the degradation of HMF is not due to the formation of rehydration products and the formation of levulinic or formic acid. Humins on the other hand, are formed via condensation reactions of HMF and sugars. The interaction between more than one HMF or sugar molecules to produce humins makes humins' formation a second order reaction. While fructose-HMF humin formation is possible, the almost-quantitative HMF yields suggest that this interaction is not the preferred pathway for fructose in this system. Taking this into consideration, the model was better represented as:

$$-\frac{d[F]}{dt} = \mathrm{k}_1[F] \qquad (9)$$

$$\frac{d[HMF]}{dt} = \mathrm{k}_1[F] - \mathrm{k}_3[HMF]^2 \qquad (10)$$

$$\frac{d[SP]}{dt} = \mathrm{k}_3[HMF]^2 \qquad (11)$$

Under these conditions, no side products are generated from fructose, therefore $k_1=k_f$ and $k_2=0$, and side product generation is a second order reaction from HMF. These set of equations were then modelled using Matlab Simulink (R2019a), and the kinetic constants calculated. Table 4.6 presents the values of the rate constants for the different catalysts as well as the R^2 values for each curve. Fig. 4.8-4.10 show the experimental data fitted to a kinetic model.

Table 4.6 Rate constants and R^2 values for kinetic model of fructose dehydration

	K_1- $sec^{-1}(x10^{-3})$	K_3 - $M^{-1}sec^{-1}(x10^{-7})$	R^2-Fructose	R^2-HMF	R^2-SP
PVA-10	0.8	2.57	0.932	0.853	0.892
PVA-20	1.18	9.33	0.958	0.932	0.624
PVA-30	3.36	4	0.989	0.967	0.492
PVA-40	14	9	0.994	0.985	0.567

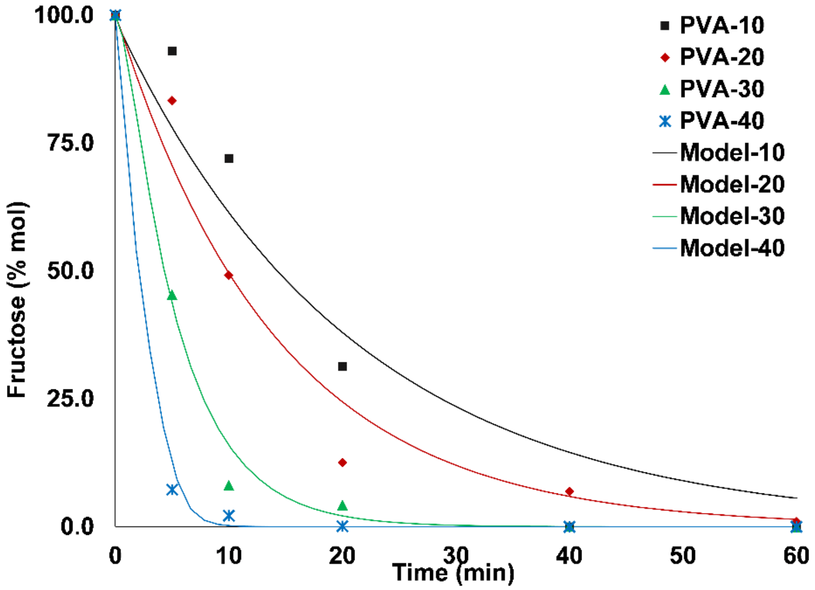


Figure 4.8 Kinetic model of fructose dehydration. Solid lines represent the calculated reaction, symbols represent experimental data.

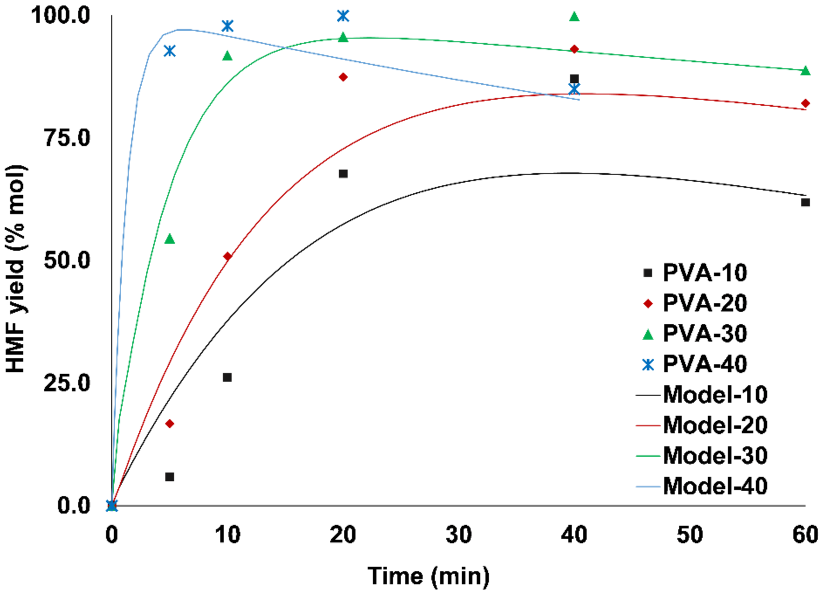


Figure 4.9 Kinetic model of HMF formation. Solid lines represent the calculated reaction, symbols represent experimental data.

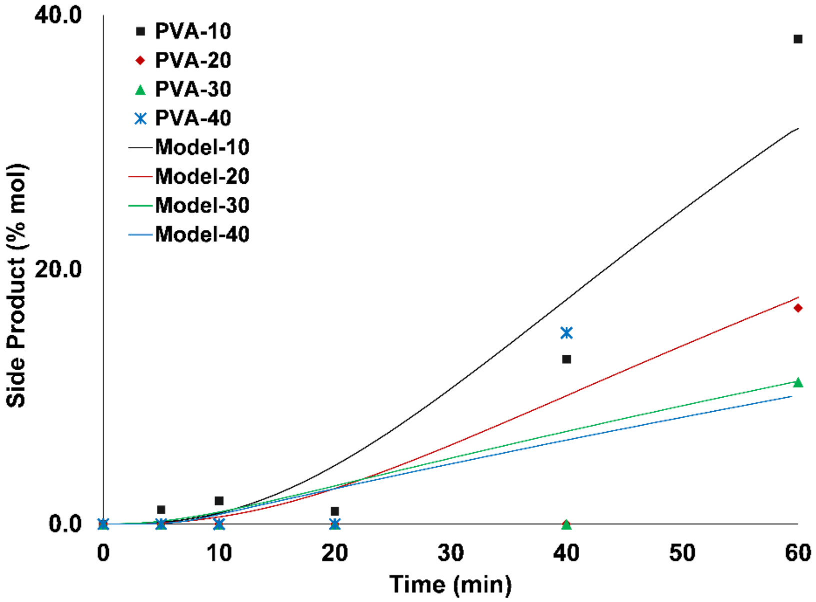


Figure 4.10 Kinetic model of side product formation. Solid lines represent the calculated reaction, symbols represent experimental data.

This model fitted the experimental data better than when assumed side products were formed from fructose or HMF rehydration. From the k values, HMF formation is several orders of magnitude faster than the humin formation reaction of two HMF molecules [415-417]. Another possible reaction is the self-etherification of HMF. This has previously been reported to be promoted by acidic catalysts, forming 5,5'-oxy(bismethylene)-2-furaldehyde (OBMF) [418-420]. The reaction was reported to take place over several hours, which agrees with the reaction rates calculated in this model.

The activation energy of the overall reaction was calculated using the Arrhenius equation $ln(K) = ln(\mathrm{A}) - {E_a}/{\mathrm{R}T}$. E_a was calculated from the slope of the plot of ln(K) vs (1/T), (Fig. 4.11) while the intercept returns the pre-exponential factor. E_a for the overall reaction was calculated as 102.3 kJ mol^{-1}, while the pre-exponential factor A was 1.27x10^{13} s^{-1}.

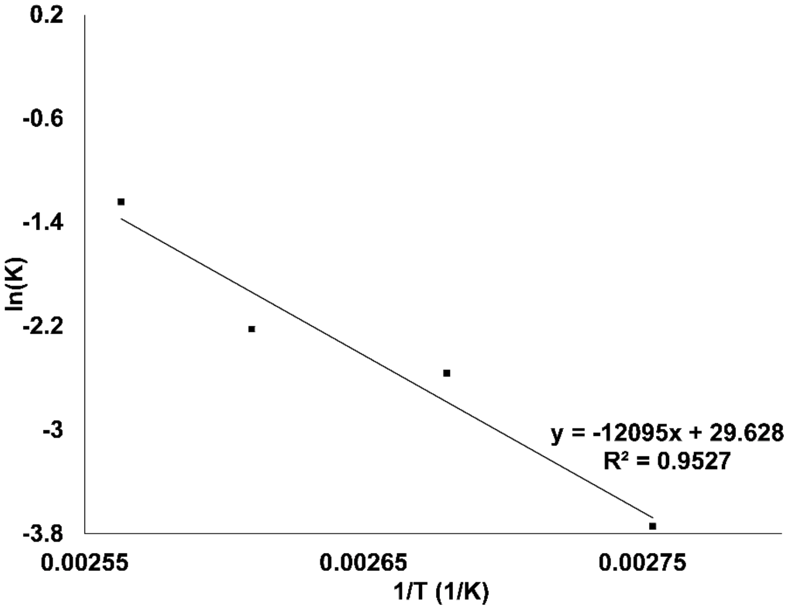


Figure 4.11 Arrhenius plot for HMF conversion using PVA-40

The turnover frequency (TOF) was also calculated for each of the catalysts and the values are shown in Fig. 4.12. The values were calculated at the 5-minute mark of the reaction by dividing the moles of HMF produced per minute by the total or SO_3H acid sites of each catalyst, where the total amount of acid sites is considered as the sum of SO_3H, COOH, and OH groups Values for both, OH and COOH are based on the remaining oxygen molecules, not part of the crosslinked SSA.PVA-40 displays the highest TOF. Given that all catalysts contain the same type of acid sites, namely SO_3H and OH groups, a possible explanation for this discrepancy is the competition for fructose between weak and strong acid sites. Sugar molecules interacting with the OH or COOH groups, not adjacent to SO_3H sites, may slow down the access to the more catalytically active SO_3H groups. This suggests a stereochemical effect on the reaction due to accessibility of the acid sites. Increasing grafting provides a two-fold beneficial effect: increasing the amount of highly active acid sites and preventing possible obstructions between the substrate and the catalytic sites.

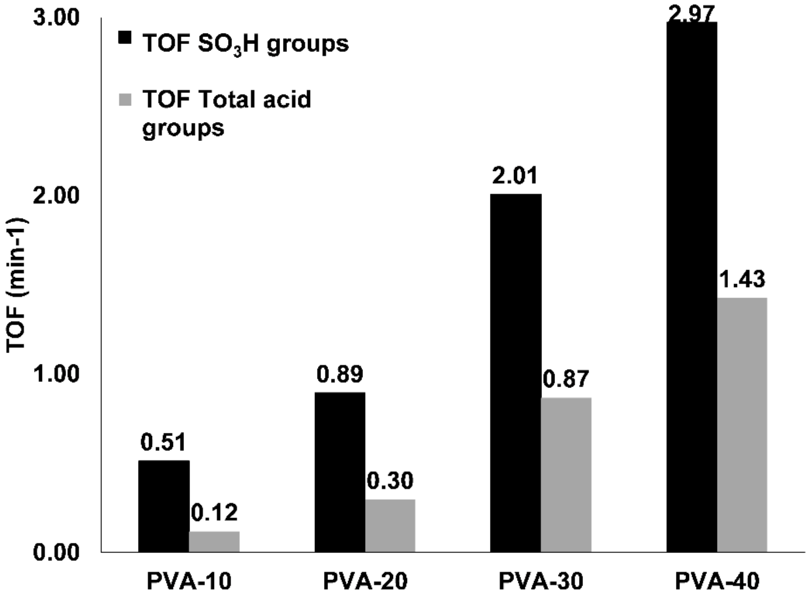


Figure 4.12 TOF for PVA catalysts

4.4.2.4 Fructose dehydration in water

To improve the sustainability of the catalytic system, fructose dehydration runs were also carried out in water. Under the same conditions as those carried out using IL-water, no HMF was detected. A screening experiment showed that a minimum temperature of 140 °C was required to obtain any HMF. This considerably limited the temperature range of the reaction, due to the likelihood of catalyst degradation at 160 °C, as shown by the TGA analysis. Reaction times were also increased, in comparison to the reactions in IL-water. Nevertheless, quantitative yields of HMF were obtained after 40 min (Fig. 4.13). This catalytic system, while requiring higher temperatures and reaction times, does have the advantages of better continuous extraction of HMF to the organic phase. Up to 85% HMF was recovered in the organic phase under these experimental conditions. Additionally, HMF recovery from water is a considerably easier process than recovery from ILs, via evaporation or crystallization. However, it should also be considered that, in the presence of water, HMF quickly degrades towards levulinic acid and formic acid. Furthermore, the increase of energy needed due to higher temperatures and longer reaction times may, at the end, make other solvents more sustainable than water. A proper life cycle analysis is needed to fully compare both alternatives.

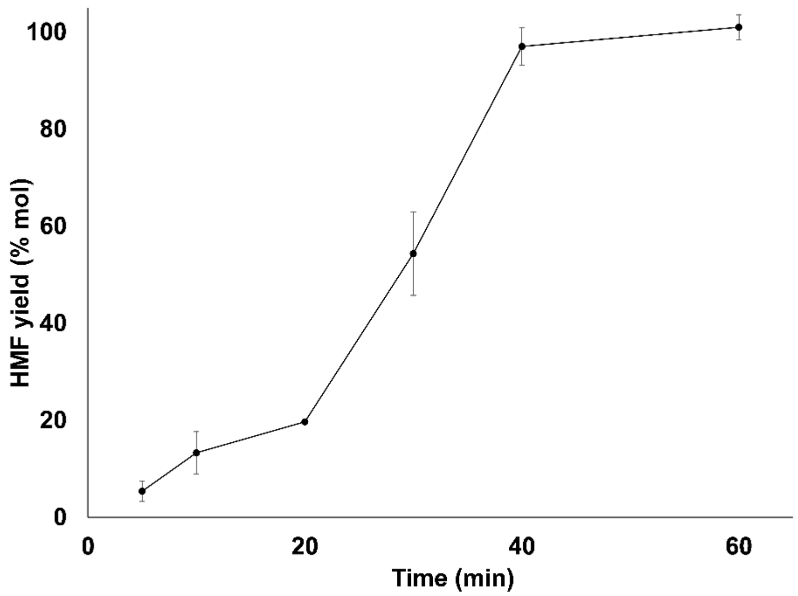


Figure 4.13 Fructose dehydration in water at 145 °C. Catalyst: PVA-40, 10 mg, fructose: 50 mg

4.4.2.5 Glucose dehydration

Further experiments were carried out using glucose at optimal conditions in IL-water, and water. As mentioned before, reactions in water are limited by the thermal stability of the catalyst, setting a cap at 145 °C. The results showed limited HMF yields, with a maximum of 25% yield after 2 h (Fig. 4.14) in IL-water. However, visual inspection of the samples showed the formation of solid material in the IL-water phase. These results suggest that, while PVA-40 does seem to catalyze the formation of HMF from glucose, the step competes with side reactions which lead to the formation of humins. According to kinetic and DFT studies by Qian, and Pidko et al. [187, 196, 281], Bronsted-catalyzed glucose dehydration does not necessarily lead to HMF formation. The reaction pathway is determined by the -OH group being protonated, with the preferred group being C_1-OH, which leads to condensation reactions rather than HMF. Protonation leading to isomerization or to HMF directly is done via C_2-OH, which happens at a much lower rate than condensation. The reaction in water resulted in much lower HMF yields, reaching only 7.6 % after 100 min (Fig. 4.14). Again, this has been explained through the interaction between the solvent and the glucose -OH groups [196], where the solvent competes with the catalyst for protons of hydroxyl groups in the sugar, as well as solvent-led mutarotation, which would make certain -OH groups more accessible.

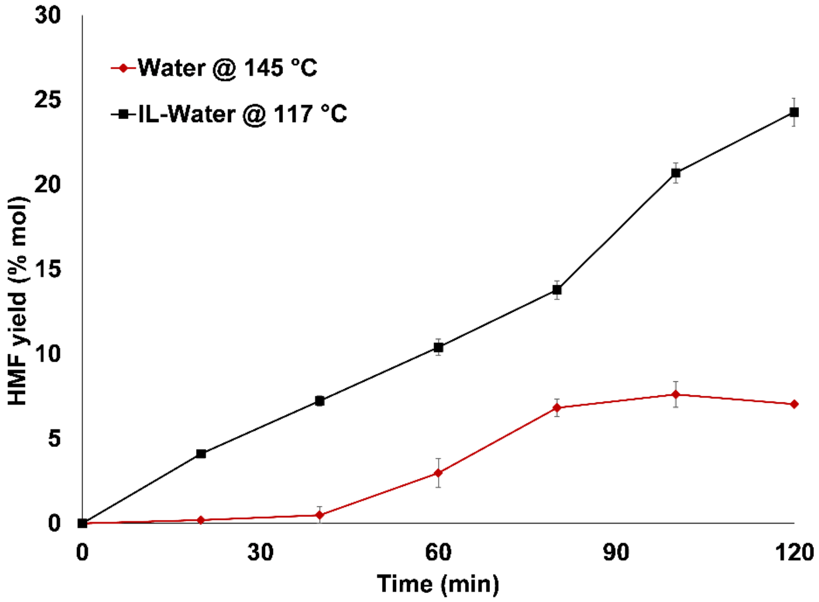


Figure 4.14 Glucose dehydration: in IL-water at 117 °C; in water at 145 °C. Catalyst: PVA-40, 10 mg, glucose: 50 mg

4.4.2.6 Sucrose dehydration

Sucrose dehydration was likewise analyzed in combination with PVA-40 in the same solvent system as glucose and fructose. Both maximum HMF yield and reaction time varied depending on solvent. As with the monosaccharides, the highest yields and shortest reaction times were obtained in the [BMIM][Cl]/water mixture. When using the IL-water system, up to 63.9 % HMF could be obtained after 60 min. The value suggests that both moieties of sucrose (fructose and glucose) were converted into HMF. In both water and IL-water (Fig. 4.15), HMF formation begins rather slowly, but the slope increases considerably after 10 min in both, water, and IL-water. A possible explanation is that at the beginning, hydrolysis of sucrose is taking place, occupying most active sites of the catalyst, creating a lag-like phase in the reaction.

As fructose and glucose begin to form, fructose quickly transforms into HMF, while glucose slowly forms either HMF or condensation products. As hydrolysis progresses, the more active sites become available for dehydration or condensation. In the IL-water system, the reaction begins more slowly, due to the limited amounts of water present in the system, which is needed for hydrolysis. This however allowed for a more controlled reaction, leading mostly to HMF. In water, the simultaneous presence of HMF, fructose and glucose can lead to the formation of condensation products, i.e. humins. In both cases, solid by-products could be observed in the aqueous phase at the time when maximum yields were obtained. Longer reaction times drastically reduced the amount of HMF obtained, with considerable formation of solid material in the aqueous phase.

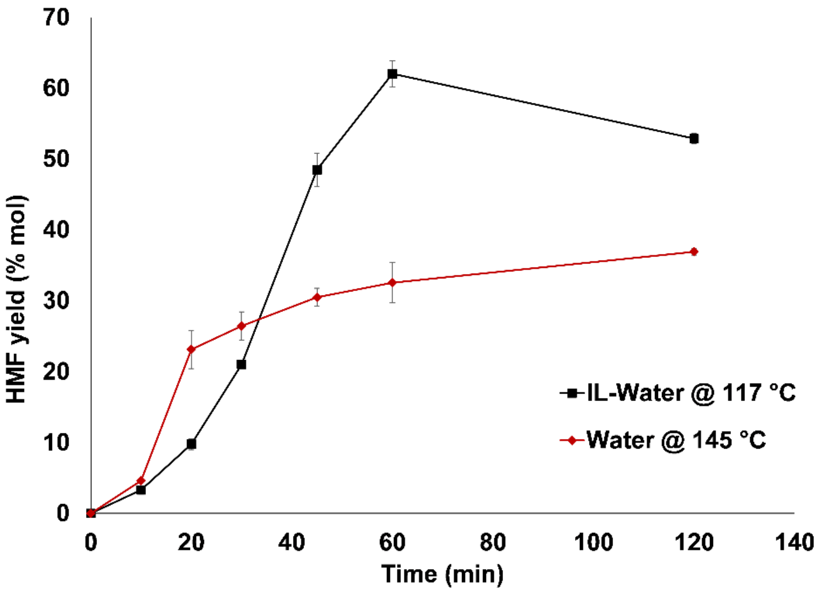


Figure 4.15 Sucrose dehydration: in IL-water at 117 °C; in water at 145 °C. Catalyst: PVA-40, 10 mg, sucrose: 50 mg

The results obtained from fructose are very competitive, when compared to those obtained from other heterogeneous catalytic systems, or even similar sulfonic resins, such as Nafion or Amberlyst (Table 4.7). Glucose dehydration remained challenging, possibly due to the lack of Lewis acid sites in the catalyst that could trigger isomerization. Nevertheless, the results obtained from sucrose were on par to those present in the literature.

Table 4.7 Sugar dehydration using different heterogeneous catalytic systems

Substrate	Solvent	Catalyst	Temperature (°C)	Time	HMF Yield (mol %)	Ref
Fructose	[BMIM][Cl]/ Water	PVA-30	117	40 min	99	This work
Fructose	[BMIM][Cl]/ Water	PVA-40	117	20 min	99	This work
Fructose	[BMIM][Cl]/ Water	PVA-40	125	4 min	94	This work
Fructose	Water	PVA-40	145	60 min	99	This work
Fructose	[BMIM][Cl]	SBA-15-SO_3H	120	60 min	81	[421]
Fructose	[BMIM][Cl]	SO_4^{-2}/ZrO_2	180	120 min	82	[422]
Fructose	[BMIM][Cl]	CCC[a]	160	15 min	81.4	[320]
Fructose	[BMIM][Cl]	$H_3PW_{12}O_{40}$	80	5 min	99	[423]
Fructose	DMSO	Cellulose/SO_4	100	45 min	93	[349]
Fructose	DMSO	HPC-P25-S[b]	130	30 min	98	[424]
Fructose	Water	Nafion	120	24 h	6	[346]
Fructose	DMSO	b-MPOS[c]	135[d]	20 min	86	[425]
Fructose	Water	Amberlyst-15	120	24 h	15	[346]
Fructose	Water-NaCl/ THF-NMP	P-TiO_2	175	105 min	98.6	[357]
Glucose	[BMIM][Cl]/ Water	PVA-40	117	120 min	25	This work
Glucose	Water	PVA-40	145	60 min	8	This work
Glucose	DMSO	Amberlyst-70	140	60 min	63.7	[305]

Glucose	THF/Water	TZ5050-$C_2H_4O_2$[e]	175	60 min	76	[39]
Sucrose	[BMIM][Cl]/ Water	PVA-40	117	60 min	64	This work
Sucrose	Water	PVA-40	145	120 min	37	This work
Sucrose	[BMIM][Cl]	Hβ zeolite	150	50 min	67.6	[259]

a) Cellulose-derived carbonaceous catalyst
b) Sulfonated hierarchically porous carbon
c) bifunctional mesoporous silica
d) Microwave heating
e) TiO_2-ZrO_2 mixed oxides

4.4.3 Catalyst recycling

In order to test the recyclability of the material, consecutive runs were used using the same catalyst. After each reaction, the catalyst was recovered by filtration using filter paper with a pore size of 2-5 μm. To ensure the removal of any traces of HMF and sugars, the recovered material was then washed using 50 ml of water. Due to their good solubility in high donor-number solvents [426], 50 ml of acetone was used to solubilize and remove any humins present. Then, the material was left to dry at 60 °C overnight. After five consecutive runs using the same catalyst, yields remained unchanged and above 90 mol % (Fig. 4.16).

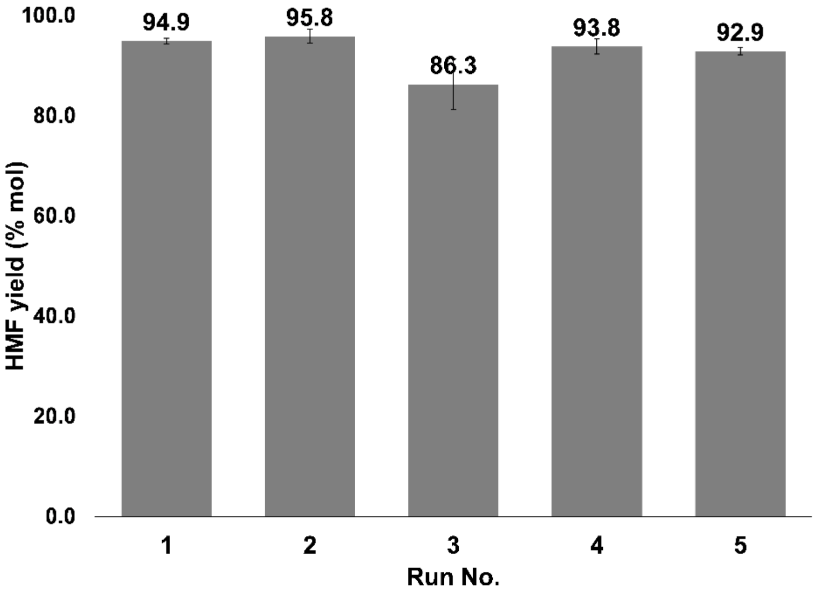


Figure 4.16 HMF yields from fructose dehydration in IL-water at 117 °C. Catalyst recycled and reused after each run.

4.5 Conclusions

A low cost SSA acid-grafted polyvinyl alcohol resin was synthesized, characterized and tested for the dehydration of carbohydrates. The characterization showed a correlation between the thermal stability of the material, functional sites, as well as its crystallinity and crosslinking degree. Several properties of the material can be tuned through the addition of SSA, such as its thermal stability, crystallinity, and functional sites. It was found that the crosslinking degree did not increase linearly with the concentration of SSA used, setting an upper limit to the amount of acid sites that can be present in the material.

The kinetic study showed that fructose dehydration and HMF formation followed a first order reaction kinetics, while HMF degradation fitted a second order reaction. This proved that HMF loss in this catalytic system was largely due to humin formation from either self-etherification or -condensation reaction between two HMF molecules. This reaction takes place slowly, when compared to HMF formation, and only prevents quantitative yields when PVA-10 is used, due to the lower amount of acid sites.

Catalytic test using different carbohydrates showed that the catalyst can efficiently and selectively synthesize HMF from fructose, as well as hydrolyze sucrose. Despite all catalyst having the same type of functional groups, PVA-40 performed the best, due to the more readily available SO_3H groups, when compared to the other materials. The sucrose results suggest that fructose was fully transformed, while glucose was only partially dehydrated. HMF formation from glucose appeared to be solvent dependent, due to possible mutarotation effects from part of the solvent on the sugar molecule, exposing certain -OH groups that can lead to either HMF or aldol condensation reactions.

PVA-40 showed great promise for HMF production in heterogeneous catalytic systems. PVA-40 can be produced very easily and in large quantities, which makes it very interesting for the upscaling of carbohydrate dehydration. Its solid nature makes it easily recoverable, and it was shown that the catalyst could be reused for several cycles. Furthermore, the material can be easily adjusted to fit the desired reaction conditions.

Connecting Statement 3

The previous chapters presented the development of acid catalysts for the dehydration of sugars, such as fructose and glucose. The results showed that fructose dehydration was very facile when sulfonic groups were present in the material. Dehydration of glucose and sucrose was also achieved with molar yields of up 25% and 64% respectively.

A key step for the industrialization of HMF and its derivate products lies in the use of cheap substrate. Generally, research has been done on utilizing cellulosic materials from agricultural and forestry waste. More recently some research has focused on valorization of food wastes and residues. These wastes are very attractive for HMF production due to the presence of simple sugars such as fructose, glucose, and sucrose, which can be more easily converted to HMF than lignocellulosic materials.

Chapter 5 focused on implementing the heterogeneous catalytic systems developed in previous chapters to convert fruit residues into the platform chemical HMF.

This chapter is based on a manuscript submitted for publication. The article was co-authored by Dr. Marie-Josée Dumont, Dr. Kayim Pineda Urbina, Dr. Roberto Muñiz Valencia, and Dr. Silvia G. Ceballos Magaña.

5 Sustainable HMF production from mango pulp using a sulfonated PVA resin.

5.1 Abstract

5-hydroxymethylfurfural (HMF) is a well-known platform chemical which can be transformed into several products, such as polymers and fuels. A strong limitation for its industrialization is its high production cost, dictated mostly by the high price of the substrate. Furthermore, the process should also remain environmentally sustainable for HMF to be competitive with oil-based products. In this work, an alternative for producing HMF from mango waste is presented. The method was developed in an environmentally and financially sustainable way using a highly tunable sulfonic solid catalyst, denoted as PVA-40. The valorization of mango was achieved using a solid, recyclable resin as catalyst, and water as solvent. The reaction was carried out in a microwave digestor using catalyst loads ranging from 8:1 to 16:1 substrate:catalyst weight ratios. The mangoes used were collected from the city's market and street waste at their highest ripening stage. Substrate concentration was set at 10 % wt. HMF yields of up to 31% mol were obtained at 140 °C, 20 min and 45 mg catalyst load. The results were comparable to those obtained using concentrated H_2SO_4, with the added benefit of an easily recyclable solid catalyst. The valorization of food waste otherwise unfit for human consumption provides an inexpensive carbohydrate source.

Keywords: HMF, heterogeneous catalysis, food waste valorization, polymeric catalyst, carbohydrate dehydration

5.2 Introduction

It has been estimated that approximately one third of all the food in the world ends up as wastes [427]. These wastes come from different steps in the supply chain, from pre-harvest to consumer. In developed countries, such as USA and Canada, approximately 40% of these wastes come from the consumer [427-429]. In Mexico, almost 70% of all food loses happen before reaching distribution, and only 15% is done by the consumer [428]. While the most accepted strategy dealing with food losses and wastes is its reduction, several strategies have been developed to deal with the fraction that is being generated today. In some developed countries, like the UK, USA and Germany, waste management hierarchies have been established [430-432]. Although there are variations in their strategies, the first three priorities are the same: reduction of wastes, consumption for humans or livestock, and industrial valorization. In Mexico, wastes are mostly consigned to landfills, with no further sorting or valorization [433, 434], with the most common wastes coming from fruits such as mango (waste of 54.4%) [428, 435].

Food waste valorization can potentially play an important role in the development of a circular economy, providing considerable sources of proteins, lipids, and carbohydrates [436-440].Recent reports showed that 12% of the global oil production is destined to the manufacturing of petrochemicals, and this number is expected to increase to 33% by 2030 [441]. A potential solution to cover this demand is through biobased platform chemicals obtained from waste. One of such building blocks is 5-hydroxymethylfurfural (HMF) [3, 4], a product of the dehydration of carbohydrates. This furanic compound has a broad spectrum of applications for the production of fuels, solvents, pharmaceuticals, and biobased polymers. The production of HMF has been shown to be acid-catalyzed, and can be readily obtained from ketohexoses, such as fructose, an important component in fruits [59, 377, 442].

In recent years, research has been focusing on developing solid catalysts and heterogeneous catalytic systems for the valorization of carbohydrates [32, 256, 257, 300, 396]. These type of reaction systems allow for the easy recovery and separation of the catalyst from the reaction medium. Additionally, they can be adjusted and customized to fit the needs of the reaction.

In previous studies, we have shown that up to 21% molar yield of HMF can be obtained from the H_2SO_4-catalyzed dehydration of mixed mango (pulp and skin) in water by microwave heating [443], as well as developed a low-cost, easily tunable solid catalyst using sulfosuccinic acid as the crosslinker, denominated as PVA-40. The catalyst was capable of dehydrating sucrose, glucose and fructose with high yields (64, 25, and 94% molar yields, respectively) [444].

Herein both studies are being expanded by incorporating a solid sulfonic catalyst into the reaction system to obtain HMF from mango pulp, in an environmentally and financially sustainable fashion.

5.3 Materials and methods

5.3.1 Materials

Sulfuric acid (96-98%) ACS reagent grade, sulfosuccinic acid (SSA) 70% in H_2O, methanol (HPLC grade), acetonitrile (HPLC grade) and water (HPLC grade) were purchased from Sigma

Aldrich (USA). Polyvinyl alcohol hydrolyzed, high molecular weight (PVA) 98-99%, was purchased from Alfa Aesar (USA). Mango pulp waste was obtained from native mango trees in the municipality of Coquimatlán, in Colima, Mexico.

5.3.2 Catalyst preparation and characterization.

The preparation and characterization of the PVA-40 catalyst has been thoroughly detailed in a previous publication [444]. In short, the material was prepared by mixing 1 g of PVA into 10 ml of H_2O under stirring at 90 °C for 6 h. Thereafter, 40% wt. SSA was added to the mixture and left to react at 70 °C for 24 h. The resulting solution was then cast in Teflon molds and left to dry for 24 h at 60 °C. Further drying was done under vacuum conditions at 110 °C for 2 hours. The final resin was then frozen with liquid nitrogen, ground, and sieved through a 0.5 mm mesh to obtain a particle size of <0.5 mm. Characterization consisted of FTIR, thermogravimetric analysis, X-ray diffraction, and elemental analysis. The presence of sulfonic sites was confirmed via FTIR and elemental analysis, and SO_3H and total acid groups were calculated to be 1.7 and 3.6 mmol/g respectively. Elemental analysis showed a total of 5 % wt of sulfur present in the catalyst.

5.3.3 Catalytic test

For the catalytic tests, mango fruits (*Manguifera indica* L.) were collected in the municipality of Coquimatlán, Colima in Mexico. The fruits were sorted out based on their ripening stage, and those in the highest stage of ripening were selected following the ripening scale of the National Mango Board [445]. These fruits were then peeled, and the seed removed to leave the pulp only.The resulting pulp was then ground in a mixture with deionized water to obtain a 10% wt solution of mango. 5 g of the mango solution was transferred into a Teflon mold with a given amount of catalyst, either PVA-40 or H_2SO_4. The samples were then brought to a Microwave Go Digestor (Anton Paar, Germany) and submitted to varying conditions of temperature, time, and catalyst amount. These conditions were determined using screening experiments and a Box Behnken experimental design where three factors were used. Combinations of experimental conditions were determined based on distance from a central point coded “0”, with these distances coded as -1, +1, $-\alpha$, and $+\alpha$. The value for α was calculated as $(2^k)^{1/4}$, where K is the number of factors. Table 5.1 shows the conditions used for H_2SO_4, and Table 5.2 shows the conditions for PVA-40.

The samples were then centrifuged using a Labogene 1580R multifunctional high velocity centrifuge (Labogene, Denmark). The supernatant was removed and filtered using syringe filters (Durapore 0.2 µm, Merk-Millipore). The HMF content of the samples was determined by liquid chromatography using an Alliance e2695 HPLC, with a diode array detector (2996 DAD, Waters) and a Hypersil ODS column (5 µm, 4.6x250mm, Varian). The column temperature was kept at 35 °C, with a mobile phase of 82:18 water:acetonitrile, and at a flowrate of 0.9 ml/min. The data were analyzed at 280 nm.

Table 5.1 Box Behnken design of catalytic test for mango using H2SO4

Coordinates	-1	1	0
Time (min)	5	25	15
Temperature (°C)	120	150	135
Catalyst (µl)	5	10	15

Table 5.2 Box Behnken design of catalytic test for mango using PVA-40

Coordinates	-1	1	0
Time (min)	5	20	12.5
Temperature (°C)	100	150	125
Catalyst (mg)	7	14	21

5.4 Results

5.4.1 Catalytic tests

The total sugar content of the mangoes was determined in a previous publication [443], and calculated to be 13.2% wt. The sugars consisted mostly of mono- and disaccharides, such as sucrose, glucose, and fructose, in percentage of 50, 12, and 33 respectively. Results obtained from previous experiments [443] showed that mango fruit wastes could be used as a potential source of carbohydrates for the production of HMF. Furthermore, previous experiments on sucrose dehydration using PVA-40 as a catalyst in a water medium proved that the material could successfully hydrolyze and dehydrate sucrose into HMF [444].

The first catalytic test results using PVA-40 were analyzed using response surface methodology to predict the optimal conditions for the reaction. It was observed that HMF yields were very low for all temperatures under 150 °C and low catalysts concentrations. Due to the large difference in HMF yields between the lower and upper conditions, the model fit was high, with an R^2=0.999. However, a predicted R^2=0 and a significant lack of fit showed that this high R^2 was due to overfitting, rather than an accurate prediction from the model. Further modification of the model and data transformation showed that the only significant factor was the temperature. An explanation for this is that the reaction only takes place at temperatures above 135 °C. This is in agreement with previous studies, where a minimum reaction temperature of 145 °C was required to obtain HMF in water using an oil bath [444]. Therefore, to improve the quality of the experimental data, a new set of conditions was selected, using larger catalyst's loads and a different range of temperature. However, due to the thermal stability of the catalyst, the highest reaction temperature was limited to 150 °C, narrowing the experimental range for this variable. This additional experimental design is shown in Table 5.3. Statistical data for both models is shown in Table 5.4.

Table 5.3 Box Behnken design of catalytic test for mango using PVA-40 at adjusted conditions

Coordinates	-1	1	0
Time (min)	10	20	15
Temperature (°C)	110	140	125
Catalyst (mg)	30	60	45

Table 5.4 Statistical data for Box-Behnken experimental designs

	Initial experimental conditions	Adjusted experimental conditions
Model	Quadratic	Quadratic
p-Value	0.019	0.0001
Lack of fit	0.0001	0.247
R^2	0.985	0.976
Adjusted R^2	0.929	0.960
Predicted R^2	0	0.914
Coefficient of variance	8.88	10.45

Under these conditions, the highest value obtained for HMF was 31.3% wt. at 140 °C, 20 min and 45 mg of catalyst, after applying the following logarithmic transformation of the data (1):

$$Data\ transformation = y' = ln\frac{(y - lower\ limit)}{(upper\ limit - y)} \quad (1)$$

Where *y*=HMF yield, *lower limit* =0.001 and *upper limit*= 99.99.

A modified quadratic model showed a good fit for the data, with an R^2=0.9764, non-significant lack of fit, and a model p-value<0.0001. Using this model, an attempt at determining optimal conditions was made, and different conditions that could result in yields >80 % were suggested. These possible scenarios required larger amounts of catalysts (>60 mg) and/or long reaction times (>25 min). However, when these conditions were used, the highest yield of HMF was only 8%, highlighting the sensitivity of the process, where differences of a few minutes, and milligrams of catalyst can have a large impact on HMF yields. While the model described quite accurately the experimental area, it did not predict adequately points outside of it. This could be due to possible thermal degradation of the catalyst at temperatures above 147 °C [444], side reactions taking place at longer times, such as humin formation, or due to concentrated microwave overheating on the catalyst particles. Fig. 5.1 shows the response surfaces of the model, in terms of desirability, where a desirability value of 1= 99.98% HMF yield, and the transformed logarithmic values.

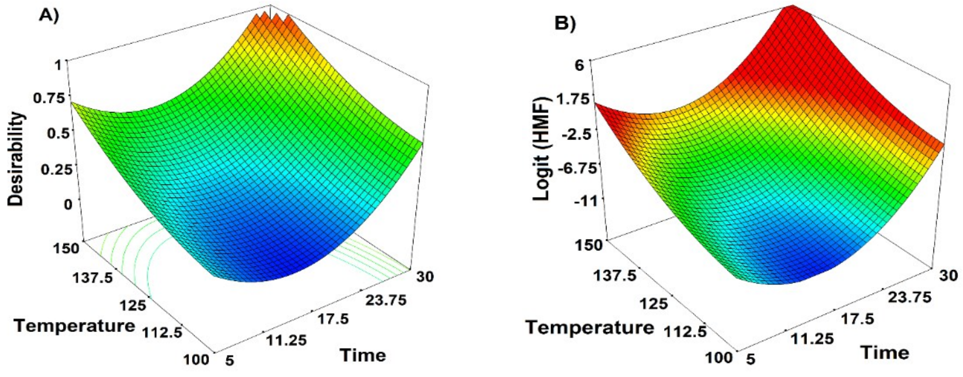


Figure 5.1 Response surface for mango sugar dehydration in water using PVA-40 and microwave heating. Catalyst load: 80 mg A) Desirability of response variable. B) Transformed variable

Nevertheless, when limiting the optimal range of the temperature and time variables to account for possible catalyst degradation and humin formation, yields of up to 31% were obtained. These results are presented in Table 5.5.

Table 5.5 Catalytic dehydration of mango pulp at different conditions

Time (min)	Temperature (°C)	Catalyst (mg)	HMF yield (% mol)
12.5	150	21	29.0
18	145	32	18.8
18	145	45	25.7
15	140	60	28.7
20	140	45	31.3

Fig. 5.2 illustrates the experimental points of both CCD models and optimization points tested for mango sugar dehydration using PVA-40. Fig. 5.2-A suggests that the reaction has a minimum temperature threshold of approximately 140 °C, while both 5.2-A and 5.2-B showed that a minimum catalyst load of 20 mg is necessary to obtain the highest possible yields. This shows that there is an optimal region of the experimental conditions where it is possible to obtain a maximum yield of approximately 32%.

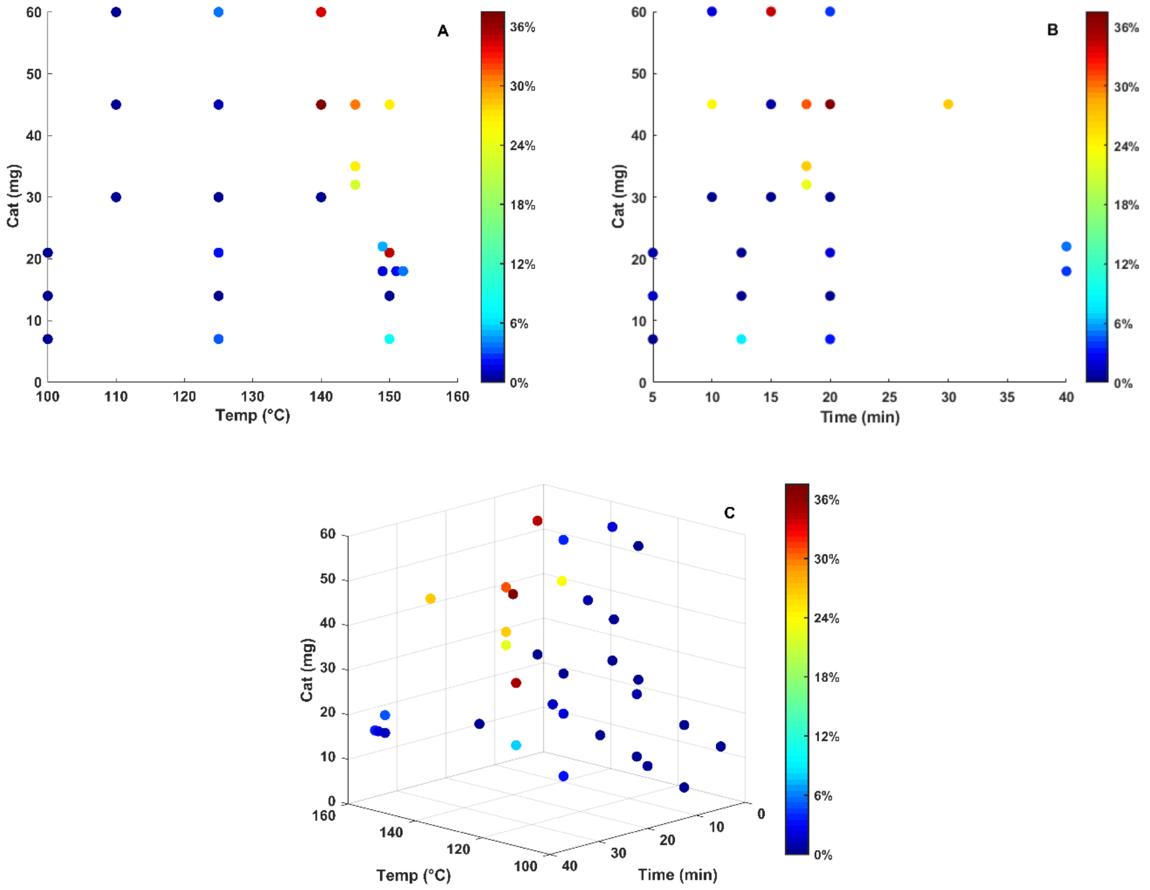


Figure. 5.2 Experimental data points showing spatial distribution of HMF yields (color bar) under different reaction conditions. A) Temperature vs catalyst load; B) Time vs catalyst load; C) spatial distribution of experimental points. Reaction medium water

For comparison purposes, a set of experiments was done using concentrated H_2SO_4 as catalyst. Similarly, the logarithmically modified data fitted the statistical quadratic model quite accurately, with a $p\text{-value} < 0.0001$ and an $R^2 = 0.9523$. The corresponding surface area plot is shown in Fig.

5.3. The model also showed that the maximum obtainable HMF yield under these conditions was 31% therefore, desirability was set to 1=31%.

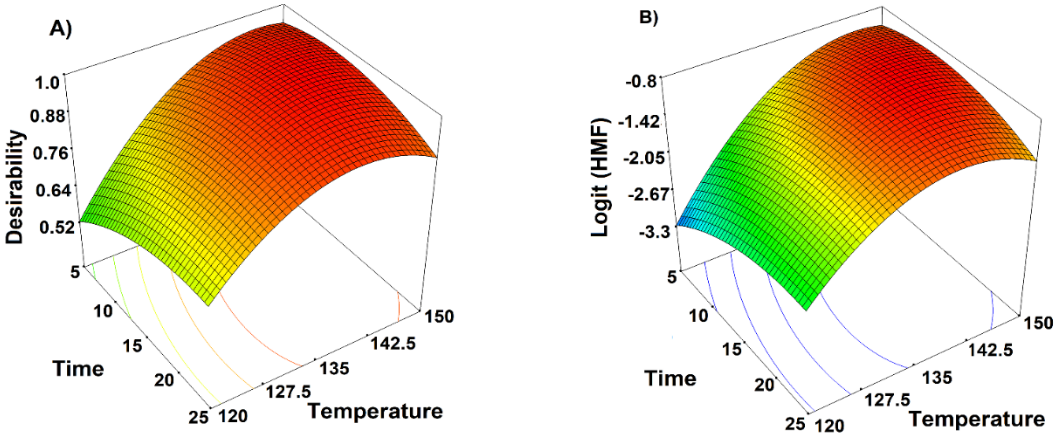


Figure. 5.3 Response surface for Mango dehydration using concentrated H_2SO_4. A) Desirability of response variable. B) Transformed variable. Catalyst load: 10 µl

As with PVA-40, a maximum value of 30.31 % yield was obtained at 135 °C after 15 min, using 10 µl of concentrated H_2SO_4, the equivalent of 0.18 mmol of SO_3H. As comparison, 60 mg of PVA-40 contain a total amount of acid sites of 0.216 mmol, 20% more than the concentrated H_2SO_4. Given the similar acid concentrations, the lower reaction times and temperatures achieved with H_2SO_4 could be attributed to the homogeneous nature of the catalytic system. The inclusion of stirring and a biphasic extraction solvent to the heterogeneous reaction could improve both reaction times and reduce the temperature.

5.5 Conclusion

Biorefineries (modeled after fossil fuel refineries) are essential for successful transition towards producing sustainable chemicals and materials from biomass. Ideally, biorefineries should be flexible and produce various fuels, chemicals, and materials from agricultural, forest and municipal residues using multiple conversion processes. Unfortunately, biorefineries do face obstacles such as the conversion of heterogeneous feedstocks, development of selective and reusable catalytic systems, and improved downstream processing. Therefore, here we presented a simple reaction system with a highly tunable solid catalyst and water as solvent was to produce HMF from mango wastes. The system could yield up to 31% HMF under microwave heating at 140 °C, 20 min and a catalyst load of 45 mg. The results were comparable to those obtained with H_2SO_4, with the added benefit of using an easily recoverable solid catalyst. Response surface model showed that 31% was the maximum HMF yield within the operational range of both catalytic systems. The use of fruit wastes, water as solvent and an easily produced solid catalyst, makes this catalytic system very promising to produce HMF. The system has a lot of potential to be implemented quickly and at a low financial cost, allowing producers, i.e., farmers, to add value to their waste and operations overall.

Connecting Statement 4

The previous work showed that using sulfosuccinic acid as crosslinker is a viable option for material functionalization. Crosslinking allowed to incorporate functional sites in a more controlled, sustainable manner. Thermal stability, chemical composition, and crystallinity were determined. A correlation between sulfonic sites, catalytic activity and HMF yields could be observed. The reaction was analyzed and optimized using response surface methodology and quantitative yields of HMF were obtained from fructose.

Metalorganic frameworks are structured solid materials with a metal center and linked via organic molecules. These organic molecules tend to be carboxylic acids such as trimesic, or terephthalic acid. The presence of a metal center and carboxylic groups can provide both Lewis and Bronsted acidities to these materials. Metals such as Cr, Zr and Ti, have been observed to isomerize glucose to fructose, with the latter easily converting to HMF.

Therefore, metalorganic frameworks were investigated in Chapter 6 as potential catalysts for sugar dehydration.

This chapter is based on a manuscript submitted to the Journal of Catalysis. The article was co-authored by Dr. Marie-Josée Dumont.

6 Sulfosuccinic acid-based metal-organic framework for the synthesis of HMF from carbohydrates.

6.1 Abstract

5-hydroxymethylfurfural (HMF) has been highlighted as a promising platform chemical and a keystone for the implementation of carbohydrate-based biorefineries. However, substrate cost remains a hurdle for the industrialization of HMF. Using different metal precursors, solid materials were developed, and their catalytic properties tested on the synthesis of HMF. The metals, Cr, Zr, and Ti were selected for their known catalytic properties in the isomerization of glucose. The solid catalysts were made using sulfosuccinic acid (SSA) as the crosslinking unit and source of Brønsted acidity. The bifunctional catalysts were characterized and tested in the dehydration of glucose. Cr-SSA was the most effective in producing HMF, reaching 60% yield after 3 h. Similar results were obtained from sucrose, reaching 60% molar yield. Kinetic models developed to provide a better understanding of the reactions' pathway, suggesting that glucose-to-fructose isomerization was the preferred pathway for HMF formation when using Cr-SSA.

Keywords: 5-hydroxymethyfurfural, heterogeneous catalysis, kinetic model, heterometallic frameworks.

6.2 Introduction

The increasing demand for oil-based fuels and chemicals has taken a heavy toll on the environment, due to the emission of greenhouse gases and unsustainable extraction practices. And yet, the demand for polymers, fuels, and fine chemicals continues to grow. It is estimate that 9% of all the oil extracted in the world is destined to the production of polymers and fine chemicals, with that number rising to 30% by 2030 [2, 441].

Several biobased alternatives have been identified to cover the demand for fuels and chemicals [3, 4]. Among those, 5-hydroxymethylfurfural (HMF) has the potential to be transformed into fuels, polymers, and fine chemicals [59, 68, 446]. HMF can be obtained from the dehydration of carbohydrates, such as fructose and glucose. Its industrialization has been halted due to the elevated cost in comparison to fossil oil-based alternatives [82, 342, 343, 345]. For this reason, research has focused on obtaining HMF from low-cost substrates, such as food, agricultural, or forestry by-products and wastes [213, 226, 364, 371, 443, 447]. However, the production of HMF from aldohexoses is not as facile as it is from ketohexoses, requiring more complex reaction systems and catalysts.

Recent studies have been oriented to developing heterogeneous catalytic systems capable of converting complex sources of biomass, such as wood or food, into HMF[368, 371, 396, 448, 449]. Metal catalysts, such as Ti, Zr, Ta, Cr, and Nb, have been commonly used [32, 353, 354, 356, 357, 363]. Watanabe et al. first observed how ZrO_2 and TiO_2 promoted glucose isomerization to fructose [15, 16], followed by studies of functionalized versions of this materials [40]. Functionalized versions of these oxides have also been developed for the dehydration of glucose [39, 40, 357, 450]. Functionalized Nb materials with both Brønsted and Lewis groups, have been developed and tested for glucose dehydration [300, 451-453].

Previous research has shown that SO_3H functional groups can efficiently catalyze HMF synthesis from fructose. Several sulfonated carbonaceous catalysts have been developed and obtained high yields from fructose, and moderate yields from glucose [25, 347, 349, 409]. Due to their incorporation of metal centers and organic acid linkers, metalorganic frameworks (MOFs) can be implemented as catalysts for carbohydrate dehydration. MIL-101(Cr) has been functionalized with SO_3H groups and tested on the synthesis of HMF from glucose [49, 454]. Hu et al. developed Zr and Hf MOFs for fructose dehydration [455]. Chen et al. sulfonated several MOFs, such as UiO-66, MIL-101, and MIL-53(Al), obtaining up to 90% HMF yield from fructose [50].

By using sulfosuccinic acid as a crosslinker, and Cr, Zr and Ti as metal centers, three different bifunctional solid catalysts were developed, characterized, and tested for the dehydration of carbohydrates. The use of sulfosuccinic acid as a crosslinker allowed for a more efficient and controlled way of incorporating SO_3H groups into the catalyst than the common sulfonation process, where H_2SO_4 is required, and considerable washing is needed to remove any remaining acid. The metal centers acted as an isomerizing agent allowing the transformation of aldohexoses to ketohexoses. Additionally, kinetic models were developed for all reaction systems, to improve the understanding of the catalysts' mechanisms, demonstrating that the catalysts followed different pathways to HMF.

6.3 Materials and Methods

6.3.1 Material

$Cr(NO_3)_3{\bullet}9H_2O$ (99%), $ZrO(NO_3)_2{\bullet}xH_2O$ (technical grade), titanium(IV) isopropoxide (97%), methyl isobutyl ketone (MIBK, 99%), acetonitrile (99.9% HPLC grade), 5-hydroxymethylfurfural (99%, food grade), butyl methyl imidazolium chloride ($[BMIM^+][Cl^-]$), D-glucose (99%), sucrose (ACS grade), ethanol (99%), and sulfosuccinic acid (SSA, 70% in H_2O), were obtained from Sigma-Aldrich (Canada), D-fructose (99%) was purchased from Alfa-Aesar (USA),

6.3.2 Catalyst preparation

Three SSA-based MOFs were prepared, and designated as Cr-SSA, Zr-SSA and Ti-SSA for chromium, zirconium, and titanium SSA-based MOF respectively. The sulfosuccinic metalorganic frameworks were synthesized by means of a solvothermal process, similar to that of Liu et al. [456] as follows. Either metal precursor was mixed with a given amount of SSA and NaOH in 65 ml of ethanol/water mixture, and poured into a stainless steel, Teflon-lined autoclave. The metal precursor, SSA, and NaOH were added in a molar ratio of 3:1.2:1 respectively. The autoclave was then heated at 130 °C for 3 days for the Cr-SSA and Ti-SSA, and 5 days for the Zr-SSA. The resulting solid material was then centrifuged and then left stirring for 24 h in an ethanol:water solution (3:1 vol ratio) for 24 h. Thereafter, the material was again centrifuged and washed until the pH of the wash water was neutral. The MOFs were then left to dry for 24 h under vacuum at 60 °C.

6.3.3 Catalysts characterization

FTIR analysis was used to determine functional groups of the organic part of the SSA-MOFs. The equipment used was a Nicolet IS10 (Thermofisher, MA, USA) with a diamond ATR crystal. The runs were done using a range of 550-4000 cm^{-1}, with a resolution of 4 cm^{-1} and 32 scans.

The atomic composition was analyzed via elemental analysis, using a Flash 2000 Organic Elemental Analyzer (Thermo Scientific, USA) following the ASTM D-5373-16. The results were used to corroborate the presence of the sulfosuccinic acid in the material.

A thermogravimetric analysis (TGA) was performed on all three materials to determine their thermal stability, functional site degradation. The experiments were run in a TGA Q50 (TA instruments, DE, USA). Samples were run under a N_2 stream at 60 ml/min, stabilized at 25 °C, and at 100 °C and further heated up at a rate of 20 °C/min, up to 800 °C.

Surface area, pore size, and pore distribution were determined via N_2 adsorption. The equipment used was a TriStar 3000 analyzed (Micromeritics, GA, USA). The samples were degassed for 24 h before analysis at 105 °C, then analyzed at -196 °C. Surface area was calculated through the Brunauer-Emmett-Teller (BET) theory, while pore size and pore distribution were determined via Barret-Joyner-Halenda (BJH) method.

The SSA-MOFs were observed under a scanning electron microscope, at different magnification levels to identify crystalline structures. The dry powder was placed onto the sample plate using a double-sided carbon sticker. A Hitachi TM 3000 was used to capture images in the range of 200-20 µm, while a Hitachi SU800 captured images in the range of 5-0.5 µm. For both devices, the analyses were performed at 30 and 15 kV acceleration voltage.

6.3.4 Kinetic study

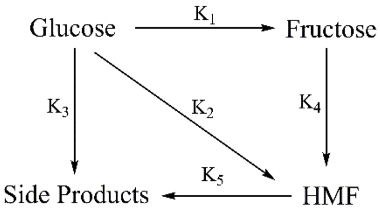
6.3.4.1 Catalytic tests

The catalytic properties of the SSA-MOFs were tested for the dehydration reaction of carbohydrates to produce HMF. Glucose and sucrose were chosen as model substrates since glucose is a main component of cellulose, and sucrose is a disaccharide present in most fruits. The reaction was carried out in a biphasic system using an organic solvent for continuous extraction of HMF. The bottom layer consisted of either a solvent mixture of ionic liquid [BMIM][Cl] and water in either 500 mg of a 4:1 w/w ratio (IL-water) solution, or 500 mg of water. 3 ml of MIBK were used for the extracting phase. 100 mg of substrate were added to the mixture, along with 20 mg of catalyst. The reaction was monitored over an interval of 3 h. Temperature was set at 140 °C using an oil bath, and continuous stirring was kept throughout the reaction at 300 rpm. Afterwards, the reaction was quenched in an ice bath at -4 °C, and both phases were filtered using a syringe filter (Whatman RC 13, 0.2 µm).

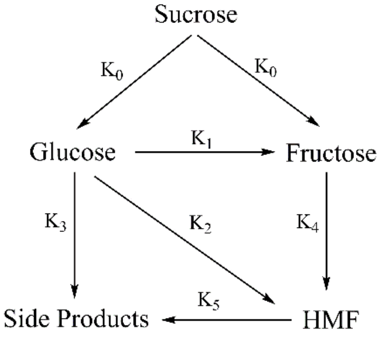
The quantification of HMF and carbohydrates was done by liquid chromatography, using an Agilent 1260 HPLC with a RI and VW detectors. A C18 Zorbax Eclipse Plus column (3.5 µm, 4.6x100 mm) and a mobile phase of 20:80 methanol:water were used for HMF quantification. The flow rate was kept at 0.6 ml/min, the column temperature was set at 30 °C, and the wavelength detection was set at 280 nm. A Hi-Plex Ca duo column (8 µm, 4x250 mm) and a mobile phase of pure HPLC grade water were used for carbohydrate quantification. The flow rate and column temperature were set at 0.8 ml/min and 80 °C respectively, and the RI cell temperature was set at 50 °C.

6.3.4.2 Kinetic model

The data obtained from the catalytic test were analyzed to obtain a kinetic model to better understand the reaction pathways. The mathematical model was developed using MatLab R2019a Simulink and fitted to the experimental data using the built-in parameter estimator. The model considered the transformation of glucose to fructose, HMF and side products (SP). The formation of SP from fructose was considered negligible, and HMF proceeded to form SP either via rehydration or condensation reactions (Scheme 6.1). The model for sucrose dehydration followed the same principles, with the addition of the hydrolyzation of sucrose to glucose and fructose (Scheme 6.2).



Scheme 6.1 Glucose dehydration reaction pathway



Scheme 6.2 Sucrose dehydration reaction pathway

6.4 Results and discussion

6.4.1 Material characterization

6.4.1.1 FTIR

The FTIR analysis confirmed the formation of the metal-organic framework by the presence of characteristic functional groups. The spectra of the SSA MOFs are shown in Fig. 6.1. All three materials display the characteristic -OH stretching in the range of 3550-300 cm^{-1}, attributed to adsorbed water and intermolecular bonding from -OH groups. The small bands at ≈2970 correspond to the symmetric and asymmetric vibrations of -CH groups present in the SSA. Two strong peaks can be observed at 1580 and 1440 cm^{-1} for all three materials. These two bands are attributed to the asymmetrical C-O and symmetrical O-C-O vibrational stretches of carboxylate groups, formed between the sulfosuccinic acid and the metal ions [457-459]. The bands at 796 and 634 cm^{-1} in the Zr-SSA spectra are associated to the Zr-O vibrations. Cr-SSA exhibits a broad band at 550 cm^{-1}, which can be assigned to Cr-O and O-Cr-O vibrations [460-462]. Similarly, the bands <800 cm^{-1}, i.e., the peaks at 790 cm^{-1}, and 686 cm^{-1}, are related to Ti-O and O-Ti-O vibrations [463-465]. The absence of a peak in the range of 1760-1660 cm^{-1} suggests that no ester bonds formed between SSA molecules and the solvent ethanol, nor that there are carboxylic groups due to free SSA present in the material.

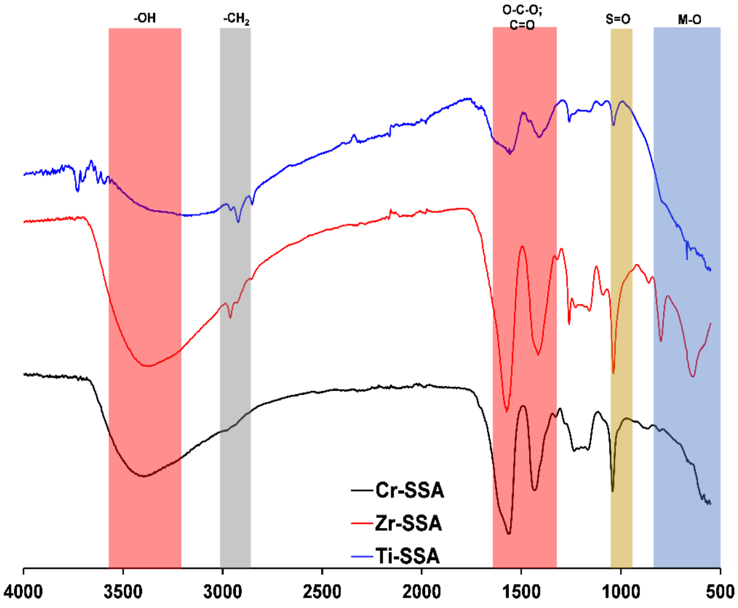


Figure 6.1 FTIR spectra of Cr-SSA, Zr-SSA and Ti-SSA. M-O= metal oxide

6.4.1.2 Thermogravimetric analysis

The thermal stability of the materials was tested by TGA (Fig. 6.2). All three materials showed similar degradation curves in the range of 25-140 °C, with an approximate weight loss of 7%, which can be attributed to adsorbed water. At 150 °C further degradation could be observed, which is related to the loss of SO_3H groups. This weight loss continues until approximately 300 °C after which point, further degradation takes place, causing the curve to drop more steeply for Cr-SSA and Zr-SSA. Of the three catalysts, Cr-SSA shows the largest weight loss in the temperature range of 300-500 °C. This loss could be attributed to the breaking of the bonds between the crosslinker and the Cr[OH] groups. A possible reason for such large difference between Cr-SSA and the other catalysts could be the larger proportion of SSA present in its structure. The opposite could be observed for Ti-SSA, with no increased weight loss at this stage. Between 500 and 800 °C, a slow and steady degradation can be observed. This could be related to the aromatization and carbonization of what is left of the crosslinking units, which eventually gasify at 800 °C. A large portion of Ti-SSA remains after reaching 800 °C, suggesting a larger proportion of Ti present in the sample, which would indicate a lower crosslinking degree, compared to the other two materials. A possible explanation for the lack of crosslinking is the very reactive nature of the Ti(IV) ion, which quickly precipitates in contact with water and forms TiO_2, a much more stable form of Ti, and thus less prone to form ligands with the linker [466].

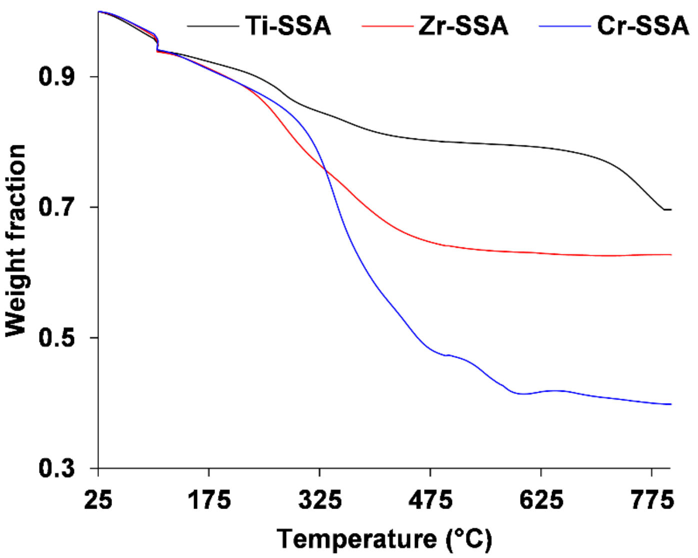


Figure 6.2 TGA analysis of SSA-based catalysts

6.4.1.3 Porosity and surface area analysis

Surface area was determined by the BET method. The obtained isotherms are shown in Fig. 6.3. Cr-SSA exhibited a low-hysteresis type II isotherm, characteristic of macro/non-porous materials, which agrees with its low surface area, and large pore width. However, the narrow H_1 type hysteresis loop at high pressures suggests some degree of mesoporosity, confirmed by BJH analysis. Zr-SSA's type II – type IV composite isotherm suggests a mesoporous solid with some macroporosity, and its $H_{2(b)}$ hysteresis, indicates a disordered porosity and possible network effects, reflected in the larger surface and pore volume. The BJH analysis confirmed the mesoporous nature of the material. Similarly, Ti-SSA's isotherm is also a composite of type II – type IV with a $H_{2(a)}$ hysteresis loop. This type of curve suggests a narrower range of pore necks. Additionally, Ti-SSA shows a larger proportion of micropores than Cr-SSA or Zr-SSA. The results of the BET and BJH analysis are shown in table 6.1.

Table 6.1 Surface area of SSA-based solid catalysts

	BET surface area (m^2/g)	BJH pore volume (cm^3/g)	Average pore width (nm)
Cr-SSA	30.56	0.07337	13.2
Zr-SSA	361.24	0.407	5.08
Ti-SSA	212.19	0.133	3.04

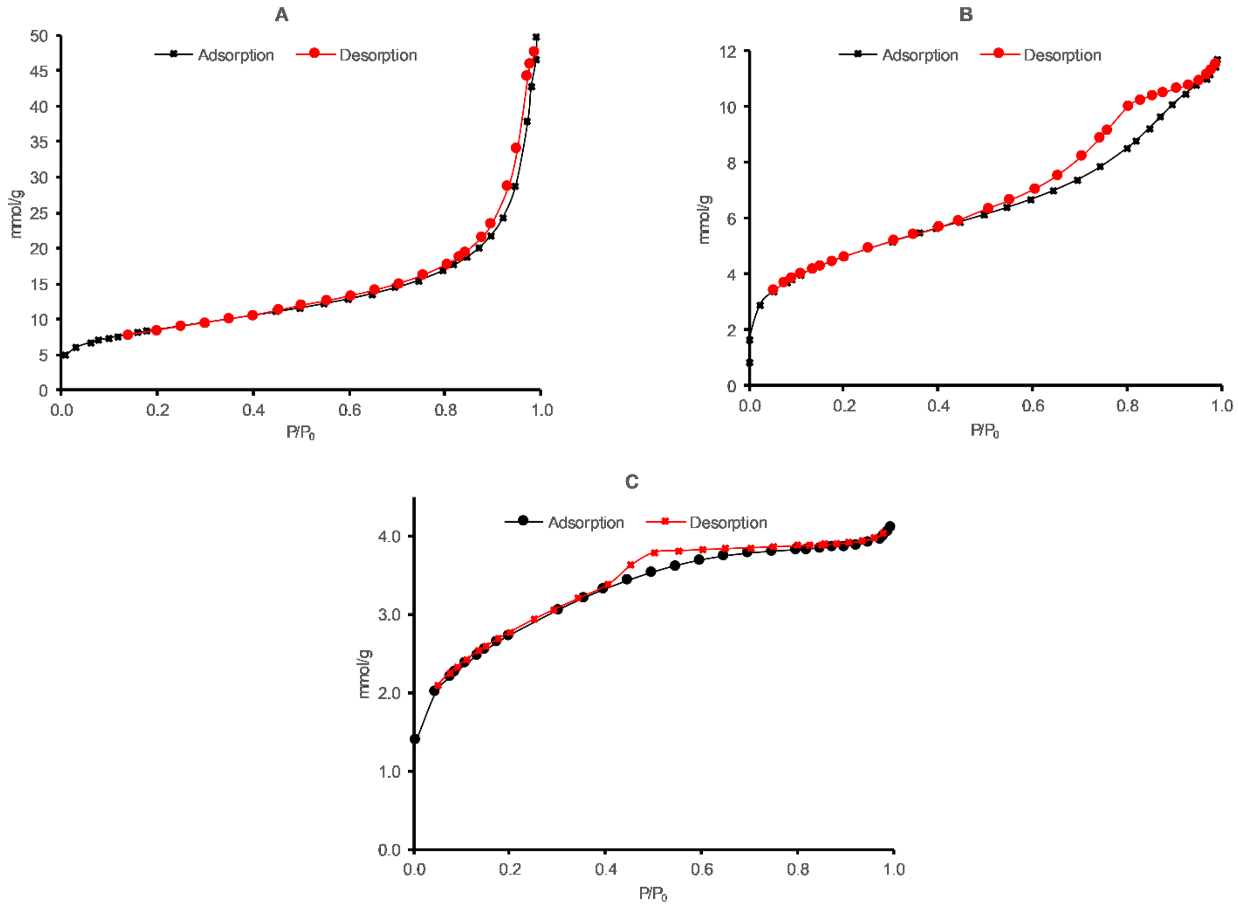


Figure 6.3 N2 adsorption-desorption isotherms for SSA-based catalysts. A: Cr-SSA, B: Zr-SSA, C: Ti-SSA

6.4.1.4 Elemental analysis

Elemental analyses of all three materials were performed. The results showed that the crosslinker was indeed present in the catalyst (Tables 6.2 and 6.3). Given that the sulfonic groups in SSA are the only source of sulfur, the presence of the element signalizes the functional group as well. Of the three materials, Cr-SSA contained the most SSA, with 5.6 wt%. On the other hand, Ti-SSA contained the least, and therefore was less crosslinked. These observations are in accordance with those observed in the TGA analysis. Indeed, Ti-SSA has much lower proportions of all organic elements. The mass not attributed to the C, H, O, or S is assumed to be the remaining metals and sodium molecules. The large proportion of missing mass from Ti-SSA suggests that crosslinking was not as effective as with the other metal centers, due to the formation of the more stable TiO_2, which may remain present in the matrix.

Table 6.2 C, H, O, S in % weight

	C	H	O	S	Metal
Cr-SSA	11.76 ±0.1	3.17±0.15	34.4 ±0.5	5.6 ±0.23	45±0.98
ZrSSA	9.32 ±0.1	2.69 ±0.15	18.9 ±1.1	2.3 ±0.73	66.8±2.08
TiSSA	4.3 ±0.11	1.27 ±0.02	8.3 ±0.1	1.6 ±0.01	84.5±0.24

Table 6.3 Atomic ratio based on S

	C	H	O	S
Cr-SSA	5.6	18.0	12.2	1.0
ZrSSA	10.8	37.4	16.4	1.0
TiSSA	7.0	24.8	10.1	1.0

6.4.1.5 SEM

SEM imaging was used to observe the morphology of the materials. Cr-SSA appeared to consist of microspheres at 20 µm. However, a closer inspection at 0.5 µm revealed the more amorphous nature of the material (Fig. 6.4), where large clumps of smaller particles can be observed. The images of Zr-SSA showed a more organized structure, with smaller crystals agglomerating into larger formations. These crystals' length ranged between 10 and 5 µm (Fig. 6.5). Ti-SSA showed two different structures: sphere-like particles, which can be attributed to titanium oxide, and flat, amorphous particles (Fig. 6.6). The presence of these two types of agglomerates suggests that the crosslinking was not as thorough as it was in the other two materials. This is also in accordance with the results observed in the TGA analysis, where a large mass fraction remained after 900 °C.

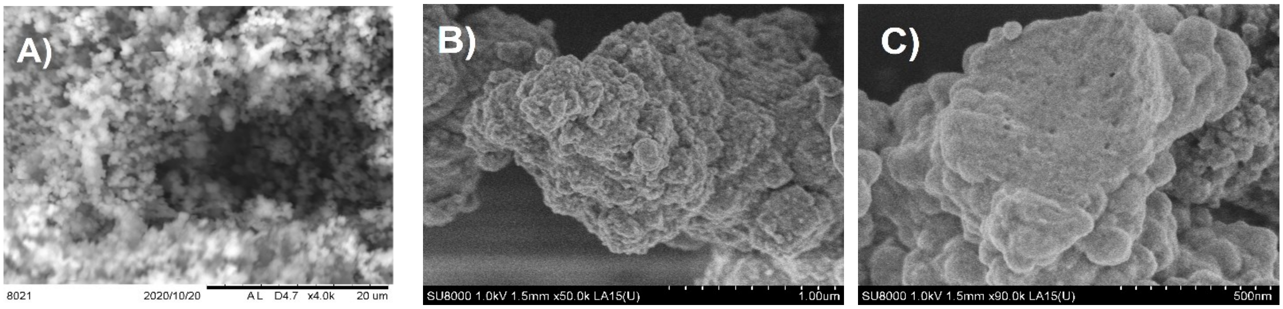


Figure 6.4 SEM images of Cr-SSA. A) 20 µm B) 1 µm C) 0.5 µm

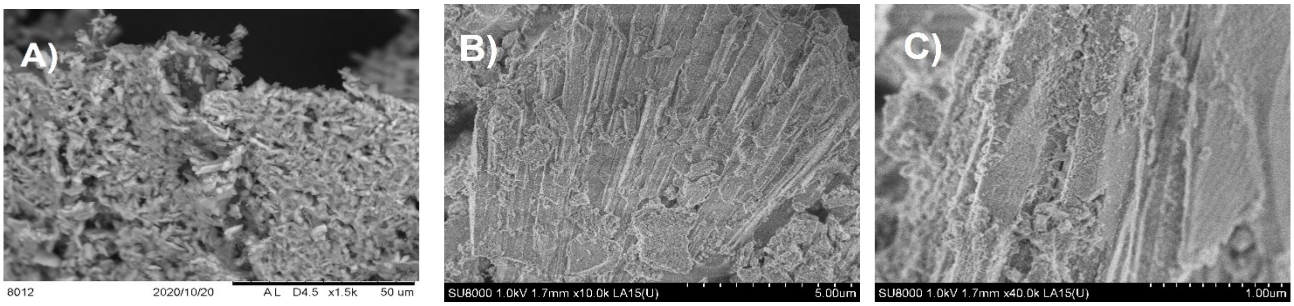


Figure 6.5 SEM images of Zr-SSA. A) 50 µm B) 5 µm C) 1 µm

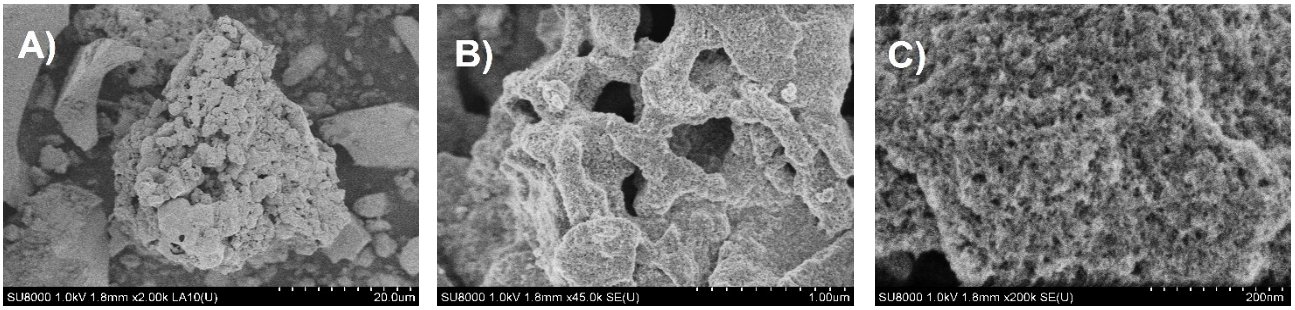


Figure 6.6 SEM images of Ti-SSA. A) 20 µm B) 1 µm C) 0.2 µm

6.4.2 Catalytic studies

6.4.2.1 Glucose dehydration

All SSA-based solid materials were tested as catalysts for the dehydration reaction of carbohydrates. Glucose was chosen as model substrate for the reaction, given its abundance and low cost when obtained from cellulosic waste. The reactions were carried out for 3 h and monitored every 30 minutes. All three catalysts obtained a 100% carbohydrate conversion rate during this time but exhibited very different selectivity towards HMF. Furthermore, while Cr-SSA led to glucose-to-fructose isomerization, Zr-SSA and Ti-SSA, did not so in a considerable way. Nevertheless, fructose was still detected in small amounts when using both Zr-SSA and Ti-SSA. After 3 h, an HMF yield of 60.5 mol % was obtained using Cr-SSA, while using Zr-SSA, or Ti-SSA as catalysts resulted in 39.5 % and 34.3 mol % respectively. With both, Zr-SSA and Ti-SSA, the amount of fructose detected was negligible. It is well established in literature that both, ZrO_2 and TiO_2 lead to isomerization of glucose to fructose [16, 39, 40]. However, the values obtained here suggest that the Cr-SSA was more effective in this process. The reaction progression can be observed in Fig. 6.7.

Further runs were carried out using only water as solvent and Cr-SSA as catalyst, given the higher yields achieved by this material. The reaction conditions were similar to those used with the IL-water system, with additional water substituting the IL proportion. Under these conditions, HMF was produced in small amounts, reaching a maximum of 19 % molar yield. SP were the main products generated from this system. While isomerization of glucose-to-fructose can be observed already after 30 min, SP begins to form very early in the reaction. Also of note is the fact that, while in the IL-water system, fructose was transformed almost immediately into HMF, in water, fructose conversion happened much more slowly, being detected after 4 h reaction. The synergistic effect that ILs can have with certain catalysts has been previously documented [18, 467-469], changing the mutarotation of glucose from its α-form to a mixture of α and β forms, and lowering the reaction energy. These results suggest that a similar synergy takes place between [BMIM][Cl] and Cr-SSA. Fig. 6.8 shows the progress of the reaction in water.

6.4.2.2 Sucrose

Due to its abundance in fruit, and therefore in food and agricultural wastes, sucrose was tested as a substrate for HMF synthesis. The results showed the complete hydrolysis of sucrose within 1 h.

Glucose accumulated in larger quantities than fructose, due to the rapid dehydration into HMF of the latter. Fructose was almost depleted after 1.5 h. HMF yields continued to increase until complete conversion of both glucose and fructose. The final maximum HMF yield obtained was 60 mol % ± 2.17. From these results, it was found that hydrolysis of sucrose is quite facile in this system, as well as fructose dehydration. Glucose-to-fructose isomerization appeared to be considerably slower. Fig. 6.9 shows the course of the sucrose to HMF reaction. The limited yields from sucrose could be explained by the possible formation of humins from glucose-HMF and glucose-fructose interactions.

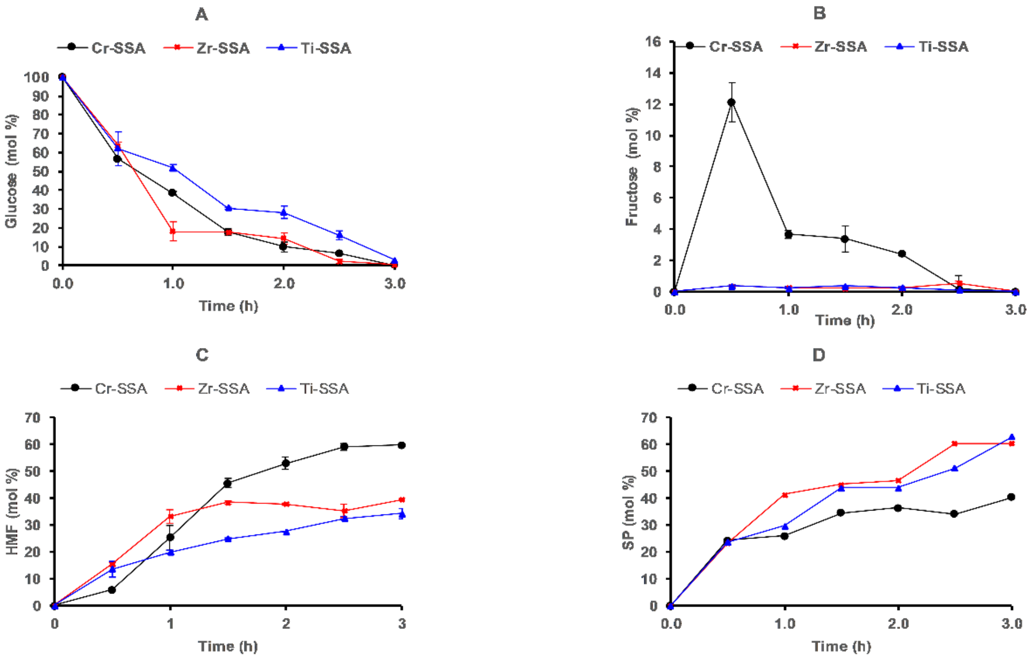


Figure 6.7 Glucose dehydration using SSA-Based solid catalysts. A) Glucose conversion. B) Fructose formation. C) HMF formation. D) SP formation. Reaction conditions: 140 °C, 500 mg IL-water, 20 mg of catalyst.

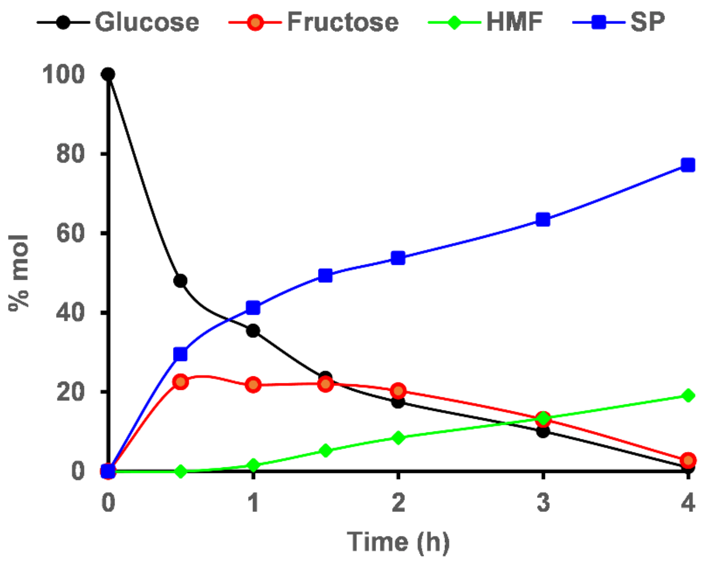


Figure 6.8 Glucose dehydration in water using Cr-SSA as catalyst. Reaction conditions: 140 °C, 500 mg water, 20 mg of catalyst.

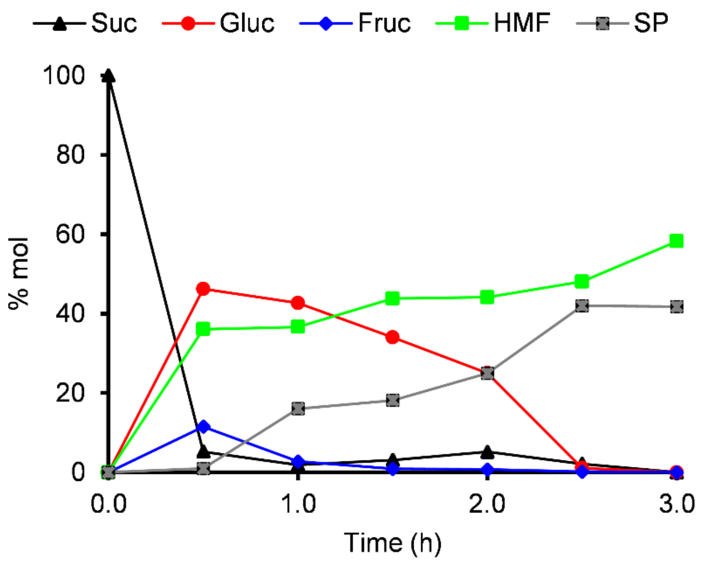


Figure 6.9 Sucrose transformation using Cr-SSA as catalyst. Reaction conditions: 140 °C, 500 mg IL-water, 20 mg of catalyst.

6.4.2.3 Kinetic model

Using the reaction pathways shown in Scheme 6.1, the following reaction systems were considered:

$$[G] \overset{k_1}{\rightarrow} [F] \quad (1)$$

$$[G] \overset{k_2}{\rightarrow} [HMF] \quad (2)$$

$$[G] \overset{k_3}{\rightarrow} [SP] \quad (3)$$

$$[F] \overset{k_4}{\rightarrow} [HMF] \quad (4)$$

$$[HMF] \overset{k_5}{\rightarrow} [SP] \quad (5)$$

Where [G], [F], [HMF], and [SP] are the concentrations of glucose, fructose, HMF and SP respectively, and $k_{1\text{-}5}$ are the rate constants for each of the reactions.

Using eq (1) to (5), the derivate rate laws for each compound can be written as:

$$-\frac{d[G]}{dt} = k_1[G] + k_2[G] + k_3[G] = k_g[G] \quad (6)$$

$$\frac{d[F]}{dt} = k_1[G] - k_4[F] \quad (7)$$

$$\frac{d[HMF]}{dt} = k_2[G] + k_4[F] - k_5[HMF] \quad (8)$$

$$\frac{d[SP]}{dt} = k_3[G] + k_5[HMF]^2 \quad (9)$$

The experimental data for all three catalysts was fitted using this model, and the rate constants were calculated. A comparison between the model and the experimental data can be observed in Fig. 6.10-6.12. The calculated rate constants are shown in Table 6.4.

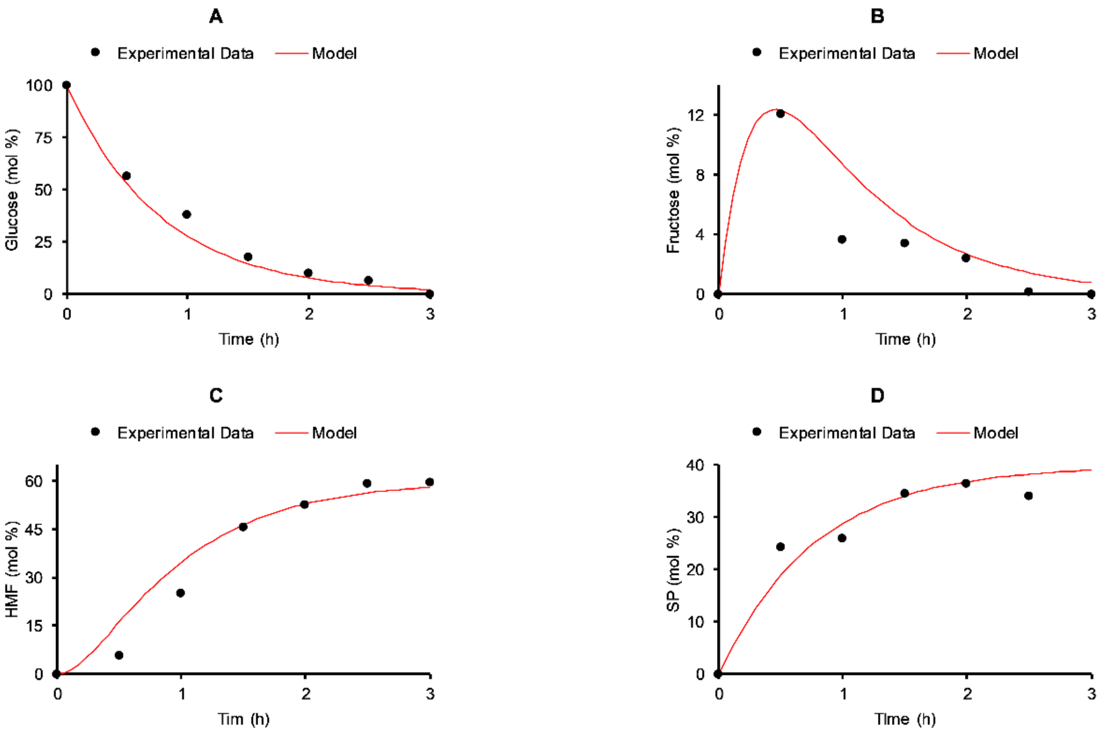


Figure 6.10 Model fitting for Cr-SSA catalyst. A) Glucose conversion. B) Fructose formation. C) HMF formation. D) SP formation

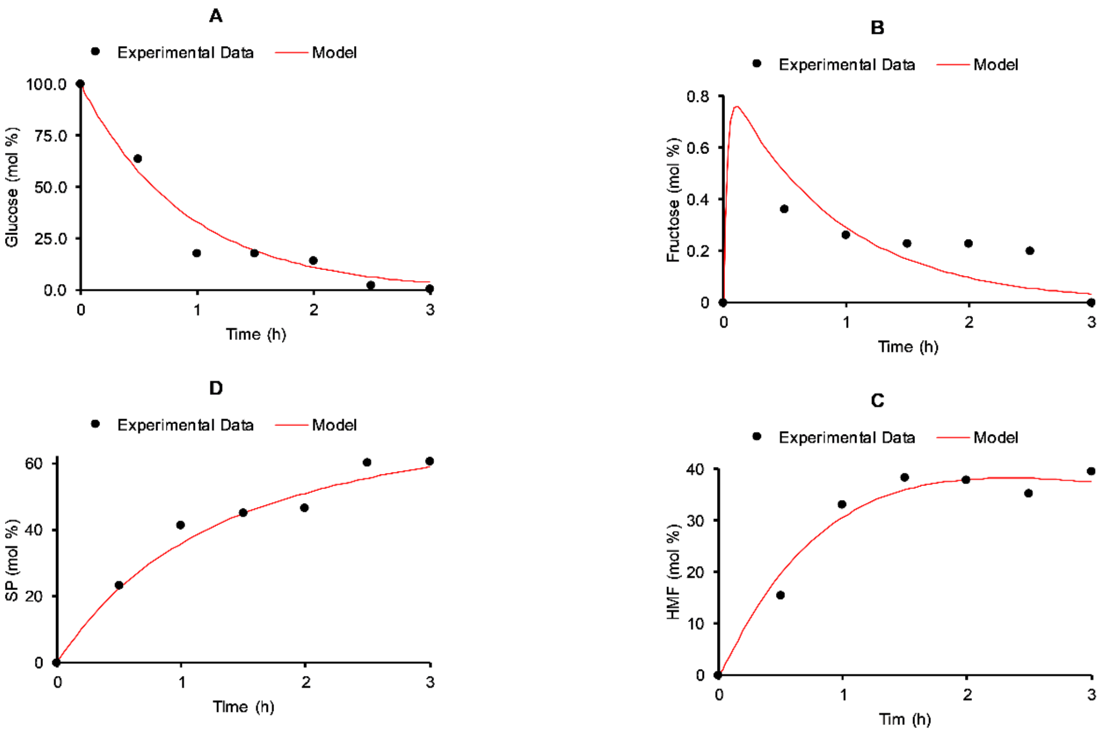


Figure 6.11 Model fitting for Zr-SSA catalyst. A) Glucose conversion. B) Fructose formation. C) HMF formation. D) SP formation

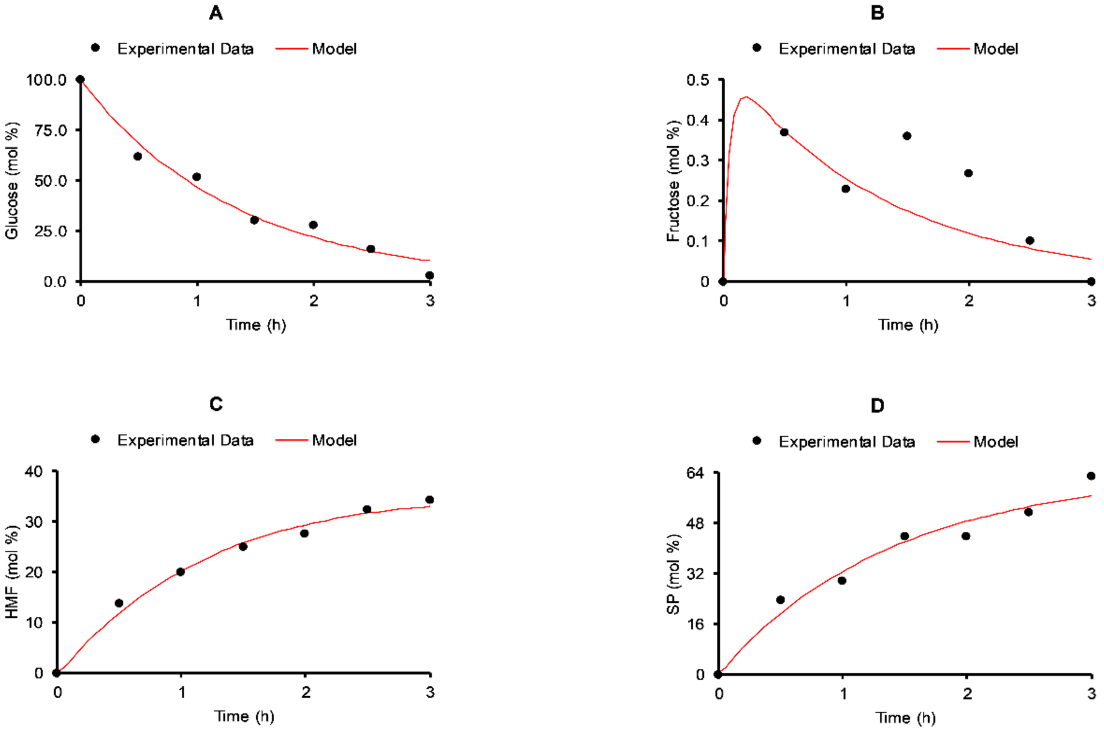


Figure 6.12 Model fitting for Ti-SSA catalyst. A) Glucose conversion. B) Fructose formation. C) HMF formation. D) SP formation

A first calculation, assuming the rehydration of HMF, did not accurately describe the generation of side products observed in the reaction. Therefore, a second order condensation reaction was then used, which improved the accuracy of the model. Condensation reactions are more likely in this reaction system, given the limited amount of water available for rehydration [418-420]. The resulting model showed a good fit for most signals, with R^2 values above 0.95, (Table 6.5) except for fructose, whose low fitting values can be attributed to the very low concentration values and relatively large standard deviations, due to the detection range of the equipment.

The calculated kinetic rate constants suggest different reaction pathways between Cr-SSA, and Ti-SSA and Zr-SSA. Both Zr-SSA and Ti-SSA showed low K_1 values, causing them to have a slower isomerization rate than Cr-SSA. Indeed, an approximate of 26 and 12 mol % of glucose was isomerized with Zr-SSA and Ti-SSA respectively, while Cr-SSA isomerized 60% of all the glucose. However, K_2, the glucose-to-HMF formation pathway, is almost nonexistent for the Cr-

SSA reaction, while for Zr-SSA and Ti-SSA, this was responsible for a third of the HMF produced in the reaction. Fructose dehydration was the main process of HMF formation for Cr-SSA, yet Zr-SSA and Ti-SSA exhibit K_4 values of an order of magnitude higher than for the Cr counterpart, practically transforming any fructose formed instantly, despite the fact of containing a lower amount of SO_3H groups. In all three cases, SP formation resulted mainly from glucose degradation, with a small proportion of HMF condensation.

A kinetic model, similar to the glucose reaction, was developed for the reaction with sucrose. The model follows the reaction pathway shown in Scheme 6.2. The equation system remains the same as before, with the addition of a hydrolyzation step, and a sugar formation step for eq. 6 and 7:

$$[S] \overset{k_0}{\rightarrow} [F] + [G] \qquad (10)$$

$$-\frac{d[S]}{dt} = k_0[S] \qquad (11)$$

$$\frac{d[G]}{dt} = \frac{1}{2}k_0[S] - (k_1[G] + k_2[G] + k_3[G]) \qquad (12)$$

$$\frac{d[F]}{dt} = \frac{1}{2}k_0[S] + k_1[G] - k_4[F] \qquad (13)$$

The model showed a good fit for sucrose, fructose, and SP, but both glucose and HMF R^2 values did not describe completely the observed reaction. Other interactions, such as condensation reactions between glucose and HMF were also simulated but resulted in lower R^2 values than the initial model. Nevertheless, both simulated signals followed the trend of the experimental data, albeit with some variations (Fig. 6.13). These variations could be due to factors not considered in the model, such as solvent-catalyst or solvent-product interactions.

It can be surmised from both the experimental data and the calculated rate constants, that hydrolyzation is a very quick process, happening at one order of magnitude faster than all the other reactions, while isomerization to fructose happens more slowly than when glucose is used as the starting substrate. While the reaction rate of HMF formation from glucose is considerably faster, fructose-to-HMF remains the main pathway for HMF formation.

Table 6.4 Calculated kinetic constant

	K_0 (min^{-1})	K_1 (min^{-1})	K_2 (min^{-1})	K_3 (min^{-1})	K_4 (min^{-1})	K_5 (min^{-1})
Ti-SSA	-	1.7x10^{-3}	3.2x10^{-3}	7.7x10^{-3}	3.2x10^{-1}	1.5x10^{-5}
Zr-SSA	-	5.0x10^{-3}	3.8x10^{-3}	9.6x10^{-3}	5.9x10^{-1}	4.6x10^{-5}
Cr-SSA	-	1.3x10^{-2}	3.7x10^{-16}	8.5x10^{-3}	5.7x10^{-2}	8.6x10^{-9}
Cr-SSA[1]		7.5x10-3	7.5x10-12	1.4x10-2	6.1x10-3	2.2x10-4
Cr-SSA[2]	7.4x10^{-2}	1.8x10^{-3}	4.4x10^{-5}	6.7x10^{-3}	8.3x10^{-2}	1.2x10^{-3}

[1] Rate values for reaction in water

[2] Rate values for sucrose reaction

Table 6.5 R^2 values for the fitted data

	R^2 Sucrose	R^2 Glucose	R^2 Fructose	R^2 HMF	R^2 SP
Ti-SSA	-	0.970	0.581	0.986	0.957
Zr-SSA	-	0.968	0.414	0.971	0.975
Cr-SSA	-	0.980	0.735	0.950	0.940
Cr-SSA[1]	-	0.9528	0.7821	0.8645	0.9502
Cr-SSA[2]	0.990	0.782	0.992	0.789	0.928

[1] Rate values for reaction in water

[2] Rate valu n es for sucrose reaction

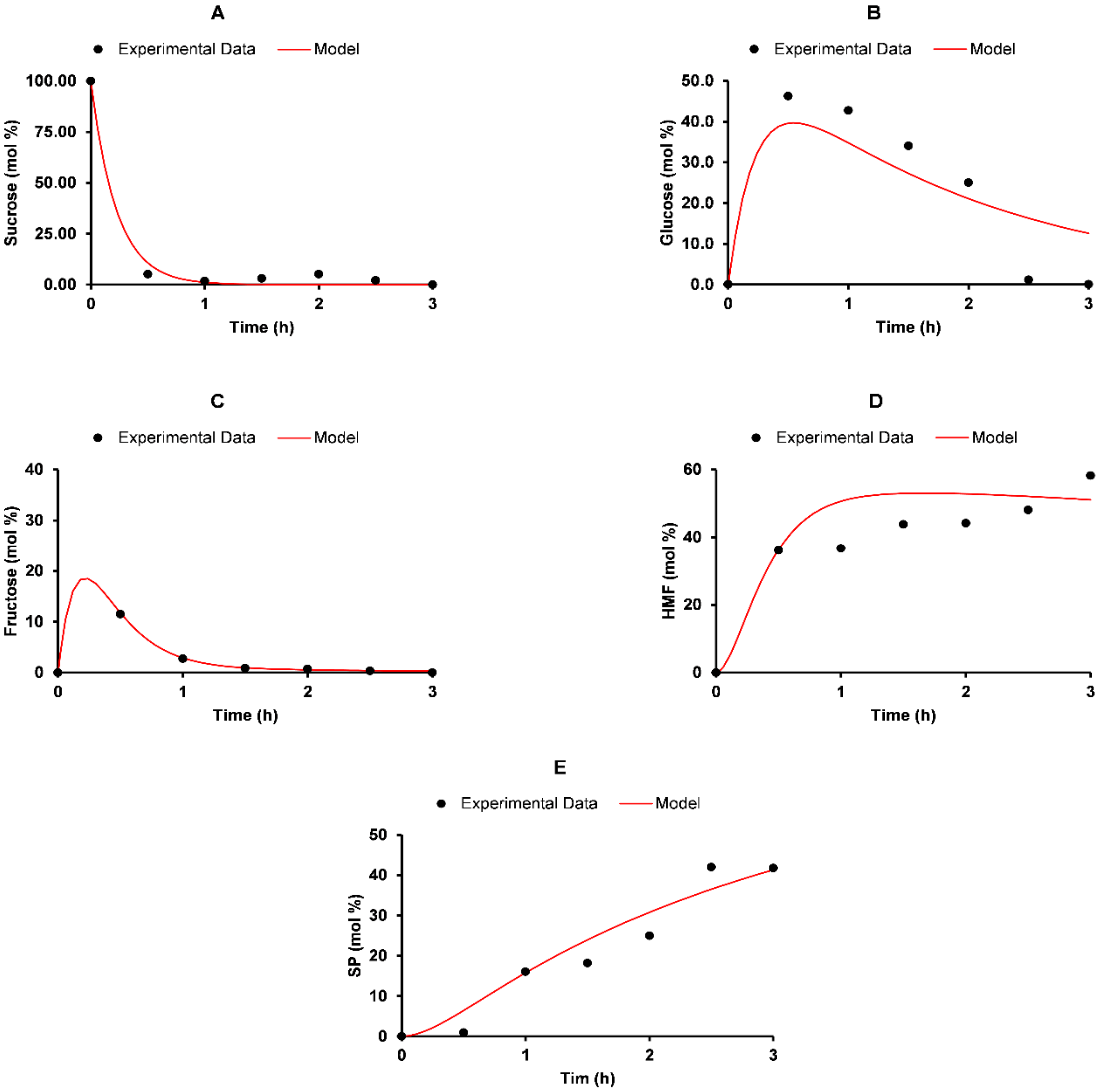


Figure 6.13 Model fitting for Sucrose dehydration using Cr-SSA catalyst. A) Sucrose hydrolysis. B) Glucose formation. C) Fructose formation. D) HMF formation. E) SP formation

6.5 Conclusions

Three novel metalorganic frameworks, Ti-SSA, Zr-SSA, Cr-SSA, were developed using SSA as the crosslinking unit. The materials were characterized and the presence of their respective metal, as well as the SO_3H acidic groups was confirmed. Both Ti-SSA and Zr exhibit large surface areas, with Ti showing microporosity, and Zr meso- and macroporosity. On the other hand, Cr-SSA exhibited the smallest surface area of the three materials, with almost no porosity. All three materials showed similar degradation profiles up to 300 °C, after which point the different amounts of crosslinking present in the samples caused a divergence in their degradation's patterns. SEM imaging showed that both Cr-SSA and Ti-SSA were amorphous materials, and Ti displayed two different phases, suggesting incomplete crosslinking. Zr on the other hand showed a more crystalline structure, with crystals agglomerating into larger particles.

Of the three catalysts, Cr-SSA was the most efficient in converting glucose to HMF, reaching up to 60 % molar yield. All three catalysts were capable of isomerizing glucose to fructose and produce HMF. Cr-SSA was also tested for the hydrolysis and dehydration of sucrose to HMF, also reaching 60% molar yield.

A kinetic model was developed to further understand the mechanism of the catalysts. The models suggested that Cr-SSA was more efficient in isomerizing glucose to fructose than Ti-SSA and Zr-SSA, showing that the main pathway for HMF formation using Cr-SSA was glucose-to-fructose isomerization. On the other hand, the glucose-to-HMF direct pathway was non-existent for Cr-SSA, while it accounted for a third of the HMF formed from the other two catalysts.

These results show that SSA-based bifunctional catalysts are effective to produce HMF from carbohydrates, and provide a theoretical insight into their reaction mechanisms, which can be used to modify, improve and adapt these materials to meet the reaction's needs.

Cr-SSA is a promising catalyst for the dehydration of aldohexoses due to its good HMF yields from glucose and fructose, exhibiting hydrolysing and dehydrating properties. This makes it a potential catalyst for the dehydration of more complex biomass, such as cellulosic materials. Additionally, further functionalization of these type of materials could open the door to creating multifunctional catalysts with different metal centers such as nickel, or platinum for HMF hydrogenation.

7 General conclusions and recommendations

7.1 General conclusions and summary

The focus of this work was to develop and characterize solid catalysts and their corresponding heterogeneous catalytic systems that could efficiently convert sugars into HMF. From the literature, it was observed that acid functional sites, such as sulfonic groups, were good candidates as catalysts for carbohydrate dehydration. To test this, a softwood pulp carbonaceous catalyst was developed using a two-step process of hydrothermal carbonization and sulfonation (Chapter 3). The carbonization process was optimized to obtain the maximum solid material yield. Characterization of the different HTC materials showed that no difference could be seen in the distribution of functional groups, except for samples obtained at the lowest reaction conditions. The characterization showed the presence of the sulfonic groups and suggested the aromatization of the material. While longer sulfonation times led to larger number of sulfonic sites, they also reduced the mass yield of the catalyst. Catalytic tests using [BMIM][Cl] as solvent resulted in 52% molar yield of HMF. When MIBK was used as an extracting phase, this value increased to 81.4%. Further optimization via response surface methodology improved the yield to 98.4%.

To improve efficiency and sustainability of the catalyst synthesis, a crosslinked polymeric material was developed. The inclusion of functional sites was done by using a crosslinker with sulfonic sites already present (Chapter 4). For this purpose, sulfosuccinic acid was selected. Functionalization via crosslinking resulted in a more efficient reaction, with less use of reagents and more controlled addition of sulfonic groups to the material. Characterization of the materials showed that the thermal stability and crystallinity correlated with the crosslinker concentration. The thermal stability improved with initial crosslinker concentration up to 20% and started to decrease afterwards due to steric effects and the autocatalytic activity of the sulfonic sites on the polymer chain. Reaction rates also correlated directly to the functional site density, with PVA-40 displaying the highest HMF yields in the shortest time (100% in 20 min at 117 °C). Optimization of the reaction conditions by response surface methodology further reduced the reaction time to 4 min, albeit with an increase in reaction temperature (125 °C). A kinetic model for the reaction was developed, fitting the experimental data. It was observed that the formation of side products did not properly fit a first order reaction, but a second order, suggesting that degradation of HMF did not follow the rehydration route to levulinic and formic acid, but probably the one of humin formation via condensation reactions.

The best performing catalyst, PVA-40, was tested for the valorization of fruit residues, namely mango pulp, and compared with the more conventional catalyst H_2SO_4 (Chapter 5). Water was selected as solvent to improve sustainability and reduce process costs. Both catalytic systems resulted in complete conversion of all substrates and reached up to 31 mol% HMF yield after 20 min. Statistical analysis of the data showed that the maximum yield possible from both reaction systems was indeed 31 mol %. However, the combination of water as solvent, and PVA-40, an easily synthesized recyclable catalyst, improves the potential sustainability of the process, while at the same time keeping production costs low.

Further exploring functionalization via SSA, a series of metalorganic frameworks were developed using known metal catalysts Cr, Ti, and Zr (Chapter 6). All three metals have shown isomerizing properties, transforming glucose to fructose, and in the case of $CrCl_3$, producing HMF directly. SSA once again granted Brønsted acidity to the material via its SO_3H groups, while the metal groups acted as Lewis acid center, creating a bifunctional catalytic metal organic framework. All three materials were characterized via FTIR, elemental, analysis, TGA, BET, and SEM. The characterization showed that Cr and Zr contain a larger proportion of crosslinker than Ti, which can be explained due to the fact that, in the presence of water, Ti(IV) tends to form TiO_2, a more stable and less reactive form of Ti, preventing it from forming links with SSA. Catalytic tests showed that Cr-SSA was more effective in producing HMF from glucose than the other two catalysts. The kinetic study suggested that, while all three catalysts could isomerize glucose to fructose, Cr-SSA did so to a lesser extent than Ti-SSA and Zr-SSA. HMF yields of up to 60% were obtained from both glucose and fructose. When glucose was dehydrated using Cr-SSA in water, sugar conversion was complete, but yields reached only 20% HMF, highlighting the importance of solvent selection.

7.2 Contributions to knowledge

HMF has been regarded for many years now as a promising platform chemical. Despite this, scaling-up and industrialization are yet to take off, mainly due to high substrate costs. This work focused on developing solid catalytic materials that could efficiently convert sugars into HMF while being easily recoverable and recyclable. In that sense, this work contributed to the knowledge of the field as follows:

1. A sulfonated carbonaceous material was synthesized from softwood to produce HMF from fructose. The material was fully characterized, and a possible structure was suggested. Effect of sulfonation on mass yield of the catalyst was documented. The material was highly effective and selective in producing HMF from fructose. Incorporation of an extracting layer of MIBK further increased the reaction. The effectiveness of sulfonic groups as catalytic sites for HMF was well demonstrated.
2. An easily synthesized polymeric resin was developed using SSA as a crosslinker. Analysis of the material demonstrated a correlation between functional sites, thermal stability, and crystallinity, as well as allowed to elucidate the structure of the polymer. These results increased the knowledge and understanding of the effect on chemical and physical properties of crosslinker concentration on PVA polymers. Moreover, the material proved to be a very efficient catalyst, obtaining HMF from fructose in reaction times as short as 4 min. A kinetic study of the reaction demonstrated that HMF degradation on a catalytic system of [BMIM][Cl] and limited amounts of water did not lead to rehydration formation but more likely to condensation products and humin formation.
3. A series of novel metalorganic frameworks were developed with SSA as the organic binder, and Cr, Ti, and Zr as metal centers. Characterization of the materials showed the presence of sulfonic groups and metal centers, demonstrating that the selected reaction was successful in producing the desired solid materials. All three materials were successfully tested as catalysts for glucose dehydration to produce HMF. A kinetic study showed that Zr-SSA and Ti-SSA isomerize glucose to fructose more effectively than Cr-SSA, and that Cr-SSA produce HMF directly from glucose, as opposed to the expected glucose-fructose-HMF pathway.

4. PVA-40 was shown to successfully transform complex fruit waste biomass to HMF. Mango waste was selected as the test substrate. The results for mango pulp were the highest obtained in literature so far.

7.3 Recommendations for future research

The successful synthesis of bifunctional solid catalysts, and valorization of fruit waste, opens several potential research ideas to bring the biorefinery concept closer to fruition:

1. Solvent-catalyst synergy has been shown to play an important role on selectivity and reaction temperature. Screening of potential sustainable solvents, such as choline chloride deep eutectic mixtures, biobased ionic liquids, or biomass-derived solvents like γ-valerolactone, could improve sustainability and efficiency of the reaction system.
2. Most research on HMF production has focused on one-pot reactions. While batch processes have advantages, such as ease of setup and costs, they can be more time consuming and require more energy than continuous processes. A series of fixed bed reactors using solid catalysts could potentially allow for more efficient reactions systems, with conditions tailored for each step of HMF production, such as hydrolysis, isomerization, and dehydration, preventing formation of undesired side products. Moreover, HMF is an intermediate product, which can then be directly transformed into final products requiring considerably different reaction conditions, such as 2,5-furandicarboxylic acid (FDCA), or 2,5-dimethyfuran (DMF).
3. Alternatively, one-pot reactions can be designed to carry out the reaction from carbohydrate to HMF, to final product. By designing multifunctional catalysts with the according reaction media, it could be possible to obtain a catalytic reaction system which can transform carbohydrates to HMF, and then to FDCA or DMF. A multifunctional system with both Brønsted and Lewis acid sites, as well as a hydrogenation catalyst, such as ruthenium, could lead to obtaining DMF in a one-pot reaction system.

4. Substrate cost remains the main hurdle to realization of the biorefinery concept. On the other hand, household waste accounts for up to 40% of all food waste in developed countries. This potential substrate is rich in proteins, lipids, and carbohydrates, all of which can be potentially transformed into valuable platform chemicals. Valorization of such substrate requires developing a process capable of extracting and purifying each of these biomolecules for their respective transformation.

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