

Review

Catalytic Systems for 5-Hydroxymethylfurfural Preparation from Different Biomass Feedstocks: A Review

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Abstract: The preparation of high-value-added platform compounds from biomass materials provides an important method for solving fossil energy shortages. Known as the “sleeping giant”, 5-HMF is one of the most important biomass platform compounds with promising applications. At present, raw materials for the preparation of 5-HMF mainly comprise sugar compounds and non-food biomass. The current systems for preparing 5-HMF are disadvantaged by poor selectivity and a low conversion rate. This paper focuses on the catalytic mechanisms and catalytic systems for the synthesis of 5-HMF from different biomass feedstocks and reviews a series of existing techniques for the preparation of 5-HMF. Catalytic systems for the synthesis of 5-HMF from different feedstocks are also discussed in depth, providing theoretical support for its subsequent in-depth study. The development of efficient catalysts and catalytic systems for the conversion of polysaccharide raw materials into 5-HMF is anticipated.

Keywords: monosaccharides; polysaccharides; 5-hydroxymethylfurfural; catalytic systems



Citation: Tao, J.; Pan, Y.; Zhou, H.; Tang, Y.; Ren, G.; Yu, Z.; Li, J.; Zhang, R.; Li, X.; Qiao, Y.; et al. Catalytic Systems for 5-Hydroxymethylfurfural Preparation from Different Biomass Feedstocks: A Review. *Catalysts* **2024**, *14*, 30. <https://doi.org/10.3390/catal14010030>

Academic Editor: Maria A. Goula

Received: 20 November 2023

Revised: 24 December 2023

Accepted: 25 December 2023

Published: 29 December 2023



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1. Introduction

Resource shortages and environmental pollution have become two prominent barricades for the development of human society. With the dramatic increase in demand for fuels, bulk chemicals and other products [1], traditional petrochemical resources, that is, their basic raw materials, are becoming increasingly scarce and non-renewable, and their biodegradability has caused serious ecological pollution. Therefore, the search for clean, renewable resources is urgent [2]. As a natural, clean, renewable, zero-carbon energy source that is widely available, abundant and inexpensive, biomass has the potential to transform into a variety of important, high-value-added fuels and chemicals that can replace traditional fossil energy sources [3,4]. The search for more efficient ways to use biomass resources is currently attracting widespread interest from academia and industry.

Importantly, 5-Hydroxymethylfurfural is an important biomass platform compound known as the “sleeping giant” [5]. The main physical characteristics of HMF are shown in Table 1. HMF contains a furan ring, an aldehyde group and a hydroxymethyl group, which is chemically active and can be transformed into various downstream derivatives such as 5-hydroxymethyl furfural acid (HMFC), 5-formyl furfural acid (FFCA), levulinic acid (LA), 2,5-furandicarboxylic acid (FDCA), 2,5-diformyl furan (DFF), furfuryl alcohol,

ethylene glycol (EEG), ethoxymethyl furfural, etc. through reactions such as oxidation, hydrogenation, hydration, decarbonylation and etherification. These chemicals have great market potential as precursors for bioplastics, biofuel additives, functional polymers and macromolecules (Figure 1) [6].

Table 1. Physical properties of HMF.

Physical Properties Items	Values
Molecular weight	126.11
Colour	Yellow
State	Solid
Odour	The odour of chamomile flowers
Density	1.243 at 25 °C
Boiling point	114–116 °C at 1 hPa
Melting point	31.5 °C
Solubility	Soluble
Refractive index	1.5627 at 18 °C
Flash point	79 °C
UV absorption maximum	283 nm

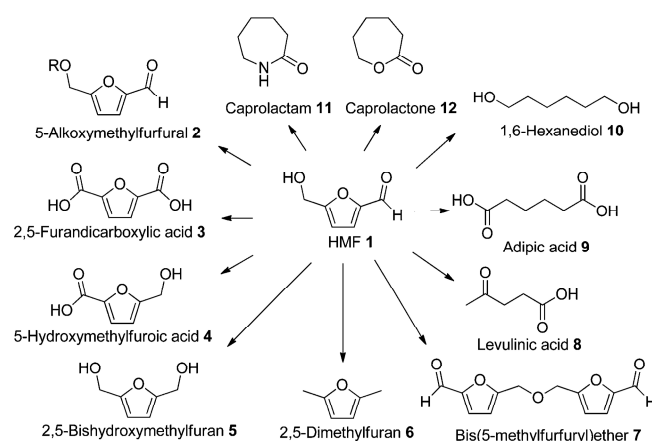


Figure 1. Pathways of high-value HMF utilisation [6].

A variety of synthetic routes for HMF have been reported in recent years [7–10]. Relevant review studies have mainly focused on catalysts, catalytic systems and solvent effects, and a few reports have comprehensively reviewed the conversion of HMF from the perspective of different biomass-derived feedstocks, especially non-food biomass, inulin and watermelon rind.

Feedstock for the preparation of 5-HMF can be divided into two types according to the preparation method. One is converted from saccharides, whereby sugar can be dehydrated directly to form HMF, glucose needs to be isomerised to fructose and then dehydrated to produce HMF, and polysaccharides such as inulin and cellulose need to be hydrolysed to produce monosaccharides first, which are then dehydrated to prepare HMF. The second type is non-food biomass such as agricultural waste (straw, bagasse, etc.), wood, forestry processing waste, etc. [11]. This type of biomass can be used to prepare HMF directly using the one-pot method. Current commonly used catalytic systems can be classified into homogeneous and non-homogeneous phases. The most commonly used homogeneous catalysts are inorganic acid catalysts [12], such as H_2SO_4 and HCl . Due to the problems of large corrosion damage to equipment and difficulties in recycling and disposal of homogeneous catalysts, researchers have begun to explore non-homogeneous solid acid catalysts, such as zeolite molecular sieves, carbon-based solid acids and ion exchange resins. Compared with the homogeneous phase, the non-homogeneous phase has the advantages of good catalytic ability, high stability and less damage to equipment.

Therefore, researchers should focus more on the catalytic conversion of non-food biomass by solid acids with a high catalytic effect in the future.

Moreover, 5-HMF is a promising biomass-based chemical feedstock, and studying the catalytic system for its synthesis is of great significance. This paper reviews the research progress on the catalytic system for the synthesis of 5-HMF from different biomass feedstocks, discusses in detail the conversion mechanisms of monosaccharides and polysaccharides into 5-HMF, extends the discussion on studies on the one-pot conversion of non-food biomass into HMF and finally explores the separation and purification treatments of HMF after its production, providing theoretical support for its subsequent in-depth research.

2. Catalytic System for HMF Synthesis from Different Raw Materials

This paper focuses on the synthesis of HMF based on different biomass feedstocks. The reaction system for the conversion of C6 monosaccharides to HMF as feedstock is presented first, followed by the catalytic system for the conversion of polysaccharides to HMF as feedstock. Finally, the catalytic system for the conversion of non-food biomass to HMF as feedstock is also presented.

Glycoconjugates are the most abundant and dominant components of biomass resources. The sugars can be divided into polysaccharides (cellulose and starch) and monosaccharides (glucose and fructose). Generally, 5-HMF can be prepared via the acid-catalysed dehydration of carbohydrates such as fructose, glucose, inulin and cellulose, in increasing order of difficulty. HMF can be produced from both glucose and fructose. Fructose is an isomer of glucose, and the structure of fructose hexoketose requires less energy to produce HMF than the hexose structure of glucose. Glucose is more stable and can be converted into fructose via enolisation; however, this process requires energy uptake, and glucose readily polymerises into oligosaccharides, which also readily cross-link with HMF. Therefore, producing HMF from glucose is more difficult than from fructose, but glucose is less costly.

2.1. Monosaccharide-Based Catalytic Systems

Monosaccharides mainly include C5 and C6 sugars. The dehydration of raw material monosaccharides via acid catalysts has been considered to produce a large number of products. HMF is among these products, mainly formed by the dehydration of C6 monosaccharides. This part discusses the catalytic conversion of two C6 monosaccharides, fructose and glucose, as raw materials and the conversion of glucose, which often produces a harmful by-product of polymerisation, that is, humic substances.

2.1.1. Fructose as a Raw Material

HMF was first isolated from the decomposition of fructose oxalic acid in an aqueous solution. It was not until the middle of the twentieth century that the reaction mechanism of fructose-catalysed dehydration for the preparation of HMF was proposed, and until now, the dehydration mechanism was inconclusive. There are two possible mechanisms, as shown in Figure 2. In the first, fructose removes one molecule of water to form an allylic structural compound, and then removes two molecules of water to form HMF. In the second, fructose molecules remove two molecules of water in the form of a straight chain and then one molecule of water to form a ring-shaped HMF [13].

Catalysts are essential in the conversion of sugars to HMF. Except for fructose, which can be produced under subcritical conditions (513 K and 3.35 MPa) to produce lower yields of HMF [14], remaining sugars require the presence of an acidic catalyst to produce a good HMF yield [15]. In initial studies, liquid acids were the first catalysts to be recognised as having catalytic functions. Asghari et al. [16] and Salak et al. [17] compared the catalytic performance of several common inorganic (phosphoric acid, etc.) and organic (oxalic acid, etc.) acids for the conversion of HMF from fructose at reaction pressures of 473–590 K and 1.55–11.28 MPa and at reaction times of 75–180 s. The results showed that the catalytic performance of fructose was very good in the conversion of HMF to fructose. The catalytic performance of HMF conversion from fructose at 473–590 K, 1.55–11.28 MPa and 75–180 s

reaction time showed that the highest catalytic activity was obtained when the reaction was carried out with an aqueous phosphoric acid solution at pH = 2.0 and 513 K. However, it was also found that the reaction was carried out in the presence of saline salt. Moreover, the conversion of fructose at 513 K for 10 s in a hydrochloric acid system yielded more than 64% HMF. Chheda et al. [18] used inorganic acids such as hydrochloric acid, sulphuric acid and phosphoric acid, obtaining 89%, 91% and 53% of HMF using fructose, xylose and glucose as substrates, respectively, in a water/DMSO system with 7:3 MIBK-butanol as the extractant at 140 °C and a pH of 1–2. Hansen et al. used the microwave hydrothermal method to convert 27 wt % fructose using 0.10 M hydrochloric acid as a catalyst at 200 °C for 60 s to obtain HMF in a 53% yield, with 95% conversion of fructose [19]. However, liquid acids are gradually eliminated due to the inconvenience in the recovery of the reaction and the disposal of the waste liquid, and they can cause corrosion to the reaction equipment. Room-temperature ionic liquids have attracted much attention in recent years due to their unique properties, and from Table 2, it can be seen that high HMF yields were achieved when ionic liquids were used as catalysts. However, using ionic liquids as catalysts increases the cost of the reaction. Therefore, developing an efficient IL catalyst system for the production of 5-HMF from fructose with a greener and simpler synthesis method that can be reused several times remains a challenge of great practical significance.

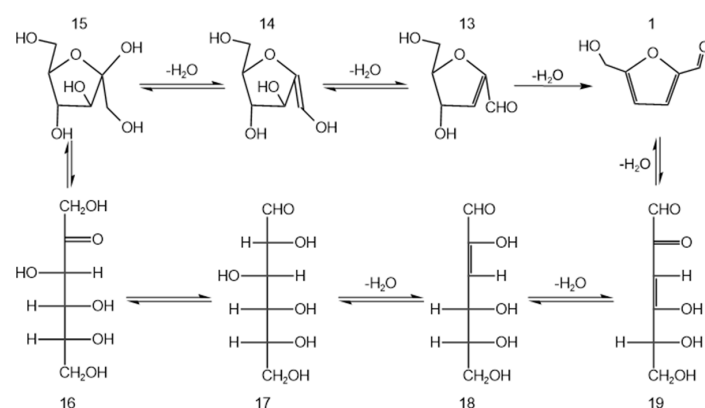


Figure 2. Two reactive fructose conversion pathways.

Compared to homogeneous liquid acids, non-homogeneous solid acids have the advantages of easy separation from the reaction system, easy recycling and reuse after recovery and suitability for industrial production, among others. Non-homogeneous catalysts include zeolite molecular sieves, composite metal oxides, heteropolyacids, acidic ion-exchange resins, carbon-based solid acids, etc. [20]. As seen from Table 2, when using non-homogeneous catalysts, HMF achieved moderate-to-high yields, and catalysts could be recycled, remaining active. Additionally, we found that the reaction could be carried out under mild conditions when using ionic liquids as solvents. Although many catalytic systems have been developed, there is still a great need to explore efficient catalysts for the synthesis of HMF from carbohydrate dehydration under mild reaction conditions.

Table 2. Preparation of HMF from fructose as a raw material.

Saccharides	Catalyst	Solvent	Temperature/°C	Time/min	Yield/%	Ref.
Fructose	[BMIM]OH	DMSO	160	480	91.6	[21]
Fructose	[CMIm]Cl	DMSO	120	120	95.7	[22]
Fructose	LF	DMSO	393K	90	~90	[23]
Fructose	N3P3Cl6	[Bmim]Cl	80	20	92.8	[24]
Fructose	CM-SO3H	[BMIM]Cl	80	30	83.5	[25]
Fructose	P-TiO2	water-THF	175	30	98.6	[26]
Fructose	C16-SO3H- γ -Al2O3-650 °C	DMSO/H2O	110	240	84	[27]
Fructose	GO	DMSO	120	240	60.8	[28]

2.1.2. Glucose as a Raw Material

The conversion of glucose to HMF is more difficult compared to fructose, as glucose is difficult to convert to HMF in acidic aqueous media, and it is generally necessary to first convert glucose to fructose [29], a process that requires the involvement of alkaline or Lewis acids to complete isomerisation. This is followed by dehydration in the presence of Brønsted's acid to produce HMF [30]. There are two reaction mechanisms in the isomerisation of glucose to fructose: cyclic and acyclic dehydration (as shown in Figure 3). Fructose in acyclic dehydration is mainly converted through an enol-type intermediate converted by glucose, which generates 5-HMF via two-step sequential dehydration and one-step ring closure to eliminate water molecules. On the other hand, in cyclic dehydration, glucose is converted to fructose through an isomerisation reaction, and fructose is used as an intermediate in the form of a furano-keto sugar, of which the hemiacetal on the carbon atom in the second position is first dehydrated to form the tertiary carbon-positive ion and is subsequently dehydrated in two more sequential steps on a furan ring to generate 5-HMF [31]. It is clear from the relevant literature that researchers are more supportive of the cyclic route process because of the presence of the cyclic intermediates found in the process, as demonstrated using NMR spectroscopy and isotopic labelling methods by Amarasekara et al. [32]. Antal et al. [33] demonstrated that HMF can be generated from several cyclic furan intermediates by the dehydration of fructose. Moreau et al. [34] predicted that the enediol pathway is essential in the formation of HMF, and enediols are thought to be intermediates in the isomerisation reaction of glucose to fructose. Fructose is then converted to HMF by keto-enol isomerisation with the loss of three water molecules. It is worth noting that the presence of active functional groups in sugars causes many side reactions under acidic conditions, such as hydroxyaldol condensation, reversal reaction, molecular isomerisation, cleavage, water and other reactions, during which polymers and putrescine are readily generated, and the obtained HMF is prone to further hydrolysis to form acetylpropionic acid and formic acid (shown in Figure 4), which leads to a decrease in the yield of HMF.

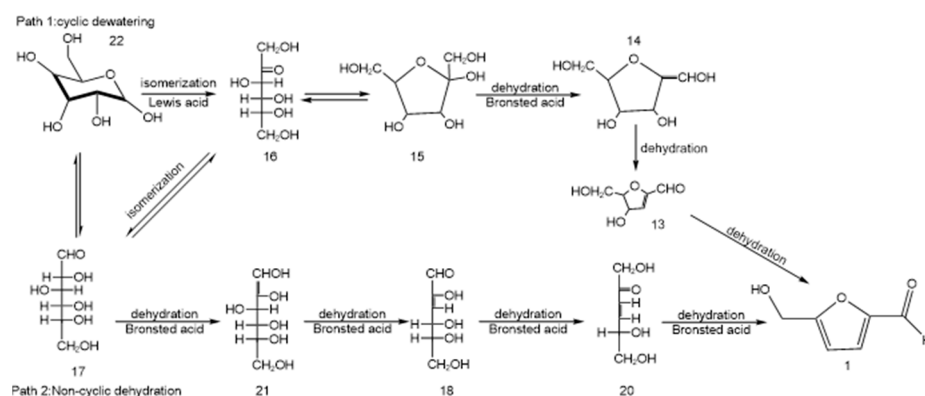


Figure 3. Cyclic versus acyclic dehydration of glucose.

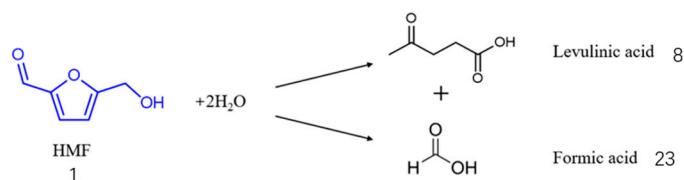


Figure 4. Rehydration products of HMF.

Previously, the main catalysts used for the conversion of glucose to HMF were homogeneous catalysts, including acidic catalysts such as Lewis acid and Brønsted acid; soluble metal salts such as AlCl_3 [35], LaCl_3 [36], InCl_3 [37], CrCl_3 [38], SnCl_4 [39] and FeCl_3 [40]; and inorganic acids such as hydrochloric acid, sulfuric acid and phosphoric acid. Among

metal salts, chromium salts were able to achieve higher yields in the catalytic conversion of glucose. However, when inorganic acids and metal salts were used as catalysts, there were problems such as corrosion of equipment, hazardous operation and difficulty in recycling; hence, researchers turned their attention to non-homogeneous catalysts. Feng et al. [41] catalysed the conversion of glucose to HMF using 2-SZ-5-HM-550 as a catalyst at 195 °C and reacted in biphasic solvents such as a NaCl solution and DMSO for 90 min, obtaining a 61.14% yield of HMF. Some studies on the catalysis of glucose with non-homogeneous catalysts are shown in Table 3. Due to the numerous advantages of solid catalysts, in line with the requirements of green chemistry, the use of solid catalysts to catalyse the preparation of 5-HMF from sugars has gradually become a research hot spot, and the search for the development of solid acid catalysts with high activity will be an important research direction in the future.

Table 3. Glucose-based HMF preparation.

Saccharides	Catalyst	Solvent	Temperature/°C	Time/min	Yield/%	Ref.
Glucose	RCP160M	H ₂ O-NMP-NaCl/MIBK	120	480	84.92	[42]
Glucose	Cu-Cr/ZSM-5	DMSO	140	240	50.4	[43]
Glucose	SPPS	ILs	140	240	87.2	[44]
Glucose	Sn-Mont	THF/DMSO	160	180	53.5	[45]
Glucose	AlCl ₃ + [NMP]Br	DMA	120	120	57	[46]

2.1.3. High-Fructose Corn Syrup

High-fructose corn syrup (HFCS), an enzymatically produced product, was first introduced in the United States in 1967 and is used primarily as a liquid sweetener in the food and beverage industry because it is inexpensive and easy to handle [47]. The demand for HFCS is reflected in the amount of HFCS used, which ranged from 0.5 pounds per capita in 1970 to 62.4 pounds per capita in 1997 and was still as high as 59.0 pounds per capita in 2005 [48].

Jeong et al. [49] achieved an 80% yield of HMF by mixing industrially produced high-fructose corn syrup (HFCS-90) as a raw material and cation exchange resin Amberlyst-15 as a catalyst in 1,4-dioxane at 100 °C for 3 h. Rao et al. [50] catalysed HFCS (HFCS-90/55/42) with 15P-TiO₂, achieving 50%, 48% and 45% HMF yields, respectively. Lin et al. [51] catalysed high-fructose corn syrup (HFCS-55) with biooxidative in situ production of gluconic acid as a catalyst, obtaining HMF yields as high as 85%. Given the current high consumption of HFCS in beverages, which can easily lead to obesity or other related diseases, limiting its application in the food industry, the use of HFCS to produce HMF could create a useful alternative market for current HFCS producers [52].

2.2. Polysaccharide-Based Catalytic Systems

Glucose and fructose are mainly derived from food crops, and their use as feedstock for conversion may have an adverse impact on global food supplies. Research into the more widely sourced and cheaper cellulose-based polysaccharide compounds as feedstocks for the synthesis of HMF is currently more promising for application. Whichever biomass resource is used as a feedstock for HMF production, unique catalytic strategies have to be explored to form efficient catalytic systems.

Polysaccharides are polymeric sugar macromolecular carbohydrates consisting of glycosidically bonded sugar chains with at least over 10 monosaccharides. In a broad sense, they can be divided into homogeneous polysaccharides and inhomogeneous polysaccharides. Homogeneous polysaccharides are polysaccharides formed by the condensation of one type of monosaccharide molecule. The most abundant homogeneous polysaccharides in nature are cellulose, starch and glycogen, which are all composed of glucose. In addition to these, there is inulin, a polyfructose that has a low degree of polymerisation, is easily hydrolysed and is found mainly in the roots of plants in the Asteraceae family. Compared with the preparation of HMF from monosaccharides, polysaccharides have the challenges

of low conversion and poor selectivity, so it is necessary to design suitable catalysts and select suitable catalytic systems.

2.2.1. Cellulose-Based Raw Materials

Cellulose is the most abundant biomass resource on Earth, mainly in the form of wood and crop residues. Cellulose is a straight-chain macromolecule consisting of glucose molecules linked by β -1,4-glycosidic bonds, and it is generally believed that the conversion from cellulose to HMF occurs via three steps (as shown in Figure 5): (i) hydrolysis of cellulose to glucose, (ii) isomerisation of glucose to fructose and (iii) fructose dehydration reaction to obtain 5-HMF. The acid-catalysed hydrolysis of cellulose to glucose [13] consists of three steps: (i) protonation at the glycosidic oxygen, (ii) cleavage at the glycosidic bond and (iii) nucleophilic attack by water.

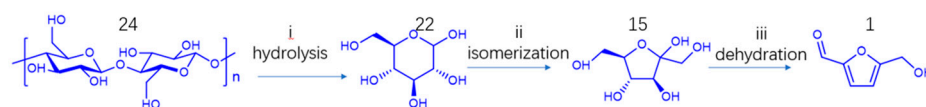


Figure 5. Conversion of cellulose to HMF.

Cellulose is structurally stable and not susceptible to chemical and physical changes; therefore, the hydrolysis of cellulose is usually carried out in the presence of a catalyst. The main homogeneous catalysts reported so far to catalyse the conversion of cellulose to HMF include traditional inorganic acids and metal salts. Inorganic acids were first used as catalysts in the study of cellulose dehydration to generate HMF due to their numerous and common types. In such cases, the HMF yields were high, but inorganic acids were gradually eliminated due to the serious corrosion of equipment. Some studies on the preparation of HMF from cellulose as a raw material are shown in Table 4. From Table 4, it can be seen that the yield of HMF when non-homogeneous catalysts are used as catalysts is not very high, and the exploration of efficient and green, recyclable, non-homogeneous catalysts still has a long way to go.

Table 4. Preparation of HMF from cellulose-based feedstock.

Saccharides	Catalyst	Solvent	Temperature/ $^{\circ}$ C	Time/min	Yield/%	Ref.
MCC (microcrystalline cellulose)	HCl	ZnCl ₂ aq	150	40	80.6	[53]
Microcrystalline cellulose	RuCl ₃	NaCl _{aq} -butanol	220	30	83.3	[54]
Cellulose	CrCl ₃ ·6H ₂ O	TBAC	140	90	43.7	[55]
Cellulose	HPW/Nb ₂ O ₅	Acetone/H ₂ O	200	30	20.6	[56]
Microcrystalline cellulose	HfO(PO ₄) ₂	NaCl-H ₂ O/THF	190	240	69.8	[57]
Cellulose	γ -AlOOH	(BmimCl) + DMSO	160	120	58.4	[58]
Microcrystalline cellulose	NBO	H ₂ O	230	120	7	[59]

2.2.2. Starch-Based Raw Materials

Starch is a glucan made of glucose linked by α -glycosidic bonds. Compared with cellulose, the α -glycosidic bonds in starch are more easily utilised by hydrogenolysis, which is promising for application in the field of biomass conversion, and the lower cost of starch compared to monosaccharides and disaccharides is conducive to the industrial production of HMF. The synthesis of HMF from starch requires the following three processes: (i) degradation of starch to monosaccharides, (ii) isomerisation of glucose to fructose and (iii) dehydration of fructose to form HMF.

The original catalytic system used inorganic acids and bases and metal salts as catalysts. Chheda et al. [60] catalysed starch with HCl in a biphasic system with a conversion rate of up to 43%. Yang et al. [35] tested the conversion of starch by AlCl₃·6H₂O in a biphasic H₂O/THF solvent containing NaCl additive, with yields up to 50%. Chun et al. [61] found that the addition of HCl to starch in the presence of the ionic liquid [OMIM]Cl was

able to increase the yield of HMF. Moreover, when cassava starch was dissolved in 0.5 M HCl, the addition of a certain amount of CrCl_2 increased the HMF yield on average by two times, reaching as high as 73% yield. Yi et al. [62] examined the effect of chromium fluoride on the yield of 5-hydroxymethylfurfural in ionic liquids using a two-step method and found that when the concentration of CrF_3 was 1%, the yield of HMF could reach 52.6%. Moreover, when using a combined addition of CrF_3 and CrBr_3 , the HMF yield was 1.3 times higher, presumably due to a synergistic effect between the two catalysts. Recently, solid catalyst systems more conducive to industrial-scale production have been developed. Zhang et al. [63] used gC_3N_4 -loaded UiO-66-type MOF catalysts to catalyse starch in an IL system, with an HMF yield of 33.9%. Cao et al. [64] prepared aluminium ion-exchanged calcium montmorillonites with different concentrations, applied them to the preparation of HMF and found that two types of acid sites existed in the resulting catalysts. The two types of acid sites were Lewis acid for glucose isomerisation and Brønsted acid sites for fructose dehydration; finally, 60.1% HMF was obtained by catalysing starch using Al-mont-10 as a catalyst. Atanda et al. [26] used phosphorylated TiO_2 to catalyse starch from rice and potatoes at 180 °C, obtaining an 80 to 85% yield of HMF. At this stage, glucose isomerisation, starch solubility, glycosidic bond hydrogenolysis, etc. are all urgent issues to be solved in the industrial application of starch to HMF, and the development of catalytic systems that can catalyse the degradation of polysaccharides as well as efficiently catalyse the isomerisation of glucose and the dehydration of fructose is a good direction for research.

2.2.3. Inulin as a Raw Material

Inulin is an indigestible oligosaccharide, a biopolymer composed of fructose and a small amount of glucose with a degree of polymerisation between 2 and 70, which is mainly found in plants such as inulin tubers and chicory roots [65]. Raw chicory root can be used for direct conversion to HMF due to its high inulin content (70–75% by dry weight). In particular, about 80–90% of the total carbohydrate content of chicory root consists of inulin-type fructans, and these fractions can be used for the synthesis of HMF [66]. Inulin is first hydrolysed to fructose, and fructose is then dehydrated to produce HMF, both of which can be catalysed by an acid catalyst so that HMF can be produced using a one-pot method, reducing the loss of intermediate steps [67]. Therefore, inulin-rich plant materials can be used as an excellent biofeedstock for the production of HMF [68].

Heo et al. [68] summarised a number of studies on the production of HMFs from inulin and found that the product yields of HMFs obtained from inulin-rich plant materials were generally higher than those of other carbohydrate-rich plant sources. Perez et al. [69] summarised the yields of HMF in ChoCl /citric and ChoCl /oxalic with inulin as the raw material and the yields of HMF in the presence of homogeneous and non-homogeneous catalysts, which were relatively good. Cao et al. [64] carried out the catalytic conversion of inulin with Al-mont-10 inulin with a final HMF yield of 81.6%. Yang et al. [70] carried out the catalytic conversion of inulin with pre-treated hydrated niobium pentoxide in a water-THF biphasic system at 433 K, with a final HMF yield of 54%. However, when inulin was hydrolysed by inulin exo-enzymes, the HMF yield could reach up to 74%, which may be due to the slow hydrolysis of inulin in this non-homogeneous catalytic system, which in turn affects HMF production. Hu et al. [22] achieved an 88.4% HMF yield of inulin at 120 °C using dimethyl sulfoxide as a solvent and the acidic ionic liquid 1-hydroxypropyl-3-methylimidazolium chloride ($[\text{CMIm}]\text{Cl}$) as a catalyst. As seen from Table 5, moderate-to-high HMF yields can generally be achieved when using inulin as a raw material.

Table 5. Preparation of HMF from inulin as a raw material.

Saccharides	Catalyst	Solvent	Temperature/°C	Time/min	Yield/%	Ref.
Inulin	Sn-CP/HCl	H ₂ O/DMSO	170	240	55.9	[71]
Inulin (enzymatically hydrolysed)	NA-p	Water-2-butanol	433K	80	74	[70]
Inulin	CM-SO ₃ H	[BMIM][Cl]	80	60	59.2	[25]
Inulin	GO	DMSO	160	100	58.2	[28]
Inulin	GO	THF-H ₂ O	160	100	61.2	[28]
Inulin	SCFC	DMSO	393K	180	80.1	[72]
Inulin	SBBA	[bmim]HSO ₄	120	300	88	[73]

2.3. Catalytic Systems for Non-Food Biomass Feedstocks

Of the previously discussed feedstocks, glucose and fructose, in particular, mainly originate from food crops, and their use as feedstocks for conversion could have a negative impact on the global food supply. China is a large agricultural country with abundant biomass resources, and wheatgrass, straw, dead twigs, leaves, bagasse and household wastepaper generated from agricultural production contain a large amount of lignocellulose that can be utilised. Hence, the direct conversion and utilisation of these non-edible cellulose sources is at the core of the development of biomass energy and has been the focus of the work of many researchers. Therefore, food wastes, such as starch-rich food waste [74], straw [75], fruit peels [76], sugar beets [77], etc., can be selected as feedstock for the synthesis of 5-HMF. Shao et al. [76] used microwave hydrothermal liquefaction (MHTL) technology to convert watermelon rind into the biomass high-value-added chemical, 5 hydroxymethylfurfural (HMF), with 1% hydrochloric acid as a catalyst, a holding temperature of 135 °C, a holding time of 6 min, and a liquid-to-solid ratio of 12:1; the highest yield of HMF (3.8%) was obtained in a similar hydrothermal system. Mo et al. [78] degraded cotton stalks with a solid, ultra-strong acid, and the maximum yield of HMF was 27.2% when the reaction temperature was 503 K and the reaction time was 75 min. Cao et al. activated pyrolysed pine woodchip biochar with phosphoric acid at 600 °C as a solid acid catalyst to catalyse the synthesis of 24.5, 22.2 and 14.7 Cmol% HMF from starch-rich food wastes (bread, rice and spaghetti) by reacting them at 180 °C for 20 min, respectively. Ryoya et al. [79] obtained an HMF yield of 4.5 wt% after reacting the wood in [EMIM]HSO₄ ionic liquid for 10 h at 140 °C. The creation of these catalytic feedstocks and catalytic systems provides new ideas for the high-value and resourceful utilisation of non-food crops and solid wastes.

3. Isolation and Purification of 5-HMF

The separation and purification processes available for 5-HMF include extraction, nanofiltration, ionic liquids, distillation and adsorption [80]. For example, Jeong et al. [49] used dioxane as a solvent in their study and found that dioxane could be evaporated under mild conditions to recover the crude reaction mixture, which was later dissolved in ethyl acetate, washed with water and then evaporated from the ethyl acetate to obtain HMF. Kougioumtzis et al. [81] used dichloromethane (DCM) as a solvent and purified HMF via liquid–liquid extraction, achieving 98% HMF recovery potential. In recent years, many adsorbents for the selective adsorption of 5-HMF, such as zeolites, activated carbons, polymers and resins, have been investigated. In order to enhance the solid–liquid adsorption separation, Zhang et al. [82] combined adsorption isotherms with DFT calculations to gain insights into the adsorption properties and mechanisms of HMF. A porous polymeric adsorbent (H-PAP) with a hollow structure was developed, showing a 20-fold scale-up potential. A more innovative approach to the recovery of 5-HMF is the use of loaded hydrophobic deep eutectic solvent (DES) liquid membranes. Dietz et al. [83] prepared and characterised 12 deep eutectic solvent (DES) liquid membranes with different carriers and determined their stability in water and air. Subsequently, the loaded DES liquid membranes were applied for the recovery of HMF from aqueous solutions. However, due to the

high costs associated with DES, more efficient regeneration methods are required before industrial-scale HMF separation can be considered economically viable.

The isolation and purification of 5-HMF can account for up to 70% of the overall production cost [84], but relatively few studies have been carried out on the isolation and purification of HMF compared to studies on the production of HMF; therefore, the isolation and purification of HMF from the reacted mixtures is still a challenging problem.

4. Conclusions and Outlook

Efforts to reduce carbon emissions in various countries in response to global warming issues and dependence on fossil energy sources have also led to increasingly popular research into the conversion of biomass into fuels and chemicals. For many years, HMF, a product of hexose dehydration, has also been considered one of the most promising platform compounds. The conversion of biomass into HMF, a high-value-added platform compound, has long-lasting and far-reaching implications for alleviating energy problems. This paper summarises the biomass feedstocks that are commonly used to produce HMF. Among the many feedstocks, polysaccharide feedstocks such as cellulose and inulin are more complex and difficult to utilise in the preparation of HMF than monosaccharide feedstocks such as glucose and fructose. This also poses a greater challenge for the development of efficient catalysts and catalytic systems for the conversion of polysaccharide feedstocks to HMF.

- (1) For the conversion of cellulose-based polysaccharides to HMF via a hydrolysis–isomerisation–dehydration cascade, multifunctional catalytic systems for improving the overall reaction efficiency should be further enriched, and the design of new catalysts with adjustable B and L acids is of significance for improving the efficiency of the reaction.
- (2) Solvent systems also have a potential impact on the synthesis of HMF. A suitable solvent system can inhibit the production of by-products and facilitate the conversion of raw materials, thus improving the selectivity of the reaction. Aqueous solutions are the most economical and green reaction solvents, but they reduce product yields due to easy evaporation during the reaction compared to expensive ionic liquids. Therefore, there is a need to continue to explore efficient and inexpensive reaction solvent systems.
- (3) Future research should still focus on exploring green, economic and sustainable conversion strategies that are compatible with the environment. Emphasis will be placed on the feasibility of industrial production while focusing on environmental issues to harmonise economic development with environmental protection. There is a need to design and develop high-performance, non-homogeneous catalytic systems and enhance their catalyst stability to allow for multiple reuses and cost savings.
- (4) The by-products from the synthesis of HMF can be resourcefully utilised and considered for conversion into valuable materials or fuels. HMF has very good application prospects and is one of the important platform compounds with great research value and significance.

Author Contributions: Conceptualisation, J.T., J.X., X.L. (Xuebin Lu) and Z.Y.; methodology, X.L. (Xuebin Lu) and Z.Y.; software, J.T.; validation, J.T., G.R. and J.L.; formal analysis, X.L. (Xuebin Lu) and Z.Y.; investigation, J.X.; data curation, Y.P., H.Z., Y.T., X.L. (Xiaoyun Li) and R.Z.; writing—original draft preparation, J.T.; writing—review and editing, X.L. (Xuebin Lu) and Z.Y.; visualisation, R.Z. and Y.Q.; supervision, J.T. and R.Z.; project administration, J.T. and G.R.; funding acquisition, X.L. (Xuebin Lu) and Z.Y. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the National Natural Science Foundation of China (grant numbers: 51908400, 52066017 and 51876180), the Central Financial Support Special Funds for Local Colleges and Universities ((2023) No. 1 and (2024) No. 1), the Tibet University Postgraduate High Level Talent Training Programme (Grant No. 2020-GSP-B017), Tibet University Talent Development Incentive Scheme—Young Scholars Project Grant.

Data Availability Statement: No new data were created or analysed in this study. Data sharing is not applicable to this article.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Tilman, D.; Socolow, R.; Foley, J.A.; Hill, J.; Larson, E.; Lynd, L.; Pacala, S.; Reilly, J.; Searchinger, T.; Somerville, C.; et al. Beneficial Biofuels—The Food, Energy, and Environment Trilemma. *Science* **2009**, *325*, 270–271. [\[CrossRef\]](#) [\[PubMed\]](#)
2. Zhang, Z. Synthesis of γ -Valerolactone from Carbohydrates and its Applications. *ChemSusChem* **2016**, *9*, 156–171. [\[CrossRef\]](#) [\[PubMed\]](#)
3. George, W.; Huber, S.I.; Corma, A. Synthesis of Transportation Fuels from Biomass: Chemistry, Catalysts, and Engineering. *Chem. Rev.* **2006**, *106*, 4044–4098. [\[CrossRef\]](#)
4. Zhu Chenjie, D.F.; Hanjie, Y.; Pingkai, O. Catalytic production of liquid hydrocarbon fuels and fuel additives from lignocellulosic platform molecules. *CIESC J.* **2015**, *66*, 2785–2792. [\[CrossRef\]](#)
5. Weng, R.; Lu, X.; Ji, N.; Fukuoka, A.; Shrotri, A.; Li, X.; Zhang, R.; Zhang, M.; Xiong, J.; Yu, Z. Taming the butterfly effect: Modulating catalyst nanostructures for better selectivity control of the catalytic hydrogenation of biomass-derived furan platform chemicals. *Catal. Sci. Technol.* **2021**, *11*, 7785–7806. [\[CrossRef\]](#)
6. Van Putten, R.-J.; van der Waal, J.C.; de Jong, E.; Rasrendra, C.B.; Heeres, H.J.; de Vries, J.G. Hydroxymethylfurfural, A Versatile Platform Chemical Made from Renewable Resources. *Chem. Rev.* **2013**, *113*, 1499–1597. [\[CrossRef\]](#)
7. Yong, G.; Zhang, Y.; Ying, J.Y. Efficient Catalytic System for the Selective Production of 5-Hydroxymethylfurfural from Glucose and Fructose. *Angew. Chem. Int. Ed.* **2008**, *47*, 9345–9348. [\[CrossRef\]](#)
8. Lee, S.-B.; Jeong, G.-T. Catalytic Conversion of Chitosan to 5-Hydroxymethylfurfural Under Low Temperature Hydrothermal Process. *Appl. Biochem. Biotechnol.* **2015**, *176*, 1151–1161. [\[CrossRef\]](#)
9. Oh, S.J.; Park, J.; Na, J.G.; Oh, Y.K.; Chang, Y.K. Production of 5-hydroxymethylfurfural from agarose by using a solid acid catalyst in dimethyl sulfoxide. *RSC Adv.* **2015**, *5*, 47983–47989. [\[CrossRef\]](#)
10. Jia, S.; He, Y.; Wang, G. Dimethylsulfoxide/Water Mixed Solvent Mediated Synthesis of 5-Hydroxymethylfurfural from Galactose with Aluminum Salt Catalyst. *ChemistrySelect* **2017**, *2*, 2356–2362. [\[CrossRef\]](#)
11. Liu, D.; Xiao, R.; Ying, H.; Chen, Y.; Zhu, C.; Du, F.; Zhang, H.; Ouyang, P. Research progress in catalytic valorization of lignocellulose. *Sci. Sin. Chim.* **2015**, *45*, 454–478. [\[CrossRef\]](#)
12. Marcotullio, G.; De Jong, W. Chloride ions enhance furfural formation from d-xylose in dilute aqueous acidic solutions. *Green Chem.* **2010**, *12*, 1739–1746. [\[CrossRef\]](#)
13. Xin, L.; Gaofeng, S.; Zhao, W.; Fenfang, L.; Yawen, H.; Kaiqiang, Y. Research progress on the preparation of 5-hydroxymethylfurfural by converting biomass resources. *Mod. Chem. Ind.* **2020**, *40*, 22–26. [\[CrossRef\]](#)
14. Asghari, F.S.; Yoshida, H. Dehydration of fructose to 5-hydroxymethylfurfural in sub-critical water over heterogeneous zirconium phosphate catalysts. *Carbohydr. Res.* **2006**, *341*, 2379–2387. [\[CrossRef\]](#) [\[PubMed\]](#)
15. Li, Y.; Lu, X.; Yuan, L.; Liu, X. Fructose decomposition kinetics in organic acids-enriched high temperature liquid water. *Biomass Bioenergy* **2009**, *33*, 1182–1187. [\[CrossRef\]](#)
16. Asghari, F.S.; Yoshida, H. Kinetics of the Decomposition of Fructose Catalyzed by Hydrochloric Acid in Subcritical Water: Formation of 5-Hydroxymethylfurfural, Levulinic, and Formic Acids. *Ind. Eng. Chem. Res.* **2007**, *46*, 7703–7710. [\[CrossRef\]](#)
17. Yoshida, F.S.A.H. Acid-Catalyzed Production of 5-Hydroxymethyl Furfural from D-Fructose in Subcritical Water. *Ind. Eng. Chem. Res.* **2006**, *45*, 2163–2173.
18. Chheda, J.N.; Huber, G.W.; Dumesic, J.A. Liquid-Phase Catalytic Processing of Biomass-Derived Oxygenated Hydrocarbons to Fuels and Chemicals. *Angew. Chem. Int. Ed.* **2007**, *46*, 7164–7183. [\[CrossRef\]](#)
19. Hansen, T.S.; Woodley, J.M.; Riisager, A. Efficient microwave-assisted synthesis of 5-hydroxymethylfurfural from concentrated aqueous fructose. *Carbohydr. Res.* **2009**, *344*, 2568–2572. [\[CrossRef\]](#)
20. Lopes, M.; Dussan, K.; Leahy, J.J.; da Silva, V.T. Conversion of d -glucose to 5-hydroxymethylfurfural using Al₂O₃-promoted sulphated tin oxide as catalyst. *Catal. Today* **2017**, *279*, 233–243. [\[CrossRef\]](#)
21. Qu, Y.S.; Song, Y.L.; Huang, C.P.; Zhang, J.; Chen, B.H. Dehydration of Fructose to 5-Hydroxymethylfurfural Catalyzed by Alkaline Ionic Liquid. *Adv. Mater. Res.* **2011**, *287–290*, 1585–1590. [\[CrossRef\]](#)
22. Hu, Z.; Liu, B.; Zhang, Z.; Chen, L. Conversion of carbohydrates into 5-hydroxymethylfurfural catalyzed by acidic ionic liquids in dimethyl sulfoxide. *Ind. Crops Prod.* **2013**, *50*, 264–269. [\[CrossRef\]](#)
23. Tang, H.; Li, N.; Li, G.; Wang, W.; Wang, A.; Cong, Y.; Wang, X. Dehydration of Carbohydrates to 5-Hydroxymethylfurfural over Lignosulfonate-Based Acidic Resin. *ACS Sustain. Chem. Eng.* **2018**, *6*, 5645–5652. [\[CrossRef\]](#)
24. Song, J.; Zhang, B.; Shi, J.; Ma, J.; Yang, G.; Han, B. Dehydration of Carbohydrates to 5-Hydroxymethylfurfural in Ionic Liquids Catalyzed by Hexachlorotriphosphazene. *Chin. J. Chem.* **2012**, *30*, 2079–2084. [\[CrossRef\]](#)
25. Li, X.; Wang, Y.; Xie, X.; Huang, C.; Yang, S. Dehydration of fructose, sucrose and inulin to 5-hydroxymethylfurfural over yeast-derived carbonaceous microspheres at low temperatures. *RSC Adv.* **2019**, *9*, 9041–9048. [\[CrossRef\]](#)

26. Atanda, L.; Shrotri, A.; Mukundan, S.; Ma, Q.; Konarova, M.; Beltramini, J. Direct Production of 5-Hydroxymethylfurfural via Catalytic Conversion of Simple and Complex Sugars over Phosphated TiO_2 . *ChemSusChem* **2015**, *8*, 2907–2916. [[CrossRef](#)] [[PubMed](#)]
27. Lin, F.; Wang, K.; Gao, L.; Guo, X. Efficient conversion of fructose to 5-hydroxymethylfurfural by functionalized $\gamma\text{-Al}_2\text{O}_3$ beads. *Appl. Organomet. Chem.* **2019**, *33*, e4821. [[CrossRef](#)]
28. Nie, G.; Tong, X.; Zhang, Y.; Xue, S. Efficient Production of 5-Hydroxymethylfurfural (HMF) from d-Fructose and Inulin with Graphite Derivatives as the Catalysts. *Catal. Lett.* **2014**, *144*, 1759–1765. [[CrossRef](#)]
29. Yang, L.; Tsilomelekis, G.; Caratzoulas, S.; Vlachos, D.G. Mechanism of Brønsted Acid-Catalyzed Glucose Dehydration. *ChemSusChem* **2015**, *8*, 1334–1341. [[CrossRef](#)]
30. Mimura, N.; Sato, O.; Shirai, M.; Yamaguchi, A. 5-Hydroxymethylfurfural Production from Glucose, Fructose, Cellulose, or Cellulose-based Waste Material by Using a Calcium Phosphate Catalyst and Water as a Green Solvent. *ChemistrySelect* **2017**, *2*, 1305–1310. [[CrossRef](#)]
31. Hongyan Yang, J.L.; Lu, J.; Lan, P.; Zhang, H. Study on Catalytic Conversion of Cellulose to 5-Hydroxymethyl Furfural by Directional Degradation in Deep Eutectic Solvents. *BioResources* **2020**, *15*, 3344–3355. [[CrossRef](#)]
32. Amarasekara, A.S.; Williams, L.D.; Ebede, C.C. Mechanism of the dehydration of d-fructose to 5-hydroxymethylfurfural in dimethyl sulfoxide at 150 °C: An NMR study. *Carbohydr. Res.* **2008**, *343*, 3021–3024. [[CrossRef](#)] [[PubMed](#)]
33. Antal, M.J., Jr.; Mok, W.S.; Richards, G.N. Mechanism of formation of 5-(hydroxymethyl)-2-furaldehyde from D-fructose and sucrose. *Carbohydr. Res.* **1990**, *199*, 91–109. [[CrossRef](#)] [[PubMed](#)]
34. Moreau, C.; Finiels, A.; Vanoye, L. Dehydration of fructose and sucrose into 5-hydroxymethylfurfural in the presence of 1-H-3-methyl imidazolium chloride acting both as solvent and catalyst. *J. Mol. Catal. A Chem.* **2006**, *253*, 165–169. [[CrossRef](#)]
35. Yang, Y.; Hu, C.-w.; Abu-Omar, M.M. Conversion of carbohydrates and lignocellulosic biomass into 5-hydroxymethylfurfural using $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ catalyst in a biphasic solvent system. *Green Chem.* **2012**, *14*, 509–513. [[CrossRef](#)]
36. Wang, T.; Pagán-Torres, Y.J.; Combs, E.J.; Dumesic, J.A.; Shanks, B.H. Water-Compatible Lewis Acid-Catalyzed Conversion of Carbohydrates to 5-Hydroxymethylfurfural in a Biphasic Solvent System. *Top. Catal.* **2012**, *55*, 657–662. [[CrossRef](#)]
37. Shen, Y.; Sun, J.; Yi, Y.; Wang, B.; Xu, F.; Sun, R. 5-Hydroxymethylfurfural and levulinic acid derived from monosaccharides dehydration promoted by InCl_3 in aqueous medium. *J. Mol. Catal. A Chem.* **2014**, *394*, 114–120. [[CrossRef](#)]
38. Jia, S.; Xu, Z.; Zhang, Z.C. Catalytic conversion of glucose in dimethylsulfoxide/water binary mix with chromium trichloride: Role of water on the product distribution. *Chem. Eng. J.* **2014**, *254*, 333–339. [[CrossRef](#)]
39. Hu, S.; Zhang, Z.; Song, J.; Zhou, Y.; Han, B. Efficient conversion of glucose into 5-hydroxymethylfurfural catalyzed by a common Lewis acid SnCl_4 in an ionic liquid. *Green Chem.* **2009**, *11*, 1746–1749. [[CrossRef](#)]
40. Zhou, X.; Zhang, Z.; Liu, B.; Zhou, Q.; Wang, S.; Deng, K. Catalytic conversion of fructose into furans using FeCl_3 as catalyst. *J. Ind. Eng. Chem.* **2014**, *20*, 644–649. [[CrossRef](#)]
41. Feng, Y.; Zuo, M.; Wang, T.; Jia, W.; Zhao, X.; Zeng, X.; Sun, Y.; Tang, X.; Lei, T.; Lin, L. Efficient synthesis of glucose into 5-hydroxymethylfurfural with $\text{SO}_4^{2-}/\text{ZrO}_2$ modified H^+ zeolites in different solvent systems. *J. Taiwan Inst. Chem. Eng.* **2019**, *96*, 431–438. [[CrossRef](#)]
42. Pumrod, S.; Kaewchada, A.; Roddech, S.; Jaree, A. 5-HMF production from glucose using ion exchange resin and alumina as a dual catalyst in a biphasic system. *RSC Adv.* **2020**, *10*, 9492–9498. [[CrossRef](#)] [[PubMed](#)]
43. Chung, N.H.; Oanh, V.T.; Thoa, L.K.; Hoang, P.H. Catalytic Conversion of Glucose into 5-Hydroxymethyl Furfural Over Cu–Cr/ZSM-5 Zeolite. *Catal. Lett.* **2019**, *150*, 170–177. [[CrossRef](#)]
44. Li, Z.; Su, K.; Ren, J.; Yang, D.; Cheng, B.; Kim, C.K.; Yao, X. Direct catalytic conversion of glucose and cellulose. *Green Chem.* **2018**, *20*, 863–872. [[CrossRef](#)]
45. Wang, J.; Ren, J.; Liu, X.; Xi, J.; Xia, Q.; Zu, Y.; Lu, G.; Wang, Y. Direct conversion of carbohydrates to 5-hydroxymethylfurfural using Sn-Mont catalyst. *Green Chem.* **2012**, *14*, 2506–2512. [[CrossRef](#)]
46. Yang, Y.; Liu, W.; Wang, N.; Wang, H.; Li, W.; Song, Z. Effect of Different Ionic Liquids on 5-Hydroxymethylfurfural Preparation from Glucose in DMA over AlCl_3 : Experimental and Theoretical Study. *Chin. J. Chem.* **2015**, *33*, 583–588. [[CrossRef](#)]
47. Casey, J.P. High Fructose Corn Syrup. A Case History of Innovation. *Starch—Stärke* **2006**, *29*, 196–204. [[CrossRef](#)]
48. Lo, C.; Li, S.; Wang, Y.; Tan, D.; Pan, M.; Sang, S.; Ho, C. Reactive dicarbonyl compounds and 5-(hydroxymethyl)-2-furfural in carbonated beverages containing high fructose corn syrup. *Food Chem.* **2008**, *107*, 1099–1105. [[CrossRef](#)]
49. Jeong, J.; Antonyraj, C.A.; Shin, S.; Kim, S.; Kim, B.; Lee, K.-Y.; Cho, J.K. Commercially attractive process for production of 5-hydroxymethyl-2-furfural from high fructose corn syrup. *J. Ind. Eng. Chem.* **2013**, *19*, 1106–1111. [[CrossRef](#)]
50. Rao, K.T.V.; Souzanchi, S.; Yuan, Z.; Xu, C. One-pot sol–gel synthesis of a phosphated TiO_2 catalyst for conversion of monosaccharide, disaccharides, and polysaccharides to 5-hydroxymethylfurfural. *New J. Chem.* **2019**, *43*, 12483–12493. [[CrossRef](#)]
51. Lin, C.; Wu, H.; Wang, J.; Huang, J.; Cao, F.; Zhuang, W.; Lu, Y.; Chen, J.; Jia, H.; Ouyang, P. Preparation of 5-Hydroxymethylfurfural from High Fructose Corn Syrup Using Organic Weak Acid in Situ as Catalyst. *Ind. Eng. Chem. Res.* **2020**, *59*, 4358–4366. [[CrossRef](#)]
52. Souzanchi, S.; Nazari, L.; Rao, K.T.V.; Yuan, Z.; Tan, Z.; Xu, C. 5-HMF production from industrial grade sugar syrups derived from corn and wood using niobium phosphate catalyst in a biphasic continuous-flow tubular reactor. *Catal. Today* **2023**, *407*, 274–280. [[CrossRef](#)]

53. Zhang, Y.-R.; Li, N.; Li, M.-F.; Fan, Y.-M. Highly efficient conversion of microcrystalline cellulose to 5-hydroxymethyl furfural in a homogeneous reaction system. *RSC Adv.* **2016**, *6*, 21347–21351. [\[CrossRef\]](#)
54. Yan, L.; Ma, R.; Wei, H.; Li, L.; Zou, B.; Xu, Y. Ruthenium trichloride catalyzed conversion of cellulose into 5-hydroxymethylfurfural in biphasic system. *Bioresour. Technol.* **2019**, *279*, 84–91. [\[CrossRef\]](#) [\[PubMed\]](#)
55. Wang, S.; Du, Y.; Zhang, W.; Cheng, X.; Wang, J. Catalytic conversion of cellulose into 5-hydroxymethylfurfural over chromium trichloride in ionic liquid. *Korean J. Chem. Eng.* **2014**, *31*, 1786–1791. [\[CrossRef\]](#)
56. Nogueira, J.S.M.; Santana, V.T.; Henrique, P.V.; Aguiar, L.G.d.; Silva, J.P.A.; Mussatto, S.I.; Carneiro, L.M. Production of 5-Hydroxymethylfurfural from Direct Conversion of Cellulose Using Heteropolyacid/Nb₂O₅ as Catalyst. *Catalysts* **2020**, *10*, 1417. [\[CrossRef\]](#)
57. Cao, Z.; Fan, Z.; Chen, Y.; Li, M.; Shen, T.; Zhu, C.; Ying, H. Efficient preparation of 5-hydroxymethylfurfural from cellulose in a biphasic system over hafnium phosphates. *Appl. Catal. B Environ.* **2019**, *244*, 170–177. [\[CrossRef\]](#)
58. Tang, Z.; Su, J. Direct conversion of cellulose to 5-hydroxymethylfurfural (HMF) using an efficient and inexpensive boehmite catalyst. *Carbohydr. Res.* **2019**, *481*, 52–59. [\[CrossRef\]](#)
59. Wen, Z.; Yu, L.; Mai, F.; Ma, Z.; Chen, H.; Li, Y. Catalytic Conversion of Microcrystalline Cellulose to Glucose and 5-Hydroxymethylfurfural over a Niobic Acid Catalyst. *Ind. Eng. Chem. Res.* **2019**, *58*, 17675–17681. [\[CrossRef\]](#)
60. Chheda, J.N.; Román-Leshkov, Y.; Dumesic, J.A. Production of 5-hydroxymethylfurfural and furfural by dehydration of biomass-derived mono- and poly-saccharides. *Green Chem.* **2007**, *9*, 342–350. [\[CrossRef\]](#)
61. Chun, J.A.; Lee, J.W.; Yi, Y.B.; Hong, S.S.; Chung, C.H. Direct conversion of starch to hydroxymethylfurfural in the presence of an ionic liquid with metal chloride. *Starch—Stärke* **2010**, *62*, 326–330. [\[CrossRef\]](#)
62. Yi, Y.-B.; Ha, M.-G.; Lee, J.-W.; Chung, C.-H. New role of chromium fluoride: Its catalytic action on the synthesis of hydroxymethylfurfural in ionic liquid using raw plant biomass and characterization of biomass hydrolysis. *Chem. Eng. J.* **2012**, *180*, 370–375. [\[CrossRef\]](#)
63. Zhang, Y.; Guan, W.; Song, H.; Wei, Y.; Jin, P.; Li, B.; Yan, C.; Pan, J.; Yan, Y. Coupled acid and base UiO-66-type MOFs supported on g-C₃N₄ as a bi-functional catalyst for one-pot production of 5-HMF from glucose. *Microporous Mesoporous Mater.* **2020**, *305*, 110328. [\[CrossRef\]](#)
64. Cao, J.; Ma, M.; Liu, J.; Yang, Y.; Liu, H.; Xu, X.; Huang, J.; Yue, H.; Tian, G.; Feng, S. Highly effective transformation of carbohydrates to 5-Hydroxymethylfurfural with Al-montmorillonite as catalyst. *Appl. Catal. A Gen.* **2019**, *571*, 96–101. [\[CrossRef\]](#)
65. Fachri, B.A.; Abdilla, R.M.; Rasrendra, C.B.; Heeres, H.J. Experimental and modeling studies on the acid-catalyzed conversion of inulin to 5-hydroxymethylfurfural in water. *Chem. Eng. Res. Des.* **2016**, *109*, 65–75. [\[CrossRef\]](#)
66. Menegazzo, F.; Ghedini, E.; Signoretto, M. 5-Hydroxymethylfurfural (HMF) Production from Real Biomasses. *Molecules* **2018**, *23*, 2201. [\[CrossRef\]](#)
67. Qi, X.; Watanabe, M.; Aida, T.M.; Smith, R.L., Jr. Efficient one-pot production of 5-hydroxymethylfurfural from inulin in ionic liquids. *Green Chem.* **2010**, *12*, 1855–1860. [\[CrossRef\]](#)
68. Heo, J.B.; Lee, Y.-S.; Chung, C.-H. Raw plant-based biorefinery: A new paradigm shift towards biotechnological approach to sustainable manufacturing of HMF. *Biotechnol. Adv.* **2019**, *37*, 107422. [\[CrossRef\]](#)
69. Portillo Perez, G.; Mukherjee, A.; Dumont, M.-J. Insights into HMF catalysis. *J. Ind. Eng. Chem.* **2019**, *70*, 1–34. [\[CrossRef\]](#)
70. Yang, F.; Liu, Q.; Bai, X.; Du, Y. Conversion of biomass into 5-hydroxymethylfurfural using solid acid catalyst. *Bioresour. Technol.* **2011**, *102*, 3424–3429. [\[CrossRef\]](#)
71. Jiang, N.; Qi, W.; Wu, Z.; Su, R.; He, Z. “One-pot” conversions of carbohydrates to 5-hydroxymethylfurfural using Sn-ceramic powder and hydrochloric acid. *Catal. Today* **2018**, *302*, 94–99. [\[CrossRef\]](#)
72. Tang, H.; Li, N.; Chen, F.; Li, G.; Wang, A.; Cong, Y.; Wang, X.; Zhang, T. Highly efficient synthesis of 5-hydroxymethylfurfural with carbohydrates over renewable cyclopentanone-based acidic resin. *Green Chem.* **2017**, *19*, 1855–1860. [\[CrossRef\]](#)
73. Walia, M.; Sharma, U.; Agnihotri, V.K.; Singh, B. Silica-supported boric acid assisted conversion of mono- and poly-saccharides to 5-hydroxymethylfurfural in ionic liquid. *RSC Adv.* **2014**, *4*, 14414–14418. [\[CrossRef\]](#)
74. Cao, L.; Yu, I.K.M.; Tsang, D.C.W.; Zhang, S.; Ok, Y.S.; Kwon, E.E.; Song, H.; Poon, C.S. Phosphoric acid-activated wood biochar for catalytic conversion of starch-rich food waste into glucose and 5-hydroxymethylfurfural. *Bioresour. Technol.* **2018**, *267*, 242–248. [\[CrossRef\]](#) [\[PubMed\]](#)
75. Xu, S.; Pan, D.; Wu, Y.; Xu, N.; Yang, H.; Gao, L.; Li, W.; Xiao, G. Direct Conversion of Wheat Straw Components into Furan Compounds Using a Highly Efficient and Reusable SnCl₂-PTA/ β Zeolite Catalyst. *Ind. Eng. Chem. Res.* **2019**, *58*, 9276–9285. [\[CrossRef\]](#)
76. Shao, Y.; Long, Y.; Zhou, Y.; Jin, Z.; Zhou, D.; Shen, D. 5-Hydroxymethylfurfural production from watermelon peel by microwave hydrothermal liquefaction. *Energy* **2019**, *174*, 198–205. [\[CrossRef\]](#)
77. Piñkowska, H.; Krzywonos, M.; Wolak, P.; Seruga, P.; Górniak, A.; Złocińska, A.; Ptak, M. Sustainable Production of 5-Hydroxymethylfurfural from Pectin-Free Sugar Beet Pulp in a Simple Aqueous Phase System-Optimization with Doehlert Design. *Energies* **2020**, *13*, 5649. [\[CrossRef\]](#)
78. Mo, H.-b.; Chen, X.-p.; Liao, X.-y.; Zhou, T. Sustainable synthesis of 5-hydroxymethylfurfural from waste cotton stalk catalyzed by solid superacid-SO₄²⁻/ZrO₂. *J. Cent. South Univ.* **2017**, *24*, 1745–1753. [\[CrossRef\]](#)
79. Ito, R.; Miyafuji, H.; Miyazaki, Y.; Kawai, T. Production of 5-hydroxymethylfurfural from wood by ionic liquid treatment. *J. Wood Sci.* **2016**, *62*, 349–355. [\[CrossRef\]](#)

80. Slak, J.; Pomeroy, B.; Kostyniuk, A.; Grilc, M.; Likozar, B. A review of bio-refining process intensification in catalytic conversion reactions, separations and purifications of hydroxymethylfurfural (HMF) and furfural. *Chem. Eng. J.* **2022**, *429*, 132325. [[CrossRef](#)]
81. Kougioumtzis, M.A.; Marianou, A.; Atsonios, K.; Michailof, C.; Nikolopoulos, N.; Koukouzas, N.; Triantafyllidis, K.; Lappas, A.; Kakaras, E. Production of 5-HMF from Cellulosic Biomass: Experimental Results and Integrated Process Simulation. *Waste Biomass Valorization* **2018**, *9*, 2433–2445. [[CrossRef](#)]
82. Zhang, Y.-B.; Luo, Q.-X.; Lu, M.-H.; Luo, D.; Liu, Z.-W.; Liu, Z.-T. Controllable and scalable synthesis of hollow-structured porous aromatic polymer for selective adsorption and separation of HMF from reaction mixture of fructose dehydration. *Chem. Eng. J.* **2019**, *358*, 467–479. [[CrossRef](#)]
83. Dietz, C.H.J.T.; Kroon, M.C.; Di Stefano, M.; van Sint Annaland, M.; Gallucci, F. Selective separation of furfural and hydroxymethylfurfural from an aqueous solution using a supported hydrophobic deep eutectic solvent liquid membrane. *Faraday Discuss.* **2018**, *206*, 77–92. [[CrossRef](#)] [[PubMed](#)]
84. Zheng, J.; He, X.; Cai, C.; Xiao, J.; Liu, Y.; Chen, Z.; Pan, B.; Lin, X. Adsorption isotherm, kinetics simulation and breakthrough analysis of 5-hydroxymethylfurfural adsorption/desorption behavior of a novel polar-modified post-cross-linked poly (divinylbenzene-co-ethyleneglycoldimethacrylate) resin. *Chemosphere* **2020**, *239*, 124732. [[CrossRef](#)]

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