

Review

Novel Challenges on the Catalytic Synthesis of 5-Hydroxymethylfurfural (HMF) from Real Feedstocks

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Abstract: The depletion of fossil resources makes the transition towards renewable ones more urgent. For this purpose, the synthesis of strategic platform-chemicals, such as 5-hydroxymethylfurfural (HMF), represents a fundamental challenge for the development of a feasible bio-refinery. HMF perfectly deals with this necessity, because it can be obtained from the hexose fraction of biomass. Thanks to its high reactivity, it can be exploited for the synthesis of renewable monomers, solvents, and bio-fuels. Sustainable HMF synthesis requires the use of waste biomasses, rather than model compounds such as monosaccharides or polysaccharides, making its production more economically advantageous from an industrial perspective. However, the production of HMF from real feedstocks generally suffers from scarce selectivity, due to their complex chemical composition and HMF instability. On this basis, different strategies have been adopted to maximize the HMF yield. Under this perspective, the properties of the catalytic system, as well as the choice of a suitable solvent and the addition of an eventual pretreatment of the biomass, represent key aspects of the optimization of HMF synthesis. On this basis, the present review summarizes and critically discusses the most recent and attractive strategies for HMF production from real feedstocks, focusing on the smartest catalytic systems and the overall sustainability of the adopted reaction conditions.

Keywords: 5-hydroxymethylfurfural; waste biomass; catalytic conversion; solvent system; biomass pretreatment

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1. Introduction

The strong dependence on fossil resources has produced several economic, social, and environmental problems, such as their progressive depletion, as well as environmental issues. All these problems are becoming even more relevant, considering that the global energy demand is expected to increase up to 37% by 2040 [1]. Therefore, to reduce dependence on fossil resources, the exploitation of renewable ones will be of paramount importance in both scientific and industrial communities. In particular, the exploitation of biomass to create valuable products has attracted great interest in recent years, because it is the only renewable carbon-based and abundant feedstock, with a global production of about 120 billion tons per year [2]. In this perspective, 5-hydroxymethylfurfural (HMF) is considered a versatile key platform-chemical, potentially synthesizable from carbohydrate-rich biomasses. The HMF chemical structure consists of a furanic ring, an aldehyde, and an alcohol group (Figure 1), thus resulting in a particularly reactive molecule, exploitable for the synthesis of many added-value chemicals, ranging from monomers, bio-fuels, and food additives to pharmaceuticals [2].

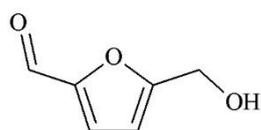


Figure 1. Chemical structure of HMF.

It is well-known that hexoses, such as fructose and glucose, are effective feedstocks for HMF production. Remarkably, fructose is a direct precursor of HMF, so its use as the starting feedstock allows the achievement of higher selectivity than glucose [3]. However, the availability of fructose in nature is quite limited, resulting in an expensive feedstock for HMF production, while the employment of glucose or, even better, the cellulosic fraction of the abundant biomass, should be preferred. Considering the synthesis of HMF from cellulose, it generally involves three fundamental steps, each catalyzed by a specific acidity: (i) hydrolysis of cellulose into glucose, catalyzed by Brønsted acid; (ii) isomerization of glucose to fructose, catalyzed by Lewis acid or Brønsted base; (iii) dehydration of fructose to HMF, catalyzed by Brønsted acid (Figure 2).

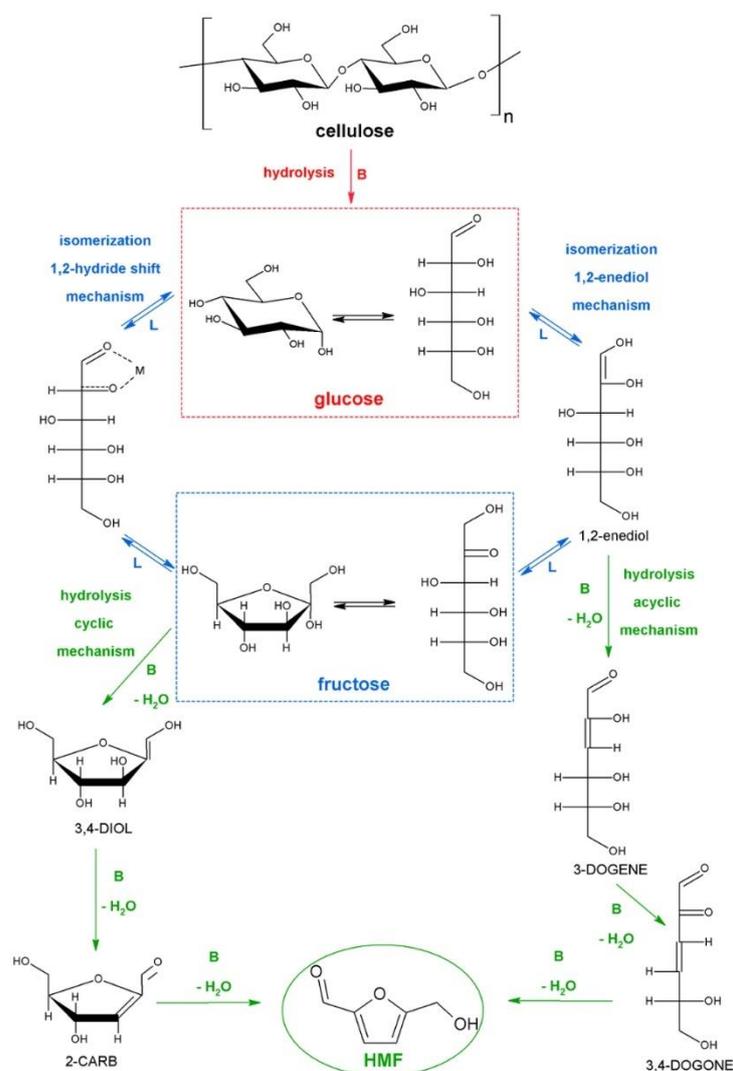


Figure 2. Mechanism of HMF synthesis from cellulose, carried out in the presence of both Brønsted (B) and Lewis (L) acids. “M” stands for “metal center”.

In the first step, the protons released by the Brønsted acid break the C–O bonds of the β -1,4-glycosidic bonds, thus leading to the formation of glucose [4]. Then, depending

on the catalytic system, glucose can be isomerized to fructose or it can be directly converted to HMF (Figure 3), but, in both cases, this represents the rate-limiting step of the whole process. When a Lewis acid is employed in combination with a Brønsted acid, the isomerization route is promoted via the 1,2-enediol or 1,2-hydride shift mechanism [5]. The isomerization involving 1,2-enediol formation usually occurs through the formation of a catalyst–monosaccharide complex, whereas the 1,2-hydride shift mechanism involves coordination between a carbonyl group, an alcoholic hydroxyl group, and a Lewis acid center, generally represented by a metal center (M) (Figure 2). On the other hand, when only a Brønsted acid is adopted, the direct conversion of glucose to HMF takes place by the mechanism reported in Figure 3 [6].

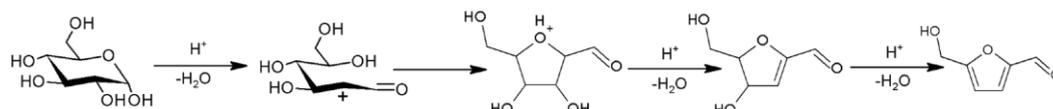


Figure 3. Mechanism of direct HMF synthesis from glucose, catalyzed by Brønsted acid.

The isomerization of glucose to fructose leads to higher selectivities in HMF, thus the combination of Brønsted and Lewis acids is the most investigated strategy for HMF synthesis [7]. Finally, regarding the pathway of fructose dehydration to HMF, two different mechanisms have been proposed in the literature, the acyclic and the cyclic ones (Figure 2). In the acyclic mechanism, the open-chain structure of fructose is in equilibrium with the 1,2-enediol that undergoes two consecutive dehydration steps, generating 3-deoxyglucos-2-ene (3-DOGENE) and 3,4-deoxyglucosone (3,4-DOGONE), followed by a chain closure, resulting in the elimination of the last molecule of water, thus affording HMF as the final product [8,9]. On the other hand, according to the cyclic mechanism, the first step involves the dehydration of D-fructofuranose at the C2 position to form a tertiary carbenium cation, which is further converted to 2-(hydroxymethyl)-5-(hydroxymethylene)tetrahydrofuran-3,4-diol (3,4-DIOL) and then to 4-hydroxy-5-(hydroxymethyl)-4,5-dihydrofuran-2-carbaldehyde (2-CARB). Finally, the latter undergoes further dehydration to form HMF [8]. At the moment, the most accepted mechanism is the cyclic one. In fact, under the same reaction conditions, fructose is more reactive and selective toward HMF than glucose, probably due to their different conformations in water [10]: in this solvent, glucose is almost found in the stable pyranose structure, whereas fructose results for 21% in the furanose conformation, making it promptly available for HMF synthesis, according to the cyclic mechanism shown in Figure 2. For this reason, glucose isomerization to fructose, catalyzed by a Brønsted base or a Lewis acid, is necessary to obtain a high HMF yield starting from glucose, thus underlining the importance of fructose as the precursor of HMF [11,12]. On the other hand, according to the acyclic mechanism, glucose and fructose have in common the formation of 1,2-enediol as an intermediate, and this aspect cannot explain the different reactivity and selectivity experimentally observed in the two sugars. The same conclusions in support of the cyclic mechanism are confirmed working in organic solvents. For instance, Akien et al. studied the dehydration of fructose in DMSO and other organic solvents by the ^{13}C NMR, confirming the presence of 2-(hydroxymethyl)-5-(hydroxymethylene)tetrahydrofuran-3,4-diol (3,4-DIOL), whose formation is ascribable to the cyclic pathway [13] (Figure 2).

A critical point of HMF synthesis is given by the several obtainable by-products, such as levulinic and formic acids, originating from the subsequent rehydration of HMF (Figure 4) [14], but also black tarry by-products, known as humins, characterized by a very complex structure mainly including furanic, aromatic, and oxygen-containing functionalities, such as carboxyl, carbonyl, and hydroxyl ones [15,16].

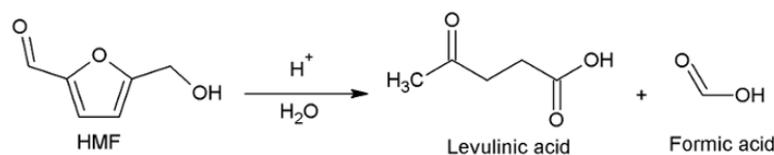


Figure 4. Rehydration of HMF to levulinic and formic acids.

It is well-known that humins formation is strongly activated by a combination of high temperature and acidity [15,17]. However, up to now, the mechanism of their formation has still not been clarified, due to the complex composition of the reaction medium, which includes hexose, HMF, and degradation products, all these components potentially being involved in the reaction mechanism. From an economical and technological perspective, the formation of these by-products is strongly undesired, because it worsens HMF selectivity, making its separation and purification much more difficult. However, several recent studies focused on the valorization of humins in different fields, such as in environmental remediation, as support for catalysts and the preparation of foams and adhesives, thus turning the problem of their formation into a partial advantage [16,18,19].

As mentioned above, the importance of HMF is due to its importance as the precursor of many added-value bio-products, as reported in Figure 5.

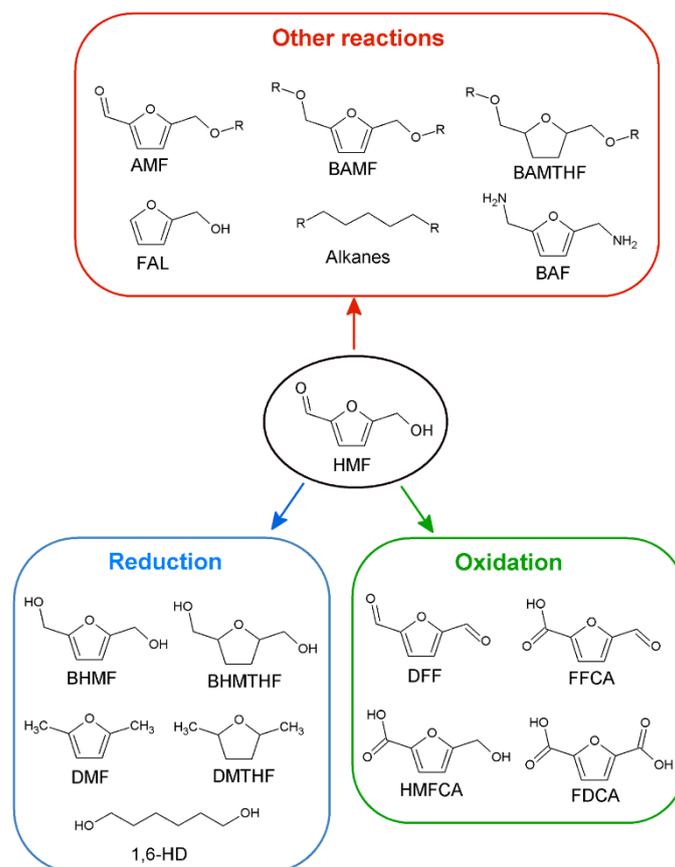


Figure 5. Possible pathways for the production of added-value bio-products from HMF.

The two pathways of greatest interest are oxidation and reduction. The first one allows the production of many important HMF derivatives: 5-formyl-2-furancarboxylic acid (FFCA), having promising applications as fuel and chemical intermediate [20]; 5-hydroxymethyl-2-furancarboxylic acid (HMFCA), exploitable for the production of furanic polyesters and anticancer agents [21]; 2,5-diformylfuran (DFF), which finds ap-

plication in the production of novel polymers, antifungal agents, and medical intermediates [22]; and in particular, 2,5-furandicarboxylic acid (FDCA) [23,24], an important renewable alternative to terephthalic acid for the preparation of bio-based polymers, such as polyethylene furanoate (PEF), the bio-based alternative replacing polyethylene terephthalate (PET) [25]. In addition, this dicarboxylic acid can be further converted into adipic acid, a key monomer for the synthesis of nylon 6,6 [26]. On the other hand, the reductive pathway allows the production of monomers for the synthesis of polyurethanes and polyesters, such as 2,5-bis(hydroxymethyl)furan (BHMF) [27,28]; 2,5-bis(hydroxymethyl)tetrahydrofuran (BHMTHF) [27–29]; 1,6-hexanediol (1,6-HD) [28,30] (which is also employed as an additive in plastics and as a precursor of caprolactone [31]); and bio-fuels, such as 2,5-dimethylfuran (DMF) [32,33] and 2,5-dimethyltetrahydrofuran (DMTHF) [33]. Moreover, HMF and its derivatives can also undergo other reactions, such as etherification, to give 5-alkoxymethylfurfural (AMF) [34,35], 2,5-bis(alkoxymethyl)furan (BAMF) [36,37], and, very recently, 2,5-bis(alkoxymethyl)tetrahydrofuran (BAMTHF) [36], all employable as bio-fuels. HMF can also be involved in aldol condensation and hydrodeoxygenation reactions to produce long-chain alkanes; to be used as fuels [38]; to be used in a decarbonylation reaction to obtain furfuryl alcohol (FAL), which can be adopted as a monomer for the production of furan resin [39]; finally, to be used in a reductive amination reaction to give 2,5-bis(aminomethyl)furan (BAF), a promising monomer for the synthesis of polyurethanes and polyamides [40].

However, despite the great interest in HMF and its derivatives, no large-scale HMF plant is still running, mainly due to its high production costs, reflected in the high HMF selling cost (about 3500 €/kg in 2019) [41,42]. In fact, up to now, most of the bio-refinery approaches proposed for HMF production involve the use of pure first-generation feedstocks, such as hexose sugars, which are more favorable but too expensive for the synthesis of HMF, compared with cheap lignocellulosic biomass, wherein the strong interactions between cellulose, hemicellulose, and lignin hinder the reaction [43]. On this basis, it is evident that the development of a bio-refinery process that exploits raw biomasses as starting feedstocks is a challenge of great relevance to render the production of HMF cost-effective in the future. From this perspective, AVA Biochem, a subsidiary of AVALON Industries AG, is the pioneer in the industrial production of HMF, having in Muttenz (Switzerland) a plant with an operating capacity of about 300 tonnes per year. This company has patented a process for the conversion of lignocellulosic biomass to HMF through the hydrothermal carbonization (HTC) route [44]. According to this process, the substrate is subjected to HTC under high temperature and pressure, producing two main streams, (1) the char, that can be used as an energy source [45], and (2) the HMF aqueous solution. The latter is then extracted with a solvent in a counter-current mix-settler column, followed by a distillation step [46]. On this basis, HMF is produced as a co-product of the char, making the whole process more economically sustainable and allowing the HTC technology to be scaled-up at commercial small scale to produce HMF. However, in addition to the challenge of the employment of raw lignocellulosic biomass, the scale-up of HMF production at large scale requires the solution of other technological problems, such as the formation of by-products, in particular solid humins, and the separation of HMF from the reaction medium and its further purification. By-products formation strongly depends on the adopted reaction conditions, which also affects the separation and purification steps and, consequently, the process costs. Also for these reasons, the majority of the available HMF processes are still at a very early stage of development and the reaction media and process parameters are the main focus of the next optimization studies [47].

Therefore, several studies have been reported, aimed at the synthesis of HMF starting from raw biomasses, investigating the influence of homogeneous/heterogeneous catalysts, solvent systems, heating methods, and pretreatment steps on HMF yield. However, to date, the published reviews have mainly focused on the synthesis of HMF

from model compounds, such as monosaccharides, disaccharides, and polysaccharides, [5,7,48–52], and the most recent review regarding the synthesis of HMF from biomasses dated back to 2018 [53]. Nevertheless, new achievements in this field are constantly obtained; thus, an in-depth and up-to-date review summarizing the most recent results on the synthesis of HMF from raw biomass is missing. On this basis, this review aims to emphatically discuss the effect of different reaction parameters on the HMF yield reached starting from a real substrate, to make sustainable the rational employment of raw or waste biomasses.

2. Synthesis of HMF from Raw Biomass

Biomasses are mainly composed of three biopolymers: hemicellulose (20–35 wt%), cellulose (30–50 wt%), and lignin (15–20 wt%). Hemicellulose is a heteropolysaccharide, consisting of both pentoses, such as D-xylose and L-arabinose; hexoses, such as D-glucose, D-galactose, and D-mannose; and uronic acids, such as D-glucuronic and D-galatturonic acids. Its structure includes several ramifications, which make it prone to hydrolysis [54]. Instead, cellulose is the linear homopolymer of D-glucose, making it the most important source of hexoses and, therefore, an ideal candidate for HMF production. The units of glucose are linked through β -(1,4) glycosidic bonds, which make it stable and stiff. The D-glucose units of cellulose are also engaged in the formation of intra- and inter-molecular hydrogen bonds among the hydroxyl groups, giving crystallinity to its structure, which is responsible for its low solubility in water and its elevated mechanical and chemical stability. In addition, cellulose is characterized by the presence of amorphous domains that result in it being more easily accessible to water than crystalline ones, thus requiring milder hydrolysis conditions than the latter [55]. Lignin is a three-dimensional highly cross-linked polymer composed of three types of phenylpropanolic monomers (*p*-cumaryl alcohol, coniferyl alcohol, and synapyl alcohol) linked through carbon–carbon and ether bonds. Lignin is fundamental for conferring good mechanical resistance to the biomass but its chemical stability, together with the crystallinity of cellulose, makes biomass mostly recalcitrant towards the conversion [56]. For this reason, in addition to the high instability of HMF in water under acidic conditions, the synthesis of HMF from waste biomasses is still challenging, and several strategies have been proposed, aiming at the optimization of HMF selectivity. Generally, the variables that influence HMF production are the presence of a pretreatment step, the type of solvent, the biomass loading, and the adopted catalytic system. In fact, as will be better explained in Section 2.2, the pretreatment favors the deconstruction of the lignocellulosic matrix, thus improving the interaction between the catalyst and the cellulose fraction and hence increasing the conversion rate of cellulose to HMF [3]. On the other hand, the type of solvent plays a key role in directing the selectivity of the process, in some cases inhibiting the side reactions (rehydration of HMF and humins formation) but also showing synergistic effects with the catalyst or having catalytic effects by itself [3]. On this basis, several solvent systems have been adopted for the synthesis of HMF from waste biomasses, such as water, organic solvents (both protic and aprotic ones), biphasic systems involving water as the reaction medium and an organic solvent as the extraction one, and innovative solvents such as ionic liquids and deep eutectic solvents. Finally, the properties of the catalyst, mainly in terms of amount and type of acidity, strongly influence the reaction, having a key effect on HMF selectivity. In this regard, both homogeneous and heterogeneous systems have been investigated for the production of HMF from biomasses. Generally, homogeneous catalysts have better performance and low cost but their recycling is more difficult than heterogeneous ones, which, on the other hand, have a limited contact with a possible substrate, thus resulting in less efficiency. Anyway, the increase in biomass loading causes an increase in HMF concentration but also a decrease in its molar yield, due to the higher extent of by-products formation.

To highlight the different approaches adopted up to now for the synthesis of HMF from real biomasses, the literature references have been commented on in the following

paragraphs, considering the presence of a pretreatment step, the type of solvent system, and the employed catalyst. The HMF yield, unless otherwise specified, has been reported as mol% and calculated as follows:

$$Y_{\text{HMF}} (\text{mol}\%) = [(\text{HMF moles})/(\text{anhydroglucose moles in biomass})] \times 100$$

2.1. Not Pretreated Biomass

2.1.1. One-Solvent Systems

Table 1 summarizes the available data for the synthesis of HMF from not-pretreated biomasses in one-solvent systems, including both water and organic systems.

Table 1. HMF production starting from raw biomasses in one-solvent systems.

Entry	Feedstock (wt%)	Catalyst (wt _{biomass} /wt _{catalyst})	Solvent	T (°C)	t (min)	Heat ¹	Y _{HMF} (mol%)	Ref
1	Food waste (4.0%)	/	H ₂ O	230	15	MW	7	[57]
2	Sugar beet thick juice (14.7%)	H ₂ SO ₄ (166.7)	H ₂ O	180	106	Conv.	27	[58]
3	Mango pulp and skin (5.0%)	H ₂ SO ₄ (1000.0)	H ₂ O	150	20	MW	21	[59]
4	Spruce wood (2.4%)	H ₂ SO ₄ (5.1)	H ₂ O	200	40	Conv.	10	[60]
5	Beach wood (2.4%)	H ₂ SO ₄ (5.1)	H ₂ O	200	40	Conv.	11	[60]
6	Recycled pulp paper towel waste (5.0%)	H ₂ SO ₄ (3.8)	H ₂ O	200	5	MW	6	[61]
7	Macroalgae <i>Gracilaria verrucosa</i> sp. (6.3%)	H ₂ SO ₄ (20.8)	H ₂ O	175	35	Conv.	18	[62]
8	Poppy stalks (4.8%)	CuCl ₂ (12.5)	H ₂ O	200	60	Conv.	12	[63]
9	Microalgae <i>Chlorella</i> sp. (5.0%)	Al ₂ (SO ₄) ₃ (1.3)	H ₂ O	165	30	Conv.	23	[64]
10	Corn cob (1.5%)	ZnCl ₂ nH ₂ O (0.5) + HCl (75.0)	H ₂ O	1°: 80 2°: 120	1°: 300 2°: 60	Conv.	30	[65]
11	Softwood chips (1.5%)	ZnCl ₂ nH ₂ O (0.5) + HCl (75.0)	H ₂ O	1°: 80 2°: 120	1°: 300 2°: 60	Conv.	22	[65]
12	Algae <i>Ulva lactuca</i> sp. (2.5%)	ZnCl ₂ nH ₂ O (0.8) + HCl (122.0)	H ₂ O	1°: 80 2°: 120	1°: 300 2°: 60	Conv.	25	[65]
13	Algae <i>Porphyridium cruentum</i> sp. (4.3%)	ZnCl ₂ nH ₂ O (1.4) + HCl (217.0)	H ₂ O	1°: 80 2°: 120	1°: 300 2°: 60	Conv.	35	[65]
14	Vegetable waste (5.0%)	Amberlyst-36 (1.0)	H ₂ O	120	5	MW	5	[66]
15	Macroalgae <i>Gracilaria verrucosa</i> sp. (11.7%)	Amberlyst-15 (6.7)	H ₂ O	130	120	Conv.	19	[67]
16	Sugarcane bagasse (4.8%)	D001-cc ion-exchange resin (1.0)	H ₂ O	140	25	MW	9	[68]
17	Sugarcane bagasse (4.8%)	D001-cc ion-exchange resin (1.0)	DMSO	140	25	MW	18	[68]
18	Waste fluff (2.0%)	BT300S ² (2.0)	H ₂ O	200	120	Conv.	64	[69]
19	Cotton linter (2.0%)	BT300S ² (2.0)	H ₂ O	200	240	Conv.	29	[69]
20	Corn straw (2.0%)	BT300S ² (2.0)	H ₂ O	200	60	Conv.	52	[69]
21	Sugarcane bagasse (1.1%)	SPPTPA ³ (5.0)	DMSO	140	60	MW	20 ⁴	[70]
22	Sugarcane	SPPTPA ³ (5.0)	NMP ⁵	140	60	MW	19 ⁴	[70]

23	bagasse (1.2%) Corncob (1.3%)	SPPTPA ³ (4.2)	GVL	175	30	Conv.	32	[71]
24	Used clothing (0.7%)	Ca ₃ (PO ₄) ₂ (0.1)	H ₂ O	200	120	Conv.	10	[72]
25	Used paper (0.7%)	Ca ₃ (PO ₄) ₂ (0.1)	H ₂ O	200	120	Conv.	8	[72]
26	Japanese cedar (1.5%)	Ca ₃ (PO ₄) ₂ (0.26)	H ₂ O	200	120	Conv.	14	[72]
27	Waste cotton stalks (3.2%)	SO ₄ ²⁻ /ZrO ₂ (3.3)	H ₂ O	230	75	Conv.	27	[73]
28	Microalgae <i>Chlorococcum sp.</i> (1.0%)	H-ZSM-5 (1.5)	H ₂ O	200	120	Conv.	39	[74]
29	Wood ear mushroom (5.0%)	[NMP][CH ₃ SO ₃] ⁶ (5.5)	DMA ⁷ -LiCl	140	2	MW	58	[75]
30	Wood ear mushroom (5.0%)	[DMA][CH ₃ SO ₃] ⁸ (5.5)	DMA ⁷ -LiCl	140	2	MW	64	[75]
31	Wood ear mushroom (5.0%)	[BBIM-SO ₃ H][OTf] ⁹ (5.5)	DMA ⁷ -LiCl	140	2	MW	63	[75]
32	Wood ear mushroom (5.0%)	[BBIM-SO ₃ H][NTf ₂] ¹⁰ (5.5)	DMA ⁷ -LiCl	140	2	MW	69	[75]

¹ “Conv.” and “MW” stand for “Conventional” and “Microwave”. ² Wheat-straw-derived sulfonated solid acid carbonaceous catalyst. ³ Highly porous polytriphenylamine sulfonated. ⁴ Calculated as wt%. ⁵ N-methyl-2-pyrrolidone. ⁶ N-methyl-2-pyrrolidone methylsulfonate. ⁷ N,N-dimethylacetamide. ⁸ N,N-dimethylacetamide methylsulfonate. ⁹ 1-butyl-3-(4-sulfobutyl)imidazolium trifluoromethanesulfonate. ¹⁰ 1-butyl-3-(4-sulfobutyl)imidazolium bis((trifluoromethyl)sulfonyl)amide.

Within one-solvent systems, water is the most used. In fact, water is abundant, cheap, environmentally compatible, non-toxic, and non-flammable, thus being the preferred choice. Moreover, according to the mechanism reported in the Introduction Section, water can promote the hydrolysis of cellulose to glucose, which is the first step in biomass conversion. Although the employment of an acid catalyst is generally involved, recently the autocatalytic conversion of a real feedstock, properly a food waste, has also been investigated for the synthesis of HMF, working at high temperature (230 °C) under MW irradiation and reaching a modest HMF yield of 7 mol% (run 1, Table 1) [57]. However, due to the scarce efficiency of the autocatalytic reaction, this represents an isolated example. On the other hand, a large variety of catalysts have been tested for the conversion of not-pretreated biomass, in particular mineral acids, such as H₂SO₄, which is the most effective at HMF production from simple sugars [3]. Abdilla-Santes et al. carried out the conversion of a sugar beet thick juice rich in sucrose, reaching an HMF yield of 27 mol% (run 2, Table 1), higher than that obtained starting from pure sucrose, under the same reaction conditions (about 18 mol%), thanks to a lower formation of by-products (levulinic acid and humins) [58]. This has been addressed to the presence of sulfate ions in the thick juice, which can react with monoalcohol groups of the reaction intermediates, stabilizing them [76] and thus preventing by-products formation. Muñoz-Valencia et al. performed the reaction starting from mango pulp and skin under milder reaction conditions, in terms of sulfuric acid concentration and temperature, with the support of the MW heating that allowed the reduction of reaction time (run 3, Table 1) [59]. Mango waste’s sugar profile is mainly composed of sucrose and, in lesser amounts, fructose and glucose, disaccharides and monosaccharides, that can be more easily converted to HMF, reaching a yield of 21 mol%. Although promising results were obtained from the sugar beet thick juice and mango waste, the most employed feedstocks are lignocellulosic biomasses. Anyway, these are more recalcitrant than the previous ones, due to their complex structure, thus requiring harsher reaction conditions, mainly in terms of higher acid concentrations, to obtain satisfactory HMF yields. Świątek et al. performed the reaction in

a semi-continuous process starting from spruce and beach woods, reaching a HMF yield of 10 and 11 mol%, respectively, working at 200 °C and employing a biomass/catalyst weight ratio of 5.1 (runs 4 and 5, Table 1) [60]. Dutta et al. carried out the conversion of recycled pulp paper towel in a MW reactor under analogous reaction conditions in terms of temperature and biomass/catalyst weight ratio, but, in this case, the prevailing products were glucose and levulinic acid, and HMF with a yield of only 6 mol% (run 6, Table 1) [61]. Another kind of feedstock that is attracting great interest is algal biomass. In fact, algae grow quickly, and their cultivation does not require the use of fertilizers or other inputs, and their use can contribute to reducing the environmental problem of coastal eutrophication. Algae contain many carbohydrates and a low amount of lignin, resulting in a cheap and easy hydrolyzable feedstock. Jeong et al. proposed the red algae *Gracilaria verrucosa* as a substrate for HMF synthesis catalyzed by H₂SO₄ (run 7, Table 1) [62]. *Gracilaria verrucosa* is composed of agar, a polymer made up of D-galactose and 3,6-anhydrogalactopyranose units, both easily hydrolyzable to HMF. The authors optimized the HMF synthesis through a five-level three-factor central composite rotatable experimental design, reaching the highest yield of 18 mol%. Remarkably, the authors highlighted that the HMF production was promoted by short reaction time/low reaction temperature/low catalyst concentration, the two latter parameters being more influential than the reaction time.

Furthermore, inorganic salts, characterized by the presence of Brønsted and Lewis acid sites, have been employed as homogeneous catalysts. For example, different chlorides were tested by Hoşgün for the conversion of poppy stalks, and CuCl₂ strongly catalyzed the reaction, despite being a divalent chloride (run 8, Table 1) [63]. In fact, it is well-known that higher amounts of chloride ions improve cellulose conversion, so trivalent metal chlorides should be preferred over divalent ones [77]. However, according to Hoşgün, sugars form with Cu²⁺ a more stable complex than those with other divalent metals, due to the Jahn–Teller distortion [78], which is responsible for the characteristic activity of CuCl₂. Jeong et al. tested aluminum sulfate as the catalyst for the conversion of the microalgae *Chlorella*, which was optimized by a Box–Behnken design, evaluating the reaction temperature, the catalyst amount, and the reaction time as the independent variables (run 9, Table 1) [64]. The optimized reaction conditions, corresponding to low temperature, low catalyst amount, and low/medium reaction time, allowed the achievement of a maximum HMF yield of 23 mol%. Moreover, a combination of inorganic salts with mineral acids could be an even more promising strategy, because it allows the tuning of the Brønsted and Lewis acidities, as reported by Bodachivskyi et al. [65]. These authors carried out the conversion of two lignocellulosic biomasses (corn cob and softwood chips) and two algae (*Ulva lactuca* and *Porphyridium cruentum*), which were catalyzed by combining ZnCl₂ and HCl (runs 10–13, Table 1). The authors found that the acidity of ZnCl₂ strongly depends on the level of hydration: lower hydration states ($n = 2–3$) correspond to stronger acidity, while higher hydration states ($n = 3.25–4.5$) correspond to milder acidity. For this reason, ZnCl₂·4.25 H₂O was efficient towards the dissolution of microcrystalline cellulose, selectively providing HMF and avoiding the formation of humins. However, the addition of HCl further improved the HMF yield, and this combined system (ZnCl₂·4.25 + HCl) was tested by the authors on different biomasses (runs 10–13, Table 1) in two steps, the first one at mild temperature (80 °C) and the second one at higher temperature (120 °C), to hydrolyze the biomasses to glucose and convert the latter to HMF, respectively. Under these reaction conditions, the conversion of the softwood chips (run 11, Table 1) was less efficient than that of the other biomasses, due to its recalcitrance, leading to an HMF yield of 22 mol%. However, in this case, the possible formation of humins has not been considered. Besides, heterogeneous catalysts have been widely adopted for HMF synthesis from real feedstocks, but, in this case, the interaction of the catalyst with biomass was less efficient, due to the mass transfer issue. Regarding heterogeneous systems, sulfonated solid acid catalysts were efficient in HMF synthesis from biomasses. In this regard, Chen et al. adopted amberlyst-36 for the hy-

hydrolysis of vegetable wastes under MW heating, reaching an HMF yield of 5 mol% and proving that HMF could be formed via direct glucose dehydration, without the intermediate production of fructose (run 14, Table 1) [66]. Jeong et al. used amberlyst-15 for the conversion of the macroalgae *Gracilaria verrucosa*, achieving a promising HMF yield of 19 mol%, probably due to the high amount of galactose that can be converted to HMF more easily than glucose (run 15, Table 1) [67]. Li et al. carried out HMF synthesis from sugarcane bagasse in the presence of the commercial D001-cc ion-exchange resin, under MW heating (runs 16 and 17, Table 1) [68]. This resin has pores with a large enough size to enable a large contact area between the substrate and the catalyst active sites, thus improving the biomass conversion to HMF. The authors performed the reaction in water and DMSO, obtaining maximum HMF yields of 8 and 18 mol%, respectively, proving that the organic solvent hampered HMF degradation. Not only commercial sulfonated heterogeneous catalysts have been adopted but also synthesized sulfonated catalysts obtained, for example, from wastes, as reported in the work of Ozsel et al., who prepared the catalyst by the sulfonation of wheat straw carbonaceous residue (runs 18–20, Table 1) [69]. The obtained catalyst (BT300S) was characterized by an elevated acid density (1.76 mmol/g of $-\text{SO}_3\text{H}$ group), making it active towards the hydrolysis reaction. The synthesized sulfonated catalyst was able to interact with the carbohydrate substrate mainly through: (i) hydrogen bonds between the $-\text{OH}$ groups of carbohydrates and the oxygenated functional groups on the catalyst surface ($-\text{COOH}$ and $-\text{OH}$) and (ii) van der Waals forces between the CH groups of carbohydrates and the aromatic rings of the carbon structure of the catalyst. This catalyst was employed in the conversion of several biomasses (waste fluff, cotton linter, and corn straw) at 200 °C, reaching very promising yields at different reaction times, ascribable to the different chemical compositions and cellulose crystallinities of the three biomasses. For example, the extension of the reaction time up to 240 min for the conversion of cotton linter was necessary to reach a high HMF yield, due to the high degree of cellulose crystallinity in the adopted biomass (loading of only 2 wt%). This is reflected in the percentage of cotton linter hydrolysis at 200 °C, which was only 27 wt%, lower than that achieved under the same reaction conditions from corn straw and waste fluff, equal to 61 and 43 wt%, respectively. Mondal et al. prepared a highly porous polytriphenylamine sulfonated catalyst (SPPTPA), which was used for the conversion of sugarcane bagasse in organic solvents, such as DMSO and N-methylpyrrolidone (NMP), under MW irradiation, leading to HMF yields of about 20 mol%, probably thanks to the good MW-absorbing ability of these solvents (runs 21 and 22, Table 1) [70]. The same catalyst was also adopted, with better performance in the conversion of corncob under conventional heating in the renewable solvent GVL, which is particularly active towards HMF synthesis, a hydrophilic lactone, which is generally more suitable than the hydrophobic ones in this reaction (run 23, Table 1) [71]. Furthermore, heterogeneous catalysts having both Brønsted acid/basic sites and Lewis acid sites have also been adopted for HMF synthesis from raw biomasses. Mimura et al. performed the conversion of several wastes and natural cellulose-based materials, in particular used clothing, used paper, and Japanese cedar, proposing the inorganic catalyst $\text{Ca}_3(\text{PO}_4)_2$ but reaching a modest HMF yield of 10, 8, and 14 mol%, respectively, despite the low substrate loadings (0.7–1.5 wt%) (runs 24–26, Table 1) [72]. As reported in Figure 2, the conversion of cellulose to HMF generally requires: (i) hydrolysis of cellulose to glucose, catalyzed by Brønsted acids; (ii) isomerization of glucose to fructose, catalyzed by Lewis acids or Brønsted bases; (iii) conversion of fructose to HMF, catalyzed by Brønsted acids. For this reason, $\text{Ca}_3(\text{PO}_4)_2$ was an active catalyst of HMF synthesis from cellulose-based materials, having both Brønsted acid sites, due to the PO_4^{3-} groups, and base sites, ascribed to the Ca–O groups. A higher HMF yield of 27 mol% was claimed by Mo et al., who carried out the conversion of waste cotton stalks to HMF with the super acid $\text{SO}_4^{2-}/\text{ZrO}_2$, which was stable after four cycles, giving a yield of 25 mol% (run 27, Table 1) [73]. The heterogeneous catalysts with both Brønsted and Lewis acid sites have been adopted for the conversion of algae in an aqueous medium. Wang et al. carried out HMF

synthesis starting from the microalgae *Chlorococcum* sp., working at low biomass loading (1 wt%) and in the presence of the commercial H-ZSM-5 zeolite, which led to a good HMF yield (39 mol%). This yield was higher than that achieved with H₂SO₄ (10 mol%), working under the same reaction conditions, thus confirming the importance of both types of acid sites for improving HMF production (run 28, Table 1) [74]. Moreover, the authors found that HMF was particularly stable during the conversion of microalgae, which is ascribable to the presence of proteins and lipids in the reaction mixture deriving from the disruption of the adopted biomass. In fact, proteins partially occupied the acid sites, thus preventing the rehydration of HMF to levulinic and formic acids, whereas hydrophobic lipids formed a micro-biphasic system with water, moving HMF away from acid sites [79]. These results are interesting because they show that complicated separation and purification steps of microalgae from nutrients are not necessary and that raw *Chlorococcum* sp. can be directly employed as feedstock for HMF production. Lastly, a N,N-dimethylacetamide–lithium chloride (DMA–LiCl) medium was reported as an efficient solvent system for the conversion of wood ear mushrooms, carried out in the presence of different ionic liquids as catalysts. Literature reports that this medium is effective towards biomass dissolution, due to the formation of (DMA)_nLi⁺ macrocations. The latter lead to a higher concentration of Cl[−] ions that can interact with –OH groups of biomass, promoting the disruption of intra and inter-chain H-bonds of polysaccharides [80]. Moreover, the adopted Brønsted acid ionic liquids also promote the biomass conversion by donating protons, and their effectiveness, depending on their different proton donating abilities, follows the order: [BBIM-SO₃][NTf₂] > [DMA][CH₃SO₃] > [BBIM-SO₃][OTf] > [NMP][CH₃SO₃] (runs 29–32, Table 1) [75]. At the end of the reaction, HMF was obtained in high yield (about 60 mol%), and then it was separated through diethyl ether extraction. The reaction mixture, containing the spent catalyst and DMA–LiCl, was recycled, and only a slight decrease of HMF yield of about 5 mol% was obtained after three cycles, proving that the ionic liquids can be effectively recycled.

2.1.2. Ionic Liquids (ILs) and Deep Eutectic Solvents (DESs)

The complex structure of lignocellulosic biomass hampers its solvation and conversion in conventional solvents (water and organic systems), so alternative ones, such as ionic liquids (ILs) and deep eutectic solvents (DES), have recently attracted great interest. ILs are organic salts typically composed of large cations and small anions, which can destroy the hydrogen bonds network between the polysaccharides, at the same time improving the solvation and acting as catalysts [81]. However, ILs show some drawbacks, such as difficult synthesis, low biodegradability, high cost, and low vapor pressure, the latter making HMF recovery through distillation unfeasible. Therefore, recent research has developed a new type of ionic liquid, called DES. In general, DESs are composed of a hydrogen bond acceptor, usually a quaternary ammonium salt such as choline chloride (ChCl), and a hydrogen bond donor, such as urea, citric acid, and glycerol [82]. DESs originating from the combination of ChCl with one of these hydrogen bond donors are cheap and eco-friendly and have low vapor pressure, thus being more attractive than ILs for the synthesis of HMF from real biomasses [83]. Table 2 summarizes the available data for HMF synthesis from not-pretreated biomasses in ionic liquids and deep eutectic solvents.

Table 2. HMF production from raw biomasses in ionic liquids and deep eutectic solvents.

Entry	Feedstock (wt%)	Catalyst (wt _{biomass} /wt _{catalyst})	Solvent	T (°C)	t (min)	Heat ¹	Y _{HMF} (mol%)	Ref
33	Wood chips (4.8%)	CrCl ₃ ·6H ₂ O (1.3)	[BMIM]Cl ²	120	120	Conv.	41	[84]
34	Rice straw (4.8%)	CrCl ₃ ·6H ₂ O (1.3)	[BMIM]Cl ²	120	120	Conv.	35	[84]
35	Wheat straw (10.0%)	CrCl ₃ (1.2)	[BMPy]Cl ³	130	120	Conv.	50	[85]
36	Rice husk (10.0%)	CrCl ₃ (1.0)	[BMPy]Cl ⁴	130	60	Conv.	26	[86]

37	Wheat husk (10.0%)	CrCl ₃ (1.0)	[BMPy]Cl ⁴	130	60	Conv.	45	[86]
38	Corn stover (10.0%)	CrCl ₃ (1.0)	[BMPy]Cl ⁴	130	60	Conv.	39	[86]
39	Sugarcane bagasse (10.0%)	CrCl ₃ (1.0)	[BMPy]Cl ⁴	130	60	Conv.	16	[86]
40	Coconut shells (10.0%)	CrCl ₃ (1.0)	[BMPy]Cl ⁴	130	60	Conv.	26	[86]
41	Almond shells (10.0%)	CrCl ₃ (1.0)	[BMPy]Cl ⁴	130	60	Conv.	30	[86]
42	Junegrass (3.8%)	CuCl ₂ (8.3)	[Et ₃ NH][HSO ₄] ⁴	180	41	MW	45	[87]
43	Mixed herb residue (4.8%) <i>Anemarrhena</i>	SnCl ₄ ·5H ₂ O (0.3)	ChCl ⁵ /formic acid (1/8 mol/mol)	140	30	Conv.	55	[88]
44	<i>asphodeloides Bunge</i> (4.8%)	SnCl ₄ ·5H ₂ O (0.2)	ChCl ⁵ /formic acid (1/8 mol/mol)	140	30	Conv.	77	[88]
45	<i>Caulis Polygoni Multiflori</i> (4.8%)	SnCl ₄ ·5H ₂ O (0.2)	ChCl ⁵ /formic acid (1/8 mol/mol)	140	60	Conv.	14	[88]
46	Sugarcane bagasse (4.8%)	D001-cc ion-exchange resin (1.0)	[BMIM]Cl ²	140	25	MW	21	[68]
47	Sugarcane bagasse (4.8%)	D001-cc ion-exchange resin (1.0)	[BMIM]OAc ⁶	140	25	MW	25	[68]
48	Babool wood (4.8%)	Sulfonated activated carbon (2.0)	[BMIM]Cl ³	120	60	Conv.	33	[89]
49	Corn stalk (4.8%)	HCSS ⁷ (1.0)	[BMIM]Cl ²	150	30	Conv.	44	[90]
50	Corn stalk (20.0%)	Biochar-Mg-Sn (5.0)	AMIMBF ₄ ⁸	100	180	Conv.	43	[91]
51	Corn stalk (20.0%)	Biochar-Mg-Sn (5.0)	AMIMBr ⁹	100	180	Conv.	49	[91]
52	Corn stalk (20.0%)	Biochar-Mg-Sn (5.0)	AMIMCl ¹⁰	100	180	Conv.	61	[91]
53	Corn husk (4.8%)	ChCl ⁵ /oxalic acid (0.05)	ChCl ⁵ /oxalic acid (1/1 mol/mol)	80	60	Conv.	14	[92]

¹ "Conv." and "MW" stand for "Conventional" and "Microwave". ² 1-butyl-3-methylimidazolium chloride. ³ 1-butyl-3-methylpyridinium chloride. ⁴ Triethylammonium hydrogen sulfate. ⁵ Choline chloride. ⁶ 1-butyl-3-methylimidazolium acetate. ⁷ Hydrothermal carbonized corn stalk sulfonated. ⁸ 1-allyl-3-methylimidazolium tetrafluoroborate. ⁹ 1-allyl-3-methylimidazolium bromide. ¹⁰ 1-allyl-3-methylimidazolium chloride.

Even in the presence of these solvents, both of which are homogeneous, in particular inorganic salts and heterogeneous catalysts have been adopted for the synthesis of HMF from biomasses. Regarding the inorganic salts, CrCl₃ has been proposed, leading to a good HMF yield of 41, 35, and 50 mol%, starting from wood chips, rice straw, and wheat straw, respectively, working under conventional heating (runs 33–35, Table 2) [84,85]. Remarkably, Naz et al. proved the beneficial role of CrCl₃ towards HMF yield, due to its Lewis acidic properties that promoted the isomerization step [85]. Moreover, the authors, comparing different ILs anions, demonstrated that Cl⁻ allowed the highest conversion due to being the stronger bond acceptor, thus increasing the acidity of ILs and promoting the dehydration step. More recently, the same authors investigated the employment of CrCl₃ as the catalyst for the conversion of other biomasses, underlining the possibility of performing the one-pot delignification and simultaneous conversion of the cellulose fraction to HMF (runs 36–41, Table 2). The authors found that the agricultural residues gave higher HMF yields than dry fruit shells. They obtained the highest HMF yield of 45 mol% from wheat husk and the maximum lignin recovery, about 65 wt%, from rice husk [86]. Due to the high polarity of ILs, these can well absorb MWs, in this way further promoting the breaking of intermolecular hydrogen bonds between polysaccharides and consequently improving their conversion [81]. Therefore, MW heating has been adopted for HMF synthesis from biomasses, by combining ILs and inorganic salts. In particular, a protic IL, such as triethylammonium hydrogen sulfate ([Et₃NH][HSO₄]), was employed as the solvent for HMF synthesis from Junegrass catalyzed by CuCl₂, reaching a HMF

yield of 45 mol% (run 42, Table 2) [87]. The mechanism proposed by the authors also involves $[\text{Et}_3\text{NH}][\text{HSO}_4]$ as the active species in biomass conversion. In fact, they supposed that the reaction of CuCl_2 with the reaction medium led to the formation of a Cu^{2+} hexa-aquo complex; SO_4 ; the amine Et_3N , which acted as Brønsted base; and HCl , which boosted the rupture of the glycosidic bond of cellulose, thus producing glucose. The latter can be converted to HMF through the isomerization step to fructose, catalyzed by the Brønsted base Et_3N and/or the Cu^{2+} hexa-aquo complex, followed by the dehydration of fructose to HMF, exploiting the HCl acidity. Yu et al. reported the employment of SnCl_4 as the catalyst in the HMF synthesis from herb residues, working in DES composed of choline chloride and formic acid, in which the catalyst was soluble at temperatures higher than $100\text{ }^\circ\text{C}$ (runs 43–45, Table 2) [88]. The highest HMF yield of 77 mol% was achieved with the herb *Anemarrhena asphodeloides* Bunge, which comprises a higher amount of soluble carbohydrates, especially fructose and sucrose, than other investigated biomasses.

Regarding the heterogeneous catalysts, both commercial and ad hoc synthesized ones have been used as catalysts in IL-systems. Li et al. carried out the synthesis of HMF from sugarcane bagasse, employing D001-cc ion-exchange resin under MW heating, in two different ILs, e.g., $[\text{Bmim}]\text{OAc}$ and $[\text{Bmim}]\text{Cl}$. The authors achieved higher HMF yield in the presence of $[\text{Bmim}]\text{OAc}$, thanks to its more efficient MW energy absorption and lower viscosity, thus improving its accessibility to the sugarcane bagasse, which is more prone to the conversion (runs 46 and 47, Table 2) [68]. Moreover, the HMF yields obtained working in the two ILs were higher than those achieved in water and DMSO (runs 16 and 17, Table 1), confirming the beneficial role of ILs. In addition to the commercial heterogeneous catalysts, several works reported the synthesis and use of ad hoc synthesized catalysts for the conversion of wastes to HMF. An example was proposed by Tyagi et al., who prepared sulfonated activated carbon, which was tested for HMF synthesis from Babool wood in $[\text{BMIM}][\text{Cl}]$, reaching a maximum yield of 33 mol% (run 48, Table 2) [89]. Similarly, Yan et al. synthesized a carbonaceous material including sulfonic, acid, and phenolic groups through the hydrothermal carbonization of corn stalk followed by the sulfonation step of the produced hydrochar. The as-prepared catalyst (HCSS) was tested for the conversion of corn stalk in $[\text{BMIM}][\text{Cl}]$, leading to the best HMF yield of 44 mol% (run 49, Table 2) [90]. The authors attributed the good catalytic activity of HCSS to the synergistic effect of its functional groups. In fact, acid and phenolic groups on the catalyst surface can adsorb the cellulose dissolved in IL, whereas the sulfonic groups can hydrolyze the cellulose. Another example of a synthesized acid catalyst was reported by Liu et al., who prepared a promising biochar from corn stalk and tested it in HMF production in ILs. The authors prepared the biochar through the carbonization of the corn stalk and improved its physical and chemical catalytic properties by the addition of ions, such as Mg^{2+} and Sn^{4+} , which enhanced the delignification of corn stalk, thus promoting the dissolution of biomass in the reaction medium. The authors investigated the effect of different anions (BF_4^- , Br^- , Cl^-) composing the employed IL in HMF production, identifying the highest HMF yield, of 61 mol%, with the Cl^- , which strongly enhanced the biomass conversion (runs 50–52, Table 2) [91]. This is a promising HMF yield, especially considering that a high substrate loading (20 wt%) was employed. The adopted catalyst was recycled up to five consecutive runs, showing only a slight decrease in activity, thus proving to be a stable and reusable system. Lastly, a recent work investigated the potentialities of DES, composed of choline chloride and oxalic acid, as both the solvent and catalyst of the reaction mixture for the conversion of corn husk. The acidic medium was sufficiently active to promote the conversion of the biomass, but the authors found that the high acid strength of the system promoted the formation of humins, leading to a low HMF yield equal to 14 mol% (run 53, Table 2) [92].

2.1.3. Biphasic and/or Multiple-Solvent Systems

The combined use of different solvents generally allows the formation of a biphasic system, which includes a reaction phase, wherein HMF synthesis occurs, and an extracting phase, which allows the HMF prompt isolation, thus enhancing its yield limiting the formation of by-products. The most employed biphasic system is composed of water (reaction phase) and an organic solvent (extracting phase), but also ILs and DESs have recently been adopted as the reaction phase for the biomass conversion to HMF. Due to the strong enhancement of HMF yield afforded in a biphasic system, this is surely the most adopted reaction medium. The following tables summarize the available data for the synthesis of HMF starting from not-pretreated biomasses, in the presence of mineral and organic acids (Table 3), inorganic salts and their combinations with acids (Table 4), heterogeneous catalysts (Table 5), and other catalytic systems (Table 6).

Table 3. HMF production starting from raw biomasses in biphasic and/or multiple-solvent systems with mineral and organic acids.

Entry	Feedstock (wt%)	Catalyst (wt _{biomass} /wt _{catalyst})	Solvent	T (°C)	t (min)	Heat ¹	Y _{HMF} (mol%)	Ref
54	Sugar beet juice (3.7%)	H ₂ SO ₄ (35.0)	H ₂ O-NaCl/MeTHF ² (1/4 v/v)	150	20	Conv.	96 ³	[93]
55	Microalgae <i>Chlorella sorokiniana</i> (1.6%)	H ₂ SO ₄ (3.6)	H ₂ O-LiCl/DMSO (1/3 v/v)	150	120	Conv.	52	[94]
56	Bamboo (0.6%)	HCl (21.4)	H ₂ O/MIBK (1/19 v/v)	177	60	MW	42	[95]
57	Bamboo culm (0.6%)	HCl (21.4)	H ₂ O/MIBK (1/19 v/v)	177	60	MW	37	[96]
58	Bamboo leaves (0.6%)	HCl (21.4)	H ₂ O/MIBK (1/19 v/v)	177	60	MW	35	[96]
59	Macroalgae <i>Ulva prolifera</i> (2.0%)	Formic acid (1.6)	H ₂ O-NaCl/THF (1/1 v/v)	200	60	Conv.	31	[97]
60	Pinewood (2.0%)	Levulinic acid (4.0)	H ₂ O/MeTHF ² (1/1 v/v)	200	60	Conv.	21	[98]
61	Straw (1.0%)	Sulfanilic acid (6.0)	H ₂ O, DMSO/ 2-butanol, MIBK (1/2 v/v)	150	60	Conv.	41	[99]
62	Barley husk (1.0%)	Sulfanilic acid (7.1)	H ₂ O, DMSO/ 2-butanol, MIBK (1/2 v/v)	150	60	Conv.	41	[99]

¹ “Conv.” and “MW” stand for “Conventional” and “Microwave”. ² 2-methyltetrahydrofuran. ³ Calculated with respect to moles of fructose.

Abdilla-Santes et al. carried out HMF synthesis starting from sugar beet juice (3.7 wt%), in the presence of H₂SO₄ as the catalyst and different biphasic systems. They found that a higher HMF selectivity was reached using MeTHF instead of MIBK (82 and 75 mol%, respectively) due to the higher partition coefficient of HMF in the biphasic system MeTHF/H₂O than MIBK/H₂O (1.9 and 1.0, respectively), proving the beneficial effect of the more efficient removal of HMF from the acid phase. The authors also investigated the influence of salt addition, such as NaCl, claiming that the salting-out effect allowed the increase of the partition coefficient (from 1.9 to 3.7 for MeTHF/H₂O and from 1.0 to 1.8 for MIBK/H₂O) and the improvement of HMF yield up to 96 mol% in a H₂O-NaCl/MeTHF system (run 54, Table 3) [93]. Furthermore, Amoah et al. adopted H₂SO₄ as the catalyst for HMF production from the microalgae *Chlorella sorokiniana* in a H₂O-LiCl/DMSO system, adopting a low substrate loading (1.6 wt%). DMSO was chosen as the organic phase, due to its good thermal stability. However, due to its high polarity, it is miscible with water,

giving a monophasic solution that acts as a biphasic one, thus stabilizing the HMF and reducing the formation of by-products. However, the addition of a salt, such as LiCl, reduced the mutual solubility of DMSO and H₂O, leading to a significant improvement in HMF yield up to 52 mol% (run 55, Table 3) [94]. Although the formation of by-products was reduced in H₂O–LiCl/DMSO, the authors also attributed the good HMF yield to the contribution of the high amount of lipids present in the microalgae *Chlorella sorokiniana* that, forming a micro-biphasic system, can further limit the formation of by-products. HCl was adopted by Sweygers et al. for the conversion of bamboo under MW heating in the H₂O/MIBK system, employing a very low substrate loading (0.6 wt%). The authors identified the optimal reaction conditions adopting a statistical model starting from pure cellulose, and these were subsequently applied on bamboo, achieving an analogous HMF yield of about 42 mol% (run 56, Table 3) [95]. More recently, the same authors successfully applied the optimized reaction conditions to produce HMF from bamboo culm and bamboo leaves, reaching yields of 37 and 35 mol%, respectively (run 57 and 58, Table 3) [96]. In addition to mineral acids, organic acids, such as formic and levulinic acids, both deriving from HMF rehydration, have been also tested as catalysts for HMF production. Formic acid was proposed for the conversion of the macroalgae *Ulva prolifera*, and it strongly promoted the depolymerization of polysaccharides and the dehydration of monosaccharides, thus accelerating HMF formation and increasing its yield. The presence of THF suppressed HMF rehydration and polymerization, and the addition of NaCl led to the formation of a biphasic system (H₂O–NaCl/THF), achieving the highest HMF yield of about 31 mol% (run 59, Table 3) [97]. On the other hand, levulinic acid was employed as the catalyst for the conversion of pinewood in the H₂O/MeTHF system, and the prevailing acid distribution in the two solvents depended on their ratio. In fact, the increase in the H₂O/MeTHF ratio reduced the levulinic acid amount in the organic phase. In addition, the H₂O/MeTHF ratio influenced the polarity of the system and the catalytic behavior. Remarkably, an increase in water amount accelerated the cleavage of glycosidic bonds, enhancing the hydrolysis step, but an excessive amount of water significantly promoted the HMF rehydration and polymerization, thus causing a decrease in its yield. On this basis, a 1:1 volume ratio was optimal, leading to the highest HMF yield of 21 mol% (run 60, Table 3) [98]. Other researchers reported the employment of a bifunctional organocatalyst, such as sulfanilic acid, for the conversion of biomasses to HMF. Sulfanilic acid has both sulfonic and amino groups, e.g., Brønsted acidity and basicity properties, thus being effective in hydrolysis/dehydration and isomerization steps, respectively. The authors adopted a complex biphasic system, wherein the reactive phase was composed of H₂O and DMSO, with the extracting phase composed of 2-butanol and MIBK. DMSO was added to water to increase the amount of β-D-fructofuranose tautomer, which undergoes dehydration, whereas 2-butanol was added to the organic phase to enhance HMF extraction. Under the best reaction conditions, the authors achieved an HMF yield of 41 mol% starting from both straw and barley husk, and the recycled catalyst in the aqueous phase was active for up to five consecutive runs (runs 61 and 62, Table 3) [99]. However, this good yield was achieved by adopting a very low biomass loading (only 1 wt%), an aspect that weakens the effectiveness of the result.

A larger number of examples have been reported for inorganic salts and their combinations with acids, because this catalytic system allowed an easier modulation of Brønsted and Lewis acidity, an aspect of paramount importance to reach promising HMF yields (Table 4).

Table 4. HMF production starting from raw biomasses in biphasic and/or multiple-solvent systems with inorganic salts and combinations of them with acids.

Entry	Feedstock (wt%)	Catalyst (wt _{biomass} /wt _{catalyst})	Solvent	T (°C)	t (min)	Heat ¹	Y _{HMF} (mol%)	Ref
63	Eucalyptus pulp	Fe ₂ (SO ₄) ₃ (1.3)	H ₂ O/MIBK	200	60	Conv.	32	[100]

64	(1.2%) Mixed spruce, pine and fir pulp (1.2%)	Fe ₂ (SO ₄) ₃ (1.3)	(1/5 v/v) H ₂ O/MIBK (1/5 v/v)	200	90	Conv.	29	[100]
65	Eucalyptus pulp (1.2%)	Fe ₂ (SO ₄) ₃ (1.3)	H ₂ O/MIBK (1/5 v/v)	170	20	MW	27	[100]
66	Mixed spruce, pine and fir pulp (1.2%)	Fe ₂ (SO ₄) ₃ (1.3)	H ₂ O/MIBK (1/5 v/v)	170	20	MW	25	[100]
67	Macroalgae <i>Enteromorpha prolifera</i> (2.1%)	FeCl ₃ (9.9)	H ₂ O-NaCl/THF (1/1 v/v)	190	60	Conv.	33	[101]
68	Bamboo (4.8%)	NaCl (6.7)	H ₂ O/sulfolane (1/7 v/v)	200	120	Conv.	18	[102]
69	Bamboo (4.8%)	MgCl ₂ (6.7)	H ₂ O/sulfolane (1/7 v/v)	200	120	Conv.	18	[102]
70	Bamboo (4.8%)	CaCl ₂ (6.7)	H ₂ O/sulfolane (1/7 v/v)	200	120	Conv.	20	[102]
71	Bamboo (4.8%)	AlCl ₃ (6.7)	H ₂ O/sulfolane (1/7 v/v)	200	120	Conv.	22	[102]
72	Bamboo (4.8%)	CrCl ₃ (6.7)	H ₂ O/sulfolane (1/7 v/v)	200	120	Conv.	27	[102]
73	Bamboo (4.8%)	ZnCl ₂ (6.7)	H ₂ O/sulfolane (1/7 v/v)	200	120	Conv.	29	[102]
74	Bamboo (4.8%)	CuCl ₂ (6.7)	H ₂ O/sulfolane (1/7 v/v)	200	120	Conv.	30	[102]
75	Bamboo (4.8%)	FeCl ₃ (6.7)	H ₂ O/sulfolane (1/7 v/v)	200	120	Conv.	36	[102]
76	Bamboo (4.8%)	SnCl ₄ (6.7)	H ₂ O/sulfolane (1/7 v/v)	200	120	Conv.	41	[102]
77	Bread waste (4.8%)	SnCl ₄ (3.5)	H ₂ O/DMSO (1/1 v/v)	140	20	MW	17	[103]
78	Unskinned kiwi fruit (4.8%)	SnCl ₄ (3.5)	H ₂ O/DMSO (1/1 v/v)	140	20	MW	32	[104]
79	Watermelon flesh (4.8%)	SnCl ₄ (3.5)	H ₂ O/DMSO (1/1 v/v)	140	20	MW	39	[104]
80	Rice waste (4.8%)	SnCl ₄ (3.5)	H ₂ O/DMSO (1/1 v/v)	140	20	MW	13	[104]
81	Rice waste (4.8%)	SnCl ₄ (3.5)	H ₂ O/DMSO (1/1 v/v)	140	40	MW	33	[104]
82	Rice waste (4.8%)	AlCl ₃ (6.8)	H ₂ O/DMSO (1/1 v/v)	140	40	MW	29	[104]
83	Rice waste (4.8%)	CrCl ₃ (5.7)	H ₂ O/DMSO (1/1 v/v)	140	40	MW	23	[104]
84	Rice waste (4.8%)	AlCl ₃ (6.8)	H ₂ O/DMSO (1/1 v/v)	140	100	MW	35	[105]
85	Rice waste (4.8%)	SnCl ₄ (3.5)	H ₂ O/DMSO (1/1 v/v)	140	80	MW	36	[106]
86	Rice waste (4.8%)	SnCl ₄ (3.5)	H ₂ O/acetone (1/1 v/v)	140	20	MW	32	[106]
87	Bread waste (4.8%)	SnCl ₄ (3.5)	H ₂ O/DMSO (1/1 v/v)	160	20	MW	38	[107]
88	Bread waste (4.8%)	AlCl ₃ (6.8)	H ₂ O/DMSO	160	20	MW	33	[107]

89	Bread waste (4.8%)	SnCl ₄ (3.5)	(1/1 v/v) H ₂ O/DMSO	140	60	MW	35	[108]
90	Bread waste (4.8%)	SnCl ₄ (3.5)	(1/1 v/v) H ₂ O/THF	140	120	MW	10	[108]
91	Bread waste (4.8%)	SnCl ₄ (3.5)	(1/1 v/v) H ₂ O/CAN ²	140	10	MW	33	[108]
92	Bread waste (4.8%)	SnCl ₄ (3.5)	(1/1 v/v) H ₂ O/acetone	140	10	MW	33	[108]
93	Bread waste (4.8%)	SnCl ₄ (3.5)	(1/1 v/v) H ₂ O/acetone	120	50	MW	22	[109]
94	Bread waste (4.8%)	SnCl ₄ (3.5)	(1/1 v/v) H ₂ O/GVL	120	40	MW	31	[109]
95	Bread waste (4.8%)	SnCl ₄ (3.5)	(1/1 v/v) H ₂ O/PC ³	120	7	MW	26	[109]
96	Corn waste (4.8%)	SnCl ₄ (3.5)	(1/1 v/v) H ₂ O/acetone	140	10	MW	27	[110]
97	Taro waste (4.8%)	SnCl ₄ (3.5)	(1/1 v/v) H ₂ O/acetone	140	10	MW	30	[110]
98	Rice waste (10.0%)	SnCl ₄ (3.5)	H ₂ O-NADES ⁴ /MIBK (1/25 v/v)	130	120	Conv.	61	[111]
99	Bread waste (10.0%)	SnCl ₄ (3.5)	H ₂ O-NADES ⁴ /MIBK (1/25 v/v)	130	120	Conv.	55	[111]
100	Rice waste (4.8%)	AlCl ₃ ·6H ₂ O (0.5)	H ₂ O-ChCl/GVL (1/1 v/v)	140	60	Conv.	19	[112]
101	Molasses (12.8%)	AlCl ₃ (61.5)	H ₂ O/GVL (1/4 v/v)	160	180	Conv.	24	[113]
102	Sunn hemp fibres (2.0%)	CuCl ₂ (6.3)	H ₂ O/[BMIM]Cl ⁵ (1/4 v/v)	180	46	MW	34	[114]
103	Junegrass (3.8%)	CuCl ₂ (10.0)	H ₂ O/[BMIM]Cl ⁵ (1/3.3 v/v)	180	36	MW	31	[87]
104	Fir sawdust (3.2%)	CoCl ₂ ·6H ₂ O (1.4)	H ₂ O/isopropanol (1/2.3 v/v)	180	180	Conv.	19	[115]
105	Mixed spruce, pine, and fir pulp (1.2%)	Fe ₂ (SO ₄) ₃ (1.3) + HCl (33.3)	H ₂ O/MIBK (1/5 v/v)	200	80	Conv.	38	[100]
106	Eucalyptus pulp (1.2%)	Fe ₂ (SO ₄) ₃ (12.5) + HCl (16.7)	H ₂ O/MIBK (1/5 v/v)	200	30	Conv.	29	[100]
107	Corn stover (4.8%)	AlCl ₃ (46.9) + HCl (41.7)	H ₂ O/dioxane (1/4 v/v)	200	5	MW	69	[116]
108	Loblolly pine (4.8%)	AlCl ₃ (46.9) + HCl (41.7)	H ₂ O/dioxane (1/4 v/v)	200	5	MW	60	[116]
109	Switchgrass (4.8%)	AlCl ₃ (46.9) + HCl (41.7)	H ₂ O/dioxane (1/4 v/v)	200	5	MW	65	[116]
110	Hybrid poplar (4.8%)	AlCl ₃ (46.9) + HCl (41.7)	H ₂ O/dioxane (1/4 v/v)	200	5	MW	67	[116]
111	Rice waste (4.8%)	SnCl ₄ (3.5) + maleic acid (31.0)	H ₂ O/DMSO (1/1 v/v)	140	40	MW	35	[106]
112	Rice waste (4.8%)	SnCl ₄ (3.5) + maleic acid (31.0)	H ₂ O/acetone (1/1 v/v)	140	10	MW	30	[106]
113	Rice waste (4.8%)	AlCl ₃ (6.8) + maleic acid (31.0)	H ₂ O/DMSO (1/1 v/v)	140	100	MW	17	[105]

114	Sugarcane bagasse (9.0%)	AlCl ₃ (6.7) + oxalic acid dihydrate (1.0) + HCl (17.9)	DMSO/ 2-butanol, MIBK (1/1 v/v)	130	360	Conv.	43	[43]
115	Raw potato (9.0%)	AlCl ₃ (6.7) + oxalic acid dihydrate (1.0) + HCl (17.9)	DMSO/ 2-butanol, MIBK (1/1 v/v)	130	360	Conv.	40	[43]

¹ "Conv." and "MW" stand for "Conventional" and "Microwave". ² Acetonitrile. ³ Propylene carbonate. ⁴ Natural deep eutectic solvent composed of glucose and choline chloride. ⁵ 1-butyl-3-methylimidazolium chloride.

The salts can act as both Brønsted and Lewis acids. In fact, in aqueous media, they dissociate into cations and anions; cations are solvated by water, forming aqueous complex ions that release protons through hydrolysis, whereas the anions react with water to form the respective acid, thus conferring Brønsted acid properties to the salt. Moreover, the cations can form an adduct with saccharides, thus weakening the intra-molecular bonds of polysaccharides and consequently accelerating their hydrolysis. In addition, they can act as a Lewis acid, promoting the isomerization of glucose to fructose [100]. In this regard, Mukherjee et al. employed Fe₂(SO₄)₃ for the conversion of eucalyptus pulp (hardwood) and mixed pulp of spruce, pine, and fir (softwoods) in a H₂O/MIBK solvent system. Under conventional heating, the authors achieved an HMF yield of 32 and 29 mol% after 60 and 90 min starting from eucalyptus pulp and mixed pulp of spruce, pine, and fir, respectively, finding that hardwood was easier to hydrolyze than softwood (runs 63 and 64, Table 4) [100]. The authors attributed the lower catalytic performance of Fe₂(SO₄)₃ in the conversion of softwoods to their higher amount of extractives, which can form complexes with Fe³⁺, thus reducing its ability to bind with cellulose and limiting its depolymerization. Because MW are effective in cellulose depolymerization [117], the authors also performed the reaction under MW heating, reaching analogous yields to those previously reported but at a lower temperature and after a shorter reaction time, thanks to the high efficiency of the MW heating system (runs 65 and 66, Table 4). However, despite the interesting yields reported in this work, the low substrate loading (1.2 wt%) makes the process not very appealing. Chen et al. adopted a ferric salt for the synthesis of HMF. In particular, the authors reported the employment of FeCl₃ as the catalyst for the conversion of the macroalgae *Enteromorpha prolifera* in H₂O–NaCl/THF 1/1 v/v, achieving the highest HMF yield of 33 mol% thanks to the extraction of HMF by THF and the presence of NaCl, which improved the partition coefficient (run 67, Table 4) [101]. The authors found that the heating of FeCl₃ in water led to the formation of a red precipitate, mainly composed of α-Fe₂O₃ and β-FeOOH, highlighting the fact that FeCl₃ was unstable and easily hydrolyzable. On the other hand, when FeCl₃ was heated with biomass, the red precipitate was absent. Therefore, the authors supposed that sugars, intermediates, or furans prevented the FeCl₃ hydrolysis and that the complex of Fe³⁺ with polysaccharides was the active species for the catalysis. Liu et al. not only tested FeCl₃ but also several other chloride salts as catalysts for the conversion of bamboo to HMF in H₂O/sulfolane. The authors found that SnCl₄ led to the highest HMF yield of 41 mol%, together with a biomass conversion of 93 wt%, due to the hydrolysis of SnCl₄ that provided the appropriate amount of Brønsted and Lewis acid species (runs 68–76, Table 4) [102]. For this purpose, the presence of water was of paramount importance in facilitating salt hydrolysis, but an excess of water also promoted the HMF hydration to acids, thus a ratio of 1/7 v/v H₂O/sulfolane was selected as optimal. The authors highlighted the fact that sulfolane had an important role in the catalytic activity, limiting the hydrolysis of SnCl₄ to HCl and SnO₂, and maintaining the stability of the Sn⁴⁺ aqueous complex, which is the effective Lewis acid species. On this basis, the proposed mechanism included the hydrolysis of cellulose to glucose, which was catalyzed by HCl released from the hydrolysis of SnCl₄,

then the isomerization of glucose to fructose, which was catalyzed by the Sn^{4+} aqueous complex, and the final dehydration of fructose to HMF, catalyzed by HCl. SnCl_4 was surely the preferred salt for HMF synthesis from raw biomasses, and other researchers have tested it as a catalyst. For example, Yu et al. investigated HMF synthesis in the presence of SnCl_4 under MW heating, starting from different food wastes, such as bread waste [103,107–109], unskinned kiwi fruit [104], watermelon flesh [104], rice waste [104,106], corn waste [110], and taro waste [110]. Performing the reaction under the same conditions (140 °C and 20 min) in the solvent system $\text{H}_2\text{O}/\text{DMSO}$ (1/1 *v/v*), the authors reported different HMF yields depending on the starting biomass (runs 77–81, Table 4) [103,104]. They tested two different types of biomass, a starch-rich one, such as bread waste and rice waste, and a sugar-rich one, such as unskinned kiwi fruit and watermelon flesh, finding that the latter led to a higher HMF yield (32 and 39 mol%, respectively). This was due to the presence in the two sugar-rich biomasses of a higher amount of fructose, which is easily and quickly converted to HMF. On the other hand, in the two starch-rich biomasses, despite the metal-catalyzed hydrolysis being efficient, the subsequent isomerization was kinetically limited and required a longer reaction time, as evidenced by the improvement in HMF yield from 13 (run 80, Table 4) to 33 mol% (run 81, Table 4), prolonging the reaction time from 20 to 40 min. The authors also investigated the employment of trivalent salts, such as AlCl_3 and CrCl_3 , for the conversion of rice waste, finding that they were less active than the tetravalent SnCl_4 because they produced milder acidity (pH of the solution equal to 3.3, 2.6, and 1.5 for AlCl_3 , CrCl_3 , and SnCl_4 , respectively). For this reason, AlCl_3 and CrCl_3 led to lower HMF yields than SnCl_4 , working under the same reaction conditions (runs 82 and 83, Table 4) [104], and a similar HMF yield was obtained only after a longer time (100 min) (run 84, Table 4) [105]. On this basis, the use of SnCl_4 resulted in the most promising inorganic salt, and the authors focused their attention on its use in the optimization of HMF synthesis starting from rice waste. They prolonged the reaction time up to 80 min, further improving the HMF yield to 36 mol% and obtained an analogous yield after a shorter reaction time (20 min), employing acetone instead of DMSO (runs 85 and 86, Table 4) [106]. Analogous conclusions were also obtained starting from bread waste. The authors performed the conversion in $\text{H}_2\text{O}/\text{DMSO}$ at 160 °C with SnCl_4 or AlCl_3 (runs 87 and 88, Table 4) [107]. The increase in temperature from 140 to 160 °C allowed the improvement of HMF yield from 17 (run 77, Table 4) to 38 mol%, and SnCl_4 was more efficient than AlCl_3 , which generated lower HMF yield due to humins formation. In fact, AlCl_3 induced significant polymerization, due to its strong Lewis acidity and the binding ability of Al^{3+} to the reaction intermediates, making them susceptible to the attack of 2,5-dioxo-6-hydroxyhexanal (DHH), a by-product deriving from HMF degradation and identified as the initiator of humins formation [118]. Moreover, the solid residue recovered at the end of the reaction with SnCl_4 did not contain unconverted starch, whereas the residue from the AlCl_3 -catalyzed reaction still contained unexploited starch, underlining the higher efficiency of SnCl_4 . Regarding solvent composition, the authors carried out the conversion of bread waste not only in $\text{H}_2\text{O}/\text{DMSO}$ but also in $\text{H}_2\text{O}/\text{THF}$, $\text{H}_2\text{O}/\text{ACN}$, and $\text{H}_2\text{O}/\text{acetone}$ at 140 °C under MW heating (runs 89–92, Table 4) [108]. They found that the hydrolysis of biomass was always fast, but an accumulation of glucose was observed working with $\text{H}_2\text{O}/\text{DMSO}$ and $\text{H}_2\text{O}/\text{THF}$, due to its slower isomerization to fructose in these solvent systems. The glucose conversion was particularly slow in $\text{H}_2\text{O}/\text{THF}$, achieving an HMF yield of only 10 mol% after 120 min, probably due to its low dielectric constant and low dipole moment that disfavored the MW absorption and heat transfer. On the other hand, ACN and acetone did not improve the HMF selectivity but only speeded up the glucose conversion, thus the highest HMF yields achieved with $\text{H}_2\text{O}/\text{DMSO}$, $\text{H}_2\text{O}/\text{ACN}$, and $\text{H}_2\text{O}/\text{acetone}$ were similar but were ascertained after different reaction times (60, 10 and 10 min, respectively) and were higher than obtained with $\text{H}_2\text{O}/\text{THF}$, wherein HMF was more susceptible to rehydration. The authors hypothesized that ACN and acetone were able to arrange themselves near the hydroxyl groups of sugars and the carbonyl group of HMF,

thus protecting them from side reactions [119,120]. Moreover, the authors investigated the employment of green solvents in combination with water, such as propylene carbonate (PC), which is a scarcely toxic and highly biodegradable solvent [121], and GVL, which is a biomass-derived solvent [122,123]. In this context, the catalytic activity of SnCl₄ in these solvents was compared with that obtained in H₂O/acetone in the conversion of bread waste at 120 °C (runs 93–95, Table 4) [109]. In this work, the authors deeply investigated the effect of the organic solvents on the catalytic activity and supposed that, analogously to sulfolane [102], the kinetic of SnCl₄ hydrolysis could be slowed down, thus suppressing the formation of inactive SnO₂. As a consequence, the Sn⁴⁺ effective Lewis acid, which promotes glucose isomerization, was maintained and cooperated with HCl to promote the HMF synthesis. In addition, they found a positive correlation between the dipole moment of the organic solvent and the HMF yield. In particular, the greater the dipole moment was, the more efficiently the molecule can act as a ligand to coordinate with Sn⁴⁺, thus suppressing the salt hydrolysis to the inactive SnO₂ and improving the HMF yield. Lastly, the authors tested the promising solvent system H₂O/acetone in the conversion of other biomasses, such as corn waste and taro waste, achieving the highest HMF yield from taro (30 mol% respect to 27 mol%), probably due to the higher amount of available sugars in this biomass (runs 96 and 97, Table 4) [110]. SnCl₄ was also adopted by Zuo et al. for the conversion of wastes with aqueous-assisted natural deep eutectic solvent (A-NADES) as the reaction medium, composed of water and the natural deep eutectic solvent formed by glucose and choline chloride, with MIBK as the extraction medium [111]. The addition of water to this natural deep eutectic solvent was very important, because it facilitated the reduction of viscosity and improved fluidity and thermal conductivity. In this way, water enhances the conduction of the reaction and hampers the coordination of SnCl₄ with choline chloride, which is responsible for the reduction of its catalytic activity. Moreover, the addition of water played an important role in the hydrolysis of SnCl₄, leading to the formation of the strong Lewis acid complex (Sn(OH)_x(H₂O)_yⁿ⁺) and HCl. On the other hand, the authors supposed that the choline chloride in A-NADES was able to inhibit the HMF rehydration to levulinic and formic acids, thanks to the contribution of both the anion and cation of choline chloride, which can adsorb water, forming hydration ions and thus limiting the degradation pathways of HMF. However, HMF formed strong hydrogen bonds with choline chloride, making its separation from the reaction medium difficult. Therefore, the employment of MIBK was important for in situ extraction, which allowed the timely and convenient recovery of HMF. Thanks to all these peculiarities of the reaction system, very promising HMF yields were achieved starting from rice waste and bread waste, equal to 61 and 55 mol%, respectively (runs 98 and 99, Table 4). It must be underlined that these performances were achieved working with a biomass loading of 10 wt%, which is much higher with respect to the loading generally reported in the literature. Moreover, at the end of the reaction, A-NADES, containing the SnCl₄, was easily separated from MIBK and re-used many times. Remarkably, the catalytic activity decreased after the fifth cycle, due to the accumulation of humins that could influence the interaction between glucose and choline chloride, thus lowering the HMF yield. However, when the A-NADES enriched in humins was purified through filtration and centrifugation, the catalytic activity was restored. Choline chloride was also adopted in a ternary reaction system together with H₂O and GVL for HMF synthesis from rice waste catalyzed by AlCl₃·6H₂O [112]. This ternary system afforded the highest HMF yield of 19 mol%, due to the stability conferred by the synergistic effect of choline chloride and GVL (run 100, Table 4). In fact, the chlorine atom of choline chloride can combine with the hydroxymethyl group of HMF, thus increasing its stability, while GVL extracts HMF from the aqueous phase, thus limiting the formation of by-products and increasing the HMF yield. The authors also investigated the recyclability of the reaction system, considering that AlCl₃·6H₂O and choline chloride were dissolved in the aqueous phase without any transfer to GVL during the reaction. For this purpose, at the end of the reaction, the aqueous and organic phases

were separated, fresh rice waste and GVL were added to the aqueous solution containing $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ and choline chloride to perform the reaction, and this procedure was repeated six times. With the progress of the reaction recycling, the HMF yield decreased from 19 to 9 mol% after the sixth cycle, due to the damaging of the catalyst quality or to the catalyst loss.

In addition to SnCl_4 and AlCl_3 , which are the most adopted salts for the conversion of biomass to HMF, other chloride salts, such as CuCl_2 and CoCl_2 , were also tested as catalysts. In this regard, Paul et al. employed CuCl_2 for the conversion of sunn hemp, a non-edible, herbaceous, fast-growing, sub-tropical annual bioenergy crop [114]. This biomass seemed promising for the synthesis of HMF, due to its low lignin and high cellulose contents, but its conversion was challenging, due to the high crystallinity and high polymerization degree of cellulose, which limited the cleavage of the glycosidic bond. This problem was overcome by employing a combination of water and the ionic liquid [BMIM]Cl as the reaction medium and CuCl_2 as the catalyst. All these components formed a supramolecular complex with cellulose, which was subsequently hydrolyzed by water to produce glucose and then HMF, the latter with a yield of 34 mol% after 46 min (run 102, Table 4) under MW heating. Roy et al. carried out the conversion of Junegrass to HMF under MW heating and the same temperature of 180 °C, reaching an HMF yield of 31 mol% (run 103, Table 4) [87]. Pan et al. employed CoCl_2 as the catalyst for HMF synthesis from fir sawdust, reaching the highest yield of 19 mol% at 180 °C after 3 h with the H_2O /isopropanol solvent system (run 104, Table 4) [115]. Interestingly, most of the Co^{2+} was present in the aqueous phase and could be easily recovered by precipitation. The amount of aromatic compounds formed during the reaction and deriving from the decomposition of lignin was very low, indicating that CoCl_2 selectively catalyzed the conversion of polysaccharides, leaving the almost pure lignin as the residual hydrochar. The authors also valorized this by-product through the pyrolysis process, obtaining some light hydrocarbons (mainly benzene and toluene), phenols and vanillin, pyrolysis gas, and nanoparticles of biochar stabilized with Co, usable for the elimination of pollutants.

In addition to the employment of only inorganic salts, their combination with homogeneous acids has also been investigated, aimed at the quicker depolymerization of cellulose. Mukherjee et al. added diluted HCl to $\text{Fe}_2(\text{SO}_4)_3$ for HMF synthesis from eucalyptus pulp (hardwood) and mixed spruce, pine, and fir pulp (softwood), already converted with $\text{Fe}_2(\text{SO}_4)_3$ alone (runs 63 and 64, Table 4) [100]. Starting from mixed spruce, pine, and fir pulp, the presence of HCl facilitated an improvement in HMF yield, equal to 38 mol% after 80 min (run 105, Table 4), with respect to 29 mol% achieved with only $\text{Fe}_2(\text{SO}_4)_3$ (run 64, Table 4). On the other hand, starting from eucalyptus pulp, a higher amount of humins was formed and the HMF yield of 29 mol% (run 106, Table 4), slightly lower than that reached with $\text{Fe}_2(\text{SO}_4)_3$ alone (32 mol%, run 63, Table 4), was achieved after a shorter reaction time (30 min instead of 60 min). These results confirm that longer reaction times and harsher reaction conditions were necessary to depolymerize softwood pulp. Besides, Mittal et al. employed HCl as a homogeneous acid, in combination with AlCl_3 as an inorganic salt [116]. The authors carried out the conversion of several biomasses in a H_2O -dioxane solvent system under the same reaction conditions and exploiting MW heating. Similar HMF yields were achieved starting from corn stover, switchgrass, and hybrid poplar (65–69 mol%) and slightly lower yield (60 mol%) from loblolly pine (runs 107–110, Table 4). Probably, this was due to the higher amount of glucans in loblolly pine than the other tested biomasses, whose hydrolysis resulted in the increased formation of humins and other degradation products, such as levulinic acid. The authors investigated the influence of the H_2O /dioxane volume ratio, finding that the value of 1/4 *v/v* was optimal because at least 20% (*v/v*) of the reaction solvent should be water to achieve the effective hydrolysis of cellulose fraction to glucose. Yu et al. investigated the influence of maleic acid on the conversion of rice waste, carried out in the presence of SnCl_4 as the inorganic salt [106]. In this case, the addition of a homogeneous organic acid did not improve the HMF yield, and the authors supposed that maleic acid

played a complementary role in the catalysis, simply giving malic acid through its hydration, which could disrupt the hydrogen bond in starch, thus making it more accessible to the hydrolysis of glycosidic bonds. For this reason, maleic acid only speeded up the conversion, having reduced the time required to obtain HMF, with yields like those previously obtained with SnCl₄ alone, working with H₂O/DMSO and H₂O/acetone (compare runs 111 and 112 with 85 and 86 Table 4, respectively). On the contrary, when maleic acid was added to AlCl₃, the rate of HMF production from rice waste was lower, reaching, under the same reaction conditions (140 °C, 100 min), a yield of 17 mol% (run 113, Table 4) instead of 35 mol% (run 84, Table 4), together with less sugar conversion [105]. However, maleic acid allowed the improvement of HMF selectivity, thanks to the moderation of Lewis acidity through the formation of malic acid, which acted as the ligand of Al³⁺. Lastly, Kumar et al. tested a complex catalytic system composed of an inorganic salt (AlCl₃), an organic acid (oxalic acid dihydrate), and a mineral acid (HCl) to produce HMF from sugarcane bagasse and raw potato and supposed that each component catalyzed a specific step of the reaction [43]. Oxalic acid dihydrate might provide the acidity for the hydrolysis of cellulose to glucose; AlCl₃ might act as Lewis acid promoting the isomerization of glucose to fructose, and HCl might catalyze the dehydration of fructose to HMF. However, this acid system was not effective in most solvents, such as water, THF, and DMF, but was effective only in the biphasic-solvent system [DMSO/2-butanol, MIBK]. In this solvent, HMF yields of 43 and 40 mol% were claimed starting from sugarcane bagasse and raw potato, respectively, and working at a 500 g scale, larger than a laboratory one, with a biomass loading of 9 wt% (runs 114 and 115, Table 4).

Inorganic salts, alone or in combination with homogeneous acids, are the most common catalytic systems used up to now for the conversion of biomass to HMF, but heterogeneous acid catalysts have also been proposed, despite the less efficient interaction between solid substrate and solid catalyst. The available data for HMF synthesis from not-pretreated biomass catalyzed by heterogeneous acids in the biphasic medium are summarized in Table 5.

Table 5. HMF production from raw biomasses in biphasic and/or multiple-solvent systems with heterogeneous catalysts.

Entry	Feedstock (wt%)	Catalyst (wt _{biomass} /wt _{catalyst})	Solvent	T (°C)	t (min)	Heat ¹	Y _{HMF} (mol%)	Ref
116	Vegetable waste (5.0%)	Amberlyst-36 (1.0)	H ₂ O/DMSO (1/1 v/v)	135	5	MW	17	[66]
117	Salvia miltiorrhiza residue (0.7%)	PDVB-SO ₃ H ² (2.0)	H ₂ O/GBL (1/4 v/v)	170	30	Conv.	14	[124]
118	Corn stalk (2.4%)	PTSA-POM ³ (2.0)	H ₂ O/GVL (1/10 v/v)	190	100	Conv.	20	[125]
119	Microalgae <i>Chlorococcum</i> sp. (1.0%)	HZSM-5 (1.5)	H ₂ O/MIBK (3/2 v/v)	200	120	Conv.	44	[74]
120	Microalgae <i>Chlorococcum</i> sp. (1.0%)	HZSM-5 (1.5)	H ₂ O-NaCl/THF (3/2 v/v)	200	120	Conv.	48	[74]
121	Wheat straw (2.7%)	FePO ₄ ·2H ₂ O (10.0)	H ₂ O-NaCl/THF (1/3 v/v)	160	150	Conv.	18	[126]
122	Wheat straw (2.7%)	FePO ₄ ·2H ₂ O (5.0) + NaH ₂ PO ₄ (50.0)	H ₂ O-NaCl/THF (1/3 v/v)	160	60	Conv.	44	[126]
123	Wheat straw (2.7%)	SnCl ₂ -PTA/β ⁴ (1.7)	H ₂ O-NaCl/THF (1/3 v/v)	180	120	Conv.	33	[127]
124	Corn stover (1.3%)	SO ₃ H-NG-C ⁵ (2.0)	H ₂ O/GVL (1/6.5 v/v)	190	80	Conv.	30	[128]

125	Bread waste (4.3%)	Sulfonated biochar (1.0)	H ₂ O/DMSO (1/3 v/v)	180	20	MW	38	[129]
126	Bread waste (4.3%)	H ₃ PO ₄ -activated biochar (2.5)	H ₂ O/DMSO (1/3 v/v)	180	30	MW	38	[130]
127	Rice waste (4.3%)	H ₃ PO ₄ -activated biochar (2.5)	H ₂ O/DMSO (1/3 v/v)	180	20	MW	24	[130]
128	Corn stalk (20.0%)	Biochar-Mg-Sn (5.0)	Isopropanol/ AMIMCl ⁶ (n.a. ⁷)	100	180	Conv.	82	[91]
129	Corn stalk (20.0%)	Biochar-Mg-Sn (5.0)	DMSO/AMIMCl ⁶ (n.a. ⁷)	100	180	Conv.	81	[91]
130	Corn stalk (20.0%)	Biochar-Mg-Sn (5.0)	DMC ⁸ /AMIMCl ⁶ (n.a. ⁷)	100	180	Conv.	76	[91]
131	Corn stalk (20.0%)	Biochar-Mg-Sn (5.0)	THF/AMIMCl ⁶ (n.a. ⁷)	100	180	Conv.	75	[91]
132	Corn stalk (20.0%)	Biochar-Mg-Sn (5.0)	MIBK/AMIMCl ⁶ (n.a. ⁷)	100	180	Conv.	71	[91]
133	Peanut shell (3.8)	PSC ⁹ (0.6)	EMIMCl ¹⁰ / ChCl ¹¹ -DMSO (1/1 v/v)	150	60	Conv.	11	[131]
134	Water hyacinth (3.8)	PSC ⁹ (0.6)	EMIMCl ¹⁰ / ChCl ¹¹ -DMSO (1/1 v/v)	150	60	Conv.	6	[131]
135	Stalk (3.8)	PSC ⁹ (0.6)	EMIMCl ¹⁰ / ChCl ¹¹ -DMSO (1/1 v/v)	150	60	Conv.	15	[131]

¹ "Conv." and "MW" stand for "Conventional" and "Microwave". ² Polydivinylbenzene sulfonated. ³ Copolymer p-toluenesulfonic acid and paraformaldehyde. ⁴ SnCl₂ on zeolite H/β-supported phosphotungstic acid. ⁵ Sulfonated N-doped porous carbon. ⁶ 1-allyl-3-methylimidazolium chloride. ⁷ "n.a." stands for "not available". ⁸ Dimethyl carbonate. ⁹ Sulfonated peanut shells catalyst. ¹⁰ 1-ethyl-3-methylimidazolium chloride. ¹¹ Choline chloride.

Chen et al. studied the catalytic activity of the commercial amberlyst-36 towards the conversion of vegetable wastes, comparing H₂O (run 14, Table 1) and H₂O/DMSO (run 116, Table 5), as the solvents. They found that a higher HMF yield (17 mol%) was achieved in the biphasic solvent, obtaining a higher HMF selectivity [66]. In fact, the hydrogen bonds between the Brønsted acid sites of amberlyst-36 and the polar aprotic solvent DMSO were weaker than with water; thus, the protonation of glucose was more pronounced due to the accessibility of a larger number of protons to its hydroxyl groups, which represents the rate-limiting step of the glucose conversion. Moreover, HMF was solvated by DMSO, thus suppressing the nucleophilic attack at its carbonyl group and slowing the rehydration to levulinic and formic acids. Zhang et al. employed a sulfonated polymer, e.g., polydivinylbenzene sulfonated, for the HMF synthesis [124]. In this case, the authors synthesized the catalyst and reached negligible HMF yields starting from cottonseed hull and sugarcane bagasse, whereas a modest yield of 14 mol% was obtained starting from salvia miltiorrhiza residue (run 117, Table 5), a Chinese herbal medicine, thanks to the presence of starch, which was more easily hydrolyzable than cellulose. However, the authors obtained a modest yield working with a very low substrate loading (0.7 wt%); thus, these results are scarcely promising. Xu et al. prepared the copolymer between p-toluenesulfonic acid and paraformaldehyde, which was proposed for the conversion of corn stalk, reaching an HMF yield of 20 mol% working in the solvent system H₂O/GVL (run 118, Table 5) [125]. In addition to commercial and ad hoc synthesized organic polymers, inorganic heterogeneous catalysts, such as zeolites, have also been used, as reported in the work of Wang et al., who performed the conversion of the microalgae *Chlorococcum* (only 1 wt%) in the presence of HZSM-5 as the catalyst [74]. Two different biphasic systems were investigated, e.g., H₂O/MIBK and H₂O-NaCl/THF, and the highest HMF yield of 48 mol% was achieved in the latter system, because THF had a higher extraction efficiency than MIBK (runs 119 and 120, Table 5). The catalyst showed a

slight decrease in activity after six recycle runs, leading to an HMF yield of 37 mol%, caused by the deposition of humins and proteins on the catalyst surface, but the activity was almost completely restored after a calcination treatment at 500 °C for 4 h. The promising H₂O–NaCl/THF solvent system was also adopted by Xia et al. for the conversion of wheat straw in the presence of FePO₄·2H₂O, alone or in combination with NaH₂PO₄, reaching HMF yields of 18 and 44 mol%, respectively (runs 121 and 122, Table 5) [126]. FePO₄·2H₂O was able to catalyze the cellulose conversion to HMF, showing not only Brønsted acidity, deriving from its hydrolysis, but also Lewis acidity, deriving from the formation of soluble hydroxylated iron species. Anyway, the proper addition of NaH₂PO₄ facilitated the improvement of the HMF yield, due to the introduction of other Brønsted acid sites, which further improved the HMF synthesis. At the end of the reaction, the authors valorized the solid residue, containing the catalyst, unconverted cellulose, and lignin, through catalytic pyrolysis, obtaining a bio-oil rich in acetic acid, furans (2,5-dimethylfuran and 2-methylfuran, originating from the hydrogen transfer of HMF catalyzed by FePO₄·2H₂O), and aromatic compounds (*p*-cresol, phenol, guaiacol). Together with bio-oil, the pyrolysis treatment also resulted in a solid residue composed of bio-char, containing elements such as P and Na, and FePO₄·2H₂O, which was employed for the production of phosphate fertilizers. The wheat straw was also converted in H₂O–NaCl/THF by an ad hoc prepared catalyst, such as SnCl₂ on zeolite H/β-supported phosphotungstic acid (SnCl₂–PTA/β), achieving an HMF yield of 33 mol% (run 123, Table 5) [127]. The catalytic activity was synergistically influenced by acid and textural properties. Regarding the acid ones, the introduction of PTA and SnCl₂ strongly increased the acid density and the acid sites' strength in the catalytic system. In addition, a higher amount of SnCl₂ led to a higher ratio of Lewis/Brønsted acid sites, which were beneficial for the conversion of cellulose to glucose, the isomerization to fructose, and the HMF production. Regarding the textural properties, the increase of SnCl₂ amount led to the increase of the pore diameter and the decrease of the pore volume of the catalyst, thus gradually shortening the pore channels of SnCl₂–PTA/β. The shorter channels contributed to the improvement of the catalytic performance, because the contact of the substrate with the active sites was easier, and the diffusion of the HMF was faster, preventing its degradation. The authors also evaluated the catalyst stability, performing thermal calcination at 450 °C before each of the four recycle runs. The HMF yield decreased from 33 to 19 mol%, ascribed to the partial collapse of the pores, the slight loss of SnCl₂, and the relevant loss of PTA after the recycling. However, the catalyst was reactivated thanks to the reimpregnation of SnCl₂ and PTA, reaching an HMF yield of 24 mol%, indicating that, despite the collapse of the pores, the restored amount of SnCl₂ and PTA in the catalytic system was sufficient to restore the starting activity almost completely. In addition to polymers and inorganic materials, carbonaceous acid catalysts have also been prepared and employed for the conversion of biomass to HMF in two or even more solvents. Yang et al. synthesized a sulfonated N-doped porous carbon (SO₃H-NG-C), which was adopted for the conversion of corn stover in H₂O/GVL, achieving an HMF yield of 30 mol% (run 124, Table 5) [128]. GVL was shown to be a promising solvent for HMF production, because it limited undesired reactions, maintaining the product stability. Moreover, being a polar aprotic solvent, GVL enhanced the reactivity of protons, stabilizing them by solvation and promoting biomass hydrolysis. Moreover, water had a fundamental role in the reaction, influencing the –SO₃H ionization and, consequently, the catalytic activity of the solid acid. For this reason, the HMF yield was improved from 17 to 30 mol% when water was added to GVL, confirming the beneficial role of water towards the hydrolysis of the glycosidic bonds of cellulose. At the end of the reaction, the authors recovered a solid composed of the catalyst and unconverted corn stover and directly used it for the next runs. The HMF yield strongly decreased after each run, due to the presence of corn stover residue that inhibited the catalyst activity and to the leaching of the sulfonic acid after five cycles. Cao et al. prepared sulfonated biochar through the slow pyrolysis of forestry food waste (*Acacia confusa* and *Celtis sinensis*) and employed it

for HMF synthesis in H₂O/DMSO starting from bread waste. An HMF yield of 38 mol%, together with a low amount of by-products (levulinic and formic acids), was reached thanks to the presence of DMSO that limited the collateral reactions (run 125, Table 5) [129]. The catalyst recovered at the end of the reaction was washed with water, ethanol, and acetone; dried; and reused in four further consecutive runs. The HMF yield dropped to 4 mol% after the fourth run, due to the sulfonic acid leaching that caused a decrease in the catalyst acidity. To solve this problem, the authors regenerated the catalyst by treatment with H₂SO₄, which allowed the almost complete restoration of the highest HMF yield. The same authors proposed another carbonaceous catalyst, obtained by the H₃PO₄ treatment of biochar derived from the pyrolysis of the pinewood sawdust, for the conversion of bread and rice wastes. The highest HMF yield of 38 mol% was obtained starting from the first biomass, thanks to the enhanced porosity and starch accessibility given by the previous roasting process (runs 126 and 127, Table 5) [130]. Liu et al., once having identified AMIMCl as the best ionic liquid for realizing the conversion of corn stover with biochar-Mg-Sn (run 52, Table 2), also considered different organic solvents, such as isopropanol, DMSO, DMC, THF, and MIBK, as the HMF extraction medium, reaching the highest HMF yield of 82 mol% working with isopropanol (runs 128–132, Table 5) [91]. The authors attributed this improvement to the synergy between the isopropanol/AMIMCl solvent medium and the catalyst. They proposed that the Mg²⁺ ions of the catalyst react with isopropanol, giving active hydrogen and isopropyl radicals. The first attacks the C–O and C–C bonds of polysaccharides in corn stover, promoting its degradation. The ionic liquid AMIMCl is also involved in the mechanism, through the formation of electron-donor–electron-acceptor complexes between its charged species and the oxygen/hydrogen of cellulose. In particular, the cation of AMIMCl binds to oxygen atoms, whereas the Cl[−] binds to the hydrogen ones, leading to the breakage of inter- and intra-molecular hydrogen bonds of cellulose, thus facilitating its hydrolysis. As already found in previous works, Sn⁴⁺ can convert biomass into fructose and HMF. It is important to underline that the elevated HMF yields reported in this work acquire further value considering that they have been obtained starting from a high biomass loading of 20 wt%. Recently, Chang et al. prepared a sulfonated peanut shells catalyst (PSC) by treating the pulverized peanut shells with sulfuric acid, and this catalyst was tested for HMF synthesis from peanut shells, water hyacinth, and stalk, reaching HMF yields of 11, 6, and 15 mol%, respectively (runs 133–135, Table 5) [131].

Finally, other systems, such as DES, which can be simultaneously employed as solvent and catalyst, and heteropolyacids have been proposed as catalysts for the conversion of not-pretreated biomass to HMF in biphasic medium. The available data are summarized in Table 6.

Table 6. HMF production from raw biomasses in biphasic and/or multiple-solvent systems with other catalysts.

Entry	Feedstock (wt%)	Catalyst (wt _{biomass} /wt _{catalyst})	Solvent	T (°C)	t (min)	Heat ¹	Y _{HMF} (mol%)	Ref
136	Corn husk (1.8%)	DES ² (0.05)	DES ² /ethyl acetate (1/2.3 v/v)	100	120	Conv.	13	[92]
137	Corn husk (1.8%)	DES ² (0.05)	DES ² /MIBK (1/2.3 v/v)	100	120	Conv.	9	[92]
138	Corn cob (1.8%)	DES ² (0.05)	DES ² /MIBK (1/2.3 v/v)	100	120	Conv.	11	[92]
139	Macroalgae <i>Ulva lactuca</i> (1.8%)	DES ² (0.05)	DES ² /MIBK (1/2.3 v/v)	100	120	Conv.	7	[92]
140	Microalgae <i>Porphyridium cruentum</i> (1.8%)	DES ² (0.05)	DES ² /MIBK (1/2.3 v/v)	100	120	Conv.	9	[92]

141	Corn stover (2.2%)	ChH ₂ PW ₁₂ O ₄₀ (0.3)	H ₂ O/MIBK (1/10 v/v)	140	600	Conv.	28 ³	[132]
142	Pinewood (2.2%)	ChH ₂ PW ₁₂ O ₄₀ (0.3)	H ₂ O/MIBK (1/10 v/v)	140	600	Conv.	12 ³	[132]
143	Husk of xanthoceras (2.2%)	ChH ₂ PW ₁₂ O ₄₀ (0.3)	H ₂ O/MIBK (1/10 v/v)	140	600	Conv.	13 ³	[132]
144	Corn stover (3.2)	Ch5-AgPW ⁴ (1.3)	H ₂ O/MIBK (2/3 v/v)	170	180	Conv.	26	[133]
145	Rice straw (3.2)	Ch5-AgPW ⁴ (1.3)	H ₂ O/MIBK (2/3 v/v)	170	180	Conv.	20	[133]
146	Bagasse (3.2)	Ch5-AgPW ⁴ (1.3)	H ₂ O/MIBK (2/3 v/v)	170	180	Conv.	19	[133]

¹ "Conv." and "MW" stand for "Conventional" and "Microwave". ² The deep eutectic solvent (DES) is composed by choline chloride/oxalic acid. ³ Calculated as wt%. ⁴ Chitin-AgH₂PW₁₂O₄₀ containing 5 wt% chitin.

Bodachivskiy et al., in addition to the conversion of corn husk only in DES (run 53, Table 2), tested different extraction solvents, such as ethyl acetate and MIBK, and also applied a biphasic system to the conversion of other biomasses (corn cob, macroalgae *Ulva lactuca*, and microalgae *Porphyridium cruentum*), in all cases keeping the same loading of only 1.8 wt% (runs 136–140, Table 6) [92]. Complete cellulose conversion was achieved only starting from algae, underlining that polysaccharides in the terrestrial substrates are more resistant to hydrolysis than those of marine sources. However, despite the complete cellulose conversion, analogous HMF yields, in the range of 7 to 13 mol%, were reached from terrestrial and marine feedstocks, probably due to the larger amount of by-products obtained with the latter.

Another class of emerging catalysts for the conversion of biomasses to value products is represented by the heteropolyacids [134]. Zhang et al. synthesized a heteropolyacid catalyst starting from choline chloride and H₃PW₁₂O₄₀, giving ChH₂PW₁₂O₄₀ that was employed as a catalyst for the conversion of corn stover, pinewood, and husk of xanthoceras to HMF, working with H₂O/MIBK (runs 141–143, Table 6) [132]. The catalyst was insoluble in water at room temperature but became soluble at temperatures higher than 60 °C, so when the reaction was performed at 140 °C, the ChH₂PW₁₂O₄₀ acted as a homogeneous catalyst. According to the authors, ChH₂PW₁₂O₄₀ could be self-assembled as micellar spheres of polar H₂PW₁₂O₄₀[−] outside and Ch⁺ inside, providing a sort of nanoreactor. During the hydrolysis, cellulose could be adsorbed by hydrophilic H₂PW₁₂O₄₀[−], which promoted the conversion to HMF. Subsequently, the formed HMF was stabilized by the hydrophobic Ch⁺ and extracted by MIBK that, together with the low Brønsted acidity of ChH₂PW₁₂O₄₀, allowed the enhancement of the HMF yield, limiting the formation of levulinic and formic acids. Lai et al. prepared the catalyst treating the heteropolyacid H₃PW₁₂O₄₀ with AgNO₃, obtaining the exchange of a proton of the heteropolyacid with Ag⁺, and chitin, which introduced Lewis acid sites and increased the stability of the catalyst, respectively [133]. The authors employed the prepared catalyst in the synthesis of HMF from 3.2 wt% of corn stover, rice straw, or bagasse, achieving, under the same reaction conditions, HMF yields of 26, 20, and 19 mol%, respectively (runs 144–146, Table 6).

2.2. Pretreated Biomass

As previously introduced, biomass pretreatment generally causes the rupture of the complex network between its components (cellulose, hemicellulose, and lignin) and the reduction of cellulose crystallinity, thus favoring its conversion into HMF and increasing its yield. The available pretreatment techniques are classified into physical, chemical, and biological ones. Among the physical pretreatments, ball-milling leads to the decrease in particle sizes and cellulose crystallinity, due to the breakage of hydrogen bonds in cellulose, together with the increase of the number of β-1,4-glycosidic bonds accessible to the catalyst [135]; ultrasonic and MW pretreatments allow the destruction of the crystalline structure of cellulose, thus improving the hydrolysis efficiency, but these technologies require expensive equipment, so their application on a large scale is rather limited [136,137]; instead, a steam explosion leads to the destruction of the biomass texture

through the decompression of steam [138]. On the other hand, the chemical pretreatments include the hydrothermal one, which is generally carried out at 150–260 °C, releasing sugars [139]; the use of dilute acid, which employs inorganic acids (e.g., H₂SO₄, HCl, H₃PO₄) or organic acids (e.g., oxalic acid, peracetic acid) for the hydrolysis of polysaccharides to sugars [140]; alkali pretreatments, aiming at lignin dissolution in NaOH, KOH, or Ca(OH)₂ aqueous solutions, by destroying the network structure of biomass and weakening the hydrogen bonds between cellulose and hemicellulose [141]. Lastly, biological pretreatments require the use of appropriate microorganisms, which release ligninolytic and hydrolytic enzymes. In this way, the depolymerization of lignin and the hydrolysis of polysaccharides take place without the generation of wastes and under low-energy-demand conditions. However, in comparison with other pretreatments, the biological ones require the strict control of the reaction parameters and very long reaction times [142]. All these pretreatment strategies have been adopted for the synthesis of HMF from real biomasses, and in the following paragraphs the most relevant results are described.

2.2.1. One-Solvent Systems

The conversion of pretreated biomasses in one-solvent systems involves the employment of water as the reaction medium and both homogeneous and heterogeneous catalysts, as evidenced by the literature results reported in Table 7.

Table 7. HMF production from raw pretreated biomasses in one-solvent systems.

Entry	Feedstock (wt%)	Catalyst (wt _{biomass} /wt _{catalyst})	Solvent	T (°C)	t (min)	Heat ¹	Y _{HMF} (mol%)	Ref
147	Sugar beet pulp ² (5.0%)	/	H ₂ O	193	51	Conv.	10	[143]
148	Polyester/cotton mixed fabric waste ³ (1.0%)	Citric acid (1.0)	H ₂ O	225	60	Conv.	12 ⁴	[144]
149	Eucalyptus ⁵ (1.0%)	InCl ₃ (7.3)	H ₂ O	200	120	Conv.	14	[145]
150	Seaweed <i>Gracilaria dura</i> ⁶ (4.8%)	KHSO ₄ (250.0)	H ₂ O	110	540	Conv.	61	[146]
151	Corn stover ⁷ (1.0%)	AlCl ₃ (3.8) + Maleic acid (4.3)	H ₂ O	180	20	MW	16	[147]
152	Used clothing ³ (0.7%)	Ca ₃ (PO ₄) ₂ (0.1)	H ₂ O	200	120	Conv.	31	[72]
153	Used paper ³ (0.7%)	Ca ₃ (PO ₄) ₂ (0.1)	H ₂ O	200	120	Conv.	22	[72]
154	Japanese cedar ³ (1.5%)	Ca ₃ (PO ₄) ₂ (0.26)	H ₂ O	200	120	Conv.	36	[72]
155	Microalgae <i>Chlorococcum</i> ³ (1.0%)	H-ZSM-5 (1.5)	H ₂ O	200	120	Conv.	47	[74]
156	Corn cob ⁸ (10.0%)	HSO ₃ -ZSM-5 (3.3)	H ₂ O	150	300	Conv.	24	[148]
157	Corn stalk ⁹ (1.6%)	SO ₄ ²⁻ /ZrO ₂ (5.0)	H ₂ O	230	120	Conv.	60	[149]

¹ "Conv." and "MW" stand for "Conventional" and "Microwave". ² Hydrothermal extraction of pectin. ³ Ball-milled pretreated. ⁴ Calculated as wt%. ⁵ Extraction of cellulose. ⁶ Extraction of agarose. ⁷ Fractionated. ⁸ Solvent extraction. ⁹ Delignification.

As for the not-pretreated biomass, in this case the autocatalytic HMF synthesis in water has been investigated. Pińkowska et al. optimized the conversion of pectin-free sugar beet pulp through the support of a Doehlert statistical design, achieving the highest HMF yield of 10 mol% (run 147, Table 7) [143]. However, the autocatalytic reaction does not provide sufficient acidity to promote the HMF production, thus the employment of an acid catalyst is required. Therefore, Kawamura et al. carried out the conversion of ball-milled polyester/cotton mixed fabric waste, at a loading of only 1 wt%, and in the presence of citric acid as the catalyst. The authors reported a highest HMF yield of 12 wt%, together with 14 wt% of glucose, without the co-production of levulinic acid, proving that the adopted reaction conditions were sufficiently mild to avoid the relevant formation of by-products (run 148, Table 7) [144]. Wei et al. extracted the cellulose frac-

tion from dewaxed eucalyptus by treating it with nitric acid and ethanol and finally obtaining a white fiber. This was subsequently hydrolyzed at low substrate loading (1 wt%), working in the presence of InCl_3 as the catalyst and obtaining an HMF yield of only 14 mol%, due to the promoted rehydration pathway (run 149, Table 7) [145]. A higher HMF yield, equal to 61 mol%, was reported by Kholiya et al., who prepared an agarose aqueous solution from the seaweed *Gracilaria dura*. The authors supposed that only the 3,6-anhydrogalactopyranose unit of agarose was converted to HMF in the presence of KHSO_4 as the catalyst, whereas the other agarose units gave humins, and galactose was stable in the aqueous phase (run 150, Table 7) [146]. KHSO_4 showed not only Brønsted acidity, which contributed to the break of glycosidic bonds and the dehydration of 3,6-anhydrogalactopyranose units to HMF, but also Lewis acidity, responsible for the isomerization step. The recyclability of KHSO_4 was investigated, by extracting HMF with an organic solvent and recycling the KHSO_4 aqueous solution in nine consecutive runs, each time adding newly extracted agarose. Surprisingly, the HMF yield increased with the increase of cycles, probably as a consequence of the salt-out process, occurring during the recycling. In fact, the extracted agarose also contains potassium, sodium, and other metal ions whose concentrations increased with the increase of the recycling tests, thus contributing to the salt-out process that enhances the HMF selectivity and yield. In addition to the use of only inorganic salts, their combination with organic acid has also been investigated for the conversion of pretreated biomass, as reported by Jin et al., who prepared formylated cellulose through the treatment of corn stover with formic acid and adopted it as the feedstock for HMF production. They employed AlCl_3 and maleic acid as the catalytic system, working under MW heating but obtaining a HMF yield of only 16 mol%, despite the low substrate loading (1 wt%), due to the high hydrophobicity, crystallinity, and thermal stability of the prepared formylated cellulose (run 151, Table 7) [147]. However, the reached HMF yield was higher than that achieved starting from α -cellulose and microcrystalline cellulose, in both cases about 10 mol%. Mimura et al. introduced the ball-milling pretreatment for the conversion of used clothing, used paper, and Japanese cedar, in the presence of the heterogeneous catalyst $\text{Ca}_3(\text{PO}_4)_2$, allowing a marked improvement of HMF yields from 10, 8, and 14 mol% (runs 24–26, Table 1) to 31, 22, and 36 mol% (runs 152–154, Table 7), respectively, but still working at low substrate loadings (0.7–1.5 wt%) [72]. In fact, the ball-milling contributed to the decrease of cellulose particles and the increase of the amorphous fraction of cellulose, at the expense of the crystalline one, thus increasing the superficial contact area between substrate and catalyst and enhancing the reactivity of the substrate. A slight improvement in the HMF yield from 39 (run 28, Table 1) to 47 mol% was also reported by Wang et al., who ball-milled the microalgae *Chlorococcum* and converted it in the presence of H-ZSM-5 as the catalyst, adopting the low biomass loading of 1 wt% (run 155, Table 7) [74]. On the other hand, other pretreatments have been adopted. In this regard, Hoang et al. pretreated the corn-cob with a mixture of ethanol and acetone for 6 h to remove the extractives, and then the residue was adopted as the feedstock for HMF synthesis. A sulfonic acid-functionalized mesoporous ZSM-5 zeolite ($\text{HSO}_3\text{-ZSM-5}$) was synthesized and tested for this reaction, reaching an unsatisfactory HMF yield of 24 mol%, due to the high formation of humins and rehydration acids (run 156, Table 7) [148]. Finally, the delignification pretreatment was also investigated for the conversion of biomass in water. In fact, this could represent a very promising approach to activate the cellulose conversion and enhance HMF synthesis, because cellulose becomes more accessible to the acid sites of the catalyst. This pretreatment was adopted by Zhang et al., who delignified the corn stover with sodium chlorite at 75 °C for 2 h and converted the pretreated biomass, with the low loading of 1.6 wt%, in the presence of the solid super acid $\text{SO}_4^{2-}/\text{ZrO}_2$ [149]. The authors found that the sodium chlorite amount strongly affected the cellulose conversion to HMF, obtaining the highest HMF yield of 61 mol% when the concentration of sodium chlorite in the pretreatment was 6 wt% (run 157, Table 7). Moreover, the adopted catalyst was stable and

recyclable in five further consecutive cycles, allowing the achievement of an HMF yield of 55 mol% at the end of the fifth cycle.

2.2.2. Ionic Liquids (ILs) and Deep Eutectic Solvents (DESs)

The employment of ILs and DESs as the reaction medium is not limited to the conversion of not pretreated biomasses, but it can also be proposed for the pretreated ones, as shown by the literature results reported in Table 8.

Table 8. HMF production from raw pretreated biomasses in ionic liquids and deep eutectic solvents.

Entry	Feedstock (wt%)	Catalyst (wt _{biomass} /wt _{catalyst})	Solvent	T (°C)	t (min)	Heat ¹	Y _{HMF} (mol%)	Ref
158	Wood dust ² (n.a. ³)	H ₂ SO ₄ (20.0 ⁴)	ChCl ⁵ /citric acid (2/1 mol/mol)	130	5	Conv.	24 ⁶	[150]
159	Wood chips ⁷ (4.8%)	CrCl ₃ ·6H ₂ O (1.3)	[BMIM]Cl ⁸	120	120	Conv.	79	[84]
160	Rice straw ⁷ (4.8%)	CrCl ₃ ·6H ₂ O (1.3)	[BMIM]Cl ⁸	120	120	Conv.	76	[84]
161	Waste cottonseed hull ⁹ (4.0%)	CuCl ₂ ·2H ₂ O (5.0)	[EMIM]Ac ¹⁰ + [BMIM][TOS] ¹¹ (1/6 v/v)	120	150	Conv.	42	[151]
162	Waste cottonseed hull ⁹ (4.0%)	H ₄ [Si(W ₃ O ₁₀) ₄]·xH ₂ O (5.0)	[EMIM]Ac ¹⁰ + [BMIM][TOS] ¹¹ (1/6 v/v)	120	150	Conv.	40	[151]
163	Apple waste ¹² (6.3%)	D001-cc ion-exchange resin (1.0)	[BMIM]Cl ⁸	140	60	Conv.	45	[152]
164	Orange waste ¹² (6.3%)	D001-cc ion-exchange resin (1.0)	[BMIM]Cl ⁸	140	60	Conv.	42	[152]
165	Sugarcane bagasse ¹³ (4.8%)	D001-cc ion-exchange resin (1.0)	[BMIM]OAc ¹⁴	140	25	MW	66	[68]
166	Wheat straw ⁹ (2.0%)	ChCl ⁵ / <i>p</i> -TSA (0.02)	ChCl ⁵ / <i>p</i> -TSA (n.a. ³)	80	30	Conv.	72	[153]
167	Rice husk ⁹ (2.0%)	ChCl ⁵ / <i>p</i> -TSA (0.02)	ChCl ⁵ / <i>p</i> -TSA (n.a. ³)	80	30	Conv.	68	[153]
168	Bagasse ⁹ (2.0%)	ChCl ⁵ / <i>p</i> -TSA (0.02)	ChCl ⁵ / <i>p</i> -TSA (n.a. ³)	80	30	Conv.	70	[153]

¹ "Conv." and "MW" stand for "Conventional" and "Microwave". ² Acid pretreatment (H₂SO₄ at 4 wt%) followed by steam explosion and enzymatic hydrolysis. ³ "n.a." stands for "not available". ⁴ Calculated respect to glucose present in the hydrolyzate deriving from pretreatment steps. ⁵ Choline chloride. ⁶ Calculated with respect to the moles of glucose. ⁷ Basic pretreatment. ⁸ 1-butyl-3-methylimidazolium chloride. ⁹ Isolation of cellulose by acid treatment. ¹⁰ 1-ethyl-3-methylimidazolium acetate. ¹¹ 1-butyl-3-methylimidazolium tosylate. ¹² Ultrasonic-[BMIM]Cl pretreatment. ¹³ Ultrasonic-[BMIM]OAc pretreatment. ¹⁴ 1-butyl-3-methylimidazolium acetate.

Chen et al. prepared a glucose-rich hydrolyzate from wood dust through an acid pretreatment, followed by a steam explosion and enzymatic hydrolysis, and adopted this hydrolyzate as feedstock for HMF synthesis in DES composed of choline chloride/citric acid [150]. The latter was a promising DES system, wherein choline chloride acted as a hydrogen bond acceptor and citric acid was chosen as a hydrogen bond donor, due to its high biodegradability. Despite the high viscosity of the DES, a temperature of 130 °C allowed the reduction of the hydrogen bond strength, thus reducing the viscosity of the solvent and leading to efficient HMF production. In fact, in the presence of H₂SO₄ as the catalyst, an HMF yield of 24 mol% was achieved (run 158, Table 8), which was like that

obtained starting from pure glucose. Nguyen et al. pretreated wood chips and rice straw with an alkaline solution (NaOH) that could cause a structural change in lignin, swelling, and the partial de-crystallization of cellulose, as well as the partial removal of hemicellulose, thus making the cellulose more prone to the conversion. The pretreated biomasses were catalytically hydrolyzed by $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ in the ionic liquid [BMIM]Cl, obtaining analogous HMF yields of 79 and 76 mol% starting from wood chips and rice straw, respectively (runs 159 and 160, Table 8) [84]. On the other hand, Ge et al. performed an acid pretreatment with sulfuric acid solution, aiming at the isolation of cellulose from waste cotton seed hull [151]. Successively, the authors employed two different catalysts for HMF synthesis from the isolated cellulose, in particular, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and the heteropolyacid $\text{H}_4[\text{Si}(\text{W}_3\text{O}_{10})_4] \cdot x\text{H}_2\text{O}$ in the solvent system composed of the ionic liquids [EMIM]Ac and [BMIM][TOS], achieving HMF yields of 42 and 40 mol%, respectively (runs 161 and 162, Table 8). When $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was employed as the catalyst, the two ionic liquids, [EMIM]Ac and [BMIM][TOS], had a synergistic role, the first having a strong dissolving ability towards the isolated cellulose, while the second one was able to form a complex with CuCl_2 ($[\text{CuCl}_2(\text{TOS})]^-$) active in the glucose conversion to HMF. Ji et al. adopted the ionic liquid [BMIM]Cl in the pretreatment of food wastes, such as apple and orange wastes, assisted by ultrasound sonication [152]. This approach facilitated a decrease in the crystallinity index, due to the synergistic effect of the ionic liquid, which is able to destroy the hydrogen bonds between the cellulose chains, and ultrasounds, which promoted the accessibility of the ionic liquid into the biomass through the generation of shear forces, shock waves, and a cavitation phenomenon. The authors found that ultrasounds strongly enhanced the dissolution of cellulose, destroying the dense structure of the not-pretreated biomass, which became rough and irregular, showing cracks and pores as a consequence of the pretreatment. The pretreated biomass was subsequently converted under conventional heating in the same ionic liquid, because [BMIM]Cl was a powerful solvent towards the cellulose dissolution, adopting commercial heterogeneous acid resins as catalysts. The best results were achieved with the macroporous strong acid-exchange resin D001, obtaining HMF yields of 45 and 42 mol% starting from apple waste and orange waste, respectively (runs 163 and 164, Table 8). These promising results could be explained by considering the textural properties of the D001 resin, which is characterized by large pore diameter, high surface area, and the easy and fast exchange of protons, all favorable properties for promoting the interaction between the substrate and the acid sites. Moreover, the catalyst was stable and recyclable, keeping the HMF yield almost constant after five consecutive runs. The same authors also adopted the ultrasound pretreatment for the conversion of sugarcane bagasse, using [BMIM]OAc as the solvent for both the pretreatment and the reaction step, due to its promising performance already shown in the conversion of not-pretreated sugarcane bagasse (run 47, Table 2) [68]. The introduction of this pretreatment strongly enhanced the HMF yield, and the authors found that ultrasound frequency positively influenced the reaction. In particular, the increase of ultrasound frequency from 20 to 40 kHz promoted the disruption of cellulose structure, resulting in a significant increase in the HMF yield from 36 to 66 mol% (run 165, Table 8). Finally, DESs were investigated in the dual role of solvent and catalyst for the HMF synthesis from cellulose extracted from wheat straw, rice husk, and bagasse [153]. In particular, the DES composed of choline chloride/*p*-toluenesulfonic acid gave the highest HMF yields with respect to the other tested DESs (choline chloride/oxalic acid and choline chloride/citric acid) due to its higher acidic properties. In this way, HMF yields equal to 72, 68, and 70 mol% were achieved from wheat straw, rice husk, and bagasse cellulose, respectively (runs 166–168, Table 8). Moreover, the recyclability of the system was tested for four cycles by adding fresh cellulose isolated from the wheat straw without any considerable loss in activity, thus proving that the system kept the efficiency almost constant.

2.2.3. Biphasic and/or Multiple-Solvent Systems

As previously described for the conversion of not-pretreated biomasses, for the pretreated ones the use of two or more solvents represents the most adopted approach. Both homogeneous and heterogeneous catalysts have been employed: the literature results for the homogeneous catalytic systems are reported in Table 9.

Table 9. HMF production from raw pretreated biomasses in biphasic and/or multiple-solvent systems with homogeneous catalysts (mineral acids, inorganic salts, and a combination of them).

Entry	Feedstock (wt%)	Catalyst (wt _{biomass} /wt _{catalyst})	Solvent	T (°C)	t (min)	Heat ¹	Y _{HMF} (mol%)	Ref
169	Melon rind ² (2.7%)	H ₂ SO ₄ (10.2)	H ₂ O-NaCl/THF (1/3 v/v)	180	30	Conv.	14	[154]
170	Melon rind ² (2.7%)	H ₂ SO ₄ (10.2)	H ₂ O-NaCl/THF (1/3 v/v)	180	30	MW	13	[154]
171	Eucalyptus ³ (1.0%)	InCl ₃ (7.3)	H ₂ O-NaCl/THF (1/3 v/v)	200	120	Conv.	43	[145]
172	Eucalyptus ³ (1.0%)	AlCl ₃ (12.1)	H ₂ O-NaCl/THF (1/3 v/v)	200	120	Conv.	40	[145]
173	Eucalyptus ³ (1.0%)	FeCl ₃ (9.8)	H ₂ O-NaCl/THF (1/3 v/v)	200	120	Conv.	38	[145]
174	Bagasse ³ (1.0%)	InCl ₃ (7.3)	H ₂ O-NaCl/THF (1/3 v/v)	200	120	Conv.	46	[145]
175	Birch wood ⁴ (2.2%)	Salts (0.3)	Seawater/THF (1/6 v/v)	200	300	Conv.	43	[155]
176	Beech wood ⁴ (2.2%)	Salts (0.3)	Seawater/THF (1/6 v/v)	200	300	Conv.	44	[155]
177	Pine wood ⁴ (2.2%)	Salts (0.3)	Seawater/THF (1/6 v/v)	200	300	Conv.	46	[155]
178	Corn stalks ⁴ (2.2%)	Salts (0.3)	Seawater/THF (1/6 v/v)	200	300	Conv.	50	[155]
179	Molasses ⁵ (12.8%)	AlCl ₃ (61.5)	H ₂ O/GVL (1/4 v/v)	160	180	Conv.	28	[113]
180	Corn straw ⁶ (1.0%)	Al ₂ (SO ₄) ₃ (2.8)	H ₂ O-NaCl/GVL (1/4 v/v)	165	50	Conv.	30	[156]
181	Rice straw ⁶ (1.0%)	Al ₂ (SO ₄) ₃ (2.8)	H ₂ O-NaCl/GVL (1/4 v/v)	165	50	Conv.	35	[156]
182	Cow dung ⁶ (1.0%)	Al ₂ (SO ₄) ₃ (2.8)	H ₂ O-NaCl/GVL (1/4 v/v)	165	50	Conv.	35	[156]
183	Poplar sawdust ⁶ (1.0%)	Al ₂ (SO ₄) ₃ (2.8)	H ₂ O-NaCl/GVL (1/4 v/v)	165	50	Conv.	66	[156]
184	Corn waste ⁷ (4.8%)	SnCl ₄ (3.5)	H ₂ O/acetone (1/1 v/v)	140	10	MW	27	[110]
185	Taro waste ⁷ (4.8%)	SnCl ₄ (3.5)	H ₂ O/acetone (1/1 v/v)	140	10	MW	32	[110]
186	Corn straw ⁸ (2.5%)	SnCl ₄ (0.7)	DES ⁹ /DMSO (1/1 v/v)	140	60	Conv.	28	[157]
187	Waste coffee grounds ² (2.4%)	Al(NO ₃) ₃ ·9H ₂ O (2.7) + H ₂ SO ₄ (8.5)	H ₂ O/DMSO (3/2 v/v)	n.a. ¹⁰	20	MW	14 ¹¹	[158]
188	Spent coffee grounds ¹² (5.0% ¹³)	AlCl ₃ (79.0) + HCl (465.0)	H ₂ O-NaCl/GVL (1/2 v/v)	170	20	Conv.	8 ¹¹	[159]
189	Pistachio hull ¹²	AlCl ₃ (79.0) +	H ₂ O-NaCl/GVL	170	20	Conv.	8 ¹¹	[159]

190	Potato peels ¹⁴ (5.0% ¹³) (4.0%)	HCl (465.0) 1°: LiBr (0.2) + H ₂ SO ₄ (8.2) 2°: AlCl ₃ (2.0) ¹⁵	(1/2 v/v) 1°: H ₂ O 2°: H ₂ O/2-butanol (1/3 v/v)	1°: 140 2°: 160	1°: 60 2°: 180	Conv.	54	[160]
191	Corn stover ¹⁶ (1.0%)	AlCl ₃ (3.8) + Maleic acid (4.3)	H ₂ O/acetone (2/1 v/v)	180	20	MW	31	[147]
192	High-fructose corn syrup ¹⁷ (2.2%)	CaCl ₂ (1.1) + Gluconic acid (1.2)	H ₂ O/MeTHF (1/4 v/v)	150	120	Conv.	82	[161]
193	High-fructose corn syrup ¹⁷ (2.2%)	CaCl ₂ (0.2) + Gluconic acid (1.2)	H ₂ O/MeTHF (1/4 v/v)	150	10	MW	86	[161]

¹ "Conv." and "MW" stand for "Conventional" and "Microwave". ² Solvent extraction. ³ Extraction of cellulose. ⁴ Lignin depolymerization. ⁵ Tricalcium phosphate with hydrochloric acid treatment. ⁶ Ball-milling with Al₂(SO₄)₃. ⁷ Supercritical CO₂ extraction. ⁸ Ultrasound pretreatment. ⁹ Choline chloride/oxalic acid (1/1 mol/mol). ¹⁰ "n.a." stands for "not available". ¹¹ Calculated as wt%. ¹² Fractionation, enzymatic hydrolysis, and glucose isomerization. ¹³ Fructose concentration employed for the HMF synthesis at the end of the pretreatment steps. ¹⁴ Ultrasound extraction of antioxidants. ¹⁵ Calculated respect to glucose formed in the first step. ¹⁶ Fractionation. ¹⁷ Enzymatic oxidation.

To the best of our knowledge, only the work of Lucas-Torres et al. reported the use of mineral acid as the catalyst for the conversion of pretreated biomass in the biphasic system [154]. The authors valorized the melon rind through the extraction of fatty acids and polar compounds, such as antioxidant polyphenols, with cyclohexane and ethanol, respectively. The solid residue recovered at the end of this pretreatment was converted to HMF, adopting H₂SO₄ as the catalyst under both conventional and MW heating systems with H₂O–NaCl/THF, obtaining analogous results with the two heating approaches (runs 169 and 170, Table 9). However, modest HMF yields (14 mol%) were obtained under the adopted reaction conditions, because H₂SO₄ was efficient in the hydrolysis of cellulose to glucose but not suitable for the conversion of glucose to HMF. Many papers described the use of inorganic salts as catalysts. Wei et al. adopted the H₂O–NaCl/THF solvent for the conversion of extracted cellulose from dewaxed eucalyptus catalyzed by InCl₃ [145]. The authors found that the use of a biphasic system strongly improved the HMF yield from 14 mol%, achieved in water (run 149, Table 7), to 43 mol% (run 171, Table 9), ascribable to the continuous separation of HMF from the aqueous phase to the organic phase. Comparing the catalytic performance of InCl₃ with other chlorides, such as AlCl₃ and FeCl₃ (runs 172 and 173, Table 9), the authors proved that InCl₃ was the best one, due to the combined effect of In³⁺, acting as Lewis acid in the isomerization of glucose to fructose, and the partially hydrolyzed In–OH group, acting as the Brønsted acid in the dehydration of fructose to HMF. InCl₃ was also employed for the conversion of pretreated bagasse, leading to the HMF yield of 46 mol% (run 174, Table 9). Lastly, the whole reaction medium was easily recycled. For this purpose, the organic phase, containing THF and HMF, was distilled to recover the product and recycle THF in subsequent runs together with the aqueous phase containing the InCl₃ deriving from the previous run. During the recycling, the HMF yield gradually decreased, due to the loss of InCl₃. However, despite the interesting HMF yields achieved by Wei et al., the low adopted biomass loading (1 wt%) makes the process not very attractive at a larger scale. Taking into consideration that the presence of the inorganic salt was important to improving the separation between water and THF and also to enhancing the hydrolysis of biomass, Guo et al. did not use pure water as the reaction medium, but seawater that naturally contains a large amount of salts and proposed the full valorization of several lignocellulosic biomasses, such as birch wood, beech wood, pine wood, and corn stalks [155]. The first step provided the depolymerization of lignin to alkyl methoxy phenols, which was catalyzed by Pd/C and Yb(OTf)₃, and performed in methanol at 200 °C for 2 h with 20 bar of H₂. At the end, the solid residue contained Pd/C, hemicellulose, and cellulose, while the liquid phase included methylated C5 sugars, lignin monomers, and Yb(OTf)₃. These latter were

separated through rotary vapor, aimed at the removal of the solvent, followed by water extraction, for the recovery of methylated C5 sugars and $\text{Yb}(\text{OTf})_3$, and extraction with ethyl acetate, for the recovery of lignin monomers. $\text{Yb}(\text{OTf})_3$ was separated from methylated C5 sugars and reused in the next run, whereas the lignin monomers were converted into aromatic hydrocarbons through a hydrodeoxygenation reaction, adopting $\text{Ru}/\text{Nb}_2\text{O}_5$ as catalyst and 2-propanol as hydrogen donor. In this approach, the valorization of lignin is proposed as the pretreatment step, leading to a solid residue rich in hemicellulose and cellulose, also containing the heterogeneous adopted catalyst Pd/C. This residue was converted to furfural and HMF in a biphasic system of seawater/THF, leading to an HMF yield of 43, 44, 46, and 50 mol%, starting from birch wood, beech wood, pine wood, and corn stalks, respectively (runs 175–178, Table 9). The proposed acid-free process was effective for the production of HMF in good yields, also enabling the recovery of Pd/C as solid residue, which was recycled in the delignification step. At the end, the organic phase, containing furfural and HMF, was separated from the aqueous phase, containing salts, and the latter was directly recycled in subsequent runs, keeping unaltered the HMF yield for three cycles. However, despite the full valorization of biomasses and the interesting HMF yields, the process is complex, expensive, and not so safe, due to the employment of a noble metal (Pd/C) and hydrogen in the first step.

Besides THF, GVL was also largely investigated as an organic solvent in the biphasic system, being more promising than THF, thanks to its renewable origin. An example is reported in the work of Tian et al., who highlighted a low HMF yield starting from molasses (run 101, Table 4). For this reason, they pretreated this biomass with tricalcium phosphate and hydrochloric acid to remove inorganic salts and organic impurities, thus slightly enhancing the HMF yield up to 28 mol%, working in $\text{H}_2\text{O}/\text{GVL}$ under the same experimental conditions and the same promising biomass loading of 12.8 wt% (run 179, Table 9) [113]. Shen et al. pretreated several biomasses through ball-milling in the presence of $\text{Al}_2(\text{SO}_4)_3$, and the resulting mixture was treated in the biphasic system $\text{H}_2\text{O}-\text{NaCl}/\text{GVL}$, to carry out the hydrolysis catalyzed by $\text{Al}_2(\text{SO}_4)_3$ [156]. The presence of $\text{Al}_2(\text{SO}_4)_3$ during the ball-milling step allowed a greater destruction of cellulose, generating more cracks in the surface than the simple ball-milling because the salt entered into the crystalline region of cellulose and broke the hydrogen bonds, thus reducing the size of biomass particles and destroying the cellulose crystal structure. Thanks to this pretreatment, the biomasses were successfully converted to HMF, leading to yields of about 30, 35, 35, and 66 mol%, starting from corn straw, rice straw, cow dung, and poplar sawdust, respectively, employed at a loading of only 1 wt% (runs 180–183, Table 9). Yu et al. have deeply investigated the synthesis of HMF starting from biomasses catalyzed by inorganic salts in the biphasic system [103–108,110]. They also performed the pretreatment with supercritical CO_2 , aiming at the extraction of saturated and unsaturated fatty acids from corn and taro wastes [110]. This pretreatment step, in addition to allowing the separation and the potential exploitation of waxes and fatty acids, could also improve the solubility of polysaccharides, enabling a better contact between catalyst and substrate. However, only limited changes in the biomass structure were observed after the pretreatment, and HMF yields like those previously reported for the not-pretreated biomasses (runs 96 and 97, Table 4) were obtained (runs 184 and 185, Table 9). A possible explanation for this evidence could be that the release of CO_2 was not fast enough to disrupt the biomass structure or to solubilize polysaccharides. Different inorganic salts were also investigated in natural deep eutectic solvents (NATDES). Lu et al. found that the DES composed of choline chloride/oxalic acid and SnCl_4 were, respectively, the most promising solvent and catalyst for the synthesis of HMF from corn straw pretreated by ultrasound [157]. Sonication at 40 kHz produced cavitation, obtaining a local increase of temperature and pressure, which was effective for destroying the structure of biomass and increasing the superficial area, thus improving the extraction of cellulose. However, the high viscosity of NATDES hampered the progress of the conversion of hexose to HMF, resulting in the imperative addition of a co-solvent, such as DMSO, that lowered

the viscosity of the reaction medium, helped NATDES to dissolve lignocellulose and improved sugars conversion, leading to the highest HMF yield of 28 mol% (run 186, Table 9).

The combination of inorganic salts with mineral and organic acids has also been proposed for the conversion of the pretreated ones. Ganado et al. pretreated the waste coffee grounds through extraction with water for the recovery of valuable extractives, such as caffeine and chlorogenic acid, and subsequently converted the solid residue to HMF in a H₂O/DMSO system, working in the presence of Al(NO₃)₃·9H₂O and H₂SO₄ as the catalytic system [158]. The authors performed the reaction under MW heating and optimized the HMF yield thanks to the support of the Box–Behnken experimental design, reaching the highest HMF yield of 14 wt% (run 187, Table 9). Spent coffee grounds, together with pistachio hull, were also proposed as substrates by Pereira et al. [159]. The authors fractionated the wastes through an organosolv process, employing H₂SO₄ as catalyst and water–MIBK, water–ethanol, or water–acetone as the solvent, thus obtaining a water-solubilized fraction predominantly deriving from hemicellulose, a cellulose-enriched solid residue and a lignin-enriched organic phase. The cellulose-enriched solid residue was then enzymatically hydrolyzed to glucose in the presence of cellulase from *Aspergillus niger*. Glucose was isomerized to fructose in the presence of glucose isomerase from *Streptomyces murinus*, and fructose was converted to HMF, adopting AlCl₃ and HCl as the catalytic system in the sustainable biphasic solvent H₂O–NaCl/GVL, giving comparable HMF yields of only 8 wt% starting from both spent coffee grounds and pistachio hull (runs 188 and 189, Table 9). On the other hand, to achieve the complete exploitation of the biomass, the authors also investigated the valorization of the other two obtained fractions. In particular, the water-solubilized fraction containing hemicellulose sugars was fermented in the presence of the oleaginous yeast *Metshnikowia pulcherrima* to produce bio-oil, whereas the high heating value of the lignin-enriched organic phase was evaluated to propose this fraction as a liquid fuel. Also Ebikade et al. investigated the complete exploitation of the waste potato peels, carrying out the first ultrasonic-assisted extraction of antioxidants, followed by the conversion of the cellulosic fraction to HMF and, finally, the pyrolysis of lignin to biochar [160]. The conversion of the cellulosic fraction was performed in two steps. In the first one, the extracted potato peels were hydrolyzed in 25 wt% LiBr and 0.05 M H₂SO₄ solution to produce glucose. A glucose yield of about 90 mol% was achieved under the best reaction conditions, and then it was converted to HMF in the same reactor, adding AlCl₃ as the Lewis catalyst and 2-butanol as the organic solvent, to create a biphasic system that reduced the formation of by-products. This second step was optimized through the support of a Box–Behnken design, considering temperature, reaction time, and AlCl₃ concentration as the independent variables, reaching the highest HMF yield of 54 mol% (run 190, Table 9). For the recycling test, the aqueous phase containing LiBr, H₂SO₄, and AlCl₃ was separated from the organic one and reused in two subsequent reactions, leading to the HMF yield of 50 mol% after the third recycling, underlining that only a slight decrease of activity occurred, probably due to the partial loss of LiBr in the organic phase confirmed by the ICP-MS analysis. The solid residue recovered at the end of the HMF synthesis was pyrolyzed, and the obtained biochar proved to be effective in removing pesticides from water and employable also as soil enrichment. AlCl₃ was also adopted in combination with an organic acid, such as maleic acid, for the conversion to HMF of formylated cellulose (loading of only 1 wt%), obtained from the pretreatment of corn stover with formic acid [147]. In particular, the combined employment of acetonitrile and water as the reaction medium strongly promoted the HMF formation, because the organophilic formyl group in the formylated cellulose had stronger interaction with the organic solvent rather than with only water, thus promoting the conversion of the formylated cellulose to glucose and increasing the HMF yield from 16 (run 151, Table 7) to 31 mol% (run 191, Table 9). Noteworthy, Lin et al. generated in situ organic acid by the enzymatic oxidation of high-fructose corn syrup, thus converting glucose to gluconic acid [161]. However, this is a weak acid and did not

provide sufficient protons to catalyze the fructose conversion to HMF. Therefore, to improve the dissociation constant of gluconic acid, the authors added a salt, because it is well-known that strong electrolytes improve the dissociation degree of a weak electrolyte. CaCl₂ was shown to be very effective for this purpose, allowing complete fructose conversion when associated with gluconic acid. On the other hand, low fructose conversion was reached when the salt was adopted alone, thus confirming the synergistic effect of the two catalysts. The authors carried out the reaction in the biphasic system H₂O/MeTHF and achieved a HMF yield of 82 mol% after 120 min under conventional heating (run 192, Table 9) and 86 mol% after only 10 min under MW heating (run 193, Table 9), working at the same temperature of 150 °C and adopting a low biomass loading (2.2 wt%).

Pretreated biomasses were also converted into HMF working in a biphasic medium in the presence of heterogeneous catalytic systems (Table 10).

Table 10. HMF production from raw pretreated biomasses in biphasic and/or multiple-solvent systems with heterogeneous catalysts.

Entry	Feedstock (wt%)	Catalyst (wt _{biomass} /wt _{catalyst})	Solvent	T (°C)	t (min)	Heat ¹	Y _{HMF} (mol%)	Ref
194	Food and beverage waste-derived high-fructose syrup ² (3.8%)	Amberlyst-36 (1.0)	H ₂ O/DMSO (1/1 v/v)	140	40	MW	71 ³	[162]
195	Apple waste ⁴ (4.0)	Sn-amberlyst-15 (0.3)	H ₂ O/MIBK (1/1 v/v)	120	120	Conv.	29	[163]
196	Melon rind ⁵ (2.7%)	Montmorillonite KSV (1.0)	H ₂ O-NaCl/THF (1/3 v/v)	180	30	Conv.	22	[154]
197	Melon rind ⁵ (2.7%)	Montmorillonite KSV (1.0)	H ₂ O-NaCl/THF (1/3 v/v)	180	30	MW	28	[154]
198	Microalgae <i>Dunaliella salina</i> ⁵ (4.6%)	H-ZSM-5 (6.0)	H ₂ O-NaCl/THF (1/1.7 v/v)	180	60	Conv.	39	[164]
199	Corn cob ⁵ (10.0%)	HSO ₃ -ZSM-5 (3.3)	H ₂ O/DMSO (1/3 v/v)	150	300	Conv.	63	[148]
200	Corn cob ⁵ (10.0%)	HSO ₃ -ZSM-5 (2.5)	H ₂ O/THF (1/3 v/v)	160	300	Conv.	63	[148]
201	Rice straw ⁶ (1.0%)	APG-SO ₃ H ⁷ (2.0)	H ₂ O-NaCl/GVL (1/4 v/v)	180	480	Conv.	31	[165]
202	Banana plant waste ⁸ (2.0%)	Al ₂ O ₃ -TiO ₂ -W (2.5)	H ₂ O-NaCl/THF (1/3 v/v)	175	180	Conv.	76	[166]
203	Banana plant waste ^{6,8} (2.0%)	Al ₂ O ₃ -TiO ₂ -W (2.5)	H ₂ O-NaCl/THF (1/3 v/v)	175	60	Conv.	80	[166]
204	Yellow dent corn ⁶ (30.0%)	Activated carbon (3.9) + Maleic acid (73.8) + AlCl ₃ (32.1)	H ₂ O/DMSO/ acetonitrile (2/2/1 v/v)	180	3	Conv.	85	[167]
205	Pineapple peels ⁹ (2.0%)	Sulfonated activated carbon (2.0)	H ₂ O/[BMIM]Cl ¹⁰ (4/1 v/v)	120	60	Conv.	50	[168]
206	Banana peels ⁹ (2.0%)	Sulfonated activated carbon (2.0)	H ₂ O/[BMIM]Cl ¹⁰ (4/1 v/v)	120	60	Conv.	45	[168]
207	Catalpa ^{6,9} (2.4%)	Sulfonated activated carbon (1.0) + AlCl ₃ (1.2)	H ₂ O/[BMIM]Cl ¹⁰ (n.a. ¹¹)	120	60	Conv.	86	[169]

208	Indian rosewood ^{6,9} (2.4%)	Sulfonated activated carbon (1.0) + AlCl ₃ (1.2)	H ₂ O/[BMIM]Cl ¹⁰ (n.a. ¹¹)	120	60	Conv.	70	[169]
209	Chinaberry ^{6,9} (2.4%)	Sulfonated activated carbon (1.0) + AlCl ₃ (1.2)	H ₂ O/[BMIM]Cl ¹⁰ (n.a. ¹¹)	120	60	Conv.	62	[169]
210	Babool ^{6,9} (2.4%)	Sulfonated activated carbon (1.0) + AlCl ₃ (1.2)	H ₂ O/[BMIM]Cl ¹⁰ (n.a. ¹¹)	120	60	Conv.	75	[169]
211	Corncob ⁹ (3.2%)	MCMP ¹² -Al (30.3)	H ₂ O/[moMIM][PF ₆] ¹³ (1/3 v/v)	200	180	Conv.	52	[170]
212	Corncob ⁹ (3.2%)	MCMP ¹² -Al (30.3) + MCMP ¹² -Cr (30.3) + MCMP ¹² -Mg (30.3)	H ₂ O/[moMIM][PF ₆] ¹³ (1/3 v/v)	200	180	Conv.	68	[170]

¹ "Conv." and "MW" stand for "Conventional" and "Microwave". ² Enzymatic hydrolysis, impurity removal, and enzymatic isomerization of glucose to fructose. ³ Calculated respect to fructose. ⁴ Milling, filtration on ceramic candle filter, neutralization with Na₂CO₃. ⁵ Solvent extraction. ⁶ Ball-milling. ⁷ Sulfonic acid functionalized attapulgite. ⁸ Extraction of cellulose. ⁹ Acid pretreatment. ¹⁰ 1-Butyl-3-methylimidazolium chloride. ¹¹ "n.a." stands for "not available". ¹² Magnetic-chitosan metalloporphyrin particles. ¹³ 1-Methyl-3-n-octylimidazolium-hexafluorophosphate.

Yu et al. employed industrial food (potato chips and oatmeal products) and beverage wastes (fruit juice, sport drink, and soft drink) as feedstock. This mixture was enzymatically pretreated by glucoamylase and sucrase enzymes to obtain glucose syrup, which was purified and further isomerized to fructose by a glucose isomerase enzyme [162]. The as-obtained fructose syrup was further purified and converted to HMF in a biphasic H₂O/DMSO system, employing the commercial acid resin amberlyst-36 as the catalyst. Under the optimal reaction conditions, the achieved HMF yield was 70 mol% (run 194, Table 10), and it also remained almost constant after being recycled four times, confirming the stability of the catalyst. Recently, Tempelman et al. employed the commercial resin amberlyst-15 exchanged with SnCl₂ (Sn-amberlyst-15) as the catalyst for the conversion of apple waste to HMF [163]. In this case, the authors milled the starting feedstock, which was filtered under vacuum, and the filtrate was neutralized by a Na₂CO₃ aqueous solution. After this pretreatment, MIBK (extraction solvent) and Sn-amberlyst-15 (catalyst), were added to the aqueous solution, and the reaction was carried out at 120 °C for 2 h, leading to an HMF yield of 29 mol% (run 195, Table 10). In addition, Lucas-Torres et al. investigated the HMF production from the food waste melon rind, which was pretreated by solvent extraction [154]. The authors obtained higher yields in the presence of the heterogeneous catalyst montmorillonite KSV (runs 196 and 197, Table 10) rather than with the mineral acid H₂SO₄ (runs 169 and 170, Table 9) working under the same reaction conditions both under conventional and microwave heating in the biphasic system H₂O–NaCl/THF. H₂SO₄ was mainly effective in the cellulose hydrolysis to glucose, but it was scarcely active towards the further conversion of glucose to HMF, whereas montmorillonite KSV was effective also for this last step. Moreover, in the presence of montmorillonite KSV, the highest HMF yield (28 mol%) was obtained under MW heating, further confirming the efficiency of this alternative heating system. The biphasic system H₂O–NaCl/THF was adopted for the conversion of the microalgae *Dunaliella salina* into HMF, in the presence of the commercial zeolite H-ZSM-5 as the catalyst [164]. Before the hydrothermal conversion, the microalgae was extracted by hexane to remove lipophilic compounds, such as carotenoids and triglycerides, and then it was converted to HMF, leading to a yield of 39 mol% (run 198, Table 10). In the work of Hoang et al., the H-ZSM-5 zeolite was sulfonated (HSO₃–ZSM-5) and employed for HMF synthesis from corncob, after extractive removal with a mixture of ethanol and acetone

[148]. Compared with the water medium (run 156, Table 7), both the adopted biphasic systems H₂O/DMSO and H₂O/THF allowed the improvement of the HMF yield from 24 (in water) up to 63 mol% (runs 199 and 200, Table 10), thanks to the enhancement of the biomass solubilization in the presence of the organic solvent and to the suppression of both HMF rehydration to acids and HMF polymerization to humins. Remarkably, the H₂O/DMSO system was particularly effective, giving the same HMF yield of the H₂O/THF system but at a lower temperature. On the other hand, DMSO has a very high boiling point (189 °C, at atmospheric pressure), making its recovery from the reaction mixture difficult. On this basis, H₂O/THF was further considered for the study of catalyst recyclability: after five subsequent runs, an HMF yield of 51 mol% was reached, confirming the absence of significant catalyst deactivation. The proposed process is interesting, thanks to the good biomass loading (10 wt%), which is higher than most of those reported up to now. Sun et al. proposed a green and facile strategy for the preparation of sulfonic-acid-functionalized attapulgite (APG-SO₃H) via a wet mechanical ball-milling method, employing 3-mercaptopropyltrimethoxysilane as the source of -SH groups. These were grafted on the clay and subsequently oxidized to -SO₃H with H₂O₂ at room temperature [165]. The synthesized catalyst was employed in the HMF synthesis from ball-milled rice straw (only 1 wt%) in a H₂O-NaCl/GVL system. Attapulgite is a natural clay mineral widely adopted as catalyst support, due to its low cost and high specific surface area. Moreover, being an aluminum-magnesium silicate clay, the magnesium of this clay could promote the isomerization of glucose to fructose, whereas the sulfonic groups could promote the hydrolysis of cellulose to glucose and the hydrolysis of fructose to HMF, thus the prepared APG-SO₃H catalyst was efficient, allowing the achievement of an HMF yield of 31 mol% (run 201, Table 10). The effectiveness of the ball-milling pretreatment for the improvement of HMF production was also demonstrated by Flores-Velázquez et al. [166]. The authors extracted the cellulose from banana plant waste through soft alkaline and acid treatments, thus recovering pure cellulose free of hemicellulose and lignin. This cellulose was converted to HMF in the H₂O-NaCl/THF biphasic system, employing Al₂O₃-TiO₂-W (with 5 wt% of tungsten) as the catalyst, obtaining the highest HMF yield of 76 mol% at 175 °C after 180 min (run 202, Table 10). However, when the cellulose was ball-milled, it was possible to speed up its conversion to HMF, achieving a maximum HMF yield of 80 mol% after only 60 min at 175 °C (run 203, Table 10). This study proved that the depolymerization of the long cellulose chains positively affected HMF production. The ball-milling pretreatment was also adopted by Overton et al. for the conversion of yellow dent corn at high loading (30 wt%), working in the H₂O/DMSO/acetonitrile medium, together with activated carbon, maleic acid, and AlCl₃ [167]. The activated carbon facilitated the increase in HMF yield up to 85 mol% (run 204, Table 10) by adsorbing the impurities originating from the dehydration of fructose, which can reduce the efficiency of the isomerization step and lead to the higher formation of by-products [171]. This result is very promising not only for the high achieved HMF yield but also for the highest adopted substrate loading (30 wt%) reported up to now, in agreement with the “high-gravity” approach, which allows the production of concentrated HMF streams. However, the substrate is largely employed in the food supply chain, thus its exploitation for HMF synthesis on a large scale could be poorly socially sustainable. Tyagi et al. prepared a sulfonated activated carbon catalyst, which was adopted for the conversion of acid-pretreated pineapple and banana peels to HMF in the H₂O/[BMIM]Cl solvent system [168]. The reaction conditions were optimized with a statistical model and the highest HMF yields of 50 and 45 mol% were achieved from pineapple and banana peels, respectively (runs 205 and 206, Table 10). In another work, the same authors proved that the addition of an electrolyte, such as AlCl₃, to the sulfonated activated carbon strongly improved the HMF yield starting from acid-pretreated hardwood biomasses [169]. The Lewis acidity of AlCl₃ can facilitate the isomerization step, thus enhancing the HMF yield. Among the investigated hardwood biomasses, the maximum disruption of the crystalline matrix was observed for Catalpa wood and the

highest HMF yield, equal to 86 mol% (run 207, Table 10), was obtained starting from this biomass, whereas HMF yields of 70, 62 and 75 mol% were achieved from Indian rosewood, chinaberry, and babool, respectively (runs 208–210, Table 10). At the end of the reaction, ethyl acetate was added to the mixture to separate HMF from the aqueous phase, composed of [BMIM]Cl and AlCl₃, and the last ones were reused in successive runs after evaporation under vacuum to remove moisture. The HMF yield gradually decreased from 86 to 26 mol%, after the sixth recycling runs, thus proving that a worsening of the [BMIM]Cl and AlCl₃ activities took place after each cycle. Yuan et al. also performed the conversion of the acid-pretreated biomass corncob to HMF [170]. The authors carried out the reaction in the H₂O/[moMIM][PF₆] solvent system, with magnetic-chitosan metalloporphyrin particles (MCMP-M) as catalyst. It was composed of Fe₃O₄, which represented the magnetic core, covered by a chitosan surface linked to metalloporphyrins, wherein the metallic species acted as the acid site. The employment of this type of catalyst had an evident positive effect on corncob hydrolysis. In particular, the MCMP-Al exhibited the best catalytic performances, leading to an HMF yield of 52 mol% (run 211, Table 10), but the mixed catalytic system involving MCMP-Al, MCMP-Cr, and MCMP-Mg allowed the further improvement of the HMF yield up to 68 mol%, under the same reaction conditions (run 212, Table 10). Noteworthy, these catalysts had magnetic properties, thus they can be easily separated from the reaction medium by the application of an external magnetic field and recycled in subsequent runs. In this regard, both the ionic liquid and the catalytic system were recycled in subsequent runs, and the catalytic efficiency started to decrease after the seventh recycling, probably due to the destruction of the magnetic-chitosan metalloporphyrin particles structure.

Lastly, DES and ILs have also been employed as the catalyst for the conversion of pretreated biomasses in two or more solvents, as reported in Table 11.

Table 11. HMF production starting from raw pretreated biomasses in biphasic and/or multi-solvent systems with ionic liquid and deep eutectic solvent as catalyst.

Entry	Feedstock (wt%)	Catalyst (wt _{biomass} /wt _{catalyst})	Solvent	T (°C)	t (min)	Heat ¹	Y _{HMF} (mol%)	Ref
213	Sugarcane bagasse ² (8.5%)	DES ³ (0.1)	H ₂ O/DES ³ (n.a. ⁴)	110	240	Conv.	57	[172]
214	<i>Camelia oleifera</i> fruit shell ⁵ (1.6%)	[BMIM]HSO ₄ ⁶ (0.2)	H ₂ O/1,4-dioxane (1/10 v/v)	180	20	MW	21	[173]

¹ "Conv." and "MW" stand for "Conventional" and "Microwave". ² Pretreatment with DES (choline chloride/lactic acid) at 100 °C for 4 h. ³ The deep eutectic solvent (DES) is composed by choline chloride/lactic acid. ⁴ "n.a." stands for "not available". ⁵ Extraction of lipophilic compounds. ⁶ 1-butyl-3-methylimidazolium hydrogen sulfate.

Ji et al. performed the lignin removal and, partially, that of the hemicellulose from sugarcane bagasse through an acid pretreatment by a DES composed of choline chloride and lactic acid [172]. The high efficiency of the acid DES for this pretreatment was assessed to the organic acid that can break the hydrogen bond and van der Waals forces between cellulose and hemicellulose and the benzyl ether bonds between lignin and polysaccharides, thus causing the partial hydrolysis of hemicellulose, as well as cellulose and lignin removal. Moreover, Cl⁻ in choline chloride can contribute to the cleavage of the β-O-4 bonds of the lignin [174], thus improving lignin dissolution. The acidic properties of the adopted DES are effective for promoting the HMF synthesis starting from the cellulose-rich residue obtained from sugarcane bagasse. However, the highest HMF yield (57 mol%; run 213, Table 11) was achieved when the DES was employed together with the proper amount of water, because this facilitated the desirable reduction of viscosity. On the other hand, Huang et al. employed [BMIM]HSO₄ for the conversion of *Camelia oleifera* fruit shell feedstock, previously subjected to the solvent extraction of the lipo-

philic compounds [173]. The authors carried out the reaction under MW heating in a biphasic system composed of [BMIM]HSO₄ and water as the reactive phase and 1,4-dioxane as the extractive one. Under the best reaction conditions, they obtained furfural as the major product and HMF as the co-product, due to the higher recalcitrance of cellulose towards the hydrolysis, reaching the highest furfural and HMF yields of 68 and 21 mol% (run 214, Table 11), respectively. The authors also tested the recyclability of the catalyst by adding fresh feedstock to the phase composed of ionic liquid and water, and almost constant yields were obtained after three recycling runs.

3. Strategies and Future Perspectives to Wake up the “Sleeping Giant”

HMF has been considered a “sleeping giant” because of its enormous potential as a platform-chemical but also due to the drawbacks related to its selective synthesis (by-products formation) and its scarce stability, which hamper its production on a larger scale [175]. Moreover, to develop the bio-refinery process, industrial HMF production should become a feasible possibility starting from real biomasses, rather than from model compounds, such as monosaccharides, which are more expensive and contribute to making the process not economically sustainable. Nevertheless, the employment of real biomass as the starting feedstock is even more challenging, due to its complex matrix and the issue of the HMF separation/purification representing a crucial aspect, up to now still scarcely investigated in the literature. In fact, starting from model compounds, the criticism is due primarily to the formation of by-products, whereas starting from real biomasses the other components, mainly hemicellulose and lignin, can release in the solution other compounds, such as C5 sugars, furfural, and soluble lignin [176], thus further complicating the HMF work-up. On this basis, biomasses rich in C6 sugars, such as paper waste, bread waste, rice waste, sugar beet juice, and high-fructose corn syrup [58,61,72,93,103–109,111,112,129,130,161,162], could represent very promising feedstocks for the industrial scale, being easier hydrolyzable and producing lesser amounts of other compounds than the conversion of lignocellulosic feedstocks, depending on their composition. The easy hydrolysis of these C6 sugar-rich biomasses is confirmed by the absence of works that performed any pretreatment steps starting from them. In this context, only Lin et al. [161] carried out a previous enzymatic oxidation step on high-fructose corn syrup but with the purpose of generating *in situ* the catalyst, namely gluconic acid, from the oxidation of glucose. Importantly, starting from these C6 sugar-rich biomasses, in particular sugar beet juice, the highest HMF yield of 96 mol% was obtained with the H₂O–NaCl/MeTHF system, employing H₂SO₄ as the catalyst (run 54, Table 3) [93]. However, high-fructose corn syrup is preferably used within the food supply chain, thus its employment for HMF synthesis is not socially sustainable. For this reason, generally, research is focusing on the possibility of adopting lignocellulosic or algal wastes as starting feedstock, thus avoiding competition with the food supply chain [177]. However, when starting from lignocellulosic biomass, a pretreatment step aiming at the fractionation of biomass into its components is usually necessary to optimize the HMF synthesis, facilitating its separation/purification and also valorizing each biomass component, thus making the whole process sustainable. In fact, only the valorization of each biomass component can justify the addition of a pretreatment step, which could require expensive and energy-intensive equipment, such as a ball mill and ultrasound/microwave reactors, and other chemicals, such as alkali/acid solutions and/or enzymes. Even the catalyst could complicate the separation and purification of HMF, particularly when it is homogeneous, such as mineral and organic acids and/or inorganic salts. For this reason, heterogeneous catalysts often represent an effective alternative, due to their easier separation and recycling. Nevertheless, when biomasses are adopted as the starting feedstock, the efficiency of the heterogeneous catalysts is generally lower than that of homogeneous ones due to the limited interactions between the catalyst active sites and the substrate, both being in the solid state. Moreover, the separation and recycling of the heterogeneous catalyst is not so easy when employed in the conversion of lignocellulosic biomass, be-

cause it is recovered at the end of the reaction in the solid residue, together with the unconverted biomass and humins. This problem is not often faced, and only few works have reported the recyclability of the heterogeneous catalyst involving a calcination step at temperatures higher than 400 °C, which allows the burning of the carbonaceous material. However, this procedure is feasible only for thermally stable catalysts, such as commercial and modified zeolites [74,127], but not for polymeric resins that are not stable at the required temperature. Moreover, the employed heterogeneous catalysts are often ad hoc synthesized systems to tune the acid properties, in terms of total acidity, Brønsted/Lewis acid ratio and their strength, that have a crucial role in the HMF production, but the results are expensive and hardly scalable on a larger scale. On this basis, the homogeneous catalysts, in particular the inorganic salts, which are commercial and cheap and show both Brønsted and Lewis acidities are more promising than heterogeneous systems for the synthesis of HMF from biomasses, despite the problems of their separation and recycling. Remarkably, this problem can be resolved thanks to the proper choice of reaction medium. In fact, biphasic water/organic solvent systems allow the confinement of the homogeneous catalyst in the aqueous phase wherein the reaction takes place and the continuous selective extraction of HMF in the organic phase [178]. Thus, these systems contribute to: (i) improving the selectivity of the reaction, preventing HMF degradation, which is particularly active in the aqueous medium; (ii) isolating HMF from the other components of the reaction mixture, allowing an easier purification step; (iii) recycling the homogeneous catalyst contained in the aqueous phase through the further addition of fresh biomass and organic solvent [99,112,145,146,155,160,169]. The choice of the organic solvent is a key aspect of improving the sustainability of this process. The ideal solvent should have a low miscibility with water and a low boiling point, making feasible its recovery from HMF by vacuum distillation. Moreover, this solvent should be safe and preferably from a renewable source. On this basis, MIBK, GVL, and MeTHF represent promising renewable organic solvents characterized by lower boiling points than that of the largely adopted DMSO, and they are safer than THF, which can generate peroxides that are potentially dangerous [179]. Moreover, to improve the separation between the aqueous and organic phases, often the “salting-out” phenomenon has been exploited by the addition of a salt, generally NaCl, to water [178]. Other solvent systems have been proposed for the synthesis of HMF from biomasses, such as ILs and DESs. They are promising and are particularly active towards the deconstruction of the lignocellulosic biomass matrix and act themselves as the catalyst of the reaction. However, ILs have complicated synthesis, high viscosity, low vapor pressure, low biodegradability, and high cost. On the other hand, DESs are cheap and biodegradable, but, analogously to ILs, they have low vapor pressure and high viscosity, the latter causing mass transfer limitations [179]. Nevertheless, the main drawback of their use is represented by their difficult separation from HMF, due to their high boiling points, that make their removal by distillation impossible. In addition, the strong interactions established between ILs/DESs and HMF make its extraction with organic solvents difficult [180]. On this basis, despite ILs and DESs being claimed to be green solvents, their greenness is rather questionable, and their employment as the solvent for the synthesis of HMF from real biomasses is not advantageous. Another aspect scarcely considered in the synthesis of HMF from biomasses but that could be of paramount importance in the work-up operations is related to the loading of starting biomass. In fact, the proposal of a “high-gravity” approach, indicating the preference of elevated biomass loadings (generally higher than 20 wt%) could allow the production of concentrated HMF streams, thus reducing separation costs [47,134]. However, it is well-known that a high biomass loading leads to a higher concentration of by-products, thus causing a decrease in HMF yields, as well as mass transfer problems [181]. For these reasons, biomass loadings below 10 wt% have been generally proposed in the literature, aimed at the optimization of HMF selectivity. Nevertheless, if, from one site, the optimized HMF yields could be promising, the HMF concentrations are still scarcely interesting from an industrial per-

spective because they make the HMF separation and purification steps economically onerous. Therefore, more in-depth studies should be carried out in the future to find the best compromise between the yield and the concentration of HMF. Furthermore, the heating system influences the reaction selectivity. In fact, MW heating is more efficient than conventional heating, and it facilitates a shorter heating time, thus reducing the energy demand and improving HMF selectivity. However, it is well-known that the scale-up of MW heating on an industrial scale faces some unsolved issues, such as the technological difficulties in constructing the reactor to have a geometry that allows the homogeneous penetration of MW into the reaction medium, which implies a high equipment cost. To solve this problem, the few industrial processes that exploit MW heating have preferred a continuous reactor rather than a batch one, thus reducing the volumes to be treated [182]. This solution could also be considered to produce HMF from biomass, regardless of the adopted heating system. Up to now, the research has focused mainly on the adoption of batch reactors, but the possibility of carrying out the reaction in flow reactor could allow the optimization of the HMF residence time in the reactor, thus limiting the HMF degradation to by-products and maximizing its yield. In conclusion, the optimization of HMF production from real biomass should be investigated in an integrated way, considering not only the reaction conditions but also the type of biomass, the solvent, the catalyst, the heating system, and the reactor configuration.

4. Conclusions

HMF is one of the most important platform-chemicals obtainable from the C6 fraction of biomass, and it is a valuable precursor of several renewable monomers, solvents, and fuels. However, its synthesis faces several problems, such as by-product formation and instability, which up to now have hampered its production on an industrial scale. Moreover, to develop a real sustainable bio-refinery process, industrial HMF production should be performed starting from biomasses rather than from model compounds, such as monosaccharides and polysaccharides, but this choice still represents a demanding challenge. For this purpose, several works have proposed HMF synthesis from different biomasses, such as food, agricultural and industrial wastes, and algae, developing different strategies, in terms of kinds of catalysts, solvents, heating systems, and eventually pretreatment steps. All of the process information reported up to now in the literature for HMF synthesis from biomasses have been summarized and detailed in the present review, which aims at providing a comprehensive and critical update of the state of the art. In particular, the study of the literature allowed us to conclude that a feasible process should involve the employment of a C6-rich biomass as the starting feedstock, inorganic salts as the catalyst, and a biphasic system as the solvent medium, preferentially constituted by water and a renewable organic solvent, such as MIBK, GVL, or MeTHF. On the other hand, the presence/type of pretreatment step strongly depends on the characteristics of the starting biomass, and it could be advantageous only if each biomass component is properly valorized. The application of microwave heating could be interesting, but technical problems should be overcome before its adoption on an industrial scale. Furthermore, in a scale-up perspective, the starting biomass loading represents a critical aspect, because the “high-gravity” approach should be preferred to obtain concentrated HMF streams, but a compromise with the HMF yield, which drops at elevated biomass loadings, should be found as a consequence of a dedicated optimization study. Under this perspective, the highest yield (85 mol%) obtained from the conversion of ball-milled yellow dent corn catalyzed by [activated carbon + maleic acid + AlCl_3] mixture in a $\text{H}_2\text{O}/\text{DMSO}/\text{acetonitrile}$ medium is very promising because a substrate loading of 30 wt%, higher than the majority reported up to now in the literature, was employed. However, if the process conditions can be considered sustainable and both an elevated HMF yield and concentration can be obtained, the employment of this substrate is not socially sustainable, because it is largely adopted within the food supply chain. In conclusion, the present hot topic needs further investigations, wherein only an integrated

analysis of the HMF process could facilitate the better identification of optimal conditions on an industrial scale.

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