

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 the 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, and due to its great reactivity, it can be exploited as a strategic intermediate for the synthesis of renewable monomers, solvents, and bio-fuels as bio-substitutes of those produced, at the moment, from fossil resources. In order to consider the sustainable HMF synthesis, it should be performed from biomass, in particular wastes, thus finding them a valorization, rather than starting from model compounds, such as monosaccharides or polysaccharides, at the same time 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 complexity of the starting matrix and to the HMF reactivity, e.g. instability, thus. On this basis, different strategies have been adopted to maximize the HMF yield. Under this perspective, the properties of the catalytic system, together with as well as the adopted choice of a suitable solvent and the possible presence addition of an eventual pretreatment of biomass step, play a key role in represent key aspects for the optimization of HMF synthesis. On this basis, the present review summarized and critically discussed the most recent and attractive strategies for the HMF production from real feedstocks, will summarize and critically discuss the main different strategies up to now reported for the HMF production from real feedstocks, focusing on the different smartest catalytic systems and the overall sustainability of the adopted reaction conditions and on the overall sustainability of the adopted reaction conditions.

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1. Introduction

The strong dependence on fossil resources has resulted in produced several economic, social, and environmental problems, such as their progressive depletion, as well as environmental issues of resources, emission of pollutants, and CO₂ causing, as a consequence, the global climate change. All these problems become more and are becoming even more relevant, considering that the global energy demand is expected to increase up to 37% by 2040 [1]. Therefore, in order to reduce the dependence on fossil resources, the exploitation of the renewable ones is will be of paramount importance in both scientific and industrial communities. In particular, the exploitation of biomass to give valuable products has attracted great interest in the recent years, because it is the only renewable carbon-based resource employable as feedstock, cheap and abundant feedstock,

being available with a global biomass 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, and has received growing attention in chemical industries. In fact, HMF can be produced from monosaccharides, disaccharides, and polysaccharides present in the biomass and HMF chemical structure, consisting consists of a furanic ring, an aldehyde, and an alcohol group (Figure 1), makes HMF thus resulting a particularly reactive molecule, exploitable for the synthesis and susceptible to a large variety of reactions, thus making it the building block of many important added-value chemicals, ranging from monomers, bio-fuels, food additive and pharmaceuticals [2].

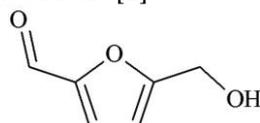
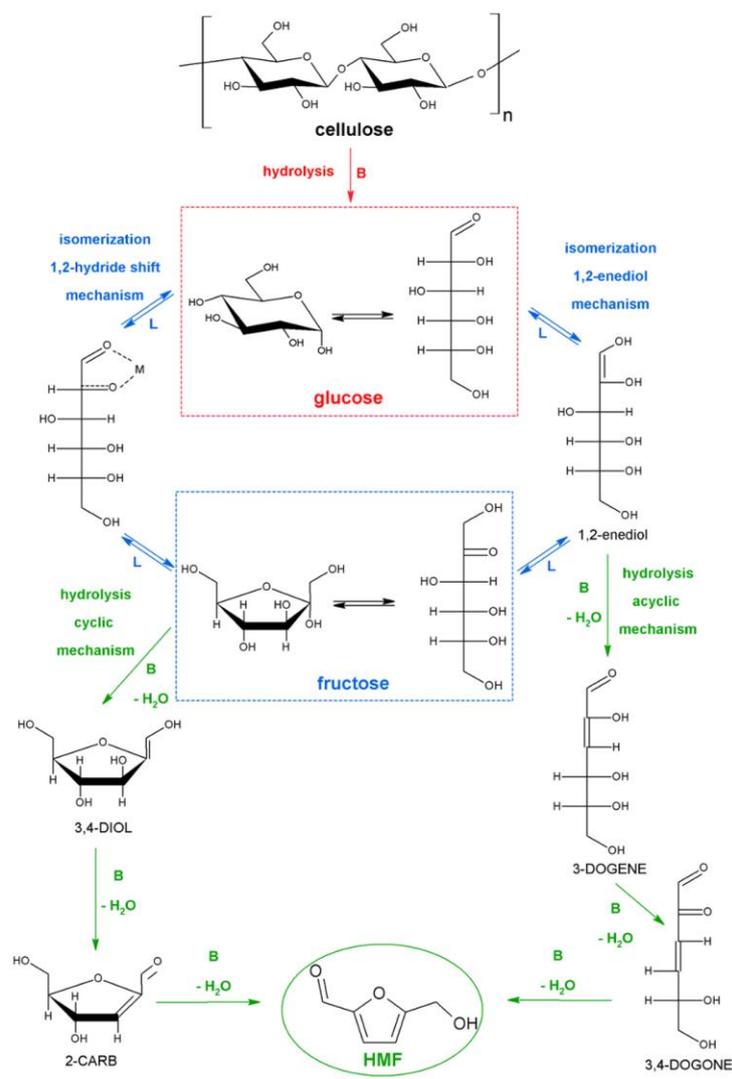
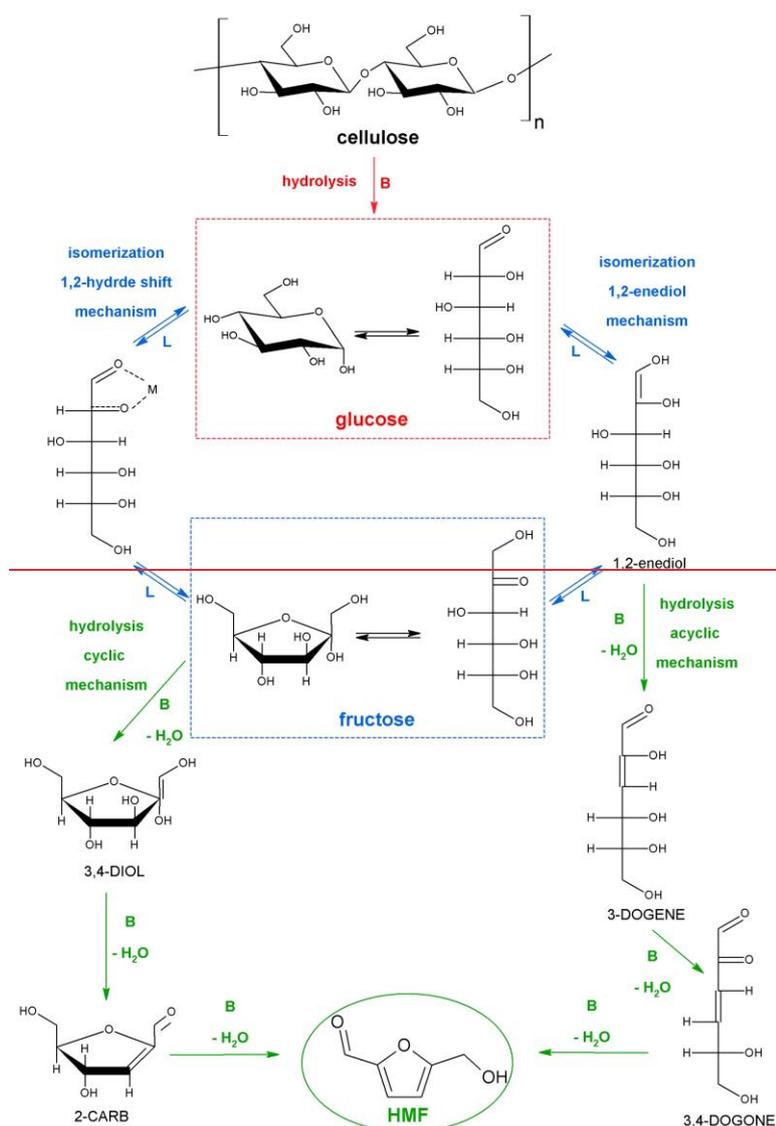


Figure 1. Chemical structure of HMF.

Regarding the synthesis of HMF, it is well-known that hexoses, such as fructose and glucose, are the main reactants to produce effective feedstocks for the HMF production, and in particular Remarkably, fructose is easier to be converted being the direct precursor of HMF, so its use as the starting feedstock allows the achievement of and requiring fewer steps, thus leading to higher selectivity than glucose [3]. However, the presence availability of fructose in nature is quite limited, resulting an expensive feedstock for the HMF production thus its cost is high and for this reason, under industrial application, whilst the employment of glucose, or, even much better, the cellulosic fraction of the abundant biomass, must should be preferred. Considering the synthesis of HMF from cellulose, it generally involves three fundamental steps, each of them 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).





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

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In the first step, the protons released by Brønsted acid attack-break the C–O bonds of the β -1,4-glycosidic bonds, thus leading to the formation of leading to the cut off of the C–O bonds, forming 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 a 1,2-enediol formation as intermediate usually causes-occurs by the formation of a catalyst-monosaccharide complex, whereas the 1,2-hydrde shift mechanism involves the coordination between carbonyl group, alcoholic hydroxyl group and 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 following the mechanism reported in Figure 3 [6].

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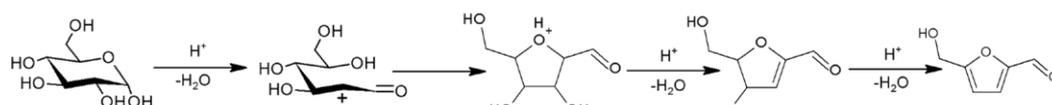
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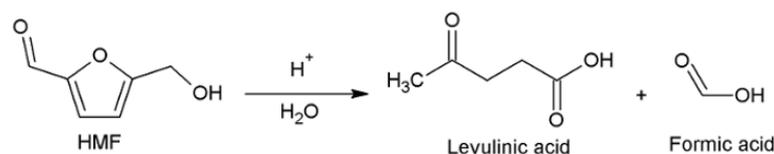


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Figure 3. Mechanism of the direct HMF synthesis from glucose, catalyzed by Brønsted acid.

However, the route involving the isomerization of glucose to fructose leads to higher selectivities to HMF, resulting thus the combination of Brønsted and Lewis acids results the most investigated strategy for the 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-ring 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 ring-chain closure, resulting in the elimination of the last molecule of water, thus and with the last water elimination to affording HMF as the final product [8,9]. On the other hand, according to the cyclic mechanism, the first step involves the α -dehydration of D-fructofuranose at the C2 position, to form a tertiary carbenium cation, that 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, this latter undergoes is subjected to a further dehydration to form HMF [8]. At the moment, the most accredited mechanism is the cyclic one. In fact, under the same reaction conditions, fructose results more reactive and selective toward HMF than glucose, probably due to their different conformations in water [10]: in this solvent, glucose is almost exclusively found in the stable pyranose structure, whereas fructose results for 21% in the furanose conformation, being immediately active resulting promptly available for the HMF synthesis, according to the cyclic mechanism shown in Figure 2. For this reason, the glucose isomerization to fructose, catalyzed by a Brønsted base or a Lewis acid, is necessary in order to have get 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 the in common the formation of intermediate 1,2-enediol as intermediate, and this aspect cannot explain the different reactivity and selectivity experimentally observed of the two sugars. The same conclusions supporting in support of the cyclic mechanism can be also ascertained are confirmed working in other organic solvents than water. For instance, Akien et al. studied the dehydration of fructose in DMSO and other organic solvents by the ^{13}C NMR, identifying in the recorded spectrum the peak of confirming the presence of 2-(hydroxymethyl)-5-(hydroxymethylene)tetrahydrofuran-3,4-diol (3,4-DIOL), intermediate supposed in whose formation is ascribable led to the cyclic pathway [13] (Figure 2).

A critical point of the HMF synthesis is represented given by the several obtainable by-products that can be co-produced during the HMF synthesis, such as levulinic and formic acids, that originate originating from the subsequent rehydration of HMF (Figure 4) [14], but also and, last but not least, black tarry by-products, called known as humins, characterized by a very complex structure combining mainly including mainly furanic, aromatic and oxygen-containing functionality 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 the humins formation is strongly activated by the combination of high temperature and an acid medium acidity [15,17]. However but, up to today now, their formation mechanism of their formation is has not been still not clarified, due to the complex composition of the reaction medium, which includes in which where not only

hexose, ~~and~~ HMF, ~~and but also the~~ degradation products, ~~all these components potentially involved in the reaction mechanism are present and all of them are~~ ~~can be involved in the reaction mechanism~~ reaction. From an economical and technological perspective, the formation of these by-products is strongly undesired, because it ~~lowers~~ ~~worsens~~ the HMF selectivity, making its separation and purification much more difficult. However, ~~recently~~ several ~~recent~~ researches focused on the valorization of humins in different fields, such as in environmental remediation, as support for catalysts and ~~for~~ 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 ~~key role~~ ~~importance~~ as ~~reagent for a large variety of reactions~~ ~~the precursor of many added-value bio-products~~, as reported in Figure 5.

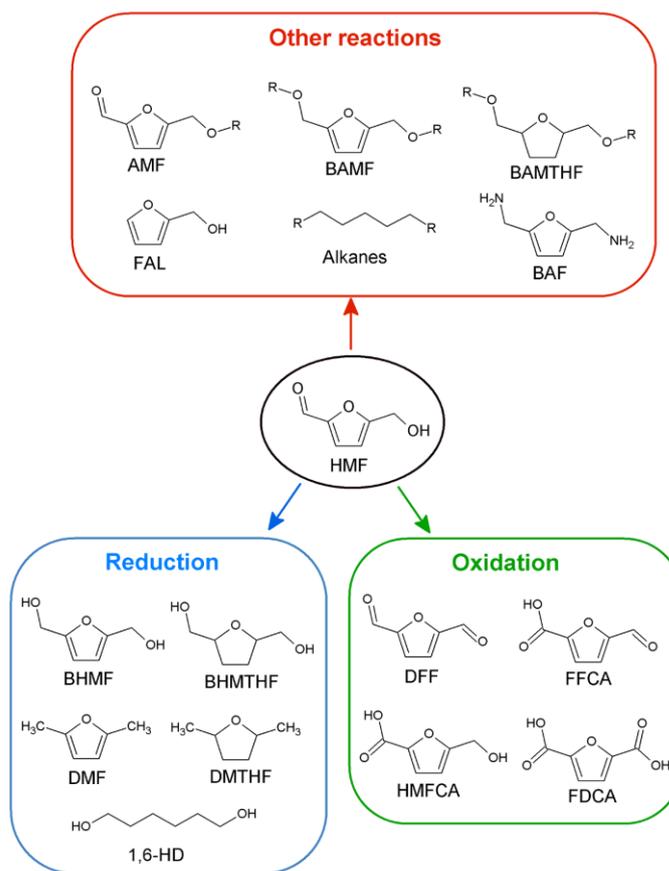


Figure 5. Possible pathways for the production of ~~valuable compounds starting~~ ~~added-value~~ ~~bio-products~~ from HMF.

The two ~~mainly relevant~~ pathways ~~of greatest interest~~ are ~~the~~ oxidation and ~~the~~ reduction ~~ones~~. The first one allows ~~the production of~~ ~~to produce~~ many important HMF derivatives: 5-formyl-2-furancarboxylic acid (FFCA), ~~that has~~ ~~having~~ promising applications as fuel and chemical intermediate [20]; 5-hydroxymethyl-2-furancarboxylic acid (HMFCFA), ~~exploitable for that is a relevant compound in~~ the production of furanic polyesters and ~~as antitumoral anticancer tumoral agents~~ [21]; 2,5-diformylfuran (DFF), that finds application 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 the polyethylene furanoate (PEF), the bio-based alternative ~~replacing to~~ ~~replace~~ polyethylene terephthalate (PET) [25]. In addition, this dicarboxylic acid can be further converted into adipic acid, ~~a crucial key~~ monomer for the synthesis of Nylon 6,6

[26]. On the other hand, the reductive pathway allows ~~the production of potential to~~ produce 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], ~~the this~~ latter also employed as ~~an~~ additive in plastics and as ~~a~~ precursor of caprolactone ~~through lactonization reaction~~ [31]; bio-fuels, such as 2,5-dimethylfuran (DMF) [32,33] and 2,5-dimethyltetrahydrofuran (DMTHF) [33]. Moreover, HMF and its derivatives can ~~be subjected also~~ ~~undergo to~~ 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 ~~of them~~ employable as bio-fuels. ~~Moreover,~~ HMF can be involved ~~also~~ in aldol condensation and hydrodeoxygenation reactions, to produce long-chain alkanes, ~~to be used that already found an application~~ as fuels [38]; in decarbonylation ~~reaction~~ to ~~lead get~~ furfuryl alcohol (FAL), which can be adopted as ~~a~~ monomer for the production of furan resin [39] ~~and;~~ finally, in the 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 ~~towards in~~ HMF and its derivatives, ~~none~~ large-scale HMF plant is ~~still~~ running, mainly due to its high production costs, that reflects on the high HMF selling cost (about 3500 €/kg in 2019) [41,42]. In fact, up to ~~now-day~~, most of the bio-refinery approaches proposed for ~~the~~ HMF production ~~involve the use of are of the first generation, employing purified pure feedstocks of first generation,~~ like hexose sugars, which are more favorable ~~and much more but too~~ expensive for the synthesis of HMF, ~~if compared with than cheap~~ lignocellulosic biomass, where 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 ~~material feedstocks~~ is a challenge of great relevance ~~that could contribute to the make~~ cost-effective ~~the~~ production of HMF ~~already~~ in the next future. ~~Under 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 and having has~~ patented a process for the conversion of lignocellulosic biomass to HMF through ~~a~~ hydrothermal carbonization (HTC) route [44]. According to this process, the substrate is subjected to HTC under high temperature and pressure, ~~producing and~~ two main streams ~~comes from the reactor,~~ 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 ~~separation 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 already scaled-up ~~at commercial small-scale,~~ to produce HMF ~~at commercial small-scale~~. However, in addition to the challenge of the employment of raw lignocellulosic biomass, the scale-up of HMF production at large-scale ~~meets requires the solution of~~ other technological problems ~~that should be solved in the future~~, such as the formation of by-products, in particular solid humins, the separation of HMF from the reaction ~~media medium~~ and its ~~further~~ purification. The by-products formation strongly depends on the adopted reaction conditions, ~~also affecting and it influences also~~ the separation ~~and a~~ purification steps ~~and, consequently,~~ ~~affecting in this way~~ the process costs. Also for these reasons, the majority of the ~~available HMF~~ processes ~~proposed up to now for the synthesis of HMF~~ are still at a very early stage of development and the reaction media and process parameters are the main focus of the ~~next~~ optimization [47].

Therefore, several studies have been reported, ~~over the past years aiming aimed~~ at the synthesis of HMF starting from raw biomasses, investigating the influence of homogeneous/heterogeneous catalysts, solvent system, heating method and pretreatment step on the HMF yield. However, up to date, the published reviews are 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, the 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, the aim of this review is this review aims to emphatically discuss the role of the different reaction parameters on the HMF yield reached starting from a real substrate, in order to make sustainable a rational employment of raw or waste biomasses.

2. Synthesis of HMF from raw biomass

Biomasses are mainly composed of by three biopolymers: hemicellulose (20–35 wt%), cellulose (30–50 wt%), and lignin (15–20 wt%). Hemicellulose is a heteropolysaccharide, being consisted 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 is characterized by several ramifications, which make it prone to hydrolysis that make hemicellulose an amorphous polymer easy to be hydrolyzed [54]. As previously reported Instead, cellulose is the linear homopolymer of D-glucose, representing in this way resulting the most important feedstock source of hexoses and, therefore, of an ideal candidate for HMF production. The units of glucose are linked through β -(1,4) glycosidic bonds, which make it and this conformation makes cellulose a stable and stiff polymer. The D-glucose units of cellulose are also engaged in the formation of intra- and inter-molecular hydrogen bonds between among the hydroxyl groups, making the cellulose chains mainly packed in a crystalline structure 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 less ordered amorphous regions domains, that resulting more easily accessible to water than crystalline ones, these g. requiring milder hydrolysis conditions than the latter that are amorphous and these portions can adsorb water and be more easily hydrolyzed than the crystalline area, which is involved under harsher conditions [55]. Lignin is a three-dimensional highly cross-linked polymer composed of by 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 the lignin's 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 a challenge today challenging and several strategies have been proposed, aiming at the optimization of HMF yield selectivity. Generally, the variables that influence the HMF production are the presence of a pretreatment step, the type of solvent, the biomass loading, and the adopted catalytic system. In fact, as it is will be better explained in the Paragraph 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 to direct the selectivity of the process, because some of them can in some cases inhibiting the side reactions (rehydration of HMF and humins formation), can but also showing synergistic effects with the catalyst or can have having catalytic effects themselves by alone, controlling the pathways of the biomass conversion [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 extracting medium extraction one, and innovative solvents such as ionic liquids and deep eutectic solvents. Finally, the properties of the catalyst, in particular mainly in terms of amount and type of acidity, strongly influence the reaction, directly controlling the mechanism and having key effect on the HMF selectivity. In this regard, both homogeneous and heterogeneous systems have been investigated for the production of HMF

from biomasses. Generally, homogeneous catalysts have higher performances and low cost but their recycle is more difficult than the heterogeneous ones, which, on the other hand, have a limited contact with a possible substrate, thus resulting in less efficiency. In every case anyway, the increase of the 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.

In order to highlight the different approaches adopted up to now for the synthesis of HMF from real biomasses and how they can affect the reaction, the literature references have been commented 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-One-solvent systems

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

Table 1. HMF production starting from raw biomasses in one-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 bagasse (1.2%)	SPPTPA ³ (5.0)	NMP ⁵	140	60	MW	19 ⁴	70
23	Corn cob (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.

It is evident that within the one-solvent systems, water is the most employed solvent for the conversion of biomass to HMF in the presence of only one solvent. In fact, water is abundant, cheap, environmentally compatible, non-toxic, and non-flammable, thus resulting being the preferred choice from a green chemistry point of view. Moreover, according to the mechanism reported in the Introduction section, water can promote the hydrolysis of cellulose to glucose, which is the first step of the biomass conversion. Although the employment of an acid catalyst is generally involved, recently also the autocatalytic conversion of a real feedstock, such as properly a food waste, has been also investigated for the synthesis of HMF, working at high temperature (230 °C) under microwave-MW irradiation, reaching the modest HMF yield of 7 mol% under the optimized reaction conditions (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, such as in particular mineral acids, as and in particular H₂SO₄, which because it results the most effective for the HMF production starting from simple sugars [3]. Abdilla-Santes et al. carried out the conversion of a sugar beet thick juice rich in sucrose, with a biomass loading of 14.7 wt% reaching the 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%), ~~due 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. In fact, the authors found that sulfate anion~~ can react with monoalcohol groups ~~present in of~~ the ~~reaction~~ intermediates stabilizing them ~~of the reaction stabilizing them~~ [76], ~~and~~ thus preventing the 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 ~~microwave-MW~~ heating that allowed the reduction of reaction time (run 3, Table 1) [59]. Mango waste's sugar profile is mainly ~~characterized composed of by~~ sucrose and, in lesser amounts, by fructose and glucose, disaccharides and monosaccharides, that can be ~~more~~ easily converted to HMF, reaching the yield of 21 mol%. Although ~~the promising results were~~ obtained from the sugar beet thick juice and mango's waste, the most employed feedstocks are lignocellulosic biomasses, ~~that Anyway, these~~ are more recalcitrant ~~than the previous ones, towards the conversion and the selective synthesis of HMF~~ due to their complex ~~matrixstructure~~, thus ~~their conversion requires requiring generally~~ harsher reaction conditions, ~~mainly in terms of and in particular~~ higher acid concentrations, ~~to get satisfactory HMF yields. Therefore,~~ Świątek et al. performed the reaction in a semi-continuous process starting from spruce and beach woods, reaching the 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 ~~microwave-MW~~ reactor under analogous reaction conditions in terms of temperature and biomass/catalyst weight ratio but, in this case, the ~~major prevailing~~ products were glucose and levulinic acid, and ~~only the HMF with a yield of only 6 mol% was obtained~~ (run 6, Table 1) [61]. Another kind of feedstock that ~~in the last years~~ is attracting great interest is ~~the~~ algal biomass. In fact, algae grow quickly, ~~and~~ their cultivation does not require the use of fertilizers or other ~~particular care inputs~~, and their employment can contribute to ~~reduc~~ing the environmental problem of coastal eutrophication. Algae contain many carbohydrates and a low amount of lignin, resulting ~~in~~ a cheap ~~and easy hydrolysable~~ feedstock ~~potentially easy to be hydrolyzed. On this basis,~~ Jeong et al. proposed the red algae *Gracilaria verrucosa* as ~~the~~ substrate for the ~~HMF synthesis of HMF~~ catalyzed by H₂SO₄ (run 7, Table 1) [62]. ~~In fact, Gracilaria verrucosa is a promising feedstock for the HMF production being~~ composed ~~of by~~ agar, a polymer made up of ~~units of~~ D-galactose and 3,6-anhydrogalactopyranose ~~units, both easily~~ hydrolysable to HMF. The authors optimized the ~~HMF synthesis of HMF~~ through a five-level three-factor central composite rotatable experimental design, reaching the highest yield of 18 mol%, ~~and Remarkably, the authors highlighted finding~~ that the ~~HMF production of HMF~~ was promoted by short reaction time/low reaction temperature/low catalyst concentration, being the two latter parameters more influential than the reaction time.

~~Not only H₂SO₄ has been employed as homogeneous catalyst but A~~ also inorganic salts, ~~that differently from the mineral acids are~~ characterized by the presence of Brønsted and Lewis acid sites, ~~have been employed as homogeneous catalysts~~. For example, different chlorides were ~~adopted tested~~ by Hoşgün for the conversion of poppy stalks and ~~the author found that~~ CuCl₂ strongly catalyzed the reaction, despite ~~being it is~~ a divalent chloride (run 8, Table 1) [63]. ~~It In fact, it is well-known that the higher amounts of chloride ion amount could promote the improve the~~ cellulose conversion, so ~~generally,~~ trivalent metal chlorides ~~should be preferred over the have a stronger effect on the biomass conversion than the~~ 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 ~~particular characteristic~~ activity of CuCl₂. Jeong et al. tested aluminum sulfate as ~~the~~ catalyst for the conversion of the microalgae *Chlorella*, ~~which was~~ optimized ~~through the support of the by a~~ Box-Benken design, ~~where evaluating the~~ reaction temperature, ~~the~~ catalyst amount, and ~~the~~ reaction time ~~were considered 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 the maximum HMF yield of 23 mol%. ~~Also~~ Moreover, the combination of inorganic salts with mineral acids could be an even more promising strategy, because it allows the tuning of the Brønsted and Lewis acidity/acidities of the homogeneous catalytic system, as in the work of reported by Bodachivskiy et al. [65]. ~~They~~ These authors carried out the conversion of two lignocellulosic biomasses (corn cob and softwood chips) and two algae (*Ulva lactuca* and *Porphyridium cruentum*), which was catalyzed by combining ZnCl₂ together with and HCl (runs 10–13, Table 1). The authors found that the acidity of ZnCl₂ strongly depends on the level of hydration, in particular, lower hydration states (n=2–3) correspond to stronger acidity, and whilst higher hydration states (n=3.25–4.5) correspond to milder acidity. For this reason, ZnCl₂·4.25 H₂O was efficient in towards the selective dissolution of microcrystalline cellulose, selectively providing HMF and avoiding the formation of humins of humins. However, the addition of HCl allowed the further increase of 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), in order to hydrolyze the biomasses to glucose and convert the this latter to HMF, respectively. Under these reaction conditions, the conversion of the softwood chips (run 11, Table 1) was less efficient with respect to than those of the other biomasses, due to its recalcitrance, leading to the HMF yield of 22 mol%. However, in this case, the possible formation of humins has not been considered. ~~Also~~ Besides, the heterogeneous catalysts have been widely adopted for the HMF synthesis from real feedstocks but, in this case, the interaction of with the catalyst with biomass results less efficient, than the homogeneous systems due to mass transfer issue the more difficult contact between the substrate and the active sites of the catalyst. Regarding the heterogeneous systems, sulfonated solid acid catalysts resulted to be efficient in towards the HMF synthesis of HMF from biomasses. In this regard, Chen et al. adopted Amberlyst-36 for the hydrolysis of vegetable wastes under microwave-MW heating, reaching the HMF yield of 5 mol% and proving that HMF could be formed via direct glucose dehydration, without the intermediate production of fructose, considering that the Brønsted acid sites are inefficient in the isomerization step of glucose to fructose (run 14, Table 1) [66]. Jeong et al. used Amberlyst-15 for the conversion of the macroalgae *Gracilaria verrucosa*, achieving the 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 the HMF synthesis of HMF from sugarcane bagasse in the presence of the commercial D001-cc ion-exchange resin, under microwave-MW heating (runs 16 and 17, Table 1) [68]. This resin has pores with enough large sizes that to enable both biomass and solvent molecules to enter easily into the channels, providing a large contact area between the substrate and the catalyst active sites and, as consequence thus improving the biomass conversion, a favorable conversion of biomass to HMF. The authors performed the reaction in water and DMSO, obtaining under the same reaction conditions the maximum HMF yields of 8 and 18 mol%, respectively, proving that the organic solvent hampered the HMF degradation and allowed the achieving of a higher yield. 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 –SO₃H group), resulting active in towards the hydrolysis reaction. ~~and~~ The synthesized sulfonated catalyst was able to interact with the carbohydrate substrate mainly through two forces: i) hydrogen bonds between the –OH groups of carbohydrates and the oxygenated functional groups on the catalyst surface (–COOH and –OH); 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 for the conversion of several biomasses (waste fluff, cotton linter, and corn

straw) at 200 °C, reaching very promising yields at different reaction times, due 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, because its hydrolysis was resulted difficult due to the high degree of cellulose crystallinity of the adopted biomass (loading of only 2 wt%). This is reflected in the percentage of cotton linter hydrolysis at 200 °C, which that was only 27 wt%, lower than those achieved under the same reaction conditions from of corn straw and waste fluff, equal to 61 and 43 wt% respectively, when employed under the same reaction conditions at low biomass loading (2 wt%). Mondal et al. prepared a highly porous polytriphenylamine sulfonated catalyst (SPPTPA), which was and used it for the conversion of sugarcane bagasse in organic solvents, such as DMSO and N-methylpyrrolidone (NMP), under microwave-MW irradiation, leading to HMF yields of about 20 mol%, probably thanks to the good microwave-MW absorbing ability of these solvents (runs 21 and 22, Table 1) [70]. The same catalyst was also adopted, with better performances, for the conversion of corncob under conventional heating in the renewable solvent GVL, particularly active in the synthesis towards the of HMF synthesis, being a hydrophilic lactone, generally more suitable than the hydrophobic ones in this reaction (run 23, Table 1) [71]. Furthermore Besides, heterogeneous catalysts having both Brønsted acid/basic sites and Lewis acid sites have been also adopted for the 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 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 towards the HMF synthesis from cellulose-based materials, having both Brønsted acid sites, due to the PO_4^{3-} groups, and base sites, possibly due ascribed to the Ca–O groups. A higher HMF yield, equal to of 27 mol%, was reached 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 also after four cycles, giving the yield of 25 mol% (run 27, Table 1) [73]. The heterogeneous catalysts with both Brønsted and Lewis acid sites have been adopted also in for the conversion of algae in the aqueous medium. In fact, Wang et al. carried out the HMF synthesis of HMF 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 adopting with H_2SO_4 (10 mol%), working under the same reaction conditions, thus confirming the importance of both types of acid sites for improving the HMF production (run 28, Table 1) [74]. Moreover, the authors found that HMF was particularly stable during the conversion of microalgae, which is and they proved that this could be ascribable to the presence of proteins and lipids in the reaction mixture deriving from 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 away HMF from acid sites [79]. These results are interesting because show that complicated separation and purification steps of microalgae from nutrients are not necessary and the raw *Chlorococcum* sp. can be directly employed as feedstock for HMF production. Finally/Lastly, the employment of N,N-dimethylacetamide-Lithium-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. In fact, literature reports that this medium is effective in towards the biomass dissolution, of biomass due to the formation of $(\text{DMA})_n\text{Li}^+$ 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 extraction with 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 ing 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 that makes unfeasible the HMF recovery through distillation. Therefore, recent the research has developed a new type of ionic liquids, called DESs. 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]. The DESs deriving-originating from the combination of ChCl with one of these hydrogen bond donors are low cost cheap, low vapor pressure, and eco-friendly, and eco friendly, thus resulting more promising-attractive than ILs for the HMF synthesis of HMF from real biomasses [83]. Table 2 summarizes the available data for the HMF synthesis of HMF 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	June grass (3.8%)	CuCl ₂ (8.3)	[Et ₃ NH][HSO ₄] ⁴	180	41	MW	45	87
43	Mixed herb residue (4.8%)	SnCl ₄ ·5H ₂ O (0.3)	ChCl ⁵ /formic acid (1/8 mol/mol)	140	30	Conv.	55	88

44	<i>Anemarrhena asphodeloides</i> Bunge (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.

Also-Even in the presence of these solvents both homogeneous, in particular inorganic salts, and heterogeneous catalysts, have been adopted for the synthesis of HMF from biomasses. Regarding the inorganic salts, the most largely adopted one was CrCl₃ has been proposed, which that led to leading to 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]. In particular Remarkably, Naz et al. proved the beneficial role of CrCl₃ in increasing the towards the 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 being the stronger bond acceptor, thus increasing the acidity of ILs and promoting the dehydration step. In a more recent work 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 under the proposed reaction conditions (runs 36–41, Table 2). The authors found that the agricultural residues led to gave higher HMF yields with respect to the than dry fruit shells and, they They obtained the highest HMF yield of 45 mol% from the wheat husk and the maximum lignin recovery, of about 65 wt%, from the rice husk [86]. Due to the high polarity of ILs, they these are able to can well absorb microwaves-MWs, by this way and this can further promote promoting the rupture breaking of intermolecular hydrogen bonds between polysaccharides, and consequently improving their conversion [81]. Therefore, the microwave-MW heating has been adopted for the HMF synthesis of HMF from biomasses, by combining -in ILs and in the presence of inorganic salts as catalysts. In particular, a protic ionic liquid IL, the such as triethylammonium hydrogen sulfate ([Et₃NH][HSO₄]), was employed as the solvent for the HMF synthesis of HMF from June grass catalyzed by CuCl₂, reaching the HMF yield of 45 mol% (run 42, Table 2) [87]. The mechanism proposed by the authors involves also [Et₃NH][HSO₄] as active specie in biomass conversion. In fact, they supposed that the reaction of CuCl₂ with the reaction medium led to the formation of a Cu²⁺

hexa-aquo complex, SO_4 , the amine Et_3N , which acted as Brønsted base, and HCl that 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 thanks to HCl acidity. On the other hand, Yu et al. reported the employment of inorganic salt (SnCl_4) as the catalyst in the HMF synthesis of HMF from herb residues, performed working in DES, composed of by choline chloride and formic acid, in which the catalyst resulted soluble at temperature higher than $100\text{ }^\circ\text{C}$ (runs 43–45, Table 2) [88]. The highest HMF yield, equal to of 77 mol%, was ascertained with *Anemarrhena asphodeloides* Bunge herb, that includes is composed of by a higher amount of soluble carbohydrates, especially fructose and sucrose, with respect to the than other investigated biomasses, especially fructose and sucrose, which are easier converted to HMF than polysaccharides.

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 microwave-MW heating in, in two different ILs, e.g. [Bmim]OAc and [Bmim]Cl under the same reaction conditions. The authors achieved higher HMF yield in the presence of [Bmim]OAc, than with [Bmim]Cl due thanks to its more efficient microwave-MW energy absorption and lower viscosity, which enable [Bmim]OAc to make the catalyst more accessible thus improving its accessibility to the sugarcane bagasse, thus promoting its which is more prone to the conversion (runs 46 and 47, Table 2) [68]. Moreover, the HMF yields obtained performing the reaction working in the two ILs resulted were higher than those achieved working 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 preparation-synthesis and the employment use of *ad-hoc* synthesized catalysts for the conversion of wastes to HMF. An example is the work of proposed by Tyagi et al., who prepared a sulfonated activated carbon, which was tested and adopted it for the HMF synthesis of HMF from Babool wood in [BMIM][Cl], reaching the maximum yield of 33 mol% under the optimal reaction conditions (run 48, Table 2) [89]. Analogously Similarly, Yan et al. synthesized a carbonaceous material characterized by 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 in for the conversion of corn stalk in [BMIM][Cl], leading to an 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 all its functional groups. In fact, acid and phenolic groups on the catalyst surface are able to can adsorb the cellulose dissolved in IL, whereas the sulfonic groups can hydrolyze the cellulose. Another example of a synthesized acid catalyst is reported by Liu et al., who prepared a promising biochar for the production of HMF from corn stalk, and tested it for the HMF production in ILs. The authors prepared the biochar through the carbonization of the corn stalk itself 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 influence-effect of different anions (BF_4^- , Br^- , Cl^-) composing the employed IL on the HMF production, finding that, under the same reaction conditions, identifying the highest HMF yield of 61 mol% with the was reached with chloride 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 ef activity, thus proving to be a stable and reusable system. Finally Lastly, a recent work investigated the potentialities of DES, composed of by choline chloride and oxalic acid, as both 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 employment combined use of two or more different solvents generally allows the formation of a biphasic system, which includes where it is possible to identify a reaction phase, in which the catalyst is confined and the reaction takes place where HMF synthesis occurs, and an extracting phase that removes HMF, 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 been recently adopted as the reaction phase for the biomass conversion of biomass to HMF. Due to the strong enhancement of HMF yield afforded in a biphasic system, this is surely the most adopted reaction medium, and in the following Tables are summarized the available data for the synthesis of HMF starting from not pretreated biomasses, in presence of mineral and organic acids (Table 3), inorganic salts and their combinations of them 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 respect to the moles of fructose.

Abdilla-Santes et al. carried out the HMF synthesis of HMF starting from sugar beet juice (3.7 wt%), in the presence of H₂SO₄ as the catalyst and the authors investigated the role of the solvent composition different biphasic systems. They found that a higher HMF selectivity was reached using MeTHF than 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 investigated also investigated the influence of the 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 H₂O-NaCl/MeTHF

system (run 54, Table 3) [93]. Also, Amoah et al. adopted H_2SO_4 as the catalyst for the HMF production from the microalgae *Chlorella sorokiniana* in the H_2O -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 H_2O , leading to a significant improvement of HMF yield up to 52 mol% (run 55, Table 3) [94]. Although the formation of by-products was reduced in H_2O -LiCl/DMSO, the authors attributed the achieved good HMF yield also 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 H_2O /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 the 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, also organic acids, such as formic and levulinic acids, both deriving both from the HMF rehydration of HMF, have been also tested as catalysts for the 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 the HMF formation and increasing its yield. The presence of THF suppressed the HMF rehydration and polymerization, and the addition of NaCl to water allowed to the formation of a biphasic system (H_2O -NaCl/THF), where the organic phase extracted the HMF, 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 H_2O /MeTHF system, where and the prevailing acid distribution in the two solvents depended on their ratio. In fact, the increase in of the H_2O /MeTHF ratio reduced the levulinic acid amount in the organic phase. In addition, the H_2O /MeTHF ratio influenced the polarity of the system and the catalytic behavior, thus Remarkably, an increase in of 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 of HMF causing a decrease of its yield. On this basis, a 1:1 volume ratio was selected as optimum optimal, because it led 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 the sulfanilic acid, for the conversion of biomasses to HMF. In fact, sulfanilic acid has both sulfonic and amino groups, e.g. that give it Brønsted acidity and basicity properties, thus resulting effective active in towards hydrolysis/dehydration and isomerization steps, respectively. The authors adopted a complex biphasic system, where the reactive phase was composed of H_2O and DMSO, whilst the extracting phase by 2-butanol and MIBK. DMSO was added to water with the aim of increasing to increase the amount of β -D-fructofuranose tautomer, which is the real form subjected to undergoes dehydration, whereas 2-butanol was added to the organic phase in order to enhance the HMF extraction. Under the best reaction conditions, the authors achieved the HMF yield of 41 mol% starting from both straw and barley husk, and the recycled catalyst in the aqueous phase showed to be was active up to five consecutive runs (runs 61 and 62, Table 3) [99]. However, it must be underlined that 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 combination with acids, because this catalytic system allowed an easier modulation of

Brønsted and Lewis acidity, ~~that, as previously commented, is an aspect~~ of paramount importance ~~in order~~ 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 (1.2%)	Fe ₂ (SO ₄) ₃ (1.3)	H ₂ O/MIBK (1/5 v/v)	200	60	Conv.	32	100
64	Mixed spruce, pine and fir pulp (1.2%)	Fe ₂ (SO ₄) ₃ (1.3)	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 (1/1 v/v)	160	20	MW	33	107
89	Bread waste (4.8%)	SnCl ₄ (3.5)	H ₂ O/DMSO (1/1 v/v)	140	60	MW	35	108
90	Bread waste (4.8%)	SnCl ₄ (3.5)	H ₂ O/THF (1/1 v/v)	140	120	MW	10	108
91	Bread waste (4.8%)	SnCl ₄ (3.5)	H ₂ O/ACN ² (1/1 v/v)	140	10	MW	33	108
92	Bread waste (4.8%)	SnCl ₄ (3.5)	H ₂ O/acetone (1/1 v/v)	140	10	MW	33	108
93	Bread waste (4.8%)	SnCl ₄ (3.5)	H ₂ O/acetone (1/1 v/v)	120	50	MW	22	109
94	Bread waste (4.8%)	SnCl ₄ (3.5)	H ₂ O/GVL (1/1 v/v)	120	40	MW	31	109
95	Bread waste (4.8%)	SnCl ₄ (3.5)	H ₂ O/PC ³ (1/1 v/v)	120	7	MW	26	109
96	Corn waste (4.8%)	SnCl ₄ (3.5)	H ₂ O/acetone (1/1 v/v)	140	10	MW	27	110
97	Taro waste (4.8%)	SnCl ₄ (3.5)	H ₂ O/acetone (1/1 v/v)	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	June grass (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 ~~are able to act~~ can act as both Brønsted and Lewis acids. In fact, in aqueous media they dissociate into cations and anions, the first ones are solvated by water, forming aqueous complex ions that ~~through their hydrolysis~~ 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 ~~as consequence~~ consequently accelerating their hydrolysis, ~~and it~~ In addition, they can act as Lewis acid promoting the isomerization of glucose to fructose [100]. In this regard, Mukherjee et al. employed Fe₂(SO₄)₃ ~~as the catalyst~~ for the conversion of eucalyptus pulp (hardwood) and mixed pulp of spruce, pine, and fir (softwoods) in a H₂O/MIBK solvent system. Under the conventional heating, the authors achieved the 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 ~~in this case~~ hardwood was easier to hydrolyze than softwood (runs 63 and 64, Table 4) [100]. The authors attributed the lower catalytic performances of Fe₂(SO₄)₃ in the conversion of softwoods to their higher amount of extractives ~~than hardwood~~, which can form complexes with Fe³⁺, thus reducing its ability to bind with cellulose, ~~thus and~~ limiting its depolymerization. Because ~~microwaves MW have been demonstrated able~~ are effective towards the cellulose depolymerization ~~to depolymerize cellulose~~ [117], the authors performed the reaction also under ~~microwave MW~~ heating, reaching analogous yields ~~than~~ those previously reported but at a lower temperature and after a shorter reaction time, ~~due thanks~~ to the high efficiency of ~~the microwave MW as~~ heating system (runs 65 and 66, Table 4). However, despite the interesting yields reported in this work, the low ~~adopted~~ substrate loading (1.2 wt%) makes the process not very appealing. ~~Also~~ 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 that led to~~ 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 ~~mainly of~~ α-Fe₂O₃ and β-FeOOH, highlighting that FeCl₃ was unstable and easily hydrolysable. On the other hand, when FeCl₃ was heated with biomass, the red precipitate was absent, ~~therefore~~ ~~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 other several chloride salts as catalysts for the conversion of bamboo to HMF in H₂O/sulfolane. The authors found that ~~among all the employed salts~~, SnCl₄ led to

the highest HMF yield of 41 mol% together with the 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 the salt hydrolysis, but an excess of water promoted also promoted the HMF hydration of HMF to rehydration acids, thus a ratio of 1/7 v/v H₂O/sulfolane was selected as optimal. The authors highlighted that sulfolane had an important role in the catalytic activity, limiting the hydrolysis of SnCl₄ to HCl and SnO₂, and maintaining stable the Sn⁴⁺ aqueous complex, which is the effective Lewis acid species. the latter inactive in the dehydration and isomerization steps, maintaining stable the Sn⁴⁺ aqueous complex, which is the effective Lewis acid species. On this basis, the proposed mechanism reported included the hydrolysis of cellulose to glucose, which was catalyzed by HCl released from the hydrolysis of SnCl₄, then the successive isomerization of glucose to fructose, which was catalyzed by the Sn⁴⁺ aqueous complex, and the final dehydration of fructose to HMF catalyzed by HCl. SnCl₄ was surely the most adopted preferred salt for the HMF synthesis of HMF from raw biomasses and other researchers have tested it as the catalyst. For example, Yu et al. investigated the HMF synthesis of HMF in the presence of SnCl₄ under microwave-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 H₂O/DMSO (1/1 v/v), the authors reported different HMF yields depending on the starting biomass (runs 77–81, Table 4) [103,104]. In fact, they tested two different types of biomass, the starch-rich one, such as bread waste and rice waste, and the sugar-rich one, such as unskinned kiwi fruit and watermelon flesh, and found founding that the latter second ones allowed the achieving of led to the higher HMF yield of (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 was efficient, the subsequent isomerization was kinetically limited and required a longer reaction time, as evidenced by the improvement of 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 salt catalysts, such as AlCl₃ and CrCl₃, for the conversion of rice waste, finding that they were less active than the tetravalent SnCl₄ because they produced a milder acidity being the (pH of the solution equal to 3.3, 2.6 and 1.5 for AlCl₃, CrCl₃, and SnCl₄, respectively). For this reason, AlCl₃ and CrCl₃ led to lower HMF yields with respect to that ascertained with SnCl₄, working under the same reaction conditions (runs 82 and 83, Table 4) [104] and similar HMF yield was obtained only after a longer time (100 min) (run 84, Table 4) [105]. On this basis, SnCl₄ resulted in the most promising inorganic salt and the authors focused their attention on its employment 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 regarding the good catalytic performances of SnCl₄ and the influence of the solvent system on the HMF synthesis were also obtained also starting from bread waste. The authors performed the conversion of this biomass in H₂O/DMSO at 160 °C with SnCl₄ or AlCl₃ and compared the achieved catalytic performances with those shown by the trivalent AlCl₃ (runs 87 and 88, Table 4) [107]. The increase of increment of temperature from 140 to 160 °C allowed the improvement of HMF yield from 17 (run 77, Table 4) to 38 mol%, and SnCl₄ led to better results was more efficient than AlCl₃, which generated lower HMF yield due to humins formation. In fact, AlCl₃ induced significant polymerization, due to its strong Lewis acidity and binding ability of Al³⁺ to the reaction intermediates, of the reaction 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 for humins formation [118]. Moreover, the solid

residue recovered at the end of the reaction performed with SnCl₄ did not contain unconverted starch, whereas the residue from AlCl₃-AlCl₃-catalyzed reaction still contained unexploited starch, underlining the higher efficiency of SnCl₄. Regarding the solvent composition, the authors carried out the conversion of bread waste not only in H₂O/DMSO, but also in H₂O/THF, H₂O/ACN, and H₂O/acetone at 140 °C under microwave-MW heating (runs 89–92, Table 4) [108]. They found that the hydrolysis of biomass was always fast, in all the investigated solvents but an accumulation of glucose was observed working with H₂O/DMSO and H₂O/THF, they observed an accumulation of glucose due to its slower isomerization to fructose in these solvent systems that led, as consequence, to a slower HMF formation. The glucose conversion resulted particularly slow in H₂O/THF, achieving the HMF yield of only 10 mol% after 120 min, probably due to its low dielectric constant and low dipole moment, that disfavored the microwave-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 H₂O/DMSO, H₂O/ACN, and H₂O/acetone, were similar but ascertained after different reaction times (60, 10 and 10 min, respectively) and higher than that obtained in H₂O/THF, where HMF was more susceptible to rehydration. In fact, the authors hypothesized that ACN and acetone were able to arrange 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 γ -valerolactone (GVL), which is a biomass biomass-derived solvent [122,123]. In this context, and compared 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 deeper deeply investigated the effect of the organic solvents on the catalytic activity and supposed that they, analogously to the sulfolane [102], can slow down 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 the glucose isomerization, was maintained and it cooperated/cooperated with HCl, responsible for hydrolysis and dehydration steps, to promote the HMF synthesis, thus allowing the achievement of promising yields. 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, 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. Finally/Lastly, the authors tested the promising solvent system H₂O/acetone in the conversion of other biomasses, such as corn waste and taro waste, reaching the highest HMF yield starting 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 in the 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 allowed the reduction of viscosity and improved the fluidity and thermal conductivity, thus. By this way, water enhancing/enhances the conduction of the reaction, and hampered/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 present in the A-NADES was able to inhibit the HMF rehydration to levulinic and formic acids, thanks to the action/contribution of both anion and cation of choline chloride, that can adsorb water, forming hydration ions and thus limiting the degradation pathways of HMF and leading to higher HMF yield. However, the produced HMF formed strong hydrogen bonds with choline chloride, making diffi-

cult its separation from the reaction ~~phase medium~~. Therefore, ~~thus~~ the employment of MIBK was important ~~in order~~ to have the *in situ* extraction, which allowed a 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 reached 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, the A-NADES, containing the ~~catalyst~~ SnCl₄, was easily separated from MIBK and reused ~~in many subsequent runs many times and~~. 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 the HMF synthesis ~~of HMF~~ from rice waste catalyzed by AlCl₃·6H₂O ~~that provided both Bronsted and Lewis acidity necessary for hydrolysis/dehydration and isomerization mechanisms, respectively~~ [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, whilst 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 AlCl₃·6H₂O and choline chloride to perform the reaction and this procedure was repeated six times. With the ~~increase progress~~ of the reaction cycles, the HMF yield decreased from 19 to 9 mol% after the sixth cycle, due to the damaging of the catalyst quality, or ~~probably due to the loss of catalyst loss during the recycles~~.

~~Finally, i~~n addition to SnCl₄ and AlCl₃, which are the most adopted salts for the conversion of biomass to HMF, also other chloride salts, such as CuCl₂ and CoCl₂, were ~~also~~ tested as catalysts. In this regard, Paul et al. employed CuCl₂ for the conversion of the 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 ~~amount of~~ lignin and high cellulose contents, but its conversion was ~~however~~ challenging, due to high crystallinity and high polymerization degree of cellulose, that 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 CuCl₂ as ~~the~~ catalyst. All these components formed a supramolecular complex with cellulose, that was subsequently hydrolyzed by water to produce glucose and then HMF, the latter with the yield of 34 mol% after 46 min (run 102, Table 4), ~~thanks to the employment of under the MW-microwave~~ heating. Roy et al. carried out the conversion of june grass to HMF under ~~microwave-MW~~ heating and the same temperature of 180 °C, reaching the HMF yield of 31 mol% (run 103, Table 4) [87]. Pan et al. employed CoCl₂ as ~~the~~ catalyst for the HMF synthesis ~~of HMF~~ from fir sawdust, reaching the highest yield of 19 mol% at 180 °C after 3 h in the ~~solvent system~~ H₂O/isopropanol ~~solvent system~~ (run 104, Table 4) [115]. Interestingly, most of the Co²⁺ 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 CoCl₂ selectively catalyzed the conversion of polysaccharides, leaving the almost pure lignin as the residual hydrochar. The authors ~~valorized 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, also their combination with homogeneous acids has been investigated, ~~aimed at for the conversion of biomass to HMF because generally this strategy allows a more quick quicker~~ depolymerization of cellulose. Mukherjee et al. added diluted HCl to $\text{Fe}_2(\text{SO}_4)_3$ for the 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 allowed the improvement of 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 ascertained after 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. ~~Also Besides~~, Mittal et al. employed HCl as homogeneous acid, in combination with AlCl_3 as the inorganic salt [116]. The authors carried out the conversion of several biomasses in the H_2O -dioxane solvent system under the same reaction conditions and ~~under exploiting microwave MW heating, reaching~~ 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 which produces through its hydrolysis higher initial sugar concentration resulting 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 the optimal because at least 20% (v/v) of the reaction solvent should be water, ~~in order to have an~~ effective hydrolysis of cellulose fraction to glucose. Yu et al. investigated the influence of the 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 ~~similar to like~~ those previously ~~reported in the presence of obtained with~~ SnCl_4 ~~by~~ alone, working in H_2O /DMSO and H_2O /acetone (compare runs 111 and 112 with 85 and 86 Table 4, respectively). On the contrary, when maleic acid was added to AlCl_3 , the rate of HMF production from rice waste was lower, reaching, under the same reaction conditions (140 °C, 100 min), the yield of 17 mol% (run 113, Table 4) instead of 35 mol% (run 84, Table 4), together with lower sugars conversion [105]. However, maleic acid allowed the improvement of HMF selectivity, thanks to the moderation of the Lewis acidity through the formation of malic acid, which acted as the ligand of Al^{3+} . ~~Finally Lastly~~, Kumar et al. tested a complex catalytic system composed ~~of by~~ an inorganic salt (AlCl_3), an organic acid (oxalic acid dihydrate), and a mineral acid (HCl), ~~or the production of to produce~~ HMF ~~starting~~ from sugarcane bagasse and raw potato, and supposed that each component catalyzed a specific step of the reaction [43]. ~~In particular, oxalic~~ Oxalic acid dihydrate might provide the acidity for the hydrolysis of cellulose to glucose, AlCl_3 might act as Lewis acid promoting the isomerization of glucose to fructose and HCl might catalyze the dehydration of fructose to HMF. However, this ~~particular~~ acid system was not effective in most ~~commonly used~~ solvents, such as water, THF, and DMF, but only in the biphasic solvent system [DMSO/2-butanol, MIBK]. ~~In this solvent, leading to~~ 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 that of laboratory one, with a biomass loading of 9 wt% (runs 114 and 115, Table 4).

Inorganic salts, ~~by~~ alone or in combination with homogeneous acids, ~~represent are~~ the most common catalytic systems ~~used up to now~~ for the conversion of biomass to

HMF, but **also** heterogeneous acid catalysts have been **also** 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 **starting** 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 sp.</i> (1.0%)	HZSM-5 (1.5)	H ₂ O/MIBK (3/2 v/v)	200	120	Conv.	44	74
120	Microalgae <i>Chlorococcum sp.</i> (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. ~~compared-studied~~ the catalytic activity of the commercial Amberlyst-36 ~~in-towards~~ the conversion of vegetable wastes, ~~performed-incomparing~~ H₂O (run 14, Table 1) and ~~in~~-H₂O/DMSO (run 116, Table 5), ~~as the solvents. finding-They found~~ that a higher HMF yield ~~-equal-to-(17 mol%)~~, was achieved in the ~~latter-biphasic~~ solvent, ~~system-due-to-getting~~ 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. ~~Also-~~Zhang et al. employed a sulfonated polymer, ~~e.g. the~~ polydivinylbenzene sulfonated, for the ~~HMF synthesis-of HMF~~ [124]. In this case, the authors synthesized the catalyst and reached negligible HMF yields starting from cottonseed hull and sugarcane bagasse, whereas ~~the-a modest~~ yield of 14 mol% was obtained starting from salvia miltiorrhiza residue (run 117, Table 5), a Chinese herbal medicine, ~~due-thanks~~ to the presence of starch ~~in-this biomass~~, which was easier hydrolysable 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~~scarcely promising. ~~Analogously-~~Xu et al. prepared the copolymer between p-toluenesulfonic acid and paraformaldehyde, ~~and tested-which was proposed in-for~~ the conversion of corn stalk, reaching the 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, also inorganic heterogeneous catalysts ~~have-been-used~~, such as zeolites, ~~have 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-with~~ the latter ~~system~~, because THF ~~has-hadshowered a~~ higher extraction efficiency than MIBK (runs 119 and 120, Table 5). The catalyst showed a slight decrease ~~of-in~~ activity after six recycle runs, leading to ~~the~~ HMF yield of 37 mol%, ~~due-to-caused by the deposition of~~ humins and proteins ~~deposition~~ on the catalyst surface, but the activity was almost completely restored after a calcination treatment at 500 °C for 4 h. The promising ~~solvent system~~-H₂O-NaCl/THF ~~solvent system~~ was also adopted by Xia et al. for the conversion of wheat straw in the presence of FePO₄·2H₂O, ~~by~~ alone or ~~in combination~~ with NaH₂PO₄, reaching the HMF yields of 18 and 44 mol%, respectively (runs 121 and 122, Table 5) [126]. FePO₄·2H₂O was able to catalyze the ~~cellulose~~ conversion ~~of-cellulose~~ to HMF, showing ~~both~~ Brønsted acidity, deriving from its hydrolysis ~~and-release-of protons~~, ~~and-but also~~ Lewis acidity, deriving from the formation of soluble hydroxylated iron species, ~~-but-the-addition-of-the-adequate amount~~Anyway, ~~the proper addition~~ of NaH₂PO₄ allowed the improvement of the HMF yield, due to the introduction of other Brønsted acid sites, which further ~~promoted the cellulose hydrolysis and the fructose dehydration to~~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~~of 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 ~~process-treatment~~ gave ~~as-product~~ also a solid residue composed ~~of~~by bio-char, containing elements such as P and Na, and FePO₄·2H₂O, ~~thus the authors proposed the recovered residue as material~~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 the SnCl₂ on zeolite H/β-supported phosphotungstic acid (SnCl₂-PTA/β), in H₂O-NaCl/THF, and reaching the 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 of the catalytic system. In addition, and higher amount of SnCl₂ led also to a higher ratio of Lewis/Brønsted acid sites, which were all of them beneficial properties for the conversion of cellulose to glucose, and for their isomerization to fructose and the HMF production of HMF. Regarding the textural properties, the increase of SnCl₂ amount allowed 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 gradually shortened. The shorter channels contributed to the improvement of the catalytic performances, because the contact of the substrate with the active sites was easier, and the diffusion of the produced HMF was faster, preventing its degradation. The authors evaluated also evaluated the catalyst stability, performing the a thermal calcination at 450 °C before each of the four recycle runs. The HMF yield decreased from 33 to 19 mol%, due ascribed to the partial collapse of the pores, the slight loss of SnCl₂ and the relevant loss of PTA after the recycles. However, the catalyst was reactivated thanks to the reimpregnation of SnCl₂ and PTA, reaching the 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 almost completely the starting activity.

In addition to polymers and inorganic materials, also carbonaceous acid catalysts have been prepared and employed in 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 and adopted it in the conversion of corn stover performed in H₂O/GVL, reaching the HMF yield of 30 mol% (run 124, Table 5) [128]. GVL showed to be a very promising solvent for the HMF production, because it limited undesired reactions, keeping the product stability and being. Moreover, being a polar aprotic solvent, GVL enhanced the reactivity of protons, stabilizing them by solvation, thus and promoting the biomass hydrolysis of biomass. Moreover, water had a fundamental role in the reaction, influencing the -SO₃H ionization and, as consequence 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 in towards the activation of hydrolysis of the cellulose glycosidic bonds of cellulose. At the end of the reaction, the authors recovered a solid composed of the by catalyst and unconverted corn stover and used directly 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 due to the leaching of the sulfonic acid leaching after five cycles. Cao et al. prepared a sulfonated biochar through the slow pyrolysis of forestry food waste (*Acacia confusa* and *Celtis sinensis*) and employed it the prepared catalyst for the HMF synthesis in H₂O/DMSO of HMF starting from bread waste. in H₂O/DMSO solvent system reaching the HMF yield of 38 mol%, together with a low amount of by-products (levulinic and formic acids), were reached due 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 further four-eye consecutive runs. The HMF yield dropped to 4 mol% after the fourth run, due to the sulfonic acid leaching that caused the decrease of the catalyst acidity. thus, in order to To solve this problem, the authors regenerated the catalyst by treatment with H₂SO₄, which allowed the almost complete restore of the highest HMF yield and after that the HMF yield was almost restored. 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 waste and rice wastes. reaching the highest HMF yield of 38 mol% was obtained starting from the

first biomass, ~~probably due thanks~~ to the enhanced porosity and starch accessibility ~~available thanks to 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), ~~investigated also considered the role of an different~~ organic solvents, ~~as extraction medium~~, such as isopropanol, DMSO, DMC, THF, and MIBK, ~~as the HMF extraction medium~~, reaching the highest HMF yield, ~~equal to of~~ 82 mol% ~~working~~ with isopropanol (runs 128–132, Table 5) [91]. The authors attributed ~~the this higher HMF yield obtained in this reaction system improvement~~ to the ~~synergistic role of synergy between the~~ isopropanol/AMIMCl solvent medium and the catalyst. ~~In fact, they supposed~~ They ~~proposed~~ that the Mg²⁺ ions ~~in 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. ~~Also, the~~ 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 ~~and~~/hydrogen ~~atoms~~ of cellulose. In particular, the cation of AMIMCl binds to oxygen atoms, whereas the Cl⁻ binds to the hydrogen ones, leading to the ~~breaks breakage~~ of inter-molecular and intra-molecular hydrogen bonds of cellulose, thus facilitating its hydrolysis. ~~Finally, As~~ already found in previous works, Sn⁴⁺ ~~is able to 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 the high biomass loading of 20 wt%. Recently, Chang et al. prepared ~~the a~~ sulfonated peanut shells catalyst (PSC) by ~~the treatment of treating the~~ pulverized peanut shells with sulfuric acid, ~~and this catalyst was tested and employed it as a~~ heterogeneous catalyst for the ~~HMF synthesis of HMF~~ from peanut shells, water hyacinth, and stalk, reaching the 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 ~~at the same time~~ as solvent and catalyst, and heteropolyacids, have been ~~tested proposed~~ as catalysts for the conversion of not pretreated biomass to HMF in biphasic medium, ~~and the The~~ available data are summarized in Table 6.

Table 6. HMF production ~~starting~~ 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	ChH ₂ PW ₁₂ O ₄₀ (0.3)	H ₂ O/MIBK (1/10 v/v)	140	600	Conv.	13 ³	132

	(2.2%)								
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 alone (run 53, Table 2), tested the employment of an different organic extraction solvents extraction, such as ethyl acetate and MIBK, adopting and applied the biphasic system as complex system in to the conversion of also other biomasses (corn cob, macroalgae *Ulva lactuca* and microalgae *Porphyridium cruentum*), all employed with in all cases keeping the same loading of only 1.8 wt% (runs 136–140, Table 6) [92]. Complete cellulose conversion was ascertained only starting from the algae, underlining that polysaccharides in the terrestrial substrate are more resistant to the hydrolysis than those present in of marine sources. However, despite the complete cellulose conversion, analogous HMF yields, in the range of 7–13 mol%, were reached starting 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]. On this basis, Zhang et al. synthesized an heteropolyacid catalyst starting from choline chloride and H₃PW₁₂O₄₀, obtaining giving ChH₂PW₁₂O₄₀ that that was employed as catalyst in for the conversion of corn stover, pinewood and husk of xanthoceras to HMF, working in H₂O/MIBK solvent system (runs 141–143, Table 6) [132]. The catalyst was insoluble in water at room temperature, but became soluble at a temperature higher than 60 °C, thus so performing when the reaction was performed at 140 °C, the ChH₂PW₁₂O₄₀ acted as a homogeneous catalyst. In particular, according According to the authors, ChH₂PW₁₂O₄₀ could be self-assembled as micellar spheres of polar H₂PW₁₂O₄₀⁻ outside and Ch⁺ inside, providing a sort of nanoreactors. During the hydrolysis, cellulose could be adsorbed by hydrophilic H₂PW₁₂O₄₀⁻ that concentrated cellulose around the catalyst, 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 HMF yield, limiting the formation of levulinic and formic acids. Analogously, Lai et al. prepared the catalyst treating the heteropolyacid H₃PW₁₂O₄₀ with AgNO₃, leading to getting 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, reaching, under the same reaction conditions, the HMF yields of 26, 20 and 19 mol%, respectively (runs 144–146, Table 6).

2.2. Pretreated biomass

As previously mentioned introduced, the 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 the its yield. The principal available pretreatment techniques are divided classified into physical, chemical, and biological ones. Among the physical pretreatments, ball-milling leads to the decrease of the particles 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 micro-wave-MW pretreatments allow the destruction destruct of the crystalline structure of cellulose, thus improving the hydrolysis efficiency but these last ones are characterized by technologies require the high cost of equipment, limiting so their application on large-scale is rather limited [136,137]; finally instead, the steam-explosion leads to the

rupture destruction of the biomass complex matrix 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 provides the employment of employs inorganic acids (e.g. H₂SO₄, HCl, H₃PO₄) or, due to corrosive problems, of organic acids (e.g. oxalic acid, peracetic acid) for the hydrolysis of polysaccharides to sugars [140]; alkali pretreatments, aiming at the lignin dissolution of lignin in NaOH, KOH or Ca(OH)₂ aqueous solutions, by destroying in this way the network structure of biomass and weakening the hydrogen bonds between cellulose and hemicellulose [141]. Finally/Lastly, in the biological pretreatments require the use of appropriate microorganisms, which release ligninolytic and hydrolytic enzymes, are adopted. In-By this way, the depolymerization of lignin and the hydrolysis of polysaccharides take place without the generation of wastes and under low energy demanding conditions, but/However, in comparison, compared with the other pretreatments, the biological ones require a strict control of the reaction parameters and very long reaction times [142]. All these pretreatments strategies have been adopted for the synthesis of HMF from real biomasses and in the following paragraphs the most relevant literature results are commented.

2.2.1. One-solvent systems

The conversion of pretreated biomasses in one-solvent systems involved 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 starting 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.

Analogously to As for the not pretreated biomass, also in this case the autocatalytic reaction for the HMF synthesis of HMF 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 the sufficient acidity to promote the HMF production of HMF, 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 the loading of only 1 wt%, and in the presence of citric acid as the catalyst, reaching The authors claimed the 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 ~~not produce~~ avoid the relevant formation of by-products (run 148, Table 7) [144]. Wei et al. extracted the cellulose fraction from dewaxed eucalyptus by ~~the~~ treating it with nitric acid and ethanol, and obtaining at the end a white fiber. ~~This was~~ subsequently subjected to hydrolysis hydrolyzed at low substrate loading (1 wt%), working in the presence of ~~catalyzed by the salt~~ InCl_3 as the catalyst, and leading obtaining to the the HMF yield of only 14 mol%, due to the promoted rehydration pathway under the adopted reaction conditions (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 ~~of agarose moiety~~ gave humins, and galactose was stable in the aqueous phase (run 150, Table 7) [146]. KHSO_4 showed both Brønsted acidity, which contributed to the break of glycosidic bonds and ~~to~~ the dehydration of 3,6-anhydrogalactopyranose units to HMF, and but also Lewis acidity, responsible for the isomerization step. ~~Moreover, the authors investigated~~ 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 by adding newly extracted agarose. Surprisingly, the HMF yield increased with the increase of cycles, probably due to the ~~as a consequence of~~ salt out process, occurring during the cycles. In fact, the extracted agarose also contains potassium, sodium, and other metal ions whose concentrations increased with the increase of the recycle tests, thus contributing to the salt out process that enhances the HMF selectivity and yield. In addition to the only use of inorganic salts ~~alone~~, also their combination with organic acid has been also investigated for the conversion of pretreated biomass, as ~~in the work of~~ reported by Jin et al., who prepared formylated cellulose through the treatment of corn stover with formic acid, and adopted it as the feedstock of the HMF production. They employed AlCl_3 and maleic acid as the catalytic system, working under microwave-MW heating, but obtaining and obtained the HMF yield of only 16 mol%, despite the low substrate loading ~~of~~ (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 those ascertained starting from α -cellulose and microcrystalline cellulose, which were both in both cases ~~h~~ 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 ~~the 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 ~~to~~ 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, being the amorphous fraction easier hydrolysable. A slight improvement of the HMF yield from 39 (run 28, Table 1) to 47 mol% was also obtained 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, also other pretreatments have been adopted. In this regard, Hoang et al. pretreated the corncob with a mixture of ethanol and acetone for 6 h ~~in order~~ to remove the extractives, and then the residue was adopted as the feedstock for the HMF synthesis. ~~of HMF catalyzed by~~ A ad-hoc prepared sulfonic acid-acid-functionalized mesoporous ZSM-5 zeolite ($\text{HSO}_3\text{-ZSM-5}$) was synthesized and tested for this reaction, reaching the unsatisfactory HMF yield of 24 mol%, due to the high formation of humins and rehydration acids (run 156, Table 7) [148]. Finally, also the delignification pretreatment was investigated for the conversion of biomass in water. In fact, this could represent a very promising approach to activate the cellulose conversion and enhance the HMF synthesis, because ~~in this way~~ cellulose is ~~results becomes~~ more accessible to the acid sites of the catalyst. This pretreatment was adopted by Zhang et al., who

delignified the corn stover employing 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 both the cellulose digestibility conversion and to HMF yield, leading to 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 resulted stable and recyclable in further five consecutive cycles allowing the achievement of the 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 ionic liquids ILs and deep eutectic solvents DESs as the reaction medium is not limited to the conversion of not pretreated biomasses but it they have been adopted can be proposed also for the pretreated ones, as evidenced by the literature results reported in Table 8.

Table 8. HMF production starting 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 /p-TSA (0.02)	ChCl ⁵ /p-TSA (n.a. ³)	80	30	Conv.	72	153
167	Rice husk ⁹ (2.0%)	ChCl ⁵ /p-TSA (0.02)	ChCl ⁵ /p-TSA (n.a. ³)	80	30	Conv.	68	153
168	Bagasse ⁹ (2.0%)	ChCl ⁵ /p-TSA (0.02)	ChCl ⁵ /p-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 the HMF synthesis of HMF in DES composed of choline chloride/citric acid [150]. The latter was resulted a promising DES system, where 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, the adopted temperature of 130 °C allowed the reduction of the hydrogen bond strength, thus reducing the viscosity of the solvent and leading to an efficient HMF production. In fact, in the presence of H₂SO₄ as the catalyst, the HMF yield of 24 mol% was achieved (run 158, Table 8), which was similar to like that obtained starting from pure glucose under the same reaction conditions. Nguyen et al. pretreated wood chips and rice straw with an alkaline solution (NaOH) that could cause the structural change of lignin, swelling, and partial de-crystallization of cellulose and as well as the partial removal of hemicellulose, thus making the cellulose more prone to the conversion. The pretreated biomasses were then subjected to hydrolysis catalyzed catalytically hydrolyzed by the salt CrCl₃·6H₂O in the ionic liquid [BMIM]Cl, leading to 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 the HMF synthesis of HMF from the isolated cellulose, in particular, the salt CuCl₂·2H₂O and the heteropolyacid H₄[Si(W₃O₁₀)₄]·xH₂O in the solvent system composed by the ionic liquids [EMIM]Ac and [BMIM][TOS], reaching the HMF yields of 42 and 40 mol%, respectively (runs 161 and 162, Table 8). In fact, in particular, when CuCl₂·2H₂O 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 of towards the isolated cellulose, whilst the second one being able to form a complex with CuCl₂ ([CuCl₂(TOS)]⁻) active in the glucose conversion of glucose to HMF. Ji et al. adopted the ionic liquid [BMIM]Cl in the pretreatment of food wastes, such as apple waste and orange wastes, with the support of assisted by ultrasound sonication [152]. This approach allowed the decrease of crystallinity index, due to the synergistic effect of ionic liquid, able to destroy the hydrogen bonds between the cellulose chains leading to cellulose dissolution and rupture of the crystal structure, and ultrasounds, which promoted the accessibility of the ionic liquid into the biomass through the generation of shear forces, shock waves and cavitation phenomenon could promote the penetration of ionic liquid into the biomass. In fact, 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 with cracks and pores after 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 very powerful solvent for towards the cellulose dissolution of cellulose, adopting commercial heterogeneous acid resins as catalysts. In particular, the best results were ascertained with the macroporous strong acid-exchange resin D001, which allowed the obtaining HMF yields of 45 and 42 mol% starting from apple waste and orange waste, respectively (runs 163 and 164, Table 8). These promising obtained results could be related to both the internal and external explained by considering the textural properties structure of the D001 resin, which is characterized by large pore diameter, high surface area, and easy and fast exchange of protons, all favorable properties that for promote promoting the interaction between the substrate and the acid active sites. Moreover, the catalyst resulted stable and recyclable, keeping almost constant the HMF yield after five consecutive runs. The same authors adopted the ultrasound pretreatment also for the conversion of sugarcane bagasse, using the ionic liquid [BMIM]OAc as the solvent for both the pretreatment and the reaction step, due to its promising performance already evidenced in the conversion of not pretreated sugarcane bagasse catalyzed by the D001 resin that led to the HMF yield of 25

mol% (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 of HMF yield from 36 to 66 mol% (run 165, Table 8) because the disruption of cellulose structure and its dissolution were promoted at a higher frequency. Finally, DESs were investigated in the dual role of solvent and catalyst for the HMF synthesis of HMF starting 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, allowing the achievement of. By 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 up to four cycles by adding fresh cellulose isolated from the wheat straw without any considerable loss in the activity, thus proving that the system kept the efficiency almost constant.

2.2.3. Biphasic and/or multiple solvent systems

As previously observed described for the conversion of not pretreated biomasses, also in 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 starting 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	Al ₂ (SO ₄) ₃ (2.8)	H ₂ O-NaCl/GVL	165	50	Conv.	35	156

183	(1.0%) 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 (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
190	Potato peels ¹⁴ (4.0%)	1°: LiBr (0.2) + H ₂ SO ₄ (8.2) 2°: AlCl ₃ (2.0 ¹⁵)	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/acetonitrile (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 microwave-MW heating systems in 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 for the hydrolysis of cellulose to give glucose but not very effective in suitable for the conversion of glucose to HMF. A large number of Many papers reported the employment 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 adoption-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 performances of InCl₃ with other chlorides, such

as AlCl_3 and FeCl_3 (runs 172 and 173, Table 9), the authors proved that InCl_3 resulted as the best one, due to the combined effect of In^{3+} acting as Lewis acid in the isomerization of glucose to fructose, and the partially hydrolyzed In-OH group, acting as Brønsted acid in the dehydration of fructose to HMF. InCl_3 was also employed also in the for the conversion of pretreated bagasse under the same reaction conditions, leading to the HMF yield of 46 mol% (run 174, Table 9). Finally/Lastly, the whole reaction medium was easily recycled. In fact/For this purpose, the organic phase, containing THF and HMF, was distilled in order to recover the product and recycle THF in subsequent runs together with the aqueous phase containing the catalyst InCl_3 deriving from the previous run. During the recycles, the HMF yield gradually decreased, due to the loss of InCl_3 . However, despite the interesting HMF yields ascertained by Wei et al., the low adopted biomass loading (1 wt%) makes the process not very attractive at a larger scale. Taking into consideration from these examples that the presence of the inorganic salt resulted important in order to improve the separation between water and THF and also to enhance 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]. In fact, the first step is provided the depolymerization of lignin to alkyl methoxy phenols, which was catalyzed by Pd/C and $\text{Yb}(\text{OTf})_3$, and performed in methanol at 200 °C for 2 h with 20 bar of H_2 . At the end, the solid residue contained Pd/C, hemicellulose, and cellulose, whilst in the liquid phase there were included methylated C5 sugars, lignin monomers, and $\text{Yb}(\text{OTf})_3$. These latter were separated through rotary vapor, aimed at the removing of the solvent, followed by water extraction with water, 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 hydrodeoxygenation reaction, adopting Ru/ Nb_2O_5 as catalyst and 2-propanol as hydrogen donor. In this approach, the valorization of lignin can be considered is proposed as the pretreatment step, because from the depolymerization of lignin leading to a solid residue rich in hemicellulose and cellulose, containing also containing the heterogeneous adopted catalyst Pd/C, was recovered. This residue was converted to furfural and HMF in a biphasic system seawater/THF, leading to 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 allowed not only was effective to achieve of interesting for the production of HMF in good yields, also enabling but also the recovery of Pd/C as solid residue, which was to be 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 constant unaltered the HMF yield up to for three cycles. However, despite the full valorization of biomasses and the interesting HMF yields, the process is results complex, expensive, and not so safe, due to the employment of a noble metal (Pd/C) and hydrogen in the first step.

Besides THF, also GVL was 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, due to the highlighted low HMF yield reached starting from molasses (run 101, Table 4),. For this reason, they pretreated this biomass with tricalcium phosphate and hydrochloric acid, with the aim of removing to remove inorganic salts and organic impurities, thus slightly enhancing the HMF yield up to 28 mol%, working carrying out the reaction in $\text{H}_2\text{O}/\text{GVL}$ under the same experimental conditions and the same promising promising biomass loading of 12.8 wt% (run 179, Table 9) [113]. Shen et al. pretreated several biomasses through the ball-milling in the presence of $\text{Al}_2(\text{SO}_4)_3$ and subsequently, the mixture of pretreated biomass and the inorganic salt the resulting mixture was placed in treated in the biphasic system $\text{H}_2\text{O}-\text{NaCl}/\text{GVL}$, to carry out the hydrolysis catalyzed by $\text{Al}_2(\text{SO}_4)_3$ acted as catalyst [156].

The presence of $\text{Al}_2(\text{SO}_4)_3$ during the ball-milling step allowed [a](#) greater destruction of cellulose ~~and, 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 the 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 –and in one of their works~~ 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 ~~solubility, improving in this way the enabling a better~~ contact between catalyst and substrate. However, only limited changes in the biomass structure were observed after the pretreatment, and HMF yields ~~similar to 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 of this evidence could be that probably because~~ the release of CO_2 ~~in this case~~ was not fast enough to disrupt the biomass structure and ~~to~~ solubilize polysaccharides. Different inorganic salts were also investigated in natural deep eutectic solvents (NATDES). ~~by~~ Lu et al. ~~–who~~ found that [the DES composed of](#) choline chloride/oxalic acid ~~DES~~ and SnCl_4 were respectively the most promising solvent and catalyst for the synthesis of HMF from corn straw pretreated by ultrasound [157]. The sonication at 40 kHz produced cavitation, ~~leading as consequence the getting a~~ local increase of temperature and pressure, ~~thus which was effective for~~ destroying the structure of biomass and increasing the superficial area, [thus improving the](#) ~~that enhanced the~~ extraction of cellulose. However, the high viscosity of NATDES hampered the progress of the conversion of hexose to HMF, resulting [in the](#) imperative ~~the~~ 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).

~~As previously observed for the conversion of not pretreated biomasses, the~~ [The](#) combination of inorganic salts with mineral and organic acids has been also proposed for the conversion of the pretreated ones. Ganado et al. pretreated the waste coffee grounds through ~~an~~ 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](#) $\text{H}_2\text{O}/\text{DMSO}$ system, [working](#) in the presence of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and H_2SO_4 as catalytic system [158]. The authors performed the reaction under [microwave-MW](#) heating and optimized the HMF yield thanks to the support of Box-Behnken [design experiment experimental design](#), reaching the highest HMF yield of 14 wt% (run 187, Table 9). Spent coffee grounds, together with pistachio hull, were also ~~adopted-proposed~~ as substrates by Pereira et al. [159]. The authors fractionated the wastes through an organosolv process, employing H_2SO_4 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-lignin~~-enriched organic phase. The cellulose-~~enriched~~ solid residue was ~~subsequently then~~ enzymatically hydrolyzed to glucose in the presence of cellulase from *Aspergillus niger*, ~~G~~ glucose was ~~then~~ isomerized to fructose in the presence of glucose isomerase from *Streptomyces murinus* and ~~finally~~ fructose was converted to HMF adopting AlCl_3 and HCl as [the](#) catalytic system in the sustainable biphasic solvent $\text{H}_2\text{O}-\text{NaCl}/\text{GVL}$ 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, ~~in order~~ to achieve the complete exploitation of the biomass, the authors ~~investigated 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 *Metschnikowia pulcherrima* to produce bio-oil, whereas the high heating value of lignin-enriched organic phase was evaluated, ~~to with the aim of proposing~~ this fraction as a liquid fuel. ~~Analogously, a~~ Also Ebikade et al. investigated the complete exploitation of the waste potato peels, carrying out 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. The 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, in order to~~ create a biphasic system ~~thus reducing that reduced the formation of by-products formation~~. 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% ~~in after~~ the third recycle, 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 a 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 ~~together with and~~ water as ~~the~~ reaction medium strongly promoted the HMF formation, because the organophilic formyl group ~~present in the~~ formylated cellulose had stronger interaction with the organic solvent ~~with respect to rather than with~~ the ~~only~~ water ~~alone~~, 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* the 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, thus, in order 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. ~~In particular,~~ CaCl₂ showed to be very effective for this purpose, allowing the 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 the HMF yield of 82 mol% after 120 min under conventional heating (run 192, table 9) and 86 mol% after only 10 min under ~~the microwave-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 ~~starting~~ 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	Amberlyst-36 (1.0)	H ₂ O/DMSO (1/1 v/v)	140	40	MW	71 ³	162

	syrup ² (3.8%)							
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 ^{8,6} (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	Corn cob ⁹ (3.2%)	MCMP ¹² -Al (30.3)	H ₂ O/[moMIM][PF ₆] ⁻ (1/3 v/v)	200	180	Conv.	52	170
212	Corn cob ⁹ (3.2%)	MCMP ¹² -Al (30.3) + MCMP ¹² -Cr (30.3) + MCMP ¹² -Mg (30.3)	H ₂ O/[moMIM][PF ₆] ⁻ (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 previously subjected to enzymatic hydrolysis enzymatically pretreated by, catalyzed by

glucoamylase and sucrase enzymes, ~~in order~~ to obtain glucose syrup, which was purified ~~by passing through an adsorption chromatography column, and then the obtained product was and further~~ isomerized to fructose by a glucose isomerase enzyme [162]. The as-obtained fructose syrup was further purified ~~through an adsorption chromatography column~~ and converted to HMF in a biphasic ~~H₂O/DMSO system~~ system, employing the commercial acid resin Amberlyst-36 as ~~the~~ catalyst. Under the optimal reaction conditions, the ascertained HMF yield was ~~equal to~~ 70 mol% (run 194, Table 10), and it was maintained ~~almost constant~~ also after four recycles, ~~indicating that there was negligible deactivation 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 ~~another food waste, such as~~ apple waste, to HMF [163]. In this case, the authors milled the ~~apple fruit wastes starting feedstock, which was~~ filtered ~~them on a ceramic candle filter~~ under vacuum, and ~~the filtrate was~~ neutralized ~~by a the filtrate with~~ Na₂CO₃ aqueous solution. After this pretreatment, MIBK, ~~which acted as~~ (extraction solvent), and ~~the catalyst~~ Sn-Amberlyst-15 (catalyst), were added to the aqueous solution, and the reaction was carried out at 120 °C for 2 h, ~~leading to the leading to~~ -HMF yield of 29 mol% (run 195, Table 10). ~~In addition Also~~, Lucas-Torres et al. investigated the ~~con- version HMF production from of the~~ the food waste melon rind, ~~which was~~ pretreated by solvent extraction, ~~as starting feedstock for HMF production~~ [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. ~~In fact~~, H₂SO₄ was mainly effective in the cellulose hydrolysis to glucose, but it was scarcely active ~~in towards~~ the ~~further~~ conversion of glucose to HMF, whereas montmorillonite KSV resulted effective also ~~in this last step for this last~~ step. Moreover, in the presence of montmorillonite KSV, the highest HMF yield (28 mol %) was obtained under ~~microwave MW~~ heating, ~~further confirming due to~~ 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, catalyzed by in the presence of~~ the commercial zeolite H-ZSM-5 ~~as the catalyst~~ [164]. Before the hydrothermal conversion, the microalgae was ~~subjected to extraction- extracted with by~~ hexane ~~in order~~ to remove lipophilic compounds, such as carotenoids and triglycerides, and then it was ~~directly~~ converted to HMF, ~~leading to the~~, leading to the yield of 39 mol% (run 198, Table 10). In the work of Hoang et al., the ~~zeolite~~ H-ZSM-5 zeolite was sulfonated (HSO₃-ZSM-5) and employed ~~as the catalyst~~ for the HMF synthesis ~~of HMF~~ from corncob, ~~previously extracted 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 ~~increment improve- ment 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. ~~In particular Remarkably~~, the ~~medium~~ H₂O/DMSO ~~system resulted was more particularly~~ effective ~~than H₂O/THF, allowing the achievement of 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 ~~more~~ difficult its recovery from the ~~solvent reaction~~ mixture. On this basis, H₂O/THF was ~~chosen by the authors for further investigations further considered for the study of~~, ~~such as~~ the catalyst recyclability: after five subsequent runs, the HMF yield of 51 mol% was reached, ~~showing that there was no significant confirming the absence of~~ significant catalyst deactivation. ~~Moreover, t~~ The proposed process ~~is results~~ interesting, thanks to the ~~adopted good~~ biomass loading ~~of (10 wt%), which is higher than the majority most of those~~ reported up to now. Sun et al. proposed a green and facile strategy for the preparation of sulfonic ~~acid acid~~-functionalized attapulgite (APG-SO₃H) via ~~the a~~ wet mechanical ball-milling method, employing 3-mercaptopropyltrimethoxysilane as ~~the~~ source of -SH

groups. ~~These that~~ were grafted on the clay and subsequently oxidized to $-\text{SO}_3\text{H}$ with H_2O_2 at room temperature [165]. The ~~as~~-synthesized catalyst was employed in the HMF synthesis from ball-milled rice straw (only 1 wt%), in a H_2O - NaCl / GVL system. Attapulgitte is a natural clay mineral widely adopted as catalyst support, due to its ~~characteristics, such as~~ 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, ~~thus~~ the prepared APG- SO_3H catalyst system ~~resulted was an~~ efficient catalyst allowing the achievement of the HMF yield of 31 mol% (run 201, Table 10). The effectiveness of the ball-milling pretreatment ~~in for~~ the improvement of HMF ~~synthesis production~~ was also demonstrated by Flores-Velázquez et al. [166]. The authors extracted the cellulose from a banana plant waste through soft alkaline and acid treatments, ~~thus obtaining recovering~~ pure cellulose free of hemicellulose and lignin. ~~The as prepared~~ This cellulose was converted to HMF in the H_2O - NaCl / THF biphasic system, employing Al_2O_3 - TiO_2 - 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 ~~subjected to ball milling milled, its conversion~~ it was possible to ~~was~~ speed up its conversion to HMF, ~~and the achieving a maximum~~ HMF yield of 80 mol% ~~was obtained~~ after only 60 min ~~working~~ at 175 °C (run 203, Table 10). ~~This study proved, thus proving~~ that the ~~rupture depolymerization~~ of the long cellulose chains ~~to give shorter ones~~ positively affected the 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 ~~solvent mixture~~ H_2O / DMSO / acetonitrile ~~medium, together with in the presence of~~ activated carbon, maleic acid, and AlCl_3 [167]. ~~In particular, the~~ activated carbon allowed the increase of HMF yield up to 85 mol% (run 204, Table 10), ~~thanks to its ability in by~~ adsorbing the impurities ~~formed during originating from~~ the dehydration of fructose, that can reduce the efficiency of the isomerization step and lead to the higher formation of by-products, ~~as already found by Dumesic et al.~~ [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 the literature~~, in agreement with the “high gravity” approach, that allows the production of concentrated HMF streams. However, the substrate is largely employed also in the food supply chain, thus its exploitation for the HMF synthesis ~~of HMF~~ on large scale could result poorly socially sustainable. ~~On the other hand,~~ Tyagi et al. prepared a sulfonated activated carbon catalyst, ~~and adopted it as the catalyst which was adopted~~ for the conversion of acid-pretreated pineapple and banana peels to HMF in the H_2O / $[\text{BMIM}]\text{Cl}$ solvent system [168]. The reaction conditions were optimized with a statistical model and ~~under the best reaction conditions,~~ the highest HMF yields of 50 and 45 mol% were achieved ~~starting~~ 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 AlCl_3 , to the sulfonated activated carbon strongly improved the HMF yield starting from acid-pretreated hardwood biomasses [169]. ~~The in fact, AlCl_3 , having~~ Lewis ~~properties acidity of AlCl_3~~ 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 ascertained 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, ~~in order~~ to separate HMF from the aqueous phase, composed ~~by of~~ $[\text{BMIM}]\text{Cl}$ and AlCl_3 , ~~and~~ the last ones ~~was~~ reused in successive runs after evaporation under vacuum, to remove moisture. The HMF yield gradually decreased from 86 to 26 mol%, ~~ascertained in after~~ the sixth recycle runs, thus proving that a ~~sort of degradation in worsening of~~ the activity of $[\text{BMIM}]\text{Cl}$ and AlCl_3 ~~activities~~ took place after each cycle. Also Yuan et al. performed the conversion of the acid-pretreated biomass corncob to

HMF [170]. The authors carried out the reaction in the ~~solvent system~~ 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, where the metallic specie acted as ~~the~~ acid site. The employment of this type of catalyst had an evident positive effect on ~~the~~ corn cob hydrolysis. In particular, the MCMP-Al exhibited the best catalytic performances, leading to ~~the~~ HMF yield of 52 mol% (run 211, Table 10), but the mixed catalytic system involving MCMP-Al, MCMP-Cr₂ 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 ~~after the seventh recycle~~ the catalytic efficiency started to decrease ~~after the seventh recycle~~, probably due to the destruction of the magnetic-chitosan metalloporphyrin particles structure ~~with the repeated runs~~.

~~Finally~~ ~~Lastly~~, ~~very recently~~ also DES and ILs have 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 multiple 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 ~~of lignin~~ and, partially, also ~~of that of the~~ hemicellulose from sugarcane bagasse, through an ~~acid~~ pretreatment ~~with acid by a~~ DES, composed ~~of~~ choline chloride and lactic acid [172]. The high efficiency of the acid DES ~~in for this~~ pretreatment was ~~due 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 partial hydrolysis of hemicellulose ~~and as well as~~ cellulose and lignin removal. Moreover, Cl⁻ in choline chloride can contribute to the ~~rupture cleavage~~ of the β-O-4 bonds ~~in of~~ the lignin ~~structure~~ [174], thus improving the ~~lignin~~ -dissolution ~~of lignin~~. The acidic properties of the adopted DES ~~make it active also in are effective for~~ promoting the ~~HMF~~ synthesis ~~of HMF~~ starting from the cellulose-rich residue obtained from sugarcane bagasse. However, the highest HMF yield (57 mol%; run 213, Table 11) was ascertained when ~~the~~ DES was employed together with the proper amount of water, because this allowed the ~~desirable~~ reduction of viscosity. On the other hand, Huang et al. employed ~~the ionic liquid~~ [BMIM]HSO₄ for the conversion of *Camelia oleifera* fruit shell ~~feedstock~~, previously ~~deprived subjected to solvent extraction~~ of the lipophilic compounds ~~by organic extraction~~ [173]. The authors carried out the reaction under ~~microwave-MW~~ heating in a biphasic system composed ~~of~~ [BMIM]HSO₄ and water as ~~the~~ reactive phase, and 1,4-dioxane as ~~the~~ extractive ~~phase one~~. Under the best reaction conditions, they obtained furfural as the major product and HMF as the co-product, due to the higher recalcitrance ~~towards hydrolysis~~ of cellulose ~~towards the hydrolysis than hemicellulose~~, 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~~by ionic liquid and water, and almost constant yields were obtained after three recycle runs.

3. Strategies and future perspective to wake up the “sleeping giant”

HMF has been ~~referred in the literature~~considered as a “sleeping giant” because of its enormous potential as ~~a~~ platform-chemical, but also to the drawbacks related to its selective synthesis (by-products formation) and its scarce stability, ~~these last ones~~which hampering the HMFits production on larger scale [175]. Moreover, ~~in order~~to develop the bio-refinery process, ~~the~~ industrial HMF production should become a feasible possibility starting from real biomasses, ~~rather than~~ ~~and not~~ from model compounds, such as monosaccharides, ~~which~~that are more expensive and contribute to making the process not economically sustainable. Nevertheless, the employment of ~~the real~~ biomass as ~~the~~ starting feedstock is even more challenging, due to its complex matrix and the issue of ~~the~~ HMF separation ~~and~~/purification represents a crucial aspect, up to now still scarcely investigated in the literature. In fact, ~~if~~ starting from model compounds the criticism is due primarily to the formation of by-products, whereas ~~if~~ starting from real biomasses also 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 ~~at for the~~ industrial scale, being easier ~~to be hydrolyzed~~hydrolysable, and ~~releasing few~~ ~~er~~producing lesser amounts of other ~~products~~ compounds than the conversion of lignocellulosic feedstocks ~~than a lignin rich biomass, whose degradation not only involves hemicellulose and lignin but also protein and lipids,~~ depending on ~~the biomass~~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. ~~is confirmed by the absence of works that performed any pretreatment steps starting from them, except for~~In this context, only Lin et al. [161] ~~who~~ carried out a previous enzymatic oxidation step on the high fructose corn syrup, but ~~only~~ with the purpose to generate *in situ* the catalyst, namely gluconic acid from the oxidation of glucose. Noteworthy, ~~it is~~ ~~from~~starting from these C6 sugar-rich biomasses, in particular ~~starting from~~ sugar beet juice, ~~that~~ the highest HMF yield ~~equal to~~of 96 mol% was obtained ~~in the H₂O-NaCl/MeTHF system,~~ employing H₂SO₄ as ~~the~~ catalyst ~~in the biphasic system H₂O-NaCl/MeTHF~~ (run 54, Table 3) [93]. However, ~~the~~ high fructose corn syrup is ~~preferably~~ used ~~in~~ within the food supply chain, thus its employment ~~as starting material~~ for the HMF synthesis ~~is of HMF could be~~ not socially sustainable. For this reason, generally, the research is focusing on the possibility of adopting lignocellulosic or algal wastes as ~~starting~~ feedstock, thus ~~not competing~~avoiding the competition with the food supply chain [177]. However, starting from lignocellulosic biomass usually a pretreatment step aiming at the fractionation of biomass into its components is necessary to optimize the HMF synthesis, facilitating its separation/purification and also valorizing each biomass component, thus making sustainable the whole process. ~~In fact~~In fact, only ~~valorizing all the~~the valorization of each biomass components ~~can justify~~ the ~~adding~~ addition of ~~the a~~ pretreatment step, which ~~can~~ could require expensive and energy-intensity equipment, such as ~~a~~ ball mill and ultrasound/microwave reactors, and other chemicals, such as alkali/acid solutions and/or enzymes, ~~could be economically advantageous.~~ ~~In addition to the by products that can originate during the reaction, also~~ Even the ~~adopted~~ catalyst ~~can~~ could complicate the separation and purification of HMF, ~~in particular~~particularly when it is homogeneous, such ~~such~~ as mineral and organic acids and/or inorganic salts. For this reason, ~~the~~ 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 ~~recovery separation~~ and recycling of the heterogeneous catalyst is not so easy ~~when employed in~~ when employed in the conversion of lignocellulosic biomass, because ~~at the end of the reaction~~ it is recovered ~~at the end of the reaction in~~ as the solid residue, together with the unconverted biomass and humins ~~that can be formed during the process~~. ~~Therefore, often in the literature, this~~ This problem is not often faced and ~~the only~~ few works ~~that~~ reported the recyclability of the heterogeneous catalyst, ~~involve involving~~ a calcination step at temperatures higher than 400 °C, that allows ~~the burning of~~ the carbonaceous material ~~joined together with the catalyst~~. 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, ~~in order~~ 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, ~~thus but~~ resulting expensive and hardly scalable at a larger scale. On this basis, the homogeneous catalysts, in particular the inorganic salts, which are commercial, cheap and show both Brønsted and Lewis acidities, are more promising than the heterogeneous systems for the synthesis of HMF from biomasses, despite the problem of their separation and recycle. ~~Remarkably, it is remarkable that~~ this problem can be resolved thanks to ~~the~~ proper choice of the reaction ~~medium~~ medium. In fact, biphasic ~~systems~~ water/organic solvent ~~systems~~ allow the confinement of the homogeneous catalyst in the aqueous phase where the reaction takes place and the continuous selective extraction of HMF in the organic phase [178]. Thus, these systems contribute to: *i*) improve the selectivity of the reaction, preventing the ~~HMF degradation of HMF~~, which is particularly ~~activated active~~ in ~~the~~ aqueous medium; *ii*) isolate HMF from the other components of the reaction mixture, allowing an easier purification step; *iii*) recycle the homogeneous catalyst ~~contained present~~ in the aqueous phase by ~~further addition of adding in the subsequent runs~~ fresh biomass and organic solvent [99,112,145,146,155,160,169]. ~~In order to make sustainable the process, The~~ The choice of the organic solvent is a key aspect ~~for improving the sustainability of this process. because it, in addition to~~ The ideal solvent should have a low miscibility with water ~~and~~ , ~~should be characterized by a~~ low boiling point, making ~~in this way~~ feasible ~~the its separation recovery~~ from HMF by ~~under~~ vacuum ~~evaporation distillation~~. Moreover, ~~the best~~ this solvent should be ~~also~~ safe and preferably of renewable ~~origin~~ 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 resulting potentially dangerous [179]. Moreover, ~~in order~~ 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, ~~resulting being~~ particularly active ~~in towards~~ the deconstruction of the lignocellulosic biomass matrix and acting 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 low cost 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 employment is represented by their difficult separation from HMF, due to their high boiling points, that make impossible their ~~removal by under vacuum evaporation distillation. strategy~~ In addition, ~~and~~ the strong interactions established between ~~HMF and~~ ILs/DESs ~~and HMF that~~ make difficult also ~~its~~ the extraction with organic solvents [180,79]. ~~On this basis, despite ILs and DESs are claimed as 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 ~~separation and purification of HMF~~ ~~work-up operations~~ is re-

~~lated to the adopted~~-loading of starting biomass. In fact, the ~~exploitation-proposal~~ of a "high-gravity" approach, ~~which means the adoption~~~~indicating the preference~~ of elevated biomass loadings (generally higher than 20 wt%), could allow the production of concentrated HMF streams, ~~thus~~ reducing ~~as a consequence~~ the ~~solvent~~-separation costs [47,134]. However, it is well-known that a high biomass loading leads to a ~~bigger-higher~~ concentration of by-products, thus causing a decrease ~~in of~~ HMF yields, ~~and also to as well~~ ~~as~~ mass transfer problems ~~due to a more difficult mixing of the reaction slurry~~ [1810]. For these reasons, ~~generally~~ biomass loadings below 10 wt% have been ~~adopted-generally~~ ~~proposed~~ in the literature, ~~aiming-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 perspective because make the HMF separation and purification steps economically onerous. Therefore, more in-depth studies should be carried out in the future, ~~in order~~ to find the best compromise between yield and concentration of HMF. ~~Finally, this review underlines that a~~ Also the heating system influences the reaction selectivity. In fact, ~~the microwave-MW~~ heating is more efficient than ~~the~~ conventional one, and it allows ~~to shorten the~~ heating time, thus reducing the energy demand and improving the HMF selectivity. However, it is well-known that the scale-up of ~~the microwave-MW~~ heating at ~~an~~ industrial scale faces some ~~unsolved issues, problems,~~ such as the ~~technological difficulty-difficulties~~ in constructing the reactor ~~in order~~ to have a geometry that allows the homogeneous ~~penetration of micro-waves-MW~~ ~~penetration~~ into the reaction medium, which implies high equipment cost. To solve ~~the latter this~~ problem, the few industrial processes that exploit ~~the microwave-MW~~ heating have preferred a continuous reactor rather than a batch one, thus reducing the volumes to be treated [1821]. This solution could be also considered ~~for the production of to produce~~ HMF from biomass, regardless of the adopted heating system. ~~In fact, u~~ 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 being produced~~ from ~~the~~ C6 fraction of biomass, and ~~being it is a valuable~~ precursor of several renewable monomers, solvents, and fuels. However, its synthesis faces several problems, such as ~~the~~ by-products formation and ~~its~~ instability, which up to now have hampered its production at ~~an~~ industrial scale. Moreover, ~~in order~~ to develop a real sustainable bio-refinery process, ~~the~~ industrial HMF production should be performed starting ~~directly~~ from biomasses ~~and not rather than~~ from model compounds, such as monosaccharides and polysaccharides, but this ~~approach-choice~~ still represents a demanding challenge. For this purpose, several works have ~~investigated-proposed~~ the HMF synthesis ~~of HMF starting~~ from different biomasses, such as food, agricultural and industrial wastes and algae, ~~ap-plying-developing~~ different strategies, in terms of ~~kind of~~ catalyst, solvent, heating system and eventually pretreatment step. All the process information reported up to now in the literature for the HMF synthesis from biomasses have been summarized and detailed described in the present review that 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 possible feasible process should involve the employment of C6 rich- biomass as ~~the~~ starting feedstock, inorganic salts as ~~the~~ catalyst, and a ~~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-~~and~~ type of pretreatment step strongly depends on the characteristics of the starting biomass and it could be

advantageous only if each biomass component is ~~then properly~~ valorized. The application of microwave heating could be interesting, but technical problems should be overcome before ~~their-its~~ adoption at ~~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 ~~in order~~ to obtain concentrated HMF streams, but a compromise with the HMF yield, which drops at elevated biomass loadings, should be found ~~in the final 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 + AlCl₃] mixture in H₂O/DMSO/acetonitrile medium, ~~results~~ 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 elevated HMF yield and concentration can be obtained, the employment of this substrate is not socially sustainable, because it is largely adopted ~~in within~~ the food supply chain. ~~Thus, in~~ conclusion, the present hot topic needs ~~of~~ further investigations ~~for the optimization of HMF production~~, where only an integrated analysis of the HMF process could surely allow ~~the to~~ better identification ~~of~~ the optimal conditions at ~~an~~ industrial scale.

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