

1 *Review*

# 2 **Direct alcoholysis of carbohydrate precursors and real** 3 **cellulosic biomasses to alkyl levulinates: A critical** 4 **review**

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10 **Abstract:** Alkyl levulinates (ALs) represent outstanding bio-fuels and strategic bio-products within  
11 the context of the marketing of levulinic acid derivatives. However, their synthesis by  
12 acid-catalyzed esterification of pure levulinic acid, or by acid-catalyzed alcoholysis of furfuryl  
13 alcohol, although relatively simple, is still economically disadvantageous, due to the high costs of  
14 the pure precursors. Direct one-pot alcoholysis of model C6 carbohydrates and raw biomass  
15 represents an alternative approach for the one-step synthesis of ALs. To promote the market for  
16 these bio-products and, concurrently, the immediate development of new applications, it is  
17 necessary to speed up the intensification of their production processes, and this important  
18 achievement is possible only by using low-cost or, even better, waste biomasses, as starting  
19 feedstocks. This review provides an overview of the most recent and promising advances on the  
20 one-pot production of ALs from model C6 carbohydrates and real biomasses, in the presence of  
21 homogeneous or heterogeneous acid catalysts. The use of model C6 carbohydrates allows the  
22 identification of the best obtainable ALs yields, resulting strategic for the development of new  
23 smart catalysts, whose chemical properties must be properly tuned, taking into account the  
24 involved reaction mechanism. On the other hand, the transition to the real biomass represents now  
25 a necessary choice for allowing the next ALs production on a larger scale. The improvement of the  
26 available synthetic strategies, the use of raw materials and the development of new applications for  
27 ALs will contribute to develop more intensified, greener and sustainable processes.

28 **Keywords:** alkyl levulinates; one-pot alcoholysis; solvothermal processes; levulinic acid; bio-fuels;  
29 process intensification.  
30

## 31 **1. Introduction**

32 Levulinic acid (4-oxopentanoic acid, gamma ketovaleric acid or 3-acetylpropionic acid) is a  
33 linear C5-alkyl carbon chain, which is considered one of the top 12 most promising chemicals  
34 derived from biomass [1-4]. Unfortunately, this platform chemical can be scarcely used for  
35 immediate uses, mainly requiring needful upgrading step(s) to obtain marketable bio-products of  
36 higher added-value, such as bio-fuel additives, fragrances, solvents, pharmaceuticals, plasticizers,  
37 and other polymers [5-7]. Therefore, the growth of the levulinic acid market needs the possibility of  
38 synthesizing its derivatives by the simplest synthetic strategies, thus preferring the development of  
39 the process intensification in the short term. Among these possible derivatives, alkyl levulinates  
40 (ALs) fully satisfy these requirements, in principle being easily synthesized by acid-catalyzed  
41 esterification of pure levulinic acid [8], according to the following reaction **reported in Figure 1:**  
42

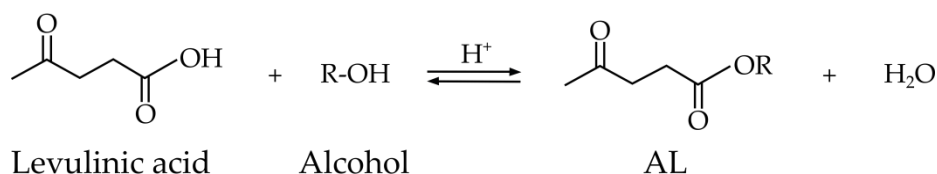


Figure 1. AL synthesis by acid-catalyzed esterification of levulinic acid.

The choice of this class of levulinic acid derivatives as starting feedstock for further up-grade is very attractive, due to the moderate reactivity of the carboxylate group, leading to remarkable advantages for the selectivity towards the final product(s) of interest. This is the reason why some levulinic acid derivatives of increasing industrial interest, such as ketals [9], alkoxy-pentanoates [10],  $\gamma$ -valerolactone, 2-methyltetrahydrofuran, valeric acid/alkyl valerates, 1,4-pentanediol, and N-substituted pyrrolidinones [11,12], are preferably produced starting from AL, rather than from levulinic acid. As an additional noteworthy advantage, esters have a lower boiling point than the corresponding carboxylic acid, thus allowing their easier and cheaper separation/purification by distillation [13]. Moreover, integrating synthesis and recovery of the ester starting from levulinic acid is a concrete possibility, achieved by reactive distillation, which improves the overall economy of the process and favors its intensification [14]. Regarding the economic evaluations, up to now, the market attention has been mainly focused on ethyl levulinate (EL) production, which is a valuable fuel-additive and a potential biomass-derived platform molecule [15], having a global market size of \$ 10.5 Million in 2019, favorably increasing up to about \$ 11.8 Million by 2022, with an estimated growth rate of 3.6% [16]. In this context, other independent economic evaluations have confirmed a promising economic outlook for the EL production [17], but only if low-cost or, even better, waste biomasses, will be used as starting feedstocks [2].

### 1.1. Reaction mechanisms

The syntheses of ALs and levulinic acid occur with similar chemistry, but the chemical structures of the reaction intermediates obtained from C6 feedstocks are different, thus expanding the possible developable applications [18-21] (Figure 2):

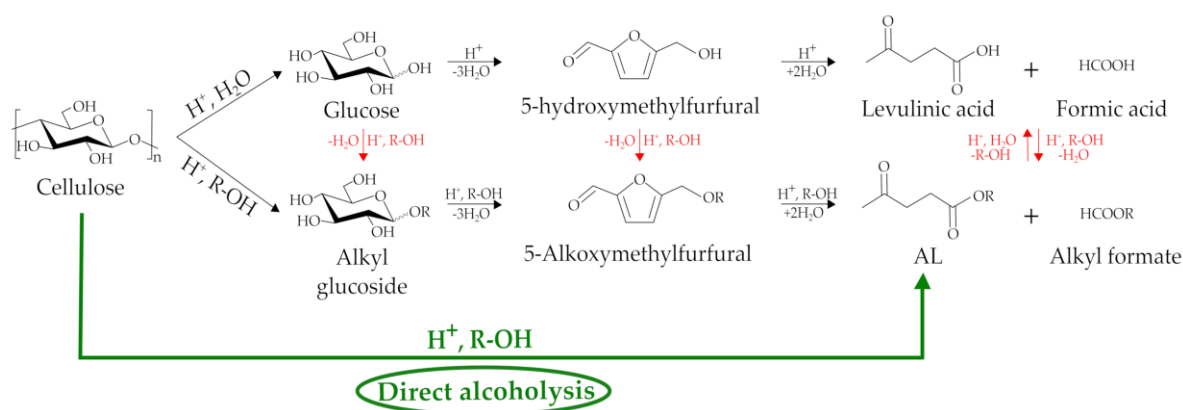
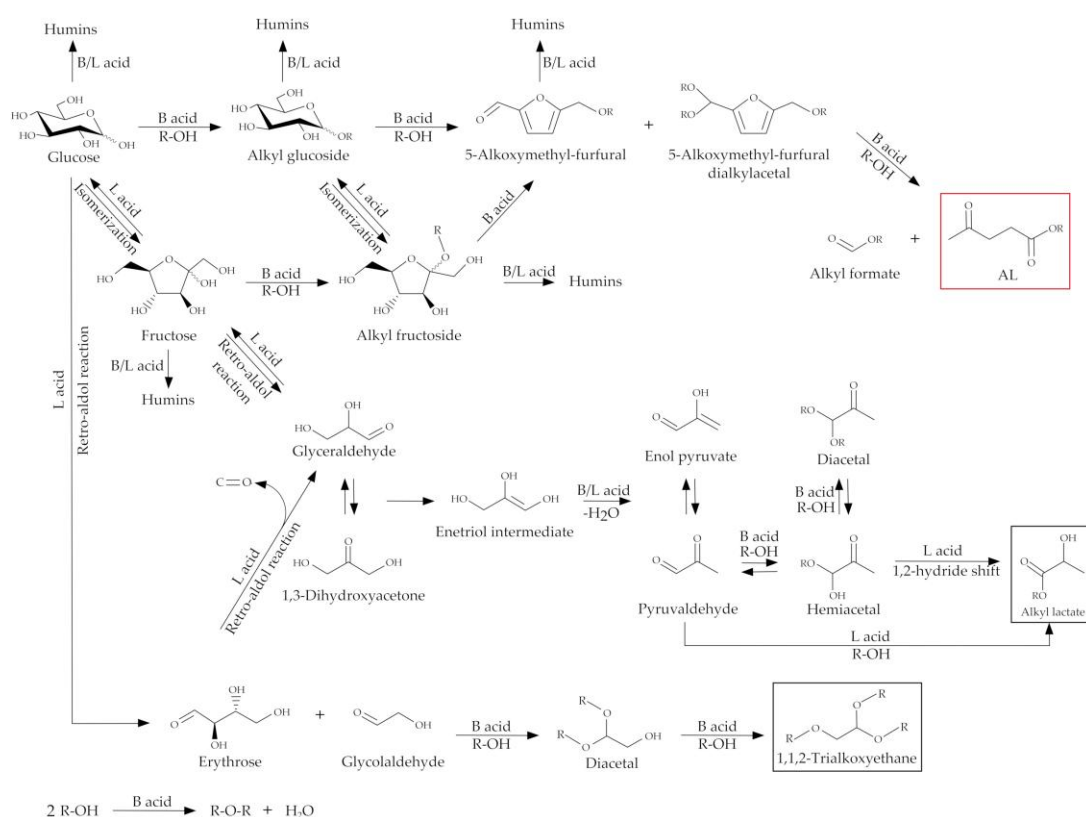


Figure 2. Comparison between the C6 routes for the production of levulinic acid and AL.

The hydrothermal process follows a series of acid-catalyzed hydrolysis/dehydration steps, *i*) hydrolysis of cellulose to glucose, *ii*) next dehydration of glucose to 5-hydroxymethylfurfural, and *iii*) hydrolysis of 5-hydroxymethylfurfural to levulinic acid. Instead, in the alcohol medium, the overall reaction occurs by *i*) cellulose alcoholysis to the alkyl glucoside, *ii*) dehydration of the alkyl glucoside to 5-alkoxy-methylfurfural, *iii*) final alcoholization of the 5-alkoxy-methylfurfural to give equimolar amounts of AL and alkyl formate [18]. However, Figure 2 also shows that the synthesis of

79 ALs can be advantageously performed starting from different reaction intermediates deriving from  
 80 the hydrothermal process, proving the good flexibility of these solvothermal processes, depending  
 81 on the market availability and the costs of the precursors. The main obstacle to the efficient use of  
 82 5-hydroxymethylfurfural for AL production is its high reactivity, which makes it prone to fast  
 83 degradation. To solve this drawback, a possible solution involves 5-chloromethylfurfural production  
 84 from C6 carbohydrates in a hydrogen chloride-saturated organic phase [22]. This furanic derivative  
 85 is more stable and hydrophobic than 5-hydroxymethylfurfural, thus allowing its quicker  
 86 simultaneous extraction into the organic phase of a biphasic system, and making its isolation easier  
 87 and more efficient. Additionally, commercial production of 5-hydroxymethylfurfural mainly  
 88 provides the use of fructose as the starting feedstock, which is more expensive than raw cellulosic  
 89 biomass, whilst the production of 5-chloromethylfurfural directly from raw biomass is more feasible  
 90 [23,24]. Based on these requirements, the choice of the real biomass as starting feedstock should be  
 91 the most appropriate for ALs production, significantly improving the process intensification, but  
 92 this goal is more difficult to achieve [25]. Starting from backward C6 precursors, and particularly  
 93 from real biomasses, the issue of the by-product formation becomes of paramount importance,  
 94 consuming carbon atoms and significantly worsening the selectivity to the desired AL, with complex  
 95 product separation and significantly increased process cost. To minimize the by-product formation,  
 96 it is necessary to properly tune the main reaction conditions and the properties of the adopted  
 97 catalysts, in particular in the specific case of the alcoholysis by C6 pathway, the Brønsted and Lewis  
 98 acidities, similarly to the corresponding hydrothermal synthesis of levulinic acid [26]. Starting from  
 99 glucose, the possible main pathways of C6 alcoholysis are reported in Figure 3, taking into account  
 100 both the Brønsted and the Lewis acidity.



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**Figure 3.** Possible pathways for the glucose alcoholysis, depending on the Brønsted (B) and Lewis (L) acidity.

The cascade conversion of C6 carbohydrates in the alcohol medium is much more complex than levulinic acid esterification, the former being carried out in the presence of a Brønsted acid or, more

107 advantageously, with bifunctional Brønsted-Lewis acid catalysts, in order to minimize the formation  
108 of reaction by-products. In this regard, according to Figure 3, C6 alcoholysis mainly involves three  
109 reaction pathways, the first one leading to the formation of the AL, the second one to that of the alkyl  
110 lactate, and the third one to that of 1,1,2-trialkoxoethane [18]. In detail, the formation of AL is mainly  
111 catalyzed by Brønsted acid sites and is further improved by the moderate presence of Lewis acid  
112 sites, which enables the glucose isomerization to fructose, together with that of the corresponding  
113 alkyl glucoside to alkyl fructoside, in this way reducing the formation of undesired by-products and  
114 shifting the reaction towards the production of the target ester [26-29]. On this basis, the balanced  
115 presence of Lewis acid sites is of paramount importance for catalyzing the aldose–ketose  
116 isomerization [30]. The subsequent Brønsted-catalysed dehydration of alkyl glucosides/fructosides  
117 leads to the formation of the 5-alkoxymethylfurfural, together with its dialkyl acetal derivative [15],  
118 which undergo ring-opening in the alcohol medium, to give the alkyl formate and the desired AL.  
119 Therefore, it is evident that Brønsted catalysts, such as traditional sulfuric or hydrochloric acid, are  
120 more effective for the fructose conversion to AL, rather than for that of glucose, which is slower [31],  
121 and that fructose should be the ideal feedstock for obtaining the highest AL yield. Instead, the  
122 reactivity of di- and poly-saccharides depends on the reactivity of their constituent monosaccharide  
123 units, up to the cellulose, which is the most complex polysaccharide to convert [15]. A proper tuning  
124 of the Brønsted-Lewis acid properties of the catalyst must take into account the interaction of the  
125 catalyst with the reaction medium, as occurs for the metal salts, which can undergo hydrolysis in the  
126 presence of the formed/added water, leading to different Brønsted-Lewis acid properties [32], which  
127 also depend on both involved cations and anions [8,33]. The main by-products deriving from the C6  
128 path are insoluble polymeric furans, named humins, deriving from acid-catalyzed condensation  
129 reactions of the reactive furanic intermediates/carbohydrate precursors [31,34]. However, their  
130 formation is particularly favored in the water medium, whilst is limited in the alcohol [35-37]. This  
131 aspect represents a remarkable advantage in favor of the alcoholysis approach. Certainly, excessive  
132 Brønsted acidity is the main reason for the humin production [38]. Therefore, considering the  
133 sulfuric acid as the catalyst of reference, to limit the humin formation, the combination of a very low  
134 acid concentration (up to 0.01 mol/L) and a higher reaction temperature, has been the preferred  
135 choice for the AL production [39]. Besides, also the use of catalysts with strong Lewis acid sites can  
136 activate the humin formation [40], thus highlighting that this side-reaction must be controlled by  
137 properly tuning the total amount of acid sites of the catalyst, the ratio of Brønsted/Lewis acid sites  
138 and their strength, as well as reaction temperature and duration. As the generation of alkyl lactate  
139 and 1,1,2-trialkoxoethane from hexoses is generally catalyzed by Lewis acids, the ratio of alkyl  
140 lactate and 1,1,2-trialkoxoethane to AL is strongly dependent on the Lewis-to-Brønsted acidity ratio  
141 of the adopted catalyst. A further side-reaction which certainly occurs is the alcohol etherification to  
142 the corresponding dialkyl ether (Figure 3) [41]. This is a well-known issue and one of the main  
143 obstacles for the development of the AL production on a greater scale, because it could cause a  
144 significant solvent loss, which cannot be recovered and recycled [42]. The addition of water as a  
145 reaction co-solvent may reduce the alcohol etherification and the coke/humin formation [32].  
146 Moreover, this side reaction can be controlled by preferring mild acid catalysis, therefore working at  
147 a very low mineral acid concentration [43], or using solid catalysts [44], thus once again highlighting  
148 the key role of catalysis in optimizing this process. However, when possible, dialkyl ether can be  
149 considered a coproduct of alcoholysis and recovered by distillation to be used for other valuable  
150 applications, in particular as bio-additives for fuels [45], thus justifying the alcohol loss.

## 151 1.2. Possible AL applications and aim of the review

153 Regarding the possible applications of ALs, in principle, they can be used as biofuels, biofuel  
154 additives, green solvents, flavoring agents, lubricants, fragrances, and polymer plasticizers [8,41].  
155 The use of short-chain ALs, in particular **methyl levulinate (ML)** and EL, as sustainable oxygenated  
156 fuel-additives, has been deeply investigated, resulting really promising for this purpose [8,41].  
157 Shrivastav *et al.* [46] blended C1-C4 ALs with conventional gasoline fuel maintaining, up to 18 mol%,  
158 density, viscosity, and compressibility within the recommended limits. The tested ALs showed good

159 octane ratings, similar C/H ratio to that of aromatics, and better local oxygen concentration than that  
160 of traditional methyl *tert*-butyl ether. The authors increased the amount of the blended AL up to 35  
161 mol%, reducing the aromatic content of gasoline. However, low-chain ALs suffer from some  
162 limitations, including a high oxygen content, good water solubility, and low-energy density. For this  
163 reason, new research trends are rather directed towards the synthesis of longer-chain ALs with  
164 higher carbon content and stronger hydrophobicity, thus improving the energy density and water  
165 insolubility. These “biodiesel-like” ALs result more appropriate as oxygenated additives for diesel  
166 blends [47-51]. However, given the more difficult synthesis of the levulinates with increasing length  
167 of the alcohol residue, only a few papers are reported for these esters, mostly synthesized starting  
168 from the more costly and pure levulinic acid, often preferring elegant catalysts, which have been  
169 synthesized *ad hoc* on the laboratory scale. To increase the development of high-volume automotive  
170 applications, it is necessary to find a compromise between the synthesis of these bio-products, which  
171 should be easily achievable, and their motor performances, which should be (at least) satisfactory.  
172 Up to now, butyl levulinate (BL) meets both these requirements, due to its feasible synthesis, even  
173 starting from real biomass, and to the related good diesel performances, also allowing a significant  
174 reduction of both CO and soot emissions [52]. In this context, Kremer *et al.* [53] have discussed in  
175 detail the engineering aspects related to the motor applications of this levulinate, also positively  
176 re-evaluating those of the di-*n*-butyl ether. This last compound, which is obtained as the main  
177 by-product from the same alcoholysis process, can be used, in addition to a pure diesel alternative,  
178 as an ignition enhancer for low-cetane biofuels, due to its high self-ignitability (Cetane Number=100)  
179 [53].

180 In principle, alcoholysis can be applied as mild biomass pre-treatment, in a biorefinery  
181 perspective, such as for the selective depolymerization/liquefaction of its components, e.g. cellulose,  
182 hemicellulose, and lignin, which can be effectively fractionated and converted into valuable  
183 bioproducts, such as alkyl glucosides/xylosides and soluble aromatics [54-56], to be used for niche  
184 added-value applications. In particular, the use of long-chain alkyl glucosides as bio-surfactants has  
185 been widely demonstrated, showing remarkable advantages of performance, biodegradability,  
186 low-toxicity and environmental compatibility [57,58]. On the other hand, alcoholysis enables also the  
187 breakdown of ether linkages of lignin, to give smaller aromatics [21,59], which can be isolated and  
188 further functionalized to obtain more value-added products, such as polymer building  
189 blocks/pharmaceuticals, or defunctionalized to simpler *drop-in* molecules (BTX, phenol, catechol,  
190 and cyclohexane), which have a large market potential [60].

191 This review provides an overview of the most recent and promising advances on the one-pot  
192 production of ALs by alcoholysis of both model C6 carbohydrates and real cellulosic biomasses, in  
193 the presence of homogeneous or heterogeneous catalysts. In the following discussion, firstly model  
194 C6 carbohydrates of progressively increasing complexity will be considered, in order to identify and  
195 discuss the drawbacks and the best solutions for the ALs production, then the attention will be  
196 focused on the conversion of real cellulosic biomasses. Up to now, the choice of real biomass  
197 feedstocks has not been properly emphasized in the literature, whilst it is particularly attractive and  
198 strategic to promote the development/intensification of this process, and it should be preferred, as  
199 well as the one-pot cascade approach, occurring without separation/purification of the reaction  
200 intermediates [61]. Other practical aspects, such as the strategic use of high feedstock loadings and  
201 diluted acids, will be specifically considered, because of the related environmental and economic  
202 concerns, of greater industrial relevance [52,62-64]. Furthermore, the issue of the catalyst  
203 heterogenization, which is highly desired already for the levulinic acid process [65], but industrially  
204 still unsolved, will be considered also for the production of ALs, in this last case being (theoretically)  
205 simpler for model and pure feedstocks, thanks to their better mass transfer with the catalyst and the  
206 reduced formation of humin by-products [44]. Anyway, the presence of the lignin component in the  
207 real biomasses makes more difficult their conversion, which is the reason why these feedstocks have  
208 not been adequately exploited in most catalytic approaches [8,21].

209 To make easier the comparison among the different available data, AL yield from model C6  
210 carbohydrates has been calculated on a molar basis, according to formula (1), this basis of calculation

211 being more useful for academic evaluations. Instead, AL yield from real biomasses was calculated  
 212 respect to the weight of the dry biomasses, according to formula (2), which is of greater practical  
 213 utility in the industrial field.

214

215 AL yield from C6 model compound ( $Y_{AL}$ ) mol% = [AL recovered (mol)/C6 units (mol)] $\times$ 100 (1)

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217 AL yield from real biomass ( $Y_{AL}$ ) wt% = [AL recovered (g)/dry biomass (g)] $\times$ 100 (2)

## 218 2. AL synthesis from model compounds

219 In the following paragraphs the state of the art regarding the synthesis of ALs from C6 model  
 220 compounds of different complexity will be discussed, taking into account the most promising  
 221 available data reached with both homogeneous and heterogeneous catalysts. For a clearer  
 222 discussion, ALs will be considered separately, methyl levulinate (ML), ethyl levulinate (EL), propyl  
 223 levulinate (PL), butyl levulinate (BL), pentyl levulinate (PeL) and hexyl levulinate (HL).

224

### 225 2.1 ML synthesis from model carbohydrates

226 Available data for ML synthesis from C6 model carbohydrates with inorganic mineral acids or  
 227 metal salts are summarized in Table 1:

228 **Table 1.** Inorganic mineral acids or metal salts for the ML production from C6 model carbohydrates.

Entry	Feedstock	Catalyst	Cat.(g)/MeOH (g) <sup>1</sup>	T (°C)	t (h)	Heat <sup>2</sup>	Y <sub>ML</sub> (mol%)	Ref.
ML_1	Fructose	H <sub>2</sub> SO <sub>4</sub> (100 wt%)	0.2/15.8	200	2	Conv.	85	[66]
ML_2	Fructose	H <sub>2</sub> SO <sub>4</sub> (96 wt%)	0.2/5.0	160	0.5	MW	90	[67]
ML_3	Fructose	H <sub>2</sub> SO <sub>4</sub> (96 wt%)	0.3/8.0	160	0.67	MW	93	[68]
ML_4	Glucose	H <sub>2</sub> SO <sub>4</sub> (96 wt%)	0.2/5.0	160	1	MW	70	[67]
ML_5	Glucose	H <sub>2</sub> SO <sub>4</sub> (96 wt%)	0.3/8.0	160	0.67	MW	72	[68]
ML_6	Cellulose	H <sub>2</sub> SO <sub>4</sub> (100 wt%)	0.2/6.9	179	0.25	Conv.	31	[69]
ML_7	Cellulose	H <sub>2</sub> SO <sub>4</sub> (100 wt%)	0.2/3.4 <sup>3</sup>	194	0.083	Conv.	45	[69]
ML_8	Cellulose	H <sub>2</sub> SO <sub>4</sub> (100 wt%)	0.1/39.6	210	2	Conv.	50	[70]
ML_9	Cellulose	H <sub>2</sub> SO <sub>4</sub> (100 wt%)	0.1/39.5	190	4.2	Conv.	55	[71]
ML_10	Cellulose	H <sub>2</sub> SO <sub>4</sub> (100 wt%)	0.2/39.5	180	4	Conv.	42	[71]
ML_11	Cellulose	H <sub>2</sub> SO <sub>4</sub> (96 wt%)	0.3/8.0	180	0.67	MW	46	[68]
ML_12	Cellulose	H <sub>2</sub> SO <sub>4</sub> (96 wt%)	0.2/5.0	160	1	MW	70	[67]
ML_13	Fructose	HReO <sub>4</sub>	0.1/22.2	160	16	Conv.	76	[72]
ML_14	Fructose	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	2.2/9.0	170	2	Conv.	25	[73]
ML_15	Glucose	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	2.2/9.0	170	2	Conv.	26	[73]
ML_16	Glucose	La <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	3.2/9.0	170	2	Conv.	30	[73]
ML_17	Glucose	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.8/15.8	200	2	Conv.	43	[66]
ML_18	Glucose	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.7/15.8	200	2	Conv.	54	[66]
ML_19	Fructose	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.6/29.8	160	1	MW	70	[67]
ML_20	Glucose	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.6/29.8	160	1	MW	70	[67]
ML_21	Cellulose	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.6/29.8	160	1	MW	20	[67]
ML_22	Cellulose	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.6/29.8	160	4	MW	49	[67]
ML_23	Cellulose	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.6/29.8	180	1	MW	61	[67]
ML_24	Glucose	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.4/35.0	160	2.5	Conv.	64	[29]
ML_25	Sucrose	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.4/35.0	160	2.5	Conv.	55	[29]
ML_26	Cellulose	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.4/35.0	180	5	Conv.	44	[29]
ML_27	Sucrose	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.4/22.4 <sup>4</sup>	180	0.25	MW	83	[32]
ML_28	Cellulose	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.4/22.4 <sup>4</sup>	170	1	MW	44	[32]

ML_29	Cellulose	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.4/22.4 <sup>4</sup>	180	0.67	MW	71	[32]
ML_30	BM-cellulose <sup>5</sup>	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.6/29.8	160	1	MW	58	[74]
ML_31	BM-cellulose <sup>5</sup>	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.6/29.8	170	0.75	MW	65	[74]
ML_32	Cellulose <sup>6</sup>	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·18H <sub>2</sub> O	0.6/35.0	180	3	Conv.	52	[75]

229 <sup>1</sup> The amounts of catalyst and MeOH have been normalized to 1g of feedstock.

230 <sup>2</sup> “Conv.” and “MW” stand for “Conventional” and “Microwave”, respectively.

231 <sup>3</sup> 6.9 g of CCl<sub>4</sub> were added to this reaction mixture.

232 <sup>4</sup> 1.2 g of water were added to this reaction mixture.

233 <sup>5</sup> “BM” stands for “Ball-Milled”.

234 <sup>6</sup> Cellulose (2.0g) was pre-oxidized at 200 °C for 10 h under O<sub>2</sub> flow (50 mL min<sup>-1</sup>) before the alcoholysis.

235

236 Sulfuric acid has been widely employed as a homogeneous Brønsted acid catalyst for the  
 237 methanolysis of C6 model feedstocks, thanks to its excellent compromise between high activity and  
 238 low-cost. Higher ML molar yields were achieved starting from fructose (runs ML\_1–ML\_3, Table  
 239 1), rather than from glucose (runs ML\_4–ML\_5, Table 1), due to the simpler conversion of the first  
 240 feedstock which, contrarily to the glucose, does not need of the Lewis acid catalysis. The use of  
 241 sulfuric acid for the one-step alcoholysis of model cellulose was proposed for the first time by  
 242 Garves [69], who reported good ML yields, working under subcritical conditions (runs  
 243 ML\_6–ML\_7, Table 1). However, sulfuric acid is also an excellent catalyst for alcohol etherification,  
 244 which may cause a progressive and significant consumption of the solvent/reactant. To solve this  
 245 issue, etherification must be controlled and limited as much as possible, in particular by minimizing  
 246 the acid concentration, a process solution that also improves the environmental sustainability and  
 247 reduces the plant costs of the alcoholysis process. This aspect was investigated more in-depth by  
 248 Peng *et al.* [43] for the glucose alcoholysis at 200 °C, in the presence of two different H<sub>2</sub>SO<sub>4</sub>  
 249 concentrations (0.1 and 0.005 mol/L). The authors found that methanol conversion to dimethyl ether,  
 250 after 2.5 h and in the presence of 0.1 mol/L of H<sub>2</sub>SO<sub>4</sub>, was remarkable (about 59 mol%), whilst it  
 251 strongly decreased (to about 2 mol%), if the use of diluted H<sub>2</sub>SO<sub>4</sub> was preferred. More recently, the  
 252 use of very dilute sulfuric acid (≤0.01 mol/L) has been rightly preferred by Li *et al.* [70], reporting  
 253 similar ML yields (about 50 mol%), only extending the reaction time (run ML\_8, Table 1). Besides,  
 254 the authors also discussed the possible ML recovery, combining atmospheric and vacuum  
 255 distillation, using *n*-dodecane for improving the separation of the heavy fraction (ML) from the light  
 256 one (MeOH). Wu *et al.* [71] achieved similar ML yields, always preferring a very low sulfuric acid  
 257 concentration (≤0.04 mol/L), and by properly optimizing reaction temperature and time (runs  
 258 ML\_9–ML\_10, Table 1). Besides, the authors compared the catalytic performances of sulfuric acid  
 259 with those of other common Brønsted acids, such as phosphoric, formic, and acetic acids, working at  
 260 the same molar concentration (0.04 mol/L). The higher catalytic activity of the sulfuric acid over  
 261 phosphoric acid was attributed the stronger acidity of the former [76], whilst organic acids, such as  
 262 formic and acetic ones, were not efficient for catalyzing this reaction, due to their unwanted  
 263 esterification, occurring under the typical reaction conditions required for ML production [77]. The  
 264 use of MW as an efficient heating system is better exploitable if applied to the conversion of more  
 265 recalcitrant substrates, such as cellulose, achieving better ML yields respect to the conventional  
 266 heating systems and reduced formation of the reaction by-products, mainly humins. In this context,  
 267 the best ML yields achieved by Feng *et al.* [68] and Chen *et al.* [67] (runs ML\_11–ML\_12, Table 1),  
 268 fully support these premises, highlighting that such efficient heating allows the use of milder  
 269 reaction conditions (temperature and time) than conventional heating systems. Up to now, the  
 270 highest ML yield from model cellulose was reported by Chen *et al.* [67] (run ML\_12, Table 1),  
 271 amounting to 70 mol%, which is the best value to consider as reference for the development of new  
 272 efficient catalysts. The innovation of the catalytic system is a very hot topic and many alternatives  
 273 have been already evaluated. Perrhenic acid (HReO<sub>4</sub>) is just an example, but certainly, this is not the  
 274 simplest and cheapest catalyst to propose as an alternative to the sulfuric acid. Its good efficiency  
 275 towards fructose methanolysis has been recently demonstrated by Bernardo *et al.* (run ML\_13, Table  
 276 1) [72], but its real use on a greater scale is not sustainable and competitive with that of the sulfuric

277 acid. Despite the high activity of sulfuric acid, separation and corrosion issues hinder its use,  
278 especially at high concentrations, thus the research is moving towards the use of other kinds of  
279 catalysts, in particular inorganic salts. In this context, cheap metal sulfates ( $\text{Na}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{MnSO}_4$ ,  
280  $\text{CoSO}_4$ ,  $\text{NiSO}_4$ ,  $\text{ZnSO}_4$ ,  $\text{CuSO}_4$ ,  $\text{Fe}_2(\text{SO}_4)_3$ ,  $\text{La}_2(\text{SO}_4)_3$  and  $\text{Ce}(\text{SO}_4)_2$ ) have been recently tested by Sun *et al.* [73] for the solvothermal conversion of glucose and fructose, evaluating different reaction media,  
281 including MeOH. As a general consideration, the metal salts provides both Lewis acid sites (due to  
282 the unsaturated metal center) and Brønsted acid ones (due to the hydrolysis/methanolysis of the  
283 salt), which catalyze the isomerization of glucose to fructose, and the dehydration of fructose to ML,  
284 respectively, whilst sulfate anions generally have a positive role towards this reaction, strongly  
285 chelating with the carbohydrates, thus preventing the formation of unwanted by-products, such as  
286 humins [73]. Among the tested metal sulfates,  $\text{Fe}_2(\text{SO}_4)_3$  and  $\text{La}_2(\text{SO}_4)_3$  gave the highest ML molar  
287 yields at 170 °C, in the range 25–30 mol% (runs ML\_14–ML\_16, Table 1), preferring the cheaper  
288  $\text{Fe}_2(\text{SO}_4)_3$ , which suppressed the humin formation. However, despite this catalyst seems interesting  
289 for ML synthesis, the reported ML yields from glucose and fructose are too low, especially if  
290 compared with the traditional sulfuric acid. A possible solution to improve the catalysis in the  
291 presence of metal salts provides the additional use of modest quantities of sulfuric acid, which  
292 favors the Brønsted acid-catalyzed steps. The catalytic effect of various metal sulfates was  
293 investigated by Peng *et al.* [66], who confirmed a significant effect of these salts on the reaction  
294 selectivity. In particular,  $\text{K}_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4$  were particularly effective for stabilizing the methyl  
295 glucoside intermediate, suppressing its further transformation, and minimizing the humin  
296 formation. Instead,  $\text{Fe}_2(\text{SO}_4)_3$  and  $\text{Al}_2(\text{SO}_4)_3$ , gave the highest ML yields (runs ML\_17–ML\_18, Table  
297 1), but favored also the formation of humins and dimethyl ether by-products. However, the  
298 formation of these by-products (in particular dimethyl ether) was significant also in the sole  
299 presence of these two metal sulfates, being the conversion of methanol to dimethyl ether equal to 19  
300 and 23 mol%, adopting  $\text{Fe}_2(\text{SO}_4)_3$  and  $\text{Al}_2(\text{SO}_4)_3$ , respectively, highlighting the importance of further  
301 optimizing the alcoholysis reaction with these more active catalytic systems [66]. The optimization of  
302 the alcoholysis of different C6 model substrates in the presence of  $\text{Al}_2(\text{SO}_4)_3$  was investigated more  
303 in-depth (runs ML\_19–ML\_32, Table 1) [29,32,67,74,75]. The addition of water reduces humin/coke  
304 formation and solvent consumption (runs ML\_28–ML\_29, Table 1) [32]. The Lewis acid species  
305  $[\text{Al}(\text{OH})_x(\text{H}_2\text{O})_y]^{n+}$  and Brønsted acid species  $\text{H}^+$ , generated by in-situ hydrolysis of  $\text{Al}_2(\text{SO}_4)_3$ , were  
306 responsible for the improved catalytic performances. The amount of water in MeOH could affect the  
307 equilibrium of metal salt hydrolysis, as well as the acid density of the reaction mixture, which would  
308 affect the salt reactivity towards cellulose conversion and the related product distribution. In  
309 particular, the addition of water significantly inhibited the etherification reaction of MeOH to  
310 dimethyl ether, which was unavoidable in the presence of Brønsted acidic catalysts at elevated  
311 temperatures. When no water was added, the dimethyl ether yield was about 20 mol%, whilst it  
312 decreased below 5 mol% by adding a low amount of water (0.6 mL). Moreover, water addition  
313 improved the cellulose solvolysis, moving the reaction towards the hydrolysis of the glycosidic C-O  
314 bonds, rather than to its thermal decomposition to coke, whose yield was reduced from about 40  
315 wt%, in the absence of water, to about 10 wt%, when the water content was over 0.6 mL. The  
316 combined use of ( $\text{Al}_2(\text{SO}_4)_3 + \text{H}_2\text{O}$ ), together with MW heating as the efficient heating system, and  
317 milder reaction conditions, allowed the improvement of the ML yield from model cellulose up to a  
318 maximum of about 70 mol% (run ML\_29, Table 1), a value similar to that reached with the  
319 traditional sulfuric acid. Similar results were obtained under conventional heating, but employing  
320 longer reaction times (run ML\_24, Table 1) [29], while harsher reaction conditions resulted  
321 detrimental for ML production (run ML\_26, Table 1). Some improvements have been recently  
322 proposed for enhancing the ML yield, always in the presence of  $\text{Al}_2(\text{SO}_4)_3$  as the main catalytic  
323 system. Chen *et al.* [74] performed a ball-milling pretreatment on the cellulose feedstock, for  
324 reducing its particle size and crystallinity index, thus improving the catalyst accessibility during the  
325 alcoholysis step. Anyway, this pre-treatment did not lead to significant improvements in ML yield,  
326 which reached the maximum value of about 65 mol%, working at 170 °C and for 45 min, under MW  
327 heating (runs ML\_30–ML\_32, Table 1). Very recently, an oxidation pretreatment has been  
328



329 considered for improving ML production from cellulose, aimed at the conversion of its  
 330 hydroxymethyl groups into carboxylic ones, thus providing the Brønsted acid sites for improving  
 331 the catalysis related to the steps of interest [75]. However, by adopting this interesting approach, the  
 332 maximum ML yield was only 52 mol%, working at 180 °C for 3 h (run ML\_32, Table 1), highlighting  
 333 that, up to now, this pre-treatment is not very functional for this purpose.

334 Sulfonic acids or/and sulfonate salts or resins have been investigated for the ML production  
 335 from C6 model carbohydrates, and the best available data are summarized in Table 2:

336 **Table 2.** Sulfonic acids, sulfonate salts, and their combinations for the ML production from C6 model  
 337 carbohydrates, under conventional heating.

Entry	Feedstock	Catalyst	Cat.(g)/MeOH(g) <sup>1</sup>	T (°C)	t (h)	Y <sub>ML</sub> (mol%)	Ref.
ML_33	Cellulose	PTSA <sup>2</sup>	0.05/39.5	180	5	20	[27]
ML_34	Cellulose	PTSA <sup>2</sup>	0.12/6.9	210	0.5	34	[69]
ML_35	Cellulose	PTSA <sup>2</sup>	0.35/39.5	180	4	46	[71]
ML_36	Cellulose	In(OTf) <sub>3</sub>	0.03/39.5	180	5	52	[27]
ML_37	Cellulose	PTSA <sup>2</sup> + In(OTf) <sub>3</sub>	0.05+0.03/39.5	180	5	70	[27]
ML_38	Cellulose	2-NSA <sup>3</sup> + In(OTf) <sub>3</sub>	0.05+0.03/39.5	180	5	75	[27]
ML_39	Glucose	BSA <sup>4</sup> + In(OTf) <sub>3</sub>	n.a. <sup>5</sup>	180	5	70	[78]
ML_40	Mannose	BSA <sup>4</sup> + In(OTf) <sub>3</sub>	n.a. <sup>5</sup>	180	5	76	[78]
ML_41	Galactose	BSA <sup>4</sup> + In(OTf) <sub>3</sub>	n.a. <sup>5</sup>	180	5	70	[78]
ML_42	Cellulose	PTSA <sup>2</sup> + Al(OEt) <sub>3</sub>	0.08+0.01/39.5	180	5	69	[79]
ML_43	Cellulose	PTSA <sup>2</sup> + Al(acac) <sub>3</sub>	0.08+0.02/39.5	180	5	72	[79]
ML_44	Cellulose	2-NSA <sup>3</sup> + Al(OH) <sub>3</sub>	0.10+0.01/39.5	180	5	74	[79]
ML_45	Fructose	Amberlyst-15	0.40/64.0	100	24	54	[80]
ML_46	Fructose	Amberlyst 15	0.28/48.3	170	15	68	[81]
ML_47	Glucose	Amberlyst 15	0.27/32.4	160	5	12	[82]
ML_48	Glucose	Amberlyst 15	0.54/32.4	160	5	75	[83]
ML_49	Fructose	Nafion NR50	0.28/48.3	170	15	73	[81]
ML_50	Fructose	PD-En-SO <sub>3</sub> H <sup>6</sup>	0.28/48.3	170	15	78	[81]
ML_51	Fructose	PSSA-g-CNT <sup>7</sup>	0.40/64.0	100	24	69	[80]
ML_52	Fructose	PSSA-g-CNF <sup>8</sup>	0.40/64.0	100	24	53	[80]
ML_53	Fructose	BSA-g-CMK-5 <sup>9</sup>	0.40/64.0	100	24	49	[80]
ML_54	Fructose	BSA-g-CNT <sup>10</sup>	0.40/64.0	100	24	12	[80]
ML_55	Fructose	5-Cl-SHPAO <sup>11</sup>	0.25/20.0	160	1	79	[84]
ML_56	Glucose	5-Cl-SHPAO <sup>11</sup>	0.25/20.0	160	12	60	[84]
ML_57	Inulin	5-Cl-SHPAO <sup>11</sup>	0.25/20.0	160	8	71	[84]
ML_58	Cellulose	Sulfonated char	0.50/31.6	200	1.25	30	[85]
ML_59	Cellulose	Sulfonated char	0.50/31.6	225	0.75	30	[85]

338 <sup>1</sup> The amounts of catalysts and MeOH have been normalized to 1g of feedstock.

339 <sup>2</sup> "PTSA" stands for "*p*-toluenesulfonic acid".

340 <sup>3</sup> "2-NSA" stands for "2-naphthalenesulfonic acid".

341 <sup>4</sup> "BSA" stands for "benzenesulfonic acid".

342 <sup>5</sup> "n.a." stands for "not-available".

343 <sup>6</sup> "PD-En-SO<sub>3</sub>H" stands for "sulfonic acid-grafted ethylenediamine-functionalized mesoporous polydivinylbenzene".

344 <sup>7</sup> "PSSA-g-CNT" stands for "poly(*p*-styrenesulfonic acid)-grafted carbon nanotubes".

345 <sup>8</sup> "PSSA-g-CNF" stands for "poly(*p*-styrenesulfonic acid)-grafted carbon nanofibers".

346 <sup>9</sup> "BSA-g-CMK-5" stands for "benzenesulfonic acid-grafted carbon mesostructured by KAIST-5".

347 <sup>10</sup> "BSA-g-CNT" stands for "benzenesulfonic acid-grafted carbon nanotubes".

348

349 <sup>11</sup> “5-Cl-SHPAO” stands for “sulfonated hyperbranched poly(arylene oxindole) with chloride substituent in the  
350 fifth position of isatin”.

351

352 *p*-Toluenesulfonic acid (PTSA) has been proposed for a long time as a reference Brønsted acid  
353 catalyst for studying the cellulose alcoholysis (runs ML\_33–ML\_35, Table 2), as an effective  
354 alternative to the already discussed sulfuric acid, achieving similar maximum ML yield (about 50  
355 mol%). Although single catalysts have been widely used for this reaction, achieving good results,  
356 recent catalytic studies are rather oriented towards the appropriate tuning of the Brønsted-Lewis  
357 acidity, generally achieved in the presence of binary catalysts. Therefore, as previously observed,  
358 Lewis acids have been used to improve the ML yield, both alone or in combination with small  
359 amounts of sulfonic acids, as Brønsted acids. In this context, In(OTf)<sub>3</sub> has been proposed by  
360 Tominaga *et al.* [27] as an efficient Lewis acid for the cellulose alcoholysis, both alone and in  
361 combination with PTSA or 2-naphthalenesulfonic acid (2-NSA), as active Brønsted acids (runs  
362 ML\_36–ML\_38, Table 2). The sole In(OTf)<sub>3</sub> showed catalytic performances similar to those of PTSA,  
363 whilst the ML yield increased up to 70-75 mol%, when In(OTf)<sub>3</sub> and PTSA or 2-NSA were used in  
364 combination. The adopted catalytic system resulted stable and recyclable, being recovered as a  
365 residue after the distillation of the solvent/products. Similar promising results were obtained by  
366 Nemoto *et al.* [78] with simpler feedstocks, such as glucose, mannose, or galactose, highlighting a  
367 similar reactivity of these carbohydrates (runs ML\_39–ML\_41, Table 2). In a more recent work of  
368 Tominaga *et al.* [79], binary catalytic systems composed of aluminum compounds (Al(OEt)<sub>3</sub>,  
369 Al(acac)<sub>3</sub>, or Al(OH)<sub>3</sub>) and organic sulfonic acids (PTSA or 2-NSA), were found to be particularly  
370 efficient for direct ML synthesis from microcrystalline cellulose (runs ML\_42–ML\_44, Table 2),  
371 achieving maximum ML yields similar to those of the best triflate-based catalytic systems (runs  
372 ML\_37–ML\_38, Table 2). Amberlyst 15 and Nafion NR50 have been considered mainly as catalysts  
373 of reference, for justifying the development of new heterogeneous catalysts, despite the available  
374 data are limited to the conversion soluble C6 carbohydrates (runs ML\_45–ML\_49, Table 2). A novel  
375 and efficient sulfonic acid-grafted ethylenediamine-functionalized mesoporous polydivinylbenzene  
376 (PD-En-SO<sub>3</sub>H) heterogeneous catalyst was synthesized by Pan *et al.* [81]. PD-En-SO<sub>3</sub>H showed  
377 excellent catalytic performances for the conversion of fructose to ML, being more active than  
378 commercial Amberlyst 15 and Nafion NR50 (compare run ML\_50 with runs ML\_46 and ML\_49,  
379 Table 2). Moreover, this new catalyst could be reused for four times, maintaining unaltered its high  
380 catalytic activity. A series of sulfonic acid-functionalized carbon materials, including  
381 poly(*p*-styrenesulfonic acid)-grafted carbon nanotubes (PSSA-g-CNT), poly(*p*-styrenesulfonic  
382 acid)-grafted carbon nanofibers (PSSA-g-CNF), benzenesulfonic acid-grafted CMK-5  
383 (BSA-g-CMK-5), and benzenesulfonic acid-grafted carbon nanotubes (BSA-g-CNT), have been  
384 applied for fructose conversion to ML (runs ML\_51–ML\_54, Table 2) [80]. The catalytic activities of  
385 these sulfonic acid-functionalized carbon materials, applied to the conversion of fructose to ML,  
386 follow the order of their acid strength and PSSA-g-CNT exhibited the highest acid density and the  
387 best catalytic performances to ML (maximum yield of 69 mol%). The authors claimed the high  
388 thermal stability and ease of recovery of these catalysts. Sulfonated hyperbranched poly(arylene  
389 oxindole)s (SHPAOs) were also used for the conversion of simple monosaccharides and inulin to  
390 ML, with high yields up to 79 mol% (runs ML\_55–ML\_57, Table 2) [84]. Due to the soluble character  
391 of the hyperbranched catalyst in the alcoholic solvent, it was easily separated from the solid humins,  
392 and recovered from the solution over a commercial low molecular weight cut-off filter. Moreover,  
393 the recovered catalyst showed in a recycle run a comparable catalytic activity (per catalyst weight)  
394 and product selectivity. To exploit more sustainable carbon bio-materials, an amorphous  
395 carbon-based catalyst was prepared by sulfonation of the bio-char obtained from fast pyrolysis (N<sub>2</sub>  
396 atm; 550 °C) of *jatropha curcas* de-oiled seed cake and tested for the cellulose methanolysis, reaching a  
397 maximum ML yield of 30 mol% (runs ML\_58–ML\_59, Table 2) [85]. The authors demonstrated that  
398 this functionalized carbon catalyst was stable for five cycles with a slight loss in catalytic activity.

399 Heteropolycompounds, or heteropolyoxometalates (POMs), consist of metal oxide clusters of  
400 early transition metals [86]. These could be heteropolyacids (HPAs) or their salts, containing one  
401 heteroatom (X = P(V), As(V), Si(IV), and B(III)) and addenda atoms (M = W(VI), Mo(VI), and V(V)).

402 The main heteropolyanion used in the field of biomass conversion is the Keggin structure  
 403 ( $\text{XM}_{12}\text{O}_{40}^{n-}$ ), but also catalysts with Wells-Dawson structure ( $\text{X}_2\text{M}_{18}\text{O}_{62}^{m-}$ ) have found applications  
 404 [87]. These catalysts are widely used in acid-catalyzed and oxidation reactions, with economic and  
 405 green benefits, but generally exhibit poor efficiency in their bulk form, due to a limited number of  
 406 exposed active sites [88]. HPAs are usually soluble in aqueous and organic solvents, making difficult  
 407 their separation/regeneration from the reaction mixture and, for this reason, many attempts for their  
 408 heterogenization have been made by immobilization on support or by the formation of an insoluble  
 409 ionic material [86]. The use of these catalysts has been proposed also for the ML production, and the  
 410 most interesting available data are summarized in Table 3:

411 **Table 3.** Polyoxometalate (POM)-based catalysts for the ML production from C6 model  
 412 carbohydrates.

Entry	Feedstock	Catalyst	Cat.(g)/MeOH(g) <sup>1</sup>	T (°C)	t (h)	Heat <sup>2</sup>	Y <sub>ML</sub> (mol%)	Ref.
ML_60	Fructose	H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	0.6/32.0	130	2	Conv.	60	[89]
ML_61	Cellulose	H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	2.0/63.0	160	5	Conv.	42	[90]
ML_62	Cellulose	H <sub>6</sub> P <sub>2</sub> W <sub>18</sub> O <sub>62</sub>	3.1/63.0	160	5	Conv.	52	[90]
ML_63	Cellulose	H <sub>4</sub> SiW <sub>12</sub> O <sub>40</sub>	0.1/31.6	195	1	Conv.	12	[91]
ML_64	Sucrose	H <sub>5</sub> PW <sub>11</sub> TiO <sub>40</sub>	1.5/42.0	100	5	Conv.	58	[92]
ML_65	Cellobiose	H <sub>5</sub> PW <sub>11</sub> TiO <sub>40</sub>	1.5/42.0	120	5	Conv.	51	[92]
ML_66	Starch	H <sub>5</sub> PW <sub>11</sub> TiO <sub>40</sub>	1.5/42.0	130	5	Conv.	47	[92]
ML_67	Cellulose	H <sub>5</sub> PW <sub>11</sub> TiO <sub>40</sub>	1.5/42.0	160	7	Conv.	51	[92]
ML_68	Cellulose	H <sub>5</sub> PW <sub>11</sub> TiO <sub>40</sub>	1.5/42.0	160	2	MW	63	[92]
ML_69	Fructose	FePW <sub>12</sub> O <sub>40</sub>	0.6/32.0	130	2	Conv.	74	[89]
ML_70	Glucose	FePW <sub>12</sub> O <sub>40</sub>	0.6/32.0	130	2	Conv.	14	[89]
ML_71	Sucrose	FePW <sub>12</sub> O <sub>40</sub>	0.6/32.0	130	2	Conv.	44	[89]
ML_72	Inulin	FePW <sub>12</sub> O <sub>40</sub>	0.6/32.0	130	2	Conv.	92	[89]
ML_73	Cellulose	FePW <sub>12</sub> O <sub>40</sub>	0.6/32.0	220	2	Conv.	14	[89]
ML_74	Fructose	Sn <sub>2</sub> SiW <sub>12</sub> O <sub>40</sub>	1.7/65.8	150	3	Conv.	57	[93]
ML_75	Fructose	AlPW <sub>12</sub> O <sub>40</sub>	0.6/7.5	160	0.5	MW	70	[94]
ML_76	Glucose	AlPW <sub>12</sub> O <sub>40</sub>	0.6/7.5	160	0.5	MW	64	[94]
ML_77	Sucrose	AlPW <sub>12</sub> O <sub>40</sub>	0.6/7.5	160	0.5	MW	65	[94]
ML_78	Cellulose	AlPW <sub>12</sub> O <sub>40</sub>	0.6/7.5	160	0.5	MW	45	[94]
ML_79	Cellulose	Cs <sub>2.5</sub> H <sub>0.5</sub> PW <sub>12</sub> O <sub>40</sub>	0.4/71.4	300	0.02	Conv.	20	[95]
ML_80	Fructose	[TMEDAPS] <sub>3</sub> [PW <sub>12</sub> O <sub>40</sub> ] <sub>2</sub> <sup>3</sup>	1.0/64.0	120	12	Conv.	80	[96]
ML_81	Sucrose	[PyPS] <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> <sup>4</sup>	5.0/46.5	150	4.5	Conv.	76	[97]
ML_82	Glucose	[PyPS] <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> <sup>4</sup>	9.4/87.8	150	4	Conv.	59	[97]
ML_83	Starch	[PyPS] <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> <sup>4</sup>	10.6/98.8	150	5	Conv.	51	[97]
ML_84	Cellulose	[PyPS] <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> <sup>4</sup>	10.6/98.8	150	5	Conv.	71	[97]
ML_85	Cellulose	[C16TA]H <sub>5</sub> P <sub>2</sub> W <sub>18</sub> O <sub>62</sub> <sup>5</sup>	3.3/63.0	160	7	Conv.	58	[90]
ML_86	Fructose	3-FPyPW <sup>6</sup>	0.5/22.2	120	10	Conv.	82	[98]
ML_87	Fructose	3-PhPyPW <sup>7</sup>	0.5/22.2	140	8	Conv.	71	[99]
ML_88	Fructose	Cs <sub>10.6</sub> [H <sub>2.4</sub> GeNb <sub>13</sub> O <sub>41</sub> ]	1.3/48.0	130	3	Conv.	53	[100]
ML_89	Glucose	Cs <sub>10.6</sub> [H <sub>2.4</sub> GeNb <sub>13</sub> O <sub>41</sub> ]	1.3/48.0	130	3	Conv.	85	[100]
ML_90	Starch	Cs <sub>10.6</sub> [H <sub>2.4</sub> GeNb <sub>13</sub> O <sub>41</sub> ]	1.3/48.0	150	4	Conv.	60	[100]
ML_91	Cellulose	Cs <sub>10.6</sub> [H <sub>2.4</sub> GeNb <sub>13</sub> O <sub>41</sub> ]	1.3/48.0	165	10	Conv.	46	[100]
ML_92	Fructose	Cs <sub>10.6</sub> [H <sub>2.4</sub> GeNb <sub>13</sub> O <sub>41</sub> ]	1.3/48.0	110	1	MW	55	[100]
ML_93	Glucose	Cs <sub>10.6</sub> [H <sub>2.4</sub> GeNb <sub>13</sub> O <sub>41</sub> ]	1.3/48.0	110	1.5	MW	89	[100]
ML_94	Starch	Cs <sub>10.6</sub> [H <sub>2.4</sub> GeNb <sub>13</sub> O <sub>41</sub> ]	1.3/48.0	120	3	MW	60	[100]
ML_95	Cellulose	Cs <sub>10.6</sub> [H <sub>2.4</sub> GeNb <sub>13</sub> O <sub>41</sub> ]	1.3/48.0	165	3	MW	50	[100]

- 413 <sup>1</sup> The amounts of catalyst and MeOH have been normalized to 1g of feedstock.  
414 <sup>2</sup> “Conv.” and “MW” stand for “Conventional” and “Microwave”, respectively.  
415 <sup>3</sup> “TMEDAPS” stands for “N,N,N,N'- tetramethyl-N,N'-dipropanesulfonic acid-1,6-hexanediammonium”.  
416 <sup>4</sup> “PyPS” stands for “1-(3-sulfopropyl)pyridinium”.  
417 <sup>5</sup> “C16TA” stands for C<sub>16</sub>H<sub>33</sub>N(CH<sub>3</sub>)<sub>3</sub>.  
418 <sup>6</sup> “3-FPyPW” stands for “3-fluoropyridine phosphotungstate”.  
419 <sup>7</sup> “3-PhPyPW” stands for “3-phenylpyridine phosphotungstate”.

420  
421

422 In the last years, HPAs have attracted great interest as homogeneous acid catalysts, due to their  
423 strong Brønsted acidity, good structural mobility, and marked multi-functionality. Among these, the  
424 Keggin-type tungstosilicic and tungstophosphoric HPAs (H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub> and H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>) have been  
425 proposed as efficient homogeneous catalysts for the alcoholysis of C6 model carbohydrates. In  
426 particular, H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> and H<sub>6</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub> showed good catalytic performances for the ML synthesis,  
427 starting from different model feedstocks, including cellulose (runs ML\_60–ML\_62, Table 3), whilst  
428 H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub> was selective for the formation of methyl glucoside intermediate and dimethyl ether  
429 by-product, rather than for ML synthesis, leading to the maximum methyl glucoside yield of 57  
430 mol%, and the corresponding conversion of methanol to dimethyl ether of 28 mol% (run ML\_63,  
431 Table 3) [91]. To improve the Lewis acidity of the HPAs, which helps the isomerization step from  
432 glucose to fructose, and to limit their solubility in alcohols, that complicates their work-up  
433 procedures, HPAs were modified by partially substituting the proton with larger cations, such as  
434 Cu<sup>II</sup>, Zn<sup>II</sup>, Cr<sup>III</sup>, Fe<sup>III</sup>, Sn<sup>IV</sup>, Ti<sup>IV</sup>, and Zr<sup>IV</sup>. Best ML yields (in the range 50-60 mol%) were achieved in the  
435 presence of the H<sub>5</sub>PW<sub>11</sub>TiO<sub>40</sub> catalyst, adopting feedstocks of different complexity, including  
436 cellulose (runs ML\_64–ML\_68, Table 3) [92]. In these cases, the addition of efficient Lewis acid sites,  
437 together with the appropriate balance between Brønsted and Lewis acidity, was responsible for the  
438 promising performances of the catalyst. Contrarily, too strong Lewis acid sites promoted C-C bond  
439 cleavage so that, for example, Fe-based HPWs gave lower ML yields than Ti-based HPWs. However,  
440 in another work of Liu *et al.* [89], the Brønsted-Lewis acidity of Fe-based HPWs catalysts was  
441 properly tuned in favor of the methanolysis pathway, thus allowing a complete conversion of simple  
442 carbohydrates, reaching good ML yields, working at 130 °C for 2 h, and ensuring satisfactory  
443 recycling tests (runs ML\_69–ML\_72, Table 3) [89]. Anyway, the use of this catalyst for cellulose  
444 conversion gave an unsatisfactory ML yield (run ML\_73, Table 3), which limits its application to  
445 simpler model feedstocks. Good performances were reported also for Sn(II) exchanged HPA Keggin  
446 Sn<sub>2</sub>SiW<sub>12</sub>O<sub>40</sub>, leading to the maximum ML yield of about 57 mol%, starting from fructose, working at  
447 150 °C for 3 h (run ML\_74, Table 3) [93]. Instead, Zhang *et al.* [94] investigated the performances of  
448 the AlPW<sub>12</sub>O<sub>40</sub> catalyst, demonstrating its effectiveness for the MW-assisted ML synthesis (ML yields  
449 in the range 45-70 mol%), starting from various carbohydrates, working at 160 °C for 30 min (runs  
450 ML\_75–ML\_78, Table 3). AlPW<sub>12</sub>O<sub>40</sub> acts as a bulk-type catalyst in a pseudo-liquid system,  
451 improving the accessibility of the active catalyst sites. The absorption of high-polar MeOH favors  
452 this liquefaction, increasing the distance between the heteropolyanion-based species, while  
453 increasing the proton mobility [94]. Among the other possible proposals of metal-exchanged HPAs,  
454 the catalytic performances of C<sub>S</sub>xH<sub>3-x</sub>PW<sub>12</sub>O<sub>40</sub> catalysts were tested for one-pot dissolution of  
455 microcrystalline cellulose and subsequent conversion to ML, in the presence of supercritical MeOH  
456 [95]. The authors identified Cs<sub>2.5</sub>H<sub>0.5</sub>PW<sub>12</sub>O<sub>40</sub> as the best performing catalyst for ML production. In  
457 the absence of a catalyst, under supercritical conditions and for short reaction times (300 °C/10  
458 MPa/1 min), the cellulose dissolution was successful, but the next conversion to ML was inefficient.  
459 On the other hand, the addition of C<sub>S</sub>xH<sub>3-x</sub>PW<sub>12</sub>O<sub>40</sub> activated the methanolysis pathway to ML  
460 (maximum yield of 20 mol%), due to its well-balanced Lewis-Brønsted acidic properties (run ML\_79,  
461 Table 3). The authors highlighted the improved accessibility of the solubilized carbohydrates to the  
462 Brønsted sites and the acid strength of Cs<sub>2.5</sub>H<sub>0.5</sub>PW<sub>12</sub>O<sub>40</sub> catalyst. However, despite cellulose  
463 solubilization was significantly improved, the performances of all these catalysts were modest,  
464 especially if compared with those achieved under milder subcritical conditions.  
465 Heteropolyanion-based ionic liquid catalysts were tested for the conversion of different model

466 compounds [96,97]. In particular, [TMEDAPS]<sub>3</sub>[PW<sub>12</sub>O<sub>40</sub>]<sub>2</sub> gave high ML yield from fructose (run  
 467 ML\_80, Table 3), whilst [PyPS]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> was used also for more complex substrates (runs  
 468 ML\_81–ML\_84, Table 3), including cellulose, in this case reaching the maximum ML yield of about  
 469 71 mol%, working for 5 h at 150 °C. In particular, the remarkable efficiency of [PyPS]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>  
 470 towards the cellulose alcoholysis was ascribed to the high acidic strength of the  
 471 sulfonic-functionalized cation and to its synergistic effects with the corresponding heteropolyanion.  
 472 Besides, the proper acidic strength of this catalyst favored the whole process consisting of cellulose  
 473 hydrolysis, levulinic acid formation and its esterification. Moreover, the authors demonstrated that  
 474 [PyPS]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> can be effectively recovered by self-separation, through simple temperature control,  
 475 also showing excellent reusability, even after ten runs. H<sub>6</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub> was properly modified with  
 476 surfactants, to prepare a micellar assembly (C<sub>16</sub>TA)<sub>x</sub>H<sub>6-x</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub> [90], which gave the maximum ML  
 477 yield of about 58 mol%, starting from cellulose (run ML\_85, Table 3). In particular, the promising  
 478 performances of the (C<sub>16</sub>TA)<sub>x</sub>H<sub>5</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub> catalyst were attributed to its micellar structure, high acidic  
 479 content, and good oxidizing ability. The assembly of HPAs with basic organic species is another  
 480 possibility to solidify the homogeneous acid and modulate its acidity. Novel substituted pyridine  
 481 phosphotungstates were prepared and tested for the direct conversion of fructose to ML [98,99].  
 482 3-fluoropyridine phosphotungstate (3-FPyPW) displayed superior catalytic activity for the synthesis  
 483 of ML from fructose (run ML\_86, Table 3), which was ascribed to its relatively higher acidity, and the  
 484 maximum ML yield of 82 mol% was achieved [98]. In another work of Fang *et al.* [99],  
 485 3-phenylpyridine phosphotungstate (3-PhPyPW) hybrid catalyst displayed good catalytic  
 486 performances in the upgrade of fructose to ML (yield of 71 mol%), after 8h at 140 °C, which was  
 487 attributed to its relatively large pore size and high hydrophobicity (run ML\_87, Table 3). As a further  
 488 improvement of HPA-based catalysis, very recently, a trifunctional polyoxometalate  
 489 Cs<sub>10.6</sub>[H<sub>2.4</sub>GeNb<sub>13</sub>O<sub>41</sub>] catalyst, which included Brønsted acid sites, Lewis acid sites, and basic sites,  
 490 was synthesized and used for this reaction, starting from different model compounds, under  
 491 conventional and MW heating (runs ML\_88–ML\_95, Table 3) [100]. The further addition of basic  
 492 sites improves the isomerization from methyl glucoside to methyl fructoside and the subsequent  
 493 formation of 5-methoxymethylfurfural. This interesting approach for the production of ML from  
 494 cellulose, allowed to achieve maximum ML yields of 53 and 55 mol%, under conventional and MW  
 495 heating, respectively, and the catalyst maintained almost unaltered its activity after six recycling  
 496 runs.

497 Zeolites are highly porous aluminosilicates, exhibiting a well-defined channel and cage-based  
 498 structure and, less commonly, a lamellar structure [101]. The molecular dimensions of their channels  
 499 and cages greatly contribute to their catalytic potential. The catalytic properties of zeolites are due in  
 500 part to the exchangeable ions and water molecules trapped in their structure, as well as their  
 501 commonly high adsorption capacity. In general, although zeolites are strong acids at high  
 502 temperatures, their acidity is relatively modest at the common temperature ranges of biomass  
 503 conversions [101]. However, it is possible to functionalize the zeolites and modulate their existing  
 504 electronic features giving rise to zeolites with enhanced acidic properties, which are more suitable  
 505 for this reaction. The most significant examples of zeolites applied to the ML production are  
 506 reported in Table 4:

507 **Table 4.** Zeolite-based catalysts for the ML production from C6 model carbohydrates.

Entry	Feedstock	Catalyst	Cat.(g)/MeOH(g) <sup>1</sup>	T (°C)	t (h)	Heat <sup>2</sup>	Y <sub>ML</sub> (mol%)	Ref.
ML_96	Glucose	H-β	0.3/32.4	160	5	Conv.	17	[82]
ML_97	Cellulose	HZSM-5	0.4/71.4	300	0.02	Conv.	12	[95]
ML_98	Cellulose	HY	0.4/71.4	300	0.02	Conv.	17	[95]
ML_99	Fructose	H-USY (6)	0.6/31.6	160	20	Conv.	51	[102]
ML_100	Glucose	H-USY (6)	0.6/31.6	160	20	Conv.	49	[102]
ML_101	Cellobiose	H-USY (6)	0.6/31.6	160	20	Conv.	53	[102]
ML_102	Maltose	H-USY (6)	0.6/31.6	160	20	Conv.	51	[102]

ML_103	Inulin	H-USY (6)	0.6/31.6	160	20	Conv.	50	[102]
ML_104	Starch	H-USY (6)	0.6/31.6	160	20	Conv.	31	[102]
ML_105	Cellulose	H-USY (6)	0.6/31.6	160	20	Conv.	13	[102]
ML_106	Fructose	H-USY-0.2	0.3/32.4	160	5	Conv.	40	[82]
ML_107	Glucose	H-USY-0.2	0.3/32.4	160	5	Conv.	32	[82]
ML_108	Mannose	H-USY-0.2	0.3/32.4	160	5	Conv.	21	[82]
ML_109	Sucrose	H-USY-0.2	0.3/32.4	160	5	Conv.	38	[82]
ML_110	Cellobiose	H-USY-0.2	0.3/32.4	160	5	Conv.	20	[82]
ML_111	Glucose	ZrY6 (0.5)	0.3/40.0	180	3	MW	68	[103]
ML_112	Mannose	ZrY6 (0.5)	0.3/40.0	180	3	MW	70	[103]
ML_113	Galactose	ZrY6 (0.5)	0.3/40.0	180	3	MW	73	[103]
ML_114	Sucrose	ZrY6 (0.5)	0.3/40.0	180	3	MW	78	[103]
ML_115	Cellobiose	ZrY6 (0.5)	0.3/40.0	180	3	MW	46	[103]
ML_116	Starch	ZrY6 (0.5)	0.3/40.0	180	6	MW	53	[103]
ML_117	Cellulose	ZrY6 (0.5)	0.3/40.0	180	6	MW	27	[103]
ML_118	Glucose	Sn-Al-Beta	0.6/33.3	160	5	Conv.	41	[104]
ML_119	Mannose	Sn-Beta + H <sub>4</sub> SiW <sub>12</sub> O <sub>40</sub>	0.2+0.3/29.0	150	3	Conv.	65	[105]
ML_120	Starch	Sn-Beta + H <sub>4</sub> SiW <sub>12</sub> O <sub>40</sub>	0.2+0.3/29.0	150	5	Conv.	58	[105]
ML_121	Cellulose	Sn-Beta + H <sub>4</sub> SiW <sub>12</sub> O <sub>40</sub>	0.2+0.3/29.0	160	10	Conv.	62	[105]

508 <sup>1</sup> The amounts of catalysts and MeOH have been normalized to 1g of feedstock.

509 <sup>2</sup> "Conv." and "MW" stand for "Conventional" and "Microwave", respectively.

510

511 Unmodified zeolites, such as H- $\beta$ , HZSM-5, and HY, were mainly proposed as catalysts of  
512 reference, to demonstrate the effectiveness of *ad hoc* synthesized catalysts [82,95]. However, the low  
513 ML yields obtained with these zeolites (runs ML\_96–ML\_98, Table 4) show that the modification of  
514 their acidic properties is fundamental to improve the ML production. Saravanamurugan *et al.* [102]  
515 demonstrated that unmodified zeolite H-USY (6) can directly transform model mono-, disaccharides  
516 and inulin polysaccharide to ML, with good yields (about 50 mol%) (runs ML\_99–ML\_103, Table 4).  
517 The H-USY (6) zeolite was preferred by the authors for its high content of Lewis acid sites, which  
518 facilitated the isomerization of glucose to fructose and the further conversion to ML. Moreover, this  
519 zeolite maintained unaltered its structural integrity in the alcohol medium, and it was reused five  
520 times without significant changes in the ML yield. However, despite these valuable data, reported  
521 ML yields from more complex feedstocks, e.g. starch and cellulose, were too low (runs  
522 ML\_104–ML\_105, Table 4), indicating that a modification of the catalyst was necessary to improve  
523 the catalysis. In fact, the microporosity of the zeolites represents an important drawback for  
524 achieving an efficient diffusion of these bulky bio-molecules. To solve these shortcomings, some  
525 additional mesopores can be introduced into the zeolite framework, for example through nitric acid  
526 treatment, which removes the extra framework aluminum species, leading to an increase of  
527 mesoporosity and a slight decrease of acidity. Hierarchical H-USY was modified in such a way by  
528 Zhou *et al.* [82], and tested for the conversion of model carbohydrates to ML (runs  
529 ML\_106–ML\_110, Table 4). However, despite the good performances declared by the authors, the  
530 comparison with the other data discussed up to now shows that these ML yields for simple model  
531 feedstocks are not striking and, even more so, cellulose was not studied. Li *et al.* [103] proposed the  
532 use of a zirconia-zeolite hybrid ZrY6(0.5) catalyst, showing a moderate acid-base site content (0.97  
533 and 0.08 mmol/g), high stability and porosity (average mesopore diameter: 6.2 nm). It was  
534 demonstrated that metal content/type and acid-base bifunctionality were closely correlated with  
535 substrate conversion and ML yield, respectively. The catalytic activity for ML production was higher  
536 than that of other zeolites (runs ML\_111–ML\_117, Table 4), but the issue of the low ML yield from  
537 cellulose remained unsolved (run ML\_117, Table 4). Anyway, the catalyst could be reused five times,  
538 maintaining stable conversion rates and ML yields. Similarly, Yang *et al.* [104] enhanced the Lewis  
539 acidity of Al- $\beta$  zeolite by loading of tin species. Mesopores were generated by hydrothermal

540 treatment of Sn/Al- $\beta$  zeolite, via desilication with tetraethylammonium hydroxide, to restructure the  
 541 zeolite and enhance the porosity of Sn-Al- $\beta$ , which facilitated the diffusion of the reactant and,  
 542 consequently, the ML production. The dual effects of Lewis acidity and mesoporosity improved the  
 543 ML yield about 2.3 folds from glucose if compared to the parent zeolite. However, the best ML yield  
 544 from glucose (run ML\_118, Table 4) is in agreement with those reported for other discussed zeolites,  
 545 hence, also in this case, the improvement deriving from the use of this catalyst is not remarkable.  
 546 Lastly, a bifunctional catalytic system composed of commercial homogeneous  $H_4SiW_{12}O_{40}$  as the  
 547 Brønsted HPA, and Sn-Beta zeolite as the Lewis acid, was recently designed by Zhou *et al.* [105], to  
 548 catalyze the direct conversion of model mono- and polysaccharides to ML (runs ML\_119–ML\_121,  
 549 Table 4). The strong Brønsted acidity and the solubility of HPA, together with the superiority of  
 550 Sn-Beta zeolite towards the isomerization reaction, make this bifunctional catalyst system highly  
 551 active for ML production, even when employing cellulose (run ML\_121, Table 4, yield to ML 62  
 552 mol%), achieving the best catalytic performances within these kinds of catalysts.

553 Another group of catalysts of great interest is that of montmorillonites (clays), which are  
 554 aluminosilicates constituted of multiple layers of polyhedrons [106]. Tetrahedral silicon oxide and  
 555 octahedral hydrous alumina are the common building blocks of these catalysts. Clays have  
 556 demonstrated remarkable catalytic activity towards many biomass conversion routes, due to their  
 557 porous structure that provides a unique environment in which molecules can interact in specific  
 558 ways allowing reactions to take place. Other remarkable advantages are high abundance, versatility,  
 559 smart modulation of the textural properties and environmental inertness. The main advances  
 560 towards the ML synthesis from model compounds in the presence of these catalysts are reported in  
 561 Table 5:

562 **Table 5.** Montmorillonite (clay)-based catalysts the ML production from C6 model carbohydrates,  
 563 under conventional heating.

Entry	Feedstock	Catalyst	Cat.(g)/MeOH(g) <sup>1</sup>	T (°C)	t (h)	Y <sub>ML</sub> (mol%)	Ref.
ML_122	Glucose	Al-clay	0.5/80.0	220	6	61	[107]
ML_123	Glucose	Cu-clay	0.5/80.0	220	6	59	[107]
ML_124	Glucose	In-clay	0.5/80.0	220	6	52	[107]
ML_125	Fructose	Sn-clay	0.5/80.0	220	6	66	[108]
ML_126	Glucose	Sn-clay	0.5/80.0	220	6	60	[108]
ML_127	Sucrose	Sn-clay	0.5/80.0	220	6	62	[108]
ML_128	Inulin	Sn-clay	0.5/80.0	220	6	55	[108]
ML_129	Starch	Sn-clay	0.5/80.0	220	6	46	[108]
ML_130	Cellulose	Sn-clay	0.5/80.0	220	6	19	[108]
ML_131	Fructose	20-SO <sub>4</sub> <sup>2-</sup> /clay	0.8/87.8	200	4	65	[109]
ML_132	Glucose	20-SO <sub>4</sub> <sup>2-</sup> /clay	0.8/87.8	200	4	48	[109]
ML_133	Sucrose	20-SO <sub>4</sub> <sup>2-</sup> /clay	0.8/87.8	200	4	60	[109]
ML_134	Starch	20-SO <sub>4</sub> <sup>2-</sup> /clay	0.8/87.8	200	4	41	[109]
ML_135	Cellulose	20-SO <sub>4</sub> <sup>2-</sup> /clay	0.8/87.8	200	4	24	[109]
ML_136	Fructose	4-HPWFe-MMTSi <sup>2</sup>	0.6/24.8	180	1	74	[110]

564 <sup>1</sup> The amounts of catalysts and MeOH have been normalized to 1g of feedstock.

565 <sup>2</sup> “4-HPWFe-MMTSi” stands for “iron-modified tungstophosphoric acid supported on silica pillared  
 566 montmorillonite”.

567

568 Various metal ion-exchanged montmorillonite catalysts were prepared, characterized, and  
 569 evaluated in glucose conversion to ML (runs ML\_122–ML\_124, Table 5) [107]. Al<sup>3+</sup>-exchanged  
 570 montmorillonite gave the best ML yield (61 mol%), due to the presence of a large number of acid  
 571 sites and a good balance of Brønsted and Lewis acid sites. The montmorillonite catalyst was easily  
 572 recovered from the reaction mixture by filtration and reused at least five times without any loss of

573 activity/selectivity after treatment with H<sub>2</sub>O<sub>2</sub> solution to remove carbon species deposited on the  
 574 catalyst surface. Similar results were reported in another work with tin-exchanged montmorillonite  
 575 catalysts (runs ML\_125–ML\_130, Table 5) [108]. A high ML yield (60–65 mol%) was obtained when  
 576 simple monosaccharides, such as glucose or fructose, were adopted as starting substrate, whilst it  
 577 significantly decreased to 19 mol%, starting from the insoluble cellulose. In a work of Xu *et al.* [109],  
 578 montmorillonites were modified by H<sub>2</sub>SO<sub>4</sub> treatment, thus introducing sulfate groups for improving  
 579 their acidity and therefore catalytic activity for ML production from different model C6 feedstocks  
 580 (runs ML\_131–ML\_135, Table 5). Under the optimal conditions, the conversions of fructose and  
 581 glucose were complete, whilst the corresponding ML yields were 65 and 48 mol% (runs  
 582 ML\_131–ML\_132, Table 5). However, also in this case cellulose conversion gave only moderate ML  
 583 yield (24 mol%, according to run ML\_135, Table 5), which restricted the use of this catalyst to simpler  
 584 soluble carbohydrates. Lastly, silica-pillared montmorillonites functionalized by iron-modified  
 585 tungstophosphoric acid were prepared by Lai *et al.* [110] and tested for fructose methanolysis. The  
 586 characterization demonstrated the high dispersion and Keggin structure of HPWFe in the  
 587 framework of the MMTSi. An optimized ML yield of around 74 mol% was obtained at 180 °C for 1 h  
 588 (run ML\_136, Table 5), and the catalyst recovered after calcination was active after five recyclings.  
 589 These catalysts showed advantageous porosity, tuned Brønsted-Lewis acidity, and high thermal  
 590 stability, making its use promising if compared with other catalysts belonging to this group.

591 It is well-known that metal oxides can be converted into more stable solid-acid catalysts by the  
 592 sulfation treatment [111]. These modified oxides show good stability in solvents, also showing  
 593 enhanced Brønsted and Lewis acidities. Their Lewis acidity is attributed to the metal atoms, whilst  
 594 the Brønsted one derives from the hydroxyl groups located on the surface of the oxides [112].  
 595 Generally, the hydroxyl groups on the surface of unmodified metal oxides have very weak Brønsted  
 596 acidity but, after having performed a sulfation treatment, the S–O bonds on the sulfuric groups  
 597 could bind strongly to the metal atoms, forming a coordination of the S=O bond with the surface  
 598 hydroxyl groups on metal oxides, thus improving the Brønsted acidity. Even these catalysts have  
 599 been tested for ML production from C6 model carbohydrates, and the main available data are  
 600 reported in Table 6:

601 **Table 6.** Modified metal oxides and tungsten disulfide catalysts for the ML production from C6  
 602 model carbohydrates.

Entry	Feedstock	Catalyst	Cat.(g)/MeOH(g) <sup>1</sup>	T (°C)	t (h)	Heat <sup>2</sup>	Y <sub>ML</sub> (mol%)	Ref.
ML_137	Fructose	TiO <sub>2</sub> nanop.	0.6/87.8	175	1	Conv.	80	[113]
ML_138	Glucose	TiO <sub>2</sub> nanop.	0.6/87.8	175	9	Conv.	61	[113]
ML_139	Starch	TiO <sub>2</sub> nanop.	1.1/175.6	175	20	Conv.	40	[113]
ML_140	Cellulose	TiO <sub>2</sub> nanop.	1.1/175.6	175	20	Conv.	42	[113]
ML_141	Fructose	SO <sub>4</sub> <sup>2-</sup> /TiO <sub>2</sub>	0.5/15.8	200	2	Conv.	59	[44]
ML_142	Glucose	SO <sub>4</sub> <sup>2-</sup> /TiO <sub>2</sub>	0.5/15.8	200	2	Conv.	33	[44]
ML_143	Sucrose	SO <sub>4</sub> <sup>2-</sup> /TiO <sub>2</sub>	0.5/15.8	200	2	Conv.	43	[44]
ML_144	Starch	SO <sub>4</sub> <sup>2-</sup> /TiO <sub>2</sub>	0.5/15.8	200	2	Conv.	28	[44]
ML_145	Cellulose	SO <sub>4</sub> <sup>2-</sup> /TiO <sub>2</sub>	0.5/15.8	200	2	Conv.	10	[44]
ML_146	Glucose	Grafted SO <sub>4</sub> <sup>2-</sup> /ZrO <sub>2</sub> /SBA-15	0.5/18.0	140	24	Conv.	24	[114]
ML_147	Fructose	SO <sub>4</sub> <sup>2-</sup> /TiO <sub>2</sub> -ZrO <sub>2</sub>	0.6/87.8	200	1	Conv.	71	[115]
ML_148	Glucose	SO <sub>4</sub> <sup>2-</sup> /TiO <sub>2</sub> -ZrO <sub>2</sub>	0.6/87.8	200	1	Conv.	23	[115]
ML_149	Sucrose	SO <sub>4</sub> <sup>2-</sup> /TiO <sub>2</sub> -ZrO <sub>2</sub>	0.6/87.8	200	1	Conv.	54	[115]
ML_150	Fructose	SO <sub>4</sub> <sup>2-</sup> /ZrO <sub>2</sub> + Sn-Beta	0.4+0.1/32.4	160	5	Conv.	54	[83]
ML_151	Glucose	SO <sub>4</sub> <sup>2-</sup> /ZrO <sub>2</sub> + Sn-Beta	0.4+0.1/32.4	160	5	Conv.	59	[83]
ML_152	Mannose	SO <sub>4</sub> <sup>2-</sup> /ZrO <sub>2</sub> + Sn-Beta	0.4+0.1/32.4	160	5	Conv.	55	[83]
ML_153	Sucrose	SO <sub>4</sub> <sup>2-</sup> /ZrO <sub>2</sub> + Sn-Beta	0.4+0.1/32.4	160	5	Conv.	31	[83]
ML_154	Cellobiose	SO <sub>4</sub> <sup>2-</sup> /ZrO <sub>2</sub> + Sn-Beta	0.4+0.1/32.4	160	5	Conv.	37	[83]



ML_155	Cellulose	NbPO <sub>4</sub>	0.2/19.0 <sup>3</sup>	180	24	Conv.	56	[18]
ML_156	Fructose	WS <sub>2</sub>	0.4/22.2	160	0.25	MW	37	[116]

603 <sup>1</sup> The amounts of catalysts and MeOH have been normalized to 1g of feedstock.

604 <sup>2</sup> "Conv." and "MW" stand for "Conventional" and "Microwave", respectively.

605 <sup>3</sup> 1.0 g of water were added to this reaction mixture.

606

607

608 Acidic TiO<sub>2</sub> (anatase) nanoparticles gave good ML yields, starting from different model  
 609 carbohydrates (runs ML\_137–ML\_140, Table 6) [113]. Remarkably, also for the challenging case of  
 610 cellulose conversion, the best ML yield was good (42 mol%), but this achievement required a very  
 611 long reaction time (20 h). The good catalytic activity of the nanoparticles was attributed to the *in-situ*  
 612 solvation on the surface and their better dispersion in the reaction medium. Also in this case, the  
 613 catalysts showed high recyclability, with only a minor loss of performance. Peng *et al.* [44] tested  
 614 many heterogeneous acids (ZSM-5(25), ZSM-5(36), NaY, H-mordenite, Zr<sub>3</sub>(PO<sub>4</sub>)<sub>4</sub>, SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub>,  
 615 SO<sub>4</sub><sup>2-</sup>/TiO<sub>2</sub>, and TiO<sub>2</sub>), identifying SO<sub>4</sub><sup>2-</sup>/TiO<sub>2</sub> as the most promising one for ML production (runs  
 616 ML\_141–ML\_145, Table 6). Besides, SO<sub>4</sub><sup>2-</sup>/TiO<sub>2</sub> avoided dimethyl ether formation, which instead  
 617 significantly occurred, for example, with ZSM-5(25) and ZSM-5(36) catalysts, which led to a  
 618 consumption of about half of the starting methanol, in favor of dimethyl ether. The heterogeneous  
 619 SO<sub>4</sub><sup>2-</sup>/TiO<sub>2</sub> catalyst was easily recovered by filtration and exhibited good catalytic activities after  
 620 calcination in five cycles of reusing. The surface structure and acidity variations of the fresh and  
 621 recycled SO<sub>4</sub><sup>2-</sup>/TiO<sub>2</sub> catalysts after calcination were characterized by XRD and NH<sub>3</sub>-TPD techniques.  
 622 The authors reported that the catalyst crystal structure was preserved after multiple cycles, but the  
 623 amount and the strength of the acid sites of the catalyst gradually decreased with the increase of  
 624 consecutive recycling runs, due to the progressive loss of sulfur, mainly occurring by solvation  
 625 during the alcoholysis and by calcination necessary for the catalyst regeneration [44]. However, the  
 626 low ML yield achieved with cellulose (10 mol%, according to run ML\_145, Table 6) demonstrated  
 627 that a further modification of this catalyst was necessary for improving the catalysis. For this  
 628 purpose, high surface area and thermally robust SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub> conformal monolayers, with tunable  
 629 Lewis-Brønsted acid site densities, were grown over a mesoporous SBA-15 template, via sequential  
 630 grafting and hydrolysis cycles, employing a zirconium isopropoxide precursor [114]. The enhanced  
 631 low-temperature activity of grafted SZ/SBA-15 was attributed to the presence of strong Lewis acid  
 632 sites that drove the glucose isomerization to fructose. Catalyst reusability was confirmed over three  
 633 consecutive runs, performing the calcination of the spent catalyst at 550 °C to remove organic  
 634 deposits, thus overcoming the extended leaching problems of commercial SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub> catalyst.  
 635 However, the optimized balance between Brønsted-Lewis acidity and density of the acid sites was  
 636 not enough for improving the ML catalysis, leading only to a moderate ML yield, starting from  
 637 glucose and working under mild reaction conditions (run ML\_146, Table 6). Further modification of  
 638 these catalysts was proposed by Njagi *et al.* [115], who synthesized sulfated mixed-metal oxides  
 639 (SO<sub>4</sub><sup>2-</sup>/TiO<sub>2</sub>-ZrO<sub>2</sub>) of high acidity, mainly ascribed to the sulfate species, and new acidic sites  
 640 generated from the charge excess. This catalyst was suitable for the high yield obtained in the  
 641 conversion of fructose or sucrose to ML (runs ML\_147 and ML\_149, Table 6), but only low yields (23  
 642 mol%) were obtained from run ML\_148, Table 6), confirming that also this mixed catalyst was not  
 643 efficient for the isomerization of glucose to fructose. However, the authors declared a high selectivity  
 644 to ML, which was attributed to the presence of large mesopores, whilst the dimethyl ether formation  
 645 was reported to be negligible. The spent catalyst was reused after a calcination step for removing  
 646 insoluble humans from the surface, maintaining its catalytic performances almost unaltered.  
 647 Another proposal of catalyst improvement was done by Jiang *et al.* [83], who reported the maximum  
 648 ML yield of about 60 mol% from fructose, by combining SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub> and Sn-Beta zeolite (run ML\_150,  
 649 Table 6). ML yields for more complex feedstocks are moderate (ML\_151–ML\_154, Table 6), in  
 650 agreement with those achieved with the zeolite-based catalysts. Sn-Beta zeolite has Lewis acidity for  
 651 allowing the isomerization of glucose to fructose and poor catalytic activity for the retro-aldol  
 652 reaction, whilst the Lewis acid sites of SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub> cannot catalyze the isomerization of glucose to

653 fructose. Recyclability studies indicated that the combined catalyst could be reused five times  
 654 without a significant decrease in product yield, proving its easy recovery and thermal stability  
 655 during regeneration. Niobium phosphate catalysts were synthesized by Ding *et al.* [18] and tested for  
 656 ML production from cellulose, showing good performances in the conversion of cellulose  
 657 (maximum ML yield of 56 mol%) (run ML\_155, Table 6). This investigation showed that the  
 658 mechanism and type of intermediates of cellulose alcoholysis in MeOH were different from those in  
 659 water and that the high Brønsted/Lewis acid ratio of these solid catalysts is needed to prevent the  
 660 generation of by-products, in particular methyl lactate and 1,1,2-trimethoxyethane. Also the  
 661 heterogeneous system WS<sub>2</sub> was tested for fructose conversion. This catalyst was synthesized by  
 662 Quereshi *et al.* [116] in a tubular furnace (600 °C), using elemental tungsten and sulfur, obtaining  
 663 multilayered flakes/sheets of WS<sub>2</sub>. Only a moderate ML yield was reached (run ML\_156, Table 6)  
 664 and the catalyst resulted very stable and showed similar activity after five consecutive runs.  
 665

## 666 2.2 EL synthesis from model carbohydrates

667 The synthesis of EL from C6 model carbohydrates have been widely investigated, and many  
 668 catalysts have been tested to increase the EL yield. The interest in this ester is enhanced by the  
 669 possible use of bioethanol as alcohol thus obtaining a fully bio-derived product. As for the synthesis  
 670 of ML ester, among the employed catalysts, mineral acids and metal salts represent the simplest and  
 671 cheapest alternatives to sulfuric acid. The most promising data for these kinds of catalysts as  
 672 reported in Table 7.

673 **Table 7.** Inorganic mineral acids and metal salts for the EL production from C6 model carbohydrates.

Entry	Feedstock	Catalyst	Cat.(g)/EtOH(g) <sup>1</sup>	T (°C)	t (h)	Heat <sup>2</sup>	Y <sub>EL</sub> (mol%)	Ref.
EL_1	Fructose	H <sub>2</sub> SO <sub>4</sub> (100 wt%)	0.04/39.2	200	1.5	Conv.	72	[117]
EL_2	Glucose	H <sub>2</sub> SO <sub>4</sub> (100 wt%)	0.01/39.4	180	0.5	Conv.	45	[118]
EL_3	Glucose	H <sub>2</sub> SO <sub>4</sub> (100 wt%)	0.02/26.5 <sup>3</sup>	200	6	Conv.	34	[119]
EL_4	Glucose	H <sub>2</sub> SO <sub>4</sub> (100 wt%)	0.04/39.2	200	1.5	Conv.	37	[117]
EL_5	Sucrose	H <sub>2</sub> SO <sub>4</sub> (100 wt%)	0.04/39.2	200	1.5	Conv.	40	[117]
EL_6	Inulin	H <sub>2</sub> SO <sub>4</sub> (100 wt%)	0.04/39.2	200	1.5	Conv.	51	[117]
EL_7	Cellulose	H <sub>2</sub> SO <sub>4</sub> (100 wt%)	0.04/39.2	200	1.5	Conv.	25	[117]
EL_8	Cellulose	H <sub>2</sub> SO <sub>4</sub> (100 wt%)	0.09/6.9	190	0.25	Conv.	12	[69]
EL_9	Cellulose	H <sub>2</sub> SO <sub>4</sub> (100 wt%)	0.13/11.8	190	0.5	Conv.	43	[120]
EL_10	Cellulose	H <sub>2</sub> SO <sub>4</sub> (96 wt%)	0.42/10.0	170	2	Conv.	51	[121]
EL_11	Fructose	HReO <sub>4</sub>	0.14/21.7	160	16	Conv.	80	[72]
EL_12	Glucose	HReO <sub>4</sub>	0.14/21.7	160	16	Conv.	27	[72]
EL_13	Sucrose	HReO <sub>4</sub>	0.14/21.7	160	16	Conv.	52	[72]
EL_14	Inulin	HReO <sub>4</sub>	0.14/21.7	160	16	Conv.	65	[72]
EL_15	Fructose	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	2.24/9.0	170	2	Conv.	29	[73]
EL_16	Glucose	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	2.24/9.0	170	2	Conv.	39	[73]
EL_17	Glucose	La <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	2.24/9.0	170	2	Conv.	29	[73]
EL_18	Glucose	Ce(SO <sub>4</sub> ) <sub>2</sub>	2.24/9.0	170	2	Conv.	29	[73]
EL_19	Cellulose	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	1.00/34.7	180	5	Conv.	45	[75]
EL_20	Cellulose	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.40/22.0 <sup>4</sup>	180	0.6	MW	54	[32]
EL_21	Cellulose	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.40/22.0 <sup>4</sup>	180	0.9	MW	70	[32]

674 <sup>1</sup> The amounts of catalyst and EtOH have been normalized to 1 g of feedstock.

675 <sup>2</sup> "Conv." and "MW" stand for "Conventional" and "Microwave", respectively.

676 <sup>3</sup> 14.3 g of glycerol were added to this reaction mixture.

677 <sup>4</sup> 1.2 g of water were added to this reaction mixture.

678 Several works have investigated the production of EL from mono- and polysaccharides,  
 679 preferring the use of diluted sulfuric acid (0.002-0.3 mol/L) (runs EL\_1–EL\_10, Table 7) [69,117-121].  
 680 Temperatures higher than 170 °C and relatively short reaction times (below 2 h) have been generally  
 681 adopted to achieve good EL yields. Taking into account the different feedstocks, as expected fructose  
 682 led to the highest EL yield (about 70 mol%), due to the easier conversion of this feedstock, in the  
 683 presence of Brønsted acids (runs EL\_1, EL\_4–EL\_7, Table 7) [117]. To inhibit the humin formation  
 684 *via* the use of non-aqueous green solvents, a binary reaction medium composed of ethanol-glycerol  
 685 was proposed for the sulfuric acid-catalyzed conversion of glucose, but an improvement of the EL  
 686 yield was not achieved (run EL\_3, Table 7) [119]. In addition, the available data for the conversion of  
 687 C6 carbohydrates to EL with H<sub>2</sub>SO<sub>4</sub>, confirm that cellulose is the most recalcitrant substrate, leading  
 688 to the lowest EL yields (runs EL\_7–EL\_8, Table 7), except when higher catalyst concentrations  
 689 (0.1-0.3 mol/L) were employed (runs EL\_9–EL\_10, Table 7) and the reaction conditions were  
 690 properly modulated [69,117,120,121]. Perrhenic acid was proposed by Bernardo *et al.* [72] as strong  
 691 Brønsted homogeneous acid for the synthesis of EL (runs EL\_11–EL\_14, Table 7). However, this  
 692 catalyst was more expensive than H<sub>2</sub>SO<sub>4</sub> and required longer reaction time to achieve interesting  
 693 yields. Analogously to the reactions performed with H<sub>2</sub>SO<sub>4</sub>, the highest EL yield of 80 mol% was  
 694 obtained starting from fructose after 16 h, whilst under the same conditions the yield from glucose  
 695 was only 27 mol% and the extension of the reaction time up to 72 h was necessary to reach the same  
 696 yield obtained starting from fructose. This catalyst was also tested for the EL synthesis from inulin  
 697 and sucrose, achieving the yields of 65 and 52 mol%, respectively, demonstrating that HReO<sub>4</sub> can  
 698 hydrolyze the glycosidic bonds of di- and polysaccharides. As reported for methanolysis, in addition  
 699 to the mineral acids, also the inorganic salts, in particular sulfates, have been successfully employed  
 700 for the EL synthesis from model C6 carbohydrates. Sun *et al.* [73] investigated different inorganic  
 701 salts, such as Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, La<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and Ce(SO<sub>4</sub>)<sub>3</sub> as the catalyst for the alcoholysis of fructose and  
 702 glucose, working at 170 °C for 2 h (runs EL\_15–EL\_18, Table 7). It was found that Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> was the  
 703 best catalyst for the glucose conversion to EL, leading to the highest EL yield of 39 mol%. Moreover,  
 704 the EL yield obtained starting from glucose was higher than that from fructose, proving that the  
 705 different chemical structures of these two sugars were affected by the chelation with Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>. For  
 706 the cellulose alcoholysis Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> was largely employed. Zhou *et al.* [75] reported the maximum EL  
 707 yield of 45 mol%, working at 180 °C for 5 h (run EL\_19, Table 7), whilst Huang *et al.* [32] achieved the  
 708 best EL yield up to 70 mol%, working at the same temperature, but prolonging the reaction only for  
 709 0.9 h under MW irradiation with an EtOH-water medium (runs EL\_20 and EL\_21, Table 7). This  
 710 yield value from a recalcitrant substrate is remarkable and analogous to that obtained by the authors  
 711 in the methanolysis of cellulose under the same reaction conditions (compare run ML\_29, Table 1,  
 712 with run EL\_21, Table 2). As already discussed for the ML synthesis, the water addition is generally  
 713 advantageous for this reaction, leading to an increase of the AL yield and improving the kinetics, at  
 714 the same time reducing the humin formation and the solvent consumption to give the dialkyl ether.  
 715 Sulfonic acids and sulfonate salts have been employed as homogeneous or heterogeneous  
 716 catalysts for the ethanolysis of C6 carbohydrates. The most interesting available data are reported in  
 717 Table 8:

718 **Table 8.** Sulfonic acids, sulfonate salts, and their combinations for the EL production from C6 model  
 719 carbohydrate.

Entry	Feedstock	Catalyst	Cat.(g)/EtOH(g) <sup>1</sup>	T (°C)	t (h)	Heat <sup>2</sup>	Y <sub>EL</sub> (mol%)	Ref.
EL_22	Cellulose	Al(OTf) <sub>3</sub>	0.47/64.0	160	4	Conv.	32	[122]
EL_23	Cellulose	In(OTf) <sub>3</sub>	0.56/64.0	160	4	Conv.	20	[122]
EL_24	Cellulose	Sn(OTf) <sub>2</sub>	0.42/64.0	160	4	Conv.	23	[122]
EL_25	Cellulose	Hf(OTf) <sub>4</sub>	0.77/64.0	160	4	Conv.	24	[122]
EL_26	Cellulose	Y(OTf) <sub>3</sub> +H <sub>3</sub> PO <sub>4</sub> (100 wt%)	0.60+0.10/64.0	180	2	Conv.	75	[122]
EL_27	Fructose	PSDVB-SO <sub>3</sub> H <sup>3</sup>	0.90/80.0	120	2	Conv.	26	[123]

EL_28	Fructose	Amberlyst-15	0.40/64.0	120	24	Conv.	73	[80]
EL_29	Fructose	Amberlyst-15	0.80/78.0	150	3.5	Conv.	75	[124]
EL_30	Cellulose	Acid resin D008	2.40/10.0	170	2	Conv.	20	[121]
EL_31	Fructose	PSSA-g-CNT <sup>4</sup>	0.40/64.0	120	24	Conv.	84	[80]
EL_32	Fructose	PSSA-g-CNF <sup>5</sup>	0.40/64.0	120	24	Conv.	69	[80]
EL_33	Fructose	BSA-g-CMK-5 <sup>6</sup>	0.40/64.0	120	24	Conv.	60	[80]
EL_34	Fructose	BSA-g-CNT <sup>7</sup>	0.40/64.0	120	24	Conv.	45	[80]
EL_35	Fructose	HDS-3.6 <sup>8</sup>	0.80/78.0	150	3.5	Conv.	70	[124]
EL_36	Glucose	HDS-3.6 <sup>8</sup>	0.40/390.0	170	8	Conv.	25	[124]
EL_37	Inulin	HDS-3.6 <sup>8</sup>	0.40/390.0	170	6	Conv.	51	[124]
EL_38	Starch	HDS-3.6 <sup>8</sup>	0.40/390.0	170	8	Conv.	18	[124]
EL_39	Cellulose	HDS-3.6 <sup>8</sup>	0.40/390.0	170	10	Conv.	12	[124]
EL_40	Fructose	5-Cl-SHPAO <sup>9</sup>	0.25/20.0	160	1	Conv.	68	[84]
EL_41	Glucose	5-Cl-SHPAO <sup>9</sup>	0.25/20.0	160	8	Conv.	61	[84]
EL_42	Sucrose	5-Cl-SHPAO <sup>9</sup>	0.25/20.0	160	6	Conv.	62	[84]
EL_43	Cellobiose	5-Cl-SHPAO <sup>9</sup>	0.25/20.0	160	8	Conv.	60	[84]
EL_44	Cellulose	5-Cl-SHPAO <sup>9</sup>	0.25/20.0	160	8	Conv.	58	[84]
EL_45	Fructose	AC-Fe-SO <sub>3</sub> H <sup>10</sup>	0.50/52.7	195	3	Conv.	58	[125]
EL_46	Fructose	AC-Fe-SO <sub>3</sub> H <sup>10</sup>	0.50/52.7	200	3	Conv.	47	[125]
EL_47	Glucose	AC-Fe-SO <sub>3</sub> H <sup>10</sup>	0.50/52.7	200	3	Conv.	19	[125]
EL_48	Sucrose	AC-Fe-SO <sub>3</sub> H <sup>10</sup>	0.50/52.7	200	3	Conv.	28	[125]
EL_49	Inulin	AC-Fe-SO <sub>3</sub> H <sup>10</sup>	0.50/52.7	200	3	Conv.	35	[125]
EL_50	Starch	AC-Fe-SO <sub>3</sub> H <sup>10</sup>	0.50/52.7	200	3	Conv.	12	[125]
EL_51	Sucrose	20 wt% Zn-SC <sup>11</sup>	0.50/47.3 <sup>12</sup>	100	12	Conv.	64	[126]
EL_52	Sucrose	20 wt% Zn-SC <sup>11</sup>	0.50/47.3 <sup>12</sup>	100	1	US	72	[126]
EL_53	Glucose	Sulfonated char	0.20/26.5 <sup>13</sup>	200	6	Conv.	37	[119]

720 <sup>1</sup> The amounts of catalyst and EtOH have been normalized to 1g of feedstock.

721 <sup>2</sup> “Conv.” and “US” stand for “Conventional” and “Ultrasound”, respectively.

722 <sup>3</sup> “PSDVB-SO<sub>3</sub>H” stands for “Polystyrene-co-divinylbenzene resin sulfonated”.

723 <sup>4</sup> “PSSA-g-CNT” stands for “poly(*p*-styrenesulfonic acid)-grafted carbon nanotubes”.

724 <sup>5</sup> “PSSA-g-CNF” stands for “poly(*p*-styrenesulfonic acid)-grafted carbon nanofibers”.

725 <sup>6</sup> “BSA-g-CMK-5” stands for “benzenesulfonic acid-grafted carbon mesostructured by KAIST-5”.

726 <sup>7</sup> “BSA-g-CNT” stands for “benzenesulfonic acid-grafted carbon nanotubes”.

727 <sup>8</sup> “HDS-3.6” stands for “Hyper-cross-linked polymer-based carbonaceous materials”.

728 <sup>9</sup> “5-Cl-SHPAO” stands for “sulfonated hyperbranched poly(arylene oxindole) with chloride substituent in the  
729 fifth position of isatin”.

730 <sup>10</sup> “AC-Fe-SO<sub>3</sub>H” stands for “Fe-impregnated sulfonated carbon”.

731 <sup>11</sup> “20 wt% Zn-SC” stands for “20 wt% ZnO doped onto acid-sulfonated carbon”.

732 <sup>12</sup> 6.0 g of tetrahydrofuran were added to this reaction mixture.

733 <sup>13</sup> 14.3 g of glycerol were added to this reaction mixture.

734

735 Regarding the organic salts, Bodachivskiy *et al.* [122] studied the EL synthesis from cellulose, in  
736 the presence of metal triflates as catalysts (runs EL\_22–EL\_26, Table 8). In particular, the authors  
737 proved that harder Lewis acids, such as Al(OTf)<sub>3</sub>, In(OTf)<sub>3</sub>, Sn(OTf)<sub>2</sub>, and Hf(OTf)<sub>4</sub>, were able to  
738 catalyze this reaction, reaching the maximum EL yield of 32 mol%, with Al(OTf)<sub>3</sub>. The catalytic  
739 performance is ascribed to the Brønsted acidity generated from the harder Lewis acids, as a  
740 consequence of the complexation of the protic solvent with the metal center, rather than hydrolysis,  
741 the latter responsible for the Brønsted acidity of inorganic salts. On the other hand, softer Lewis  
742 acids, such as Y(OTf)<sub>3</sub>, AgOTf, La(OTf)<sub>3</sub>, and Yb(OTf)<sub>3</sub> showed low activity towards the direct  
743 conversion of cellulose to EL, but their combination with a Brønsted acid, such as H<sub>3</sub>PO<sub>4</sub>,  
744 significantly increased their catalytic activity, in particular for the combined catalytic system  
745 (Y(OTf)<sub>3</sub> + H<sub>3</sub>PO<sub>4</sub>) [122]. This synergic effect derived from the favorable complexation of soft Lewis

746 acid and  $H_3PO_4$  increased the Lewis acid-assisted Brønsted acidity, leading to the highest EL yield of  
747 75 mol% starting from microcrystalline cellulose. Regarding the other sulfonated systems, both  
748 commercial and *ad-hoc* synthesized heterogeneous catalysts have been employed for the production  
749 of EL from C6 carbohydrates. For example, Zhang *et al.* [123] prepared a sulfonic acid resin by  
750 condensation of styrene and divinylbenzene (PSDVB- $SO_3H$ ), which was employed for the fructose  
751 ethanolysis, obtaining the maximum EL yield of 26 mol% (run EL\_27, Table 8). However, better EL  
752 results have been reported in the presence of commercial styrene-divinylbenzene acid resins. In fact,  
753 Liu *et al.* [80] used the commercial Amberlyst-15 for the fructose ethanolysis, working at 120 °C for  
754 24 h, achieving the highest EL yield of 73 mol% (run EL\_28, Table 8). Besides, the same authors  
755 prepared several sulfonated carbonaceous materials, such as poly(*p*-styrenesulfonic acid)-grafted  
756 carbon nanotubes (PSSA-g-CNT), poly(*p*-styrenesulfonic acid)-grafted carbon nanofibers  
757 (PSSA-g-CNF), benzenesulfonic acid-grafted CMK-5 (BSA-g-CMK-5), and benzenesulfonic  
758 acid-grafted carbon nanotubes (BSA-g-CNT), employing them under the same reaction conditions of  
759 the Amberlyst-15 (runs EL\_31–EL\_34, Table 8) [80]. The concentration of Brønsted acid sites for the  
760 synthesized catalysts decreased as follows: PSSA-g-CNT > PSSA-g-CNF > BSA-g-CMK-5 >  
761 BSA-g-CNT, and the same the trend was observed for EL yield, which was highest for the  
762 PSSA-g-CNT catalyst (84 mol%) and lowest for the BSA-g-CNT one (45 mol%). Moreover,  
763 PSSA-g-CNT gave a higher EL yield than that with the commercial Amberlyst-15, underlining that  
764 this synthesized catalyst was particularly efficient. Also Gu *et al.* [124] employed Amberlyst-15 as a  
765 catalyst for the fructose ethanolysis at 150 °C for 3.5 h, ascertaining the EL yield of 75 mol% (run  
766 EL\_29, Table 8). These catalytic performances were compared with those of several *ad-hoc*  
767 synthesized sulfonated hyper-cross-linked polymers, working under the same reaction conditions,  
768 and the authors proved that the catalyst obtained from 4,4'-bis(chloromethyl)-1,1'-biphenyl as the  
769 precursor, was the most active, due to the higher acid density and surface area (run EL\_35, Table 8)  
770 [124]. This catalyst (HDS-3.6) led to the maximum EL yield of 70 mol%, analogous to that ascertained  
771 with Amberlyst-15. The synthesized catalyst was employed also for the ethanolysis of other  
772 feedstocks, such as glucose, inulin, starch, and cellulose. The EL yields achieved starting from aldose  
773 sugars were lower than those obtained starting from ketose, due to the lack of Lewis acid sites in the  
774 adopted catalyst, which are of paramount importance for the isomerization step (runs  
775 EL\_36–EL\_39, Table 8) [124]. The same conclusion was reported by Ming *et al.* [121] for the EL  
776 synthesis from cellulose, employing the commercial sulfonic acid resin D008 (run EL\_30, Table 8).  
777 This catalyst led to the EL yield of only 20 mol%, which was lower than that obtained under the  
778 same reaction conditions with the mineral acid  $H_2SO_4$  (51 mol%, according to run EL\_10, Table 7)  
779 [121]. The lower EL yield reported with the commercial resin was attributed to the expected mass  
780 transfer limitations occurring between the protons of the heterogeneous catalyst and the solid  
781 cellulose. The detrimental absence of Lewis acid sites for EL production was confirmed for other  
782 synthesized sulfonic acid, such as the 5-chloro-sulfonated hyperbranched poly(arylene oxindole)  
783 catalyst (5-Cl-SHPAO), that was tested for the ethanolysis of several saccharides (runs  
784 EL\_40–EL\_44, Table 8) [84]. Under the optimized reaction conditions, the highest EL yield of 68  
785 mol% was obtained from fructose and it decreased as follows: fructose > sucrose > glucose >  
786 cellobiose > cellulose. Zhang *et al.* [125] synthesized Fe-impregnated sulfonated carbon of high  
787 surface area, pore volume and  $-SO_3H$  density, testing it for the ethanolysis of fructose, glucose,  
788 sucrose, inulin, and starch (runs EL\_45–EL\_50, Table 8). Also in this case, the highest EL yield was  
789 obtained starting from fructose and the EL yield progressively decreased by converting aldoses of  
790 increasing complexity. The problem of the low alkyl levulinate yields obtained from aldose  
791 carbohydrates was partially overcome by Karnjanakom *et al.* [126], who prepared different  
792 sulfonated carbon doped with metal oxides, which were tested for the sucrose conversion to EL  
793 (runs EL\_51–EL\_52, Table 8). These catalysts showed higher activity than the corresponding  
794 undoped sulfonated carbon, underlining that the synergy between Lewis and Brønsted acidity,  
795 deriving from oxides and sulfonic groups, respectively, was fundamental for this reaction. In  
796 particular, the sulfonated carbon doped with  $ZrO_2$  (Zn-SC) showed the highest selectivity towards  
797 EL, due to its acidity, that resulted sufficient to promote the reaction, but not excessive to catalyze

798 also the humin formation. The employment of THF as the reaction co-solvent improved the EL yield  
 799 from 60 to 72 mol%, because this low-polar solvent prevented the next conversion of the desired EL.  
 800 The authors also exploited the ultrasound technology as an alternative heating system for promoting  
 801 this reaction, which was proved to be particularly efficient in reducing reaction times. Bosilji *et al.*  
 802 [119] carried out the glucose ethanolysis in an (ethanol-glycerol) solvent, testing a heterogeneous  
 803 catalyst prepared by hydrothermal carbonization of the same substrate (glucose) itself, through the  
 804 addition of sodium borate. This is an interesting example because the adopted feedstock is also the  
 805 precursor of the catalytic system, in principle making the whole process cheaper and sustainable.  
 806 The synthesized catalyst had a high specific surface area and led to the maximum EL yield of 37  
 807 mol% (run EL\_53, Table 8). Moreover, the catalytic performances were comparable with those of  
 808 H<sub>2</sub>SO<sub>4</sub> (34 mol%, run EL\_3, Table 7).

809 Polyoxometalates (POMs) are another type of emerging acid catalysts adopted for the synthesis  
 810 of EL from C6 model carbohydrates. Significant results obtained with these catalysts are  
 811 summarised in Table 9:

812 **Table 9.** Polyoxometalate (POM)-based catalysts for the EL production from C6 model  
 813 carbohydrates.

Entry	Feedstock	Catalyst	Cat.(g)/EtOH(g) <sup>1</sup>	T (°C)	t (h)	Heat <sup>2</sup>	Y <sub>EL</sub> (mol%)	Ref.
EL_54	Fructose	H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	0.20/39.4	160	2	Conv.	50	[127]
EL_55	Fructose	HPW <sub>4</sub> Mo <sub>10</sub> O <sub>x</sub>	n.a. <sup>3</sup>	170	0.3	MW	74	[128]
EL_56	Glucose	HPW <sub>4</sub> Mo <sub>10</sub> O <sub>x</sub>	n.a. <sup>3</sup>	180	0.5	MW	62	[128]
EL_57	Cellulose	H <sub>4</sub> SiW <sub>12</sub> O <sub>40</sub>	0.10/31.6	180	1	Conv.	19	[91]
EL_58	Fructose	KH <sub>2</sub> PW <sub>12</sub> O <sub>40</sub>	0.75/35.5 <sup>4</sup>	150	2	Conv.	69	[129]
EL_59	Glucose	KH <sub>2</sub> PW <sub>12</sub> O <sub>40</sub>	0.75/35.5 <sup>4</sup>	150	2	Conv.	15	[129]
EL_60	Sucrose	KH <sub>2</sub> PW <sub>12</sub> O <sub>40</sub>	0.75/35.5 <sup>4</sup>	150	2	Conv.	35	[129]
EL_61	Inulin	KH <sub>2</sub> PW <sub>12</sub> O <sub>40</sub>	0.75/35.5 <sup>4</sup>	150	2	Conv.	52	[129]
EL_62	Cellulose	KH <sub>2</sub> PW <sub>12</sub> O <sub>40</sub>	0.75/35.5 <sup>4</sup>	220	2	Conv.	15	[129]
EL_63	Fructose	Ti <sub>0.75</sub> PW <sub>12</sub> O <sub>40</sub>	0.43/17.5	120	6	Conv.	63	[130]
EL_64	Glucose	Ti <sub>0.75</sub> PW <sub>12</sub> O <sub>40</sub>	0.43/17.5	120	6	Conv.	21	[130]
EL_65	Fructose	Sn <sub>2</sub> SiW <sub>12</sub> O <sub>40</sub>	1.67/65.8	150	2	Conv.	71	[93]
EL_66	Sucrose	Sn <sub>2</sub> SiW <sub>12</sub> O <sub>40</sub>	0.91/35.9	150	2	Conv.	78	[93]
EL_67	Inulin	Sn <sub>2</sub> SiW <sub>12</sub> O <sub>40</sub>	2.00/79.0	150	2	Conv.	61	[93]
EL_68	Fructose	3-PhPyPW <sup>5</sup>	0.50/21.7	140	8	Conv.	30	[99]
EL_69	Fructose	[TMEDAPS] <sub>3</sub> [PW <sub>12</sub> O <sub>40</sub> ] <sub>2</sub> <sup>6</sup>	1.00/64.0	120	12	Conv.	80	[96]
EL_70	Glucose	[TMEDAPS] <sub>3</sub> [PW <sub>12</sub> O <sub>40</sub> ] <sub>2</sub> <sup>6</sup>	1.00/64.0	150	24	Conv.	20	[96]
EL_71	Sucrose	[TMEDAPS] <sub>3</sub> [PW <sub>12</sub> O <sub>40</sub> ] <sub>2</sub> <sup>6</sup>	1.00/64.0	120	12	Conv.	45	[96]
EL_72	Cellobiose	[TMEDAPS] <sub>3</sub> [PW <sub>12</sub> O <sub>40</sub> ] <sub>2</sub> <sup>6</sup>	1.00/64.0	150	24	Conv.	18	[96]
EL_73	Inulin	[TMEDAPS] <sub>3</sub> [PW <sub>12</sub> O <sub>40</sub> ] <sub>2</sub> <sup>6</sup>	1.00/64.0	120	12	Conv.	67	[96]
EL_74	Cellulose	[TMEDAPS] <sub>3</sub> [PW <sub>12</sub> O <sub>40</sub> ] <sub>2</sub> <sup>6</sup>	1.00/64.0	150	24	Conv.	14	[96]
EL_75	Cellulose	[PyPS] <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> <sup>7</sup>	10.49/97.5	150	5	Conv.	57	[97]

814 <sup>1</sup> The amounts of catalyst and EtOH have been normalized to 1 g of feedstock.

815 <sup>2</sup> “Conv.” and “MW” stand for “Conventional” and “Microwave”, respectively.

816 <sup>3</sup> “n.a.” stands for “not-available”.

817 <sup>4</sup> 4.4 g of toluene were added to this reaction mixture.

818 <sup>5</sup> “3-PhPyPW” stands for “3-phenylpyridine phosphotungstate”.

819 <sup>6</sup> “TMEDAPS” stands for “N,N,N,N'-tetramethyl-N,N'-dipropanesulfonic acid-1,6-hexanediammonium”.

820 <sup>7</sup> “PyPS” stands for “1-(3-sulfopropyl)pyridinium”.

821 POMs, including simple HPAs and their salts, have good acidic properties. Different HPAs,  
 822 such as H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> (run EL\_54, Table 9) [127], HPW<sub>4</sub>Mo<sub>10</sub>O<sub>x</sub> (runs EL\_55–EL\_56, Table 9) [128] and  
 823 H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub> (run EL\_57, Table 9) [91], were used for the EL synthesis from fructose, glucose and

824 cellulose, obtaining satisfactory yields, in particular with the first two catalysts. In fact, analogously  
 825 to the ML synthesis,  $H_4SiW_{12}O_{40}$  strongly promoted the formation of the intermediate ethyl  
 826 glucoside, leading to a corresponding yield up to 59 mol%, and an ethanol conversion of 16 mol% to  
 827 the diethyl ether by-product. However, the main drawback of the HPA employment is their good  
 828 solubility in the reaction medium that complicates their separation/recycling. As previously  
 829 observed for ML, most of the studies have dealt with HPA salts, where one or more protons were  
 830 substituted with larger cations. In particular, as for the ML synthesis, the  $PW_{12}O_{40}^{3-}$  heteropolyanion  
 831 is that preferred for studying the alcoholysis of saccharides. For example, Zhao *et al.* [129]  
 832 substituted a proton of the Keggin-type  $H_3PW_{12}O_{40}$  with larger monovalent cations, such as  $K^+$   
 833 ( $KH_2PW_{12}O_{40}$ ) and  $Ag^+$  ( $AgH_2PW_{12}O_{40}$ ), thus decreasing the starting Brønsted acidity and making the  
 834 catalyst insoluble (runs EL\_58–EL\_62, Table 9).  $KH_2PW_{12}O_{40}$  was identified as the best catalyst,  
 835 leading to a similar maximum EL yield than that achieved with  $AgH_2PW_{12}O_{40}$ , and involving a  
 836 cheaper synthesis with KCl precursor, instead of  $AgNO_3$ . Moreover, the authors proved that the  
 837 addition of toluene strongly increased the EL yield from fructose, from 51 mol% (with pure EtOH) to  
 838 69 mol%, which was attributed to the EL extraction into the toluene phase, which prevented the  
 839 product degradation. Good EL yields were ascertained also from inulin and sucrose, whilst once  
 840 again unsatisfactory EL yields were obtained from glucose and cellulose. Similarly, Srinivasa *et al.*  
 841 [130] exchanged the protons of  $H_3PW_{12}O_{40}$  with titanium, thus adding Lewis acid sites, and reached a  
 842 maximum EL yield of 63 and 21 mol%, starting from fructose and glucose, respectively (runs  
 843 EL\_63–EL\_64, Table 9). Pinheiro *et al.* [93] synthesized several tin salts of  $H_4SiW_{12}O_{40}$ , which were  
 844 almost insoluble in an alcohol medium, and compared their performances towards the EL synthesis  
 845 starting from different saccharides (runs EL\_65–EL\_67, Table 9). The authors demonstrated that  
 846  $Sn_2SiW_{12}O_{40}$  was the most active catalyst, leading to promising EL yields starting from fructose,  
 847 sucrose, and inulin and the proton exchange by  $Sn^{2+}$  had a beneficial effect on the EL selectivity. The  
 848 very high yield from sucrose (78 mol%), the disaccharide of fructose and glucose, was ascribed to a  
 849 contribution of glucose unit, which after has been released on the catalytic site, is directly isomerized  
 850 to fructose and then is converted to EL. However, when glucose was employed as the starting  
 851 feedstock, the EL yield was very low (about 5 mol%), probably due to the significant formation of  
 852 by-products from this substrate [93]. Besides, the replacement of protons of HPAs with organic  
 853 species was proposed by Fang *et al.* [99], who synthesized different phosphotungstic acid-based  
 854 solid hybrids, through the reaction between  $H_3PW_{12}O_{40}$  and different pyridines. The  
 855 3-phenylpyridine-phosphotungstate (3-PhPyPW) resulted the most active catalyst, giving the best  
 856 EL yield of 30 mol%, starting from fructose (run EL\_68, Table 9). Recently, also ionic liquids have  
 857 been employed for modifying the acidity, polarity, surface properties and solubility of POMs. A  
 858 noteworthy example is provided by Chen *et al.* [96], who employed the ionic liquid  
 859  $N,N,N',N'$ -tetramethyl- $N,N'$ -dipropanesulfonic acid-1,6-hexanediammonium (TMEDAPS) for  
 860 preparing the corresponding POM salt,  $[TMEDAPS]_3[PW_{12}O_{40}]_2$ , which was tested for the  
 861 ethanolysis of different substrates, achieving the highest EL yield of 80 mol% from fructose (runs  
 862 EL\_69–EL\_74, Table 9). Analogously, Song *et al.* [97] proposed the use of the  
 863 1-(3-sulfopropyl)pyridinium as ionic liquid to synthesize the  $[PyPS]_3PW_{12}O_{40}$  catalyst, which gave  
 864 the best EL yield of 57 mol%, starting from cellulose (run EL\_75, Table 9).

865 The performances of acid zeolite-based catalysts have been studied for the synthesis of EL from  
 866 C6 carbohydrates, as reported in Table 10.

867 **Table 10.** Zeolite-based catalysts for the EL production from C6 model carbohydrates, under  
 868 conventional heating.

Entry	Feedstock	Catalyst	Cat.(g)/EtOH(g) <sup>1</sup>	T (°C)	t (h)	Y <sub>EL</sub> (mol%)	Ref.
EL_76	Fructose	HY	0.31/18.2	230	3	53	[131]
EL_77	Glucose	HY	1.00/64.0	170	12	39	[132]
EL_78	Glucose	H-β (19)	0.60/31.6	160	20	28	[102]
EL_79	Fructose	H-USY (6)	0.60/31.6	160	20	40	[102]

EL_80	Glucose	H-USY (6)	0.60/31.6	160	20	41	[102]
EL_81	Mannose	H-USY (6)	0.60/31.6	160	20	44	[102]
EL_82	Sucrose	H-USY (6)	0.63/32.9	160	20	35	[102]
EL_83	Maltose	H-USY (6)	0.60/31.6	160	20	47	[102]
EL_84	Cellobiose	H-USY (6)	0.63/32.9	160	20	44	[102]
EL_85	Inulin	H-USY (6)	0.68/35.9	160	20	39	[102]
EL_86	Glucose	USY	0.03/39.4	180	2	47	[118]
EL_87	Glucose	USY + H <sub>2</sub> SO <sub>4</sub> (100 wt%)	0.02+0.001/39.4	180	2	51	[133]
EL_88	Glucose	Sn-β + ZrH <sub>2</sub> PW <sub>12</sub> O <sub>40</sub>	0.40+0.10/26.4	180	3	54	[134]
EL_89	Fructose	H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> /H-ZSM-5 <sup>2</sup>	1.50/39.2	160	2	43	[127]
EL_90	Glucose	H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> /H-ZSM-5 <sup>2</sup>	1.50/39.2	160	2	19	[127]
EL_91	Sucrose	H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> /H-ZSM-5 <sup>2</sup>	1.50/39.2	160	2	27	[127]
EL_92	Inulin	H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> /H-ZSM-5 <sup>2</sup>	1.50/39.2	160	2	37	[127]

869 <sup>1</sup> The amounts of catalyst and EtOH have been normalized to 1g of feedstock.

870 <sup>2</sup> "H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>/H-ZSM-5" stands for "H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> supported on H-ZSM-5".

871

872

873 Zeolite HY was tested for the EL synthesis from fructose (run EL\_76, Table 10) [131] and glucose  
 874 (run EL\_77, Table 10) [132] reaching the yields of 53 and 39 mol%, respectively, under the optimized  
 875 reaction conditions. The catalytic performances of zeolites H-β and H-USY, having different Si/Al  
 876 ratios, were compared by Saravanamurugan *et al.* [102] for the EL synthesis from glucose. Zeolites  
 877 H-β (Si/Al ratio = 19) and H-USY (Si/Al ratio = 6) gave EL yields of 28 and 41 mol%, respectively  
 878 (runs EL\_78–EL\_85, Table 10). Zeolite H-USY (6) was effectively adopted for the ethanolysis of  
 879 other mono- and polysaccharides, leading to similar EL yields (35–47 mol%). Xu *et al.* [118]  
 880 investigated the glucose alcoholysis, in the presence of the zeolite USY as the catalyst, and compared  
 881 its performances with those of H<sub>2</sub>SO<sub>4</sub>, in both cases working at 180 °C (compare run EL\_86, Table 10  
 882 with run EL\_2, Table 7). The authors obtained similar EL yields, but the zeolite USY gave the  
 883 maximum EL yield (47 mol%) after 2 h, whereas H<sub>2</sub>SO<sub>4</sub> needed of shorter reaction time (0.5 h) to get  
 884 the maximum EL yield (45 mol%), being this difference ascribed to mass transfer limitations  
 885 occurring between the solid zeolite and the liquid phase. However, zeolite USY led to a remarkable  
 886 higher selectivity to EL, whereas diethyl ether formation was almost negligible. The combined use of  
 887 zeolites and other co-catalysts has been proposed to better tune the bulk Brønsted-Lewis acidities.  
 888 For instance, Chang *et al.* [133] proved that the addition of H<sub>2</sub>SO<sub>4</sub> to the zeolite USY strongly  
 889 improved the EL yield from glucose, which increased from 38 to 51 mol% (run EL\_87, Table 10). USY  
 890 zeolite resulted efficient for the conversion of glucose to 5-ethoxymethylfurfural, but the stronger  
 891 Brønsted acidity of H<sub>2</sub>SO<sub>4</sub> enhanced the overall alcoholysis, improving the EL yield. The zeolites  
 892 were also employed in combination with POMs. For example, Mulik *et al.* [134] used Sn-β zeolite  
 893 with ZrH<sub>2</sub>PW<sub>12</sub>O<sub>40</sub> for the synthesis of EL from glucose (run EL\_88, Table 10), demonstrating that  
 894 this synergy was fundamental to achieve the best EL yields. The POM salt contributed to the  
 895 catalysis with both Brønsted and Lewis acidity, but the latter was insufficient, and this lack is offset  
 896 just by the Sn-Beta zeolite. In particular, the ratio ZrH<sub>2</sub>PW<sub>12</sub>O<sub>40</sub>/Sn-β of 80/20 wt/wt, corresponding  
 897 to the Brønsted/Lewis ratio of 3.7, gave the best EL yield (54 mol%). Lastly, cheap H-ZSM-5 zeolite  
 898 was employed as support of high surface area for anchoring the H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, thus overcoming the  
 899 solubility drawback of the latter (runs EL\_89–EL\_92, Table 10) [127]. However, after the  
 900 immobilization, the catalytic activity of H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> decreased, and the highest EL yield of 43 mol%  
 901 was achieved starting from fructose, a lower value than that obtained in the presence of  
 902 unsupported HPA (50 mol%) (run EL\_54, Table 9) [127], although the advantage of this immobilized  
 903 catalyst lies in its good recyclability. Moreover, this catalytic system was successfully employed by  
 904 the authors also for the EL synthesis from glucose, sucrose, and inulin, achieving moderate EL  
 905 yields.

906 Metal oxides, also in combination with zeolites, resulted exploitable catalysts for the synthesis  
 of EL from fructose and glucose and the most interesting results are reported in Table 11.



907  
908**Table 11.** Metal oxides and tungsten disulfide catalysts for the EL production from C6 model carbohydrates.

Entry	Feedstock	Catalyst	Cat.(g)/EtOH(g) <sup>1</sup>	T (°C)	t (h)	Heat <sup>2</sup>	Y <sub>EL</sub> (mol%)	Ref.
EL_93	Fructose	TiO <sub>2</sub> nanoparticles	0.56/87.8	150	3	Conv.	71	[113]
EL_94	Fructose	MCM-41	0.80/78.0	150	3.5	Conv.	25	[124]
EL_95	Fructose	SO <sub>4</sub> <sup>2-</sup> /ZrO <sub>2</sub>	0.80/78.0	150	3.5	Conv.	44	[124]
EL_96	Glucose	SO <sub>4</sub> <sup>2-</sup> /ZrO <sub>2</sub>	0.02/15.8	200	3	Conv.	29	[135]
EL_97	Glucose	SO <sub>4</sub> <sup>2-</sup> /ZrO <sub>2</sub> @Al <sub>2</sub> O <sub>3</sub>	0.50/61.1	200	5	Conv.	37	[136]
EL_98	Glucose	Grafted SO <sub>4</sub> <sup>2-</sup> /ZrO <sub>2</sub> /SBA-15	0.50/25.6	140	24	Conv.	31	[114]
EL_99	Glucose	SO <sub>4</sub> <sup>2-</sup> /ZrO <sub>2</sub> -PMO-SO <sub>3</sub> H <sup>2</sup>	1.00/64.0	170	12	Conv.	42	[132]
EL_100	Fructose	Al <sub>2</sub> O <sub>3</sub> /SBA-15	1.00/78.0	190	4	Conv.	58	[137]
EL_101	Fructose	DMSi-SA <sup>3</sup>	0.81/13.3	170	24	Conv.	83	[138]
EL_102	Glucose	DMSi-SA <sup>3</sup>	0.81/13.3	170	24	Conv.	62	[138]
EL_103	Sucrose	DMSi-SA <sup>3</sup>	0.81/13.3	170	24	Conv.	90	[138]
EL_104	Glucose	SnO <sub>2</sub> + H-USY	0.03+0.48/15.8	180	3	Conv.	81	[139]
EL_105	Fructose	WS <sub>2</sub>	0.40/21.7	160	0.5	MW	23	[116]

909 <sup>1</sup> The amounts of catalyst and EtOH have been normalized to 1g of feedstock.910 <sup>2</sup> "SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub>-PMO-SO<sub>3</sub>H" stands for "Ordered mesoporous sulfonic acid functionalized ZrO<sub>2</sub>/organosilica".911 <sup>3</sup> "DMSi-SA" stands for "Sulfonated dendritic mesoporous silica nanospheres".

912 Among the commercial metal oxides, TiO<sub>2</sub> nanoparticles gave promising results in the EL  
913 synthesis from fructose affording the best EL yield of 71 mol% (run EL\_93, Table 11) [113]. Gu *et al.*  
914 [124] studied the fructose ethanolysis in the presence of commercial MCM-41 and SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub>  
915 catalysts, comparing their catalytic performances with those of synthesized sulfonated  
916 hyper-cross-linked polymers (HDS-3.6). Both commercial MCM-41 and SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub> catalysts led to  
917 moderate EL yields, equal to 25 and 44 mol% respectively (runs EL\_94–EL\_95, Table 11), whilst the  
918 synthesized HDS-3.6 gave the higher EL yield of 70 mol% (run EL\_35, Table 8). The lower EL yields  
919 with MCM-41 and SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub> catalysts were ascribed to the few acid sites and low surface area-pore  
920 volume, respectively. The use of SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub> for the alcoholysis of carbohydrates was largely  
921 investigated by other authors. For instance, Peng *et al.* [135] compared the catalytic activities of  
922 SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub>, SO<sub>4</sub><sup>2-</sup>/TiO<sub>2</sub>, SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub>-TiO<sub>2</sub>, SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts in the EL synthesis from glucose.  
923 SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup>/TiO<sub>2</sub> exhibited the best activities towards the EL production with 29 mol%  
924 yield, but SO<sub>4</sub><sup>2-</sup>/TiO<sub>2</sub> increased the formation of undesired diethyl ether, thus SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub> resulted the  
925 best catalyst system for EL production (run EL\_96, Table 11). Zhang *et al.* [136] encapsulated  
926 SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub> into a mesoporous Al<sub>2</sub>O<sub>3</sub> (SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub>@Al<sub>2</sub>O<sub>3</sub>), obtaining a catalyst with superacid  
927 properties. The latter showed both Brønsted and Lewis acid sites, affording the EL yield of 37 mol%  
928 (run EL\_97, Table 11), which was stable after four recycling tests. Morales *et al.* [114] grafted  
929 SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub> on SBA-15. ZrO<sub>2</sub> monolayers were grafted on the SBA-15 surface and then the sulfation  
930 was carried out with a solution of H<sub>2</sub>SO<sub>4</sub>. The complete coverage of the SBA-15 surface was achieved  
931 with two layers of SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub> and this catalyst had the best acid density and the appropriate  
932 Brønsted/Lewis acid ratio for EL synthesis from glucose in the presence of Lewis acid sites that  
933 promote the glucose isomerization to fructose. The best EL yield of 31 mol% was obtained with such  
934 catalyst, adopting milder reaction conditions (temperature of 140 °C) (run EL\_98, Table 11), but too  
935 long reaction time was involved. Song *et al.* [132] realized the EL synthesis from glucose with an  
936 ordered mesoporous sulfonic acid functionalized ZrO<sub>2</sub>/organosilica catalyst (SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub>-  
937 PMO-SO<sub>3</sub>H). This catalyst was characterized by the synergistic effect of super-strong Brønsted acid  
938 sites (SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub> and -SO<sub>3</sub>H) and medium Lewis ones (Zr<sup>4+</sup>), and the EL yield of 42 mol% was  
939 obtained under the optimized reaction conditions (run EL\_99, Table 11). Babaei *et al.* [137] prepared  
940 an alumina-coated mesoporous silica SBA-15 catalyst (Al<sub>2</sub>O<sub>3</sub>/SBA-15), obtaining the maximum EL  
941 yield of 58 mol% from fructose (run EL\_100, Table 11). When the amount of alumina was increased,

942 the total acidity concentration increased and the Lewis/Brønsted ratio decreased, and a lower yield  
 943 of EL was ascertained, which was ascribed to the humin formation, which is favored by an excess of  
 944 Brønsted acidity. Besides, the authors proved that the specific surface area of the final catalyst was  
 945 higher adopting a lower amount of alumina, which guaranteed a better dispersion of the active sites,  
 946 having a positive effect on the catalytic performances. Jorge *et al.* [138] prepared SBA-15, KCC-1,  
 947 MCM-41, and dendritic mesoporous silica nanospheres (DMSi), and the resulting catalyst was  
 948 functionalized with sulfonic acid. The sulfonated KCC-1, MCM-41 and SBA-15 exhibited moderate  
 949 catalytic activity towards glucose conversion, obtaining EL yields in the range 14-19 mol%, these  
 950 resulting significantly lower than that observed with the DMSi-SA catalyst (EL yield of 62 mol%)  
 951 (run EL\_102, Table 11). This catalyst gave excellent EL yields also for fructose and sucrose (EL yields  
 952 of 83 and 90 mol%, respectively) (runs EL\_101 and EL\_103, Table 11). The better performances of  
 953 DMSi-SA catalyst were attributed to its high porosity, which led to a high number of exposed  
 954 functionalizable silanol groups. The use of metal oxides in combination with other catalysts was  
 955 reported by Heda *et al.* [139], who employed SnO<sub>2</sub> with the zeolite H-USY for the synthesis of EL  
 956 from glucose. Also in this study, the synergy between the different components was fundamental  
 957 because SnO<sub>2</sub> had a high amount of strong Lewis acid sites for glucose-fructose isomerization, while  
 958 H-USY afforded the proper amount of Brønsted sites. The remarkable yield of 81 mol% was  
 959 achieved with the catalytic system SnO<sub>2</sub>+ H-USY (run EL\_104, Table 11). Lastly, tungsten disulfide  
 960 was proposed by Quereshi *et al.* [116] for the MW-assisted EL synthesis from fructose, but only a  
 961 moderate EL yield of 23 mol% was reached (run EL\_105, Table 11).

962 Ionic liquids have been also proposed as efficient catalysts for the synthesis of EL from C6  
 963 carbohydrates but only a few works reported their use for this reaction, due to their high cost,  
 964 multistep synthesis and environmental concerns. The available data are reported in Table 12.

965 **Table 12.** Ionic liquid catalysts for the EL production from C6 model carbohydrates, under  
 966 conventional heating.

Entry	Feedstock	Catalyst	Cat.(g)/EtOH(g) 1	T (°C)	t (h)	Y <sub>EL</sub> (mol%)	Ref.
EL_106	Fructose	[BMIm-SO <sub>3</sub> H][HSO <sub>4</sub> ] <sup>2</sup>	0.11/14.8	140	24	68	[140]
EL_107	Sucrose	[BMIm-SO <sub>3</sub> H][HSO <sub>4</sub> ] <sup>2</sup>	0.11/14.8	140	24	41	[140]
EL_108	Fructose	[BPyR-SO <sub>3</sub> H][HSO <sub>4</sub> ] <sup>3</sup>	0.11/14.8	140	24	70	[140]
EL_109	Sucrose	[BPyR-SO <sub>3</sub> H][HSO <sub>4</sub> ] <sup>3</sup>	0.11/14.8	140	24	43	[140]
EL_110	Fructose	[NEt <sub>3</sub> B-SO <sub>3</sub> H][HSO <sub>4</sub> ] <sup>4</sup>	0.15/14.8	140	24	74	[140]
EL_111	Sucrose	[NEt <sub>3</sub> B-SO <sub>3</sub> H][HSO <sub>4</sub> ] <sup>4</sup>	0.15/14.8	140	24	41	[140]
EL_112	Fructose	[BMIm-SO <sub>3</sub> H][NTf <sub>2</sub> ] <sup>5</sup>	0.19/14.8	140	24	77	[140]
EL_113	Sucrose	[BMIm-SO <sub>3</sub> H][NTf <sub>2</sub> ] <sup>5</sup>	0.19/14.8	140	24	43	[140]
EL_114	Fructose	[BMIm-SO <sub>3</sub> H][OMs] <sup>6</sup>	0.11/14.8	140	24	67	[140]
EL_115	Sucrose	[BMIm-SO <sub>3</sub> H][OMs] <sup>6</sup>	0.11/14.8	140	24	40	[140]
EL_116	Fructose	[BMIm-SO <sub>3</sub> H][OTf] <sup>7</sup>	0.15/14.8	140	24	69	[140]
EL_117	Sucrose	[BMIm-SO <sub>3</sub> H][OTf] <sup>7</sup>	0.15/14.8	140	24	42	[140]
EL_118	Cellulose	[PSMIm][Cl] <sup>8</sup>	0.33/2.1 <sup>9</sup>	170	12	19	[141]

967 <sup>1</sup> The amounts of catalyst and EtOH/co-solvent have been normalized to 1g of feedstock.

968 <sup>2</sup> “[BMIm-SO<sub>3</sub>H][HSO<sub>4</sub>]” stands for “1-methyl-3-(4-sulfobutyl)imidazolium hydrogensulfate”.

969 <sup>3</sup> “[BPyR-SO<sub>3</sub>H][HSO<sub>4</sub>]” stands for “1-(4-sulfobutyl)pyridinium hydrogensulfate”.

970 <sup>4</sup> “[NEt<sub>3</sub>B-SO<sub>3</sub>H][HSO<sub>4</sub>]” stands for “N,N,N-triethyl-4-sulfobutan-ammonium hydrogensulfate”.

971 <sup>5</sup> “[BMIm-SO<sub>3</sub>H][NTf<sub>2</sub>]” stands for “1-methyl-3-(4-sulfobutyl)imidazolium  
 972 bis((trifluoromethyl)sulfonyl)amide”.

973 <sup>6</sup> “[BMIm-SO<sub>3</sub>H][OMs]” stands for “1-methyl-3-(4-sulfobutyl)imidazolium methanesulfonate”.

974 <sup>7</sup> “[BMIm-SO<sub>3</sub>H][OTf]” stands for “1-methyl-3-(4-sulfobutyl)imidazolium trifluoromethanesulfonate”.

975 <sup>8</sup> “[PSMIm][Cl]” stands for “1-(1-propylsulfonic)-3-methylimidazolium chloride”.

976 <sup>9</sup> 1.7 g of water were added to this reaction mixture.

977

978 Saravanamurugan *et al.* [140] investigated the catalytic performances of several ionic liquids  
 979 with acidic functionalities for the ethanolsis of fructose and sucrose (runs EL\_106–EL\_117, Table  
 980 12). In particular, they synthesized imidazolium-, pyridinium- and ammonium-based SO<sub>3</sub>H ionic  
 981 liquids, having HSO<sub>4</sub><sup>-</sup> as the anion, and imidazolium-based ionic liquids having [NTf<sub>2</sub>]<sup>-</sup>, [OMs]<sup>-</sup> or  
 982 [OTf]<sup>-</sup> as the counter anion. Among these catalysts, [BMIm-SO<sub>3</sub>H][NTf<sub>2</sub>] gave the highest EL yield  
 983 of 77 mol% from fructose and 40–43 mol% from sucrose, indicating that only fructose moieties were  
 984 promptly converted, whilst the isomerization of glucose to fructose was more difficult. In fact, under  
 985 these reaction conditions, glucose was converted to ethyl-D-glucopyranoside, an important  
 986 non-ionic surfactant that can find applications in cosmetics and pharmaceutical formulations.  
 987 Amarasekara *et al.* [141] adopted the Brønsted acid ionic liquid  
 988 1-(1-propylsulfonic)-3-methylimidazolium chloride ([PSMIm][Cl]) for the synthesis of EL from  
 989 cellulose in a (water-EtOH) solution. The authors found that cellulose conversion in sole EtOH was  
 990 low and highlighted the key role of water co-solvent for promoting the hydrolysis of cellulose to  
 991 glucose. Once the glucose was formed in the reaction medium, [PSMIm][Cl] catalyzed the  
 992 dehydration of glucose to HMF, passing through the isomerization to fructose, and the synthesis of  
 993 EL, with a yield of 19 mol% (run EL\_118, Table 12).

994

## 995 2.3 PL synthesis from model carbohydrates

996 The available data for the PL synthesis, including the *n*-PL and *i*-PL isomers, are reported in  
 997 Table 13, taking into account the C6 model carbohydrates:

998

Table 13. Catalysts for the PL production from C6 model carbohydrates.

Entry	Feedstock	Catalyst	Cat.(g)/PrOH(g) <sup>1</sup>	T (°C)	t (h)	Heat <sup>2</sup>	Y <sub>PL</sub> (mol%)	Ref.
PL_1	Cellulose	H <sub>2</sub> SO <sub>4</sub> (100 wt%)	0.18/7.0 ( <i>n</i> ) <sup>3</sup>	190	0.25	Conv.	35	[69]
PL_2	Cellulose	H <sub>2</sub> SO <sub>4</sub> (96 wt%)	0.42/10.0 ( <i>i</i> ) <sup>4</sup>	170	2	Conv.	41	[121]
PL_3	Fructose	HReO <sub>4</sub>	0.14/21.7 ( <i>i</i> ) <sup>4</sup>	160	16	Conv.	22	[72]
PL_4	Fructose	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	2.24/9.0 ( <i>i</i> ) <sup>4</sup>	170	2	Conv.	61	[73]
PL_5	Glucose	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	2.24/9.0 ( <i>i</i> ) <sup>4</sup>	170	2	Conv.	55	[73]
PL_6	Cellulose	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.42/22.0 ( <i>i</i> ) <sup>4</sup>	180	1.3	MW	54	[32]
PL_7	Fructose	Amberlyst-15	0.40/64.0 ( <i>n</i> ) <sup>3</sup>	120	24	Conv.	80	[80]
PL_8	Cellulose	Acid resin D008	2.40/10.0 ( <i>i</i> ) <sup>4</sup>	170	2	Conv.	16	[121]
PL_9	Fructose	PSSA-g-CNT <sup>5</sup>	0.40/64.0 ( <i>n</i> ) <sup>3</sup>	120	24	Conv.	86	[80]
PL_10	Fructose	PSSA-g-CNF <sup>6</sup>	0.40/64.0 ( <i>n</i> ) <sup>3</sup>	120	24	Conv.	75	[80]
PL_11	Fructose	BSA-g-CMK-5 <sup>7</sup>	0.40/64.0 ( <i>n</i> ) <sup>3</sup>	120	24	Conv.	68	[80]
PL_12	Fructose	BSA-g-CNT <sup>8</sup>	0.40/64.0 ( <i>n</i> ) <sup>3</sup>	120	24	Conv.	54	[80]
PL_13	Cellulose	5-Cl-SHPAO <sup>9</sup>	0.25/20.0 ( <i>n</i> ) <sup>3</sup>	160	8	Conv.	60	[84]
PL_14	Glucose	H-USY (6)	0.60/32.0 ( <i>n</i> ) <sup>3</sup>	160	20	Conv.	17	[102]
PL_15	Fructose	Sn <sub>2</sub> SiW <sub>12</sub> O <sub>40</sub>	1.67/66.7 ( <i>n</i> ) <sup>3</sup>	150	2	Conv.	74	[93]
PL_16	Fructose	3-PhPyPW <sup>10</sup>	0.50/22.2 ( <i>n</i> ) <sup>3</sup>	140	8	Conv.	22	[99]
PL_17	Fructose	[TMEDAPS] <sub>3</sub> [PW <sub>12</sub> O <sub>40</sub> ] <sub>2</sub> <sup>11</sup>	1.00/64.0 ( <i>n</i> ) <sup>3</sup>	120	12	Conv.	83	[96]
PL_18	Cellulose	[PyPS] <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> <sup>12</sup>	10.49/98.7 ( <i>n</i> ) <sup>3</sup>	150	5	Conv.	37	[97]
PL_19	Cellulose	[PyPS] <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> <sup>12</sup>	10.49/98.7 ( <i>i</i> ) <sup>4</sup>	150	5	Conv.	22	[97]
PL_20	Fructose	TiO <sub>2</sub> nanoparticles	0.56/88.9 ( <i>n</i> ) <sup>3</sup>	150	3	Conv.	78	[113]
PL_21	Fructose	TiO <sub>2</sub> nanoparticles	0.56/88.9 ( <i>i</i> ) <sup>4</sup>	150	3	Conv.	13	[113]
PL_22	Glucose	Grafted SO <sub>4</sub> <sup>2-</sup> /ZrO <sub>2</sub> /SBA-15	0.50/25.6 ( <i>i</i> ) <sup>4</sup>	140	24	Conv.	10	[114]

999 <sup>1</sup> The amounts of catalyst and PrOH have been normalized to 1g of feedstock.1000 <sup>2</sup> "Conv." and "MW" stand for "Conventional" and "Microwave", respectively.1001 <sup>3</sup> "(*n*)" stands for "*n*-propanol".1002 <sup>4</sup> "(*i*)" stands for "*iso*-propanol".1003 <sup>5</sup> "PSSA-g-CNT" stands for "poly(*p*-styrenesulfonic acid)-grafted carbon nanotubes".

- 1004 <sup>6</sup> "PSSA-g-CNF" stands for "poly(*p*-styrenesulfonic acid)-grafted carbon nanofibers".
- 1005 <sup>7</sup> "BSA-g-CMK-5" stands for "benzenesulfonic acid-grafted carbon mesostructured by KAIST-5".
- 1006 <sup>8</sup> "BSA-g-CNT" stands for "benzenesulfonic acid-grafted carbon nanotubes".
- 1007 <sup>9</sup> "5-Cl-SHPAO" stands for "sulfonated hyperbranched poly(arylene oxindole) with chloride substituent in the
- 1008 fifth position of isatin".
- 1009 <sup>10</sup> "3-PhPyPW" stands for "3-phenylpyridine phosphotungstate".
- 1010 <sup>11</sup> "TMEDAPS" stands for "*N,N,N',N'*-tetramethyl-*N,N'*-dipropanesulfonic acid-1,6-hexanediammonium".
- 1011 <sup>12</sup> "PyPS" stands for "1-(3-sulfopropyl)pyridinium".

1012

1013 Garves *et al.* [69] confirmed similar molar yields for the H<sub>2</sub>SO<sub>4</sub> catalyzed production of *n*-PL and  
1014 that of the shortest ML, carried under similar reaction conditions (compare run PL\_1, Table 13 with  
1015 run ML\_6, Table 1). As above observed for the ML and EL synthesis, the production of *i*-PL from C6  
1016 carbohydrates was carried out mainly in the presence of strong Brønsted homogeneous acids, such  
1017 as H<sub>2</sub>SO<sub>4</sub> (run PL\_2, Table 13) [121], HReO<sub>4</sub> (run PL\_3, Table 13) [72], and with inorganic salts, such  
1018 as Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (runs PL\_4–PL\_5, Table 13) [73] and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (run PL\_6, Table 13) [32]. However, the  
1019 use of *i*-PrOH as the solvent/reagent caused a drastic decrease of the *i*-PL yield, respect to those  
1020 observed with lower alcohols. In fact, the *i*-PL yield was 41, 22 and 54 mol% with H<sub>2</sub>SO<sub>4</sub>, HReO<sub>4</sub> and  
1021 Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, respectively, values lower than the EL and ML yields achieved under analogous reaction  
1022 conditions (runs EL\_10–EL\_11, Table 7; run ML\_11, Table 1; run ML\_29, Table 1). Moreover, in the  
1023 presence of HReO<sub>4</sub>, also some by-products, such as HMF (4 mol%) and the corresponding  
1024 5-alkoxymethylfurfural derivative (20 mol%), were produced, proving that *i*-PrOH is not an  
1025 excellent solvent for the selective AL synthesis [72]. This can be due to the branched-chain of *i*-PrOH,  
1026 resulting in a higher steric hindrance. On the other hand, several sulfonic acids have been proposed  
1027 for the synthesis of both *n*-PL and *i*-PL. The synthesis of *n*-PL from fructose was carried out by Liu *et*  
1028 *al.* [80] in the presence of the commercial Amberlyst-15 resin, achieving the best *n*-PL yield of 80  
1029 mol% (run PL\_7, Table 13). These catalytic performances were compared with those of synthesized  
1030 sulfonated carbonaceous materials (PSSA-g-CNT, PSSA-g-CNF, BSA-g-CMK-5, BSA-g-CNT).  
1031 Promising *n*-PL yields were reached, between 54–86 mol% (runs PL\_9–PL\_12, Table 13), depending  
1032 on the adopted catalyst, and comparable with those reached employing shorter-chain EtOH (runs  
1033 EL\_31–EL\_34, Table 8). Commercial D008 sulfonic acid resin was employed for the synthesis of *i*-PL  
1034 starting from cellulose [121], but the corresponding molar yield was low (16 mol%, according to run  
1035 PL\_8, Table 13), especially if compared with that reached in the presence of the mineral acid H<sub>2</sub>SO<sub>4</sub>  
1036 (run PL\_2, Table 13). Zhang *et al.* [84] prepared a new sulfonic acid, the system 5-chloro-sulfonated  
1037 hyperbranched poly(arylene oxindole) (5-Cl-SHPAO), which was used for the synthesis of *n*-PL  
1038 from cellulose, achieving the best yield of 60 mol% (run PL\_13, Table 13), a value comparable with  
1039 that obtained from the cellulose ethanolysis (run EL\_44, Table 8). Zeolites have been poorly  
1040 investigated for the synthesis of PL from carbohydrates, leading to unsatisfactory PL yields. For  
1041 example, zeolite H-USY gave the maximum PL yield of 17 mol% from glucose (run PL\_14, Table 13)  
1042 [102]. On the contrary, POMs have been much considered for the synthesis of the two PL isomers,  
1043 starting from fructose and cellulose, and obtaining interesting results (runs PL\_15–PL\_19, Table 13)  
1044 [93,96,97,99]. In particular, Song *et al.* [97] compared the performances of [PyPS]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> towards  
1045 the cellulose alcoholysis, in the presence of *n*-PrOH or *i*-PrOH. The authors obtained the best *n*-PL  
1046 and *i*-PL yields of 37 and 22 mol%, respectively, thus confirming that the higher steric hindrance of  
1047 *i*-PrOH negatively affected the alcoholysis reaction. This conclusion is further supported by the  
1048 work of Kuo *et al.* [113], where TiO<sub>2</sub> nanoparticles were employed for the fructose alcoholysis,  
1049 achieving the maximum *i*-PL and *n*-PL yields of 13 and 78 mol%, respectively, working under the  
1050 same reaction conditions (runs PL\_20–PL\_21, Table 13). Few other metal oxides have been used for  
1051 the *i*-PL synthesis from glucose, such as grafted SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub>/SBA-15, which led to the best yield of 10  
1052 mol% (run PL\_22, Table 13), lower than that obtained from the ethanolysis reaction (run EL\_27,  
1053 Table 8) [114].

1054

1055 2.4 BL and longer-chain AL (PeL and HL) synthesis from model carbohydrates

1056 Most interesting data related to the synthesis of BL, PeL and HL from model C6 carbohydrates  
1057 are reported in Table 14:

1058 **Table 14.** Catalysts for the BL, PeL and HL production from C6 model carbohydrates.

Entry	Feedstock	Catalyst	Cat.(g)/Alcohol (g) <sup>1</sup>	T (°C)	t (h)	Heat <sup>2</sup>	Y (mol%)	Ref.
BL_1	Cellulose	H <sub>2</sub> SO <sub>4</sub> (100 wt%)	0.17/7.5 ( <i>n</i> ) <sup>3</sup>	210	0.17	Conv.	40	[142]
BL_2	Cellulose	H <sub>2</sub> SO <sub>4</sub> (100 wt%)	0.18/7.0 ( <i>i</i> ) <sup>4</sup>	210	0.25	Conv.	40	[69]
BL_3	Cellulose	H <sub>2</sub> SO <sub>4</sub> (96 wt%)	25.00/100.0 ( <i>n</i> ) <sup>3</sup>	130	20	Conv.	60	[143]
BL_4	Cellulose	H <sub>2</sub> SO <sub>4</sub> (96 wt%)	42.86/100.0 ( <i>n</i> ) <sup>3</sup>	130	5	Conv.	60	[143]
BL_5	Cellulose	H <sub>2</sub> SO <sub>4</sub> (100 wt%)	0.25/40.0 ( <i>n</i> ) <sup>3</sup>	200	0.5	Conv.	50	[144]
BL_6	Cellulose	H <sub>2</sub> SO <sub>4</sub> (100 wt%)	0.25/40.0 ( <i>i</i> ) <sup>4</sup>	200	0.5	Conv.	45	[144]
BL_7	Cellulose	H <sub>2</sub> SO <sub>4</sub> (100 wt%)	0.25/40.0 ( <i>s</i> ) <sup>5</sup>	200	0.5	Conv.	13	[144]
BL_8	Fructose	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.20/32.4 ( <i>n</i> ) <sup>3</sup>	190	3	Conv.	63	[145]
BL_9	Glucose	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.20/32.4 ( <i>n</i> ) <sup>3</sup>	190	3	Conv.	40	[145]
BL_10	Sucrose	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.20/32.4 ( <i>n</i> ) <sup>3</sup>	190	3	Conv.	50	[145]
BL_11	Inulin	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.20/32.4 ( <i>n</i> ) <sup>3</sup>	190	3	Conv.	57	[145]
BL_12	Cellulose	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.20/32.4 ( <i>n</i> ) <sup>3</sup>	220	3	Conv.	30	[145]
BL_13	Cellulose	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> +Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.48+0.025/40.8 ( <i>n</i> ) <sup>3</sup>	194	3	Conv.	40	[146]
BL_14	Cellulose	Cs <sub>2</sub> HPW <sub>12</sub> O <sub>40</sub>	0.40/40.0 ( <i>n</i> ) <sup>3</sup>	200	1	Conv.	12	[144]
BL_15	Fructose	3-PhPyPW <sup>6</sup>	0.50/22.2 ( <i>n</i> ) <sup>3</sup>	140	8	Conv.	18	[99]
BL_16	Glucose	Zeolite H-USY (6)	0.60/32.4 ( <i>n</i> ) <sup>3</sup>	160	20	Conv.	12	[102]
BL_17	Cellulose	SO <sub>4</sub> <sup>2-</sup> /ZrO <sub>2</sub>	0.40/40.0 ( <i>n</i> ) <sup>3</sup>	200	1	Conv.	13	[144]
BL_18	Glucose	SO <sub>4</sub> <sup>2-</sup> /SnO <sub>2</sub> -ZrO <sub>2</sub>	0.44/16.2 ( <i>n</i> ) <sup>3</sup>	200	2	Conv.	33	[147]
BL_19	Cellulose	SO <sub>4</sub> <sup>2-</sup> /SnO <sub>2</sub> -ZrO <sub>2</sub>	0.44/16.2 ( <i>n</i> ) <sup>3</sup>	200	2	Conv.	10	[147]
BL_20	Glucose	SO <sub>4</sub> <sup>2-</sup> /SnO <sub>2</sub> -ZrO <sub>2</sub> + (COOH) <sub>2</sub>	0.44+0.01/16.2 ( <i>n</i> ) <sup>3</sup>	200	2	Conv.	36	[147]
BL_21	Glucose	SO <sub>4</sub> <sup>2-</sup> /SnO <sub>2</sub> -ZrO <sub>2</sub> + H <sub>2</sub> SO <sub>4</sub> (100 wt%)	0.44+0.01/16.2 ( <i>n</i> ) <sup>3</sup>	200	2	Conv.	40	[147]
BL_22	Cellulose	SO <sub>4</sub> <sup>2-</sup> /SnO <sub>2</sub> -ZrO <sub>2</sub> + H <sub>2</sub> SO <sub>4</sub> (100 wt%)	0.44+0.01/16.2 ( <i>n</i> ) <sup>3</sup>	200	2	Conv.	28	[147]
BL_23	Glucose	SO <sub>4</sub> <sup>2-</sup> /SnO <sub>2</sub> -ZrO <sub>2</sub> + Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.44+0.01/16.2 ( <i>n</i> ) <sup>3</sup>	200	2	Conv.	35	[147]
BL_24	Cellulose	SO <sub>4</sub> <sup>2-</sup> /SnO <sub>2</sub> -ZrO <sub>2</sub> + Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.44+0.01/16.2 ( <i>n</i> ) <sup>3</sup>	200	2	Conv.	18	[147]
BL_25	Glucose	SO <sub>4</sub> <sup>2-</sup> /SnO <sub>2</sub> -ZrO <sub>2</sub> + CuSO <sub>4</sub>	0.44+0.01/16.2 ( <i>n</i> ) <sup>3</sup>	200	2	Conv.	39	[147]
BL_26	Cellulose	SO <sub>4</sub> <sup>2-</sup> /SnO <sub>2</sub> -ZrO <sub>2</sub> + CuSO <sub>4</sub>	0.44+0.01/16.2 ( <i>n</i> ) <sup>3</sup>	200	2	Conv.	19	[147]
BL_27	Glucose	SO <sub>4</sub> <sup>2-</sup> /SnO <sub>2</sub> -ZrO <sub>2</sub> + PTSA <sup>7</sup>	0.44+0.01/16.2 ( <i>n</i> ) <sup>3</sup>	200	2	Conv.	33	[147]
BL_28	Cellulose	SO <sub>4</sub> <sup>2-</sup> /SnO <sub>2</sub> -ZrO <sub>2</sub> + PTSA <sup>7</sup>	0.44+0.01/16.2 ( <i>n</i> ) <sup>3</sup>	200	2	Conv.	23	[147]
BL_29	Cellulose	[C <sub>4</sub> H <sub>8</sub> SO <sub>3</sub> Hmim]HSO <sub>4</sub> <sup>8</sup>	0.10/10.0 ( <i>n</i> ) <sup>3</sup>	180	0.75	Conv.	31	[148]
PeL_1	Cellulose	H <sub>2</sub> SO <sub>4</sub> (100 wt%)	25.4/101.8	138	3	Conv.	69	[150]
PeL_2	Fructose	WS <sub>2</sub>	0.39/21.7	160	0.25	MW	5	[116]
HL_1	Cellulose	H <sub>2</sub> SO <sub>4</sub> (100 wt%)	25.4/101.8	157	1	Conv.	60	[150]
HL_2	Glucose	Zn/DFNS <sup>9</sup>	0.71/58.6	200	5	Conv.	55	[151]

1059 <sup>1</sup> The amounts of catalyst and the respective alcohol have been normalized to 1g of feedstock.

1060 <sup>2</sup> "Conv." and "MW" stand for "Conventional" and "Microwave", respectively.

1061 <sup>3</sup> "(*n*)" stands for "*n*-butanol".

1062 <sup>4</sup> "(*i*)" stands for "*iso*-butanol".

1063 <sup>5</sup> "(*s*)" stands for "*sec*-butanol".

1064 <sup>6</sup> "3-PhPyPW" stands for "3-phenylpyridine phosphotungstate".

1065 <sup>7</sup> "PTSA" stands for "*p*-toluenesulfonic acid".

1066 <sup>8</sup> "[C<sub>4</sub>H<sub>8</sub>SO<sub>3</sub>Hmim]HSO<sub>4</sub>" stands for "1-(4-sulfobutyl)-3-methyl imidazolium hydrosulfate".

1067 <sup>9</sup> "Zn/DFNS" stands for "Zn modified dendritic fibrous nanosilica".

1068 Cellulose butanolysis in the presence of diluted sulfuric acid (about 0.2 mol/L) led to good BL  
1069 yields, about 40 mol%, working under the typical reaction conditions already adopted for the  
1070 previous shorter-chain ALs (runs BL\_1-BL\_2, Table 14) [69,142]. The choice of Hishikawa *et al.* [143]  
1071 of using much higher concentrations of sulfuric acid (2.0-3.5 mol/L), improved the BL yield up to the  
1072 maximum of about 60 mol% (runs BL\_3-BL\_4, Table 14), but such high acid concentrations are not  
1073 advantageous for the sustainability of the process, additionally causing to corrosion problems of the  
1074 equipment. Therefore, diluted mineral acids must be certainly preferred, to avoid these important  
1075 drawbacks. Taking into account the diluted acid approach, the best BL yield (40 mol%, according to  
1076 runs BL\_1-BL\_2, Table 14), is similar to the best one obtained for PL (41 mol%, according to run  
1077 PL\_1, Table 13), whilst is significantly lower for EL (51 mol%, according to EL\_10, Table 7) and  
1078 especially for ML (70 mol%, according to ML\_12, Table 1), thus highlighting that the synthesis of  
1079 ALs in high yield becomes progressively more difficult as the length of the alkyl chain increases. AL  
1080 yield strongly depends also on the steric hindrance of the alkyl chain, as demonstrated by Démolis *et al.*  
1081 [144] for the cellulose butanolysis. In this context, at first, the authors studied the liquefaction of  
1082 cellulose in butanol isomers (1-butanol, iso-butanol, *sec*-butanol, *tert*-butanol) in the absence of the  
1083 acid catalyst, carried out under supercritical conditions (300 °C) and with different reaction times (1  
1084 and 2 h), achieving cellulose liquefaction in the range 70–85%, to give soluble oligomers and  
1085 polymers. Despite the similar liquefaction performances of the different butanol isomers, in the case  
1086 of *tert*-butanol, a significant loss of alcohol (50 wt%) occurred, with the concomitant pressure  
1087 increase, due to the formation of gaseous products, as a consequence of the significant dehydration  
1088 of *tert*-butanol to iso-butene, thus anticipating that this butanol isomer is less attractive for  
1089 developing this reaction. Then, the authors investigated the acid-catalyzed alcoholysis of cellulose in  
1090 1-butanol under subcritical conditions, employing very diluted H<sub>2</sub>SO<sub>4</sub> (0.05 mol/L), and optimizing  
1091 the reaction temperature and time. The highest BL yield was achieved after 1 h at 200 °C (about 50  
1092 mol%), but a significant formation of dibutyl ether occurred (yield of 36 mol%). A reaction time of  
1093 0.5 h was found to be the best compromise for reducing the dibutyl ether yield (20 mol%), keeping  
1094 high the BL yield (50 mol%, according to run BL\_5, Table 14). These reaction conditions were  
1095 considered as those of reference to compare the reactivity of the butanol isomers towards the  
1096 cellulose butanolysis. Iso-butanol and *sec*-butanol isomers gave corresponding BL yields of 45 and 13  
1097 mol% (runs BL\_6-BL\_7, Table 14), whilst *tert*-butanol led only to traces of BL. Therefore, both  
1098 1-butanol and iso-butanol primary alcohols showed better performances than *sec*-butanol secondary  
1099 one, due to the higher steric hindrance of the latter. In addition, from the complementary perspective  
1100 of the by-product formation, 1-butanol and iso-butanol primary alcohols gave different dibutyl ether  
1101 yields of 20 and 2 mol%, respectively, proving the higher reactivity of the linear isomer. Instead,  
1102 *tert*-butanol was rapidly dehydrated to gaseous olefins, with remarkable loss of this alcohol (about  
1103 80 wt%), once again confirming the poor attractiveness of this butanol isomer towards this reaction.  
1104 Based on the above discussion, iso-butanol represents an excellent alcohol to use for the butanolysis,  
1105 to develop a new kind of BL-based bio-products. Instead, if *sec*- or *tert*- BLs are desired, the  
1106 alcoholysis route is not so appropriate whilst, at the actual state of the art, their synthesis can be  
1107 more effectively realized by adopting 1-butene or iso-butene as the corresponding alkylating agents  
1108 and levulinic acid as starting feedstocks, as demonstrated by Démolis *et al.* [149]. As for the previous  
1109 ALs, the catalytic activity of a series of cheap metal sulfates was proposed by An *et al.* [145], instead  
1110 of the traditional sulfuric acid. Among the investigated metal sulfates, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> resulted particularly  
1111 efficient for BL production from simpler model compounds, achieving the maximum yield of about  
1112 60 mol%, starting from simple C<sub>6</sub> carbohydrates, and about 30 mol%, starting from the more  
1113 recalcitrant cellulose feedstock (runs BL\_8-BL\_12, Table 14). However, also Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> was efficient  
1114 for this purpose, especially in combination with Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (run BL\_13, Table 14) [146], allowing the  
1115 enhancement of the BL yield up to the maximum value of about 40 mol%, thus reaching similar  
1116 performances to those with the sulfuric acid, although much longer reaction times were required in  
1117 the former case. As for the previous ALs, the use of Cs-exchanged HPAs was proposed by Démolis  
1118 *et al.* [144] also for BL synthesis from cellulose, but achieving unsatisfactory BL molar yields (run  
1119 BL\_14, Table 14). Few other catalysts have been considered, such as 3-PhPyPW or zeolite H-USY (6),

1120 but the reported BL molar yields data, already starting from simple monosaccharides, were not  
 1121 particularly noteworthy (runs BL\_15–BL\_16, Table 14) [99,102].  $\text{SO}_4^{2-}/\text{ZrO}_2$  was properly modified  
 1122 by Liu *et al.* [147] to  $\text{SO}_4^{2-}/\text{SnO}_2\text{-ZrO}_2$ , which was used alone, or in combination with  
 1123 organic/inorganic acids, or sulfates. In particular, the combination of  $\text{SO}_4^{2-}/\text{SnO}_2\text{-ZrO}_2$  with small  
 1124 amounts of  $\text{H}_2\text{SO}_4$ ,  $(\text{HCOOH})_2$ , PTSA,  $\text{Fe}_2(\text{SO}_4)_3$  or  $\text{CuSO}_4$ , was effective for improving this reaction  
 1125 (runs BL\_17–BL\_28, Table 14). Lastly, the good BL yield of about 30 mol% was reported by Ma *et al.*  
 1126 [148] for the cellulose conversion in the acidic ionic liquid  $[\text{C}_4\text{H}_8\text{SO}_3\text{Hmim}]\text{HSO}_4$  (run BL\_29, Table  
 1127 14), which was identified as a stable and water-tolerant catalyst.

1128 On the other hand, only very few works have studied the synthesis of PeL and HL from C6  
 1129 model feedstocks, due to their lower reactivity. Yamada *et al.* [150] carried out the synthesis of PeL  
 1130 and HL starting from cellulose and working at the boiling point of the respective solvent (runs PeL\_1  
 1131 and HL\_1, Table 14). Very interesting yields were ascertained for both PeL and HL, equal to 69 and  
 1132 60 mol% respectively, but the concentration of  $\text{H}_2\text{SO}_4$  was too high (2.1 mol/L) so that the process  
 1133 could be considered sustainable. Also heterogeneous catalysts have been adopted for the production  
 1134 of PeL and HL. Quereshi *et al.* [116] carried out the alcoholysis of fructose under MW heating,  
 1135 employing  $\text{WS}_2$  as the catalyst and  $\text{PeOH}$  as the solvent/reagent, anyway achieving the PeL yield of  
 1136 only 5 mol% (run PeL\_2, Table 14). On the other hand, Mohammadbagheri *et al.* [151] reported the  
 1137 good HL yield of 55 mol% starting from glucose, in the presence of Zn/dendritic fibrous nanosilica  
 1138 as the catalyst (run HL\_2, Table 14), which resulted effective for this purpose, due to the balanced  
 1139 Brønsted/Lewis acidity.

### 1140 3. AL synthesis from real biomass

#### 1141 3.1 ML synthesis from real biomass

1142 ML production from real biomass has been less investigated respect to that from model  
 1143 compounds, due to its complexity and consequent much more difficult study of the fate of the large  
 1144 number of components. The best data reported in the literature are summarized in Table 15:

1145 Table 15. Available catalysts for the ML production from real biomasses.

Entry	Feedstock	Catalyst	Cat.(g)/MeOH(g) <sup>1</sup>	T (°C)	t (h)	Heat <sup>2</sup>	Y <sub>ML</sub> (wt%)	Ref.
ML_157	Bamboo	HCl (37 wt%)	0.20/8.0	180	0.5	MW	2	[68]
ML_158	Bamboo	$\text{H}_2\text{SO}_4$ (96 wt%)	0.20/5.0	180	0.5	MW	25	[68]
ML_159	Bamboo	$\text{H}_2\text{SO}_4$ (96 wt%)	0.25/8.0	180	0.67	MW	29	[68]
ML_160	Straw	$\text{H}_2\text{SO}_4$ (96 wt%)	0.25/8.0	180	0.67	MW	22	[68]
ML_161	Eucalyptus	$\text{H}_2\text{SO}_4$ (96 wt%)	0.25/8.0	180	0.67	MW	24	[68]
ML_162	Poplar	$\text{H}_2\text{SO}_4$ (96 wt%)	0.25/8.0	180	0.67	MW	25	[68]
ML_163	Pine	$\text{H}_2\text{SO}_4$ (96 wt%)	0.25/8.0	180	0.67	MW	26	[68]
ML_164	Bagasse	$\text{H}_2\text{SO}_4$ (96 wt%)	0.25/8.0	180	0.67	MW	28	[68]
ML_165	Corn stover	$\text{H}_2\text{SO}_4$ (96 wt%)	0.17/5.0	160	1	MW	9	[152]
ML_166	Corn stover	$\text{H}_2\text{SO}_4$ (100 wt%)	0.003/29.8	160	1	MW	9	[74]
ML_167	BM-corn stover 3	$\text{H}_2\text{SO}_4$ (100 wt%)	0.003/29.8	160	1	MW	11	[74]
ML_168	Paper sludge	$\text{H}_2\text{SO}_4$ (100 wt%)	0.06/15.8	222	3.58	Conv.	27	[153]
ML_169	<i>Chlorella sp.</i> KR-1	$\text{H}_2\text{SO}_4$ (100 wt%)	2.75/6.5	130	2	Conv.	7	[154]
ML_170	<i>Nannochloropsis</i> <i>gaditana</i>	$\text{H}_2\text{SO}_4$ (100 wt%)	2.75/6.5	130	2	Conv.	2	[154]
ML_171	Corn stover	$\text{Al}_2(\text{SO}_4)_3$	0.33/29.8	160	1	MW	8	[74]
ML_172	BM-corn stover 3	$\text{Al}_2(\text{SO}_4)_3$	0.33/29.8	160	1	MW	12	[74]
ML_173	Wheat straw	$\text{CuSO}_4$	0.16/7.1	182	3.3	Conv.	16	[55]

ML_174	Pretreated wheat straw <sup>4</sup>	CuSO <sub>4</sub>	0.15/7.1	183	3.9	Conv.	20	[55]
ML_175	Peanut shells	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> + H <sub>2</sub> SO <sub>4</sub> (100 wt%)	0.51+0.02/13.2	160	3.6	Conv.	18	[155]
ML_176	Bamboo	PTSA <sup>5</sup>	0.20/8.0	180	0.5	MW	19	[68]
ML_177	Cedar	Al(acac) <sub>3</sub> + PTSA <sup>5</sup>	0.12+0.06/31.6	180	5	Conv.	28	[79]
ML_178	Eucalyptus	Al(acac) <sub>3</sub> + PTSA <sup>5</sup>	0.12+0.06/31.6	180	5	Conv.	25	[79]
ML_179	Cedar	In(OTf) <sub>3</sub> + BSA <sup>6</sup>	0.04+0.06/31.6	200	5	Conv.	31	[78]
ML_180	Pine	In(OTf) <sub>3</sub> + BSA <sup>6</sup>	0.04+0.06/31.6	200	5	Conv.	26	[78]
ML_181	Eucalyptus	In(OTf) <sub>3</sub> + BSA <sup>6</sup>	0.04+0.06/31.6	200	5	Conv.	24	[78]
ML_182	Bagasse	In(OTf) <sub>3</sub> + BSA <sup>6</sup>	0.04+0.06/31.6	200	5	Conv.	25	[78]
ML_183	Bamboo	H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	0.20/8.0	180	0.5	MW	15	[68]
ML_184	Corn straw	[PyPS] <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> <sup>7</sup>	3.40/31.6	170	4.5	Conv.	18	[97]
ML_185	Bagasse	[PyPS] <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> <sup>7</sup>	3.40/31.6	170	4	Conv.	14	[97]
ML_186	Bamboo	[HSO <sub>3</sub> BMIM]HSO <sub>4</sub> <sup>8</sup>	0.20/8.0	180	0.5	MW	19	[68]
ML_187	Duckweed	[C <sub>3</sub> H <sub>6</sub> SO <sub>3</sub> HPy]HSO <sub>4</sub>	0.80/31.6	170	5	Conv.	24	[156]

1146 <sup>1</sup> The amounts of catalyst and MeOH have been normalized to 1g of feedstock.

1147 <sup>2</sup> “Conv.” and “MW” stand for “Conventional” and “Microwave”, respectively.

1148 <sup>3</sup> “BM” stands for “Ball-Milled”.

1149 <sup>4</sup> Wheat straw was pretreated in decanol for fractionating hemicelluloses, and the solid residue in 3.0 wt%

1150 NaOH for isolating lignin.

1151 <sup>5</sup> “PTSA” stands for “*p*-toluenesulfonic acid”.

1152 <sup>6</sup> “BSA” stands for “benzenesulfonic acid”.

1153 <sup>7</sup> “PyPS” stands for “1-(3-sulfopropyl)pyridinium”.

1154 <sup>8</sup> “[HSO<sub>3</sub>BMIM]HSO<sub>4</sub>” stands for “1-methyl-3-(4-sulfobutyl)imidazolium hydrogensulfate”.

1155

1156 Several biomass feedstocks, such as bamboo, straw, eucalyptus, poplar, pine and bagasse, were  
 1157 tested by Feng *et al.* [68] for the ML production adopting the efficient MW heating, mainly in the  
 1158 presence of diluted sulfuric acid (runs ML\_158–ML\_164, Table 15), whilst hydrochloric acid  
 1159 resulted inefficient for this purpose (run ML\_157, Table 15). All these biomasses have very similar  
 1160 cellulose content, approximatively 40 wt%, and this similarity makes easy the comparison of the ML  
 1161 yield results, expressed as wt% respect to the starting weight of dry biomass. About 80–85 wt% of  
 1162 the starting biomass was liquefied within 40 minutes of reaction, achieving, in most cases, ML yields  
 1163 within the range 20–30 wt%, and negligible dimethyl ether yields, due to the low sulfuric acid  
 1164 concentration, whilst other by-products, such as furfurals (5-methoxymethyl furfural and furfural)  
 1165 and methyl glucoside, were significantly produced, with corresponding yields of about 15–20 and  
 1166 10–20 wt% (runs ML\_157–ML\_164, Table 15). Among the investigated biomasses, bamboo was  
 1167 better liquefied and gave the highest ML yield (run ML\_159, Table 15) and, for this reason, it was  
 1168 studied more in-depth, comparing the hydrolysis and methanolysis routes. Approximately 84 wt%  
 1169 of the bamboo biomass was converted into liquefied products at 180 °C with MeOH, whilst only 25  
 1170 wt% of bamboo was converted with water medium. The selective catalytic conversion of biomass  
 1171 was found to be efficient for the ML production (reaching a maximum yield of approximately 30  
 1172 wt%), higher than the levulinic acid yield (14 wt%), the latter obtained carrying out the reaction in  
 1173 aqueous solution, under the same reaction conditions. The authors also demonstrated that PTSA,  
 1174 H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> or [HSO<sub>3</sub>BMIM]HSO<sub>4</sub> ionic liquid gave acceptable ML yields (runs ML\_176, ML\_183, and  
 1175 ML\_184, Table 15), and confirmed the key role of MeOH for the solubilisation of the high molecular  
 1176 weight polar products, due to their low dielectric constants, which could efficiently prevent the  
 1177 re-polymerization and re-condensation of liquefied products on the surface of biomass itself, thus  
 1178 significantly improving the diffusion and reactivity of the alcohol. However, also in the presence of  
 1179 these catalysts, the corresponding yields of furfurals and methyl glucoside were not negligible, in  
 1180 particular 20 and 18 wt% with PTSA, 13 and 16 wt% with H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, and 14 and 19 wt% with  
 1181 [HSO<sub>3</sub>BMIM]HSO<sub>4</sub> [68]. Xiao *et al.* [152] proposed the sulfuric acid-catalyzed conversion of corn



1182 stover, reporting a maximum ML yield of 9 wt%, under MW irradiation (run ML\_165, Table 15).  
1183 Despite the noteworthy positive effect of MW towards ML production, the obtained ML yields are  
1184 not competitive with those obtained from the above considered biomasses. Even the addition of a  
1185 preliminary ball-milling treatment did not allow the improvement of the ML yield from corn stover  
1186 (runs ML\_165–ML\_167, Table 15) [74], which is not a suitable feedstock for this reaction. The  
1187 conversion of a paper sludge was proposed by Peng *et al.* [153], in the presence of a very low  
1188 concentration of sulfuric acid ( $\leq 0.05$  mol/L). Response Surface Methodology (RSM) with a  
1189 four-factor, five-level central composite rotatable design, was employed to optimize the reaction.  
1190 The yields of ML and dimethyl ether, as a function of the process variables, were fitted to  
1191 second-order polynomial models through the application of multiple regression analyses, achieving  
1192 a good agreement between the experimental and modeled data. When the dimethyl ether yield was  
1193 lower than 20 mol%, a maximum ML yield of about 55 mol% was achieved, corresponding to a mass  
1194 yield of 27 wt%, calculated respect to the weight of dry paper sludge (run ML\_168, Table 15). The  
1195 authors concluded that sulfuric acid concentration and temperature were crucial for increasing ML  
1196 production and reducing that of dimethyl ether [153]. As examples of unconventional biomass  
1197 feedstocks for ML production, *Nannochloropsis* and *Chlorella* microalgal strains were compared by  
1198 Kim *et al.* [154], leading to low ML yields (2–7 wt%) (runs ML\_168–ML\_170, Table 15). As already  
1199 discussed for the model C6 feedstocks, inorganic salts can represent a good and cheap alternative to  
1200 the active sulfuric acid. The good performances of  $\text{Al}_2(\text{SO}_4)_3$  were demonstrated by Chen *et al.* [74] for  
1201 the conversion of raw and ball-milled corn stover (runs ML\_171–ML\_172, Table 15), resulting in  
1202 agreement with the best results obtained with sulfuric acid (runs ML\_166–ML\_167, Table 15).  
1203 Wheat straw was effectively converted into ML, in the presence of  $\text{CuSO}_4$  as a cheap and active  
1204 catalyst (runs ML\_173–ML\_174, Table 15) [55]. In this regard, metal sulfates of the IA and IIA  
1205 groups, such as  $\text{Na}_2\text{SO}_4$ ,  $\text{MgSO}_4$ ,  $\text{K}_2\text{SO}_4$ , and  $\text{CaSO}_4$ , were not active towards ML production, due to  
1206 their too low acidities, as well as  $\text{ZnSO}_4$ ,  $\text{MnSO}_4$ , and  $\text{NiSO}_4$ . On the other hand,  $\text{Al}_2(\text{SO}_4)_3$ ,  $\text{Fe}_2(\text{SO}_4)_3$ ,  
1207  $\text{Ti}_2(\text{SO}_4)_3$  and, especially  $\text{CuSO}_4$ , exhibited good catalytic activity, due to the contemporary presence  
1208 of Lewis acid sites from metal ions and Brønsted ones, whose formation occurs via  
1209 hydrolysis/methanolysis of metal ions. A two-stage pretreatment process was developed by the  
1210 authors, where the hemicellulose fraction was first converted into decyl pentoside bio-surfactant by  
1211 an acidic decanol-based pretreatment, carried out under mild conditions and, subsequently, the  
1212 lignin component was extracted in the second stage by sodium hydroxide treatment [55]. After this  
1213 fractionation, the residual wheat straw, resulting enriched in cellulose, was used as starting  
1214 feedstock for ML production, and a maximum yield of 20 wt% was obtained, under the optimized  
1215 reaction conditions (run ML\_174, Table 15). Taking into account the interactions between reaction  
1216 time and reaction temperature or catalyst dosage, the choice of long reaction time was not in favor of  
1217 the process. Moreover, the catalyst recycling experiments showed that copper sulfate was stable and  
1218 can be reused more than five times. The combination of sulfuric acid with extremely low  
1219 concentration and  $\text{Al}_2(\text{SO}_4)_3$  was identified as the efficient mixed acid catalytic system for ML  
1220 production from waste peanut shells, reaching a ML yield of 17 wt% (run ML\_175, Table 15) [155].  
1221 Also the combination of PTSA and  $\text{Al}(\text{acac})_3$  was found to be an efficient catalytic system, applied to  
1222 the conversion of cedar and eucalyptus feedstocks (runs ML\_177–ML\_178, Table 15) [79]. The  
1223 solvolysis of the C6 fraction of the biomass was catalyzed by Brønsted acidic PTSA and the  
1224 conversion of these sugars to ML was significantly enhanced by Lewis acidic  $\text{Al}(\text{OTf})_3$ , formed in  
1225 situ from Al compounds and PTSA. Among metal triflates of group 13,  $\text{In}(\text{OTf})_3$ , used in  
1226 combination with BSA, resulted particularly efficient for the ML production, from lignocellulosic  
1227 biomasses as cedar, pine, eucalyptus and bagasse (runs ML\_179–ML\_182, Table 15) [78].  
1228 Remarkably, the highest ML yield (31 wt%) was achieved from cedar, working at 200 °C for 5 h (run  
1229 ML\_179, Table 15). As above reported for the conversion of model compounds,  
1230 heteropolyanion-based ionic liquid  $[\text{PyPS}]_3\text{PW}_{12}\text{O}_{40}$  was proposed by Song *et al.* [97] as an efficient  
1231 catalyst for the conversion of corn straw and bagasse into ML, with yields of 18 and 14 wt%,  
1232 respectively (runs ML\_184–ML\_185, Table 15). As previously reported for the alcoholysis of model  
1233 compounds, the ascertained catalytic performances were ascribed to the high acidic strength of the

1234 sulfonic-functionalized cation and to its synergistic effects with the corresponding heteropolyanion,  
 1235 which favored the whole process. Duckweed, a typical fast-growing aquatic microalgae, was  
 1236 converted into ML in the presence of acidic ionic liquid [C<sub>3</sub>H<sub>6</sub>SO<sub>3</sub>HPy]HSO<sub>4</sub> (run ML\_187, Table 15)  
 1237 [156]. Under the best reaction conditions (170 °C, 5 h), about 88% of the starting duckweed feedstock  
 1238 was converted, leading to the maximum ML yield of 24 wt% and levulinic acid yield of 2 wt%, these  
 1239 good catalytic performances being partly attributed to the low lignin content of the starting biomass.  
 1240 In agreement with the previous data, it was confirmed that the solvent had a remarkable intensified  
 1241 effect on the process efficiency (as levulinic acid yield plus ML yield), which dramatically decreased  
 1242 from 82 to 54 mol% when MeOH was replaced by water.

1243

### 1244 3.2 EL synthesis from real biomass

1245 Up to now, also for the EL synthesis from real biomasses, homogeneous catalysts have been  
 1246 preferred over heterogeneous ones. The most promising available data are reported in Table 16:

1247 **Table 16.** Catalysts for the EL production from real biomasses.

Entry	Feedstock	Catalyst	Cat.(g)/EtOH(g) <sup>1</sup>	T (°C)	t (h)	Heat <sup>2</sup>	Y <sub>EL</sub> (wt%)	Ref.
EL_119	Grey pine wood	H <sub>2</sub> SO <sub>4</sub> (96 wt%)	0.04/5.0	190	1.6	Conv.	16	[157]
EL_120	Paper pulp	H <sub>2</sub> SO <sub>4</sub> (96 wt%)	0.04/5.0	190	1.6	Conv.	26	[157]
EL_121	Switchgrass	H <sub>2</sub> SO <sub>4</sub> (96 wt%)	0.04/5.0	190	1.6	Conv.	14	[157]
EL_122	Wheat straw	H <sub>2</sub> SO <sub>4</sub> (100 wt%)	0.51/19.8	183	0.6	Conv.	18	[158]
EL_123	Chipped laminated particleboard	H <sub>2</sub> SO <sub>4</sub> (96 wt%)	0.19/7.4	200	0.5	Conv.	24	[159]
EL_124	<i>Chlorella sp.</i> KR-1	H <sub>2</sub> SO <sub>4</sub> (100 wt%)	2.75/6.5	130	2	Conv.	11	[154]
EL_125	<i>Nannochloropsis gaditana</i>	H <sub>2</sub> SO <sub>4</sub> (100 wt%)	2.75/6.5	130	2	Conv.	3	[154]
EL_126	Mandarin peels	H <sub>2</sub> SO <sub>4</sub> (100 wt%)	0.90/5.3 <sup>3</sup>	150	2	Conv.	28	[160]
EL_127	Cassava	H <sub>2</sub> SO <sub>4</sub> (96 wt%)	0.25/3.9 <sup>4</sup>	160	3	Conv.	14	[161]
EL_128	Cassava <sup>5</sup>	H <sub>2</sub> SO <sub>4</sub> (96 wt%)	0.25/3.9 <sup>4</sup>	160	3	Conv.	21	[161]
EL_129	Cassava <sup>5</sup>	H <sub>2</sub> SO <sub>4</sub> (96 wt%)	0.17/5.3 <sup>6</sup>	160	5	Conv.	27	[161]
EL_130	Bamboo	H <sub>2</sub> SO <sub>4</sub> (96 wt%)	0.04/30.1	210	2.1	Conv.	51	[162]
EL_131	Bamboo <sup>7</sup>	H <sub>2</sub> SO <sub>4</sub> (96 wt%)	0.04/30.1	210	2.1	Conv.	63	[162]
EL_132	Corn stover	H <sub>2</sub> SO <sub>4</sub> (96 wt%)	0.42/15.0	190	0.5	Conv.	7	[163]
EL_133	Corn stover	H <sub>2</sub> SO <sub>4</sub> (96 wt%)	0.42/15.0	190	0.5	MW	17	[163]
EL_134	Corn stover	H <sub>2</sub> SO <sub>4</sub> (96 wt%)	0.20/20.0	180	0.5	MW	13	[164]
EL_135	Corn stover <sup>8</sup>	H <sub>2</sub> SO <sub>4</sub> (96 wt%)	0.20/20.0	180	0.5	MW	14	[164]
EL_136	Corn stover	H <sub>2</sub> SO <sub>4</sub> (96 wt%)	0.15/5.0	180	0.5	MW	12	[25]
EL_137	Wheat straw	H <sub>2</sub> SO <sub>4</sub> (96 wt%)	0.15/5.0	180	0.5	MW	11	[25]
EL_138	Rice straw	H <sub>2</sub> SO <sub>4</sub> (96 wt%)	0.15/5.0	180	0.5	MW	11	[25]
EL_139	Rape straw	H <sub>2</sub> SO <sub>4</sub> (96 wt%)	0.15/5.0	180	0.5	MW	6	[25]
EL_140	Poplar wood	H <sub>2</sub> SO <sub>4</sub> (96 wt%)	0.15/5.0	180	0.5	MW	9	[25]
EL_141	Cassava	H <sub>2</sub> SO <sub>4</sub> (96 wt%)	0.10/19.0	200	6	Conv.	31	[165]
EL_142	Cassava	NaHSO <sub>4</sub>	0.10/19.0	200	6	Conv.	15	[165]
EL_143	Cassava	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.10/19.0	200	6	Conv.	36	[165]
EL_144	Cassava	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.10/19.0	200	6	Conv.	9	[165]
EL_145	DHFW <sup>9</sup>	H <sub>2</sub> SO <sub>4</sub> (96 wt%) +AlCl <sub>3</sub> ·6H <sub>2</sub> O	0.16+0.16/15.8	180	4	Conv.	15	[166]

EL_146	KW <sup>10</sup>	H <sub>2</sub> SO <sub>4</sub> (96 wt%) +AlCl <sub>3</sub> ·6H <sub>2</sub> O	0.16+0.16/15.8	180	4	Conv.	32	[166]
EL_147	FVS <sup>11</sup>	H <sub>2</sub> SO <sub>4</sub> (96 wt%) +AlCl <sub>3</sub> ·6H <sub>2</sub> O	0.16+0.16/15.8	180	4	Conv.	11	[166]
EL_148	OFMSW <sup>12</sup>	H <sub>2</sub> SO <sub>4</sub> (96 wt%) +AlCl <sub>3</sub> ·6H <sub>2</sub> O	0.16+0.16/15.8	180	4	Conv.	14	[166]
EL_149	Coniferous wood	1,5-NSA <sup>13</sup>	0.20/7.9	200	4	Conv.	46	[167]
EL_150	Coniferous wood	2-NSA <sup>14</sup>	0.20/7.9	200	4	Conv.	49	[167]
EL_151	Furfural residue	USY + H <sub>2</sub> SO <sub>4</sub> (96 wt%)	0.03+0.04/39.9	219	1.8	Conv.	19	[133]
EL_152	Wheat straw	[HSO <sub>3</sub> -BMIM] [HSO <sub>4</sub> ]	0.26/15.0	200	1	Conv.	16	[168]
EL_153	OPEFB <sup>15,16</sup>	[HMIM][HSO <sub>4</sub> ]	n.a. <sup>17</sup>	90	12	Conv.	12	[169]
EL_154	OPMF <sup>18,16</sup>	[HMIM][HSO <sub>4</sub> ]	n.a. <sup>17</sup>	90	12	Conv.	14	[169]
EL_155	OPEFB <sup>15,19</sup>	[HMIM][HSO <sub>4</sub> ] + InCl <sub>3</sub>	n.a. <sup>17</sup>	90	10	Conv.	13	[170]
EL_156	OPMF <sup>18,19</sup>	[HMIM][HSO <sub>4</sub> ] + InCl <sub>3</sub>	n.a. <sup>17</sup>	90	10	Conv.	15	[170]
EL_157	OPEFB <sup>15,20</sup>	[HMIM][HSO <sub>4</sub> ] + InCl <sub>3</sub>	n.a. <sup>17</sup>	105	12.2	Conv.	19	[171]
EL_158	OPMF <sup>18,20</sup>	[HMIM][HSO <sub>4</sub> ] + InCl <sub>3</sub>	n.a. <sup>17</sup>	105	12.2	Conv.	21	[171]
EL_159	Corn stover <sup>21</sup>	[HSO <sub>3</sub> -BMIM][HSO <sub>4</sub> ] + Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.51+0.14/20.0	170	2	MW	11	[172]

1248 <sup>1</sup> The amounts of catalyst and EtOH have been normalized to 1g of feedstock.

1249 <sup>2</sup> "Conv." and "MW" stand for "Conventional" and "Microwave", respectively.

1250 <sup>3</sup> 10.0 g of chloroform were added to this reaction mixture.

1251 <sup>4</sup> 4.8 g of water were added to this reaction mixture.

1252 <sup>5</sup> The biomass was pre-hydrolyzated at 100 °C for 1 h.

1253 <sup>6</sup> 3.2 g of water were added to this reaction mixture.

1254 <sup>7</sup> The biomass was pretreated in water with MgO under O<sub>2</sub> pressure (1 MPa) at 170 °C for 3h.

1255 <sup>8</sup> The biomass was pretreated by 120 min of ball milling.

1256 <sup>9</sup> "DHFV" stands for "Dried household food waste".

1257 <sup>10</sup> "KW" stands for "Kitchen waste".

1258 <sup>11</sup> "FVS" stands for "Fruit and vegetables scraps".

1259 <sup>12</sup> "OFMSW" stands for "Organic fraction of municipal solid waste".

1260 <sup>13</sup> "1,5-NSA" stands for "1,5-naphthalenesulfonic acid".

1261 <sup>14</sup> "2-NSA" stands for "2-naphthalenesulfonic acid".

1262 <sup>15</sup> "OPEFB" stands for "Oil palm empty fruit bunch".

1263 <sup>16</sup> The biomass was previously depolymerized at 160 °C for 3h.

1264 <sup>17</sup> "n.a." stands for "not-available".

1265 <sup>18</sup> "OPMF" stands for "Oil palm mesocarp fiber".

1266 <sup>19</sup> The biomass was previously depolymerized at 160 °C for 5h.

1267 <sup>20</sup> The biomass was previously depolymerized at 177 °C for 4.8h.

1268 <sup>21</sup> The biomass was pretreated by 60 min of ball milling.

1269

1270 Also in this case, sulfuric acid is the catalyst of greatest practical interest. Different biomasses,  
1271 such as wheat straw, chipped laminated particleboard, algae, cassava, bamboo, grey pine wood,  
1272 paper pulp, switchgrass, mandarin peels, corn stover, rice straw, rape straw, and poplar wood, have  
1273 been adopted as starting feedstocks, in the presence of H<sub>2</sub>SO<sub>4</sub> as the catalyst, achieving EL yields in

1274 the range 6–63 wt%, evaluated respect to the weight of the starting dry biomass. This wide range of  
1275 the best EL yields depends on the different cellulose content of the adopted biomasses. Le Van Mao  
1276 *et al.* [157], compared the ethanolysis of three different biomasses (grey pine wood, paper pulp,  
1277 switchgrass) (runs EL\_119–EL\_121, Table 16), demonstrating that EL yield decreased in the order  
1278 paper pulp > grey pine wood > switchgrass, retracing the same trend of cellulose amount in the three  
1279 biomasses, equal to 78, 42, and 35 wt%, respectively. The authors also confirmed the presence of  
1280 some interesting reaction by-products, such as ethyl formate, with yields of 8, 7, and 5 wt%, starting  
1281 from paper pulp, grey pine wood and switchgrass, respectively, and diethyl ether, with  
1282 corresponding yields of 3, 2, and 2 wt%, both properly exploitable after their efficient separation.  
1283 Chang *et al.* [158] carried out the conversion of wheat straw to EL, optimizing the reaction conditions  
1284 through a Box-Behnken experimental design, claiming the highest EL yield of 18 wt%, working at  
1285 183 °C for 36 min with much more concentrated acid (run EL\_122, Table 16). Olson *et al.* [159]  
1286 performed the ethanolysis of chipped laminated particleboard, reaching an optimal EL yield of 24  
1287 wt% (run EL\_123, Table 16). Starting from the results of ML synthesis, Kim *et al.* [154] studied also  
1288 that of EL from *Chlorella* and *Nannochloropsis* microalgal strains, achieving the EL yield of 11 and 3  
1289 wt%, respectively, this difference of reactivity being ascribed to the higher carbohydrate content in  
1290 the *Chlorella* strain (runs EL\_124–EL\_125, Table 16). Yang *et al.* [160] proposed the conversion of  
1291 mandarin peels, employing chloroform as co-solvent for increasing the EL yield (from 4 to 28 wt%,  
1292 under the optimized reaction conditions) (run EL\_126, Table 16). This improvement was ascribed to  
1293 the higher solubilization of EL in chloroform, rather than in the (water-EtOH) system, where  
1294 chloroform enables as a continuous extraction medium for EL, at the same time limiting the humin  
1295 formation. EL yield was also improved by adopting appropriate biomass pre-treatments of the  
1296 starting raw biomass to overcome its recalcitrance and improve the interaction between the catalyst  
1297 and the cellulose. On this basis, Zhao *et al.* [161] pre-hydrolyzed cassava biomass at 100 °C for 1 h  
1298 and, subsequently, carried out its ethanolysis at 160 °C for 3h, comparing the results with those  
1299 achieved starting from the untreated cassava (runs EL\_127–EL\_129, Table 16). The authors found  
1300 that when cassava was pre-hydrolyzed, the maximum achieved EL yield was higher, and the EL  
1301 yield from pre-hydrolyzed cassava was further increased up to the maximum value of 27 wt%, after  
1302 having properly optimized the reaction conditions. Gong *et al.* [162] hydrothermally pre-treated  
1303 bamboo biomass, working in the presence of MgO and O<sub>2</sub> pressure (1 MPa), at 170 °C for 3 h. As a  
1304 consequence of this pre-treatment, the authors obtained a significant removal of the lignin fraction,  
1305 thus making easier the next sulfuric acid-catalyzed ethanolysis step (runs EL\_130–EL\_131, Table 16).  
1306 Zhang *et al.* [163] investigated the corn stover ethanolysis, exploiting the efficient MW heating,  
1307 which improved the EL production (17 wt%) respect to the conventional heating (7 wt%) (runs  
1308 EL\_132–EL\_133, Table 16). Also Liu *et al.* [164] preferred the MW heating for studying the  
1309 ethanolysis of ball-milled corn stover, adopting similar reaction conditions of Zhang *et al.* [163],  
1310 anyway not obtaining appreciable improvements in the EL yield (runs EL\_134–EL\_135, Table 16).  
1311 Zhao *et al.* [25] compared the MW-assisted conversion of different biomasses (corn stover, wheat  
1312 straw, rice straw, rape straw, poplar wood) (runs EL\_136–EL\_140, Table 16). In this work, the  
1313 authors proved that EL yield depended not only on the cellulose content but also on the crystallinity  
1314 index of the cellulose fraction. In fact, the cellulose amount decreased, as follows: rice straw ≈ poplar  
1315 wood > corn stover > wheat straw > rape straw. However, the EL yield decreased as follows: corn  
1316 stover > rice straw ≈ wheat straw > poplar wood > rape straw. In particular, the EL yield from poplar  
1317 wood was lower than that obtained from rice straw, despite they had a similar cellulose amount (37  
1318 wt%), and this difference was explained with the higher crystallinity index of poplar wood, leading  
1319 to a lower EL yield. Bifunctional Brønsted-Lewis acid behavior of inorganic salts has been exploited  
1320 also for the EL synthesis from real biomasses. Tan *et al.* [165] compared the catalytic activity of H<sub>2</sub>SO<sub>4</sub>  
1321 and several inorganic salts towards the ethanolysis of cassava (runs EL\_141–EL\_144, Table 16). The  
1322 authors found that Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> gave the highest EL yield of 36 wt%, thanks to its better synergistic  
1323 effect between Brønsted and Lewis acidity, generated from the salt hydrolysis/ethanolysis.  
1324 Analogously to the ethanolysis of model compounds, also for the real biomasses, H<sub>2</sub>SO<sub>4</sub> was  
1325 employed in combination with inorganic salts, for example by Di Bitonto *et al.* [166], who choose the

1326 catalytic system ( $\text{H}_2\text{SO}_4 + \text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ) for the conversion of organic wastes, such as dried household  
 1327 food waste (DHFV), kitchen waste, fruit (KWF), fruit and vegetable scraps (FVS) and organic  
 1328 fractions of municipal solid waste (OFMSW), obtaining the maximum EL yields of 15, 32, 11 and 14  
 1329 wt%, respectively (runs EL\_145–EL\_148, Table 16).

1330 Other catalysts, such as sulfonic acids, zeolites and ionic liquids have been tested for this  
 1331 reaction. Regarding the sulfonic acids, such as 1,5-NSA and 2-NSA, their use for the coniferous  
 1332 wood ethanolysis was discussed by Bianchi *et al.* [167]. The authors claimed the highest EL yields of  
 1333 46 and 49 wt%, employing 1,5-NSA acid and 2-NSA, respectively (runs EL\_149–EL\_150, Table 16).  
 1334 Chang *et al.* [133] employed a combination of zeolite USY and  $\text{H}_2\text{SO}_4$  for optimizing, through a  
 1335 Box-Behnken experimental design, the ethanolysis of a cellulosic waste deriving from the furfural  
 1336 factory, achieving the highest EL yield of 19 wt%, working at 219 °C for 107 min (run EL\_151, Table  
 1337 16). Guan *et al.* [168] compared the catalytic performances of three ionic liquids ([BMIM][Cl],  
 1338 [BMIM][HSO<sub>4</sub>] and [HSO<sub>3</sub>-BMIM][HSO<sub>4</sub>]) for the conversion of wheat straw, and selected  
 1339 [HSO<sub>3</sub>-BMIM][HSO<sub>4</sub>] thanks to its higher efficiency (runs EL\_152, Table 16). An in-depth  
 1340 investigation of the synthesis of EL with ionic liquids, starting from oil palm empty fruit bunch  
 1341 (OPEFB) and oil palm mesocarp fiber (OPMF), was carried out by Tiong *et al.* [169]. The authors  
 1342 developed a one-pot cascade approach, which provided i) a depolymerization step, carried out in  
 1343 the presence of the ionic liquid at 160 °C for 5 h in a 20 wt% of aqueous EtOH and ii) an esterification  
 1344 step in EtOH excess, working under reflux at 90 °C for 12 h (runs EL\_153–EL\_154, Table 16). This  
 1345 study demonstrated that [HMIM][HSO<sub>4</sub>] was the most efficient catalyst, leading to the best EL yields  
 1346 of 12 and 14 wt%, starting from OPEFB and OPMF, respectively. The same authors added the  
 1347 inorganic salt  $\text{InCl}_3$  to the ionic liquid [HMIM][HSO<sub>4</sub>] and performed the reaction carrying out the  
 1348 depolymerization step with  $\text{InCl}_3$ -[HMIM][HSO<sub>4</sub>] at 160 °C for 3 h in a 20 wt% aqueous–EtOH  
 1349 solution and the esterification step in EtOH excess, under reflux at 90 °C for 10 h (runs  
 1350 EL\_155–EL\_156, Table 16) [170]. The addition of  $\text{InCl}_3$  improved the reaction, weakening the  
 1351 glycosidic bonds of polysaccharides, thus promoting the depolymerization and the conversion of  
 1352 cellulose to levulinic acid, the direct EL precursor. By this way, higher EL yields of 13 and 15 wt%,  
 1353 were obtained starting from OPEFB and OPMF, respectively, after shorter reaction time, employing  
 1354  $\text{InCl}_3$ -[HMIM][HSO<sub>4</sub>] as the catalytic system. Lastly, the authors optimized both the  
 1355 depolymerization and the esterification steps, through the central composite design (CCD) model,  
 1356 achieving the maximum EL yields of 19 and 21 wt%, starting from OPEFB and OPMF, respectively  
 1357 (runs EL\_157–EL\_158, Table 16) [171]. Liu *et al.* [172] employed the ionic liquid [HSO<sub>3</sub>-BMIM][HSO<sub>4</sub>]  
 1358 together with  $\text{Al}_2(\text{SO}_4)_3$  as catalyst for the MW-assisted EL synthesis from ball-milled corn stover.  
 1359 When  $\text{Al}_2(\text{SO}_4)_3$  was applied as the only catalyst, under the adopted reaction conditions  
 1360 ethyl-D-glucoside was the main product, achieving yield up to 16 wt%, whilst levoglucosenone  
 1361 yield up to 4 wt% was obtained with [HSO<sub>3</sub>-BMIM][HSO<sub>4</sub>], due to the strong acidity of the ionic  
 1362 liquid. Instead, the combined use of the ionic liquid and inorganic salt showed a synergistic positive  
 1363 effect, leading to the highest EL yield of 11 wt% (run EL\_159, Table 16).

### 1364 3.3 PL, BL and longer-chain AL (PeL and HL) synthesis from real biomass

1366 Up to now, the most investigated ALs from real biomass are ML and EL, whilst few data have  
 1367 been reported for the synthesis of PL, BL, PeL and HL. These data are summarized in Table 17:

1368 **Table 17.** Catalysts for the PL, BL, PeL and HL production from real biomasses.

Entry	Feedstock	Catalyst	Cat.(g)/Alcohol (g) <sup>1</sup>	T (°C)	t (h)	Heat <sup>2</sup>	Y (wt%)	Ref.
PL_23	Coniferous wood	2-NSA <sup>3</sup>	0.20/8.0 (i) <sup>4</sup>	200	4	Conv.	46	[167]
PL_24	Duckweed	[C <sub>3</sub> H <sub>6</sub> SO <sub>3</sub> HPy]HSO <sub>4</sub> <sup>5</sup>	0.80/32.0 (n) <sup>6</sup>	170	5	Conv.	20	[156]
BL_30	Softwood Kraft pulp	H <sub>2</sub> SO <sub>4</sub> (100 wt%)	42.86/100.0 (n) <sup>7</sup>	117	3	Conv.	53	[150]
BL_31	Hardwood	H <sub>2</sub> SO <sub>4</sub> (100 wt%)	42.86/100.0 (n) <sup>7</sup>	117	3	Conv.	43	[150]

	Kraft pulp							
BL_32	Papermaking sludge "A" ADW	H <sub>2</sub> SO <sub>4</sub> (100 wt%)	42.86/100.0 (n) <sup>7</sup>	117	3	Conv.	11	[150]
BL_33	<i>Eucalyptus Nitens</i> <sup>8</sup>	H <sub>2</sub> SO <sub>4</sub> (100 wt%)	0.10/3.9 (n) <sup>7</sup>	183	2.4	MW	38	[52]
BL_34	<i>Arundo donax</i>	H <sub>2</sub> SO <sub>4</sub> (100 wt%)	0.10/6.0 (n) <sup>7</sup>	190	0.25	MW	37	[173]
BL_35	Coniferous wood	2-NSA <sup>3</sup>	0.20/8.1 (n) <sup>7</sup>	200	4	Conv.	43	[167]
PeL_3	Softwood Kraft pulp	H <sub>2</sub> SO <sub>4</sub> (100 wt%)	25.4/101.8	138	3	Conv.	62	[150]
PeL_4	Hardwood Kraft pulp	H <sub>2</sub> SO <sub>4</sub> (100 wt%)	25.4/101.8	138	3	Conv.	56	[150]
PeL_5	Papermaking sludge "G"	H <sub>2</sub> SO <sub>4</sub> (100 wt%)	25.4/101.8	138	3	Conv.	45	[150]
HL_3	Softwood Kraft pulp	H <sub>2</sub> SO <sub>4</sub> (100 wt%)	25.4/101.8	157	1	Conv.	59	[150]
HL_4	Hardwood Kraft pulp	H <sub>2</sub> SO <sub>4</sub> (100 wt%)	25.4/101.8	157	1	Conv.	54	[150]
HL_5	Papermaking sludge "G"	H <sub>2</sub> SO <sub>4</sub> (100 wt%)	25.4/101.8	157	1	Conv.	42	[150]

1369 <sup>1</sup> The amounts of catalyst and the respective alcohol have been normalized to 1g of feedstock.

1370 <sup>2</sup> "Conv." and "MW" stand for "Conventional" and "Microwave", respectively.

1371 <sup>3</sup> "2-NSA" stands for "2-naphthalenesulfonic acid".

1372 <sup>4</sup> "(i)" stands for "iso-propanol".

1373 <sup>5</sup> "[C<sub>3</sub>H<sub>6</sub>SO<sub>3</sub>HPy]HSO<sub>4</sub>" stands for "1-(3-sulfopropyl)-pyridinium bisulfate".

1374 <sup>6</sup> "(n)" stands for "n-propanol".

1375 <sup>7</sup> "(n)" stands for "n-butanol".

1376 <sup>8</sup> "ADW" stands for "autohydrolyzed-delignified wood".

1377

1378 Bianchi *et al.* [167] proposed the use of 2-NSA as a homogeneous catalyst for the synthesis of  
 1379 *i*-PL from coniferous wood, obtaining a promising PL yield of 46 wt% (run PL\_23, Table 17).  
 1380 Moreover, Chen *et al.* [156] synthesized *n*-PL directly from duckweed biomass, employing the ionic  
 1381 liquid [C<sub>3</sub>H<sub>6</sub>SO<sub>3</sub>HPy]HSO<sub>4</sub> as the reaction catalyst (run PL\_24, Table 17). Under the best reaction  
 1382 conditions, the authors achieved the maximum *n*-PL yield of 20 wt%, which was significantly lower  
 1383 than those achieved by the authors with shorter-chain alcohols, such as MeOH and EtOH.

1384 Few data are available for the conversion of real biomasses to BL. Sulfuric acid has been the  
 1385 almost exclusively used catalyst, highlighting that the interest in the heterogeneous catalyst is rather  
 1386 limited by the difficulties of performing out this reaction and achieving satisfactory yields. Some  
 1387 interesting biomasses deriving from the papermaking production were tested for this reaction, in the  
 1388 presence of sulfuric acid as the reaction catalyst, achieving BL yields in the range 40-50 wt%, under  
 1389 the best circumstances (runs BL\_30–BL\_32, Table 17) [150]. However, the authors' choice of  
 1390 employing a low reaction temperature (117 °C) involved the requirement of a very high acid  
 1391 concentration, about 3.5 mol/L, which is not sustainable for a sustainable industrial process. To solve  
 1392 this drawback, a higher reaction temperature should be preferred, thus allowing the use of lower  
 1393 acid concentrations. Very recently, Antonetti *et al.* [52] and Raspolti Galletti *et al.* [173] preferred this  
 1394 last approach, carrying out the MW-assisted butanolysis of ADW *Eucalyptus Nitens* and *Arundo*  
 1395 *donax*, respectively. In particular, the former optimized the reaction with a multivariate approach,  
 1396 achieving a maximum BL yield of about 40 wt% (run BL\_33, Table 17), in agreement with the other  
 1397 best BL data reported in Table 19. Lastly, in a patent of Bianchi *et al.* [167], coniferous wood was  
 1398 converted in the presence of dilute 2-NSA (0.1 mol/L), also in this case achieving a good BL yield  
 1399 (run BL\_35, Table 17).

1400 As in the previous cases, also for the production of PeL and HL, sulfuric acid has been the only  
1401 adopted catalyst. To the best of our knowledge, only Yamada *et al.* [150] have considered the  
1402 synthesis of these two longer-chain AL directly from real biomasses (Table 17). The authors carried  
1403 out the alcoholysis of different biomasses, softwood kraft pulp, hardwood kraft pulp, some  
1404 papermaking sludges, by refluxing PeOH and HeOH at their boiling points, in the presence of  
1405 highly concentrated acid, and optimizing the reaction time (runs PeL\_3–PeL\_5, Table 17; runs  
1406 HL\_3–HL\_5, Table 17). For both these ALs, the highest yields were ascertained starting from the  
1407 softwood kraft pulp and the yield from the different substrates followed the trend: softwood kraft  
1408 pulp >hardwood kraft pulp> papermaking sludge “G”. This was mainly due to the very different  
1409 hexose content of the three biomasses that was about 90, 80, and 50 wt% for softwood kraft pulp,  
1410 hardwood kraft pulp, and papermaking sludge “G”, respectively.

#### 1411 4. Considerations on the catalysis issues, main process bottlenecks and improvable aspects

1412 To identify the main bottlenecks and improvable aspects of the alcoholysis process, it is  
1413 necessary to consider more critically the overall available data and, consequently, evaluate the most  
1414 appropriate choices, especially those related to the target ALs, the starting feedstocks, and the  
1415 catalysts of greatest interest.

1416 Regarding the choice of the most suitable ALs, the comparison among the available data from  
1417 both model and real feedstocks confirms that ML and EL are undoubtedly the most studied esters  
1418 and, consequently, the most successful candidates for the possible development of valuable  
1419 applications in the immediate future. The first pioneering work of Silva *et al.* [17] on the economic  
1420 feasibility of the EL production on a greater scale, together with the acknowledged use of ML and EL  
1421 as bio-additives for improving the properties of different transportation fuels [41], indirectly confirm  
1422 this tendency. In particular, Tian *et al.* [174] reported that blends of ML or EL (10 vol.%) in Euro 95  
1423 gasoline have a superior anti-knock quality to the reference Euro 95 gasoline. However, even if the  
1424 antiknock index of ML is high, its full miscibility with water and its separation from gasoline at cold  
1425 temperatures makes practically disadvantageous its use for this purpose [47]. Also in the field of  
1426 diesel fuels, the use of EL as bio-based cold-flow improvers in bio-diesel fuels has been  
1427 demonstrated [47,175] but hindered by miscibility issues [176]. To further increase the AL miscibility  
1428 in diesel fuels, now the attention is moving rather towards higher molecular-weight alcohols. In this  
1429 context, the use of PL as a fuel-blender does not lead to remarkable advantages on fuel properties,  
1430 and this poor interest is indirectly confirmed by the few available catalytic data, whilst that of BL has  
1431 recently aroused great interest, allowing cleaner combustion, mainly in terms of low CO and soot  
1432 emissions [52,53]. Therefore, longer-chain ALs are certainly more appropriate for diesel-fuel blends  
1433 [177] but, according to the available data, their syntheses are more difficult, being realized mostly  
1434 starting from the expensive pure levulinic acid, thus making more appropriate the use of these ALs  
1435 for niche applications, rather than for high-volume ones. Definitely, among the possible candidates,  
1436 EL and BL represent the most promising ALs for the real development of high-volume fuel  
1437 applications, already in the immediate future.

1438 The choice of the appropriate starting feedstock is fundamental and strategic for improving the  
1439 alcoholysis process, for the exploitation of the C6 fraction of biomass. Most of the available data  
1440 reported in this review have been obtained adopting model C6 feedstocks, especially soluble mono-  
1441 and disaccharides, with loadings generally below 4 wt%. The preference of soluble C6 mono- and  
1442 disaccharides is certainly convenient for demonstrating the good performances of *ad hoc* synthesized  
1443 catalysts, thus minimizing substrate-catalyst mass transfer problems. Besides, recycling tests of the  
1444 synthesized heterogeneous catalysts generally provide satisfactory results, because the issue of solid  
1445 humin formation for the alcoholysis of these model carbohydrates is not so relevant as in the  
1446 hydrothermal process. Therefore, the use of these convenient feedstocks minimizes the char  
1447 formation, enabling a more agile recovery of the catalysts, which generally maintain almost  
1448 unaltered their physicochemical properties, after many recycling runs. Anyway, from an applicative  
1449 perspective, the adoption of these model feedstocks is concretely unsustainable for the development  
1450 of this process intensification, which should instead prefer the use of cheap or, even better, waste

1451 real biomasses: this is certainly the main bottleneck to face for the development of the alcoholysis  
1452 process [61]. Already moving towards the more complex model cellulose, the issue of by-product  
1453 formation is significant and this issue becomes much more considerable by using the real  
1454 lignocellulosic biomass, where the final solid residue includes the contribution of both humin and  
1455 lignin components. For these reasons, catalyst heterogenization becomes a difficult issue to solve,  
1456 also taking into account that the new catalysts should have increasingly satisfactory performances  
1457 and maintain prolonged recyclability. Based on these considerations, in the case of real biomass  
1458 alcoholysis, the use of very dilute mineral acids (in particular  $\text{H}_2\text{SO}_4$ ) is preferred over that of  
1459 heterogeneous catalysts, whose application is instead almost limited to AL synthesis from simple  
1460 model carbohydrates. The range of the catalyst loading adopted for the conversion of model  
1461 compounds and real biomasses is wide (0.02-30 wt%), the chosen value depending on the type of  
1462 catalyst and the reaction conditions. Lower catalyst loadings are generally used for the mineral  
1463 acids, requiring a higher reaction temperature to achieve the highest AL yield, about 50-60 mol% in  
1464 the most difficult cases, e.g. starting from the recalcitrant cellulose or real biomass. The preference of  
1465 the homogeneous acids for the alcoholysis of real biomass also favors the use of higher feedstock  
1466 loadings (6-10 wt%), if compared with those of the model compounds. The use of higher loadings is  
1467 strategic for increasing the AL concentration in the reaction mixture, in agreement with the *high*  
1468 *gravity* approach [63], reducing the AL separation costs and making the whole process economically  
1469 more profitable.

1470 According to the available data, the chemical properties of the catalyst can be adjusted and  
1471 improved. Alkyl lactate and 1,1,2-trialkoxyethane are formed with an excess of Lewis acidity, while  
1472 humins with an excess of Brønsted or Lewis acids. In addition to these reaction by-products, the  
1473 preference of a very low concentration of Brønsted acids is of paramount importance for limiting the  
1474 dialkyl ether formation, which is responsible for a significant consumption and loss of the solvent,  
1475 with dialkyl ether yields up to 60 mol% [41,43]. Anyway, a limited formation of dialkyl ether is  
1476 allowed, thanks to its valuable fuel properties [178], and its separation from the reaction mixture is  
1477 generally simple. The proper balance between Brønsted and Lewis acidity appears of paramount  
1478 importance for maximizing the AL production and, consequently, minimizing that of by-products.  
1479 Many authors have strategically chosen fructose as starting feedstock, avoiding the Lewis-catalyzed  
1480 isomerization from glucose to fructose, thus proposing Brønsted acids and obtaining very high  
1481 yields in AL. Again, this solution is academically convenient but industrially uninteresting, whilst  
1482 the use of real feedstocks must take into account the Lewis-catalysed steps. Taking into account the  
1483 alcoholysis of the model cellulose, which is the most difficult model substrate to convert into ALs,  
1484 the combined use of traditional Brønsted acids (such as  $\text{H}_2\text{SO}_4$ , PTSA, NSA or  $\text{H}_3\text{PO}_4$ ) and Lewis  
1485 acids, in particular aluminum derivatives (e.g.  $\text{Al}_2(\text{SO}_4)_3$ ,  $\text{Al}(\text{acac})_3$ ,  $\text{Al}(\text{OEt})_3$ ,  $\text{Al}(\text{OH})_3$ ) [79] and metal  
1486 triflates (e.g.  $\text{In}(\text{OTf})_3$  or  $\text{Y}(\text{OTf})_3$ ) [27,122], is particularly promising, given the very high AL yields  
1487 (70-75 mol%), if compared with the sole Brønsted acid (50-60 mol%, for the synthesis of ALs with the  
1488 most efficient  $\text{H}_2\text{SO}_4$ ). In this context, it is interesting that already the Brønsted-Lewis acidity of the  
1489 sole  $\text{Al}_2(\text{SO}_4)_3$  is enough to achieve the highest AL yields (about 70 mol% for ML and EL) [32], thus  
1490 avoiding the addition of mineral acid as co-catalyst, and achieving considerable advantages on the  
1491 separation/recovery of the spent catalyst. Eventually, it is possible to further modulate the  
1492 Brønsted-Lewis acidity of  $\text{Al}_2(\text{SO}_4)_3$ , by using other metal salts as co-catalysts, such as with the  
1493 system  $[\text{Al}_2(\text{SO}_4)_3+\text{Fe}_2(\text{SO}_4)_3]$ , adopted for the BL synthesis from model cellulose, reaching  
1494 performances similar to those of sulfuric acid (40 mol%, in both cases) [146]. Lastly, the ML synthesis  
1495 in the presence of a sulfonated hydrochar as the heterogeneous catalyst appears interesting [85].  
1496 Despite the reported ML yield from cellulose is not particularly high (30 mol%) and the bio-char was  
1497 obtained from a different process (biomass pyrolysis), the possibility of sulfonating the char  
1498 recovered from the same solvothermal processes deserves further research and development,  
1499 allowing the valorization of waste by-products produced within the same process, rather than using  
1500 more costly acid sulfonic resins, thus supporting the biorefinery and the intensification concepts  
1501 [61]. In this context, the addition of Lewis acids as the reaction co-catalysts, should be evaluated also  
1502 in this case, extending the research towards the synthesis of longer-chain ALs.



1503 Moving towards the alcoholysis of real biomasses, the comparison of the catalyst performances  
1504 becomes more difficult, due to the different chemical composition of the starting biomass feedstocks,  
1505 which is often untold. As a general consideration, the use of diluted Brønsted acids (in particular  
1506  $\text{H}_2\text{SO}_4$ , PTSA and BSA), together with Lewis ones (especially Al salts, e.g.  $\text{Al}_2(\text{SO}_4)_3$ ,  $\text{Al}(\text{acac})_3$ , or  
1507  $\text{AlCl}_3$ , but also  $\text{CuSO}_4$ ), actually represents the best and simplest solution for maximizing the  
1508 production of short-chain ALs, e.g. ML and EL, achieving similar yields to those obtained with the  
1509 traditional  $\text{H}_2\text{SO}_4$ , generally in the range 20-30 wt%. Eventually, the sole use of inorganic salts,  
1510 endowed with Lewis/Brønsted acidity, deserves further investigation for this one-pot approach,  
1511 given the acceptable AL yields reported in the literature [55,74], thus completely avoiding the use of  
1512  $\text{H}_2\text{SO}_4$ , and preferring the conversion of biomasses which are rich in cellulose and poor in lignin.  
1513 When longer-chain ALs are desired, the one-pot alcoholysis of the real biomass requires stronger  
1514 acid catalysts, which is why  $\text{H}_2\text{SO}_4$  is still the preferred catalyst, thus giving less importance to the  
1515 careful balance of the Brønsted-Lewis acidity. Moreover, the addition of any pretreatment steps, for  
1516 example, to improve the accessibility of the cellulose and/or fractionate the biomass components  
1517 (e.g. mechanical ball-milling, organosolv or ionic liquid pre-treatments), should lead to an  
1518 improvement of the AL yields, by this way compensating for the added costs. However, the  
1519 reported data for the different ALs clearly show that up to now these pre-treatments do not lead to  
1520 such striking improvements, further supporting the proposed simpler choices, e.g. the preference of  
1521 the direct biomass conversion, aided by cheap diluted and tunable catalysts. Moreover, especially in  
1522 the case of real low-cost or waste biomass, the unjustified addition of expensive treatments would  
1523 create evident contradictions.

## 1524 5. Conclusions

1525 Alkyl levulinates are valuable chemicals having a strong market potential, mainly as  
1526 oxygenated bio-fuels. However, to enhance their production on a larger industrial scale, it is  
1527 necessary to start directly from cheap precursors, such as C6 carbohydrates and, even better,  
1528 lignocellulosic or waste biomasses, rather than from more expensive and pure levulinic acid.  
1529 Therefore a direct cascade approach should allow to postpone and reduce the number of purification  
1530 steps, with remarkable advantages on the alkyl levulinate yield and, more generally, on the total  
1531 costs of the process. For these prime reasons, this review has been focused on the use of model C6  
1532 carbohydrates and real biomasses in the direct alcoholysis to give different levulinates, dealing with  
1533 the most interesting and recent advances in catalysis. Diluted sulfuric acid results the most  
1534 performing catalyst for the alkyl levulinate production, leading to the highest yield of about 90  
1535 mol%, and the reference for the development of new catalysts. The use of model C6 carbohydrates  
1536 has been preferred by researchers to demonstrate the effectiveness of *ad hoc* synthesized catalysts,  
1537 which are often very elegant, but too expensive and of little practical use. In this context, the choice  
1538 of fructose as the starting substrate makes it possible to simplify the catalysis, which is mainly of  
1539 Brønsted-acid type, thus generally achieving very high yields, whilst glucose and its polymers  
1540 require an additional isomerization step, catalyzed by Lewis acids. The tunability between these  
1541 different acidities has been the subject of many studies and, among many proposed catalytic  
1542 systems, the use of metal salts, especially  $\text{Al}_2(\text{SO}_4)_3$ , alone or in combination with very diluted  
1543 mineral acids, represents the best compromise between catalytic performances and costs. These  
1544 catalysts result attractive also for the alcoholysis of the more recalcitrant cellulose and even for that  
1545 of real biomass, reaching performances similar to that of the traditional sulfuric acid, whilst other  
1546 systems, such as heteropolyacids, sulphonic acids, zeolites, clays, sulfated metal oxides, and  
1547 properly modified catalysts, are still poor performing for the alcoholysis of these tough substrates.  
1548 Moreover, in the case of the real biomass alcoholysis, the issue of recovery/recycling of the  
1549 heterogeneous catalyst becomes even more problematic, due to the co-presence of char, which  
1550 includes carbonaceous degradation products, mainly humins and lignin. In principle, the use of  
1551 sulfonated char, which is produced within the same solvothermal process, as a heterogeneous  
1552 catalyst for the alcoholysis reaction, could satisfy the concepts of sustainability and biorefinery, but  
1553 low alkyl levulinate yield from soluble carbohydrates hinders its use for the biomass alcoholysis

1554 shortly. On this basis, dilute sulfuric acid remains the preferred choice for the alcoholysis of real  
1555 substrates, leading to yields up to about 60 wt%. To favor the intensification of the process, the  
1556 conversion of cellulose-rich biomasses, such as wastes deriving from the papermaking process,  
1557 should be preferred for improving the yield to alkyl levulinates, being less recalcitrant towards the  
1558 alcoholysis. Moreover, the use of cellulose-rich feedstocks, which do not include the lignin  
1559 component, is particularly appropriate for improving the employment of heterogeneous catalysts,  
1560 simplifying their recovery. Therefore, the topic is surely of great interest and offers real prospects for  
1561 industrial applications but it is necessary to deep the research by both proposing appropriate  
1562 feedstocks and carefully tuning the adopted catalytic systems and reaction conditions.

1563  
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