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1 Simultaneous production of furfural and levulinic acid from pine sawdust via acid-  
2 catalysed mechanical depolymerization and microwave irradiation

3

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13

14 Abstract

15 In this work pine sawdust was converted into levulinic acid (LA) and furfural. Sawdust  
16 was first pre-treated with sulfuric acid-catalysed mechanical depolymerization. The  
17 conversion reactions were then performed with microwave heating at 180 °C. To  
18 enhance the furfural yield and the efficient separation of furfural and LA, a biphasic  
19 water-toluene reaction system was used. The effect of an additional catalyst, AlCl<sub>3</sub>, on  
20 the yield of LA and furfural was also studied. According to the results the pre-treatment  
21 method enhanced the yields of LA. In addition, due to the microwave heating the  
22 reaction times were short. Additional AlCl<sub>3</sub> catalyst enhanced the LA yield, however  
23 excellent furfural yields were achieved even without it. Best LA yield (38%) was

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24 achieved with 6 h of milling combined with 30 min of microwave heating while the best  
25 furfural yield (85%) was achieved with 4 h of milling and 20 min of microwave heating.

26

27 Keywords: Acid catalysis; Mechanical depolymerization; Microwave irradiation;  
28 Levulinic acid; Furfural; Biomass;

29

## 30 1. Introduction

31 Most of the industrial chemicals are currently being prepared from fossil resources.

32 However, the oscillating increase in fossil fuel prices as well as the depletion of the  
33 fossil resources is driving forward the search for alternative renewable feedstocks in the  
34 production of so called platform chemicals, which could replace the oil-based  
35 chemicals. [1]

36 Among the most important platform chemicals are levulinic acid (LA) and  
37 furfural [2-4]. LA can be used as a raw material for e.g. resins, plasticizers, textiles,  
38 animal feed, coatings, antifreeze, fuel additives, polymer precursors, herbicides,  
39 pharmaceuticals and flavour substances. Due to its chemical structure with ketone  
40 carbonyl and carboxylic functional groups, it can be converted into various other  
41 important chemicals such as succinic acid,  $\gamma$ -valerolactone, calcium levulinate, 1,4-  
42 butanediol, tetrahydrofuran (THF), acrylic acid and ethyl levulinate. [1,5-7] Furfural on  
43 the other hand is used for the preparation of many small commercially available  
44 chemicals employed for the synthesis of polymeric materials or bioactive compounds  
45 [8]. Such chemicals include furoic acid [9], furfuryl alcohol [10] or 2-furonitrile [11].  
46 Furfural is also used as the starting material for the synthesis of organic solvents such as  
47 2-methyltetrahydrofuran (2-MTHF) [12] and THF [8].

48 Cellulose and hemicellulose rich lignocellulosic biomasses, such as  
49 sawdust, are currently the most studied and abundant raw materials in the production of  
50 LA and furfural. Both conversion reactions have already been known for a long time.  
51 E.g. Adams and Voorhees reported the production of furfural from corn cob in 1921  
52 [13] and McKenzie produced levulinic acid from cane sugar in 1929 [14]. More recent  
53 literature includes the production of LA e.g. from post-harvest tomato plants [15],  
54 Jerusalem artichoke [16], lignocellulosic fibres of paper waste [17], red algae [18],  
55 wheat straw [19,20], silver grass [21], poplar sawdust, olive tree pruning and paper  
56 sludge [20], while furfural has been produced e.g. from aspen and maple chips [22] as  
57 well as silver grass [21]. However, there are some challenges related to the conversion  
58 of biomass to those valuable chemicals. First, the recalcitrance of the lignocellulose  
59 causes a major challenge for its utilization. The cellulose and hemicellulose components  
60 of the biomass are tightly linked together and to the lignin, the third main component of  
61 lignocellulose, which makes the structure highly resistant to treatment. [23,24]  
62 Therefore pre-treatment of lignocellulose prior to the conversion reactions is critical.  
63 Second, furfural, which is formed during the conversion reactions, can further react with  
64 sugars present in the reaction solution to form humins, which are dark-brown solid by-  
65 products [5].

66 The pre-treatment techniques can be classified into chemical, physical,  
67 physicochemical and biological methods. One of the commonly used physical methods  
68 is mechanical disruption by milling, which can reduce biomass particle size and  
69 increase its surface area, break the hydrogen bonds between cellulose, hemicellulose  
70 and lignin components as well as enable the access of the acid catalysts. [25] In our  
71 recent study the mechanical pre-treatment method was combined with acid catalysis by  
72 mixing biomass i.e. pine sawdust (PSD) with concentrated H<sub>2</sub>SO<sub>4</sub> prior to the milling

73 process. The resulting one-step acid-catalysed mechanical depolymerization method led  
74 to the fast disruption of lignocellulosic structure and converted the PSD into total  
75 reducing sugars and increased the water-solubility of the PSD considerably. [26]

76 In this work we have studied the conversion of lignocellulosic biomass,  
77 PSD, to LA and furfural. In order to accelerate the conversion of PSD acid-catalysed  
78 mechanical depolymerization was used as the pre-treatment method and microwave  
79 irradiation as the heating method for the conversion reaction. It has been found in  
80 previous studies that microwave heating accelerates the conversion reaction as well as  
81 enhances the product selectivity [8,20,27-31]. There is also a significant, up to 85-fold,  
82 energy saving involved in the microwave-assisted processes [32]. In order to prevent  
83 furfural from forming humins, and to separate LA and furfural from each other during  
84 the conversion reactions a biphasic (water-toluene) system was used. To our knowledge  
85 pine sawdust, has not been converted simultaneously into LA and furfural before using  
86 mechanical depolymerization and microwave heating.

87

## 88 2. Materials and methods

### 89 2.1 Pine sawdust

90 Pine sawdust was received from the Biofuel Technology Centre in Umeå. It consisted  
91 mainly of cellulose (42 - 44%), hemicellulose (25 - 26%) and lignin (27 - 29%). [26]  
92 Before use it was sieved through 1 mm sieve and dried in an oven at 50 °C overnight.

93 Toluene, 2-methyltetrahydrofuran and anhydrous AlCl<sub>3</sub> were purchased  
94 from Sigma Aldrich and H<sub>2</sub>SO<sub>4</sub> (98%) from VWR. All chemicals were analytical grade  
95 and used without further purification.

96

97

98 2.2 Pre-treatment of pine sawdust by acid-catalysed mechanical depolymerization

99 In a typical experiment PSD (2.5 g) and concentrated H<sub>2</sub>SO<sub>4</sub> (0.113 g, corresponding to  
100 0.45 mmol of H<sub>2</sub>SO<sub>4</sub>/g of PSD) were mixed in a 45 ml stainless steel bowl. The mixture  
101 was milled in a planetary micro mill (FRITSCH, planetary micro mill pulverisette 7  
102 premium line) with approximately 8 ml (46.5 g) of 3 mm diameter grinding balls  
103 prepared from ZrO<sub>2</sub>. The temperature of the milling process was controlled by a “1 min  
104 milling/1 min pause” alternation mode at 13.3 Hz [26]. Temperature was checked with  
105 an electronic thermometer at the end of the milling through a pressure relief valve of the  
106 mill and was found to remain at 50 - 55 °C during all the milling processes. The total  
107 milling time was 2, 4 or 6 h corresponding thus to 1, 2 or 3 h of active milling.

108

109 2.3 Conversion of pre-treated pine sawdust to levulinic acid and furfural in microwave  
110 reactor

111 In a typical experiment the pre-treated PSD (0.2 g, containing ca. 9 mg of H<sub>2</sub>SO<sub>4</sub>) and  
112 additional acid catalyst, AlCl<sub>3</sub>, (0 or 5 mg (0.037 mmol)) were weighed into a  
113 microwave reactor vessel (size 2 - 5 ml) equipped with a stirring bar. Water (1 ml) and  
114 toluene (4 ml) were added. The mixture was heated in the microwave reactor (Biotage  
115 Initiator with a single-mode microwave unit) at 180 °C for 10, 20, 30 or 60 minutes.

116 After the reaction, a 1 ml sample was taken from the toluene layer and 0.5  
117 ml sample from the water layer. To separate the levulinic acid from the water layer, the  
118 layer was extracted twice with 0.5 ml of 2-MTHF and the 2-MTHF layers were  
119 combined. Internal standard (0.2 ml, prepared by dissolving 1 ml of undecane in 250 ml  
120 of 2-MTHF) was added to the sample as well as to the sample taken from the toluene  
121 layer. All samples were analysed with GC-MS.



147

148           The theoretical amount of furfural was based on the xylose content of pine  
149 sawdust and was estimated to be 5% [33]. The theoretical amount of LA was based on  
150 the total holocellulose content of PSD reduced by the estimated amount of xylose, i.e.  
151  $70\% - 5\% = 65\%$ .

152           Besides the presence of furfural and LA that of 5-hydroxymethylfurfural  
153 (HMF) was also determined from the samples with GC-MS by using the same method  
154 as for LA and furfural. The retention time of HMF was 7.4 min and its yield-% was  
155 calculated with the equation 3:

156

157 
$$\text{HMF Yield (\%)} = \left[ \frac{\text{the amount of HMF produced}}{\text{the theoretical amount of HMF from}} \right. \\ 158 \left. \frac{\text{the holocellulose content of PSD}}{\text{}} \right] * 100\% \quad (3)$$

159

### 160 3. Results and discussion

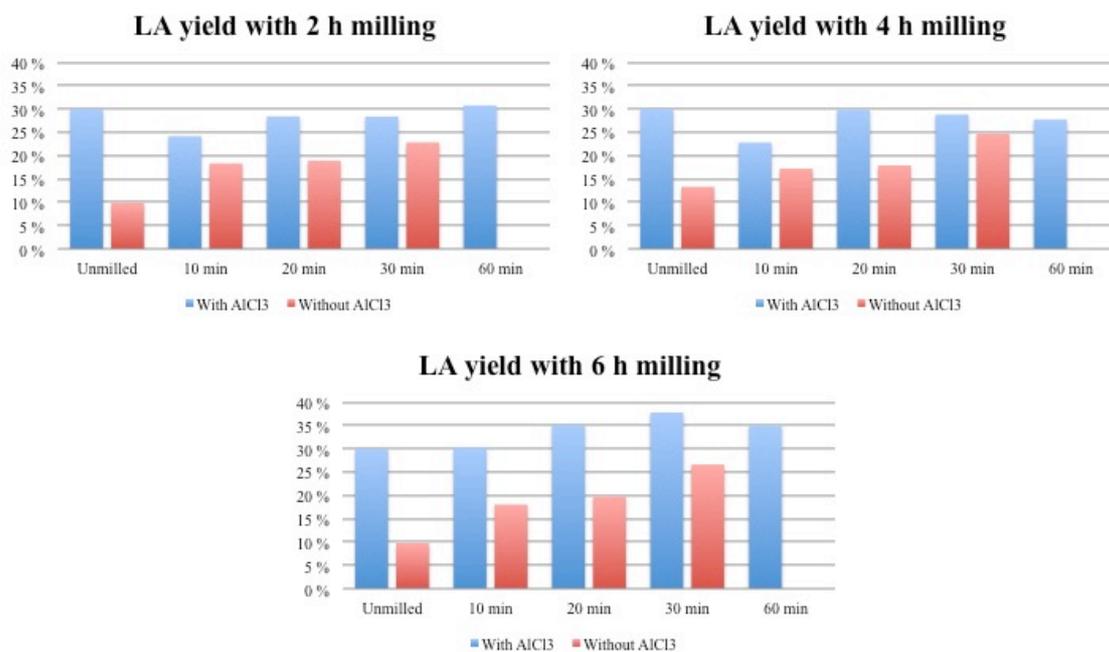
161 The pine sawdust was pre-treated prior to the conversion reactions by direct acid-  
162 catalysed depolymerization method.  $\text{H}_2\text{SO}_4$  was used as the acid catalyst and its  
163 concentration, 0.45 mmol/g of sawdust, was kept constant. The amount of acid was  
164 based on our previous study [26] according to which, that concentration was the most  
165 effective towards PSD depolymerization but not too high to cause PSD burning during  
166 milling i.e. turning to black sticky substance, which would adhere to the walls of the  
167 milling bowl and milling balls [34]. The burning of the PSD was also avoided by  
168 controlling the temperature increase inside the milling bowl by performing the milling  
169 in cycles. One cycle consisted of 1 min milling and 1 min pausing. With such milling  
170 cycle the temperature inside the mill remained at 50 - 55 °C during all the milling  
171 processes. In addition, the milling was performed with 3 mm grinding balls, since it was

172 found previously that the 3 mm balls provided the greatest impact on the reduction of  
173 the PSD size [26].

174           The effect of milling time was studied with total milling times of 2, 4 or 6  
175 hours. After the milling the pine sawdust samples, which had been ground into fine  
176 powder, were subjected to conversion reactions in a water-toluene biphasic system with  
177 microwave irradiation as the heating method. The temperature of the conversion  
178 reactions was kept at 180 °C, which was the maximum operating temperature of the  
179 microwave reactor. Lower conversion reaction temperatures were not studied, since it  
180 has been found in previous studies that the conversion of lignocellulosic biomass into  
181 LA requires high temperatures, usually 180 °C or higher. [35,16-18]

182           Toluene was selected as the organic solvent for the biphasic system, since  
183 as a non-polar solvent it dissolves furfural well and LA poorly [36-39]. In fact, toluene  
184 had great effect on the furfural yield. Some reference reactions were performed without  
185 toluene in the same reaction conditions as the actual conversion reactions and in those  
186 reactions the furfural yield was 21% at best (data not shown). Without the toluene layer  
187 furfural was able to react further into levulinic acid, side products or humins. However,  
188 according to GC-MS the increase in levulinic acid yield was only 2% units at best,  
189 when the conversion reaction was performed without the toluene layer. This suggests  
190 that some of the furfural reacted also into side products or humins. However, no clear  
191 new peaks were detected from the gas chromatograms with the used GC method.

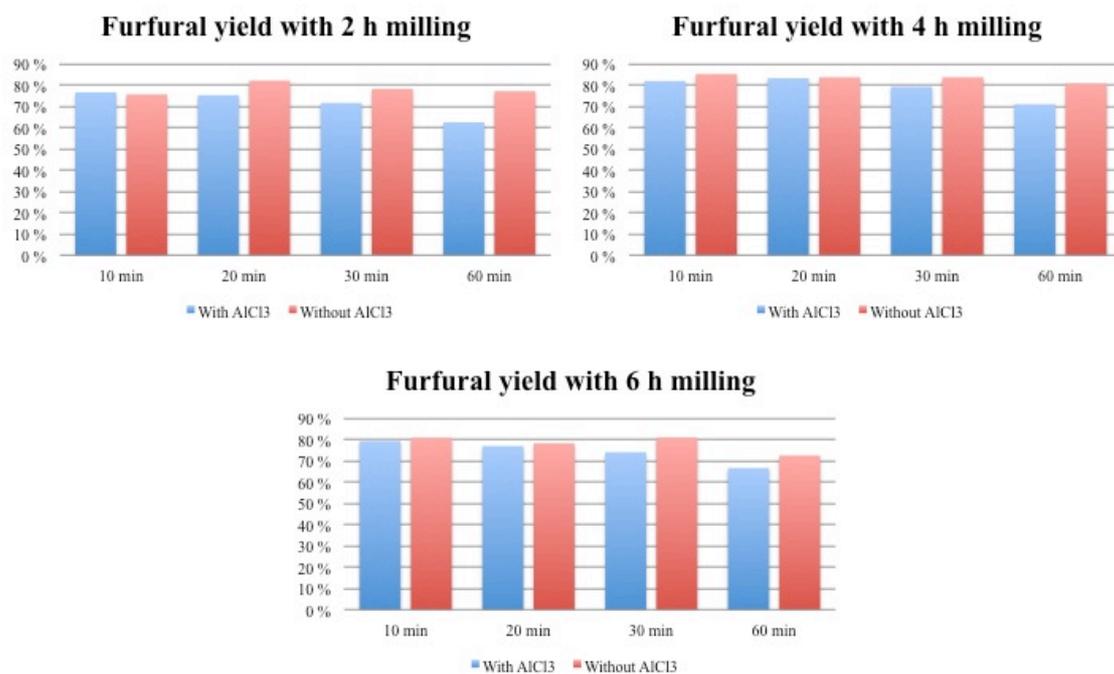
192           The results of the study are presented in Figures 1 and 2.



194

195 Figure 1. The effect of the milling time and the conditions of the subsequent conversion  
 196 reaction on the LA yield. Conversion reaction temperature (180 °C) and the amount  
 197 AlCl<sub>3</sub> catalyst (5 mg, when used) were kept constant. The conversion reaction time for  
 198 the unmilled pine sawdust was 60 min.

199



200

201 Figure 2. The effect of the milling time and the conditions of the subsequent conversion  
 202 reaction on the furfural yield. Conversion reaction temperature (180 °C) and the amount  
 203 AlCl<sub>3</sub> catalyst (5 mg, when used) were kept constant.

204

205 3.1 The effect of the milling time

206 The conversion of PSD to LA was greatly influenced by the milling time, which can be  
 207 seen from Figure 1. When milling time was shortest, 2 h, the highest LA yield was 31%,  
 208 which was reached after 60 min of microwave heating, and with AlCl<sub>3</sub> present in the  
 209 reaction. Similar LA yield (30%) was obtained in a reference reaction performed with  
 210 the same heating time, but with an unmilled PSD sample (Figure 1). When milling time  
 211 was increased to 4 h, the highest LA yield remained at 30% but was reached  
 212 considerable faster, in 20 min. Furthermore, when milling time was 6 h, the yield of LA  
 213 was increased noticeable to 38% and was achieved already after 30 min of microwave  
 214 heating (Figure 1).

215                   The great effect of the pre-treatment method can also be seen from the  
216 conversion reactions performed without  $\text{AlCl}_3$  (Figure 1). The reference reaction  
217 performed with unmilled PSD yielded only 18% of LA after 60 min of microwave  
218 heating (Figure 1). However, when PSD was milled 2, 4 or 6 h, the LA yield after 60  
219 min of microwave heating was higher, 23, 25 or 26%, respectively (Figure 1).

220                   The positive effect of the milling time on the LA yield and on the  
221 conversion reaction time can be explained by the formation of total reducing sugars  
222 during the milling, which has been shown in previous studies [26,34,40]. In this study,  
223 due to the biphasic system, LA is mainly formed from hexose monosaccharides via 5-  
224 hydroxymethylfurfural intermediate. In the case of PSD, the most abundant hexose is  
225 glucose. However, it is present as anhydroglucose units, part of the cellulose and  
226 hemicellulose chains. Therefore, before the conversion reaction to LA can take place,  
227 the cellulose and hemicellulose components need to be hydrolysed into hexose  
228 monosaccharides. The pre-treatment of PSD by milling with acid increased the amount  
229 of reducing sugars in the biomass [26]. The reducing sugars were then hydrolysed faster  
230 into glucose during the conversion reaction than the cellulose or hemicellulose in the  
231 unmilled PSD. In addition, the longer the milling time was during the pre-treatment  
232 step, the more reducing sugars were formed in the PSD.

233                   Longer milling times than 6 h were not studied, since milling is considered  
234 as an energy consuming process [41] and very reasonable LA yields were achieved after  
235 4 or 6 h of milling. It has also been found in recent studies that longer milling times  
236 may cause the burning of the biomass material, when there is acid present during the  
237 milling. [26,34,40]

238                   The milling time or additional Lewis acid catalyst did not have much  
239 effect on the furfural yield (Figure 2). Excellent furfural yields were achieved with and

240 without the additional  $\text{AlCl}_3$  catalyst and already after 10 min of microwave irradiation.  
241 The highest furfural yield slightly increased, from 82 to 85%, when milling time  
242 increased from 2 to 4 h, respectively. However, when milling time was 6 h the highest  
243 furfural yield was 81% indicating that furfural started to convert into LA or other  
244 products. Furfural is mainly formed from pentose (C5) sugars, i.e. xylose, which is only  
245 found in hemicellulose component of lignocellulose [8]. Compared to cellulose,  
246 hemicellulose is less tightly bound in the lignocellulosic structure and thus reacts more  
247 easily. Therefore, even short, 2 h, milling time loosened the lignocellulosic structure  
248 enough enabling the conversion of pentose sugars to furfural with good yield with short  
249 reaction time (10 - 20 min, Figure 2).

250

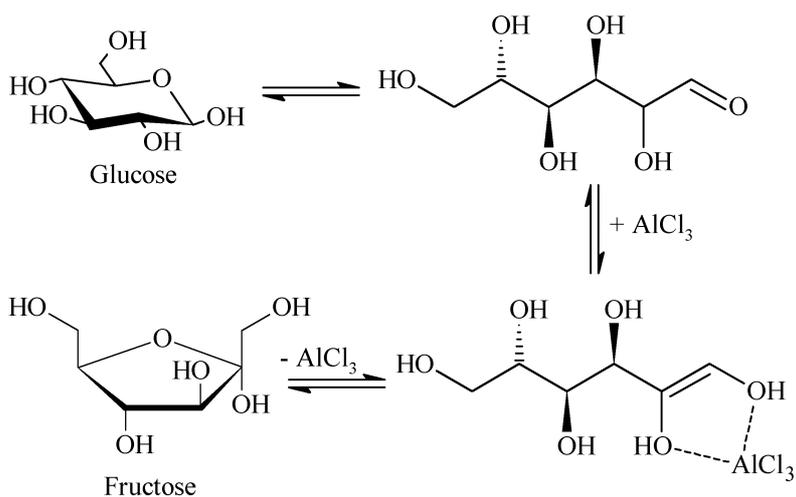
### 251 3.2 The effect of the additional Lewis acid catalyst

252 The yield of LA benefited greatly from the  $\text{AlCl}_3$  catalyst. The highest LA yield in the  
253 study, 38% (Figure 1), was obtained after 30 min of microwave irradiation with PSD  
254 milled for 6 h and  $\text{AlCl}_3$  as an additional catalyst. The corresponding LA yield for the  
255 PSD conversion reaction performed without the additional catalyst was only 20%  
256 (Figure 1). It has been reported in previous studies that Lewis acid catalysts, such as  
257  $\text{AlCl}_3$  or  $\text{CrCl}_3$ , combined with Brønsted acids help to overcome the glucose to fructose  
258 isomerization limitations and thus enhance the decomposition of biomass into 5-  
259 hydroxymethylfurfural, which is the pre-cursor of LA. [1,39,42] The exact route for the  
260 Lewis acid catalyzed isomerization is not known but based on the recent literature, a  
261 plausible route is presented in Figure 3. [43,44]

262

263

264



265

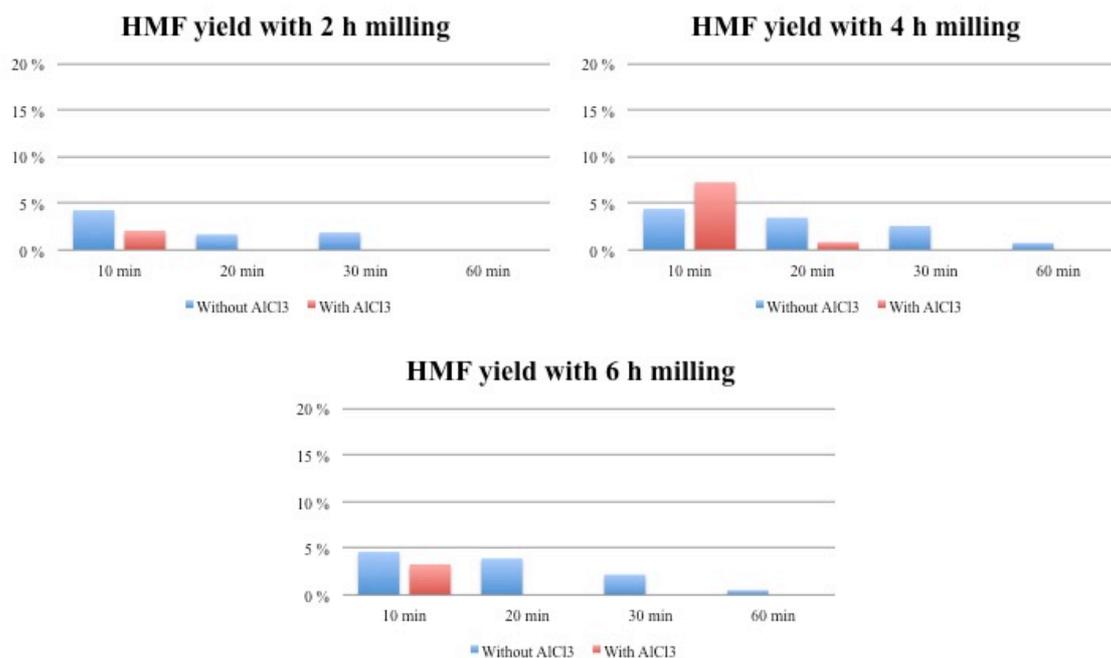
266 Figure 3. Proposed route for the  $\text{AlCl}_3$  catalyzed isomerization of glucose to fructose.

267 [43,44]

268

269 The efficiency of  $\text{AlCl}_3$  catalyst was also observed by monitoring the  
 270 HMF contents of the samples taken after the conversion reactions (Figure 4). When  
 271  $\text{AlCl}_3$  was used in the conversion reaction, small amount of HMF (yield < 7%) was  
 272 present after 10 min of microwave irradiation. After 20 min of microwave heating  
 273 practically all the HMF had reacted further into LA. However, when conversion  
 274 reactions were performed without the additional catalyst, small amounts of HMF (yield  
 275 < 5%) could be detected from the reaction samples after 30 min of microwave  
 276 irradiation and trace amounts even after 60 min of heating.

277



278

279 Figure 4. The effect of the milling time and the conditions of the subsequent conversion  
 280 reaction on the HMF yield. Conversion reaction temperature (180 °C) and the amount  
 281 AlCl<sub>3</sub> catalyst (5 mg, when used) were kept constant.

282

283 On the other hand, the effect of the Lewis acid catalyst, AlCl<sub>3</sub> on the yield  
 284 of furfural was not significant. In fact, with the exception of the conversion reactions  
 285 performed after 4 h of milling, furfural yield was higher, when no AlCl<sub>3</sub> was used in the  
 286 conversion reactions. The recent literature suggests that the furfural yield is favoured by  
 287 the use of Lewis acid catalysts. The catalysts enhance the isomerization of xylose into  
 288 xylulose, which has been found to dehydrate more rapidly into furfural than xylose  
 289 (Figure S1 in Supplementary material). [37] The result achieved in this study, i.e. that  
 290 the AlCl<sub>3</sub> catalyst does not seem to have an effect into the furfural yield, might be  
 291 because AlCl<sub>3</sub> is a powerful catalyst. Therefore it could have enhanced the conversion  
 292 of furfural to LA even though a biphasic system was used. [45]

293

294 AlCl<sub>3</sub> was chosen to this study, since it has been proven previously to be  
 an efficient catalyst for biomass conversion reactions [45,46]. However, some other

295 catalysts were also studied to see, if similar LA or furfural yields could be achieved.  
 296 The studied catalysts are presented in Table 1. Chromium chloride hexahydrate was  
 297 chosen since it is a Lewis acid, like AlCl<sub>3</sub> and according to literature has shown to  
 298 enhance the glucose to fructose isomerization step and thus the conversion of biomass  
 299 to LA [42,47]. Amberlyst 15 and p-TsOH were chosen since they have the sulfonic acid  
 300 group and may thus enhance the conversion reaction of biomass similarly to sulfuric  
 301 acid. Boric acid has been proposed in a recent study by computational modelling and  
 302 deuterium-labelling studies to enhance the isomerization pathway from glucose to  
 303 fructose [48]. Also in another study it was found to be indispensable in the conversion  
 304 of glucose to 5-hydroxymethylfurfural [49]. The molar amount of studied catalysts was  
 305 kept the same as the amount of AlCl<sub>3</sub> and the experiments were performed with the PSD  
 306 sample milled for 6 h.

307

308 Table 1. The effect of various catalysts on the conversion of PSD to LA and furfural.  
 309 The milling time (3 h) and conversion reaction temperature (180 °C) were kept constant.  
 310 The molar amount of the studied catalyst was kept the same as the amount of AlCl<sub>3</sub>  
 311 catalyst (0.037 mmol).

| Catalyst                              | Furfural (%) / LA (%) |         |         |         |
|---------------------------------------|-----------------------|---------|---------|---------|
|                                       | 10 min                | 20 min  | 30 min  | 60 min  |
| CrCl <sub>3</sub> (6H <sub>2</sub> O) | 67 / 26               | 63 / 28 | 57 / 30 | 59 / 29 |
| Amberlyst 15                          | 81 / 14               | 76 / 18 | 75 / 25 | 71 / 26 |
| <i>p</i> -TsOH                        | 73 / 5                | 77 / 18 | 78 / 23 | 71 / 23 |
| Boric acid                            | -                     | -       | -       | 69 / 25 |
| AlCl <sub>3</sub>                     | 79 / 30               | 77 / 35 | 74 / 38 | 67 / 35 |

312

313

314 Based on the results, none of the studied catalysts was as effective as  
315  $\text{AlCl}_3$  in the same reaction conditions.  $\text{CrCl}_3$  gave the best results for the LA yield with  
316 the highest yield of 30% (Table 1). However the furfural yield was lowest with  $\text{CrCl}_3$   
317 catalyst. This indicates that  $\text{CrCl}_3$  enhanced the conversion reactions of furfural to LA  
318 or other products. When Amberlyst 15 and *p*-TsOH were used as the catalyst the  
319 furfural yields were good but did not differ at all from furfural yields achieved without  
320 any catalyst (Figure 1). On the other hand,  $\text{AlCl}_3$  did not enhance the furfural yields  
321 either. To improve the LA yields with Amberlyst and *p*-TsOH higher concentrations  
322 should be used and Amberlyst and *p*-TsOH should be combined with Lewis acid  
323 catalyst like  $\text{AlCl}_3$  instead of sulfuric acid. Boric acid should have worked similarly to  
324  $\text{CrCl}_3$  and  $\text{AlCl}_3$  and enhance the LA yield. However, the boric acid concentrations may  
325 have been too low. Further research is needed to see if it could replace  $\text{AlCl}_3$  as the  
326 catalyst in biomass conversion reactions.

327

### 328 3.3 Comparison with literature

329 The combination of acid-catalysed depolymerization by ball milling and microwave  
330 heating proved to be an efficient method to produce furfural and LA from PSD  
331 (holocellulose concentration of ca.  $0.86 \text{ mol L}^{-1}$ ).  $\text{H}_2\text{SO}_4$  was added only before the  
332 milling step so its concentration during the microwave heating was low ( $0.09 \text{ mol L}^{-1}$ )  
333 compared to many of the studies reported in literature. Also the amount of additional  
334 Lewis acid catalyst was low,  $0.037 \text{ mol L}^{-1}$ , compared to studies reported in literature.  
335 Furthermore, reasonable furfural and LA yields were achieved with short heating times,  
336 10-30 min. Thus the conditions used in this study during the conversion reactions were  
337 mild compared to reaction conditions found in previous literature. For example Rong et  
338 al. [39], prepared furfural (with the yield of 83%) from pure xylose ( $0.067 \text{ mol L}^{-1}$ ) with

339 H<sub>2</sub>SO<sub>4</sub> and Lewis acid (FeCl<sub>3</sub>) concentration of 1 mol L<sup>-1</sup> and 0.37 mol L<sup>-1</sup>, respectively  
340 and the reaction time of 5 h, while according to Mazar et al. [22] a furfural yield of 78%  
341 can be achieved from wood chips pre-hydrolysate with H<sub>2</sub>SO<sub>4</sub> concentration of 0.04  
342 mol L<sup>-1</sup> and total heating time of 98 min. Weiqi and Shubin [42] prepared LA (54%)  
343 from pure glucose (0.056 mol L<sup>-1</sup>) with H<sub>3</sub>PO<sub>4</sub> and CrCl<sub>3</sub> concentrations of 0.02 mol L<sup>-1</sup>  
344 and the reaction time of 2 h and Jeong [16] prepared LA (approximately 40%) from  
345 Jerusalem artichoke (0.39 mol L<sup>-1</sup>) with H<sub>2</sub>SO<sub>4</sub> concentration of 0.31 mol L<sup>-1</sup> and the  
346 reaction time of 34 min. According to kinetic models produced by Dussan et al. [21] the  
347 furfural yield of 27% and LA yield of 70% could be produced from silver grass (0.39  
348 mol L<sup>-1</sup>) in 3 and 112 min, respectively with the sulfuric acid concentration of 0.5 mol  
349 L<sup>-1</sup>. The kinetic model of Chang et al. [19], on the other hand, predicts the LA yield of  
350 20% from wheat straw in 38 min with H<sub>2</sub>SO<sub>4</sub> concentration of 0.36 mol L<sup>-1</sup>.

351

### 352 3.4 Microwave irradiation as the heating method

353 In this study microwave irradiation proved to be an efficient heating method for the  
354 conversion of pre-treated PSD to LA. The reactions were performed in a single-mode  
355 microwave reactor, for which the maximum reaction volume was 5 ml. Using the  
356 single-mode reactor allowed the safe processing of the small volume reactions in sealed  
357 reaction vessels. Also the used technology enabled fast heating of the reaction vessel  
358 and similar reaction conditions for all the performed reactions, since the irradiation was  
359 focused directly to the reaction liquid and the reaction temperature was carefully  
360 controlled by the microwave equipment software. It has been suggested in the literature  
361 that the rapid heating of the reaction mixture as well as the ability to use high reaction  
362 temperatures in sealed reaction vessels enable the short reaction times, improved purity  
363 as well as good yields of the products. [50,51]

364 From industry point of view it is important to be able to scale the small  
365 volume reactions into larger scale. However, there are some physical limitations, e.g.  
366 magnetron power and penetration depth of the irradiation, which restrain the  
367 microwave-assisted heating from becoming a viable heating method for large scale  
368 systems/the scale up of the traditional batch-type microwave processes. [51,52] There  
369 have been some improvements over the past few years with the batch-type systems in  
370 translation of the optimized small-scale conditions (mL) to larger scale (L). [51-53] Yet,  
371 the irradiation penetration depth issues may still inhibit the batch-type technology from  
372 achieving the product quantities that are industrially relevant. In addition, there are  
373 some safety concerns related to large, pressurized vessels. [51,52]

374 The limitations related to large-scale batch processes have made a  
375 continuous-flow technique a preferable option for processing volumes greater than 1000  
376 mL. In such systems the reaction mixture is passed through a microwave transparent  
377 coil, which is placed in the microwave reactor cavity. [51,52] Several examples can be  
378 found in literature, where microwave-assisted continuous-flow synthesis has been  
379 performed in kg scale. [54,55] Also, Morschhäuser et al. [52] demonstrated recently the  
380 synthesis of four relevant chemicals in a continuous microwave system on industrial  
381 scale.

382

### 383 Conclusions

384 Mechanocatalytical depolymerization performed by ball milling and with sulphuric acid  
385 as the catalyst was an efficient pre-treatment method when PSD was converted into LA  
386 and furfural with microwave irradiation as the heating method for the conversion  
387 reaction. The biphasic water-toluene reaction system enabled the separation of LA and  
388 furfural during the reaction. Due to the effective pre-treatment method the concentration

389 of sulfuric acid was low ( $0.09 \text{ mol L}^{-1}$ ), and it was enough to add it only prior to the  
390 milling step. Additional Lewis acid catalyst,  $\text{AlCl}_3$  enhanced the conversion reaction of  
391 the pre-treated PSD to LA but did not have an effect on the furfural yield. The highest  
392 LA yield in this study, 38%, was achieved with 6 h of milling and 30 min of microwave  
393 heating and the highest furfural yield, 85%, with 4 h of milling and 10 min of  
394 microwave heating. Compared to current literature the LA and furfural yields can be  
395 considered reasonable, since the starting material was biomass instead of e.g. pure  
396 cellulose. However, it has to be kept in mind that the study was performed at small-  
397 scale and transferring of the whole process into large-scale may not be straightforward.  
398 Milling is a known operation for particle size reduction and microwave-assisted  
399 synthesis has already been demonstrated at kg scale. Yet, there are issues related e.g. to  
400 corrosion resistance of the large-scale mills, the safety of the large-scale microwave  
401 reactors and re-optimization of the process conditions.

402

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407

#### 408 Supplementary material

409 Supplementary material associated with this article can be found in the online version.

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