

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

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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, AlCl₃, 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 AlCl₃ 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, γ -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 H₂SO₄ 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 AlCl₃ were purchased
94 from Sigma Aldrich and H₂SO₄ (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 H₂SO₄ (0.113 g, corresponding to
100 0.45 mmol of H₂SO₄/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 ZrO₂. 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 H₂SO₄) and
112 additional acid catalyst, AlCl₃, (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.

122 The reference reactions were performed similarly. The untreated PSD (0.2
123 g) and AlCl₃ (5 mg (0.037 mmol)) were weighed into the reaction vessel. Water (1 ml)
124 was added and the mixture was heated at 180 °C for 30 or 60 min. A sample was taken
125 from the water layer and extracted and analysed as mentioned above.

126

127 2.4 Analytical methods

128 The samples taken after the conversion reactions were analysed with Agilent GC-MS
129 (7890A series GC with a 5975D MS detector) equipped with a HP-1 capillary column
130 (0.25 mm x 30 m x 0.25 µm; Agilent Technologies Inc.). The GC oven temperature
131 program was 2 min at 50 °C and then from 50 to 250 °C at the ramping temperature of
132 20 °C/min. Finally the temperature was kept 1 min at 250 °C. The injection volume was
133 1 µl and the split ratio 50:1. The flow rate of the carrier gas (helium) was 0.9 ml/min.
134 Under these conditions the retention time of furfural and LA was 3.8 and 6.2 min,
135 respectively.

136 The concentrations of furfural and LA, determined with the GC-MS and
137 based on the concentration of the internal standard, were used to calculate the yields of
138 the products. In this work the yield of levulinic acid or furfural means the yield-% of
139 those compounds. The yield-% is the ratio between the actual amount of the compound
140 produced in the study and the theoretical amount of the compound, which could be
141 produced from the PSD. The yield-% were calculated with equations 1 and 2.

142

143 LA Yield (%) = [the amount of LA produced/the theoretical amount of LA from the
144 holocellulose content of PSD]*100% (1)

145 Furfural Yield (%) = [the amount of furfural produced/the theoretical amount of furfural
146 from the xylose of PSD]*100% (2)

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

159

160 3. Results and discussion

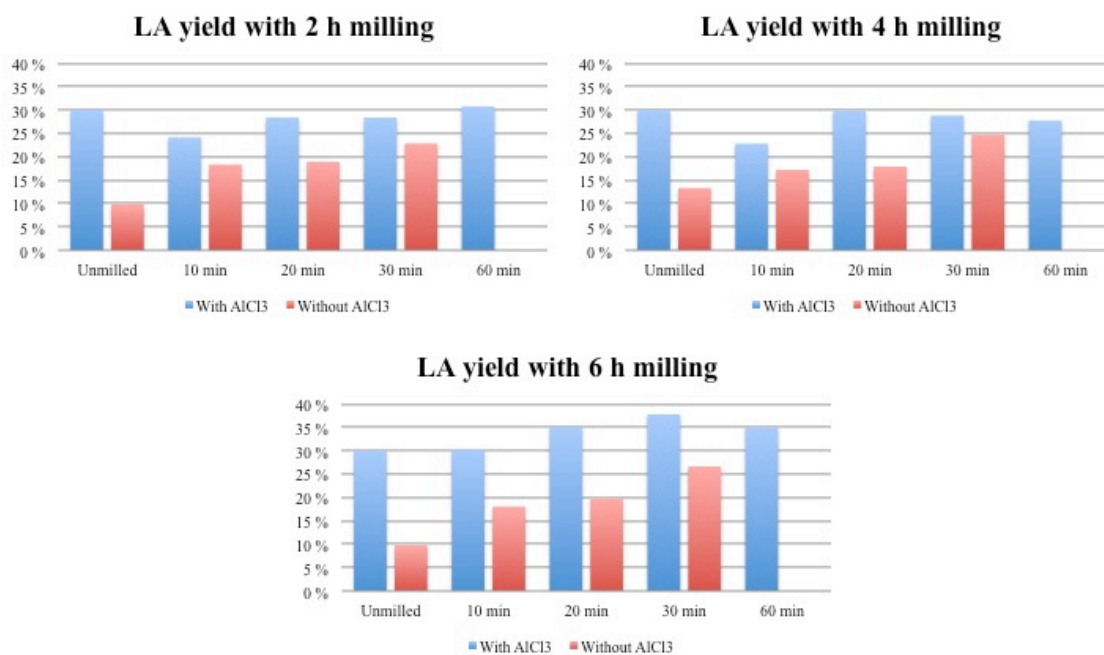
161 The pine sawdust was pre-treated prior to the conversion reactions by direct acid-
162 catalysed depolymerization method. H_2SO_4 was used as the acid catalyst and its
163 concentration, 0.45 mmol/g of sawdust, was kept constant. The amount of acid was
164 based on our previous study [26] according 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.

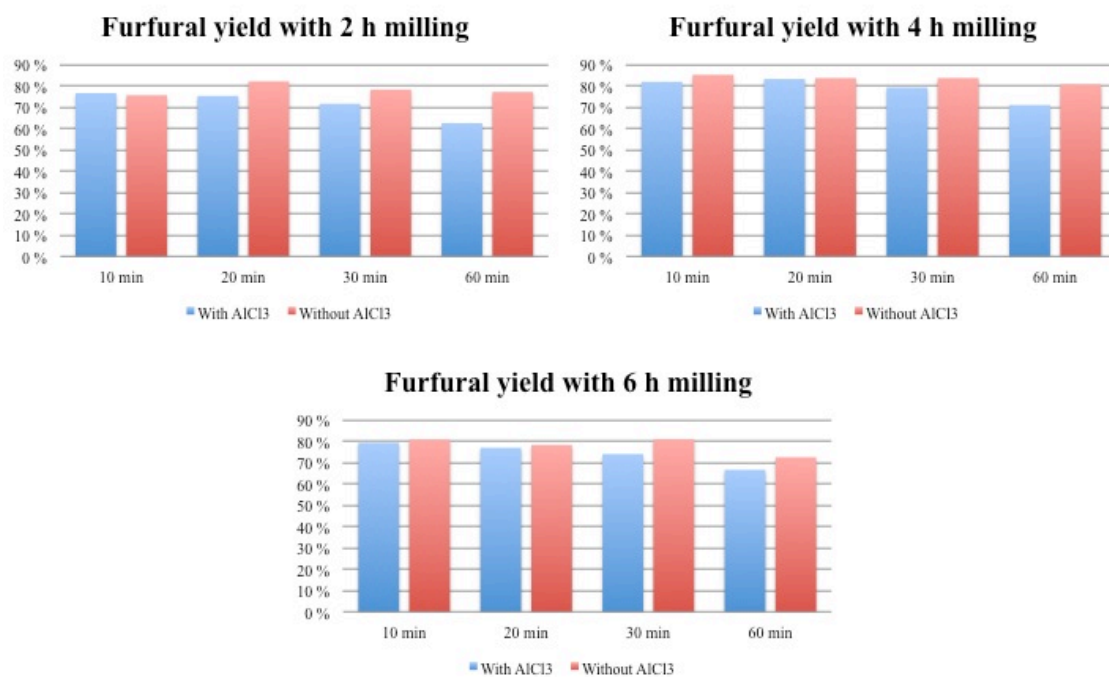
192 The results of the study are presented in Figures 1 and 2.



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 AlCl₃ 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 AlCl₃ 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 AlCl₃ 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 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 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

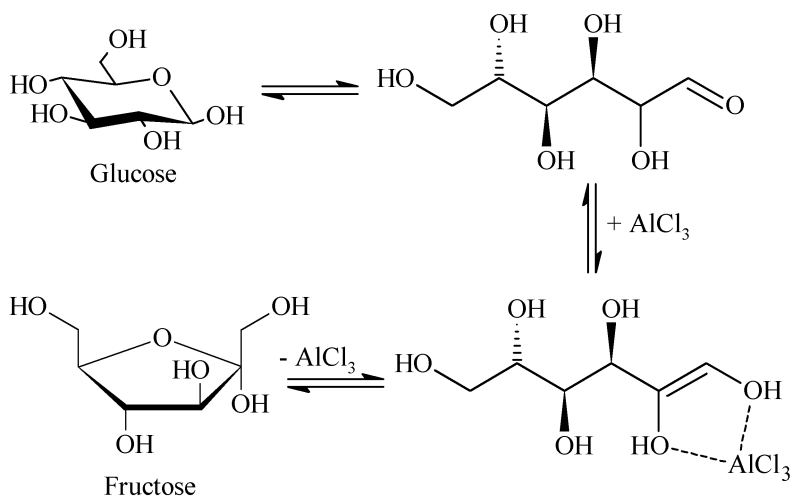
251 3.2 The effect of the additional Lewis acid catalyst

252 The yield of LA benefited greatly from the 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 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 AlCl_3 or 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]

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263

264



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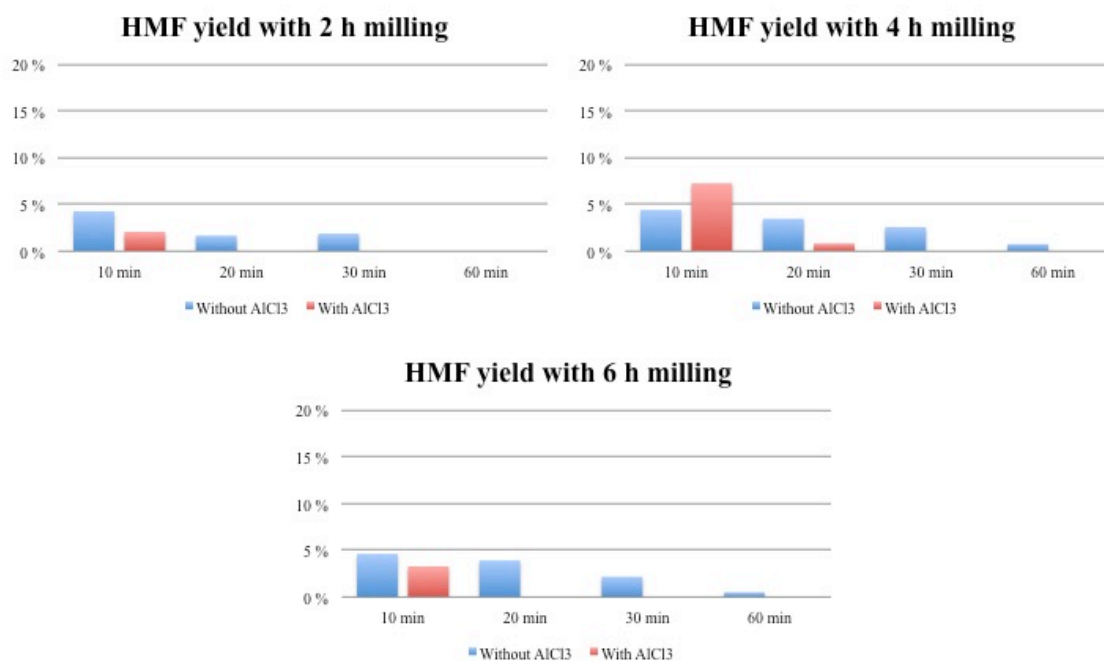
266 Figure 3. Proposed route for the AlCl_3 catalyzed isomerization of glucose to fructose.

267 [43,44]

268

269 The efficiency of AlCl_3 catalyst was also observed by monitoring the
 270 HMF contents of the samples taken after the conversion reactions (Figure 4). When
 271 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 AlCl₃ catalyst (5 mg, when used) were kept constant.

282

283 On the other hand, the effect of the Lewis acid catalyst, AlCl₃ 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 AlCl₃ 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 AlCl₃ catalyst does not seem to have an effect into the furfural yield, might be
 291 because AlCl₃ 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 AlCl₃ 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 AlCl₃ 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 AlCl₃ 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 AlCl₃
 311 catalyst (0.037 mmol).

Catalyst	Furfural (%) / LA (%)			
	10 min	20 min	30 min	60 min
CrCl ₃ (6H ₂ 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 ₃	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 AlCl_3 in the same reaction conditions. 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 CrCl_3
317 catalyst. This indicates that 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, 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 AlCl_3 instead of sulfuric acid. Boric acid should have worked similarly to
324 CrCl_3 and 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 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 mol L^{-1}). H_2SO_4 was added only before the
332 milling step so its concentration during the microwave heating was low (0.09 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 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 mol L^{-1}) with

339 H₂SO₄ and Lewis acid (FeCl₃) concentration of 1 mol L⁻¹ and 0.37 mol L⁻¹, 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 H₂SO₄ concentration of 0.04
342 mol L⁻¹ and total heating time of 98 min. Weiqi and Shubin [42] prepared LA (54%)
343 from pure glucose (0.056 mol L⁻¹) with H₃PO₄ and CrCl₃ concentrations of 0.02 mol L⁻¹
344 and the reaction time of 2 h and Jeong [16] prepared LA (approximately 40%) from
345 Jerusalem artichoke (0.39 mol L⁻¹) with H₂SO₄ concentration of 0.31 mol L⁻¹ 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⁻¹) in 3 and 112 min, respectively with the sulfuric acid concentration of 0.5 mol
349 L⁻¹. 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 H₂SO₄ concentration of 0.36 mol L⁻¹.

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 mol L^{-1}), and it was enough to add it only prior to the
390 milling step. Additional Lewis acid catalyst, 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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