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

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Abstract

In this work pine sawdust was converted into levulinic acid (LA) and furfural. Sawdust was first pre-treated with sulfuric acid-catalysed mechanical depolymerization. The conversion reactions were then performed with microwave heating at 180 °C. To enhance the furfural yield and the efficient separation of furfural and LA, a biphasic water-toluene reaction system was used. The effect of an additional catalyst, $AlCl_3$, on the yield of LA and furfural was also studied. According to the results the pre-treatment method enhanced the yields of LA. In addition, due to the microwave heating the reaction times were short. Additional $AlCl_3$ catalyst enhanced the LA yield, however excellent furfural yields were achieved even without it. Best LA yield (38%) was

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

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

1. Introduction

Most of the industrial chemicals are currently being prepared from fossil resources. However, the oscillating increase in fossil fuel prices as well as the depletion of the fossil resources is driving forward the search for alternative renewable feedstocks in the production of so called platform chemicals, which could replace the oil-based chemicals. [1]

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

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

The pre-treatment techniques can be classified into chemical, physical, physicochemical and biological methods. One of the commonly used physical methods is mechanical disruption by milling, which can reduce biomass particle size and increase its surface area, break the hydrogen bonds between cellulose, hemicellulose and lignin components as well as enable the access of the acid catalysts. [25] In our recent study the mechanical pre-treatment method was combined with acid catalysis by mixing biomass i.e. pine sawdust (PSD) with concentrated H_2SO_4 prior to the milling process. The resulting one-step acid-catalysed mechanical depolymerization method led to the fast disruption of lignocellulosic structure and converted the PSD into total reducing sugars and increased the water-solubility of the PSD considerably. [26]

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

2. Materials and methods

2.1 Pine sawdust

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

Toluene, 2-methyltetrahydrofuran and anhydrous $AlCl_3$ were purchased from Sigma Aldrich and H_2SO_4 (98%) from VWR. All chemicals were analytical grade and used without further purification.

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

In a typical experiment PSD (2.5 g) and concentrated H_2SO_4 (0.113 g, corresponding to 0.45 mmol of H_2SO_4/g of PSD) were mixed in a 45 ml stainless steel bowl. The mixture was milled in a planetary micro mill (FRITSCH, planetary micro mill pulverisette 7 premium line) with approximately 8 ml (46.5 g) of 3 mm diameter grinding balls prepared from ZrO_2. The temperature of the milling process was controlled by a "1 min milling/1 min pause" alternation mode at 13.3 Hz [26]. Temperature was checked with an electronic thermometer at the end of the milling through a pressure relief valve of the mill and was found to remain at 50 - 55 ºC during all the milling processes. The total milling time was 2, 4 or 6 h corresponding thus to 1, 2 or 3 h of active milling.

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

In a typical experiment the pre-treated PSD (0.2 g, containing ca. 9 mg of H_2SO_4) and additional acid catalyst, $AlCl_3$, (0 or 5 mg (0.037 mmol)) were weighed into a microwave reactor vessel (size 2 - 5 ml) equipped with a stirring bar. Water (1 ml) and toluene (4 ml) were added. The mixture was heated in the microwave reactor (Biotage Initiator with a single-mode microwave unit) at 180 ºC for 10, 20, 30 or 60 minutes.

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

The reference reactions were performed similarly. The untreated PSD (0.2 g) and $AlCl_3$ (5 mg (0.037 mmol)) were weighed into the reaction vessel. Water (1 ml) was added and the mixture was heated at 180 ºC for 30 or 60 min. A sample was taken from the water layer and extracted and analysed as mentioned above.

2.4 Analytical methods

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

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

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

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

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

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

HMF Yield (%) = [the amount of HMF produced/the theoretical amount of HMF from the holocellulose content of PSD]*100% (3)

3. Results and discussion

The pine sawdust was pre-treated prior to the conversion reactions by direct acid-catalysed depolymerization method. H_2SO_4 was used as the acid catalyst and its concentration, 0.45 mmol/g of sawdust, was kept constant. The amount of acid was based on our previous study [26] according to which, that concentration was the most effective towards PSD depolymerization but not too high to cause PSD burning during milling i.e. turning to black sticky substance, which would adhere to the walls of the milling bowl and milling balls [34]. The burning of the PSD was also avoided by controlling the temperature increase inside the milling bowl by performing the milling in cycles. One cycle consisted of 1 min milling and 1 min pausing. With such milling cycle the temperature inside the mill remained at 50 - 55 ºC during all the milling processes. In addition, the milling was performed with 3 mm grinding balls, since it was found previously that the 3 mm balls provided the greatest impact on the reduction of the PSD size [26].

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

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

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

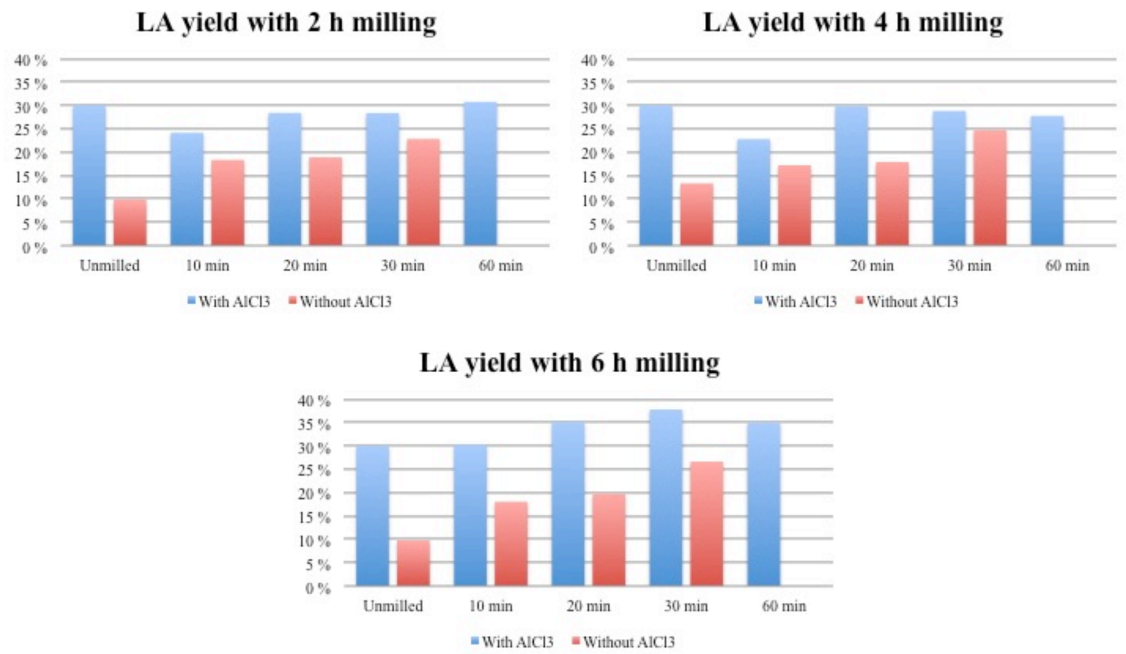

Figure 1. The effect of the milling time and the conditions of the subsequent conversion reaction on the LA yield. Conversion reaction temperature (180 ^{o}C) and the amount $AlCl_3$ catalyst (5 mg, when used) were kept constant. The conversion reaction time for the unmilled pine sawdust was 60 min.

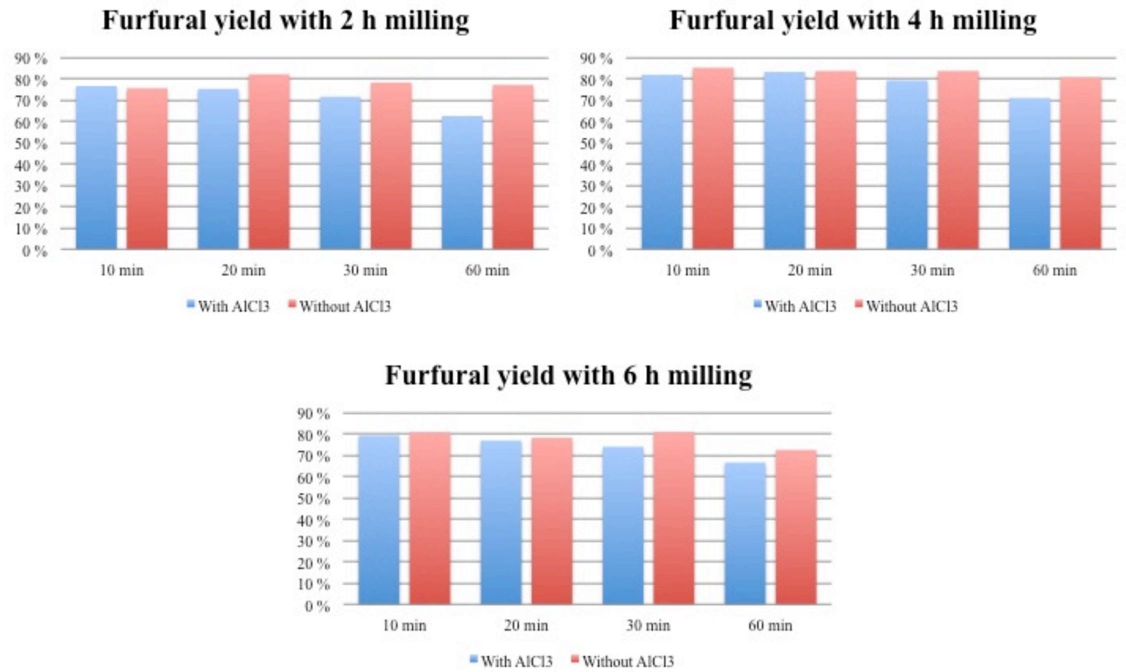

Figure 2. The effect of the milling time and the conditions of the subsequent conversion reaction on the furfural yield. Conversion reaction temperature (180 ^{o}C) and the amount $AlCl_3$ catalyst (5 mg, when used) were kept constant.

3.1 The effect of the milling time

The conversion of PSD to LA was greatly influenced by the milling time, which can be seen from Figure 1. When milling time was shortest, 2 h, the highest LA yield was 31%, which was reached after 60 min of microwave heating, and with $AlCl_3$ present in the reaction. Similar LA yield (30%) was obtained in a reference reaction performed with the same heating time, but with an unmilled PSD sample (Figure 1). When milling time was increased to 4 h, the highest LA yield remained at 30% but was reached considerable faster, in 20 min. Furthermore, when milling time was 6 h, the yield of LA was increased noticeable to 38% and was achieved already after 30 min of microwave heating (Figure 1).

The great effect of the pre-treatment method can also be seen from the conversion reactions performed without $AlCl_3$ (Figure 1). The reference reaction performed with unmilled PSD yielded only 18% of LA after 60 min of microwave heating (Figure 1). However, when PSD was milled 2, 4 or 6 h, the LA yield after 60 min of microwave heating was higher, 23, 25 or 26%, respectively (Figure 1).

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

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

The milling time or additional Lewis acid catalyst did not have much effect on the furfural yield (Figure 2). Excellent furfural yields were achieved with and without the additional $AlCl_3$ catalyst and already after 10 min of microwave irradiation. The highest furfural yield slightly increased, from 82 to 85%, when milling time increased from 2 to 4 h, respectively. However, when milling time was 6 h the highest furfural yield was 81% indicating that furfural started to convert into LA or other products. Furfural is mainly formed from pentose (C5) sugars, i.e. xylose, which is only found in hemicellulose component of lignocellulose [8]. Compared to cellulose, hemicellulose is less tightly bound in the lignocellulosic structure and thus reacts more easily. Therefore, even short, 2 h, milling time loosened the lignocellulosic structure enough enabling the conversion of pentose sugars to furfural with good yield with short reaction time (10 - 20 min, Figure 2).

3.2 The effect of the additional Lewis acid catalyst

The yield of LA benefited greatly from the $AlCl_3$ catalyst. The highest LA yield in the study, 38% (Figure 1), was obtained after 30 min of microwave irradiation with PSD milled for 6 h and $AlCl_3$ as an additional catalyst. The corresponding LA yield for the PSD conversion reaction performed without the additional catalyst was only 20% (Figure 1). It has been reported in previous studies that Lewis acid catalysts, such as $AlCl_3$ or $CrCl_3$, combined with Brønsted acids help to overcome the glucose to fructose isomerization limitations and thus enhance the decomposition of biomass into 5-hydroxymethylfurfural, which is the pre-cursor of LA. [1,39,42] The exact route for the Lewis acid catalyzed isomerization is not known but based on the recent literature, a plausible route is presented in Figure 3. [43,44]

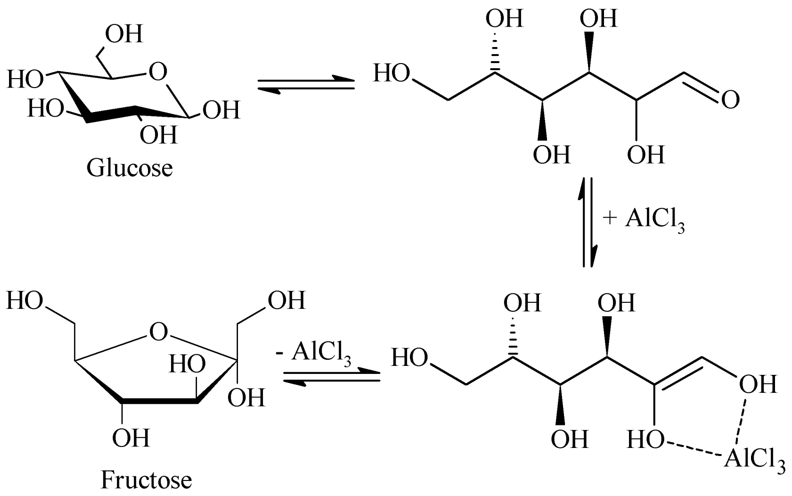

Figure 3. Proposed route for the $AlCl_3$ catalyzed isomerization of glucose to fructose. [43,44]

The efficiency of $AlCl_3$ catalyst was also observed by monitoring the HMF contents of the samples taken after the conversion reactions (Figure 4). When $AlCl_3$ was used in the conversion reaction, small amount of HMF (yield < 7%) was present after 10 min of microwave irradiation. After 20 min of microwave heating practically all the HMF had reacted further into LA. However, when conversion reactions were performed without the additional catalyst, small amounts of HMF (yield < 5%) could be detected from the reaction samples after 30 min of microwave irradiation and trace amounts even after 60 min of heating.

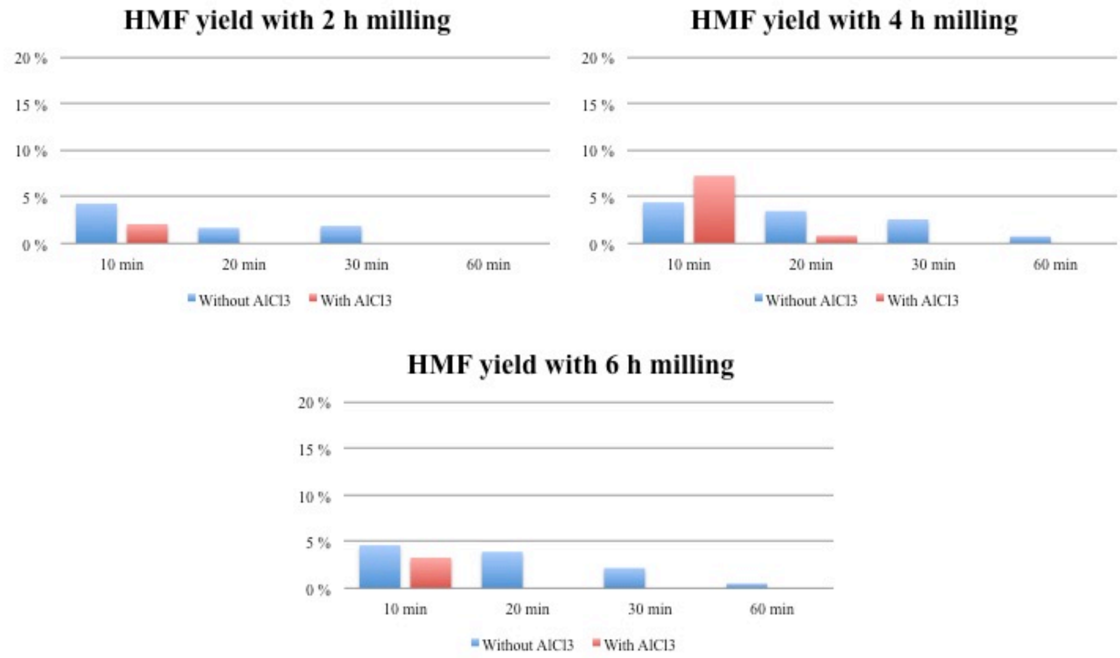

Figure 4. The effect of the milling time and the conditions of the subsequent conversion reaction on the HMF yield. Conversion reaction temperature (180 ^{o}C) and the amount $AlCl_3$ catalyst (5 mg, when used) were kept constant.

On the other hand, the effect of the Lewis acid catalyst, $AlCl_3$ on the yield of furfural was not significant. In fact, with the exception of the conversion reactions performed after 4 h of milling, furfural yield was higher, when no $AlCl_3$ was used in the conversion reactions. The recent literature suggests that the furfural yield is favoured by the use of Lewis acid catalysts. The catalysts enhance the isomerization of xylose into xylulose, which has been found to dehydrate more rapidly into furfural than xylose (Figure S1 in Supplementary material). [37] The result achieved in this study, i.e. that the $AlCl_3$ catalyst does not seem to have an effect into the furfural yield, might be because $AlCl_3$ is a powerful catalyst. Therefore it could have enhanced the conversion of furfural to LA even though a biphasic system was used. [45]

$AlCl_3$ 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 catalysts were also studied to see, if similar LA or furfural yields could be achieved. The studied catalysts are presented in Table 1. Chromium chloride hexahydrate was chosen since it is a Lewis acid, like $AlCl_3$ and according to literature has shown to enhance the glucose to fructose isomerization step and thus the conversion of biomass to LA [42,47]. Amberlyst 15 and p-TsOH were chosen since they have the sulfonic acid group and may thus enhance the conversion reaction of biomass similarly to sulfuric acid. Boric acid has been proposed in a recent study by computational modelling and deuterium-labelling studies to enhance the isomerization pathway from glucose to fructose [48]. Also in another study it was found to be indispensable in the conversion of glucose to 5-hydroxymethylfurfural [49]. The molar amount of studied catalysts was kept the same as the amount of $AlCl_3$ and the experiments were performed with the PSD sample milled for 6 h.

Table 1. The effect of various catalysts on the conversion of PSD to LA and furfural. The milling time (3 h) and conversion reaction temperature (180 ^oC) were kept constant. The molar amount of the studied catalyst was kept the same as the amount of $AlCl_3$ catalyst (0.037 mmol).

Catalyst	Furfural (%) / LA (%)			
	10 min	20 min	30 min	60 min
$CrCl_3$ ($6H_2O$)	67 / 26	63 / 28	57 / 30	59 / 29
Amberlyst 15	81 / 14	76 / 18	75 / 25	71 / 26
p-TsOH	73 / 5	77 / 18	78 / 23	71 / 23
Boric acid	-	-	-	69 / 25
$AlCl_3$	79 / 30	77 / 35	74 / 38	67 / 35

Based on the results, none of the studied catalysts was as effective as $AlCl_3$ in the same reaction conditions. $CrCl_3$ gave the best results for the LA yield with the highest yield of 30% (Table 1). However the furfural yield was lowest with $CrCl_3$ catalyst. This indicates that $CrCl_3$ enhanced the conversion reactions of furfural to LA or other products. When Amberlyst 15 and *p*-TsOH were used as the catalyst the furfural yields were good but did not differ at all from furfural yields achieved without any catalyst (Figure 1). On the other hand, $AlCl_3$ did not enhance the furfural yields either. To improve the LA yields with Amberlyst and *p*-TsOH higher concentrations should be used and Amberlyst and *p*-TsOH should be combined with Lewis acid catalyst like $AlCl_3$ instead of sulfuric acid. Boric acid should have worked similarly to $CrCl_3$ and $AlCl_3$ and enhance the LA yield. However, the boric acid concentrations may have been too low. Further research is needed to see if it could replace $AlCl_3$ as the catalyst in biomass conversion reactions.

3.3 Comparison with literature

The combination of acid-catalysed depolymerization by ball milling and microwave heating proved to be an efficient method to produce furfural and LA from PSD (holocellulose concentration of ca. 0.86 mol L^{-1}). H_2SO_4 was added only before the milling step so its concentration during the microwave heating was low (0.09 mol L^{-1}) compared to many of the studies reported in literature. Also the amount of additional Lewis acid catalyst was low, 0.037 mol L^{-1}, compared to studies reported in literature. Furthermore, reasonable furfural and LA yields were achieved with short heating times, 10-30 min. Thus the conditions used in this study during the conversion reactions were mild compared to reaction conditions found in previous literature. For example Rong et al. [39], prepared furfural (with the yield of 83%) from pure xylose (0.067 mol L^{-1}) with

H_2SO_4 and Lewis acid ($FeCl_3$) concentration of 1 mol L^{-1} and 0.37 mol L^{-1}, respectively and the reaction time of 5 h, while according to Mazar et al. [22] a furfural yield of 78% can be achieved from wood chips pre-hydrolysate with H_2SO_4 concentration of 0.04 mol L^{-1} and total heating time of 98 min. Weiqi and Shubin [42] prepared LA (54%) from pure glucose (0.056 mol L^{-1}) with H_3PO_4 and $CrCl_3$ concentrations of 0.02 mol L^{-1} and the reaction time of 2 h and Jeong [16] prepared LA (approximately 40%) from Jerusalem artichoke (0.39 mol L^{-1}) with H_2SO_4 concentration of 0.31 mol L^{-1} and the reaction time of 34 min. According to kinetic models produced by Dussan et al. [21] the furfural yield of 27% and LA yield of 70% could be produced from silver grass (0.39 mol L^{-1}) in 3 and 112 min, respectively with the sulfuric acid concentration of 0.5 mol L^{-1}. The kinetic model of Chang et al. [19], on the other hand, predicts the LA yield of 20% from wheat straw in 38 min with H_2SO_4 concentration of 0.36 mol L^{-1}.

3.4 Microwave irradiation as the heating method

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

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

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

Conclusions

Mechanocatalytical depolymerization performed by ball milling and with sulphuric acid as the catalyst was an efficient pre-treatment method when PSD was converted into LA and furfural with microwave irradiation as the heating method for the conversion reaction. The biphasic water-toluene reaction system enabled the separation of LA and furfural during the reaction. Due to the effective pre-treatment method the concentration of sulfuric acid was low (0.09 mol L^{-1}), and it was enough to add it only prior to the milling step. Additional Lewis acid catalyst, $AlCl_3$ enhanced the conversion reaction of the pre-treated PSD to LA but did not have an effect on the furfural yield. The highest LA yield in this study, 38%, was achieved with 6 h of milling and 30 min of microwave heating and the highest furfural yield, 85%, with 4 h of milling and 10 min of microwave heating. Compared to current literature the LA and furfural yields can be considered reasonable, since the starting material was biomass instead of e.g. pure cellulose. However, it has to be kept in mind that the study was performed at small-scale and transferring of the whole process into large-scale may not be straightforward. Milling is a known operation for particle size reduction and microwave-assisted synthesis has already been demonstrated at kg scale. Yet, there are issues related e.g. to corrosion resistance of the large-scale mills, the safety of the large-scale microwave reactors and re-optimization of the process conditions.

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Supplementary material

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

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