

## Brønsted and Lewis Acid Catalyzed Conversion of Pulp Industry Waste Biomass to Levulinic Acid

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Enormous amounts of fiber sludge are generated annually by the pulp industry as a by-product. As a cellulose-rich material, its current usage, mainly as fuel, is inefficient from a material efficiency point of view. This work studied the utilization of fiber sludge from a Finnish and a Swedish pulp mill as a potential feedstock to produce levulinic acid, a valuable platform chemical. The conversion experiments of fiber sludge to levulinic acid were performed in a microwave reactor with a mixture of H<sub>2</sub>SO<sub>4</sub> and Lewis acid as the catalyst. The reaction conditions, which included reaction time and temperature as well as the H<sub>2</sub>SO<sub>4</sub> and Lewis acid concentrations, were studied in detail. The highest levulinic acid yield, 56%, was obtained with Swedish fiber sludge after 60 min at 180 °C with the H<sub>2</sub>SO<sub>4</sub> concentration of 0.3 mol/L and a CrCl<sub>3</sub> concentration of 7.5 mmol/L which indicated that the fiber sludge had the potential to be used as feedstock for levulinic acid production.

*Keywords:* Fiber sludge; Levulinic acid; Microwave irradiation; Catalytic conversion; Brønsted acid; Lewis acid

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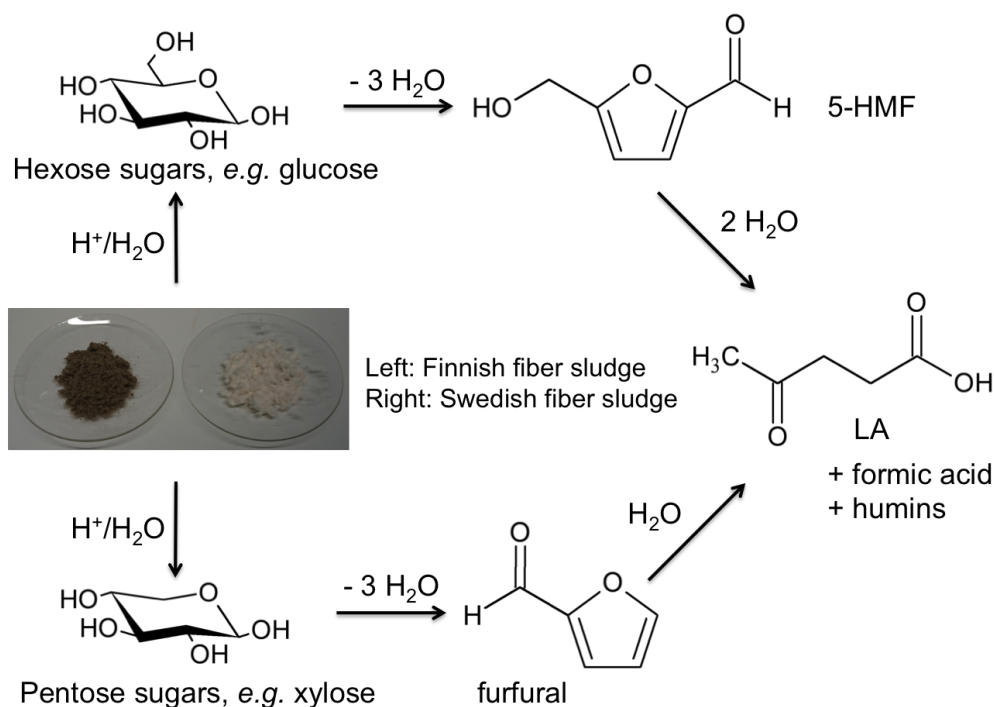
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### INTRODUCTION

Finnish pulp industries generate *ca.* 300,000 tons (dry matter) of fiber sludge as a by-product per year, and Swedish pulp industries generate 450,000 tons (dry matter) of fiber sludge per year (Holm *et al.* 2013; Kuokkanen *et al.* 2018). Presently, fiber sludge is mainly incinerated. According to the waste legislation, the Landfill of Waste Directive (Council Directive 1999/31/EC 1999), the landfilling of organic waste has been restricted since 2016, and there are no other suitable applications for the utilization of the sludge. However, fiber sludge has high cellulose content, so its usage as fuel seems inefficient from a material utilization viewpoint. According to current EU strategies, the waste materials should be primarily used as material sources and secondarily as energy sources (Kuokkanen *et al.* 2018). Therefore, new applications are actively sought for fiber sludge utilization.

Levulinic acid (LA, Fig. 1) is one of the most important platform chemicals (Werpy *et al.* 2004). It is a keto-acid, which can be converted to numerous value-added chemicals and hence be used as a raw material for resins, plasticizers, textiles, coatings, and fuel additives (Hayes *et al.* 2008; Antonetti *et al.* 2016; Silva *et al.* 2018). LA can be derived from various C6- or C5-based polysaccharides such as cellulose and hemicellulose (Mukherjee *et al.* 2015), which are, along with lignin, the main components in lignocellulosic biomasses and side streams (Singh *et al.* 2016). The cellulose and

hemicellulose components are first hydrolyzed to monomeric sugars, which are then dehydrated to 5-hydroxymethylfurfural (5-HMF) or furfural. 5-HMF and furfural are then converted to LA (Fig. 1). Formic acid and soluble and insoluble humins are formed as side products in the reactions (Mukherjee *et al.* 2015).



**Fig. 1.** Reaction scheme for the conversion of lignocellulosic biomass such as fiber sludge to levulinic acid (Mukherjee *et al.* 2015)

The conversion reaction of biomass to LA is usually enhanced by either a homogeneous or a heterogeneous acid catalyst. Homogeneous catalysts include mineral acids, such as  $H_2SO_4$  (Chang *et al.* 2007; Girisuta *et al.* 2007) and  $HCl$  (Yan *et al.* 2008); organic acids like *p*-toluene sulfonic acid (Ji *et al.* 2019); and Lewis acids like  $CrCl_3$ ,  $FeCl_3$ , and  $AlCl_3$  (Peng *et al.* 2010; Zhi *et al.* 2015). The combinations of mineral acids and Lewis acids in LA production have been studied. For example, Wei and Wu found recently that the mixture of  $CrCl_3$  and  $H_3PO_4$  as a catalyst has a positive catalytic effect on the conversion of glucose to LA compared to a single  $CrCl_3$  or  $H_3PO_4$  catalyst (Wei and Wu 2017). Heterogeneous catalysts, on the other hand, include various zeolites (Zeng *et al.* 2010; Ya'aini *et al.* 2012; Guzmán *et al.* 2016), solid superacid catalysts,  $S_2O_8^{2-}/ZrO_2-SiO_2-Sm_2O_3$  (Chen *et al.* 2011), zirconium dioxide (Joshi *et al.* 2014), and metal halide salts physically incorporated with Nafion supported on amorphous silica (Potvin *et al.* 2011). There are several problems associated with the use of homogeneous and heterogeneous catalysts. Mineral acids are said to cause pollution and promote equipment corrosion (Peng *et al.* 2010; Ya'aini *et al.* 2012; Guzmán *et al.* 2016). Along with Lewis acids, they are also said to be difficult to recycle. Heterogeneous catalysts on the other hand are said to suffer from low yields and long reaction times and are not easily recovered from the solid residues remaining after the reaction (Ji *et al.* 2019).

Numerous biomasses have been studied as potential feedstocks for LA production.

These include poplar sawdust (Galletti *et al.* 2012; Ji *et al.* 2019), sugarcane bagasse (Yan *et al.* 2008), beech (Efremov *et al.* 1998), aspen (Efremov *et al.* 1997), corn stalk (Zhi *et al.* 2015), wheat and rice straw (Chang *et al.* 2007; Chen *et al.* 2011), mushrooms (Yan *et al.* 2008; Lappalainen *et al.* 2018), and potato peel waste (Lappalainen *et al.* 2018). In this work, fiber sludge from two pulp mills was used as the feedstock to produce LA. The conversion reactions were performed in an aqueous solution with a mixture of H<sub>2</sub>SO<sub>4</sub> and a Lewis acid as the catalyst. In order to accelerate the conversion of the sludge to LA, microwave irradiation was used as the heating method. It has been found in several studies that microwaves enhance the reaction rates as well as the product selectivity in organic synthesis (Guenic *et al.* 2015; Delbecq *et al.* 2016; Guenic *et al.* 2016; Delbecq *et al.* 2018; Wang *et al.* 2018). Energy savings of up to 85-fold can be involved in microwave-assisted processes (Dallinger and Kappe 2007). The effects of reaction conditions, *i.e.* the reaction temperature, time, and the concentrations of H<sub>2</sub>SO<sub>4</sub> and Lewis acid catalysts, on the yield of LA were studied in detail. To the authors' knowledge, fiber sludge has not been used before as the raw material in LA production.

## EXPERIMENTAL

### Materials and Methods

The fiber sludges used in this study were received from Finnish and Swedish pulp mills UPM (Pietarsaari, Finland) and Domsjö Fabriker AB (Örnsköldsvik, Sweden). A simplified flow sheet of the production process of each fiber sludge can be found in Supplementary material (Fig. S1 and S2) in the Appendix. Before use, the sludges were air-dried until a constant weight was achieved and were used as such in the conversion reactions. The color of the Finnish fiber sludge (FFS) was gray (Fig. 1). Its cellulose, hemicellulose, and lignin contents were 75%, 11%, and 14%, respectively (Dong *et al.* 2016). The color of Swedish fiber sludge (SFS) was white (Fig. 1). Its composition was determined using known methods (NREL LAP-004 1996; Yokoyama *et al.* 2002; Rowell *et al.* 2005; TAPPI T203 cm-09 standard 2009; Sluiter *et al.* 2011; Styarini *et al.* 2012). The cellulose, hemicellulose, and lignin contents were found to be 98%, 1%, and 0%, respectively. A detailed description of the whole biomass composition determination process can be found from a recent study by Rusanen *et al.* (2018). Other reagents, *i.e.*, H<sub>2</sub>SO<sub>4</sub> (95-97%, Merck), CrCl<sub>3</sub>·6H<sub>2</sub>O (98%, Alfa Aesar), FeCl<sub>3</sub>·6H<sub>2</sub>O (99%, Merck), CuCl<sub>2</sub>·2H<sub>2</sub>O (99%, Merck), ZnCl<sub>2</sub> (98-100%, VWR), and NiCl<sub>2</sub>·6H<sub>2</sub>O (97%, J.T. Baker) were used as received from the suppliers.

#### *Experimental procedure for the conversion of fiber sludge to levulinic acid*

In a typical experiment, fiber sludge (0.25 g, 5 wt%) was weighted into a microwave reactor vessel (size 2 to 5 mL) equipped with a magnetic stirring bar. A Lewis acid catalyst in the amount corresponding to the final concentration of 1.9 mmol/L to 19 mmol/L (Tables 1 to 4) and 5 mL of aqueous H<sub>2</sub>SO<sub>4</sub> (0.1 mol/L to 0.5 mol/L, Tables 1 to 4) were added. The mixture was heated in the microwave reactor (Biotage Initiator with a single-mode microwave unit) at a temperature and reaction time of 140 °C to 180 °C and 15 min to 120 min, respectively (Tables 1 to 4). After the reaction, a sample (1.5 mL) was taken from the mixture, filtered with a 0.45 μm syringe filter, and analyzed with high performance liquid chromatography coupled with a photodiode array detector (HPLC-PDA).

### Analytical Methods

The LA concentration of the samples taken after each conversion reaction was analyzed with HPLC-PDA. The HPLC equipment consisted of a Waters 2695 Separation module (Milford, CT, USA) fitted with an Atlantis dC18 column with dimensions of 4.6 mm x 150 mm and particle size of 5  $\mu\text{m}$ , and a Waters 996 PDA detector. The mixture had a water:methanol ratio of 90:10 with 0.1% (v/v) of trifluoroacetic acid; this was used as the mobile phase with a flow rate of 1 mL/min. The injection volume was 4  $\mu\text{L}$ . The column temperature was kept constant at 30  $^{\circ}\text{C}$  and the calibration was performed using the LA analytical standard (Sigma Aldrich). The UV detection was done at 267 nm for LA. Each sample was analyzed in duplicate.

The yield of the LA was calculated with Eq. 1,

$$\text{Yield} = c_{LA}/c_{theor} \times 100 \quad (1)$$

where *Yield* is the yield of LA (%),  $c_{LA}$  is the concentration of LA in a sample (g/L), and  $c_{theor}$  is the theoretical maximum yield of LA which could be in the sample (g/L). The theoretical maximum yield of LA was calculated from the holocellulose content, *i.e.*, the combined cellulose and hemicellulose content of the starting material, which was 86% for the Finnish fiber sludge and 99% for the Swedish sludge.

### Experimental Design

The full 2<sup>4</sup>-factorial design was chosen as the experimental design in order to perform a preliminary study of the effect of the reaction conditions on the conversion of fiber sludge into LA. The purpose was to estimate which factors had the clearest effect on the LA yield and which required more detailed study. The experiments included in the experimental design were conducted with the Finnish fiber sludge. The factors (time, temperature, H<sub>2</sub>SO<sub>4</sub>, and Lewis acid concentration) and their levels used in the experiments are given in Table 1. The factors were studied in two levels, high and low. The design also contained three center point experiments, which were performed to estimate the experiment uncertainty. The levels for the factors were selected based on some previous studies (Peng *et al.* 2010; Wei and Wu 2017; Zheng *et al.* 2017) and preliminary test reactions. The design consisted in total of 19 experiments, which were carried out in a random order. The LA yield (%) was used as the response. Once the LA yields were gained, the data was fitted using the multiple linear regression method in MODDE 9.1 (Umetrics, Umeå, Sweden) computer software. The statistical validation was determined using an ANOVA test at a 95% confidence level (Supplementary Table S1).

**Table 1.** The Factors and their Levels Used in the Full 2<sup>4</sup>-Factorial Design

Factors	Low	Center	High
Time (min)	15	37.5	60
Temperature ( $^{\circ}\text{C}$ )	140	160	180
H <sub>2</sub> SO <sub>4</sub> (mol/L)	0.1	0.3	0.5
CrCl <sub>3</sub> ·6H <sub>2</sub> O (mmol/L)	1.9	4.7	7.5

## RESULTS AND DISCUSSION

### Preliminary Experiments with 2<sup>4</sup>-Factorial Design

The potential of two fiber sludges, FFS and SFS, to be used to produce LA was studied. The full 2<sup>4</sup>-factorial experimental design with FFS was first used to study the effect of various factors on the yield of LA, which was used as the response in the design (Table 2).

**Table 2.** Reaction Conditions Used in the 2<sup>4</sup>-Factorial Design Experiments for the Finnish Fiber Sludge, and the Yield (%) of LA

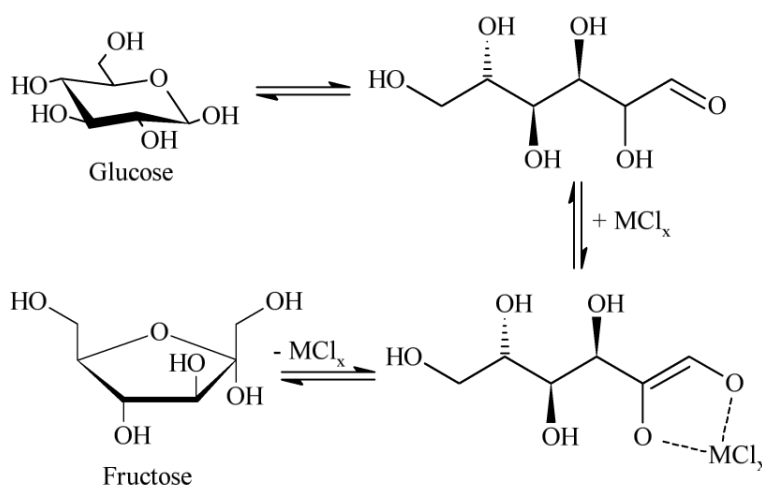
Exp.	Time (min)	Temp. (°C)	H <sub>2</sub> SO <sub>4</sub> (mol/L)	CrCl <sub>3</sub> (mmol/L)	LA (%)
1	15	140	0.1	1.9	0
2	60	140	0.1	1.9	0
3	15	180	0.1	1.9	3
4	60	180	0.1	1.9	14
5	15	140	0.5	1.9	0
6	60	140	0.5	1.9	2
7	15	180	0.5	1.9	29
8	60	180	0.5	1.9	31
9	15	140	0.1	7.5	0
10	60	140	0.1	7.5	0
11	15	180	0.1	7.5	5
12	60	180	0.1	7.5	18
13	15	140	0.5	7.5	0
14	60	140	0.5	7.5	3
15	15	180	0.5	7.5	31
16	60	180	0.5	7.5	30
17	37.5	160	0.3	4.7	9
18	37.5	160	0.3	4.7	9
19	37.5	160	0.3	4.7	9

According to the analyzed data, the reaction time and temperature as well as the H<sub>2</sub>SO<sub>4</sub> concentration had a statistically significant effect on the LA yield. This can be seen from the data presented in Table 2 as well as from Supplementary Table S2, which shows the scaled and centered coefficients for the fitted model of the yield of LA. The LA yield generally increased when the time, temperature, and H<sub>2</sub>SO<sub>4</sub> concentration increased. The model for the LA yield also contained interaction terms between temperature and H<sub>2</sub>SO<sub>4</sub> concentration as well as between time and temperature (Supplementary Table S2).

Based on the model obtained from the factorial design, it was concluded that the reaction temperature and the concentration of H<sub>2</sub>SO<sub>4</sub> had the greatest impact on the yield of LA. The optimum reaction temperature was 180 °C, and 0.5 M was the optimum H<sub>2</sub>SO<sub>4</sub> concentration. Regarding the reaction time, high LA yields of 30% to 31% (Table 2) were achieved in 60 min (exps. 8 and 16, Table 2) as well as in 15 min (exp. 15, Table 2). However, when the reaction time was short, *i.e.*, 15 min, or when the Lewis acid concentration was low, *i.e.*, 1.9 mmol/L, the reaction solutions still contained 5-HMF and furfural, which are the precursors of LA. This behavior indicated that a longer reaction time was needed for the conversion reaction to be completed.

The model obtained from the factorial design suggested that the Lewis acid catalyst had no effect on the yield of LA. However, Lewis acids have been found to improve the conversion of biomass to LA, since they catalyze the glucose to fructose during the

isomerization step, which is necessary for the conversion reaction to occur (Choudhary *et al.* 2013; Kumar *et al.* 2015; Wei and Wu 2017). The exact mechanism for the Lewis acid catalyzed isomerization is not known, but based on previous studies (Li *et al.* 2009; Peng *et al.* 2010) a plausible route is presented in Fig. 2. As mentioned above, the highest LA yield (31%) during the factorial experiments was achieved in 60 min at 180 °C with an H<sub>2</sub>SO<sub>4</sub> concentration of 0.5 mol/L and a CrCl<sub>3</sub> concentration of 1.9 mmol/L. However, a similar yield was achieved in 15 min when the CrCl<sub>3</sub> concentration increased to 7.5 mmol/L. This indicated that the Lewis acid concentration had some effect on the LA yield. Therefore, some additional reactions were performed to study the effect of the Lewis acid as well as the reaction time in more detail.



**Fig. 2.** The proposed route for the Lewis acid catalyzed isomerization of glucose to fructose (Li *et al.* 2009; Peng *et al.* 2010).

### Additional Experiments with Finnish Fiber Sludge

The additional conversion reactions were first performed with only the H<sub>2</sub>SO<sub>4</sub> as the catalyst. It was considered that the upper level of the H<sub>2</sub>SO<sub>4</sub> concentration (0.5 mol/L, Tables 1 and 2) during the factorial experiments was so high that its effect hid the effect of the Lewis acid catalyst. Therefore, it was first determined whether the H<sub>2</sub>SO<sub>4</sub> concentration could be reduced without significantly reducing the LA yield. Thus, the conversion reaction was performed without the Lewis acid catalyst but with the same H<sub>2</sub>SO<sub>4</sub> concentration of 0.5 mol/L (exp. 3, Table 3) as in experiment 8, shown in Table 2. The reaction was also performed with a reduced concentration of H<sub>2</sub>SO<sub>4</sub>, 0.3 mol/L (exp. 1, Table 3). Indeed, similar LA yields of 31% (Table 3) were achieved with both new reactions as during the factorial experiments. This verified that H<sub>2</sub>SO<sub>4</sub> itself was enough to produce the 31% LA yield and that the H<sub>2</sub>SO<sub>4</sub> concentration could be reduced noticeably to 0.3 mol/L. After 60 min of heating, there was still some 5-HMF and furfural left in the reaction mixtures. This supported the importance of the Lewis acid catalyst in the conversion reaction. Therefore, the reaction time was increased and after 120 min of heating, no more 5-HMF or furfural could be detected in the reaction mixtures. Also, the LA yields increased slightly with the increasing reaction time and were similar with both studied H<sub>2</sub>SO<sub>4</sub> concentrations of 34% (Table 3). Based on these results, the H<sub>2</sub>SO<sub>4</sub> concentration was decreased, and in the following reactions a sulfuric acid concentration of 0.3 mol/L was used.

Next, the effect of the Lewis acid catalyst on the LA yield was studied.  $\text{CrCl}_3$  was used as the Lewis acid, and its concentration as well as the reaction time was varied (exps. 5 to 14, Table 3). The results indicated that the presence of Lewis acid reduced the reaction time compared to the reactions, which were done with only the  $\text{H}_2\text{SO}_4$  as the catalyst. Similar LA yields of 33% (exps. 7, 10, and 14, Table 3) were achieved in 60 min with all the studied  $\text{CrCl}_3$  concentrations. Also, when there was 7.5 mmol/L or 19 mmol/L of  $\text{CrCl}_3$  present in the reaction mixture, no 5-HMF or furfural was detected from the mixtures after 60 min of heating. Based on this set of reactions, the reaction time of 60 min and Lewis acid concentrations of 7.5 mmol/L and 19 mmol/L were used in the following reactions.

**Table 3.** Reaction Conditions Used in the Additional Reactions with the Finnish Fiber Sludge and the Yield (%) of LA.

Exp.	Lewis acid	$C_{\text{Lewis acid}}$ (mmol/L)	Time (min)	LA (%)	
1	-	-	60	31	
2			120	34	
3*	-	-	60	31	
4*			120	34	
5	$\text{CrCl}_3$	1.9	15	25	
6			30	31	
7			60	33	
8		7.5	15	29	
9			30	32	
10			60	33	
11			120	32	
12		19	15	22	
13			30	30	
14			60	33	
15		$\text{FeCl}_3$	7.5	60	32
16			19	60	29
17		$\text{ZnCl}_2$	7.5	60	34
18			19	60	31
19	$\text{CuCl}_2$	7.5	60	29	
20		19	60	30	
21	$\text{NiCl}_2$	7.5	60	33	
22		19	60	34	

\* The sulfuric acid concentration was 0.5 mol/L.  
Unless otherwise noted, the reaction temperature and the sulfuric acid concentration of all reactions were 180 °C and 0.3 mol/L, respectively.

To complete the reactions with the FFS as the starting material, some preliminary conversion reactions were performed with other Lewis acids besides  $\text{CrCl}_3$  in order to study if similar LA yields could be produced.  $\text{CrCl}_3$  is a Lewis acid that is commonly used for LA production, but there are some studies in which also other Lewis acids have been used (Peng *et al.* 2010; Yang *et al.* 2013; Zhi *et al.* 2015; Zheng *et al.* 2017; Boonyakarn *et al.* 2019). The other Lewis acids used in this study were  $\text{FeCl}_3$ ,  $\text{ZnCl}_2$ ,  $\text{CuCl}_2$ , and  $\text{NiCl}_2$ . The results of the preliminary reactions are presented in Table 3. According to the results, similar LA yields of 29% to 34% were achieved with the studied Lewis acids (exps. 15 to 22, Table 3), and it seemed that the lower concentration of Lewis acid (7.5 mmol/L) was enough to catalyze the conversion reactions. The LA yields were also similar to those achieved with  $\text{CrCl}_3$  as the Lewis acid catalyst. Furthermore, the results were in accordance with a previous study where  $\text{ZnCl}_2$ ,  $\text{CrCl}_3$ ,  $\text{FeCl}_3$ , or  $\text{CuCl}_2$  was used as a mixed catalyst

with H<sub>2</sub>SO<sub>4</sub> and produced LA yields of 26%, 33%, 36%, or 28% (Yang *et al.* 2013). On the other hand, the results differed from those of Boonyakarn *et al.* (2019) and Peng *et al.* (2010). In their studies, the CrCl<sub>3</sub> was clearly a better catalyst for LA production from cellulose than ZnCl<sub>2</sub>, CuCl<sub>2</sub>, or FeCl<sub>3</sub> (Peng *et al.* 2010; Boonyakarn *et al.* 2019). It should be noted though that in their studies, the Lewis acid was used as a single catalyst, whereas in this study it was used in a catalyst mixture with H<sub>2</sub>SO<sub>4</sub>.

### Conversion of Swedish Fiber Sludge to Levulinic Acid

The results achieved with FFS suggested that the best reaction conditions for the fiber sludge conversion to LA were 180 °C for reaction temperature, 0.3 mol/L for the H<sub>2</sub>SO<sub>4</sub> concentration, 7.5 mmol/L or 19 mmol/L for Lewis acid concentration, and 60 min for reaction time. These conditions were used as the default value for the reactions with SFS.

The conversion experiments with SFS began with CrCl<sub>3</sub> as the Lewis acid catalyst. Two concentrations, 7.5 mmol/L and 19 mmol/L, were used. Some reference reactions were also performed without the Lewis acid catalyst, with the 0.3 mol/L H<sub>2</sub>SO<sub>4</sub> as the catalyst (exps. 1 to 3, Table 4). Although 60 min was found as the best reaction time for FFS, shorter reaction times were studied for SFS. One of the reasons for the recalcitrance of lignocellulose and the challenging utilization of polysaccharides in it is the presence of lignin (Zhang 2008). The SFS did not contain any lignin, whereas the lignin content of FFS was 14%. Therefore, it was considered that a shorter reaction time could be sufficient for the SFS. The results for the conversion reactions of SFS to LA are presented in Table 4. As with FFS, the reaction time of 60 min was not enough when no Lewis acid was added to the reaction mixture, since after the reaction time there was still some 5-HMF and furfural present in the reaction mixture. When CrCl<sub>3</sub> was added to the reaction, no 5-HMF or furfural was detected after 60 min of heating. With a CrCl<sub>3</sub> concentration of 7.5 mmol/L the LA yield increased with the increasing reaction time (exps. 4 to 6, Table 4) until the maximum yield of 56%, was achieved after 60 min of heating (exp. 6, Table 4). Longer heating times decreased the LA yield (exp. 7, Table 4). When the CrCl<sub>3</sub> concentration was increased to 19 mmol/L the LA yields began to decrease after 30 min of heating (exps. 8 to 11, Table 4). However, 60 min of heating was required for the conversion reaction to be completed. Furthermore, the highest LA yield obtained with the higher Lewis acid concentration was 50% (exp. 9, Table 4), which was lower than the 56% obtained with the lower CrCl<sub>3</sub> concentration. Thus, the Lewis acid concentration of 7.5 mmol/L was the best condition for the conversion reaction.

The LA yields obtained with SFS were noticeably higher than with FFS (Tables 3 and 4). This was likely due to the differences in the compositions of the sludges. SFS was almost pure cellulose, while FFS also contained hemicellulose (11%) and lignin (14%). It was possible that the lignin component facilitated the formation of humins, which are common by-products in biomass conversion reactions (Yoon *et al.* 2014). The formation mechanism of humins is complicated and not yet clearly understood, but it is known that they are derived from 5-HMF and furfural (Patil and Lund 2011; Yoon *et al.* 2014). In this study humins were formed during every experiment. Insoluble humins could be seen as black solid on the bottom of the microwave reaction tubes. Soluble humins could not be detected with the analytical method that was used in this study, but their existence was deduced from the dark orange to brown colors of the reaction liquids.

Finally, some preliminary experiments with SFS were performed with other Lewis acid catalysts besides CrCl<sub>3</sub>. The same catalysts were used as with FFS and the results



along with reaction conditions are presented in Table 4. All the studied Lewis acids produced similar LA yields that ranged from 51% to 56% (Table 4).  $\text{CuCl}_2$  seemed to be the least efficient of the tested catalysts. However, the differences in the LA yields were small, so more detailed experiments are required to determine whether any of the Lewis acids would be more or less suitable for the fiber sludge conversion to LA than the other catalysts.

**Table 4.** Reaction Conditions Used in the Reactions with the Swedish Fiber Sludge and the Yield (%) of LA

Exp.	Catalyst	$C_{\text{catalyst}}$ (mM)	Time (min)	LA (%)
1	-	-	15	47
2			60	49
3			120	49
4	$\text{CrCl}_3$	7.5	15	49
5			30	52
6			60	56
7			120	50
8		19	15	45
9			30	50
10			60	46
11	120		46	
12	$\text{FeCl}_3$	7.5	60	54
13	$\text{ZnCl}_2$	7.5	60	55
14	$\text{CuCl}_2$	7.5	60	51
15	$\text{NiCl}_2$	7.5	60	56

The reaction temperature and the sulfuric acid concentration were in all reactions 180 °C and 0.3 mol/L, respectively.

The highest LA yields achieved in this study from FFS and SFS were 34% and 56%, respectively, with a reaction temperature of 180 °C, reaction time of 60 min,  $\text{H}_2\text{SO}_4$  concentration of 0.3 mol/L, and Lewis acid concentration of 7.5 mmol/L. The results were in line with recent literature that indicated that fiber sludge from Finnish or Swedish pulp mill is a suitable feedstock for LA production. Such studies produced LA from corn stalk with a yield of 49% (Zhi *et al.* 2015; Zheng *et al.* 2017); from poplar wood powder with a yield of 58% (Ji *et al.* 2019); from cellulose with a yields of 54% and 55%, respectively (Joshi *et al.* 2014; Boonyakarn *et al.* 2019); from glucose, empty fruit bunches, and kenaf with yields of 55%, 53%, and 66%, respectively (Ya'aini *et al.* 2012); from glucose with the yields of 46% and 50%, respectively (Choudhary *et al.* 2013; Yang *et al.* 2013); and from corn stover with a yield of 57% (Li *et al.* 2016).

### The Reuse of the Catalyst Mixture

The recovery and reuse of Lewis and Brønsted acid catalysts are important points to consider from economic and ecological viewpoints. In this study, some preliminary experiments regarding the reuse of the catalysts were performed with SFS as the starting material. The reaction temperature was set to 180 °C, reaction time to 60 min,  $\text{H}_2\text{SO}_4$  concentration to 0.3 mol/L, and  $\text{CrCl}_3$  concentration to 7.5 mmol/L. The first reaction provided an LA yield of 58%. LA was extracted from the reaction mixture with ethyl acetate and the ethyl acetate layer was removed. The filtered aqueous reaction liquid, containing the  $\text{CrCl}_3$  and  $\text{H}_2\text{SO}_4$  catalysts, was used again in a new conversion reaction, with SFS again as the starting material. The second cycle provided an LA yield of 56%.

LA was removed again by extraction and the reaction liquid was used for the third time. The third cycle gave an LA yield of 59%. The reaction liquid was recycled for the fourth time and that cycle produced LA, with a yield of 58%. According to these preliminary results, the LA yield remained constant during the four cycles of the reaction liquid without the addition of H<sub>2</sub>SO<sub>4</sub> or CrCl<sub>3</sub> to the reaction mixture. The results are in accordance with Havasi *et al.* (2017) who studied the recycling of H<sub>2</sub>SO<sub>4</sub> used in the conversion of household waste into LA. However, a more detailed study of the catalyst recovery and reuse is needed, and such experiments are ongoing.

## CONCLUSIONS

1. Fiber sludge, a side stream from pulp industry, can be converted to levulinic acid (LA).
2. The composition of the sludge influenced the yield of LA. The Swedish fiber sludge, which was composed mainly from cellulose, produced a noticeably higher LA yield than the Finnish sludge, which also contained 14% lignin.
3. The reaction conditions influenced the LA yield. The combination of Brønsted and Lewis acid catalyst slightly improved the LA yield and decreased the reaction time considerably.
4. The highest LA yield, 56%, was obtained from Swedish fiber sludge, with reaction conditions as follows: a temperature of 180 °C, reaction time of 60 min, H<sub>2</sub>SO<sub>4</sub> concentration of 0.3 mol/L, and Lewis acid, CrCl<sub>3</sub>, concentration of 7.5 mmol/L. The highest LA yield of 34% was obtained from Finnish fiber sludge, when the reaction temperature was 180 °C, the reaction time was 60 min, the H<sub>2</sub>SO<sub>4</sub> concentration was 0.3 mol/L, and the Lewis acid, ZnCl<sub>2</sub>, concentration was 7.5 mmol/L.

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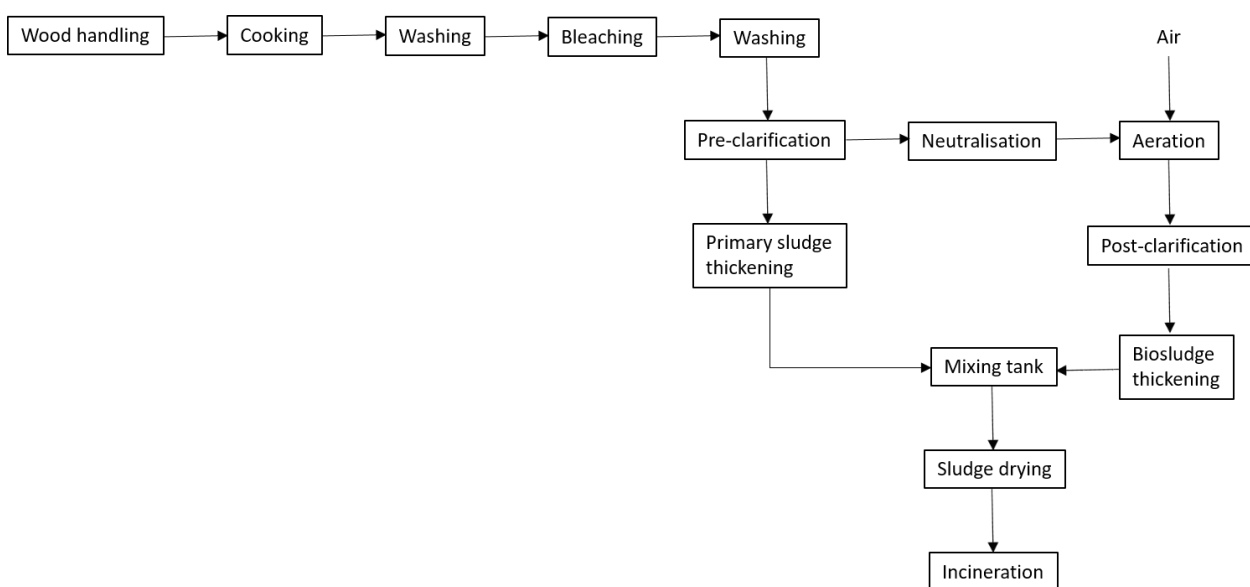
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## APPENDIX

## Supplementary Materials

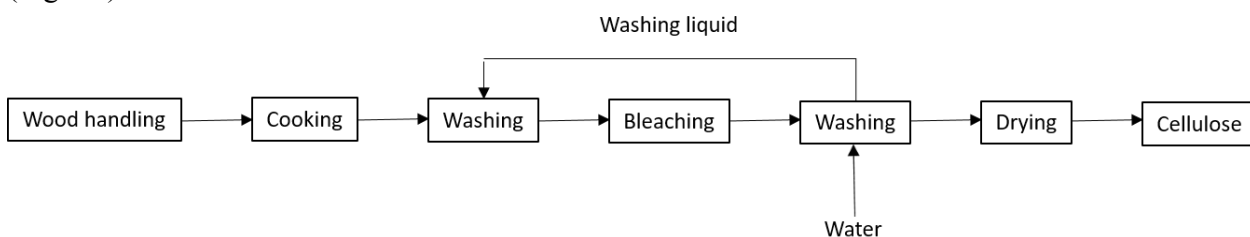
## Materials and methods

The fiber sludge from UPM (Pietarsaari, Finland) was taken from the waste stream of the pulp mill. More specifically, the sludge was taken from the stream of a mixing tank before the sludge drying process (Fig. S1).



**Fig. S1.** A simplified flow sheet of the production process of the Finnish fiber sludge. The sludge was taken from the stream of a mixing tank.

The fiber sludge from Domsjö Fabriker AB (Örnsköldsvik, Sweden) was removed from the process after bleaching and washing, as the first step of the cellulose drying process (Fig. S2).



**Fig. S2.** A simplified flow sheet of the production process of the Swedish fiber sludge. The sludge was removed from the process as the first step of the cellulose drying process.

**Table S1.** ANOVA Table for the Model of Levulinic Acid Yield with Finnish Fiber Sludge as the Starting Material

LA	DF	SS	MS (variance)	F	p	SD
Total	19	422.705	22.2476			
Constant	1	184.268	184.268			
Total Corrected	18	238.438	13.2465			3.63958
Regression	5	231.157	46.2313	82.5448	0.000	6.79936
Residual	13	7.28098	0.560075			0.748382
Lack of Fit	11	7.25511	0.659555	50.9967	0.019	0.81213
Pure Error	2	0.0258666	0.0129333			0.113725
	N = 19	Q2 = 0.927	Cond. no. = 1.09			
	DF = 13	R2 = 0.969	RSD = 0.7484			
		R2 Adj. = 0.958				

**Table S2.** The Scaled and Centred Coefficients for the Fitted Model of the Yield of Levulinic Acid with Finnish Fiber Sludge as the Starting Material

LA	Coefficient SC	Standard Error	P value	Conf. int. ( $\pm$ )
Constant	3.11421	0.171691	1.29813e <sup>-10</sup>	0.370915
Time	0.58563	0.187095	0.00797143	0.404195
Temp.	3.00687	0.187095	5.87723e <sup>-10</sup>	0.404195
H <sub>2</sub> SO <sub>4</sub>	1.64562	0.187095	7.80335e <sup>-7</sup>	0.404195
Time*Temp.	0.41688	0.187095	0.0441519	0.404195
Temp*H <sub>2</sub> SO <sub>4</sub>	1.47687	0.187095	2.58806e <sup>-6</sup>	0.404195