

This is a self-archived version of an original article. This version may differ from the original in pagination and typographic details.

Author(s): Lappalainen, Katja; Kuorikoski, Eveliina; Vanvyve, Elise; Dong, Yue; Kärkkäinen, Johanna; Niemelä, Matti; Lassi, Ulla

Title: Brønsted and Lewis acid catalyzed conversion of pulp industry waste biomass to levulinic acid

Year: 2019

Version: Published version

Copyright: © 2019 the Authors.

Rights: In Copyright

Rights url: <http://rightsstatements.org/page/InC/1.0/?language=en>

Please cite the original version:

Lappalainen, K., Kuorikoski, E., Vanvyve, E., Dong, Y., Kärkkäinen, J., Niemelä, M., & Lassi, U. (2019). Brønsted and Lewis acid catalyzed conversion of pulp industry waste biomass to levulinic acid. *Bioresources*, 14(3), 7025-7040.

<https://bioresources.cnr.ncsu.edu/resources/bronsted-and-lewis-acid-catalyzed-conversion-of-pulp-industry-waste-biomass-to-levulinic-acid/>

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

Katja Lappalainen,^{a,b,*} Eveliina Kuorikoski,^b Elise Vanvyve,^b Yue Dong,^b Johanna Kärkkäinen,^b Matti Niemelä,^b and Ulla Lassi^{a,b}

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 H₂SO₄ and Lewis acid as the catalyst. The reaction conditions, which included reaction time and temperature as well as the H₂SO₄ 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 H₂SO₄ concentration of 0.3 mol/L and a CrCl₃ 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

Contact information: a: Kokkola University Consortium Chydenius, University of Jyväskylä, Talonpojankatu 2B, Kokkola, FIN-67100, Finland; b: Research Unit of Sustainable Chemistry, University of Oulu, P.O.Box 4300, University of Oulu, FIN-90014, Finland;

* Corresponding author: katja.lappalainen@oulu.fi

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).

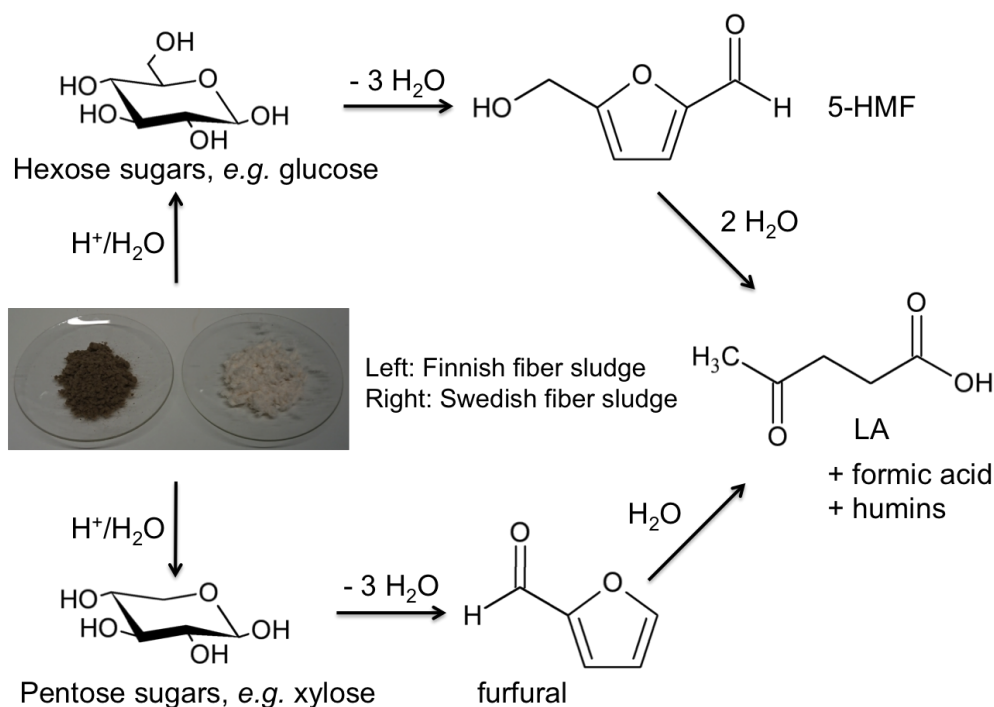


Fig. 1. Reaction scheme for the conversion of lignocellulosic biomass such as fiber sludge to levulinic acid (Mukherjee *et al.* 2015)

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, $\text{S}_2\text{O}_8^{2-}/\text{ZrO}_2\text{-SiO}_2\text{-Sm}_2\text{O}_3$ (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 H₂SO₄ 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 H₂SO₄ 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.*, H₂SO₄ (95-97%, Merck), CrCl₃·6H₂O (98%, Alfa Aesar), FeCl₃·6H₂O (99%, Merck), CuCl₂·2H₂O (99%, Merck), ZnCl₂ (98-100%, VWR), and NiCl₂·6H₂O (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 H₂SO₄ (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 μm , 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 μL . 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 2⁴-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, H₂SO₄, 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 2⁴-Factorial Design

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

RESULTS AND DISCUSSION

Preliminary Experiments with 2⁴-Factorial Design

The potential of two fiber sludges, FFS and SFS, to be used to produce LA was studied. The full 2⁴-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 2⁴-Factorial Design Experiments for the Finnish Fiber Sludge, and the Yield (%) of LA

Exp.	Time (min)	Temp. (°C)	H ₂ SO ₄ (mol/L)	CrCl ₃ (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 H₂SO₄ 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 H₂SO₄ concentration increased. The model for the LA yield also contained interaction terms between temperature and H₂SO₄ 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 H₂SO₄ had the greatest impact on the yield of LA. The optimum reaction temperature was 180 °C, and 0.5 M was the optimum H₂SO₄ 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 H₂SO₄ concentration of 0.5 mol/L and a CrCl₃ concentration of 1.9 mmol/L. However, a similar yield was achieved in 15 min when the CrCl₃ 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.

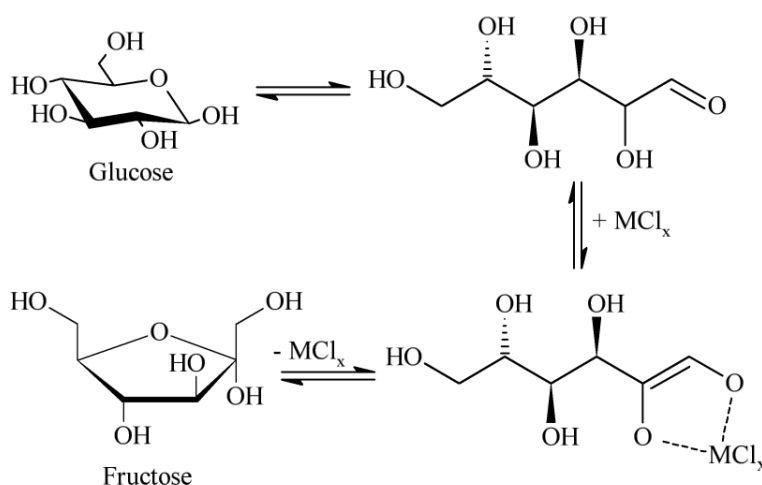


Fig. 2. The proposed route for the Lewis acid catalyzed isomerization of glucose to fructose (Li *et al.* 2009; Peng *et al.* 2010).

Additional Experiments with Finnish Fiber Sludge

The additional conversion reactions were first performed with only the H₂SO₄ as the catalyst. It was considered that the upper level of the H₂SO₄ 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 H₂SO₄ 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 H₂SO₄ 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 H₂SO₄, 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 H₂SO₄ itself was enough to produce the 31% LA yield and that the H₂SO₄ 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 H₂SO₄ concentrations of 34% (Table 3). Based on these results, the H₂SO₄ 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. CrCl₃ 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 H₂SO₄ as the catalyst. Similar LA yields of 33% (exps. 7, 10, and 14, Table 3) were achieved in 60 min with all the studied CrCl₃ concentrations. Also, when there was 7.5 mmol/L or 19 mmol/L of CrCl₃ 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 _{Lewisacid} (mmol/L)	Time (min)	LA (%)	
1	-	-	60	31	
2			120	34	
3*	-	-	60	31	
4*			120	34	
5	CrCl ₃	1.9	15	25	
6			30	31	
7			60	33	
8		7.5	15	29	
9			30	32	
10			60	33	
11		19	120	32	
12			15	22	
13			30	30	
14		60	33		
15		FeCl ₃	7.5	60	32
16			19	60	29
17		ZnCl ₂	7.5	60	34
18			19	60	31
19	CuCl ₂	7.5	60	29	
20		19	60	30	
21	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 CrCl₃ in order to study if similar LA yields could be produced. CrCl₃ 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 FeCl₃, ZnCl₂, CuCl₂, and NiCl₂. 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 CrCl₃ as the Lewis acid catalyst. Furthermore, the results were in accordance with a previous study where ZnCl₂, CrCl₃, FeCl₃, or CuCl₂ was used as a mixed catalyst

with H₂SO₄ 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 CrCl₃ was clearly a better catalyst for LA production from cellulose than ZnCl₂, CuCl₂, or FeCl₃ (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 H₂SO₄.

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 H₂SO₄ 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 CrCl₃ 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 H₂SO₄ 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 CrCl₃ was added to the reaction, no 5-HMF or furfural was detected after 60 min of heating. With a CrCl₃ 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 CrCl₃ 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 CrCl₃ 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 CrCl₃. 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). 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_{catalyst} (mM)	Time (min)	LA (%)
1	-	-	15	47
2			60	49
3			120	49
4	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	FeCl_3	7.5	60	54
13	ZnCl_2	7.5	60	55
14	CuCl_2	7.5	60	51
15	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, H_2SO_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, H_2SO_4 concentration to 0.3 mol/L, and 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 CrCl_3 and H_2SO_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 H₂SO₄ or CrCl₃ to the reaction mixture. The results are in accordance with Havasi *et al.* (2017) who studied the recycling of H₂SO₄ 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, H₂SO₄ concentration of 0.3 mol/L, and Lewis acid, CrCl₃, 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 H₂SO₄ concentration was 0.3 mol/L, and the Lewis acid, ZnCl₂, concentration was 7.5 mmol/L.

ACKNOWLEDGMENTS

This work was financially supported by Bioraff Botnia project (No. 20200327, EU/Interreg Botnia-Atlantica), Green Bioraff Solutions project (No. 20201508, EU/Interreg Botnia-Atlantica), Maj and Tor Nessling Foundation (Grant No. 201800070), Otto Malm Foundation and Oulun Läänin Talousseuran Maataloussäätiö.

REFERENCES CITED

- Antonetti, C., Licursi, D., Fulignati, S., Valentini, G., and Raspolli Galletti, A. M. (2016). "New frontiers in the catalytic synthesis of levulinic acid: from sugars to raw and waste biomass as starting feedstock," *Catalysts* 6, 196-225. DOI: 10.3390/catal6120196
- Boonyakarn, T., Wataniyakul, P., Boonnoun, P., Quitain, A. T., Kida, T., Sasaki, M., Laosiripojana, N., Jongsomjit, B., and Shotipruk, A. (2019). "Enhanced levulinic acid production from cellulose by combined Brønsted hydrothermal carbon and Lewis acid catalysts," *Industrial and Engineering Chemistry Research* 58(8), 2697-2703. DOI: 10.1021/acs.iecr.8b05332

- Chang, C., Cen, P., and Ma, X. (2007). "Levulinic acid production from wheat straw," *Bioresource Technology* 98(7), 1448-1453. DOI: 10.1016/j.biortech.2006.03.031
- Chen, H., Yu, B., and Jin, S. (2011). "Production of levulinic acid from steam exploded rice straw via solid superacid, $S_2O_8^{2-}/ZrO_2-SiO_2-Sm_2O_3$," *Bioresource Technology* 102(3), 3568-3570. DOI: 10.1016/j.biortech.2010.10.018
- Choudhary, V., Mushrif, S. H., Ho, C., Anderko, A., Nikolakis, V., Marinkovic, N. S., Frenkel, A. I., Sandler, S. I., and Vlachos, D. G. (2013). "Insights into the interplay of Lewis and Brønsted acid catalysts in glucose and fructose conversion to 5-(hydroxymethyl) furfural and levulinic acid in aqueous media," *Journal of American Chemical Society* 135(10), 3997-4006. DOI: 10.1021/ja3122763
- Council Directive 1999/31/EC. (1999). "Council Directive 1999/31/EC of 26 April 1999 on the landfill of waste," European Union, Brussels, Belgium.
- Delbecq, F., Wang, Y., and Len, C. (2016). "Conversion of xylose, xylan and rice husk into furfural *via* betaine and formic acid mixture as novel homogeneous catalyst in biphasic system by microwave-assisted dehydration," *Journal of Molecular Catalysis A: Chemical* 423, 520-525. DOI: 10.1016/j.molcata.2016.07.003
- Delbecq, F., Takahashi, Y., Kondo, T., Corbas, C. C., Ramos, E. R., and Len, C. (2018). "Microwave assisted efficient furfural production using nano-sized surface-sulfonated diamond powder," *Catalysis Communications* 110, 74-78. DOI: 10.1016/j.catcom.2018.03.020
- Dong, Y., Schneider, L., Hu, T., Jaakkola, M., Holm, J., Leveque, J. M., and Lassi, U. (2016). "Direct acid-catalysed mechanical depolymerisation of fibre sludge to reducing sugars using planetary milling," *Biomass and Bioenergy* 86, 36-42. DOI: 10.1016/j.biombioe.2016.01.006
- Efremov, A. A., Pervyshina, G. G., and Kuznetsov, B. N. (1997). "Thermocatalytic transformations of wood and cellulose in the presence of HCl, HBr and H_2SO_4 ," *Chemistry of Natural Compounds* 33(1), 84-88. DOI: 10.1007/BF02273932
- Efremov, A. A., Pervyshina, G. G., and Kuznetsov, B. N. (1998). "Production of levulinic acid from wood raw material in the presence of sulfuric acid and its salts," *Chemistry of Natural Compounds* 34(2), 182-185. DOI: 10.1007/BF02249141
- Galletti, A. M. R., Antonetti, C., De Luise, V., Licursi, D., and Nassi, N. (2012). "Levulinic acid production from waste biomass," *BioResources* 7(2), 1824-1835. DOI: 10.15376/biores.7.2.1824-1835
- Girisuta, B., Janssen, L. P. B. M., and Heeres, H. J. (2007). "Kinetic study on the acid-catalyzed hydrolysis of cellulose to levulinic acid," *Industrial and Engineering Chemistry Research* 46(6), 1696-1708. DOI: 10.1021/ie061186z
- Guenic, S. L., Delbecq, F., Ceballos, C., and Len, C. (2015). "Microwave-assisted dehydration of D-xylose into furfural by diluted inexpensive inorganic salts solution in a biphasic system," *Journal of Molecular Catalysis A: Chemical* 410, 1-7. DOI: 10.1016/j.molcata.2015.08.019
- Guenic, S. L., Gergela, D., Ceballos, C., Delbecq, F., and Len, C. (2016). "Furfural production from D-xylose and xylan by using stable Nafion NR50 and NaCl in a microwave-assisted biphasic reaction," *Molecules* 21(8), 1102-1112. DOI: 10.3390/molecules21081102
- Guzmán, I., Heras, A., Güemez, M. B., Iriondo, A., Cambra, J. F., and Requies, J. (2016). "Levulinic acid production using solid-acid catalysis," *Industrial and Engineering Chemistry Research* 55(18), 5139-5144. DOI: 10.1021/acs.iecr.5b04190
- Havasi, D., Pátzay, G., Stelén, G., Tukacs, J. M., and Mika, L. T. (2017). "Recycling of

- sulfuric acid in the valorization of biomass residues,” *Periodica Polytechnica Chemical Engineering* 61(4), 283-287. DOI: 10.3311/PPch.11175
- Hayes, D. J., Fitzpatrick, S., Hayes, M. H. B., and Ross, J. R. H. (2008). “The Biofine process - production of levulinic acid, furfural, and formic acid from lignocellulosic feedstocks,” in: *Biorefineries - Industrial Processes and Products: Status Quo and Future Directions*, B. Kamm, P. R. Gruber, M. Kamm (eds.), Wiley, Hoboken, NJ, pp 139-164.
- Holm, J., Lassi, U., and Hernoux-Villière, A. (2013). “Task-specific ionic liquid [SBMIM]Cl in one-step dissolution and hydrolysis of fiber sludge,” *Biomass and Bioenergy* 56, 432-436. DOI: 10.1016/j.biombioe.2013.05.005
- Ji, H., Dong, C., Yang, G., and Pang, Z. (2019). “Production of levulinic acid from lignocellulosic biomass with a recyclable aromatic acid and its kinetic study,” *BioResources* 14(1), 725-736. DOI: 10.15376/biores.14.1.725-736
- Joshi, S. S., Zodge, A. D., Pandare, K. V., and Kulkarni, B. D. (2014). “Efficient conversion of cellulose to levulinic acid by hydrothermal treatment using zirconium dioxide as a recyclable solid acid catalyst,” *Industrial and Engineering Chemistry Research* 53(49), 18796-18805. DOI: 10.1021/ie5011838
- Kumar, V. B., Pulidindi, I. N., and Gedanken, A. (2015). “Synergistic catalytic effect of the ZnBr₂-HCl system for levulinic acid production using microwave irradiation,” *RSC Advances* 5(15), 11043-11048. DOI: 10.1039/c4ra15083j
- Kuokkanen, M., Mäentausta, O., and Kuokkanen, T. (2018). “Eco- and material-efficient utilization applications of biotechnologically modified fiber sludge,” *BioResources* 13(1), 1457-1474. DOI: 10.15376/biores.13.1.1457-1474
- Lappalainen, K., Vogeler, N., Kärkkäinen, J., Dong, Y., Niemelä, M., Rusanen, A., Ruotsalainen, A. L., Wäli, P., Markkola, A., and Lassi, U. (2018). “Microwave-assisted conversion of novel biomass materials into levulinic acid,” *Biomass Conversion and Biorefinery* 8(4), 965-970. DOI: 10.1007/s13399-018-0334-6
- Li, C., Zhang, Z., and Zhao, Z. K. (2009). “Direct conversion of glucose and cellulose to 5-hydroxymethylfurfural in ionic liquid under microwave irradiation,” *Tetrahedron Letters* 50(38), 5403-5405. DOI: 10.1016/j.tetlet.2009.07.053
- Li, M., Li, W., Liu, Q., Jameel, H., Chang, H.-m., An, S., and Ma, L. (2016). “A two-step conversion of corn stover into furfural and levulinic acid in a water/gamma-valerolactone system,” *BioResources* 11(4), 8239-8256. DOI: 10.15376/biores.11.4.8239-8256
- Mukherjee, A., Dumont, M. J., and Raghavan, V. (2015). “Review: Sustainable production of hydroxymethylfurfural and levulinic acid: Challenges and opportunities,” *Biomass and Bioenergy* 72, 143-183. DOI: 10.1016/j.biombioe.2014.11.007
- Sluiter, A., Hames, B., Ruiz, R., Scarlata, C., Sluiter, J., Templeton, D., and Crocker, D. (2011). *Determination of Structural Carbohydrates and Lignin in Biomass* (NREL TP-510-42619), National Renewable Energy Laboratory, Golden, CO.
- Patil, S. K. R., and Lund, C. R. F. (2011). “Formation and growth of humins via aldol addition and condensation during acid-catalyzed conversion of 5-hydroxymethylfurfural,” *Energy & Fuels* 25(10), 4745-4755. DOI: 10.1021/ef2010157
- Potvin, J., Sorlien, E., Hegner, J., DeBoef, B., and Lucht, B. L. (2011). “Effect of NaCl on the conversion of cellulose to glucose and levulinic acid via solid supported acid catalysis,” *Tetrahedron Letters* 52(44), 5891-5893. DOI: 10.1016/j.tetlet.2011.09.013

- Rowell, R. M., Pettersen, R., and Tshabalala, M. A. (2005). "Cell wall chemistry," in: *Handbook of Wood Chemistry and Wood Composites*, R. M. Rowell (ed.), CRC Press, Boca Raton, LA, pp. 33-72.
- Rusanen, A., Lappalainen, K., Kärkkäinen, J., Tuuttila, T., Mikola, M., and Lassi, U. (2018). "Selective hemicellulose hydrolysis of Scots pine sawdust," *Biomass Conversion and Biorefinery*, 1-9. DOI: 10.1007/s13399-018-0357-z
- Silva, J. F. L., Grekin, R., Mariano, A. P., and Filho, R. M., (2018). "Making levulinic acid and ethyl levulinate economically viable: a worldwide techno-economic and environmental assessment of possible routes," *Energy Technology* 6 (4), 613-639. DOI: 10.1002/ente.201700594
- Singh, R., Krishna, B. B., Kumar, J., and Bhaskar, T. (2016). "Opportunities for utilization of non-conventional energy sources for biomass pretreatment," *Bioresource Technology* 199, 398-407. DOI: 10.1016/j.biortech.2015.08.117
- Styarini, D., Risanto, L., Sudiyani, Y., and Aristiawan, Y. (2012). "Comparison of two analytical methods for compositional analysis of lignocellulosic biomass for bioethanol production," *International Journal of Environment and Bioenergy* 3(2), 88-97.
- TAPPI T203 cm-09. (2009). "Alpha-, beta- and gamma-cellulose in pulp," TAPPI Press, Atlanta, GA.
- TAPPI UM 250 (2006). "Acid-soluble lignin in wood and pulp," TAPPI Press, Atlanta, GA.
- Wang, Y., Delbecq, F., Varma, R. S., and Len, C. (2018). "Comprehensive study on expeditious conversion of pre-hydrolyzed alginic acid to furfural in Cu(II) biphasic systems using microwaves," *Molecular Catalysis* 445, 73-79. DOI: 10.1016/j.mcat.2017.11.013
- Wei, W., and Wu, S. (2017). "Experimental and kinetic study of glucose conversion to levulinic acid catalyzed by synergy of Lewis and Brønsted acids," *Chemical Engineering Journal* 307, 389-398. DOI: 10.1016/j.cej.2016.08.099
- Werpy, T., Petersen, G., Aden, A., Bozell, J., Holladay, J., White, J., Manheim, A., Eliot, D., Lasure, L., and Jones, S. (2004). "Top Value Added Chemicals from Biomass. Volume 1 - Results of Screening for Potential Candidates from Sugars and Synthesis Gas," U. S. Department of Energy, Washington DC.
- Ya'aini, N., Amin, N. A. S., and Asmadi, M. (2012). "Optimization of levulinic acid from lignocellulosic biomass using a new hybrid catalyst," *Bioresource Technology* 116, 58-65. DOI: 10.1016/j.biortech.2012.03.097
- Yan, L. F., Yang, N. K., Pang, H., and Liao, B. (2008). "Production of levulinic acid from bagasse and paddy straw by liquefaction in the presence of hydrochloride acid," *CLEAN- Soil, Air, Water* 36(2), 158-163. DOI: 10.1002/clen.200700100
- Yang, F., Fu, J., Mo, J., and Lu, X. (2013). "Synergy of Lewis and Brønsted acids on catalytic hydrothermal decomposition of hexose to levulinic acid," *Energy & Fuels* 27(11), 6973-6978. DOI: 10.1021/ef401560v
- Yokoyama, T., Kadla, J. F., and Chang, H.-m. (2002). "Microanalytical method for the characterization of fiber components and morphology of woody plants," *Journal of Agricultural and Food Chemistry* 50(5), 1040-1044. DOI: 10.1021/jf011173q
- Yoon, S.-Y., Han, S.-H., and Shin, S.-J. (2014). "The effect of hemicelluloses and lignin on acid hydrolysis of cellulose," *Energy* 77, 19-24. DOI: 10.1016/j.energy.2014.01.104
- Zeng, W., Cheng, D.-g., Zhang, H., Chen, F., and Zhan, X. (2010). "Dehydration of

glucose to levulinic acid over MFI-type zeolite in subcritical water at moderate conditions,” *Reaction Kinetics, Mechanisms and Catalysis* 100(2), 377-384. DOI: 10.1007/s11144-010-0187-x

Zhang, Y. H. P. (2008). “Reviving the carbohydrate economy via multi-product lignocellulose biorefineries,” *Journal of Industrial Microbiology and Biotechnology* 35(5), 367-375. DOI: 10.1007/s10295-007-0293-6

Zheng, X., Zhi, Z., Gu, X., Li, X., Zhang, R., and Lu, X. (2017). “Kinetic study of levulinic acid production from corn stalk at mild temperature using FeCl₃ as catalyst,” *Fuel* 187, 261-267. DOI: 10.1016/j.fuel.2016.09.019

Zhi, Z., Li, N., Qiao, Y., Zheng, X., Wang, H., and Lu, X. (2015). “Kinetic study of levulinic acid production from corn stalk at relatively high temperature using FeCl₃ as catalyst: a simplified model evaluated,” *Industrial Crops and Products* 76, 672-680. DOI: 10.1016/j.indcrop.2015.07.058

Article submitted: April 5, 2019; Peer review completed: May 25, 2019; Revised version received and accepted: July 11, 2019; Published: July 17, 2019.

DOI: 10.15376/biores.14.3.7025-7040

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).

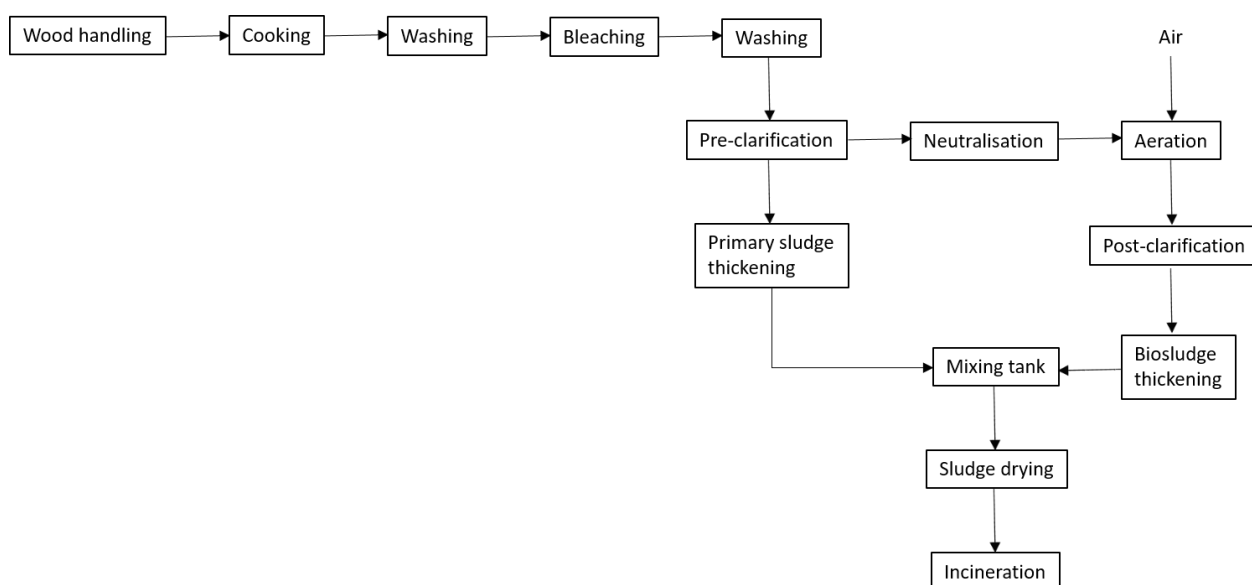


Fig. S1. A simplified flow sheet of the production process of the Finnish fiber sludge. The sludge was taken from the stream of a mixing tank.

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).

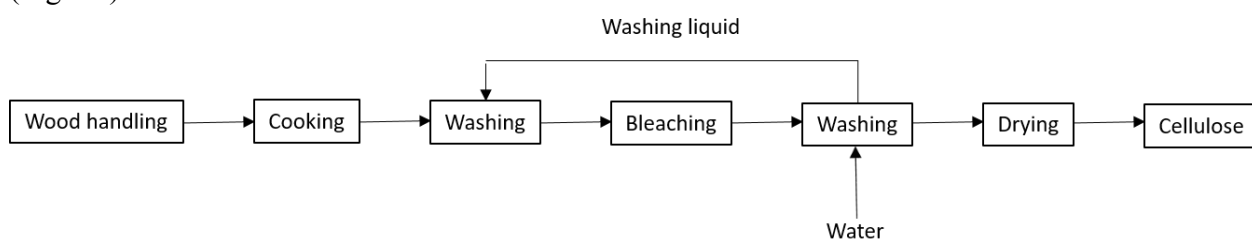


Fig. S2. A simplified flow sheet of the production process of the Swedish fiber sludge. The sludge was removed from the process as the first step of the cellulose drying process.

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 ⁻¹⁰	0.370915
Time	0.58563	0.187095	0.00797143	0.404195
Temp.	3.00687	0.187095	5.87723e ⁻¹⁰	0.404195
H ₂ SO ₄	1.64562	0.187095	7.80335e ⁻⁷	0.404195
Time*Temp.	0.41688	0.187095	0.0441519	0.404195
Temp*H ₂ SO ₄	1.47687	0.187095	2.58806e ⁻⁶	0.404195