

PRODUCTION OF CARBOXYLIC ACIDS FROM ALKALINE PRETREATMENT BYPRODUCT OF SOFTWOOD

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To reduce greenhouse gas emissions more sustainable sources of energy, fuel and chemicals are needed. Lignocellulosic biomass such as wood sawdust could be used for this purpose. The present study is concerned with production of carboxylic acids from spruce sawdust in two stages: firstly, treating sawdust increasing with temperature from 80 °C up to 160 °C with 2 °C/min with alkali during 30 min, and subsequently, treating the liquid part from the first step by partial wet oxidation at 210 °C and oxygen partial pressure of 0.6MPa for 30 min. The carboxylic acids studied include formic, acetic and lactic acids. The objective of this work was to study production of carboxylic acids from a liquid byproduct obtained by pretreatment of sawdust with sodium carbonate or green liquor. The fiber part can be used for pulp or bioethanol production. The yield of acetic acid from spruce was the highest. However, the increase (wt%) in the formation of lactic acid was the highest after pretreatment in the wet oxidation step. The case with the highest addition of Na₂CO₃ resulted in the greatest yields of acids. For extraction using n-butanol as extraction medium, distribution coefficients ranging from 0.78 to 1.69 were measured for the acids.

Keywords: wet oxidation, sawdust, lignocellulosic biomass, waste biomass, partial wet oxidation, alkaline cooking, acid cooking

INTRODUCTION

Global warming and the depletion of fossil reserves call for more effective utilization of existing resources including side and waste products. In the production of energy, fuels and chemicals existing fossil feedstock can be largely substituted by biomass and bio-based effluents and wastes, which are found in abundance on earth. The total amount of above-ground woody biomass is estimated to be 420*10¹² with an annual production calculated to be about 170*10¹² kg in biosphere.^{1,2} This makes the lignocellulosic biomass one of the potential renewable raw materials, which can be converted into energy, fuels and chemicals by different thermo-chemical processes such as pyrolysis, gasification and hydrothermal treatment.

In order to produce ethanol pretreatment, it is necessary to make the biomass more accessible to subsequent enzymatic hydrolysis. During pretreatment, the lignin holding tightly the cellulose and hemicelluloses is degraded and the complex crystalline structures of cellulose and hemicelluloses are made accessible, also resulting in increased surface area of the cellulosic biomass.³ The pretreatment method is selected based on the component that is to be extracted or utilized from

the lignocellulosic biomass. Different pretreatment methods, such as physical, chemical or microbiological, are discussed in literature.^{4,5}

Wet air oxidation (WAO) is an established treatment method for non-biodegradable waste water.^{6,7,8} It is also known as sub-critical hydrothermal oxidation. Wet air oxidation is an aqueous process where the organic/inorganic compounds present in liquid water are oxidized by dissolved oxygen. The oxidation reaction is generally carried out at temperatures above 175 °C. The pressure inside the reactor is maintained above the vapor pressure of water in order to enhance the solubility of the oxidant into the reaction mixture. The reaction is exothermic in nature, therefore it is important to remove the excess heat of the reaction. This excess heat can be removed by evaporation of liquid water or transferring heat by cooling coils. Higher pressures of oxygen/air are required for the complete oxidation of organic matter. Streams with organic content higher than 3% can sustain the reaction conditions and generate surplus energy during the reaction. The final products of wet oxidation are CO₂ and H₂O, which can further

be used to generate heat and also power a gas turbine.

The reaction mechanism for wet oxidation is not completely understood. However, it has been proposed to proceed via the free radical mechanism.⁸ The oxidation is propagated by the formation of oxygen, hydroxyl, hydroperoxyl and organic hydroxyl free radicals.

The wet oxidation process has been successfully commercialized in different parts of the world.⁹ The most widely commercialized technology is the Zimpro process, which has about 200 commercial units installed worldwide for sewage treatment purposes. Zimpro process uses the co-current bubble column reactor. The reactor is operated in the temperature range of 147-325 °C and between 2.0-12.0 MPa pressure based on the degree of oxidation required. The other popular technologies available are Wetox Process, Vertech Process, Kenox process and Oxyjet reactor system. Wetox Process uses a horizontal autoclave comprising 4-6 compartments, which together act as a series of CSTR. Vertech Process uses a sub-surface reactor consisting of two concentric cylindrical tubes. Kenox Process introduced novel concepts of static mixing and ultrasonic energy in a reactor similar to Vertech Process. On the other hand, Oxyjet reactor system used the combination of tubular reactors and jet mixers.

Many published papers report on the complete wet oxidation of organic matter in sewage sludge. Nevertheless, some of the patents discuss the incomplete oxidation for the recovery of short chain organic molecules, such as carboxylic acid anions.¹⁰ Incomplete oxidation can be carried out by

controlling the oxygen supply to the Wet air oxidation process. This process is then known as Partial Wet Air Oxidation (PWAO). During partial oxidation, the complete reaction of some components takes place, whereas others are oxidized to a smaller extent.

One alternative for the utilization of side products from biorefineries into chemicals is the partial wet oxidation (PWO) process. Moreover, energy is also produced since the process is exothermic in nature.

The separation of carboxylic acid from aqueous solution by direct distillation is unfeasible due to close and higher boiling points of the acids, compared with water. Therefore extraction is often used. Common extractants for the extraction of carboxylic acids from aqueous solutions can be roughly divided to three categories: carbon bonded oxygen-bearing extractants, phosphorus-bonded oxygen-bearing extractants and amines and amine-diluent systems. In the first two categories, the extraction is based on dissolution, but with amines, a proton transfer takes place.¹⁰

Of carbon-oxygen bearing extractants, one of the best extractants is 1-butanol, for which distribution coefficients of 0.73 for lactic acid and 1.4 for acetic acid have been reported.^{11,12} Phosphorus based extractants have also been said to be impractical and expensive to use,⁷ and therefore not many studies regarding their use in the extraction of carboxylic acids have been made. Amines, especially long chain tertiary aliphatic amines,^{12,14,15} are reported to be generally less expensive and more effective than phosphorus based extractants for the extraction of carboxylic acids from aqueous solutions.¹⁴

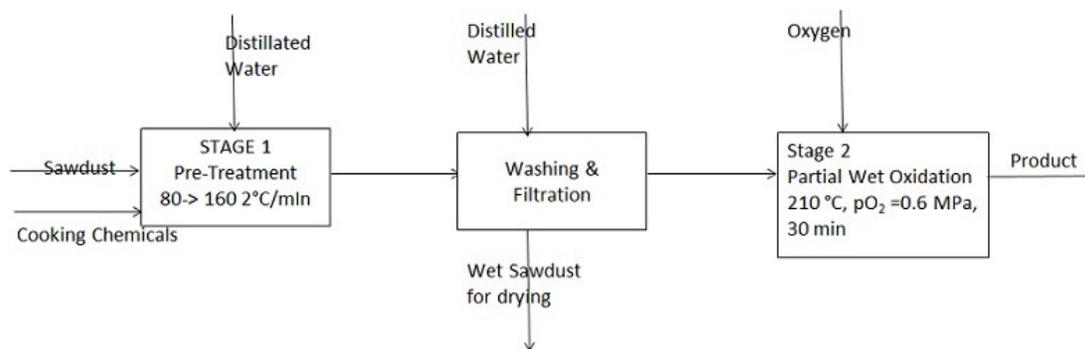


Figure 1: Flow diagram for two-stage process approach

Wet oxidation has been studied for waste water treatment and also as a pretreatment method. However, wet oxidation of a byproduct from

alkaline pretreatment for production of carboxylic acids has not been reported, according to the author's knowledge.

The objective of this study is to treat sawdust first by alkali pretreatment in order to obtain a fiber main product, which could be used for bioethanol or pulp production, and a side product, which can be further treated by partial wet oxidation in order to produce chemicals, as shown in Figure 1. Also, the recovery of acid from the wet oxidized solution was studied since the recovery of acids from the dilute aqueous solution is an important matter for the feasibility chemical production from the byproduct.

EXPERIMENTAL

Materials

The starting material used for experiments was spruce sawdust obtained from Department of Forest Product Technology, Aalto University. The saw dust was sieved using 1.41 mm mesh size in order to keep the particle size smaller than 1.50 mm. The moisture content of sawdust was found to be approximately 55%. The moisture content was determined by putting a known amount of sawdust sample in an oven for 24 h at 105 °C. Pure oxygen (99.99%) purchased from AGA, Finland, was used as oxidant in all the partial wet oxidation (PWO) experiments.

Two different cooking chemicals were used in the first stage, i.e. chemical cooking, as shown in Table 1. The reason for selecting Na_2CO_3 as a cooking chemical was because it is readily available and inexpensive. Also $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ was selected because it is already being used in the pulping mills as green liquor and it can be directly taken from the mill making the synergy easier. The cooking chemicals used are presented in Table 1. Chemicals for extraction experiments were purchased from Sigma Aldrich.

Reaction apparatus and procedure

The experiments were carried out in two stages, i.e. cooking sawdust followed by partial wet oxidation of liquid from cooked mixture. Both stages were performed in a 100 mL AISI 316 SS high pressure micro reactor (Parr model 4590) with maximum operating pressure 6MPa. The equipment was fitted with mechanically driven four blade impeller and variable speed arrangement from 0-800 rpm. The absence of mass transfer limitation was confirmed in

an earlier study by checking that the conversion of the reaction was not increased further by using higher stirring speed.¹⁶ The upper section (head) of the reactor was employed with pressure gauge, pressure release valve, gas inlet, gas sample outlet, stirring engine cooling water feed line and thermowell. The reactor vessel was mounted with an external electric heating jacket and the temperature was controlled by a temperature controller. There was no cooling in the reactor.

In the first stage, the sawdust was cooked along with distilled water and a cooking chemical i.e. Na_2CO_3 or $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$. The feedstock for cooking was prepared by mixing sawdust and cooking chemical in distilled water. The liquid wood ratio on dry wood was 10. Different amounts of cooking chemicals were used in the cooking reaction, as shown in Table 2. The prepared feed for cooking was loaded into the reactor. After closing the reactor, the temperature was slowly increased. From 80 °C to 160 °C the temperature increase rate was controlled at 2 °C/min, which took about 30 min, after which the heating was stopped and reactor was cooled down to room temperature by quenching with cool water, which took about 5 minutes. Next, the liquid and solids were separated by filtration by passing the cooked mixture through a metal sieve of mesh size 0.25 mm. The wet sawdust was then washed with 10 mL of distilled water. The separated solids were weighed accurately and dried in an oven for 24 h at 105 °C for determining the moisture content.

In the second stage, the liquid product separated from the cooked mixture was partially wet oxidized in the same reactor equipment. The reactor was closed after loading with the liquid product from the first stage and preheated to 200 °C, which is 10 °C below the actual reaction temperatures 210 °C. During the preheating stage, the reactor was closed (no oxygen was fed and no steam was purged). At temperatures between 100-105 °C, the exit line was opened for a few seconds to purge out the remaining air out of the reactor. This was done to avoid accumulation of nitrogen in the gas phase.

Table 1
Cooking chemicals used in the experiment

Compound	CAS number	Manufacturer
Na_2CO_3	497-19-8	Merck
$\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$	1313-84-4	Acros Organics

Table 2
Operating conditions and chemicals used in first stage i.e. cooking experiments

Run	Feedstock (g)				Chemicals	Temperature (°C)	Reaction time (min)	Product pH	
	SD	Na ₂ CO ₃	Na ₂ S	DW					Total
C-1	16	0.96		141.6	158.56	Na ₂ CO ₃	80->160, 2 °C/min	30	7.68
C-2	16	1.46		141.6	159.06	Na ₂ CO ₃	80->160, 2 °C/min	30	8.2
C-3	16	2.92		141.6	160.52	Na ₂ CO ₃	80->160, 2 °C/min	30	8.98
C-4	16	0.72	1.08	141.6	159.41	Na ₂ CO ₃ /Na ₂ S.9H ₂ O	80->160, 2 °C/min	30	8.25
C-5	16	1.08	1.62	141.6	160.3	Na ₂ CO ₃ /Na ₂ S.9H ₂ O	80->160, 2 °C/min	30	8.7

SD: Sawdust; DW: Distilled water

Table 3
Operating conditions used in the second stage, i.e. PWO experiments

Run	Liq. From	Amount (g)	pH		Temperature (°C)	Partial pressure of O ₂ (Mpa)	Reaction time (min)
			Feedstock	Product			
P-1	C-1	35	7.68	7.18	210	0.6	30
P-2	C-2	35	8.2	7.43	210	0.6	30
P-3	C-3	35	8.98	8.43	210	0.6	30
P-4	C-4	35	8.25	8.17	210	0.6	30
P-5	C-5	35.2	8.7	7.08	210	0.6	30

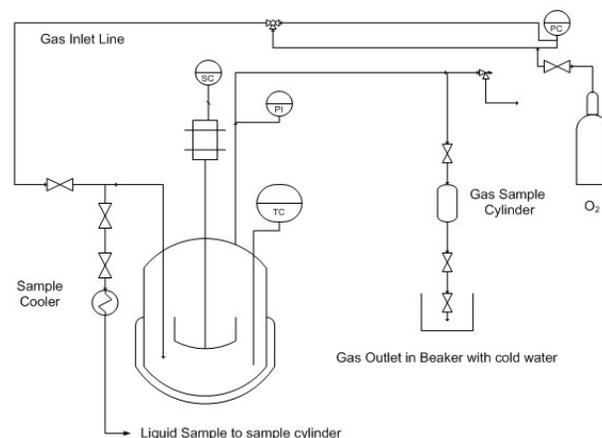


Figure 2: Experimental set-up for wet oxidation experiments

Approximately 10 °C below the desired oxidation temperature, the oxygen line was opened for very short periods to start the reaction and allowing temperature to rise to the actual reaction temperature of 210 °C and to prevent the temperature overshoot, since there was no cooling. It takes around 5 minutes to reach the set temperature and stabilize. When the reaction temperature was reached, the valve was completely opened. This was the point that was considered as the starting time of the reaction ($t=0$). The total pressure was kept constant during the run by feeding more oxygen by the pressure regulator from the oxygen bottle. The total pressure was set to 0.6 MPa higher than the vapor pressure of the feedstock at the corresponding temperature. This difference was assumed to be equal to the partial pressure of oxygen.

The reaction temperature was kept constant by a temperature controller. After 30 min, the oxygen feed was stopped and the reactor cooled down to room temperature by quenching with cool water. The quenching takes around 5 minutes. Once it cooled down, the exit line was opened and the reactor depressurized. The oxidation products were analyzed as to pH, COD, TOC. Table 3 presents the operating conditions of experiments performed in the second stage.

In the second stage i.e. PWO reaction oxygen was used as an oxidant, which was fed from a bottle via a pressure regulator, which kept the pressure of the reactor constant during the run, i.e. when oxygen was consumed in the batch reactor more oxygen from the gas bottle was injected through the pressure regulator.

The reactor set-up is presented in Figure 2.

Analysis of feedstock and products

The parameters that were analyzed for each sample were the pH, chemical oxygen demand (COD), total organic carbon (TOC), and acetic, formic and lactic acid contents. For the same feedstock the fall in pH during the runs indicates how much alkali has been consumed by the produced acids and carbon dioxide. Therefore the reduction in COD indicates how much of the feedstock has been oxidized. The total organic carbon indicates how much of the organic carbon has been converted into inorganic carbon. The inorganic carbon either remains in the liquid phase as dissolved carbon dioxide, bicarbonate or has escaped into the gas phase as carbon dioxide.

The pH was measured at atmospheric pressure and room temperature right after each oxidation run. The pH meter (VWR pH100) was calibrated before each round. COD and TOC were measured using a VIS spectrophotometer (Hach Lange, model DR 3900). The COD analysis was based on the evaluation of the green color of Cr^{3+} after the reaction between oxidizing substances with sulfuric acid–potassium dichromate solution in the presence of silver sulfate as catalyst. Since the chloride concentration can interfere in the measurement, mercury sulfate is used to mask it.

The technique used to analyze the TOC content consisted of two stages. In the first stage, the total inorganic carbon (TIC) is expelled with the help of a shaker (Hach Lange, model TOC-X5). In the second stage, the TOC is oxidized to carbon dioxide, which passes through a membrane into the indicator cuvette. The carbon dioxide causes a color change to occur, and it is this change that is evaluated with the photometer.

The cuvettes containing the reagents for COD and TOC analysis were purchased at Hach Lange (LCK 514 and LCK 387 respectively). Due to the concentration range limitations of both COD and TOC analysis programs, the samples that needed to be analyzed were previously diluted by a certain dilution factor (DF) so that the COD and TOC were in the analyzing range. In order to double-check the results, two solutions with a different DF were prepared and analyzed for each sample.

The quantification of short chain organic acid yields in the PWO reaction was determined using high pressure liquid chromatography (HPLC) analysis. The organic acids, such as acetic, formic and lactic acids, were analyzed. Glycolic acid could not be analyzed separately with HPLC due to similar retention times and it may add up to the lactic acid yield. During the sample treatment for HPLC analysis, strong alkali such as NaOH is added in some cases to adjust the pH suitable for the HPLC column. The liquid was then passed through syringe filters with a pore size of 1.2 μm to filter out any precipitates. The HPLC equipment was WATERS 2690 Alliance with RI-detector: WATERS 2414. The column used was: H+ column Hi-

Plex H 300 x 7.7 mm (Agilent Technologies). The temperature of the column was 65 °C and the eluent was 0.005 mol/L H_2SO_4 . The flow was 0.6 mL/min and injection volume 10 μL .

The composition of the raw material was measured for gravimetric Klason lignin, acetone extractives and yield of the hydrolyzed sugars. The hydrolyzed sugars were analyzed with HPLC.

Acids extraction

First the samples were acidified to pH 2.5 using 0.7 M sulfuric acid. All samples were filtered with filters having a pore size of 1.2 μm . For extraction, 1-butanol and trioctylamine/1-butanol were used. Extraction was done adding equal volumes (2.5-4 mL) of acidified and filtered sample and extraction solvent to a volumetric flask. The mixtures were kept in 30 °C water bath and stirred with magnetic stirrers for 15 minutes before letting the phases separate. Organic and aqueous phases were separated.

Samples for HPLC analysis were taken from the acidified and filtered solutions before extraction and from the aqueous phase after extraction. The amount of formic, acetic, and lactic acids in the aqueous phase before and after extraction, was measured by HPLC analysis. In addition, the amount of dissolved 1-butanol in the aqueous phase was determined. Four different samples of partially wet oxidized solutions were acidified. In the samples the carboxylic acid concentration ranged from 0.5 g/L to about 5 g/L. The distribution coefficients for the four samples were calculated for each acid, i.e. formic, acetic and lactic acids. It was based on the assumption that no dimerization or other reactions of the acids take place during extraction in the aqueous phase. By measuring the concentration of the aqueous phase before and after extraction, the difference in the mass of acid in the aqueous phase before and after extraction could be determined. This was equal to the acid dissolved into the extractant phase. Here, it also assumed that no phase mixing takes place and that the volumes of the two phases stay equal.

RESULTS AND DISCUSSION

The product analyses are shown in Table 4 for the liquid obtained from pretreatment and in Table 5 for partially wet oxidized samples.

The results of COD and TOC reduction presented in Table 5 indicate how various amounts of sodium carbonate and green liquor used in the first stage, i.e. cooking stage, influence differently COD and TOC reduction during PWO under the same reaction conditions. The maximum COD reduction of 56.5% in the second stage was achieved in run P-5, with the highest charge of green liquor compared to wood. Also the COD for liquid from C-5 was the

highest, which suggests that most lignin and hemicelluloses were dissolved during stage 1 in the experiment. The Na_2S present in the green liquor is a stronger alkali than Na_2CO_3 . Therefore more organic material is dissolved in the pretreatment. In addition, the wet oxidation reaction might be more effective at higher pH. It can be seen in Table 2 and Table 4 that generally the higher the charge of alkali, the higher the COD and TOC obtained in the liquid. Also, the final pH and acid yields were higher. Experiment C-2 was an exception since a higher COD was

obtained compared to C-3. The value of average chemical oxygen in the demand is in most cases more than twice higher compared to the average total organic carbon, as seen in Table 4 and Table 5. It indicates that components with high oxygen consumption in complete oxidation per gram of substance, such as lignin or extractives, are present in the liquid.

Table 4
Analysis results for cooking samples

Run	Average COD (g/L)	Average TOC (g/L)	Acid yields (g/100 g of dry sawdust)		
			Formic acid	Acetic acid	Lactic acid
C-1	49.8	17.1	0.4	1.1	0.1
C-2	56.1	14.2	1.3	1.4	0.2
C-3	52.8	17.2	1.9	1.4	0.3
C-4	50.9	13.6	0.5	1.2	0.1
C-5	56.9	19.0	1.4	1.3	0.2

Table 5
Analysis results for partially wet oxidized samples

Run	Average COD (g/L)	COD reduction %	Average TOC (g/L)	TOC reduction %	Acid yields (g/100 g of dry sawdust)					
					Formic acid	Diff., %	Acetic acid	Diff., %	Lactic acid	Diff., %
P-1	44.8	10.0	11.4	33.1	0.7	71.0	1.4	22.4	0.4	225.5
P-2	52.4	6.6	13.3	6.4	1.2	-5.0	1.7	21.2	0.7	217.2
P-3	52.0	1.6	23.5	-36.6	1.8	-2.9	1.9	33.3	0.7	167.5
P-4	47.0	7.7	10.5	22.4	0.6	28.0	1.4	21.1	0.4	227.8
P-5	24.8	56.5	9.9	47.9	1.0	-27.5	1.6	25.9	0.5	148.9

As shown in Table 3, the pH dropped during all runs in the second stage, which suggests that alkali was consumed by carboxylic acids and carbon dioxide in the reaction mixture during partial wet oxidation. The pH reduction was the highest in P-5 and, as shown in Table 5, the acid yield was also significant in run P-5. It can be suggested that more acids were formed during run P-5, however because of the limitation of the analytics only three acids were identified for HPLC analysis.

The amounts of different acids formed in the first stage are represented in Table 4. In Table 5 different acids formed in the second stage and the difference (wt%) are shown with respect to the first stage. It can be seen in Table 5 that generally all acid yields increased during PWO. Acetic acid is obtained already in the pretreatment step from acetyl groups in the feedstock and formic acid from degradation of sugars.

The yield was the highest for acetic acid however; the increase in the formation (wt%) of lactic acid in the second stage was the highest. The maximum yield for all three acids, i.e. formic, acetic and lactic acids, was measured to be in run P-3 – 1.8 g/100 g dry spruce, 1.9 g/100 g dry spruce and 0.7 g/100 g dry spruce, respectively. This was the run with the highest charge of alkali. However, the increase in the amount of acid in the second stage as compared to the first stage was different for different acids.

The yield of formic acid reduced during runs P-2, P3 AND P-5 in the second stage. That could be caused by the decomposition of formic acid into CO_2 and water under the harsh reaction conditions of PWO. Acetic acid was more stable during PWO reactions as there was no reduction in acetic acid yield as compared to the cooking stage (in agreement with the results obtained by Alexander).¹⁷

Generally, the acid yields were similar in PWO for feedstock cooked with Na_2CO_3 as compared to $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ for equal charge of alkali calculated as Na_2O (compare P-1 to P-4 and P-2 to P-5).

The other acids, glycolic acid, oxalic acid etc., could unfortunately not be analyzed by HPLC. The analysis of the raw material and solids obtained after pretreatment shows that the relative amount of lignin is relatively unchanged (see Table 6). With higher alkali content mannan is dissolved. According to the analysis, the extractives content of the fiber product is also significantly reduced.

Preliminary data from the extraction experiments indicate that a distribution coefficient (ratio of concentration between extraction medium and aqueous solution) ranging from 0.78 to 1.69 (shown in Table 7) was measured when

using n-butanol. The distribution coefficient was not increased when tri-octylamine was also added. However, according to literature, much higher distribution coefficients should be obtained. Possibly, the reaction time of 15 minutes was not long enough for the system to reach equilibrium or a high distribution coefficient would be obtained for a more concentrated solution. A challenge with butanol is also the high solubility in water (about 80 g/L). Therefore another extraction medium, for example an ester of butanol, would be needed to extract the dissolved butanol from the aqueous phase. The advantage of butanol is that the acids could be esterified directly with butanol to produce esters of carboxylic acids, which have important uses as solvents etc.

Table 6
Composition of original raw material and pretreated solids C3, C2 and C1

Components	Raw material wt%	Remaining solids		
		C3, %	C2, %	C1, %
Glucose	47.85	48.65	49.826	49
Mannose	10.72	5.71	8.031	9
Xylose	6.024	5.87	6.044	5.93
Arabinose	0.95	0.09	0.883	0.89
Rhamnose	0.18	0.07	0.073	0.06
Precipitated lignin	28.1	28.7	29.551	29.36
Extractives	1.45	0.22	0.2	0.26

Table 7
Measured distribution coefficients for acids between the extraction medium and the aqueous phase

	Formic acid	Acetic acid	Lactic acid
Distribution coefficient	1.02	1.69	0.78

CONCLUSION

The results confirmed the formation of short chain carboxylic acids. The charge of alkali in the pretreatment of sawdust in the first stage had significant influence on the formation of carboxylic acid formation during partial wet oxidation.

All three acids have maximum yields in PWO run P-3; acetic acid had the highest yield totally of about 4.4 g/100 g of dry sawdust. The yield could have been significantly increased by using a constant temperature of 160 °C in the

pretreatment. For industrial relevance, a lower liquid to solid ratio should be used. The ratio of 10 had to be used here because of the limitation with stirring in the equipment. A conventionally used higher solid to liquid ratio of for example 3 would give a several times more concentrated product.

The study indicates that carboxylic acids can be produced by the method described. More experiments should be done with other chemicals employed in the first stage, i.e. cooking stage. Also, acid pretreatment should be checked since no acid addition would be necessary after the PWO stage before the extraction of the acids.

Here, the fiber product obtained after pretreatment was not examined for enzymatic hydrolysis performance. However, alkaline pretreatment is known as a method to increase the yield in enzymatic hydrolysis.

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