

NOVEL TREATMENT METHOD FOR BLACK LIQUOR AND BIOMASS HYDROLYSATE WITH PARTIAL WET OXIDATION

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To reduce greenhouse gas emissions, innovative and sustainable sources of energy, fuel and chemicals are needed. Biomass side streams, such as black liquor and hydrolysate from fiber production, could be used for this purpose. Some feedstocks contain precipitates, such as silicate, which makes the evaporation to the high solid concentration needed for combustion difficult. However, as an alternative, black liquor could be partially wet oxidized to produce carboxylic salts and energy. The objective of this work is to investigate the production of carboxylic acid and hydroxyl acid in partial wet oxidation (PWO) of wheat straw black liquor (WSBL), kraft black liquor (KBL) and hydrolysate (HLP) from pulp bleach and hydrolysate (HLW) from wood under various reaction conditions. Experimental results demonstrate that for WSBL and hydrolysate the concentration of acetate and formate increased significantly in the spent liquor during the treatment.

Keywords: wet oxidation, black liquor, spent liquor, partial wet oxidation, biomass, fuel components, lignin, carboxylic acids, non-wood pulping

INTRODUCTION

Recently there has been a trend to reduce fossil fuel use, increase biomass utilization and improve the energy efficiency in energy production and industry. In order to enhance the usage of renewable energy, there should be a diversified use of biomass feedstock, which can lead to the ultimate goal of producing energy, chemicals and biofuels from cost efficient, ecologically friendly and renewable feedstock. The European commission is outlining the guidelines for sustainable energy production from biomass. Sustainable economy is the key factor in it. The implementation of sustainable economy requires innovative approaches for cost effective and diversified use of renewable feedstock.

Black liquor or spent liquor from the pulp and paper industry and hydrolysate from specialty cellulose production contain organic material and inorganic salts dissolved in water. In some cases, when the streams contain precipitating compounds, such as silicates, the evaporation of these streams to high solids concentration, which is needed in combustion, might be difficult. Also

for Kraft black liquor, a more valuable utilization, including production of chemicals and fuel components, compared to complete combustion would be desired.

Burning black liquor in the recovery boiler to generate energy and to recover the cooking chemicals is a common practice worldwide. Nevertheless, in developing countries such as China, India and Pakistan, non-wood pulping mills lack the spent liquor treatment facilities, thus spent liquor ends up in non-ecological disposal, for instance, into rivers. This causes environmental hazards and the loss of many valuable chemicals that could be recovered from the black liquor more economically compared to their extraction from wood. Besides, energy chemicals could be recovered from black liquor by utilizing methods such as partial wet oxidation (PWO). This process offers distinctive advantages over complete wet oxidation due to moderate reaction conditions. In addition to the energy production during the PWO process, the organics present in the black liquor are degraded into lower

molecular weight carboxylic acids, which can be further converted into valuable compounds. Utilizing at least part of the black liquor for feedstock in the PWO process, valuable bulk chemicals of industrial importance and intermediate components for bio-fuels can be produced, as reported by Melin *et al.* (2012).¹

In this paper, the yield of carboxylic acid salts obtained by partial wet oxidation from (WSBL) wheat straw black liquor, (KBL) Kraft mill black liquor and hydrolysate from pulp bleach (HLP) and wood (HLW) is presented. Also, other analysis results are presented for different conditions, such as reaction temperature and oxygen partial pressure, illustrating the effects of the partial wet oxidation (PWO) process on the feedstock. These are chemical oxygen demand (COD), total organic carbon (TOC), inorganic carbon, pH and average oxidation state of carbon atoms (AOSC), which reflects the oxidation state of the organic matter present in the reaction mixture. For black liquor, the organic acids present as ions and the insoluble lignin content of the feedstock are also provided.

Wet oxidation

The process of wet air oxidation (WAO) is an established technology studied by Mishra,² Salmela,³ and Debellefontaine⁴ among others. It is also termed as sub-critical hydrothermal oxidation. WAO is a chemical process in which molecular oxygen reacts with dissolved or suspended organic material present in liquid water. The reaction takes place at a temperature above 175 °C and the total pressure inside the reactor is maintained above the vapor pressure of water in order to increase the solubility of the oxidant in the reaction mixture and to keep the solution in aqueous form. The reaction is exothermic in nature, therefore it is important to remove the excess heat of the reaction. The excess heat can be easily transferred away for instance by using cooling coils and used in preheating the wet oxidation influent. Also, the excess heat can be controlled by allowing part of the liquid to

evaporate. Waste streams having organic matter higher than 3% can sustain the reaction conditions and generate surplus energy during the reaction. The products of complete wet oxidation are CO₂ and H₂O, which can be further employed to generate heat or power a gas turbine. A general schematic flow diagram of the wet oxidation process is presented in Figure 1.⁵

The reaction mechanism for wet oxidation is not completely understood. However, it has been proposed that the wet oxidation reaction proceeds via a free radical mechanism.⁴ The oxygen dissolved in the aqueous reaction mixture initiates a free radical chain reaction by reacting with weak C-H bonds in the organic compounds, causing the formation of oxygen, hydroxyl, hydroperoxyl and organic radicals.

Wet oxidation process has been successfully demonstrated on a commercial scale in different parts of the world. Among different commercial applications of the wet oxidation process, the most significant was the recovery of pulping chemicals from spent liquor and the complete oxidation of sewage sludge. This widely commercialized technology, also known as Zimpro process, has about 200 units installed worldwide for sewage treatment purposes.⁶ In the Zimpro process, a co-current bubble column reactor is used, which operates 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 commercial technologies available include Wetox process, Vertech process, Kenox process and Oxyjet reactor system. In the Wetox process, a horizontal autoclave is used consisting of 4-6 sections, which together act as a series of CSTR. In the Vertech process, a sub-surface reactor is employed consisting of two concentric tubes. In the Kenox process, the novel concepts of static mixing coupled with ultrasonic energy was introduced in the recirculation reactor. Moreover, in the Oxyjet reactor system, a combination of tubular reactors and jet mixers is used.⁶

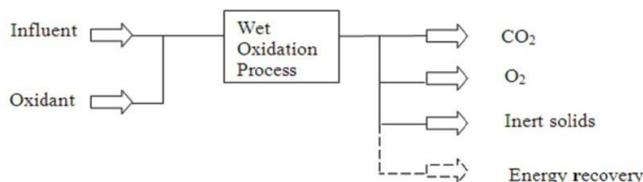


Figure 1: General schematic flow diagram of wet oxidation process⁵

Partial wet oxidation

Complete wet oxidation of organic matter in sewage sludge has been widely studied and reported, as indicated in the open source literature and patents. However, the incomplete oxidation for the recovery of valuable chemicals has also been discussed in some patents, such as Nadezhdin.⁷ Incomplete oxidation can be accomplished by limiting the flow of oxidant to the WAO process. During partial oxidation, complete conversion of some components takes place, while other components are partially oxidized. As reported by Levec⁸ and Guolin,⁹ the wet oxidation process is an energy intensive process because of the high temperature and pressure requirements of the process. Furthermore, the intense operating conditions make the process uneconomical and capital intensive, as the operating conditions directly affect the construction materials. The PWO takes place at lower temperature and pressure as compared to the complete oxidation process, resulting in the formation of safer operating environment and making the process economically advantageous.

When the conversion is not complete, acids or their salts such as acetates, formates and lactates remain in the solution. In addition, lignin might be precipitated due to pH decrease, which lowers the solubility of lignin, as suggested by Devlin.¹⁰ Also, other decomposition products of lignin or sugars such as methanol, syringaldehyde or vanillin might be obtained. The acid salts can be transferred into carboxylic acids by adding a strong acid, such as sulfuric acid, or decomposed thermally into acetone or fuel gas containing for example methane, hydrogen and other volatile organic components.¹¹ While evaluating the overall wet oxidation process, TOC and COD values are simple analysis tools to observe the status of the process. Furthermore, molar concentrations for TOC and COD are used to calculate AOSC in order to describe the oxidation state of the organic matter present in the reaction mixture.

The chemistry of the wet oxidation process for individual organic compounds and their mixtures is rather complex. The complex nature of the process is caused by the fact that various chemical reactions take place for various organics, even various chemical reactions for single organic compounds under typical wet oxidation conditions. The wet oxidation process takes place in two stages: the physical stage and the chemical

stage. During the physical stage, oxygen is transferred from the gaseous phase to the liquid phase. Therefore, if the oxygen transfer rate is not sufficient, the transfer of oxygen from the gas phase to the liquid one will determine the overall reaction rate. The chemical stage starts where oxygen reacts with the organic compound. These two stages of the wet oxidation process determine the rate of the wet oxidation process. The chemical reaction stage during the wet oxidation process takes place by means of free radical chemical reactions.¹²

The rate of chemical reaction in WO process depends on the temperature, partial pressure of oxygen, reactor geometry, reactor walls composition (if they have a catalytic effect), the pH of the solution and the nature of the organic compound.¹³

Several studies have been done to understand the effect of catalyst on the wet oxidation of the most common organic pollutants found in waste streams. Some significant studies in this area include Kolaczowski,⁶ Levec,⁸ Guolin,⁹ and Bhargava.¹³ Several catalysts, for example, heterogeneous noble metal catalyst, have been used in the wet oxidation to make the reaction conditions less harsh and the wet oxidation reaction faster. Catalysts could make the wet oxidation process more economical, if harsh conditions are required in non-catalyzed wet oxidation. In addition, several processes using homogeneous catalyst have been developed, such as LOPROX, WPO, ATHOS.⁶ The separation of catalyst can be challenging. Even though heterogeneously catalyzed wet oxidation is generally effective, it may cause problems due to leaching of metals and contamination of the feedstock, which affects downstream processes.¹⁹

Generally, a higher temperature gives a higher degree of oxidation. At a certain temperature, regardless of reaction time a fixed amount organic material remains unoxidized. Also, the feedstocks have different reactivity towards wet oxidation. The partial pressure of oxygen increases the concentration of oxygen in the liquid phase and consequently the reaction rate of wet oxidation. Also, at a higher temperature, the solubility of oxygen is higher than at the room temperature. Generally, at a fixed temperature the partial order with respect to organic compound is usually 1-1.4 order and close to 0.4 order with respect to dissolved oxygen concentration.^{12,14} However, in some cases especially with mass transfer limitation of oxygen, a higher order close to 1 has

been observed.^{15,16} Based on earlier literature review, the COD and TOC reduction, as well as the yields of some acids for Kraft liquors feedstocks have been reported under partial wet oxidation conditions. However, to the authors' knowledge, no studies have been conducted in order to investigate specifically the amount of carboxylic and hydroxyacids formed under optimum conditions for different black liquors and hydrolysates. In this work, the acid yield for different feedstocks is presented under optimal reaction conditions.

EXPERIMENTAL

Materials

Four different by-products from the pulp production process were treated in a partial wet oxidation (PWO) reaction apparatus. Wheat straw black liquor (WSBL) was obtained by lab-scale soda cooking of wheat straw. Kraft mill black liquor (KBL) was obtained from a commercial pulping plant, where birch was the raw material. A hydrolysate of bleached Kraft pulp (HLP) and a hydrolysate of wood (HLW) were obtained from lab-scale cooking. Oxygen with

purity of 99.99% (AGA, Finland) was used as oxidant for the reaction. In order to increase the solid concentration of the feedstock, evaporation was performed in an open beaker heated from the bottom with continuous stirring. Table 1 summarizes some of the characteristics of the treated feedstocks. The dissolved solids for black liquor and hydrolysates consist of sodium carbonate and sodium bicarbonate, lignin, sugars and their degradation products, different acids or their salts.

Reaction apparatus and procedure

The PWO reaction was carried out in a 100 ml 316 SS high pressure micro reactor (model 4590). The batch reactor was capable of performing experiments at a temperature up to 500 °C and pressure up to 35 MPa (Parr Instrument Co., Moline, IL). The equipment was provided with a mechanically driven four blade impeller and variable speed arrangement from 0-800 rpm. 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.

Table 1
Characteristics of feedstocks

Feedstock	pH	COD (g/L)	TOC (g/L)	Lignin (g/L)	AOSC
WSBL	10.5	227	91	47	0.26
KBL	13.6	180	80	77.7	0.6
HLP	1.6	102	47.8	-	0.79
HLW	1.45	156.9	54.4	-	-0.33

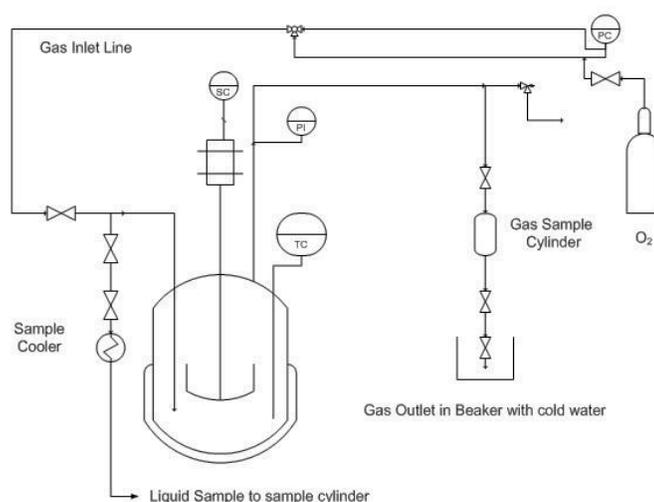


Figure 2: Experimental setup for partial wet oxidation experiments

Table 2
Operating conditions for PWO of various feedstocks

Feedstock	Temperature (°C)	Total pressure (Mpa)	O ₂ Partial pressure (Mpa)	Reaction time (min)
WSBL	180-270	1.6-6.0	0.6-2.0	80
KBL	230-275	2.4-6.0	0.6-2.0	30-80
HLP	180-240	1.5-3.5	0.4-0.7	30-80
HLW	195-225	1.5-3.6	0.4-0.7	30

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 experiments, oxygen was used as oxidant, which was fed from a bottle via the pressure regulator and the outlet gas line of the reactor was kept close. When oxygen was consumed in the reactor, the pressure decreased and the regulator at the gas bottle fed more oxygen from the gas bottle in order to keep the total pressure of the system constant. The lab-scale experimental arrangement is presented in Figure 2.

The liquid feedstock to be partially oxidized was loaded in the micro batch reactor. The reactor was closed and preheated to 30 °C below the actual reaction temperature without oxidant while stirring with the four blade impeller at 800 rpm. At temperatures between 100-105 °C, the remaining air present in the reactor was purged by opening the exit line for a few seconds. This was done in order to avoid accumulation of nitrogen in the gas phase. The oxidant i.e. oxygen was first introduced for about 5 seconds at approximately 30 °C below the desired oxidation temperature, so the heat of the reaction increased to the actual reaction temperature and not higher, since there was no cooling. It takes around 5 minutes to reach the set temperature and stabilize. When the reaction temperature is reached, the oxygen valve was completely opened. That was the point that was considered as the starting time of the reaction ($t=0$). The total pressure was 0.5-2.0MPa higher than the vapor pressure of the feedstock at the corresponding temperature. The vapor pressure was earlier tested at various temperatures in the same equipment. The reaction temperature was kept constant during the reaction by a temperature controller. After the reaction, the oxygen feed was stopped and the reactor was cooled down to room temperature by quenching with cool water. The quenching takes about 5 minutes after that the reactor is depressurized by opening the exit line. The treated feedstocks were analyzed with pH, COD, TOC, solid content, inorganic carbon.

Different feedstocks were oxidized at the temperature shown in Table 2. The reaction times in different runs were in the range of 30-80 minutes. The reaction time in the experiment was the time during which the oxygen was fed into the reactor. Liquid samples of approximately 3 ml were extracted at

various intervals during the reaction from the oxygen spurger tube positioned at the reaction bottom. While drawing samples out of the reactor, the oxygen feed was briefly shut-off. The liquid samples were then analyzed by various analytical techniques, as mentioned earlier. Table 2 presents the operating conditions during the PWO of various feedstocks.

The effect of agitation speed on the rate of oxidation in COD destruction was studied by varying the speed of agitation from 100-800 rpm. It was observed that the rate of oxidation did not depend on impeller speed when the stirring speed was sufficiently high i.e. 800 rpm, which seems to be in agreement with Joglekar¹⁶ and Miguelez.¹⁷ All the following experiments and measurements were performed at 800 rpm.

Analysis of feedstock and products

The parameters that were analyzed from each sample were pH, solid content, COD, TOC, carboxylic acid yield and FTIR analysis for some samples. The drop in the pH for some feedstock during PWO reaction indicates the increase in acid content and carbon dioxide generation. Furthermore, the COD reduction in treated samples shows how much of the feedstock has been oxidized. The TOC reduction reflects the amount of organic matter that has been converted into inorganic carbon. The inorganic carbon either remains in the aqueous phase as dissolved carbon dioxide, bicarbonate or escapes into the gaseous phase as CO₂.

The pH was measured at atmospheric pressure and room temperature right after the PWO reaction. The pH meter (VWR pH100) was calibrated before each round.

The solid content was measured in the following way: 10 g of sample was left to evaporate overnight in an oven at 120 °C and the solid content was calculated with the weight difference. The procedure was done three times for the feedstocks (WSBL, KBL, and HL), but only once for the oxidation products due to the limited amount of sample available for analysis.

Total organic carbon and inorganic carbon

In wet oxidation TOC reduction is an important parameter reflecting the efficiency of the WO process. The molar concentration for TOC is directly proportional to the organic matter present in the

solution. TOC reduction gives effectively an insight into the total oxidation, where organic matter converts into CO₂ and H₂O. However, TOC reduction exclusively is not as effective for describing the performance of PWO and therefore other parameters indicating the state of PWO have to be also taken into account.¹⁸

TOC was determined according to the standard SFS-EN 1484 with a Shimadzu TOC-V analyzer, in which the sample is oxidized by combustion and the released carbon dioxide is measured. Before the analysis, the inorganic carbon is removed by acidifying the sample and purging the formed carbon dioxide from the solution using inert gas. The carbon dioxide is separated from other volatile carbon components by absorbing the carbon dioxide.

Organic carbon containing both components left in the purged gas, and dissolved and suspended solids (for example undissolved lignin) in aqueous solution is combusted and oxidized into carbon dioxide. Finally, the carbon dioxide formed from both inorganic and organic carbon substances is determined using the Infrared spectrophotometric measurement.

Chemical oxygen demands (COD)

The determination of the chemical oxygen demand (COD) was carried out according to the standard SFS 5504, according to which the sample is oxidized with dichromate. The equipment used for the analysis includes a HACH COD reactor and a Methrom 776 Dosimat titrator.

Average oxidation state of carbon atoms (AOSC)

The AOSC represents the average oxidation state of organic carbon in the reaction mixture at a given reaction time, but cannot describe the performance of the WO process from its start. In order to represent the state of the organic matter present in the reaction mixture, measured molar concentrations for TOC and COD are combined to calculate the average oxidation state of carbon atoms. The equation for calculating AOSC is represented as follows:^{18,19}

$$\text{AOSC} = \frac{4(\text{TOC} - \text{COD})}{\text{TOC}}$$

The theoretical values of AOSC are in the range between -4 and +4. The theoretical value for methane is -4, for CO₂ +4, for oxalic acid +3, for formic acid +2 and 0 for acetic acid.¹⁸ The use of AOSC in the characterization of organics in the mixture is discussed in detail by Stumm and Mogan.²⁰

Capillary electrophoresis

For quantification of carboxylic acids present in the treated sample, capillary electrophoresis was used – it works on the basis of the difference between the molecule size and its electrical charge. The instrument used for capillary electrophoresis was a Beckman Coulter P/ACE MD Q, with capillary length ($L_{\text{det}}/L_{\text{tot}}$): 100/110 cm and internal diameter of 50 μm. Samples

were diluted 1:50 and 1:100 (v/v) with 20 mM NaOH prior to analysis. Therefore, undissolved lignin suspended in the solution was dissolved.

Fourier transform infrared spectroscopy

Literature studies indicate that significant amounts of carboxylic acid salts are present in black liquor. Furthermore, during the PWO reaction, some organics present in the black liquor are also converted into carboxylic acid salts, which can be converted into valuable products as discussed in the literature.^{11,21,22} The study by Onwudili and Williams¹¹ discusses the effects of hydrothermal decomposition on biomass containing carboxylic salts of sodium by gasifying into gaseous products. Further, the authors stated that the most valuable products obtained from carboxylic acid salts were fuel gases.

In order to study the production of fuel gases and inorganic residues from the PWO black liquor, a separate pyrolysis experiment was carried out. The treated black liquor was dried and heated in the micro reactor from room temperature up to a temperature of 470 °C without stirring. The formed gases were analyzed after each 20 seconds. Based on the analyzed gas composition in the apparatus, the average gas composition during the run was calculated. For comparison, a carboxylic acid salt sample with the composition shown in Table 12 was decomposed with the same procedure.

RESULTS AND DISCUSSION

In Tables 3 to 6, total organic carbon, inorganic carbon, average oxidation state of carbon (AOSC) and final pH are presented for all the feedstocks (WSBL; KBL; HLP; HLW). In addition, the reaction conditions are also given. Some material was lost during the reaction, as some organics converted into CO₂. There might have been a change in the liquid and solid mass during the reaction, which altered the concentration. Generally, we check that it is less than 20% of the feedstock and this has been taken into account for calculation of acid yields. In some cases, the concentration did not change. The actual change in COD and TOC could be sooner caused by the change in the mass during the reaction.

Effect of temperature on TOC and COD reduction

The total organic carbon TOC of various feedstocks without oxidation and after PWO under various temperature and pressure is presented in Tables 3 to 6. It is clear that after the reaction there is considerable reduction of TOC in the PWO reaction. The most significant decrease

in TOC after the PWO reaction can be observed for the hydrolysate (HLP and HLW) with added inorganic carbonates. TOC reduction is unfavorable, since the organic carbon is converted into inorganic carbon. The inorganic carbon can be either retained in the solution as bicarbonate or dissolved carbon dioxide or escape from the solution into the gas phase in the reactor. Generally, with more severe reaction conditions (higher temperature, higher partial pressure of oxygen and longer reaction time), higher TOC reductions are obtained. The reduction in TOC does not add up to the inorganic carbon content. Therefore, part of TOC is converted into carbon dioxide, which goes to the vapor phase. For Kraft black liquor, only a small part of the feed is lost. However, for wheat straw and especially for the hydrolysate, a large part of the feedstock converted into carbon dioxide and escaped into the gas phase. It was also observed that the pressure after the reaction when the reactor had cooled down was higher than 1 MPa. Possibly, a change in the liquid and solid mass during the reaction altered the concentration.

During the PWO, the reaction temperature had a significant effect on TOC and COD conversions. Table 3 presents the effect of temperature on TOC and COD reductions when WSBL was treated at 250 °C and 270 °C. It can be observed that in run W-1 and W-2 TOC reduction slightly increased with the increase in temperature from 36.2% (58.1 g/L) at 250 °C to 39.7% (54.9 g/L) at 270 °C. On the other hand, the COD reduction for Run W-1 was higher, i.e. 44.9%, than Run W-2, i.e. 29.9%. This is due to the significantly higher partial pressure of oxygen in W-1, compared to W-2, which increases the degree of oxidation more than the higher operating temperature. With equal partial pressure, the higher the temperature, the higher is the COD removal, which is in good agreement with Dhakhwa.²³

During the PWO of KBL at different reaction temperatures from 230-275 °C, a similar trend of increased TOC and COD reduction with the increase in temperature can be observed (Table 4). The highest TOC reduction was achieved during Run K-10, i.e. 56% (35.2 g/L at 270 °C) and the highest COD reduction was achieved for Run K-7, i.e. 49.4% (91 g/L at 260 °C). Because the partial pressure of oxygen could not be measured, but was calculated as the difference between the total pressure and the vapor pressure

of the solution, accumulated inert gases such as carbon dioxide present in the vapor phase might have led to lower partial pressures of oxygen than what has been calculated.

As presented in Table 5, during the PWO of the hydrolysate from bleached Kraft pulp, an increasing trend of COD and TOC reduction was observed with the increase in reaction temperature. The highest TOC reduction, i.e. 48% (52 g/L at 240 °C & P_{O_2} : 0.7 MPa) and COD reduction, i.e. 48.3% (51.7 g/L at 240 °C & P_{O_2} : 0.7 MPa) were reached during Run HLP-6. The addition of alkali (Na_2CO_3) further improved the reduction of TOC and COD. The highest TOC and COD reduction values for non-alkalized runs were reached in HLP-5 and HLP-1, respectively.

Moreover, for the wood hydrolysate, a similar increasing trend of TOC and COD reduction with the increase in temperature was observed when it was treated in the PWO reactor. As can be noted from the data in Table 6, temperature has a significant effect on TOC and COD reduction for the runs with and without alkali (Na_2CO_3) addition. The highest TOC and COD reduction for the runs without alkali addition was achieved in run HLW-5 with TOC reduction of 56.9% (43.1 g/L at 225 °C & P_{O_2} : 0.5 MPa) and COD reduction of 82.7% (17.3 g/L at 225 °C & P_{O_2} : 0.5 MPa). For the runs with the addition of alkali (Na_2CO_3) before the PWO reaction, the highest values for TOC and COD reduction were reached during Run HLW-2 with TOC reduction of 85.7% (14.3 g/L at 195 °C & P_{O_2} : 0.5 MPa) and COD reduction of 90% (10 g/L at 195 °C & P_{O_2} : 0.5 MPa). The alkali was added with the objective of studying the effect of HLP and HLW pH on acid yields during the PWO reaction.

Effect of temperature on final pH

The formation of acids and carbon dioxide during the run causes a drop in pH. Lignin fragments and sugars are oxidized into smaller fragments, such as short chain carboxylic acid groups and carbon dioxide. Both components consume the alkali present and decrease the pH. However, with longer reaction times, further change of pH is small. A reason for this could be the formation of lower molecular weight carboxylic acids such as acetic acid, which resist further oxidation.² Also, it might be that the final degree of oxidation for the feedstock at the given temperature has been reached.

Table 3
PWO conditions and analysis results for WSBL

Run	T (°C)	t (min)	PO ₂ (Mpa)	Oxidant	pH	TOC (g/L)	TOC reduction (%)	COD (g/L)	COD reduction (%)	IC (g/L)	AOSC
W-0	25	-	-	-	10.5	91	-	227	-	2	0.26
W-1	250	80	2	O ₂	9.6	58.1	36.2	125	44.9	1.9	0.77
W-2	270	80	0.7	O ₂	7.45	54.9	39.7	159.2	29.9	2.8	-0.35
W-3	270	80	0.6	O ₂	7.58	77	15.4	-	-	2.27	-

Table 4
PWO conditions and results of KBL

Run	T (°C)	t (min)	PO ₂ (Mpa)	Oxidant	pH	TOC (g/L)	TOC reduction (%)	COD (g/L)	COD reduction (%)	IC (g/L)	AOSC
K-0	25	-	-	-	13.6	80		180		4.1	0.6
K-1	230	60	0.6	O ₂	8.68	71	11.25	134	25.56	12.6	1.18
K-2	230	60	0.6	O ₂	9.36	77	3.75	118	34.44	13.7	1.71
K-3	230	180	0.6	O ₂	7.83	47	41.25	111	38.33	5.3	0.45
K-4	250	80	0.9	O ₂	8.04	60	25	137	23.89	6	0.6
K-5	250	80	2	O ₂	7.75	60	25	136	24.44	6.4	0.56
K-6	250	80	0.42	Air	9.31	68	15	147	18.33	6.1	0.76
K-7	260	80	0.6	O ₂	7.81	49	38.75	91	49.44	5.3	1.21
K-8	260	80	1.3	O ₂	8	56	30	127	29.44	7.8	0.58
K-9	270	80	0.5	O ₂	8.07	53	33.75	106	41.11	7.5	0.98
K-10	270	80	0.7	O ₂	9	35.2	56	114.8	36.22	6.4	-0.89
K-11	275	120	0.5	O ₂	9.17	52	35	129	28.33	7.4	0.3
K-12	275	80	0.5	O ₂	8.13	52	35	121	32.78	6.8	0.53

Table 5
PWO conditions and results of hydrolysate from bleached Kraft pulp

Run	T (°C)	PO ₂ (Mpa)	t (min)	Oxidant	Additives	pH	TOC (g/L)	TOC reduction (%)	COD (g/L)	COD reduction (%)	IC (g/L)	AOSC
HLP-0	25	-	-	-	-	1.6	100.0	-	100	-	0.011	0.79
HLP-1	160	0.4	30	O ₂	-	1.75	75.6	24.4	71.7	28.3	0	0.96
HLP-2	180	0.4	30	O ₂	5.7 wt% Na ₂ CO ₃	7.6	77.0	23	69.2	30.8	3.3	1.12
HLP-3	180	0.4	30	O ₂	-	1.74	58.0	42	72.8	27.2	0	-0.02
HLP-4	180	0.5	30	O ₂	5.9 wt% Na ₂ CO ₃	7.71	80.5	19.5	72.1	27.9	3.2	1.13
HLP-5	240	0.7	80	O ₂	-	2.22	54.4	45.6	77.2	22.8	0	-0.55
HLP-6	240	0.7	80	O ₂	7.4 wt% Na ₂ CO ₃	7.75	52.0	48	51.7	48.3	5.3	0.81

Table 6
PWO conditions and results of wood hydrolysate

Run	T (°C)	PO ₂ (Mpa)	t (min)	Oxidant	Additives	pH	TOC (g/L)	TOC reduction (%)	COD (g/L)	COD reduction (%)	IC (g/L)	AOSC
HLW-0	-	-	-	-	-	1.45	100.0	-	100.0	-	-	-0.33
HLW-1	195	0.5	30	O ₂	-	1.45	49.3	50.7	33.0	67.0	0.01	0.66
HLW-2	195	0.5	30	O ₂	4.8 wt% Na ₂ CO ₃	5.37	14.3	85.7	10.0	90.0	0.02	0.59
HLW-3	210	0.5	30	O ₂	-	1.4	45.7	54.3	33.3	66.7	0.02	0.19
HLW-4	210	0.5	30	O ₂	7.2 wt% Na ₂ CO ₃	7.35	16.9	83.1	11.3	88.7	0.01	0.54
HLW-5	225	0.5	30	O ₂	-	1.64	43.1	56.9	17.3	82.7	0.01	0.64
HLW-6	225	0.7	30	O ₂	5.8 wt% Na ₂ CO ₃	6.14	15.5	84.5	10.4	89.6	0.01	0.55

It was also observed that the higher the temperature of the oxidation reaction, the more rapid is the drop in pH. At higher temperature, the time required for the decomposition of lignin fragments shortens. Nevertheless, higher temperature also increases the rate of decomposition of short chain carboxylic acids.⁷ Generally, when no alkaline substances are added the lower the pH, the more acids and carbon dioxide are produced by wet oxidation. Also, with more severe reaction conditions, a lower final pH was achieved.

It was observed during the reaction that, as the reaction proceeded, the pH dropped. Tables 3 to 6 show the pH drop for various feedstocks under different reaction conditions. For WSBL and KBL feedstocks, the drop in pH is a simple indication that the lignin fragments have been oxidized into smaller fragments, such as short chain carboxylic acid groups and carbon dioxide. Both components consume the alkali present in the feedstock and decrease the pH. Moreover, for WSBL and KBL feedstocks, it was observed that pH drop was higher for the PWO reactions conducted at higher temperature. This is in agreement with Nadezhdin⁷, who stated that higher temperature also increases the rate of decomposition of short chain carboxylic acids. It can also be observed from the data in Tables 3 and 4 that the pH drop for KBL is higher than for WSBL during the PWO reactions. It is assumed that the lower the pH the more acids and carbon dioxide are produced during the PWO reaction. It can be concluded that at higher reaction conditions, lower final pH is achieved. However, as shown in Tables 5 and 6, for HLP and HLW feedstocks, the temperature does not have any significant effect on the pH drop during the PWO reaction.

It has also been observed that the partial pressure of the oxidant (O₂/Air) did not have any significant effect on the final pH of the product nor on TOC and COD reduction values, which is in agreement with Kindsigo and Kallas.²⁴

Average oxidation state of carbon (AOSC)

The average oxidation state of carbon is related to the average degree of oxidation. The higher the AOSC, the more oxidized is the feedstock on the average. For methane, this is most reduced component with the highest COD and lowest oxidation state -4. The most oxidized component is carbon dioxide with COD = 0 and oxidation state 4.

For WSBL and HLW feedstocks, the AOSC showed higher values when partially wet oxidized at higher temperatures, as shown in Tables 3 and 6, which is in agreement with Kindsigo and Kallas,²⁴ who state that the oxidation of the water solution improves with the rise in temperature. However, for KBL and HLP feedstocks, a different trend can be observed in Table 4 and Table 5; for some runs at higher temperature the AOSC value is lower, as compared to the runs conducted under lower temperature conditions. It is assumed that when KBL and HLP feedstocks are partially wet oxidized at elevated temperatures, the easily oxidizable organics such as sugar degraded products oxidize into gaseous products, which results in the enrichment of the reaction solution with lignin or other short chain carboxylic acid products. This is consequently reflected in lower AOSC values.

Acid yields

The material balance of the partial wet oxidation process for different feedstocks under various operating conditions is based on the results from capillary electrophoresis analysis. The highest acid formation after the partial wet oxidation reaction was achieved for wheat straw black liquor. The quantitative results presented in Table 7 indicate that the concentrations of formic acid, succinic acid, acetic acid, glycolic acid and lactic acid have increased significantly after partial oxidation. The material balances of the PWO process for WSBL, KBL, HLB and HLW are represented in Tables 7 to 10, respectively. The products include both the liquid and suspended solids, such as undissolved lignin. The acid yields are given in the form of acids, even though under those reaction conditions they might exist in their respective salt form.

During the PWO of WSBL, KBL, HLP and HLW, different reaction conditions influence the formation of acids differently. The final solutions after the PWO reaction were analyzed for different species by capillary electrophoresis. However, the formation of short chain carboxylic acids, including formic acid, acetic acid, glycolic acid and lactic acid, has been studied with special interest in this study due to their industrial importance and significant formation during the PWO, as compared to other acids. Generally, all acid yields increased during PWO, as shown in Tables 7 to 10. However, acid yields for WSBL

and HLW feedstocks were higher as compared to KBL and HLP, respectively. It can be seen in Table 7 and Table 8 that for black liquor PWO, the most significant increase in acid yield was achieved in the PWO of WSBL. The acetic acid and formic acid yields in the PWO of WSBL were 9.98 g and 3.76 g, respectively, per 100 g of

dissolved dry matter. Furthermore, the PWO of HLW yielded more acids as compared to HLP, as seen in Table 9 and Table 10. The acetic acid and formic acid yields in the PWO of HLW were 10.31 g and 5.67 g, respectively, per 100 g of dissolved dry matter.

Table 7
Material balance for PWO of WSBL

	Raw material (g)	Product (g)	% Change compared to feed
Mass total	100	86.75	-15.27
Dissolved dry matter	21.17	-	-
Water	78.83	-	-
Acid insoluble lignin	4.7	-	-
COD	21.42	18.76	-12.39
TOC	8.58	6.25	-27.15
SO ₄	0.04	0.11	179.8
Oxalic acid	0.12	0.14	12.58
Formic acid	0.28	0.8	181.24
Fumaric acid	-	0.05	-
Succinic acid	0.02	0.19	890.07
Malic acid	0.04	0.04	7.62
Acetic acid	0.71	2.11	198.45
Glycolic acid	0.14	0.78	450.99
Lactic acid	0.13	0.65	391.96
2-OH-butyric acid	0.08	0.45	426.12
Xisa (xyloisosaccharinic acid)	0.07	0.32	379.66
Gisa (glucoisosaccharinic acid)	0.13	0.38	189.03

Rxn conditions: 80 min, 250 °C; P_{O₂}, 2 MPa; Impeller speed, 800 rpm

Table 8
Material balance for PWO of KBL

	Raw material (g)	Product (g)	% Change compared to feed
Mass total	100	92.66	-7.34
Dissolved dry matter	20.4	-	-
Water	79.6	-	-
Acid insoluble lignin	9.08	-	-
COD	17.67	12.08	-31.63
TOC	7.8	4.87	-37.56
SO ₄	0.88	3.37	282.04
Oxalic acid	0.22	0.41	91.02
Formic acid	0.72	0.69	-3.18
Succinic acid	0.04	0.1	162.65
Malic acid	0.04	0.03	-28.37
Acetic acid	0.65	1.22	88.13
Glycolic acid	0.35	0.5	40.61
Lactic acid	0.35	0.44	24.69
2-OH-butyric	0.12	0.11	-4.49
Xisa (xyloisosaccharinic acid)	0.29	0.21	-29.96
Gisa (glucoisosaccharinic acid)	0.47	0.04	-92.04

Rxn conditions: 120 min; 270 °C; P_{O₂}, 0.5 MPa; Impeller speed, 800 rpm

Table 9
Material balance for PWO of HLP

	Raw material (g)	Product (g)	% Change compared to feed
Mass total	100	85.19	-14.81
Dissolved dry matter	4.36	-	-
Water	95.64	-	-
Acid insoluble lignin	0.46	-	-
COD	10	8.64	-13.61
TOC	4.69	1.60	-65.92
Oxalic acid	0.01	0.02	183.94
Formic acid	0.17	0.77	351.00
Acetic acid	0.01	0.12	695.10
Glycolic acid	0.01	0.06	313.78
Lactic acid	0.01	0.05	290.45

Rxn conditions: 80 min; 210 °C; P_{O₂}, 0.6 MPa; Impeller speed, 800 rpm

Table 10
Material balance for PWO of HLW

	Raw material (g)	Product (g)	% Change compared to feed
Mass total	100	48.39	-51.61
Dissolved dry matter	6.4	-	-
Water	93.6	-	-
Acid insoluble lignin	0.34	-	-
COD	15.38	2.49	-83.79
TOC	5.33	1.11	-79.14
Oxalic acid	-	0.02	-
Formic acid	0.35	0.55	51.9
Acetic acid	0.82	0.92	9.46
Glycolic acid	0.03	-	-
Lactic acid	0.05	0.003	-92.64

Rxn conditions: 30 min; 225 °C; P_{O₂}, 0.7 MPa; Impeller speed, 800 rpm

Thermal decomposition

As reported by Holtzapfle,²¹ carboxylic salts are suitable to produce fuel gases or biofuel components. Black liquor also contains carboxylic acids. In order to study how significant are the decomposition yields of those fuel gases or biofuel components during the decomposition reaction of black liquor solids, in comparison with the carboxylic salts responsible for producing those gases, pyrolysis was performed and the gaseous mixture was analyzed with FTIR. Two feedstocks were used for the experiment, i.e. solids from partially wet oxidized soda wood black liquor and carboxylic salts “model” mixture without lignin. The PWO soda wood black liquor was dried in an oven at 105 °C for 24 h in order to get the dried solids. The solids were loaded in a batch reactor and the temperature was increased

by an electric heating jacket from room temperature to 470 °C in about 1 hour. During the heating, the gases formed were measured after every 20 seconds, and based on that, the overall gas composition that was formed during the decomposition reaction was calculated. In Table 11, the FTIR analysis is presented for the gases formed when the solids from soda wood black liquor were decomposed at 470 °C without stirring. For comparison, a carboxylic acid sample with the composition shown in Table 12 was decomposed with the same procedure. It can be suggested that black liquor after the PWO reaction has the potential to produce a significant amount of fuel gases upon decomposition, as shown in Table 11. The yields of fuel components (acetone, methane) were higher for the carboxylic acid mixture.

Table 11
Thermal decomposition material balance for PWO soda wood black liquor solids

Feedstock		Product	
Component	Amount (g)	Product	Amount (g)
Total mass	100	Total mass	88.04
Sodium acetate	6.52	Water	27.54
Sodium formate	9.42	CO ₂	6.52
Sodium lactate	5.07	CO	2.9
Sodium glycolate	3.99	Acetone	0.72
Solid residues	75	Methanol	0.72
		Formaldehyde	0.08
		Solid residues	49.56

Rxn conditions: 60 min; 470 °C

Table 12
Thermal decomposition material balance for carboxylic salts mixture

Feedstock		Product	
Component	Amount (g)	Product	Amount (g)
Total mass	100	Total mass	96.25
Sodium acetate	44.2	Water	34.17
Sodium formate	38	CO ₂	2.92
Sodium lactate	12.9	CO	2.08
Sodium glycolate	4.9	Acetone	2.5
		Methane	0.25
		Ethanol	0.17
		Acetaldehyde	0.13
		Solid residues	54.04

Rxn conditions: 60 min; 470 °C

CONCLUSION

Four different liquors and hydrolysates from the pulp production process were partially wet oxidized in a reaction apparatus. The wheat straw black liquor oxidation carried out under 250 °C and 6 MPa total pressure (PO₂: 2 MPa) for 80 minutes showed a significant increase in the concentration of carboxylic acids. This WSBL partial wet oxidation process seems promising from the point of view of feasibility. The process approach is an interesting alternative to the conventional downstream processing in non-wood pulping mills. A more valuable utilization, including production of chemicals and fuel components, than complete combustion seems possible. Experimental results are indicative of the possible technical feasibility of converting wheat straw black liquor into carboxylic acid via an environmentally sustainable integrated process. Even though the yield of acids might be lower than for the fermentation processes, the ability to use low value or waste feedstock makes the method attractive. Furthermore, partially wet

oxidized feedstock can be more concentrated than fermentation liquors, which results in easier product separation. The optimization of operating conditions to enhance the formation of intermediate carboxylic acids will play a key role in process development. In this regard, black liquor from agricultural residues such as wheat straw and rice straw is more effective.

Unfortunately, the feedstocks were not tested under exactly the same conditions, so the experimental data are more suitable as screening results, investigating the feasibility of the method rather than to be used for experimental models. For hydrolysates, the addition of sodium carbonate resulted in a lower final COD degree value, so the oxidation was more effective.

The aim is to produce a high yield of acids under as mild reaction conditions as possible. The catalyst, which is economical to use, such as activated carbon, should be tested in the future. For the hydrolysate feedstocks, the yield of acid could be significantly higher under basic

conditions. However, due to challenges with the analytics, this could not be confirmed.

In the pyrolysis of partially wet oxidized black liquor, the chemical oxygen demand has been significantly reduced and useful fuel components are formed. However, for the black liquor case, the yields of fuel components are low and char remains in the solid residue. All the gaseous components (hydrogen and some hydrocarbons) could not be quantified in the thermal decomposition experiment (see Table 11 and Table 12), so the yields of fuel components might be underestimated.

On-going research is focused on the separation of formed acids from the oxidized black liquor and on the use of catalyst to increase the formation of intermediate carboxylic acids under milder operating conditions. Future research will include the study of techno-economic feasibility for a commercial scale integrated treatment process concept for wood and non-wood pulping mills.

Generally, the advantage of partial instead of complete wet oxidation is that milder conditions can be used, which results in lower investment and operation costs. Furthermore, extra income can be obtained from producing chemicals, besides energy.

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REFERENCES

- ¹ K. Melin, K. Parvinen, Patent Application WO2012FI50199 20120228 (2012).
- ² V. S. Mishra, V. V. Mahajani, J. B. Joshi, *Ind. Eng. Chem. Res.*, **34**, 2 (1995).
- ³ M. Salmela, R. Alén, M. T. H. Vu, *Ind. Crop. Prod.*, **28**, 47 (2008).
- ⁴ H. Debellefontaine, J. N. Foussard, *Waste Manage.*, **20**, 15 (2000).
- ⁵ D. L. Bowers, F. J. Romano, J. E. Sawicki, in *Procs. Hazardous and Industrious Wastes 27 Conference*, Bethlehem, July 9-12, 1995, pp. 333-341.
- ⁶ S. T. Kolaczowski, P. Plucinski, F. J. Beltran, F. J. Rivas, D. B. McLurgh, *Chem. Eng. J.*, **73**, 143 (1999).
- ⁷ A. Nadezhdin, Canadian patent 4756873 (1988).
- ⁸ J. Levec, A. Pintar, *Catal. Today*, **124**, 172 (2007).
- ⁹ J. Guolin, M. Luan, T. Chen, *Arabian J. Chem.*, (2012), doi:10.1016/j.arabjc.2012.01.001.
- ¹⁰ H. R. Devlin, I. J. Harris, *Ind. Eng. Chem. Res.*, **23**, 387 (1984).
- ¹¹ J. A. Onwudili, P. T. Williams, *Green Chem.*, **12**, 2214 (2010).
- ¹² H. Debellefontaine, M. Chakchouk, J. N. Foussard, D. Tissot, P. Striolo, *Environ. Pollut.*, **92**, 155 (1996).
- ¹³ S. K. Bhargava, J. Tardio, J. Prasad, K. Föger, D. B. Akolekar *et al.*, *Ind. Eng. Chem. Res.*, **45**, 1221 (2006).
- ¹⁴ J. Foussard, H. Debellefontaine, J. B. Vailhe, *J. Environ. Eng.*, **115**, 367 (1989).
- ¹⁵ J. E. Taylor, J. C. Weygandt, *Can. J. Chem.*, **52**, 1925 (1974).
- ¹⁶ H. S. Joglekar, S. D. Samant, J. B. Joshi, *Water Res.*, **25**, 135 (1991).
- ¹⁷ J. R. P. Miguelez, J. L. Bernal, E. N. Sanz, E. M. De La Ossa, *Chem. Eng. J.*, **67**, 115 (1997).
- ¹⁸ R. Hellenbrand, D. Mantzavinos, I. S. Metcalfe, A. G. Livingston, *Ind. Eng. Chem. Res.*, **36**, 5054 (1997).
- ¹⁹ D. Mantzavinos, A. G. Livingston, R. Hellenbrand, I. S. Metcalfe, *Chem. Eng. Sci.*, **51**, 4219 (1996).
- ²⁰ W. Stumm, J. J. Morgan, in "Aquatic Chemistry", John Wiley, 1981, pp. 510-511.
- ²¹ M. T. Holtzapple, R. R. Davison, M. K. Ross, S. A. Lee, M. Nagwani *et al.*, in *Procs. Twentieth Symposium on Biotechnology for Fuels and Chemicals*, Tennessee, May 3-7, 1999, pp. 609-631.
- ²² R. DiCosimo, F. G. Gallagher, U.S. Patent 7528277 (2009).
- ²³ S. Dhakhwa, S. Bandyopadhyay, T. Majazi, A. Grag, *J. Environ. Eng.*, **138**, 1194 (2012).
- ²⁴ M. Kindsigo, J. Kallas, *Proc. Estonian Acad. Sci. Chem.*, **55**, 132 (2006).