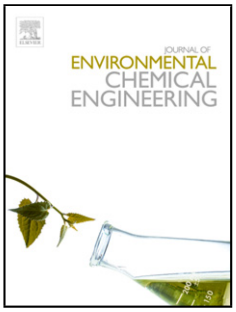

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HYDROTHERMAL PROCESSING OF KRAFT LIGNIN FOR CARBOXYLIC ACID PRODUCTION

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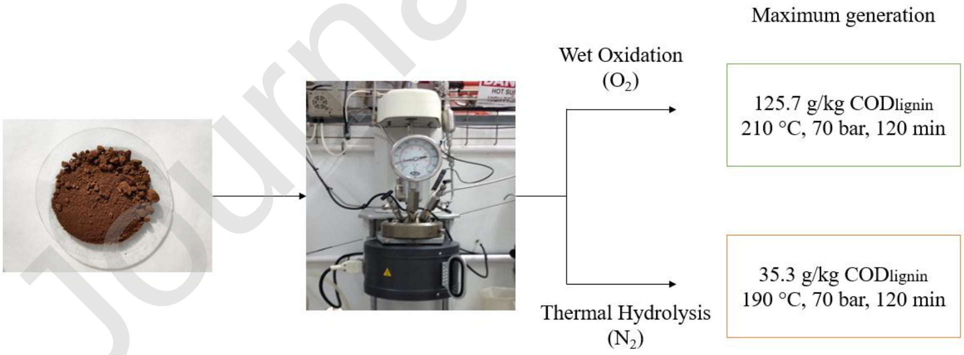
Graphical abstract



Highlights

- Wet oxidation enabled to form by up to 17% more acids than thermal hydrolysis.
- 210 °C was the optimal temperature to obtain the highest concentrations of acids.
- Selecting the operating conditions allowed to get a certain distribution of acids.
- The oxidative trends of volatile and non-volatile acids were diametrically opposed.

Abstract

The present study describes, for the first time ever, the production of organic acids by hydrothermal treatments using Kraft lignin from black liquor as feedstock, analysing the effect of the temperature and the type of atmosphere. The presence of oxygen had a positive impact on the total amount of acids, particularly, at 70 bar and 210 °C, being formed 172.8 g of acids per kg of Chemical Oxygen Demand consumed after 120 minutes of treatment. Moreover, it generated a final reaction medium mainly composed of acids, which represented 81.8% of the remaining total organic load. On the contrary, the maximum generation under an inert atmosphere was 17% lower, being reached after 120 minutes at 70 bar and 190 °C. Furthermore, selecting the operating conditions could be a tool to obtain a certain distribution of acids, increasing the proportions of lactic and acetic acid in the final mix compared to malic and formic acid during the wet oxidation process, while the latter prevailed during the thermal hydrolysis.

Keywords: Black liquor; precipitated Kraft lignin; thermal hydrolysis; partial wet oxidation; organic acids.

1. Introduction

Lignin is a natural polyphenolic macromolecule with a three-dimensional complex structure formed by the disordered polymerization of phenylpropane monomers with hydroxyl or methoxy substituents [1,2]. This compound, in conjunction with cellulose and hemicellulose, is one of the three majority components in the plant cell walls [2,3]. Owing to its highly biologically recalcitrant nature, lignin is also the major by-product from industrial activities in which lignocellulosic materials are used as feedstock. Moreover, it is also a carbon reserve with energy content, so it should not just be treated as waste or burned as low-grade fuel, as it is currently the case [4,5]. The growing worries about the search of new renewable and environmentally friendly raw materials have promoted biomass valorisation through technological advancement to produce and store clean energy and to synthesise value-added chemicals [6–8]. In fact, lignin is beginning to be seen as a potential source for the production of biofuels, biochemicals and biomaterials [9,10].

The current routes for lignin conversion include different strategies such as gasification, acid or alkali hydrolysis and biological treatments, among others [11,12]. The basic premise is to depolymerize the lignin into small molecules such as phenols and carboxylic acids [13,14]. Basically, this depolymerization is carried out by either oxidation-reduction (redox) or non-redox reactions, whereby aromatic compounds in lignin are degraded to open-ring products and, then, these components are upgraded to value-added products [15].

In particular, carboxylic acids constitute a group of important building blocks for a wide range of other chemicals, being used on a large scale in food, chemical and pharmaceutical industries. [16–18]. Most carboxylic acids are produced on an industrial scale by chemical synthesis or by fermentation; however, both methods have significant constraints. The former is driven by the high cost of petrochemical products and the depletion of world petroleum reserves, whereas the latter is dominated by feedstock cost, downstream processing and long retention times [19–21].

Carboxylic acids are considered as side products during the depolymerization of lignin towards phenols and aldehydes [22]. Lignin-derived carboxylic acids are mainly aromatic, being vanillic and syringic acid the most important ones. Nonetheless, their precursors during the lignin depolymerization (vanillin and syringaldehyde, respectively) have greater added value [13]. For this reason, research efforts are being focused on attempting to transform lignin into aliphatic acids, whose market is much larger than for aromatic acids and aldehydes [23].

Different strategies have been studied for producing aliphatic acids from lignin. Ma et al. (2014) produced dicarboxylic acids from biorefinery lignin through chalcopyrite-catalysed oxidation with H_2O_2. Mei et al. (2017) proposed a route to produce acetic acid by means of the conversion of methoxy groups of lignin by reaction with CO and water over $RhCl_3$ in the presence of $LiBF_4$ and with toluene or ionic liquids as reaction medium. Kang et al. (2019) determined that mono- and di-carboxylic acids can be produced by oxidation of depolymerized lignin compounds with different oxidation levels by Fenton and UV-Fenton processes. Lotfi et al. (2016) introduced a tow stage gas-phase catalytic process that produced carboxylic acids and aromatics from lignin using, in the first step, water vapour to crack lignin. In the second step, the effluent gas contacted with heterogeneous mixed-metal oxides or metal catalysts.

In this regard, applying hydrothermal treatments as a technique to obtain carboxylic acids from lignin is highly attractive because the reactions are carried out in an aqueous medium. Depending on the atmosphere, they are divided into two groups:

oxidative when it contains oxygen (wet oxidation) and non-oxidative when it is inert (for example, thermal hydrolysis) [26]. In particular, wet air oxidation (WAO) is a good alternative by several reasons: the use of pressurized air as the primary oxidant, relatively mild reaction conditions (200-325 °C, 50-175 bar), short residence times (1 h), no need of previous energy-intensive drying process, etc [27,28].

Nevertheless, there are only a few reported studies that apply wet oxidation on lignin and most of those are just focused on the mineralization and biodegradability of it during the treatment or on finding optimal conditions for the production of vanillin [15,29–32]. To the best of our knowledge, only a few articles in literature applied wet oxidation to the conversion of lignin to carboxylic acids specifically.

Suzuki et al. (2006) investigated the wet oxidation pathways of acetic acid production from lignin by oxidizing lignin model compounds. Hasegawa et al. (2011) reported the formation of organic acids during the oxidation of both alkali and organosolv lignin. Demesa et al. (2017) also assessed the production of carboxylic acids by partial wet oxidation of alkali lignin but using phosphotungstic or phosphomolybdic acid as catalysts. The pretreated biorefinery lignin stream of forestry residues of Douglas Fir (FS-10) was wet oxidized under alkaline conditions by Srinivas et al. (2016). Recently, Ansaloni et al. (2018) investigated the wet oxidation of a lignin-based substrate derived from the industrial waste of bioethanol production. In the first attempts, lignin was introduced as received in the WAO reactor and the presence of a perovskite oxide as catalyst improved the formation of the carboxylic acids. In a similar way, Oliveira et al. (2018) focused on the wet oxidation of the lignin obtained from coffee husk under different alkali loadings.

Nevertheless, as far as we know, the production of carboxylic acids from Kraft lignin by wet oxidation has not been studied yet, even when this kind of lignin is the most available, since it can be easily extracted from black liquor by pulp industry employing LignoForce or LignoBoost methods [38,39] and it is currently underutilized [9,40]. In this sense, using the Kraft black liquor to produce lignin is highly attractive for several reasons. Firstly, its cost is low because is a by-product. Moreover, it is pumpable liquid material, which eases its handling. Another reason is that logistics are extremely simplified as it is managed within the boundaries of the pulp and paper plant.

For this reason, the aim of this paper is to assess the formation of carboxylic acids during the hydrothermal treatment of Kraft lignin, which was obtained by acid precipitation from Kraft black liquor, paying special attention to the effect of the temperature (in a range from 170 °C to 210 °C) and the type of atmosphere (oxidizing or inert) on the acid concentration.

2. Materials and methods

2.1. Materials

Kraft lignin was obtained from the Kraft black liquor of *Eucalyptus* wood, provided by a paper mill located in Asturias (Spain), which was stored at 4 °C to maintain its characteristics until further usage.

The lignin fraction was separated from the black liquor by acid precipitation. Thus, a sulfuric acid solution 2 M was slowly added to the Kraft black liquor so as to decrease its pH below 4 and subsequently, centrifuged 20 minutes at 10,000 g. Finally, the precipitate (Kraft lignin) was redissolved, being returned to the initial volume and pH, and stored again at 4 °C until it was needed [41].

At this point, it should be explained that the lignin fraction was not washed after being precipitated in order to emulate the potential process at industrial scale. This is why the acids were detected at zero time. The main reason of not carrying out a deep cleansing of the Kraft lignin after its precipitation is the possibility of determining the stability of every single acid during the hydrothermal treatment of the Kraft lignin. Thus, comparing the evolution of the acids using their initial concentration as a reference, it can be deduced if the absence of a specific acid in the medium after the treatments is due to its no formation from the Kraft lignin or to its high degradation rate.

Table 1 shows the characterization of both the raw Kraft black liquor and the lignin fraction obtained.

Table 1. Properties of Kraft black liquor and its lignin fraction.

Parameters	**Kraft black liquor**	**Lignin fraction**
pH	12.8 ± 0.1	12.8 ± 0.1
Colour Number (CN)	147 ± 7	64 ± 10
Chemical Oxygen Demand (COD) (g O_2/L)	140 ± 7	94 ± 4
Acids (%COD)	27 ± 7	16 ± 4
Total Organic Carbon (TOC) (g C/L)	59 ± 1	40 ± 2
Dry matter (%)	13 ± 1	7.6 ± 0.1

As can be expected, the parameters of the lignin fraction were reduced due to the separation process. It contained almost 70% of the total organic matter of the black liquor, of which approximately 84% was lignin. In contrast, lignin only represented by 13% of the total COD present in black liquor. Moreover, its fraction still had a dark colour, although less strong.

2.2. Experimental setup

The hydrothermal treatments were carried out in a 1 L 316 SS batch reactor (Parr Instrument Co., Moline, IL.). In order to stir its content, the reactor was equipped with two six-bladed magnetically driven turbine agitators. Moreover, to ensure safe operation, bursting discs were placed to prevent overpressure. In addition, an electric heating jacket enabled to heat the reaction medium and the operating conditions were adjusted by means of pressure and temperature controllers and their corresponding indicators. In particular, the pressure was controlled by a back-pressure valve placed at the end of the gas line. Additionally, the gas flow (N_2 for thermal hydrolysis or O_2 for partial wet oxidation), which was provided by a compressed bottle, was saturated with humidity using a 2 L stainless steel water reservoir located before the reactor. Both the reactor and the water container were filled to 70% of their capacity to work in safe conditions.

According to preliminary experiments, 70 bar could be an optimal pressure and the working temperatures chosen were 170 °C, 190 °C and 210 °C. Furthermore, the stirrer speed was adjusted to 150 rpm and the oxygen flow rate to 1800 mL/min. Once the desired conditions were reached, they were maintained until the end of the treatment (210 minutes). Throughout the reaction time, samples were periodically withdrawn from the reactor for further analysis.

2.3. Analytical methods

The pH of the samples was measured at room temperature with a pH-meter (Basic 20 Crison), previously calibrated.

The Colour Number was calculated according to equation1 [42], using the absorbance values at three wavelengths (436 nm, 525 nm and 620 nm) measured with a spectrophotometer (T80 UV/VIS PG Instruments Ltd).

$$C.N = (ABS^2_{436} + ABS^2_{525} + ABS^2_{620})/(ABS_{436} + ABS_{525} + ABS_{620}) \qquad [1]$$

The Chemical Oxygen Demand was determined according to the standard methods recommended by the American Public Health Association [43]. Samples were digested with an excess of potassium dichromate solution and the amount of reduced dichromate was colourimetrically determined at 600 nm (HACH spectrophotometer).

The concentration of each carboxylic acid was chromatographically determined using High Performance Liquid Chromatography (HPLC) (Agilent 1200, Agilent Technologies, CA, USA), equipped with an ICSep ICE-ION-300 column (Transgenomic, CA, USA) and a refractive index detector. A solution of sulphuric acid 0.45 mM (pH = 3.2-3.3) at a flow rate of 0.3 mL/min was employed as the mobile phase. The column temperature was maintained constant at 75 °C. This chromatographic procedure enables the detection of both sugars and organic acids. Nevertheless, only six acids were identified in a significant concentration, which were divided into volatile (oxalic, malic and lactic acid) and non-volatile hydroxy acids (formic, acetic and propionic acid) [44,45].

The majority of experiments were carried out at least in duplicate and independently, getting high reproducibility (10% of standard deviation as maximum).

3. Results and discussion

3.1. Carboxylic acids

Firstly, the effect of temperature on the formation of the non-volatile hydroxy acids (oxalic, malic and lactic acid) during the hydrothermal treatments of the Kraft lignin at 70 bar is shown in Figure 1.

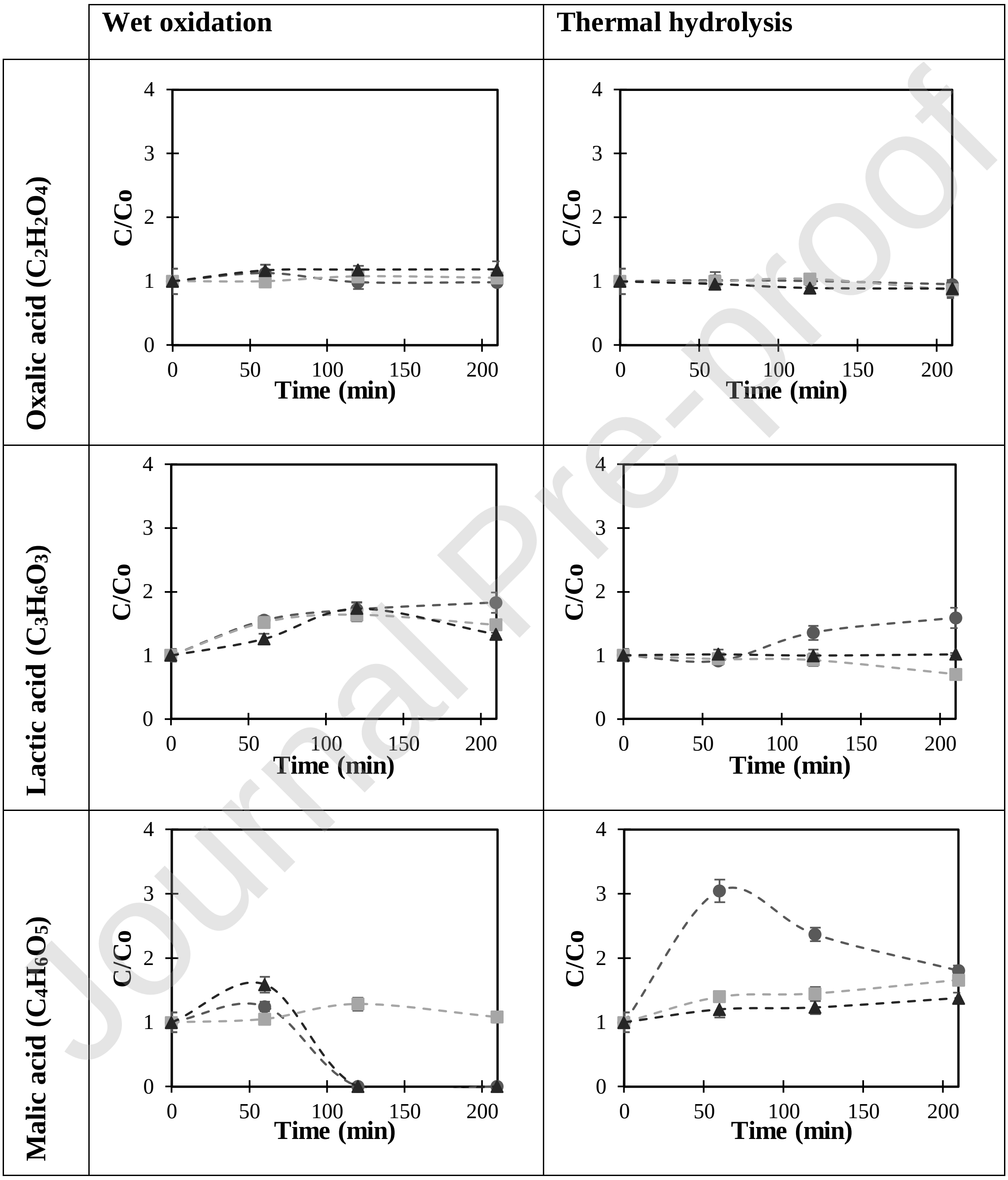


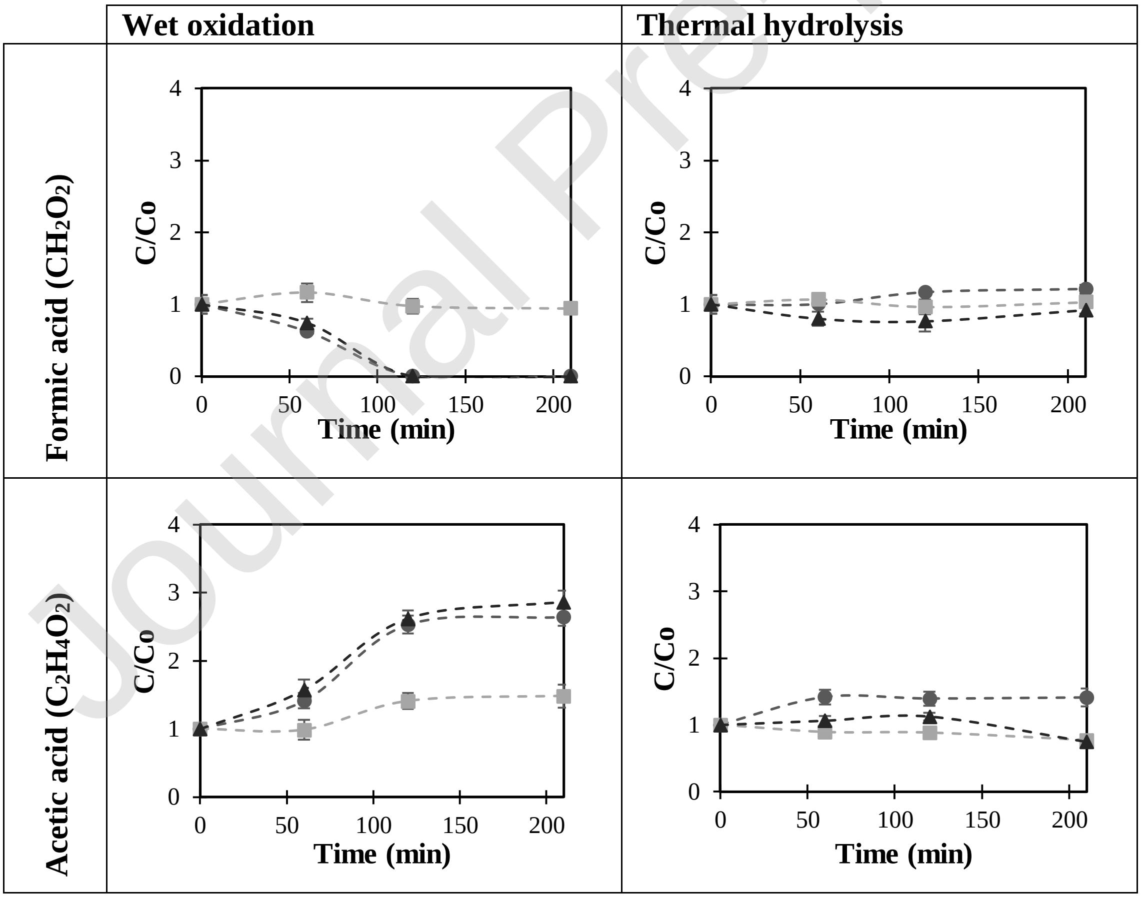
Fig. 1. Evolution of oxalic (C_o = 34 ± 3 g/L), malic (C_o = 0.5 ± 0.1 g/L), and lactic (C_o = 2.4 ± 0.2 g/L) acid throughout both hydrothermal treatments of the Kraft lignin at 70 bar and 170 °C (■), 190 °C (●) and 210 °C (▲).

As can be seen in the disparate evolutions during the whole reaction time, it is not easy to deduce a generalized relationship between the formation of non-volatile hydroxy acids and the temperature or the type of atmosphere employed. The pattern observed suggests that the longer the chain is, the faster is the formation of the acid and the lower is its stability. Thus, the concentration of the shortest acid (2 carbon atoms), that is to say, oxalic acid, remained almost unchanged for all the temperatures and atmospheres tested, showing that hydrothermal treatments do not have any remarkable effect on neither its formation nor its degradation. Suzuki et al. (2006), who oxidized different lignin model compounds (guaiacol, syringol and phenol) at 300 °C using H_2O_2 as oxidant, also reported that oxalic acid was not generated during the treatment.

However, lactic acid (3 carbon atoms) showed higher reactivity than oxalic one. Compared to its initial concentration, lactic acid increased by up to 83% during the treatment under an oxidizing atmosphere, being maximized at 190 °C. In this sense, lower temperatures (170 °C) did not result in a greater formation of this acid, whereas higher ones (210 °C) involved a faster degradation. For example, at the end of the wet oxidation (210 minutes), 18.0, 32.4 and 10.1 g of lactic acid were formed per kg of COD consumed at 170, 190 and 210 °C, respectively. Similarly, thermal hydrolysis experiments revealed that the highest concentration of lactic acid was also obtained at the intermediate temperature (190 °C). Nonetheless, the increase obtained at the end of the reaction (210 minutes) was 24% lower than that reached under the same conditions in the presence of oxygen. Hence, comparing experiments with and without oxygen, it can be concluded that the presence of an oxidizing atmosphere accelerates both the formation and degradation rates of lactic acid, being these effects more evident at higher temperatures. This behaviour agrees with that described by Lotfi et al. (2016) during the gas-solid conversion of softwood Kraft lignin. Moreover, in order to compare with other oxidants, after 15 minutes of oxidation of biorefinery lignin with a solution of H_2O_2 at 210 °C, Srinivas et al. (2016) reported that lactic acid decreased a little, reaching values of 1.89 mg/g dry biomass. In contrast, a growing tendency was detected in this work, obtaining 2.4 mg/g dry feedstock at the same time and temperature.

Finally, malic acid, which is the longest non-volatile hydroxy acid detected, showed the highest variations in its concentration with temperature and oxygen. Comparing the thermal hydrolysis and the wet oxidation experiments, it is clear that oxygen had a marked negative impact on the concentration of malic acid, especially at high temperatures. During wet oxidation, the maximum generation of this acid was 29.9 g per kg of COD consumed at 210 °C and 60 minutes of reaction; however, after this time, it was completely decomposed. Only at the lowest temperature tested (170 °C), when the degradation rate was lower, the initial concentration of malic acid hardly changed throughout this treatment. On the other hand, when an inert atmosphere was employed, the malic acid did not be decomposed. As in the case of lactic acid, the maximum concentration by thermal hydrolysis was achieved at 190 °C, tripling its initial value after 60 minutes. After this time, the concentration started to decrease significantly. However, at the lowest temperature tested, a mild but steady increase in the concentration of malic acid throughout the course of the experiment was observed, reaching 66% of formation of this acid after 210 minutes. In contrast, when the temperature was increased to 210 °C, the concentration of malic acid remained almost constant during the thermal hydrolysis, suggesting that the formation and degradation rates were more balanced. This behaviour suggests that the activation energy for the degradation reaction of malic acid is higher than for its formation, predominating the former at high temperatures. Ma et al. (2014) also observed a slight increase in the malic acid concentration during the oxidation of diluted-acid corn stover lignin and steam-exploded spruce lignin. These authors reported a mass yield of 6% during the oxidation of the first one with H_2O_2 at 60 °C, 2 hours and in the presence of chalcopyrite. Moreover, after 5 hours of oxidation of the latter under the same conditions, the yield reached was 3%.

Then, in Figure 2 the effect of temperature on the evolution of the volatile acid (formic, acetic and propionic acid) concentrations during both the partial wet oxidation and the thermal hydrolysis at 70 bar is depicted.



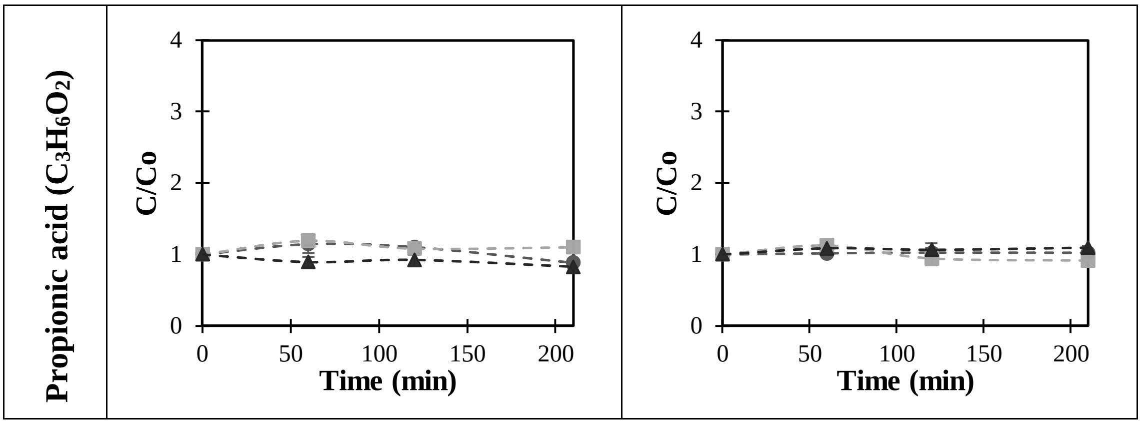


Fig. 2. Evolution of formic ($C_o = 1.0 \pm 0.1$ g/L), acetic ($C_o = 2.4 \pm 0.1$ g/L), and propionic ($C_o = 2.4 \pm 0.9$ g/L) acid throughout both hydrothermal treatments of the Kraft lignin at 70 bar and 170 °C (■), 190 °C (●) and 210 °C (▲).

Although finding a generalised behaviour pattern of the three volatile acids during the hydrothermal treatments of the Kraft lignin might be difficult at first glance, it can be observed that a negligible amount of volatile acids was produced under a non-oxidizing atmosphere, independently of the temperature tested. Thus, the concentration of formic and propionic acid remained approximately constant during the whole thermal hydrolysis experiment and only acetic acid was formed (42% of change compared to feed in terms of concentration).

On the other hand, these acids were more reactive under an oxidizing atmosphere, although the behaviour differed from one acid to another. For example, it was not possible to produce formic acid from Kraft lignin by wet oxidation. In fact, this process decomposes the residual formic acid at temperatures higher than 170 °C. Suzuki et al. (2006) reported the same fact after oxidizing different lignin model compounds (guaiacol, syringol and phenol) at 300 °C using H_2O_2 as oxidant.

By contrast, the temperature had a positive impact on the formation of acetic acid, being formed 18.3, 64.7 and 56.8 g of acid per kg of COD consumed at 170, 190 and 210 °C, respectively, after 210 minutes of oxidation. This is consistent with the reaction mechanism, according to which certain intermediate compounds are converted into acetic acid before their decomposition [28]. Suzuki et al. (2006) obtained a yield of 9% for this acid, which is quite similar to the maximum here obtained (7%).

Regarding the propionic acid, its behaviour in the presence of oxygen indicates refractoriness to both oxidation and hydrolysis reactions.

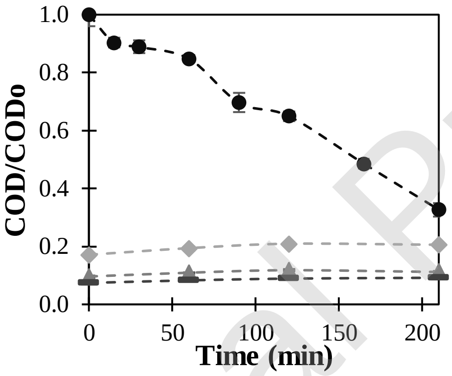
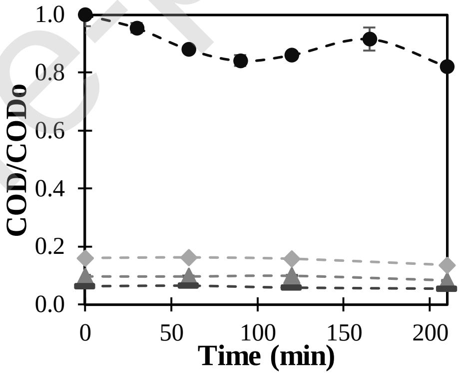
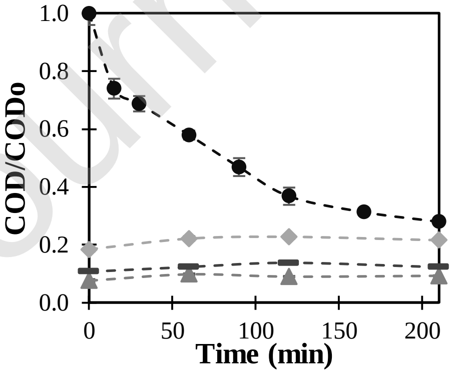
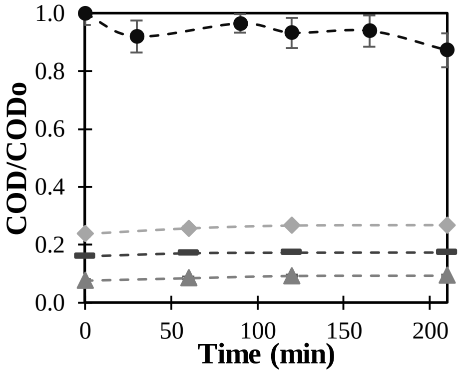
Eventually, comparing the behaviour of the non-volatile hydroxy acids with that for the volatile ones, it was observed that their trends during wet oxidation were diametrically opposed. Thus, the shortest non-volatile acid (oxalic acid), or the longest volatile one (propionic acid), had a lower formation rate and higher stability. Furthermore, the medium length acids (lactic and acetic acid) were formed until 120 minutes of reaction, when the concentration began to stabilize. Moreover, both the shortest volatile acid (formic acid) and the longest non-volatile one (malic acid) did not react at 170 °C but at the rest of the temperatures, they were decomposed. On the other hand, there was not any remarkable behaviour when an inert atmosphere was employed.

It should be pointed out that the wet oxidation also had a screening effect on the final distribution of acids, increasing the proportions of lactic and acetic acid in the final mix and reducing the corresponding to malic and formic acid, as well as the total COD. By contrast, the thermal hydrolysis caused and enrichment of the pool of acids in lactic and malic acid.

3.2. Physicochemical properties

In addition to the evolution of the different acids detected, other physicochemical properties were measured in order to study the effect of temperature and oxygen on the polluting potential of the Kraft lignin.

With this purpose, Figure 3 shows the evolution of the total Chemical Oxygen Demand, experimentally measured, and those corresponding to the theoretical one for volatile and non-volatile acids, which were calculated from the acid concentration, during the partial wet oxidation and the thermal hydrolysis of Kraft lignin at 70 bar and different temperatures.

	Wet oxidation	**Thermal hydrolysis**
170 °C		
190 °C		

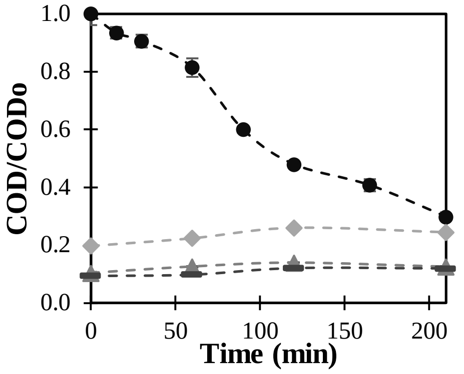
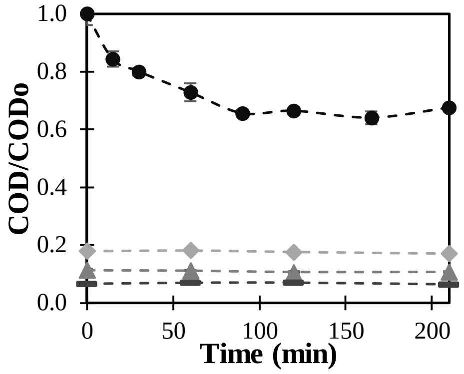
210 °C		

Fig. 3. Evolution of the non-volatile (▲) and volatile (▬) acids, expressed as Chemical Oxygen Demand, their total amount (◆) and the total Chemical Oxygen Demand (●) (COD_o = 94 ± 4 g O_2/L) throughout both hydrothermal treatments of the Kraft lignin at 70 bar and 170 °C, 190 °C and 210 °C.

Focusing on the total COD reduction, this parameter showed a great dependence on the type of atmosphere used. In the presence of oxygen, the organic load was substantially reduced during the experiments, being this reduction faster at higher temperatures. Thus, the final mineralization degrees obtained for the wet oxidation of Kraft lignin were around 70% for all the temperatures tested. Similar conclusions were achieved by other authors during the wet oxidation of other feedstocks. For example, Kindsigo and Kallas (2006) analysed the oxidation of a solution of alkali lignin (pH=12, 260 ± 10 ppm of TOC and 765 ± 15 mg O_2/L of COD). Using an oxygen pressure of 1 MPa and after 30 minutes of preheating and 120 minutes of reaction, COD removals were more significant at higher temperatures, reaching reductions above 50% at 190 °C, 19% lower than that obtained for the Kraft lignin at the same temperature after 165 minutes of reaction in this work.

By contrast, the organic load was hardly decomposed in the absence of oxygen, achieving the maximum mineralization degree (32%) at 210 °C and after 210 minutes. For the same conditions, the COD reduction in presence of oxygen was 38% higher. Moreover, hydrolysis reactions were more affected by the temperature than those of oxidation. At the end of the wet oxidation, the COD reductions reached were similar; however, after applying thermal hydrolysis there was a difference of around 15% between the final COD reduction at 190 °C and at 210 °C.

Regarding the COD due to the acids, both volatile and non-volatile acid CODs had an analogous trend under both types of atmosphere, although the latter was present in a slightly higher concentration than the former when the Kraft lignin was treated at 170 °C or at 210 °C. Contrarily, it must be pointed out that the temperature of 190 °C promoted the formation of the volatile acids in comparison to the corresponding to the non-volatile ones.

The presence of oxygen had a positive impact on the total amount of acids, particularly, at 210 °C. The maximum acid concentration was reached after 120 minutes of wet oxidation, obtaining 165.3, 70.4 and 172.8 g of acids per kg of COD consumed at 170, 190 and 210 °C, respectively. Simultaneously, the oxidation caused a significant reduction in the organic load, so the acid COD proportion increased while other by-products derived from the lignin were removed. This fact involves that the final reaction medium after a wet oxidation treatment was mainly composed of acids; specifically, the acid COD represented 62.8%, 77.0% and 81.8% of the remaining total organic load after 210 min of wet oxidation treatment. It implies that the downstream processing costs might be significantly reduced due to the fact that the membrane fouling during filtration decreases [39] and the acid extraction is simplified. Moreover, the high acid COD to total

COD ratios obtained after wet oxidation treatments open up the possibility of utilising directly the effluent obtained in different applications such as a substrate for bioplastic production or in the denitrification process, among others [46–48].

Apart from that, Figure 4 shows the evolution of pH and Colour Number during the partial wet oxidation and the thermal hydrolysis of Kraft lignin at 70 bar and at different temperatures.

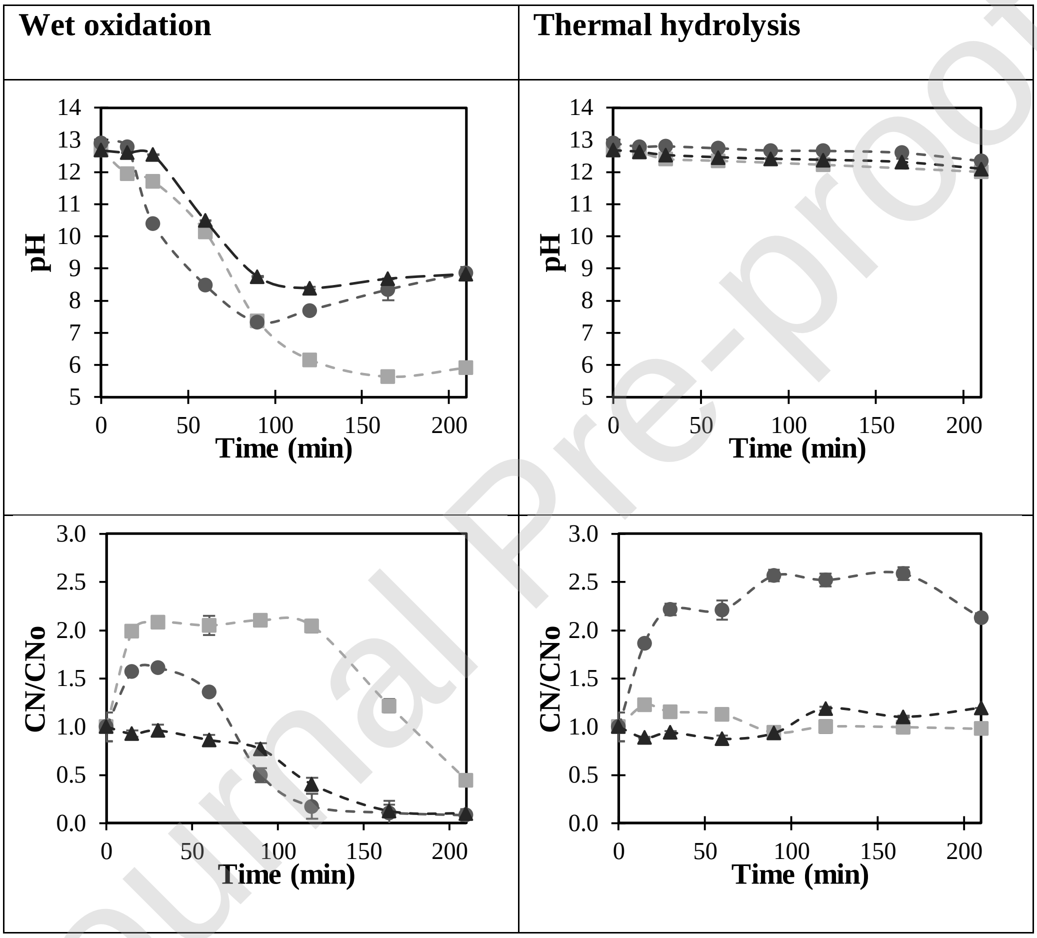


Fig. 4. Evolution of the pH ($pH_o = 12.8 \pm 0.1$) and the Colour Number ($CN_o = 64 \pm 10$) throughout both hydrothermal treatments of the Kraft lignin at 70 bar and 170 °C (■), 190 °C (●) and 210 °C (▲).

As can be seen, the temperature had a great effect on both parameters, except for pH during the thermal hydrolysis experiments. In this case, pH value remained constant for all the conditions tested, which is consistent with the low formation of acids under an inert atmosphere, previously commented. Moreover, during the thermal hydrolysis, lignin is cracked into small aromatic compounds, but oxidation products (in particular, carbon dioxide) are not produced [49]. For these reasons, the alkaline nature of this stream was maintained. On the other hand, the pH value significantly changed during the experiments when an oxidizing atmosphere was employed. This behaviour can be related to the reaction mechanism, which occurs through chain reactions that generate intermediates (alcohols, volatile acids…), some unstable and others refractory (mainly acetic acid). During the process, a part of the organic matter is decomposed into carbon dioxide and water while other compounds are converted into these intermediates [28,29]. Thus, the pH strongly dropped until achieving a constant concentration of acid intermediates. As can be seen in figures 1 and 2, working at 170 °C, neither malic nor formic acid were decomposed and the formation of lactic and acetic acid stopped after 120 minutes, so the pH continuously dropped until that time. Nevertheless, for all the other temperatures assayed, both malic and formic acid were completely oxidized at 120 minutes, when the formations of lactic and acetic acid were also stabilized. Consequently, the pH changed quicker at first and, as the production of acid intermediate compounds was slowed down, this parameter tended to increase.

The colour evolution is closely linked to the formation of coloured intermediates such as quinones or carboxylic and phenolic groups, among others [3]. According to the results, higher temperatures promote their formation and, hence, the increase in the colour number. Nevertheless, the stability of these intermediates is highly reduced under an oxidizing atmosphere, particularly at high temperatures, being further oxidized towards non-coloured products, such as hydroxy acids. This fact explains why the highest colouration with oxygen was obtained at the lowest temperature tested or why the colour number progressively decreased during all the time for the wet oxidation of Kraft lignin at 210 °C. The same behaviour was reported by Kindsigo and Kallas (2006) during the oxidation of alkali lignin (pH=12, 260 ± 10 ppm of TOC and 765 ± 15 mg O_2/L of COD) after 30 minutes of preheating, using an oxygen pressure of 1 MPa and different temperatures (110, 150 and 190 °C). It is interesting to point out that the final effluents obtained after the wet oxidation of Kraft lignin at either 190 or 210 °C are almost colourless and have the lowest pH values, which is in accordance with a reaction medium mainly composed by organic acids.

4. Conclusions

It is concluded that hydrothermal treatments could be attractive methods to obtain carboxylic acids from Kraft lignin. During the wet oxidation of Kraft lignin, the organic load was reduced by up to 70% while lactic and acetic acid were generated, so the final medium was mainly composed of acids. Moreover, it was the best technique for generating organic acids from Kraft lignin, obtaining the maximum concentration of acids (172.8 g of acids formed per kg of COD consumed) after 120 minutes at 210 °C. On the other hand, thermal hydrolysis was not useful as a technique to generate organic acids from Kraft lignin. Finally, the selection of the oxidative conditions had a screening effect on the final distribution of acids. However, this is the beginning of the study, so the extraction and the purification of these carboxylic acids would be the next challenge.

Declarations of interest

None.

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