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CHARACTERISATION OF THE WET OXIDATION OF BLACK LIQUOR FOR ITS INTEGRATION IN KRAFT PAPER MILLS

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Abstract

As a mandatory first step to assess the implementation of wet oxidation in the current approach of paper mills as biorefineries, this paper discusses for the first time ever the effect of this treatment on the chemical composition of intermediates and final products, as well as the evolution of sulphur, nitrogen, ions, Gross Calorific Value and the properties related to the subsequent handling and downstream processing of Kraft black liquor. It was found that around 50% of the initial carbon was transformed into carboxylic acids, mainly acetic and lactic; thus showing the high potential of black liquor as a renewable resource for the production of these compounds. The oxidation of organic sulphur into sulphates and the no formation of SOx involve odourless and low-polluting emissions during the wet oxidation. The wet oxidised black liquor is also less viscous (30% lower pumping costs) and easier to purify than the raw material. The treatment did not have a significant effect on evaporation rates, but decreased the Gross Calorific Value, although the heat generated per unit of total organic carbon remained constant.

Keywords

1. Introduction

It is well known that the Kraft process is currently the most widespread method to manufacture paper pulp. The main step in this process is the cooking of the wood chips with a solution of sodium hydroxide and sodium sulphide (white liquor) in order to separate the lignin from the cellulose. After washing the pulp, a waste stream called black liquor is obtained. This effluent is a highly polluted aqueous solution that mainly

contains lignocellulosic compounds from wood (lignin, resins, hemicellulose…) and inorganic compounds from the used chemicals [1].

Kraft black liquor is an alkaline wastewater, with a pH higher than 10, high organic load and content of suspended solids, low biodegradability and significant concentrations of toxic chemicals. Therefore, it strongly affects the environment and, especially, the aquatic ecosystems if it is improperly managed [2,3]. Traditionally, pulp mills have considered black liquor as a fuel [4], concentrating and burning it to obtain energy and to recover the spent chemicals in the ashes [5]. However, this recovery is operationally limited by the characteristics of the black liquor, mainly its alkalinity, viscosity and high solids concentration, [6,7] and by the release of organic sulphur compounds, associated to unpleasant odours throughout the concentration and the incineration stages [8].

Furthermore, environmental regulations have become stricter in recent years and the implementation of the Green Economy has gained relevance [9]. This methodology applied to the pulp and paper industry proposes that the mills must be converted into Green Integrated Forest Biorefineries, reducing the gas emissions and the water and fossil fuel consumption while high added-value chemicals, power, heat and fuels are produced. Between all those products, several authors have proposed the production of carboxylic acids from black liquor [10,11]. These have many industrial applications and are usually produced from petrochemical resources, which collides with one of the tasks of the Green Chemistry, or by fermentation, which requires much higher retention times [10].

Although carboxylic acids are already generated during the cooking stage, their concentrations and purity can be boosted by means of the subsequent hydrothermal treatment of the black liquor [12]. These hydrothermal treatments consist of carrying

out reactions in the aqueous phase under an oxidising atmosphere and mild working conditions (125-320 °C and 0.5 MPa-20 MPa) [13]. This alternative has been gaining interest during the last years and several studies have analysed the effect of the hydrothermal treatments on the final distribution of organic acids and/or organic load reduction [11,13–15]. Nevertheless, in addition to enhancing the generation of acids, hydrothermal treatments may also have other potential positive effects on the flow and chemical properties of the Kraft black liquor, but these have been very little explored. Surprisingly, aspects such as the impact of the hydrothermal treatments on the black liquor density, viscosity, conductivity… are unknown. Likewise, a more detailed description of the composition of the hydrothermal hydrolysates from black liquor than the mere measurement of the concentration of acids generated is neither available. There is no need to explain why the effect of the hydrothermal treatment on these metrics is essential in order to assess the potential use of black liquor as a renewable resource for the production of carboxylic acids, particularly in terms of downstream processing and integration of the hydrothermal treatment on the conventional Kraft process.

Therefore, the aim of this study is to obtain, for the first time ever, a deep knowledge of the effect of the wet oxidation on the subsequent management of Kraft black liquor. To this end, the chemical composition will be analysed in order to better understand the mechanisms involved in the treatment and to assess the production of high added-value products. After that, the changes in the main flow and thermal properties of wet oxidised Kraft black liquor will be investigated to evaluate the feasibility of the downstream processing (handling, transport, extraction of products…) and the potential integration of this technique in the conventional layout of paper mills.

2. Materials and methods

2.1. Materials

Kraft black liquor, obtained after the cooking step from *Eucalyptus* wood, was provided by a paper mill located in Asturias (Spain). In order to maintain its characteristics, it was stored at 4 °C before its usage. Table 1 shows the main physicochemical characteristics of this feedstock.

Table 1

2.2. Experimental setup

Wet oxidation reactions were carried out in a 1 L 316 SS semi-batch reactor (Parr Instrument Co., Moline, IL.). The equipment was also provided with temperature and pressure controllers and indicators and sampling systems and a heating jacket. Furthermore, the oxidising atmosphere for partial wet oxidation was provided by a compressed cylinder filled with O_2. The gas flow was previously saturated with water using a 2 L stainless steel humidifier located before the reactor. To ensure safety, both the reactor and the humidifier were loaded about 70% of their capacity and bursting disks were installed to avoid overpressures. A scheme of the experimental setup is shown in Figure 1.

Figure 1

The stirrer speed and the flow rate, which were fitted to 150 rpm and 1800 mL/min, respectively, remained constant during all the experimentation time. A more detailed description of the experimental setup can be found in Pola et al., (2019). Samples were periodically withdrawn and subsequently analysed in triplicate.

2.3. Analysis of feedstock and samples

2.3.1. Composition

The different fractions of soluble carbon (total, inorganic and organic carbon) were measured using an analyser TOC-V CSH (Shimadzu, Japan).

The elemental analysis of the dry matter was measured through the combustion technique, using an elemental analyser CHNS Vario EL Elementar AnalysenSysteme model (GmbH, Germany).

The total carbohydrates concentration was determined by means of the phenol-sulphuric acid method and the reducing sugars concentration by the dinitrosalicylic acid (DNS) method [16].

The concentration of the carboxylic acids was measured using High-Performance Liquid Chromatography (HPLC) (Agilent 1200, Agilent Technologies, CA, USA) equipped with a refractive index detector. The column used was an ICSep ICE-ION-300 (Transgenomic, CA, USA) at 75 °C and the mobile phase was a sulphuric acid 0.45 mM solution (3.1<pH<3.3) at a flow rate of 0.3 mL/min. The carboxylic acids identified were oxalic, lactic, formic, acetic and propionic acid. Regarding their structure, the first two were classified as non-volatile hydroxy acids and the rest, as volatile acids [17,18].

The concentration of the main inorganic ions was determined by means of Ion Chromatography, 883 Basic IC plus model (METROHM, Switzerland).

Absorbances at three different wavelengths (436 nm, 525 nm and 620 nm) (spectrophotometer T80 UV/VIS PG Instruments Ltd, UK) were employed to obtain the colour number according to Equation 1 [19].

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

2.3.2. Downstream processing

Density, pH and conductivity were determined at atmospheric pressure and room temperature using pycnometers, a pH-meter Basic 20 (Crison, Spain) and a conductivity-meter CM 35 (CRISON, Spain), respectively.

For samples with pH lower than 9, the viscosity was also measured with a rheometer HAAKE MARS II (Thermo Scientific, EEUU), varying the deformation rate from 0.1 to 100 s^{-1} during 180 seconds at 25 ºC and using flat plates of Titanium of 60 mm of diameter with a separation of 1 mm [20]. When the pH was alkaline, a glass viscosimeter was used at a temperature of 25 ºC.

Kinematic viscosity (ν) was calculated applying Equation 2, which relates dynamic viscosity (μ) and density (ρ).

$$\nu = \mu \, / \, \rho \qquad [2]$$

The Chemical Oxygen Demand (COD) was obtained by the Standard Dichromate Method [21].

2.3.3. Integrability in pulp mills

The evaporation rate was determined from weight loss at 105 °C, employing a thermobalance HR73 Halogen Moisture Analyzer (Mettler Toledo, USA).

The Gross Calorific Value was determined according to 1928:2009 ISO Standard for the determination of gross calorific value by the calorimeter bomb method [22].

Finally, the concentration of salts was measured by means of an Energy Dispersive X-Ray Analysis (EDX), using a Scanning Electron Microscope (SEM) JMS-6610LV (Jeol, USA). Before carrying out the analysis, it was necessary to coat the samples with gold under vacuum (sputtering) to make them conductive.

3. Results and discussion

3.1. Composition

The first step to obtain a deeper understanding of the black liquor wet oxidation was to assess its elemental composition before and after being treated, so the evolution of the four main elements (carbon, hydrogen, sulphur and nitrogen) during this treatment were analysed. The results are given in terms of concentration, as grams per litre, calculating them from the total carbon content and the relationship between carbon and the rest of the elements. Firstly, total carbon and hydrogen concentrations during the wet oxidation at different temperatures and pressures are shown in Figure 2.

Figure 2

Focusing on the major component, carbon was mainly available in the organic form, constituting around 95% of the total carbon during all the treatment, as expected from the high organic load of the Kraft black liquor. It is well known that high organic carbon content is not only dangerous for the environment but also causes problems in the equipment, such as corrosion [23,24]. During the wet oxidation, the organic carbon showed a constant decreasing trend for all the conditions tested, even during the initial heating and pressurization period, which implied the formation of carbon dioxide and/or carbonates [25]. However, the presence of the latter as a final product was discarded because the inorganic carbon content, obtained from IC analyses, remained constant and at low concentrations (< 3 g C/L) compared to the organic ones. In this sense, paying attention to the effect of the operating conditions on the carbon mineralization, it was observed that higher temperatures caused slightly greater mineralization degrees of the organic carbon content; diminishing it by 47%, 54% and 59% at 170, 190 and 210 °C, respectively, after 210 minutes. These results agree with the reductions reported by some authors after wet oxidation treatments of black liquor and other industrial

wastewaters, although under different conditions [13,25]. On the other hand, changes in pressure had a negligible effect on the mineralization, achieving reductions of around 54% in all cases.

After carbon, the second major constituent in Kraft black liquor was hydrogen. In accordance with the aforementioned, as the organic compounds were oxidised, a part of the initial organic hydrogen was turned into water, which explains why the hydrogen content dropped throughout the treatment (as can be seen in Figure 2). In this case, the reductions achieved for hydrogen were similar to those previously obtained for carbon. Therefore, after 210 minutes, the organic hydrogen concentration was reduced by 45%, 51% and 54% at 170, 190 and 210 °C (at 70 bar) and 54%, 51% and 56% at 55, 70 and 85 bar (at 190 °C).

Both elements, carbon and hydrogen, are directly related to the formation or decomposition of high added-value organic products, such as sugars and carboxylic acids. Therefore, in order to characterise the compounds responsible for this high organic carbon content, the concentrations of both reducing sugars and carboxylic acids were measured throughout the wet oxidation experiments and are shown in Figure 3 (see table 1 for initial concentrations).

Figure 3

Starting with the carbohydrates, it was checked that almost all of them corresponded to reducing ones. It can be observed that the amount of reducing sugars did not increase during the first 30 minutes of reaction, what suggests that complex polymers from black liquor (such as lignin and hemicelluloses) were firstly converted into non-reducing sugars. Afterwards, these compounds were progressively converted into reducing sugars, experimenting a peak of concentration after 60 minutes (as can be observed in Figure 3). Subsequently, reducing sugars were oxidised into carboxylic

acids and carbon dioxide until the end of the reaction (210 minutes). Focusing now on the operating conditions, it seems that they only had a significant effect during the first 90 minutes, mainly affecting the highest concentrations of reducing sugars reached during the treatment. Moreover, this effect was higher when more severe conditions were employed. In this sense, the maximum concentrations were 62% higher at 210 °C (70 bar) and 68% higher at 85 bar (190 °C) than the initial one. Afterwards, the degradations were almost complete at the end of the reaction time (210 minutes), regardless of the conditions selected.

Other important carbon compounds in Kraft black liquor, which have significant relevance in many industrial areas, are the carboxylic acids. Specifically, oxalic, lactic, formic, acetic and propionic acids were predominant in this stream. On the whole, both temperature and pressure had a significant effect on the evolution of the carboxylic acids during the wet oxidation. In any case, for all the conditions tested, the maximum concentration of total acids was reached after 60 minutes of oxidation. Taking its initial concentration as reference, these increases were very slight: 2%, 6% and 11% at 170, 190 and 210 °C (at 70 bar) and 4%, 6% and 3% at 55, 70 and 85 bar (at 190 °C). After reaching this maximum, the concentration of acids started to decrease, having the following reductions (referred to the initial value) at the end of the treatment: 12%, 14% and 21% at 170, 190 and 210 °C (at 70 bar) and 24%, 14% and 6% at 55, 70 and 85 bar (at 190 °C). It is interesting to point out that total TOC decayed notably faster than the corresponding to acids, suggesting that the refractoriness to oxidation of the latter is high [26] and that there is a preferential oxidation of the other intermediates such as, for example, carbohydrates.

As can be seen, the net effect of the treatment on the total amount of acids was a decrease in its concentration, although the behaviour of each specific acid must be

individually discussed (see Figure S.1 in Supplementary Material). In this sense, lactic and acetic acids were produced during the oxidation, while propionic acid concentration remained constant and oxalic and formic acids were degraded during the treatment. In line with the generally accepted radical-chain mechanism [26,27], some researchers have already analysed the formation of some organic acids [15,25,28]. In fact, it can be observed that wet oxidation has two effects on the organic acids present in the black liquor: the generation of a slightly less concentrated but much more purified stream of carboxylic acids and a screening effect on the final distribution of these, increasing the proportion of acetic acid mainly. These two effects result in the final obtainment of a pretty purified stream of carboxylic acids at the end of the wet oxidation. For example, after 210 minutes of wet oxidation at 210 °C and 70 bar, the COD corresponding to the acids represented the 100% of the total COD. At that time, the concentrations of acids were the following: 19.9 g/L of oxalic acid, 6.7 g/L of lactic acid, 1.5 g/L of formic acid, 10.3 g/L of acetic acid and 7.5 g/L of propionic acid. In contrast, their concentrations in the raw Kraft black liquor were: 33.9 g/L of oxalic acid, 7.0 g/L of lactic acid, 3.2 g/L of formic acid, 6.3 g/L of acetic acid and 8.4 g/L of propionic acid.

Although other organic carbon compounds, such as quinones or phenolic groups, were not directly measured, they are usually linked to the colour of the black liquor [29], so their presence is closely related to the colour number. In this sense, this parameter rose during the first 60 minutes (except for the lowest temperature and pressure), when the maximum concentrations of reducing sugars and carboxylic acids were also reached. This behaviour is caused by the decomposition of the lignin into smaller phenolic and quinone compounds, as other authors have already reported [30,31] These increases in the colour number were: 0%, 13% and 16% at 170, 190 and 210 °C (at 70 bar) and 1%, 13% and 11% at 55, 70 and 85 bar (at 190 °C). After this

time, the colour decreased until the end of the treatment, finally obtaining a yellowish-brown effluent with colour reductions of around 90% in all cases (Figure 3). This suggests that the presence of these types of compounds after 210 minutes of wet oxidation at these operational conditions is negligible. Other authors have also reported that these compounds can be easily removed by wet oxidation [32–36].

On the other hand, the presence of sulphur and/or nitrogen compounds are usually related to the appearance of harmful and odorous gaseous emissions, so knowing their evolutions (in terms of total and inorganic forms) during the wet oxidation of Kraft black liquor is essential to assess this technique. Figure 4 shows the nitrogen and sulphur elemental concentrations at the beginning and end of the wet oxidation carried out at different temperatures and pressures. The fraction of each component was calculated from the concentration of the ions (sulphate, ammonium, nitrites and nitrates), using the corresponding molecular weight ratio.

Figure 4

Regarding the sulphur content, it should be recalled that a significant portion comes from the sodium sulphide used for the cooking of the pulp [5]. Analysing its evolution during the wet oxidation, it can be observed that some organic sulphur compounds were oxidised into sulphates. This explains why the concentration of sulphate ions was approximately doubled after 210 minutes of oxidation regardless of the operating conditions. This fact also implies that sulphur remains dissolved in the medium as sulphate during the treatment, not being released as hydrogen sulphide and/or sulphur oxides to the atmosphere. From an industrial point of view, this means that the exhaust gas from the wet oxidation of Kraft black liquor is inodorous and low polluting [37,38].

Finally, focusing on the nitrogen, this was present at low concentrations and mainly in organic form. As wet oxidation proceeded, the inorganic nitrogen concentration (as ammonium, nitrites and nitrates) increased until the end (210 minutes) from 0.001 g/L to 0.04, 0.12 and 0.19 g/L at 170, 190 and 210 °C (at 70 bar) and 0.11, 0.12 and 0.09 g/L at 55, 70 and 85 bar (at 190 °C). So, higher temperatures caused greater increases in the inorganic nitrogen, while the pressures had a lesser effect. In addition, nitrate form predominated and ammonium was not detected in dissolution until the end of the reaction. For these reasons, NOx emissions are low, although more than 70% of the final total nitrogen was still organic at the end of the wet oxidation treatment.

Taking into account all the mentioned above, initially, the empirical formula for the organic matter of the black liquor (based on carbon) can be expressed as $CH_{1.07}S_{0.05}N_{0.01}$. After the corresponding wet oxidation treatment, the formula evolved into $CH_{1.05}S_{0.11}N_{0.02}$, $CH_{1.14}S_{0.12}N_{0.02}$ and $CH_{0.98}S_{0.11}N_{0.02}$ at 170, 190 and 210 °C (at 70 bar) and $CH_{1.11}S_{0.10}N_{0.02}$, $CH_{1.14}S_{0.12}N_{0.02}$ and $CH_{1.14}S_{0.12}N_{0.02}$ at 55, 70 and 85 bar (at 190 °C). Analysing these variations, the hydrogen to carbon ratio increased during the treatments, being partially due to the reduction in the average level of unsaturation of the pool of intermediates by oxidation reactions. Simultaneously, both the S/C and N/C ratios were enhanced during the treatments due to the removal of organic carbon as dioxide.

3.2. Downstream processing

The object of this section is to study the effect of wet oxidation on the properties that have an impact on the subsequent processing of the Kraft black liquor. The evolution of the main processing parameters (kinematic viscosity, pH, conductivity and

COD) during the wet oxidation treatment at different temperatures and pressures is shown in Figure 5 (see table 1 for initial concentrations).

Figure 5

Firstly, as stated in the Materials and Methods section, kinematic viscosity is defined as the quotient between the dynamic viscosity and the density. Regarding the latter parameter, it remained approximately constant throughout the wet oxidation experiments regardless of the conditions tested, with a mean value of just 7% higher than that corresponding to water at the same temperature. On the other hand, the viscosity flow curves for the raw and oxidised black liquor suggest that both had a slightly pseudoplastic rheological behaviour at very low deformation speeds. This behaviour agrees with that reported by Costa et al., (2011) for raw black liquor. Nevertheless, it can be considered as Newtonian fluid without a great error because shear stresses and deformation speeds can be lineally correlated with a good coefficient of determination (as can be seen in Figure S.2 in Supplementary Material). Once the black liquor was subjected to wet oxidation, the kinematic viscosity decreased around 31% for all tests (from $1.7*10^{-6}$ to $1.2*10^{-6}$ m^2/s), so neither the temperature nor the pressure had an appreciable influence on its reduction. For this reason, this drop may well be related to the decrease in carbohydrates and the breakage of lignin and other polymeric compounds [8], thus reducing the interactions among them and the resistance to flow. Again, industrially, this means that wet oxidation improves the transport and handling of the black liquor; achieving, for instance, a decrease of around 31% in pumping costs, for instance [39].

Aside from flow properties, another important aspect to assess the processability of a stream is its tendency to cause incrustation and corrosion phenomena in the equipment [4]. In this sense, pH and conductivity were analysed. Regarding the former,

pH experienced a sharp decrease from its initial value of 12.4 to roughly 9.0 in 90 minutes, which was caused by the oxidation of organic matter towards acidic compounds, such as organic acids and carbon dioxide, as well as by the consumption of alkalis during the oxidation [15]. However, its drop became less severe after 120 minutes, and even the medium was slightly alkalised during the last stages of treatment. This can be explained by analysing the behaviour of the acids throughout wet oxidation; because some of the short-chain acids formed started to be oxidised after a certain time of reaction [26,40]. Only the highest temperature seemed to have a slight effect on this parameter, which may be due to a greater decomposition of the organic and acid compounds. It is generally accepted that a reduction in pH increases the corrosion rate of a stream [41,42]. However, the final pH values obtained in this work at the end of the wet oxidation (210 minutes) ranged from 9 to 9.5, which largely prevents the formation of the highly corrosive carbonic acid [43]. Moreover, this acidification of the Kraft black liquor after the treatment also leads to an improvement in subsequent separation steps. For example, the filterability of oxidised Kraft black liquor would be better and the quantity of the chemical agents used for the acid precipitation of Kraft lignin would be reduced [15,18,44].

Continuing with the subject of corrosion and incrustation phenomena, conductivity is highly significant because it is closely linked to the dissolved solids and ions content. The results indicated that wet oxidation did not have a significant effect on the initial high conductivity of the black liquor. It must be taken into account that the conductivity of the raw Kraft black liquor is largely due to the different inorganic compounds added as white liquor and the products of the reactions during the previous wood cooking and the recovery stage, mainly NaOH, Na_2S and Na_2CO_3 [45]. The small fluctuations observed in this parameter for the wet oxidation experiments carried out at

different temperatures and pressures may be due to the different distributions of acids and inorganic sulphur and nitrogen previously reported, but they are dampened by the high amount of salts incorporated in the white liquor [5,45].

It is well known that the main components involved in the corrosion of metal surfaces are Cl^-, Na^+, K^+, Ca^{+2} and Mg^{+2}. Thus, Cl^- is held to be responsible for destroying the anti-corrosion layer of pipes and equipment but the rest of the ions produce corrosion inhibition, depending on the materials and the conditions tested [43]. Moreover, it is necessary to take into account that Cl^- and K^+ tend to form salts with Na^+, which cause incrustations, so their ratio needs to be controlled [4]. According to the evolution of the ions content in Kraft black liquor (see Figure S.3 in Supplementary Material), on the whole, neither the concentration of Cl^- nor those of K^+ and Na^+ varied during the oxidation. In addition, Mg^{+2} content was very low, so the incrustation and corrosion problems would hardly be affected by this cation. Moreover, Li^+, PO_4^{-3} and Br^- were not detected neither in the raw black liquor nor in the oxidised one.

All the previous parameters are focused on the effect of wet oxidation on the circulation of black liquor by the downstream equipment and piping (in terms of momentum transport and interaction with metallic surfaces). Nevertheless, another of our concerns was to know how wet oxidation influenced the subsequent separation of valuable products from the Kraft black liquor during its downstream processing. In this respect, the evolution of the total chemical oxygen demand (tCOD) was measured and compared with that corresponding to the organic acids detected for each time. Figure 5 shows that tCOD was reduced more than 50% at the end of the wet oxidation, although the final degree of mineralization varied depending on the pressure and, particularly, the temperature tested. As expected, the higher the temperature and/or pressure, the higher the tCOD removal obtained [25,40]. As an example, the degradations of organic matter

for 210 minutes were 50%, 67% and 72% at 170, 190 and 210 °C (at 70 bar) and 62%,

67% and 73% at 55, 70 and 85 bar (at 190 °C). From these results, the purification of

the acid fraction (expressed in terms of COD) in the reaction medium can be analysed.

Initially, the COD of the carboxylic acids represented almost one-third of tCOD and,

throughout the oxidation, this proportion increased gradually. Accordingly, the

percentage of acids (as COD) at the end of the reaction (210 minutes) were 65%, 96%

and 100% at 170, 190 and 210 °C (at 70 bar) and 79%, 96% and 100% at 55, 70 and 85

bar (at 190 °C) of the tCOD. This fact would simplify the subsequent separation process

of these compounds. On one hand, it enables to achieve a high degree of purity; being

transformed almost all the organic compounds into organic acids. On the other hand, the

compounds that difficult the filtration (mainly, lignin) were oxidised, so there are less

fouling membrane problems. Moreover, the efficiency of the separation process would

be better because of the purity of the acids in the solution [18,44,46].

3.3. Integrability in pulp mills

Eventually, the effect of the integration of wet oxidation operation on the

conventional recovery steps of Kraft process was studied, so the evolutions of the main

parameters involved at different temperatures and pressures are shown in Figure 6 (see

table 1 for initial concentrations).

Figure 6

The first stage of a conventional Kraft process is multiple-effect evaporation. In

order to analyse the effect of the wet oxidation of Kraft black liquor on a subsequent

concentration of this, evaporation rates were measured and compared as a function of

the temperature and the pressure employed during the wet oxidation treatment. This

parameter is key to assess energy consumption in the evaporators and, hence, the

associated costs. Nevertheless, as can be seen in Figure 6, wet oxidation barely

improved the evaporation rate. Only a slight increase in this parameter was detected (roughly, 10%) after 60 minutes; although then it almost returned back to its initial value rapidly. Therefore, neither the working conditions nor wet oxidation had a significant effect on concentrating black liquor by evaporation.

In contrast, the viscosity reduction could be beneficial owing to the fact that it would enable to reach higher solids content, which would improve the recovery process. As the solids content is increased, the viscosity rises exponentially, which in turn controls the percentage of suspended solids reached in the evaporation stage. Hence, if the initial viscosity is lower, the final solids percentage will be higher; being this also associated with an easier operation, the decrease in gas emissions and the improvement of efficiency and energy generation [7]. However, it is important to take into account that wet oxidation also reduces the solids content. For this reason, optimising the time of the reaction and the working conditions would be necessary to reduce viscosity without diminishing the solids significantly. In this case, for instance, after 120 minutes of wet oxidation at 190 ºC and 70 bar, the dry matter was slightly reduced (from 13% to 12%), but the reduction of viscosity was more important (30%).

Although wet oxidation does not reduce the evaporation costs significantly, it is necessary to point out that wet oxidation does prevent the release of odorous compounds during the evaporation due to the fact that sulphur compounds are oxidised to thiosulfates and subsequently, to sulphates, which stay dissolved in the reaction medium [44,47]. Thus, analysing the results from Figure 4, it was previously demonstrated that the odorous emissions were reduced because of the increase in sulphate concentration throughout the reaction.

The last stage of the conventional management of Kraft black liquor in papermills is its incineration. In order to know how wet oxidation affects this process,

Gross Calorific Values before and after the wet oxidation treatments at different temperatures and pressures were determined, as well as the amount of salts recovered after oxidising the stream at the reference conditions (190 ºC, 70 bar). The results revealed that the former parameter was reduced at least half of its initial value in all cases. Focusing on the effect of the working conditions, only the temperature had a significant effect on the reduction of this parameter. Accordingly, the decreases achieved at the end of the reaction (210 minutes) were 49%, 53% and 58% at 170, 190 and 210 °C (at 70 bar) and 53% at 55, 70 and 85 bar (at 190 °C). This reduction of the GCV after wet oxidation was expectable, taking into account the COD reduction during the hydrothermal treatment. This fact involves that production of energy during the incineration was also reduced because the reaction medium is enriched in compounds, mainly carboxylic acids, which have lower calorific value [18]. This is consistent with the results obtained in terms of GCV/TOC ratio, which approximately remained constant at a value of around 36 kJ/kg C until the end of the treatment for all the conditions tested. This fact suggests that the reduction of the organic matter is directly related to the decrease of the calorific value.

Analysing the recovery of the salts after the incineration stage, the differences in the composition of ashes from the initial and the wet oxidised black liquor are shown in table 2. The working conditions chosen for the wet oxidation (190 ºC and 70 bar) were those used as reference experiment in this work, whereas the operating time (120 min) was chosen in order to optimise the production of carboxylic acids. In this sense, despite the fact that the maximum concentration of acids was found after the first hour of reaction, the ratio COD_{acids}/tCOD is much higher after 120 minutes; thus improving their separation.

Table 2

As can be observed, although wet oxidation slightly reduces the percentage of dry matter and ashes, the quantity of sodium and sulphur obtained per gram of Kraft black liquor are the same. This could be explained paying again attention to the evolution of the inorganic ions (Figures 4 and S.3). Neither Na nor S was lost during the wet oxidation treatment as gaseous compounds; however, the presence of sulphates was higher, which means that a higher amount of inorganic sulphur was in the reaction medium. For this reason, the reduction in the amount of ashes recovered after the wet oxidation of black liquor was compensated by the increase in its inorganic fraction.

In view of the aforementioned, there are two main possibilities for implementing the wet oxidation stage in a pulp mill. The first one would be to oxidise all the stream in order to improve the flow properties and to reduce the gas emissions, although it would imply generating less energy as well. In fact, the savings associated with pumping would not compensate for the reduction in energy recovery during the incineration. In this sense, the second and most recommended option would be to carry out the wet oxidation of only a fraction of the Kraft black liquor stream, in parallel with the conventional incineration currently implemented, in order to obtain high added-value products without significantly decreasing the energy balance of the paper mill.

4. Conclusions

During Kraft black liquor wet oxidation, around 50% of organic carbon was mineralised. In parallel, wet oxidation has two effects on the organic acids present in the black liquor: the generation of a slightly less concentrated but much more purified stream of carboxylic acids and a screening effect on the final distribution of these, increasing the proportion of lactic and acetic acids, which eases their subsequent purification and concentration, thus making the black liquor a highly attractive renewable source of carboxylic acids. In addition, for shorter reaction times, other high

added-value compounds (sugars, phenolic compounds…) could be obtained, being their maximum concentration after 60 minutes of wet oxidation. Apart from this, the emission of odorous compounds and NOx was negligible, because the fraction of organic sulphur and nitrogen oxidised during the treatment were turned into inorganic ions (sulphates, nitrates and ammonium). Furthermore, the reduction of viscosity (up to 32%) and pH (final values around 9) improves the handling of black liquor, although its corrosiveness was not reduced. However, due to the decrease in organic matter during the wet oxidation, the gross calorific value decreased, although the heat generated per gram of carbon combusted did not change throughout the treatment. Therefore, the implementation of wet oxidation in the Kraft process would have to be optimised according to the interests pursued by each individual mill, whether they are improving process properties or obtaining high value-added products.

Acknowledgements

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Declaration of interests

X The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Figure 1

Figure 2
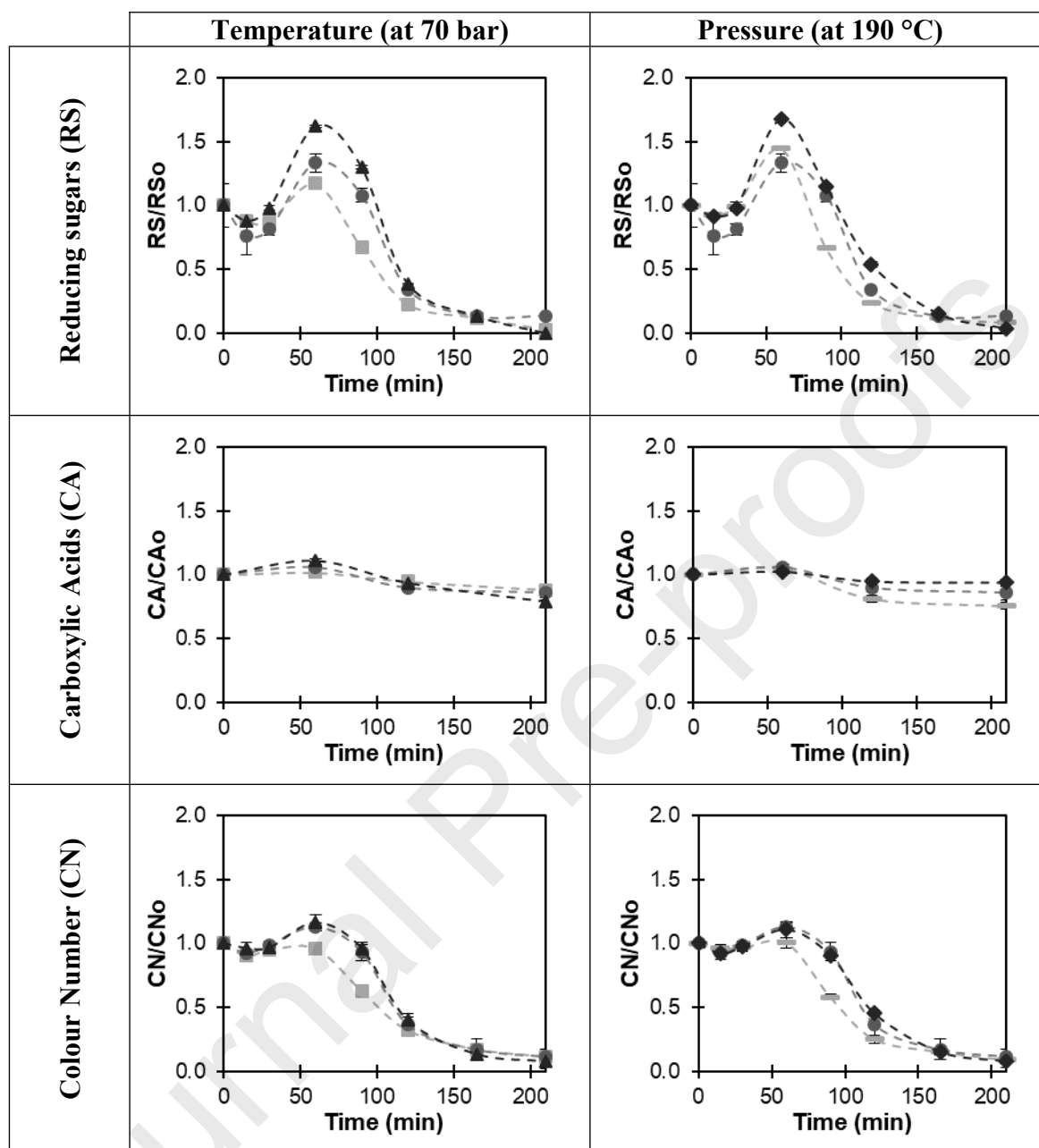
Figure 3

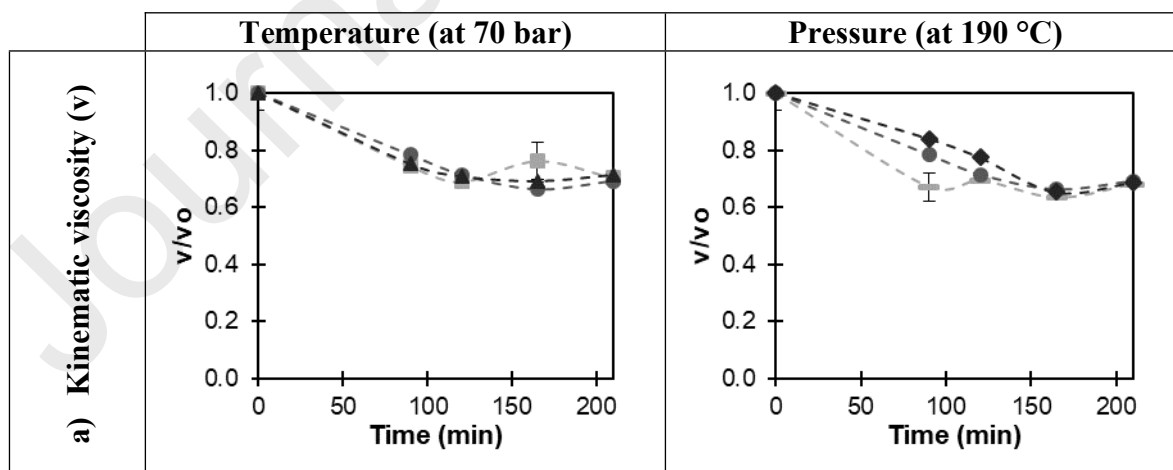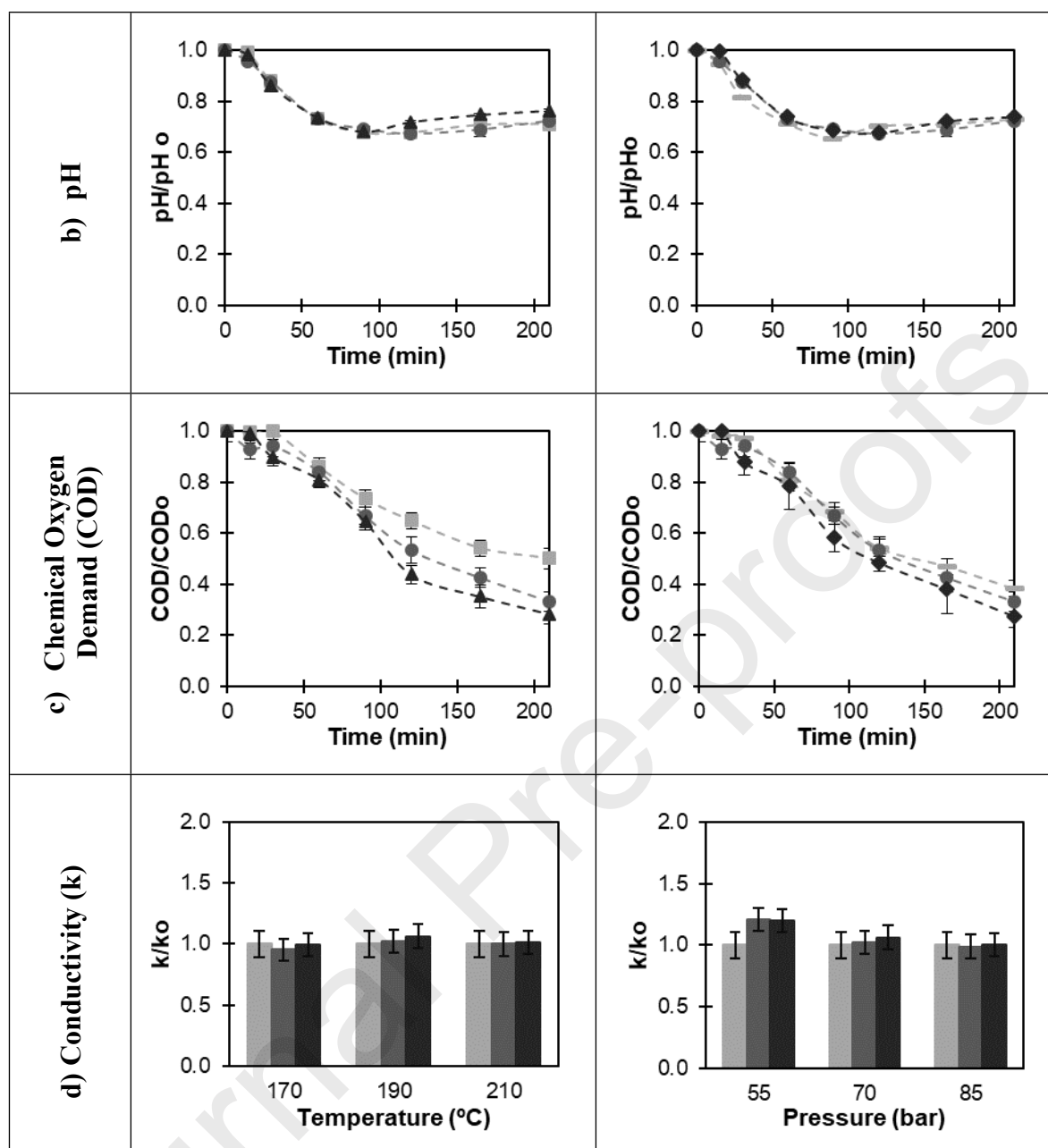|	Temperature (at 70 bar)	Pressure (at 190 °C)
Reducing sugars (RS)		
Carboxylic Acids (CA)		
Colour Number (CN)		
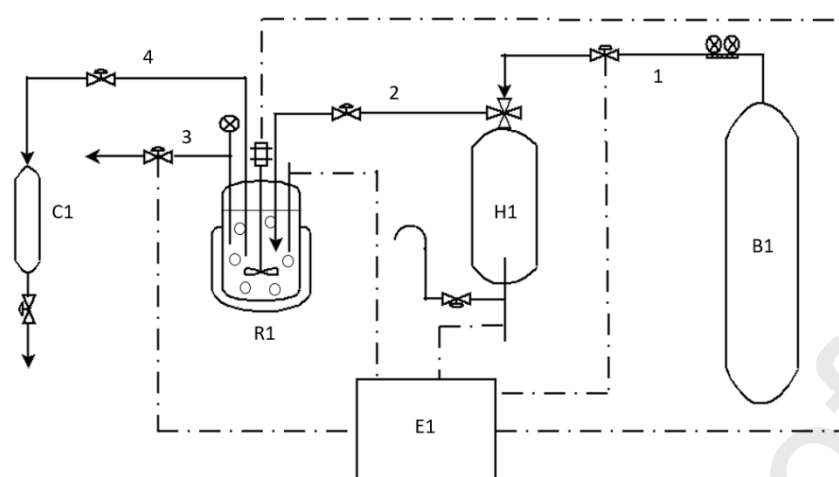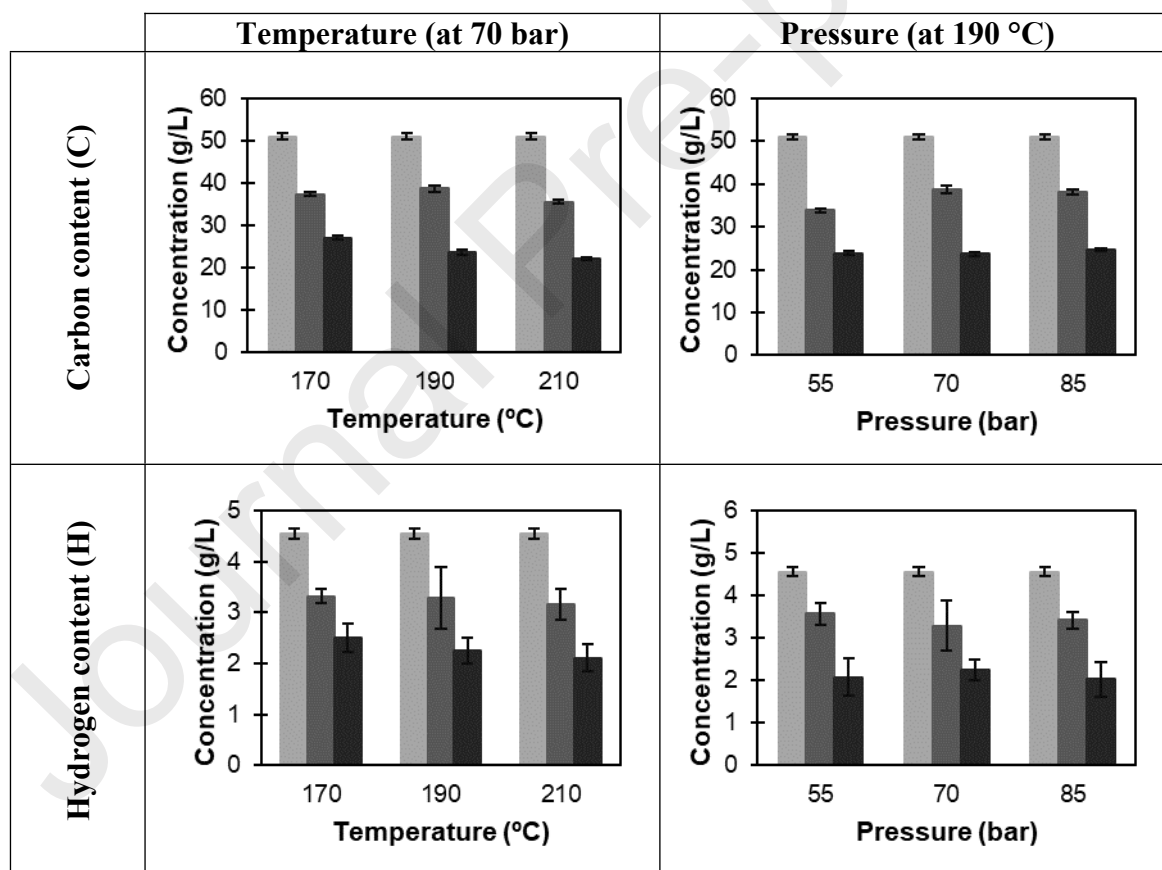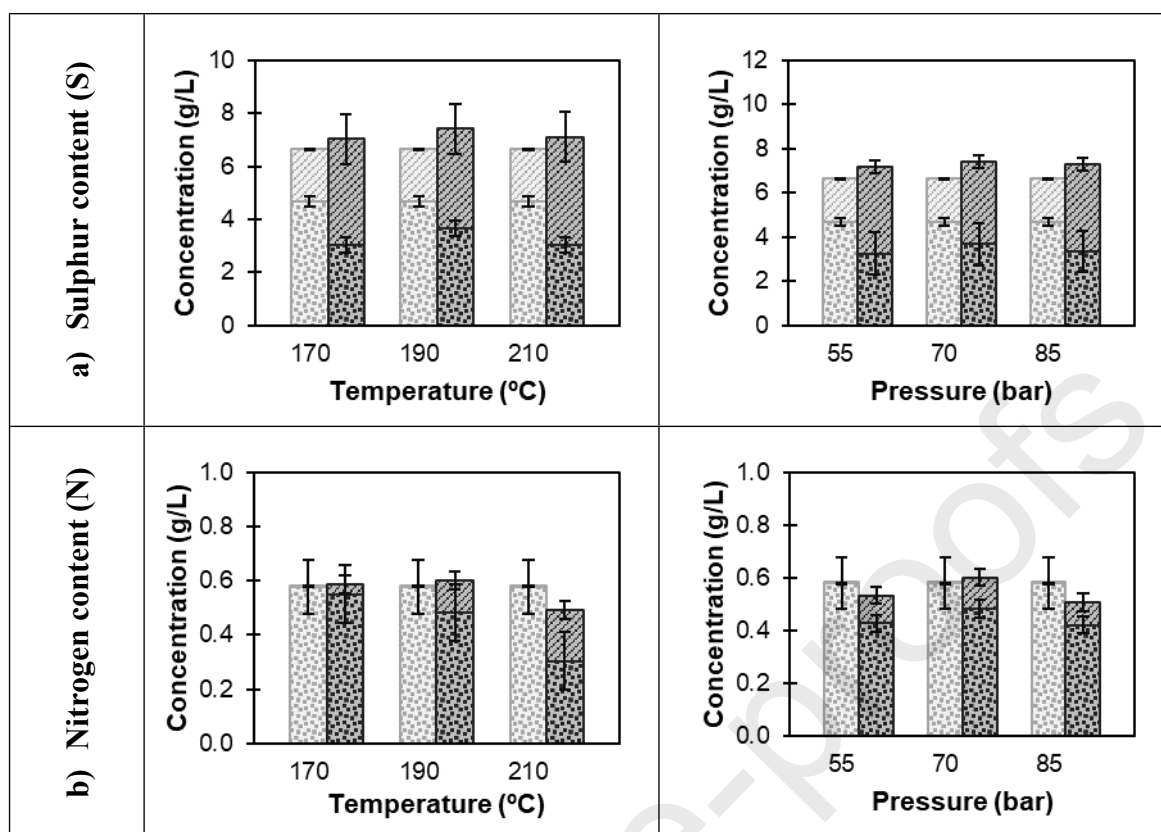
Figure 4

Figure 5

Figure 6

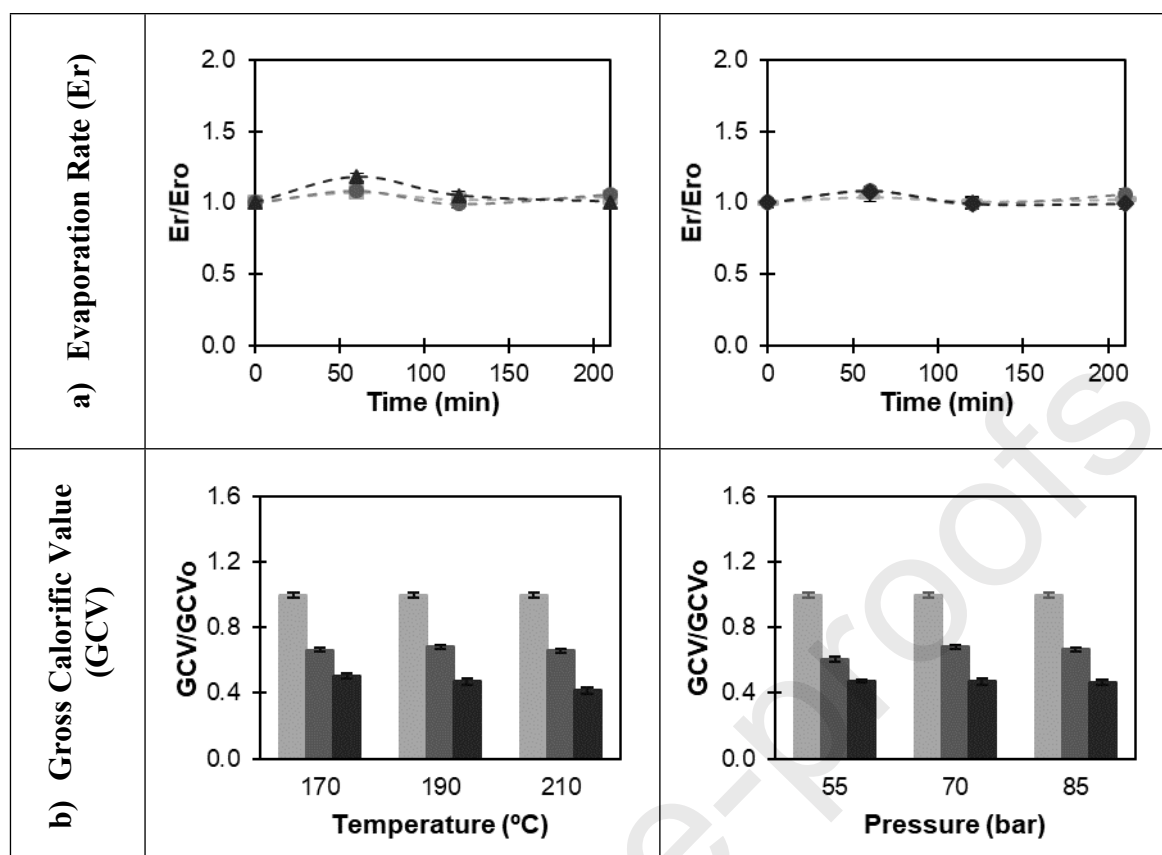| Temperature (at 70 bar)	Pressure (at 190 °C)

Figure captions

Fig. 1. Scheme of the experimental setup. Equipment: (B1) compressed bottle of oxygen, (H1) humidifier, (R1) reactor with heating jacket, (C1) condenser, (E1) PID controller (gas flow, humidifier and reactor temperatures, stirrer speed and pressure). Streams: (1) oxygen, (2) saturated oxygen, (3) gas outlet, (4) sample outlet.

Fig. 2. Total carbon and hydrogen concentrations during the wet oxidation of Kraft black liquor at different temperatures (left column) and pressures (right column) after 0 (■), 90 (■) and 210 (■) minutes. In all cases: stirrer speed, 150 rpm; oxygen flow rate, 1800 mL/min.

Fig. 3. Evolution of the organic compounds during the wet oxidation of Kraft black liquor at different temperatures (170 ■, 190 ● and 210 °C ▲ at 70 bar) and pressures (55 ▬, 70 ● and 85 ◆ bar at 190 °C). In all cases: stirrer speed, 150 rpm; oxygen flow rate, 1800 mL/min.

Fig. 4. a) Sulphur elemental concentration as sulphate ion (▨) and other forms (▦), b) nitrogen elemental concentration as ammonium, nitrite and nitrate ions (▨) and other forms (▦), of Kraft black liquor during its wet oxidation at different temperatures (left column) and pressures (right column) at 0 (■) and 210 (■) minutes. In all cases: stirrer speed, 150 rpm; oxygen flow rate, 1800 mL/min.

Fig. 5. Main processing properties (kinematic viscosity, pH and COD) evolution throughout the wet oxidation of Kraft black liquor at different temperatures (170 ■, 190 ● and 210 °C ▲ at 70 bar) and pressures (55 ▬, 70 ● and 85 ◆ bar at 190 °C) (from a to c). Conductivity of Kraft black liquor during its wet oxidation at different temperatures (left column) and pressures (right column) at 0 (■) and 210 (■) minutes (d). In all cases: stirrer speed, 150 rpm; oxygen flow rate, 1800 mL/min.

Fig. 6. a) Evaporation rate evolution at different temperatures (170 ■, 190 ● and 210 °C ▲ at 70 bar) and pressures (55 ▬, 70 ● and 85 ◆ bar at 190 °C). b) Gross Calorific Value during the wet oxidation of Kraft black liquor at different temperatures (left column) and pressures (right column) at 0 (■), 90 (■) and 210 (■) minutes during its wet oxidation. In all cases: stirrer speed, 150 rpm; oxygen flow rate, 1800 mL/min.

**Table 1.** Characterization of Kraft black liquor.

Parameters	Mean values
Carbon (g/L)	51.0 ± 0.7
Total Organic Carbon (g C/L)	48.9 ± 0.7
Hydrogen (g/L)	4.6 ± 0.1
Total Carbohydrates (g/L)	14 ± 1
Reducing Sugars (g/L)	14 ± 2
Total Acids (g/L)	59 ± 1
Colour Number	161 ± 4
Sulphur (g/L)	6.7 ± 0.1
Sulphate ions (g/L)	5.9 ± 0.1
Nitrogen (g/L)	0.6 ± 0.1
Ammonium ion (g/L)	0 ± 0
Nitrite ions ($*10^3$ g/L)	1.6 ± 0.3
Nitrate ions ($*10^3$ g/L)	3.2 ± 0.1
Dynamic viscosity ($*10^3$ Pa·s at 25°C)	1.9 ± 0.1
Density (kg/m^3 at 25°C)	1068 ± 1
pH	12.4 ± 0.1
Conductivity ($*10^{-3}$ µS/cm at 25°C)	27 ± 2

Chemical Oxygen Demand (g O_2/L)	113 ± 3
Evaporation rate ($*10^5$ kg/s·m^2)	113 ± 3
Dry matter (%)	13.0 ± 0.1
Gross Calorific Value ($*10^{-3}$ kJ/kg $_{dry\ matter}$)	14.1 ± 0.2

Table 2. Changes in the ashes of Kraft black liquor after applying wet oxidation during 120 min at 190 ºC and 70 bar.

Parameters	Initial Black Liquor	Wet Oxidised Black Liquor
Dry matter (%)	13.0 ± 0.1	11.7 ± 0.5
Ashes (%)	9.0 ± 0.1	8.3 ± 0.2
Na (mg/g black liquor)	14 ± 2	17 ± 1
S (mg/g black liquor)	1.2 ± 0.1	1.1 ± 0.2
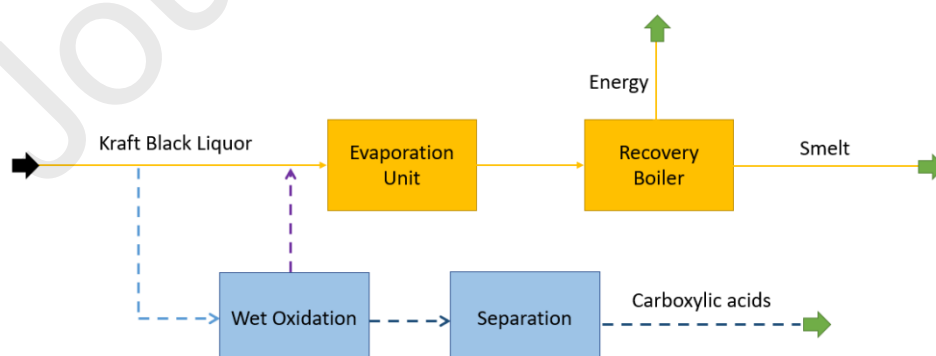
Highlights

- Kraft black liquor wet oxidation reduces sulphur and nitrogen gas emissions.

- Wet oxidation decreases black liquor viscosity up to 32%; reducing pumping costs.

- Wet oxidation generates a highly purified stream of carboxylic acids.

- Wet oxidation favours lactic and acetic acid formation and oxalic acid degradation.

- Gross calorific value per gram of carbon scarcely changes during the treatment.