



Kraft black liquor as a renewable source of value-added chemicals

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ABSTRACT

Around 1.3 billion tonnes of weak Kraft black liquor is produced every year, and is usually concentrated by evaporation and burned to produce energy. Nevertheless, this strategy implies that many valuable compounds of great industrial interest are destroyed. This article compiles the available information about valorising Kraft black liquor by obtaining chemical products. Although this topic is arousing interest, more research is needed, as only processes which have not yet been validated at industrial scale are described, except for lignin recovery. Due to the heterogeneity of the raw material, complex and integrated processes are being proposed to extract different existing and/or generated compounds. The most common approach is a first stage of lignin recovery by precipitation, followed by the use of the delignified black liquor to obtain principally organic acids, and/or as a fermentation medium, recirculating the by-product streams into the Kraft process to recover the inorganic salts.

1. Introduction

Currently, the Kraft process is the predominant method worldwide for producing pulp, employed in up to 90% of all pulp mills, due to its advantages over other pulping methods [1]. Mainly, these include obtaining stronger fibres, the ease with which it can be applied to all wood species and the recovery of the spent chemicals [2]. Basically, Kraft pulp manufacturing consists of four stages: wood preparation, pulping, bleaching and chemical recovery [3]. In more detail, the logs are firstly debarked and transformed into chips [2], which are subsequently digested with an aqueous solution (called white liquor) with 15–20% of sodium sulphide (Na_2S) and sodium hydroxide (NaOH) at high temperatures (145–170 °C) and pressures (6–7 bar) for 2–3 h [4]. During this step, the cellulose fibres (pulp) are separated from the solubilised compounds, which constitute a liquid fraction called weak black liquor [3].

The properties of Kraft black liquor depend on many factors, such as the feedstock employed (softwood, hardwood or non-wood) and the operational conditions used during the pulping stage [2,5]. However, all such liquors are alkaline aqueous solutions with a high organic load and viscosity and a dark black colour [6]. This stream comprises both organic (soaps, lignin, polysaccharides, phenolics, carboxylic acids...) and inorganic compounds (mainly, the pulping chemicals), with dry solids representing up to 15% [3–5,7]. Fig. 1 provides a summary of the typical compositions of Kraft black liquor.

Once the pulp is generated, it is bleached by chlorination and

oxidation processes in order to confer upon it the appropriate final properties for its further use, whereas Kraft black liquor is subjected to a chemical recovery process [2,3]. During this stage, black liquor is firstly concentrated up to, at least, 65% of solids and subsequently burned, thus obtaining energy and a molten smelt, rich in Na_2S and sodium carbonate (Na_2CO_3). These ashes are subsequently dissolved in water (called green liquor) and causticized with lime (CaO), so as to generate NaOH from Na_2CO_3 , Na_2S being inert. After this reaction, the resulting liquid is filtered to remove the lime mud that is formed (CaCO_3) and the liquid fraction, which is the regenerated white liquor, is recirculated to the digestion stage. Finally, the mud is washed and heated at high temperature to regenerate the spent CaO [3].

The recovery of the spent chemicals from Kraft black liquor is necessary to make the process profitable. However, this leads to some environmental and operational problems. One of the most important drawbacks is the formation of deposits and fumes of inorganic salts in evaporators and furnaces, causing an increase in the dead volume and the corrosion of the equipment, as well as a reduction in the heat transfer efficiency and net power generation [8–10]. Another problem is the emission of odorous and hazardous gases during the process, mainly caused by the release of sulphur compounds at the high temperatures reached during the regeneration [9]. Moreover, the necessary solid concentration of the black liquor to allow it to be burned more easily involves a significant increase in its viscosity, hindering its handling and favouring the blockage of pipelines and other process units [11]. It must also be stressed that incineration has a negative ecological perception

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owing to its potential for spreading dust, gases and hazardous compounds if the combustion is not complete and/or the emissions are not properly managed [12]. In addition, the recovery boiler is one of the bottlenecks of the process, limiting any desired increase in the production capacity of the pulp mills [13]. Besides the above, medium and small scale pulp mills and, especially, those located in developing countries and/or using non-wood materials as feedstock are often unable to implement a proper recovery process with enough capacity to treat all the black liquor generated during the pulping, resulting in the uncontrolled discharge of untreated black liquor into the environment [6,8,14,15].

But what is more important is that during the conventional process, high added value compounds are destroyed instead of being recovered, which is against the current waste management hierarchy and the concept of Circular Economy [15]. As an illustrative example, hydroxy acids represent one third of the dry matter of Kraft black liquor but their enthalpies of combustion are low, suggesting that their recovery would be a more profitable strategy than their complete oxidation, as is currently their fate [16,17].

For all these reasons, together with increasingly stringent environmental legislation, other approaches have been or are being developed as alternative strategies for the management of Kraft black liquor [18]. These new processes are mainly based on meeting standards of profitability, respect for the environment, efficiency and resource recovery, by turning pulp mills into biorefineries, where compounds contained in the black liquor stream are employed to generate other products of industrial interest, and not simply incinerated [1,19].

With this in mind, some authors have already reviewed some of the possible strategies of black liquor valorisation. Nevertheless, these reviews are only focused on specific types of treatments or products, mainly energetic ones. Moreover, they usually include different types of black liquor, not only that from the Kraft process, even when these feedstocks may have very different physicochemical properties from each other, making the extrapolation of results to Kraft black liquor difficult. Therefore, the aim of this study is to compile and discuss, for the first time ever, the available information dealing with alternative ways of valorising Kraft black liquor specifically, focusing in particular on those whose aim is to obtain high value-added products. Thus, this review gives a broader view of the current state of research, showing implementation possibilities and either strengths or weaknesses of the different approaches.

To provide the review with a clear and accessible structure, the studies have been classified, according to the type of treatment employed, into: direct use and physical, chemical, biochemical, thermochemical or electrochemical treatments (Fig. 2).

2. Direct use

The direct use of Kraft black liquor, without any appreciable treatment, has been subject to research for different purposes (Table 1).

Durmaz et al. [20] analysed the effectiveness of using Kraft black liquor as a substitute for copper-based chemical wood preservatives. After impregnating Scots pine sapwood (one of the feedstocks in the pulp mill from which the black liquor was taken) with different solutions of black liquor (2.5, 5.0 and 7.5% of Kraft black liquor), it was found that black liquor inhibited fungal activity, particularly, that of *Coniophora puteana* and *Poria placenta*, resulting in wood mass loss of <3%, compared to almost 30% without impregnation. The authors reported the best antifungal effects using a black liquor concentration of 5.0%.

Another alternative, proposed by Ribeiro et al. [21], was the direct use of Kraft black liquor to coat phosphorous fertilisers in order to obtain slow-release fertilisers. For this purpose, commercial monoammonium phosphate was sprayed with a solution of dried Kraft black liquor (remaining solids after the complete removal of water) in water (1:10 w/v) at different coating rates (0.5, 1.0 and 2.0 wt%). During the process, the temperature was maintained at 100–120 °C, so no further drying was required. The coatings thus obtained were found to control the phosphorus release, with this being slower as the coating concentration increased.

However, despite the simplicity of these proposals, black liquor is composed of many compounds that are of industrial interest or that can be decomposed into more valuable substances. Due to this, it is most common to treat Kraft black liquor in order to recover these compounds, as well as to reduce the polluting capacity of the residual phase that may remain.

3. Physical treatments

The physical processes here discussed include methods of fractionation, separation, extraction and/or purification of valuable compounds from Kraft black liquor (Table 2).

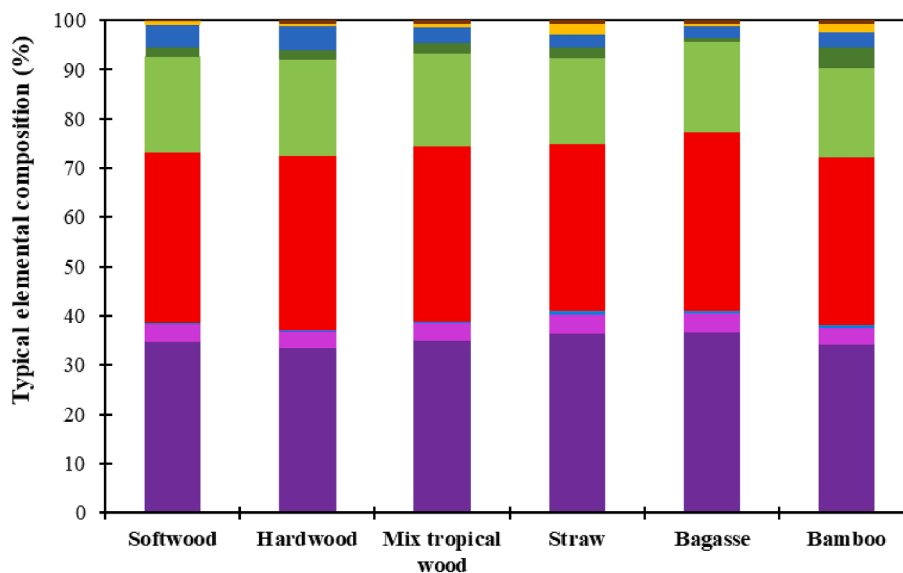


Fig. 1. Typical elemental composition of Kraft black liquor depending on the feedstock (C (purple), H (red), N (blue), O (green), Na (light green), K (dark green), S (yellow), Cl (orange) and inerts (brown)), adapted from Bajpai [2].

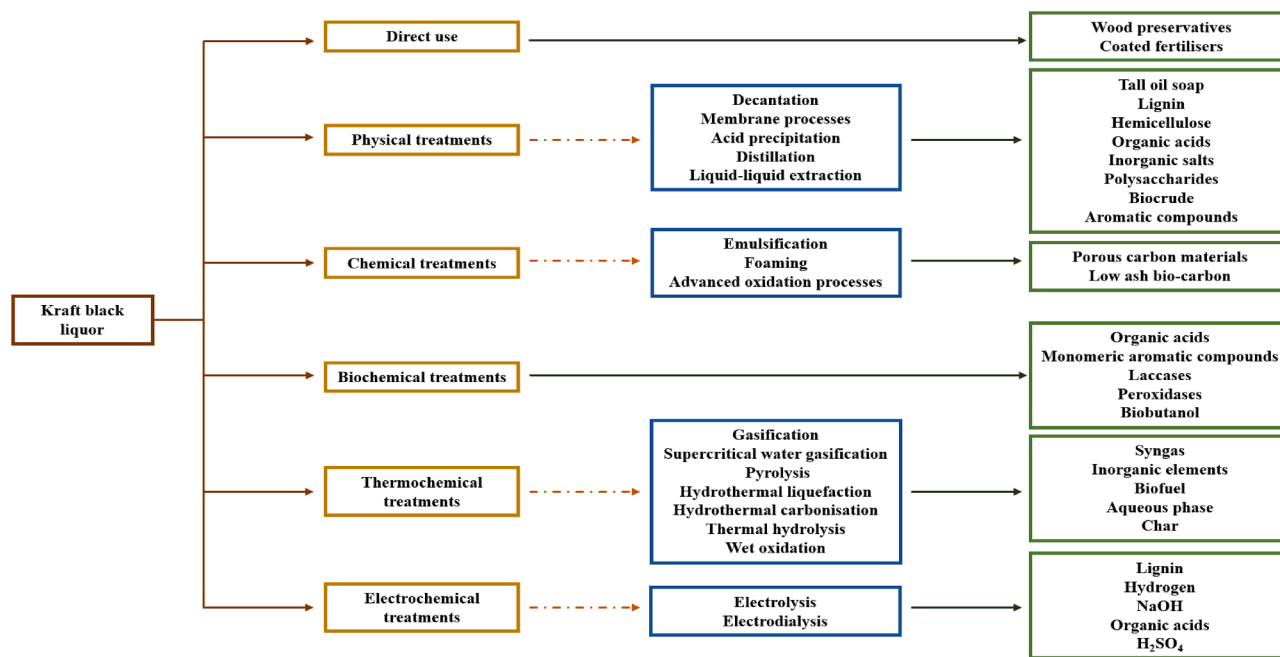


Fig. 2. Alternative treatments for the revalorisation of Kraft black liquor.

Table 1
Direct use of Kraft black liquor.

Treatments	Main operational parameters	Products	Comments	References
Direct use	–	Wood preservatives Coated fertilisers	Fungal activity inhibition Phosphorus release control	[20–21]

3.1. Decantation

Decantation is generally recognised as the simplest method for separating compounds. In this context, special attention has been paid to obtaining tall oil soap from Kraft black liquor, especially when softwood is the feedstock, via decantation. In fact, Aro and Fatehi [22] wrote a review about this topic.

Tall oil soap consists of a mixture of mainly sodium salts of fatty and rosin acids and neutral extractives, but also contains other wood constituents present in the Kraft black liquor. From this, crude tall oil, composed of 38–53 wt% saponified fatty acids, 38–53 wt% rosin acids and 6.5–20 wt% unsaponified compounds, is usually formed after an acidulation process of this soap with concentrated sulphuric acid. This product can be used as a fuel without being purified or as a feedstock to produce biodiesel or other commercially refined products [10,22].

As tall oil soap has a lower density than Kraft black liquor and becomes insoluble for solid concentrations higher than 20% (wt), the current commercial process includes a settling and skimming stage for its separation from partially concentrated black liquor (20–30 wt% of solids). However, between 20 and 40% of this soap fraction is wasted during this process because it remains soluble. For this reason, some alternatives, designed to improve decantation efficiency, have been investigated (see Fig. S.1 in the Supplementary Material) [22].

For example, the addition of a polyoxypropylene-polyoxyethylene polymer, with molecular weights ranging from 1,000 to 16,000 g/mol, increased the recovery yield of tall oil soap by around 10% due to the hydrophilic interactions between polymer and soap. Another option to

improve tall oil decantation was the addition of insoluble colloids prior to the partial concentration of black liquor by evaporation in the conventional Kraft process scheme. In this regard, the use of beta-sitosterol as colloid involved the transformation of the soap micelles into liquid crystals, with fast agglomeration behaviour and easy separation at the first decantation. After this, the black liquor can follow the traditional tall oil soap recovery method, obtaining another tall oil fraction that can be mixed with the first one [22].

The purity of the soap obtained can also be enhanced by washing the decanted tall oil soap with an alkaline solution containing Na_2SO_4 (using the spent acid from the further production of crude tall oil, neutralised with NaOH). After a subsequent second decantation, an aqueous alkaline waste with lignin and CaSO_4 (the main tall oil impurities) was removed, minimising their further precipitation during the production of crude tall oil [22].

3.2. Membrane processes

Among the different physical methods, membrane separation processes are one of the most frequently employed, because they allow the Kraft black liquor compounds to be fractionated by means of different membrane cut-offs (Fig. 3).

Its simplicity of operation, the low energy consumption, the ease of change of scale and the possibility of obtaining a stream purer in high added-value products also explain why membrane processes constitute one of the most intensively studied alternatives for the management of Kraft black liquors [23]. Particularly, membrane operations are mainly aimed at separating Kraft lignin, as it is the most abundant compound in Kraft black liquor and can be used as raw material for producing a wide range of valuable products [24]. However, the concentration of black liquor by membranes is not only employed for this purpose, but also to decrease the load of the boiler and to reduce the operating costs of the conventional incineration process for the regeneration of Kraft reagents [7]. For these reasons, much research has been done and there are reviews dealing with the treatment of Kraft black liquor with membranes (see [7,23,24]).

Kraft black liquor filtration studies include microfiltration (MF), ultrafiltration (UF) (the most common), nanofiltration (NF) and reverse osmosis (RO) [7]. Obviously, lower cut-offs allow a purer permeate to be

Table 2
Physical treatments of Kraft black liquor.

Treatments	Main operational parameters	Products	Comments	References
Decantation	Partially concentrated black liquor (20–30 wt% of solids)	Tall oil soap	Raw material for crude tall oil production by acidulation process Additives (polymers or insoluble colloids) increase the recovery yield Washing with an alkaline solution improves the soap purity	[22]
Membrane processes	Ceramic and polymeric membranes Types: microfiltration (100–5,000 kDa), ultrafiltration (15–400 kDa), nanofiltration (0.1–20 kDa) and reverse osmosis (<0.8 kDa)	Lignin Hemicellulose Organic acids Inorganic salts	Ultrafiltration is the most common method Higher cut-offs produce retentates purer in lignin and hemicelluloses Ceramic membranes withstand better the black liquor properties Combining physicochemical methods separates more valuable compounds Strong acids are commonly used	[7,23–28]
Acid precipitation	Acidifying agents: CO ₂ , H ₂ SO ₄ , HCl, HNO ₃ , H ₃ PO ₄ , CH ₂ O ₂ , C ₂ H ₄ O ₂ , C ₆ H ₈ O ₇ , C ₃ H ₆ O ₃ .	Lignin Aliphatic acids Polysaccharides	CO ₂ produced easily filtered lignin Acetic acid is a suitable green acidifying agent The lower the pH, the higher the recovery but the lower the purity Temperature changes lignin stability Adding metal cations at alkaline pH improve the lignin yield Volatile acids are released from their sodium salts	[2,13–14,25,29–46]
Distillation	Pre-treatments: acid precipitation, catalytic esterification Pressure: 0.067–0.173 kPa	Volatile fatty acids Non-volatile hydroxy acids	Previous delignification is frequently required Direct volatile fatty acid recovery Further catalytic esterification of non-volatile hydroxy acids High molecular weight hydroxy acids are recovered as bottom products Low molecular weight hydroxy acids are recovered as top products in form of esters Hydrolysis of esters is required to obtain the corresponding acids	[16–17,47]
Liquid-liquid extraction	Solvents: OP(C ₈ H ₁₇) ₃ in alkanes, C ₂₄ H ₅₁ N and C ₁₂ H ₂₇ O ₄ P with or without alkanes, C ₆ H ₁₄ , C ₄ H ₈ O ₂ , (C ₂ H ₅) ₂ O, CH ₂ Cl ₂ , C ₃ H ₆ O, C ₄ H ₁₁ NO ₂ , C ₃ H ₆ O ₃ :C ₅ H ₁₄ ClNO (11:1 M ratio).	Biocrude Organic acids Aromatic compounds Lignin	Organic solvents extract a wide range of organic compounds Green solvents extract lignin Removal of inhibitory compounds for subsequent fermentation processes	[48–55]

obtained, but at the expense of higher fouling rates and operation costs [7,25]. As an example, Costa et al. [26] fractionated Kraft black liquor using 5, 15 and 50 kDa tubular ceramic membranes, reporting significant differences in the composition of the different retentates. As expected, the membrane with the lowest cut-off generated lignin with the

highest content (>50%) of impurities, mainly carbohydrates and inorganics, while the purest lignin was obtained using the membrane with the highest cut-off. With respect to the membrane materials, both polymeric and ceramic membranes have already been implemented at pilot and, even at commercial scales. Nevertheless, the ceramic

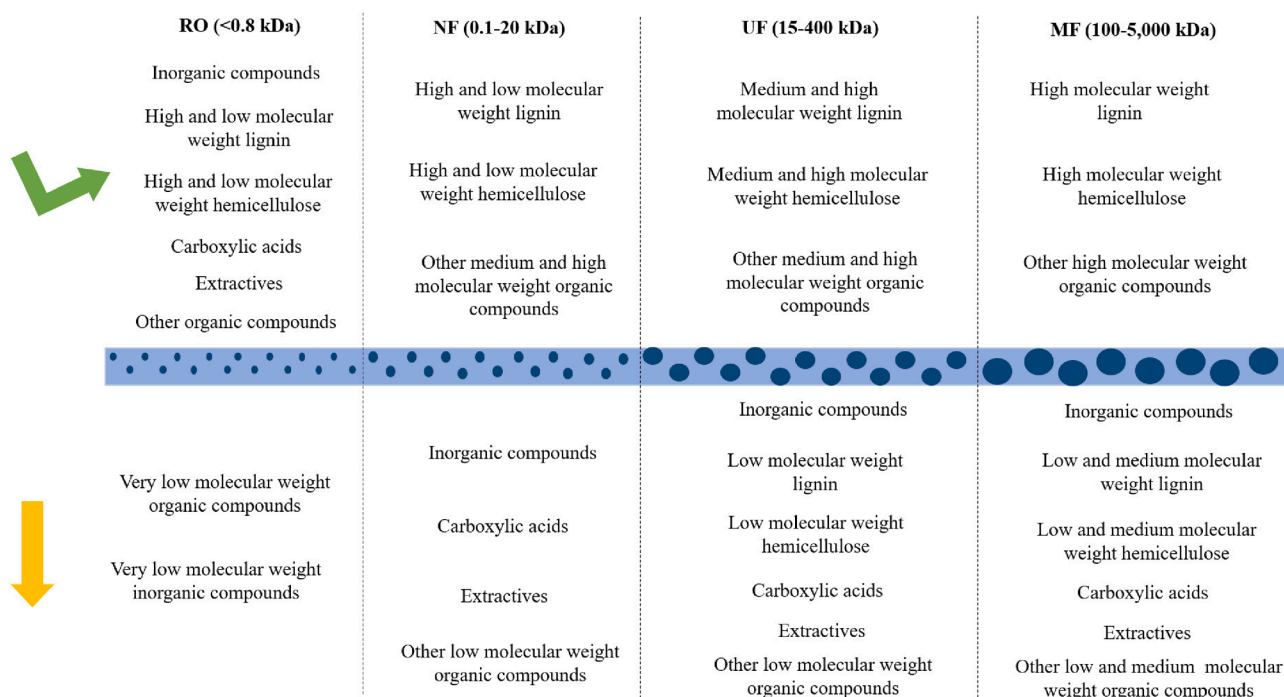


Fig. 3. Separation of Kraft black liquor components based on their molecular weight and the membrane cut-offs, adapted from Kevlich et al. [7].

membranes are preferred because of their higher chemical and thermal resistances, which implies that Kraft black liquor ($T \approx 150\text{ }^\circ\text{C}$, $\text{pH} \approx 14$) can be directly filtered without being cooled and/or pre-treated [23]. More detailed descriptions and summaries dealing with types of membranes and common operating conditions can be found in the reviews of He et al. [23] and Kevlich et al. [7].

Not only can lignin be recovered from Kraft black liquor by membrane separations, but also the purification of carboxylic acids and hemicelluloses, among others, is gaining importance, although there is still very little research. For these purposes, membrane separations are frequently combined with other physicochemical methods to simultaneously obtain valuable compounds, such as aliphatic carboxylic acids [7,17,23,27]. In many of these coupled processes, the acid precipitation of Kraft lignin with CO_2 is carried out before the membrane separation in order to purify lignin and hemicelluloses (see Section 3.4). Then, RO filtration of the resulting liquid phase would be necessary to separate small organic acids and/or inorganic salts, with the latter being reused during the cooking stage [7,23]. Thus, Mänttari et al. [27] and Niemi et al. [28] followed a similar approach, studying a 4-stage integrated process to separate and purify Kraft lignin and organic acids at the same time, based on a sequence of ultrafiltration, acidification, cooling crystallisation and nanofiltration (see Fig. S.2 in the Supplementary Material). Thus, according to Mänttari et al. [27], 75% of the total lignin was retained during the first ultrafiltration step, increasing the acid concentration from 21% to 33% of total dissolved solids in the permeate at the same time. Lignin remaining in the permeate was also recovered by precipitation with sulphuric acid ($\text{pH} = 2$). By a subsequent cooling ($-4\text{ }^\circ\text{C}$) of the delignified liquid fraction, around 50–70% of the inorganic salts were also recovered by crystallisation. Lastly, the nanofiltration of the final liquid fraction under acidic conditions resulted in the retention of between 70% and 80% of the remaining sulphates, as well as other inorganic and phenolic compounds, while most of the acids were able to pass the membrane. By means of this strategy, a final stream with an acid purity of 80% and only 2% of phenolic compounds was achieved. Mänttari et al. [27] even proposed a final adsorption step using commercial resins to remove 70% of these residual phenolic compounds from the final permeate.

3.3. Acid precipitation

Acid precipitation consists in lowering the pH of black liquor to values ranging from 9 to 2, which provokes the precipitation of lignin, and is the most widespread technique for extracting Kraft lignin. In fact, LignoBoostTM and LignoForce SystemTM are processes with acid precipitation as the main stage which have already been implemented at industrial level [14,29–31]. This technology is promising because the extraction of part of the lignin before combustion reduces the heat load of the recovery boiler, leading to a possible increase in pulp production [13].

By means of acid precipitation, up to 90% of the total Kraft lignin can be easily separated from the liquid by centrifugation, with an easy, low-energy technique. However, the properties and composition of Kraft lignin depend on the acid employed during the acidification. In fact, lignin precipitated with sulphuric acid contains Na_2SO_4 salts, whereas NaCl is the main salt when hydrochloric acid is used. It is interesting to note that, although hydrochloric acid reduces the yield of precipitation, it increases the purity and the average weight of the Kraft lignin in comparison to that obtained by acidification with sulphuric acid [32]. To make the process more cost-effective, Howell and Thring [33] analysed the implementation of an acid precipitation stage for Kraft lignin using the waste sulphuric acid from the chlorination stage to lower the pH of a hardwood Kraft black liquor (37 wt% of solids) from 12 to 8. In fact, after the lignin filtration stage, this could be washed with diluted sulphuric acid to reduce its sodium content, thus improving its potential as a fuel source. These authors also proposed the recirculation of the resulting non-lignin fraction to the conventional black liquor recovery process without any further treatment if only a small part of the total liquor stream was used to obtain lignin.

A common strategy is to carry out a first stage of precipitation with carbon dioxide until pH values of around 9 are reached, followed by a second one with a strong acid to continue the acidification to the desired pH [25]. The use of CO_2 as an acidifying agent obtains higher precipitation yields than with strong acids due to the low impact on the sodium-sulphur balance of Kraft black liquor, resulting in a lignin that can be filtered more easily [25]. In this context, LignoBoostTM and LignoForce SystemTM are processes that have already been implemented in the pulp

industry to separate Kraft lignin from black liquor, combining acid precipitation by carbon dioxide and membrane separation (see Fig. S.3 in the Supplementary Material). These processes are quite similar, with the only difference that the LignoForce SystemTM introduces a preliminary liquor oxidation stage to improve the black liquor filterability and minimise the emission of reduced sulphur compounds (TRS) (see Section 6.2 for more detailed information about wet oxidation treatments). In both cases, black liquor, previously oxidised or not, is subjected to a stage of acid precipitation by sparging carbon dioxide at 70–75 °C until pH = 9.5–10. Afterwards, lignin is filtered and the filter cake redispersed, acidified with sulphuric acid and washed. The lignin thus obtained contains 60–70% of total solids and a maximum of 0.7% of ash [2,31,34,35]. A variation on these methods, called the Sequential Liquid Lignin Recovery and Purification process (SLRPTM process), was patented by Lake and Blackburn [36]. It consists in lowering the pH to 9–10 with CO₂ at elevated temperature and pressure to separate the lignin by gravity as a dense liquid, which is further acidified to a pH of 2–3 with sulphuric acid.

It should be also pointed out that, at an industrial scale, the selection of other acids different from sulphuric acid and CO₂ could produce undesired compounds and cause higher corrosion of the equipment [33]. However, in order to make the precipitation process greener, other compounds or streams have also been evaluated as acidifying reagents. Namane et al. [37] analysed the differences between hardwood and softwood Kraft lignin precipitated with sulphuric acid or with different organic acids (formic, acetic and citric acid). Results revealed that the lowest sulphur contents were obtained by carrying out the precipitation with organic acids, especially when softwood black liquor was used. The only exception was when hardwood lignin was precipitated with formic acid, with the sulphur content being higher than that obtained with sulphuric acid. However, the presence of ashes in the precipitated lignin was higher using any organic acid than with sulphuric acid. Moreover, lignins obtained with sulphuric or formic acid were more susceptible to thermal decomposition, even when all of them presented similar functional groups. Kamble and Bhattacharyulu [38] compared the precipitation of Kraft hardwood and bamboo lignins with hydrochloric, nitric, orthophosphoric or acetic acids. Results showed that the higher the number of carbons of the acidifying agent, the higher the yield of lignin recovered; nitric acid being discarded because of the formation of dense fumes. Thermal stability did not follow this pattern, with the least stable lignin being obtained with orthophosphoric acid and the most stable with acetic acid. Da Silva et al. [14] also assessed the effectiveness of acetic, lactic and citric acids as precipitating agents for lignin recovery. The authors reported that lignins obtained by means of these organic acids were purer (lower ash and carbohydrate contents), with high antioxidant activity, but less thermally stable (except for that precipitated with acetic acid) than that obtained by conventional precipitation with sulphuric acid. Comparing organic acids with each other, lignin purities were similar for the three acids, although acetic or citric acids resulted in lignin with a better filterability. Moreover, the stronger the organic acid used, the lower the thermal stability of the lignin [14].

The most important determining factor in this technique is the pH, affecting the quantity recovered, the purity and the molecular weight of the lignin. In terms of lignin production, the lower the pH, the higher the recovery yield. However, the drawback of recovering Kraft lignin after lowering the pH to acidic values is the low quality of the product obtained due to the presence of impurities [14,25,30,39]. With a view to overcoming this difficulty, some researchers carried out a fractionation of lignin by means of gradual changes of pH, reporting that high molecular weight lignin precipitates at higher pH values than that with low molecular weight [30,40]. Thus, Velez and Thies [41] extracted different lignin fractions from softwood Kraft black liquor by varying the pH in steps of 0.5 points between 13.6 and 9.5 and using carbon dioxide at 115 °C and 6.2 bar as the acidifying reagent. The results showed that the different hydrated lignin phases thus obtained had low softening and melting points. Specifically, lignin obtained at pH = 11.1 contained the

lowest sodium, potassium, sulphur and metal contents in comparison to the feedstock. Alekhina et al. [42] also fractionated softwood Kraft lignin by means of a sequential precipitation with sulphuric acid, extracting lignin at pH values of 10.5, 5 and 2.5. In a similar way, Lourençon et al. [30] separated both softwood and hardwood Kraft lignin with hydrochloric acid at pH values of 9,7,5,3 and 1. Although the results varied depending on the type of wood, both studies stated that the more acidic the medium, the lower was the Kraft lignin purity due to the simultaneous carbohydrate precipitation.

Regarding the effects of other operating conditions, temperature has less influence on this process than pH, since it only affects the recovery yield. Its effect was studied especially between room temperature and 80 °C, with the authors concluding that it depends on the pH reached [43,44]. For alkaline pH values (>9), the precipitation yield is lower at higher temperatures due to the increase in lignin solubility [43]. On the contrary, at lower pH values, higher temperatures accelerate the protonation of the solubilised lignin, which destabilises the solution and increases the lignin recovery. Moreover, for the same pH value, it has also been reported that the higher the temperature, the greater the condensation of lignin fragments, which produces the precipitation of higher molecular weight lignin [44]. It is also noticeable that a tar-like substance is formed at temperatures higher than 80 °C [33].

Apart from this, increasing the concentration of metal cations is another adjustment that can improve the recovery yield of Kraft lignin at alkaline pH. In fact, Sundin and Hartler [45] studied the influence of Na⁺, Mg²⁺, Ca²⁺ and Al³⁺ on the precipitation of Kraft lignin by adding each of them in the form of the corresponding chloride. After adjusting the pH with HCl, it was found that all of them produced the precipitation of lignin at pH = 9, with the required concentration of these cations to precipitate Kraft lignin decreasing as their valency increased. At higher pH values, only the divalent cations produced a noticeable precipitation.

Although acid precipitation is mainly focused on obtaining lignin, it can also be applied for the recovery of other biomolecules with high added value. In this regard, this procedure favours the further recovery of aliphatic acids by releasing them from their sodium salts, which are not employed at an industrial scale [17]. Moreover, poly- and oligo-saccharides can also be selectively extracted from Kraft black liquor by acidification but using other solvents to keep almost all lignin in the solution. Following this line of research, Lisboa et al. [46] acidified a mixture of 1,4-dioxane:Kraft black liquor (2:1 v/v) with acetic acid until pH = 2–3. Then, the precipitate was washed sequentially with 1,4-dioxane, methanol and acetone and finally, vacuum dried with phosphorus pentoxide. They recovered around 20% of the initially dissolved wood saccharides, which were essentially xylan and amylopectin, in the form of oligo- and polysaccharides. The purified precipitate clearly had a very low lignin content, as could be inferred from its high neutral monosaccharide content (80–90 wt%), of which 82 wt% was xylose, 10 wt% glucose and 6 wt% galactose, approximately.

3.4. Distillation

Kraft black liquor distillation is used after lignin recovery and leads to the separation of volatile fatty acids, while non-volatile hydroxy acids need further transformations. [47]. Thus, Kumar and Alén [17] reported that after the acid precipitation of the lignin (see Section 3.3), volatile acids, which represented roughly 50% of the total acids, can be recovered by evaporation. After the removal of sodium sulphate from the bottom fraction by precipitation with methanol, low-molecular-mass hydroxy acids, which constitute around 15% of the total acids, can also be recovered by means of a catalytic esterification, with yields ranging from 70% to 86% of the theoretical ones, followed by vacuum distillation, thus obtaining their volatile methyl esters as top products. In this way, after both distillations, the final bottom stream was mainly composed of high-molecular-mass hydroxy acids (35% of the total acids) (see Fig. S.4 in the Supplementary Material).

This technique has scarcely been applied to black liquor because of

the closeness of the boiling points of the different organic acids and the required esterification. Moreover, a further hydrolysis is necessary to transform the recovered esters into the corresponding acids [47]. However, it should be taken into account that the organic acid mixtures obtained can be used without separating them from each other. For example, Mehtiö et al. [16] demonstrated that copolymers could be obtained by a catalytic melt condensation copolymerization of a mixture of glycolic, lactic and 2-hydroxybutyric acids, which are low-molecular-mass hydroxy acids present in the top stream of the distillation.

3.5. Liquid-liquid extraction

Liquid-liquid extraction is another technique used to separate a wide range of valuable compounds from Kraft black liquor by means of the selection of different organic or inorganic solvents. This technique not only allows the recovery of compounds of interest, but also improves the biodegradability of the delignified Kraft black liquor.

Focusing firstly on using organic solvents, Kalu and Andresen [48] employed hexane for extracting the organic fraction (biocrude) from Kraft black liquor. These authors analysed the effect of certain operating conditions (chip particle sizes and cooking times) of the Kraft cooking stage on the subsequent biocrude extraction from the black liquor generated. Results revealed that both small particle sizes and short cooking times improved the percentage of extractable biocrude from the liquor.

Both Kwon and Um [49] and Kim et al. [50] analysed the extraction of bioethanol fermentation inhibitors from delignified Kraft black liquor using tri-*n*-octylphosphine oxide (TOPO) 37% (w/w) diluted with an alkane, with the goal of improving the quality of the aqueous fraction to be used as the fermentation medium. Kwon and Um [49] proved that the lower the initial pH value of the delignified Kraft black liquor, the higher the recovery of aliphatic acids and aldehydes during the extraction with TOPO, while aromatic acids and sugars were not affected by this parameter. These authors also reported that the optimal temperature for extracting formic, acetic and lactic acids was 25 °C. In fact, under the best conditions of pH (0.5) and temperature (25 °C), compounds such as fumaric acid, gallic acid, vanillic acid, 4-hydroxybenzoic acid or furfural were completely extracted. In contrast, only 10% of sugars (glucose + xylose + arabinose) were extracted under the same conditions. Moreover, 53% of D-lactic acid, 60% of DL-lactic acid, 70% of acetic acid, 65% of formic acid, 76% of methyl malonic acid, 98% of 2-furoic acid and 85% of syringaldehyde were recovered in the organic phase as well. To recover compounds from the organic phase, simultaneously regenerating the solvent for subsequent extractions, a distillation stage was suggested. Kim et al. [50] followed a similar procedure and operational conditions to Kwon and Um [49], but using delignified Kraft black liquor pre-concentrated 1, 5.5 or 10 times by evaporation. It was found that the higher the pre-concentration of the feed, the lower the extraction yields. As in the previous study, sugars (glucose + xylose + arabinose) were poorly extracted and the previously explained effects of pH and temperature on the extraction were corroborated. It was also reported that the extraction time was not a determining parameter.

Navas et al. [51] tested different organic solvents (ethyl acetate, diethyl ether, dichloromethane and acetone) in order to obtain monoaromatic compounds from delignified Kraft black liquor by the Ligno-force™ method for subsequent fermentation (see Section 5). Results corroborated that the higher the solvent polarity was, the higher was the extraction yield. Acetone proved to be the most effective solvent in terms of recovery, followed by ethyl acetate, dichloromethane and finally, diethyl ether. The extraction yields of phenolic compounds (mainly guaiacol, vanillin and acetovanillone) ranged from 19 to 35%.

Núñez et al. [52] carried out a deeper screening of solvents for the recovery of short-chain organic acids from the ultrafiltration permeate of either raw, wet oxidised (190 °C, 70 bar and 120 min) or delignified Kraft black liquor. To this end, three different extractants (trioctylamine (TOA), tributylphosphate (TBP) and trioctylphosphine oxide (TOPO)),

diluted with different percentages (0–30%) of heptane or hexane, were tested at temperatures between 25 and 55 °C. Results showed that the higher the temperature, the higher the extraction yield. Regarding the effect of the extractant, the complexity of the samples led to intricate complexation mechanisms, so a general trend was not possible to obtain. On the basis of the extraction yields and the economic balance, 30% TOA 70% heptane was chosen as the best solvent. As for the extraction raw material, either of the pre-treatments of Kraft black liquor prior to ultrafiltration and liquid–liquid extraction resulted in higher organic acid recovery yield and lower operating costs, since these compounds were purer in the matrix.

Some new-generation solvents are also gaining importance because they are suitable for extracting Kraft lignin [53,54]. In this area, Saadat [55] performed Kraft lignin extractions from black liquor by means of several protic ionic liquids (PIL) and hydrophobic deep eutectic solvents (DES). After testing several solvents, authors reported that ethanollammonium acetate and lactic acid:choline chloride were the best PIL and DES, respectively, for lignin recovery, with yields of 75 and 79%. Finally, it was proved that both solvents can successfully be reused after being regenerated by vacuum distillation.

4. Chemical treatments

The chemical treatments here discussed include emulsification and advanced oxidation processes applied to Kraft black liquor (Table 3).

4.1. Emulsification and foaming

Kraft black liquor has also been studied as a feedstock for the production, by means of emulsification and foaming processes, of porous carbon materials to be used as adsorbents, catalyst supports, electrodes or capacitors, among other applications [56].

Foulet et al. [56] obtained porous polymers synthesised within high internal phase emulsions (PolyHIPes) by emulsification of black liquor with 1,2-dichloroethane and Pluronic F108, employing epichlorohydrin as the crosslinking agent. 1,2-dichloroethane was chosen on the basis of previous studies because it showed better recyclability and energy efficiency than castor oil [57]. Carbon foams (carbonHIPes) can be obtained by thermal treatment of the PolyHIPes at high temperatures (900 °C) and under inert atmospheres. CarbonHIPes thus synthesised showed specific surface areas between 500 and 1000 m²/g and micropore volumes between 0.3 and 0.5 cm³/g. The electric conductivity of the material can be increased by means of a second thermal treatment at higher temperatures (1,300 °C), thus making the material suitable for its application in the field of energy storage [56].

Highly porous carbon foams were also obtained by whipping air into Kraft black liquor in presence of a crosslinker (epichlorohydrin) and a surfactant (Hypermer 1083), followed by a pyrolysis of the lignin foams at 1,000 °C. This final product had an interconnected macropore structure with up to 88% porosity [58].

Macroporous polymeric monoliths with good thermal and sound insulation properties can be prepared from a mixture of Kraft black liquor, tannins, hexamine as the curing agent and other additives (adipic acid, phthalic acid and 1,8-octanediol) at low temperatures (85 °C). Results revealed an optimum percentage of black liquor (12 wt%) in the formulation to improve the mechanical and thermal properties of the final foam [59].

Other black liquor-based formulations to produce carbon materials have been tested as well. Thus, Amaral-Labat et al. [60] mixed Kraft black liquor with resorcinol, Ni(NO₃)₂·6H₂O and formaldehyde, with these acting as co-monomer, catalyst source and crosslinker, respectively. After a sequential procedure of hardening, curing, drying and pyrolysis, a final physical activation with CO₂ was necessary. The resulting material had a micro-mesoporous structure and electrocatalytic stability. Moreover, after the electrochemical characterisation carried out by the authors, it was proved to be a competitive Ni-based

Table 3
Chemical treatments of Kraft black liquor.

Treatments	Main operational parameters	Products	Comments	References
Emulsification and foaming	Emulsifying and crosslinking agents: C ₂ H ₄ Cl ₂ , Pluronic F108, C ₃ H ₅ ClO, CH ₂ O. Additives: C ₆ H ₁₂ N ₄ , C ₆ H ₁₀ O ₄ , C ₈ H ₆ O ₄ , C ₈ H ₁₈ O ₂ , Tween 80, Hypermer 1083, Ni (NO ₃) ₂ ·6H ₂ O, C ₆ H ₆ O ₂ .	Porous carbon materials	Porous carbon products require curation and thermal activation by pyrolysis Use as adsorbents, catalyst supports and electrodes	[56–60]
Advanced oxidation processes	Oxidising agent: H ₂ O ₂ .	Low ash bio-carbon	Use as biofuel because of its high heating value Use as bio-material because of its composition of C, N and other valuable compounds	[61–62]

electrocatalyst support for electrooxidation processes in terms of performance (ethanol oxidation current density similar to that reported in the literature) and production cost.

4.2. Advanced oxidation processes

Advanced oxidation processes are those based on the addition of oxidising agents, such as Fenton reagent, H₂O₂, O₃, UV light or HClO, alone or combined, to form hydroxyl radicals that react with the pollutants. These treatments occur at temperatures between 20 and 80 °C, and at the higher end of this temperatures range the reaction rate was faster and the degradation better in most cases [61].

These techniques are usually aimed at reducing the polluting capacity of Kraft black liquor and there is hardly any research focused on chemical valorisation. In this regard, only Al-Kaabi et al. (2020) [62] proposed an advanced oxidation process using H₂O₂ oxidation to obtain a low ash bio-carbon from dried Kraft black liquor. The solid fraction obtained (biocarbon) is suitable for use as biofuel because of its high heating value (25 MJ/kg), or as bio-material due to its content in nitrogen (0.6 wt% dry basis) and carbon (60 wt% dry basis) and the presence of other high added-value materials like aromatic compounds.

5. Biochemical treatments

Biochemical treatments revised in this Section include those in which Kraft black liquor, after being pre-treated or not, is subjected to a biotransformation by specific microorganisms with the aim of producing high added value metabolites (Table 4). At this point, it should be mentioned that there is little research on its microbial flora because not many microorganisms can withstand the extreme conditions of black liquor [63]. In fact, *Paenibacillus* has been isolated from Kraft black liquor to be used to ferment a medium rich in birchwood xylan, obtaining xylanase as the main metabolite [63,64].

The use of biochemical treatments to valorise black liquor components has been of interest for a long time due to its sugar and lignin

content [65]. For example, Potvin et al. [66] used heavy Kraft black liquor as a substrate to produce citric acid with the yeast *Candida tropicalis* ATCC 20240. Nevertheless, prior to its use, Kraft black liquor had to be delignified, diluted to about 10% of solids and supplemented with phosphorus and magnesium salts. For these conditions, the citric acid yield was around half of the maximum theoretical yield, similar to those obtained using a synthetic acetate medium. However, the presence of other organic acids in the black liquor reduced the acetate uptake and product formation rates, in comparison to the synthetic medium. The authors also suggested that better yields could be obtained if the nitrogen content of black liquor was reduced.

Analysing more recent studies, microorganisms producing laccases and peroxidases have been used as well, in order to depolymerise lignin from Kraft black liquor to produce valuable monomeric aromatic compounds (organic acids, aldehydes and alcohols, among others), reducing at the same time the organic matter content and the colour intensity of the black liquor [67]. This approach was followed by Paliwal et al. [68], who simultaneously cultured *Bacillus megaterium* ETLB-1 and *Pseudomonas plecoglossicida* ETLB-3 in Kraft black liquor at pH = 8, reporting noticeable activities (7–9 U/mL) of laccase and manganese and lignin peroxidases after 96 h. These enzymes caused the degradation of most of the initial lignin (92%) and chlorophenols (91%), forming different compounds of commercial interest, such as ferulic and cinnamic acids.

It is also interesting to point out that some Kraft black liquor fractions, apart from lignin, can also be subjected to biochemical treatments after being separated. Thus, some researchers have fermented Kraft hemicellulose to produce compounds such as ethanol and butanol. As in the case of carboxylic acids, hemicellulose has a low heating value, so its direct conversion into energy is not recommended [69]. In this regard, Kudahettige-Nilsson et al. [70] used as feedstock the filter cake (50–60% of solids) from birch Kraft black liquor, obtained after the CO₂ acidification and filtration stages of the LignoBoost™ process, a substance which is rich in xylan and lignin. After a hydrolysis with hot sulphuric acid in order to precipitate the lignin and a detoxification stage with active carbon for removing inhibitors (phenolics, hydroxymethylfurfural...), this fraction was anaerobically inoculated with *Clostridium acetobutylicum* ATCC 824, obtaining a biobutanol production of around 2 g/L (see Fig. S.5 in the Supplementary Material). However, these yields, although promising, were notably lower than those obtained with other substrates, such as xylene, arabinose or glucose. Therefore, the authors proposed that other pre-treatment methods be performed to minimise the formation of inhibitors before fermentation, thus increasing the production of bioethanol. A similar process was performed by Faisal et al. [71] in order to test a subsequent selective recovery of butanol from the broth using a commercial adsorbent (high-silica MFI zeolite). Results demonstrated that this material was very selective in adsorbing butanol, the co-adsorption of other compounds being minimised at pH = 8.

Finally, as previously explained, both extract and raffinate fractions obtained after the liquid–liquid extraction of delignified Kraft black liquor (Section 3.5) are also suitable for use as fermentation media for different microorganisms. Navas et al. [51] used the extracts obtained after the liquid–liquid extraction of aromatic compounds from delignified Kraft black liquor to test their toxicity on different microorganisms that grow on at least one of the major aromatic compounds in Kraft black liquor. After evaporating the solvents and being resuspended in dimethyl sulfoxide, extracts were added until a total aromatic concentration of 1 mM to the Lysogeny broth (LB broth). Results demonstrated that the higher the polarity of the solvents, the lower the toxicity of the extracts, with the acetone extract being the least inhibitory. All the extracts supported the growth of *Pseudomonas putida* KT2442 and *Sphingobium* sp. SYK-6, whereas they inhibited *Rhodococcus jostii* RHA1 and *Rhodococcus opacus* PD630. *Rhodococcus rhodochrous* EP4, GD01 and GD02 had long lag phases with acetone extract but their growth was inhibited by the rest of the extracts [51]. In addition, other solvents, like TOPO, have proved to be effective for extracting phenolic compounds,

Table 4
Biochemical treatments of Kraft black liquor.

Treatments	Main operational parameters	Products	Comments	References
Fermentation	Microorganisms: <i>Candida tropicalis</i> ATCC 20240, <i>Bacillus megaterium</i> ETLB-1, <i>Pseudomonas plecoglossicida</i> ETLB-3, <i>Clostridium acetobutylicum</i> ATCC 824, <i>Pseudomonas putida</i> KT2442, <i>Sphingobium</i> sp. SYK-6, <i>Rhodococcus rhodochrous</i> EP4, <i>Rhodococcus jostii</i> RHA1 and <i>Rhodococcus opacus</i> PD630.	Organic acids	Some microorganisms (like <i>Paenibacillus</i>) are present in Kraft black liquor	[40.51,63–71]
		Monomeric aromatic compounds	Kraft black liquor is a suitable fermentation broth	
		Laccases	Pretreatments, such as lignin precipitation or liquid–liquid extraction, improve the biodegradability	
		Peroxidases		
		Biobutanol		

but not sugars, from delignified black liquor. Thus, the raffinate would be more suitable for fermentation than the feedstock, due to the lower concentration of inhibitory compounds [49,50].

6. Thermochemical treatments

The main thermochemical processes applied to Kraft black liquor include gasification, pyrolysis and hydrothermal treatments. It is important to note that most of these treatments were aimed at improving the conventional Kraft black liquor recovery stage or at obtaining bio-fuels for energy purposes [72]. Nevertheless, as previously stated, this review only focusses on studies dealing with obtaining high value-added chemicals (Table 5).

6.1. Gasification and pyrolysis

Gasification has been commonly seen as the most promising method for replacing the combustion stage in Kraft pulp mills, allowing the replacement of the natural gas used in the burning stage and reducing gas emissions and water consumption. For this reason, there are many studies dealing with the gasification of Kraft black liquor, with or without catalyst, and its co-gasification with other feedstocks such as pyrolysis liquids, sludge or wood, the technology having already been successfully implemented at a pilot scale (see the reviews of Naqvi et al. [73] and Pio et al. [74] and Chapter 8 of Bajpai [2]). Nevertheless, although the concept is technically and economically feasible, there are some problems that still hinder its implementation on an industrial scale, such as corrosion phenomena, the proper purification of the syngas, the lower efficiency for recovery of cooking chemicals and the emission of toxic gases and particles [74–76].

This technique is based on the thermochemical conversion of heavy black liquor (after being concentrated in the evaporators) into syngas by heating in a partially reducing atmosphere at temperatures ranging from 600 to 1,000 °C. Although the energy required can be supplied externally (indirect gasification), this process can be conducted auto-thermally (direct gasification) by regulating the presence of air or oxygen inside the reactor. The resulting syngas, mainly composed of a mixture of carbon monoxide, hydrogen and methane, can be used not only to obtain energy, but also as a feedstock to produce other products such as methanol, ammonia, Fischer-Tropsch fuels, dimethyl ether or ethanol, among others. Regarding the slag obtained after the gasification of Kraft black liquor, composed of molten inorganic elements, this can continue through the conventional stages for white liquor recovery after being dissolved [2,73–75,77].

A promising modification of this process is to use weak black liquor as the feedstock, instead of the concentrated liquor, to carry out its gasification at operational conditions beyond the critical point of water (374 °C, 221 bar), in a process called supercritical water gasification (SCWG) (Casademont et al. [78] described some experimental and simulation studies). Depending on the temperature, different high-value streams are obtained: temperatures between 374 and 600 °C lead to final

liquid products, while gaseous ones are produced at higher temperatures [79,80]. One of the main advantages of this technique is that the evaporation stage of the black liquor during the Kraft process, which consumes a third of the steam produced in the recovery stage and reduces the energy efficiency of the conventional process, is avoided. Other benefits of SCWG include the separation of the mineral components, the regeneration of Na₂CO₃ to NaOH without additional reagents (when the temperature is between 710 and 750 °C) and the partial removal of sulphur in its elemental form. In addition, as the generated gas has a high heating value, if oxygen is properly dosed to the SCWG, this operation can also be autothermal [81–83]. Furthermore, if a chemical looping stage is added as a syngas posttreatment, not only energy but also hydrogen could be obtained [84]. Apart from this, the liquid fraction obtained is a potential source of high added value products because it contains phenolic compounds, carboxylic acids and sugars, among others [79]. Nevertheless, clogging is an important issue to be considered, as the char and salt deposits formed during the treatment can block the pipelines. In addition, the use of alkaline catalysts to improve the hydrogen yield in the syngas worsened the clogging problems, as they precipitated during the SCWG process, and compounds such as NaOH only had a slight effect, due to they were already present in high amounts in the raw black liquor [78,85]. So, to minimise this problem, Özdenkçi et al. [82] worked in semi-continuous mode, using the Stepwise Injection Method (SIM), based on periodically injecting Kraft black liquor into the reactor. After testing the effects of different operational conditions, an interdependence between temperature and residence time was found to exist. For long times (300 s), syngas production increased considerably with the temperature. On the contrary, when the residence time was short (133–162 s), this increase was only noticeable from 700 °C onwards, as reaction speed was not sufficient at lower temperatures. It was also reported that the use of Inconel® 625 alloy in the construction of the reactor promoted the degradation of the intermediates during the treatment process, leading to higher yields of syngas than were achieved using stainless steel.

Finally, some studies have proved that Kraft black liquor can be used as an alkali catalyst during the gasification of other wastes. So, Rönnlund et al. [80] proposed the use of black liquor instead of alkali salts during the catalytic SCWG of paper sludge, reporting similar results to those obtained with the addition of KOH, K₂CO₃ and NaOH.

Moving on to pyrolysis, this treatment differs from gasification in that it occurs in the absence of an oxidising agent and at lower temperatures (300–900 °C). When the residence time is very short (a few seconds), the main products are liquid biofuels and chemicals. Nevertheless, for longer residence times, a solid char is obtained, although volatile compounds, gases and tar are formed as well [75]. Although it shares similar purposes with gasification, pyrolysis has been less intensively studied. Recently, some research has focused on its application for the chemical valorisation of Kraft black liquor. In this experimental line, Peng et al. [86] pyrolyzed dried Kraft black liquor in a fixed bed reactor at temperatures between 350 and 550 °C, causing the breakage of methoxyl groups from the lignin and the formation of a bio-oil phase

Table 5
Thermochemical treatments of Kraft black liquor.

Treatments	Main operational parameters	Products	Comments	References
Gasification	Heavy/dried Kraft black liquor	Syngas (CO, H ₂ , CH ₄ , mainly)	Promising for replacing the combustion stage	[2,72–77]
	600 °C < T < 1,000 °C	Slag of molten inorganic elements	Direct gasification is autothermal Syngas is a source of energy and other valuable products (alcohols, fuels or ethers, among others)	
Supercritical water gasification	Partially reducing atmosphere		Recirculation of inorganic compounds to the conventional recovery process	[78–85]
	Weak Kraft black liquor	Syngas	Production of gas is the main objective	
	T > 374 °C	Liquid fraction rich in high added value compounds	The evaporation stage is avoided	
	P > 221 bar		It can be autothermal	
	Partially reducing atmosphere		Conversion of Na ₂ CO ₃ to NaOH at 710–750 °C Partial removal of sulphur Stepwise Injection Method can reduce clogging Kraft black liquor can be used as alkaline catalyst	
Pyrolysis	Heavy/dried Kraft black liquor	Liquid biofuel (tar) Solid (char)	Tar rich in aromatic compounds	[75,86–91]
	300 °C < T < 900 °C	Syngas	Use of char for soil remediation, catalyst support, anode material or raw material for high surface area activated carbon	
Hydrothermal liquefaction	Inert atmosphere			[75,92–99]
	Weak Kraft black liquor	Liquid biofuel	Production of biocrude is the main objective	
	250 °C < T < 350 °C	Aqueous phase Hydrochar	Organic solvents lead to the production of more phenolic compounds, organic acids and alcohols Valorisation of aqueous phase and char makes the process viable Kraft black liquor can be used as alkaline catalyst	
Hydrothermal carbonization	Inert atmosphere			[94,100–102]
	Weak Kraft black liquor	Aqueous phase Hydrochar	Production of char is the main objective Char can be revalorised but is commonly used as fuel Carbonised lignin can be recovered from the char	
	180 °C < T < 250 °C			
Thermal hydrolysis	P > saturation (40–165 bar)			[103,105]
	Inert atmosphere			
	Weak Kraft black liquor	Aqueous phase rich in sugars and organic acids	Liquid phase is the main objective Liquid phase rich in valuable compounds but not very pure Low degradation of organic matter	
Wet oxidation	100 °C < T < 200 °C			[12,15,31,104–111]
	P > saturation (1–16 bar)			
	Inert atmosphere			
Wet oxidation	Weak Kraft black liquor	Aqueous phase rich in sugars and organic acids	Liquid phase is the main objective	[12,15,31,104–111]
	100 °C < T < 325 °C		High temperatures and reaction times favour the formation and purification of short chain acids	
	P > saturation (1–120 bar)		Short reaction times increase sugar and phenolic concentrations	
	Oxidising atmosphere		High degradation of organic matter	
			Presence of catalyst reduces organic acid yields	
			Reduction of odour, viscosity, pH and calorific value of Kraft black liquor	
			Lignin and organic acids can be obtained simultaneously carrying out acid precipitation before wet oxidation Wet oxidation before lignin precipitation improves its separation	

(tar) containing the organic compounds, with yields of 50 wt% and 27 wt% for char and gas phases, respectively, regardless of the temperature tested. Results revealed that the higher the temperature, the higher the concentration of H₂, CH₄ and CO and the lower the presence of CO₂ in the gas phase because of the more complete decomposition of the methoxyl groups. The increase in the pyrolysis temperature also involved a reduction in the content of aromatic compounds with methoxyl groups but an enhancement in the content of intermediate compounds with fewer methoxyl groups in the tar composition. In this regard, the production of bio-aromatics (in particular, benzene, toluene and xylenes (BTX)) from heavy black liquors was studied by Heeres et al. [87] by means of in-situ or ex-situ catalytic pyrolysis using several zeolite catalysts at 500–600 °C. They reported the highest yield of BTX (7 wt%) using the Ga-modified H-ZSM-5 catalyst, with this yield being slightly higher for hardwood black liquors than for softwood ones. Regarding char valorisation, many alternatives have been presented in the bibliography. Chutia et al. [88] proposed its use as a liming agent for acidic soil remediation. Wang et al. [89] also assessed the potential of this biochar as a catalyst support for biodiesel production, achieving production yields of up to 91.5%. Huang et al. [90] suggested the use of biochar generated at temperatures between 750 and 950 °C as anode material in sodium-ion batteries due to its good electrochemical performance. In particular, this material possessed high rate capability and long-term cycling stability. In addition, Zhao et al. [91] prepared high surface area activated carbon from Kraft black liquor char by chemical activation with potassium hydroxide.

6.2. Hydrothermal treatments

Hydrothermal treatments are those carried out in an aqueous medium at mild temperatures (100–370 °C) and pressures (up to 175 bar). Depending on the operational conditions, they can be divided into hydrothermal liquefaction, hydrothermal carbonisation, wet oxidation and thermal hydrolysis. Supercritical water gasification, explained above, can also be considered as a hydrothermal treatment, although there are two clear differences. The first is that the target is mainly the gas phase instead of the liquid and solid phases, and the second is that the temperatures are higher (above the critical point of water) [12,92–94].

Hydrothermal liquefaction is carried out under an inert atmosphere at temperatures of around 250–350 °C, in the presence or absence of additives, such as NaOH, or cosolvents, such as alcohols or other feedstocks. The operating pressure has to be above saturation to keep the reaction medium liquid (40–165 bar). During this treatment, an oil-like organic phase is produced, as well as an aqueous phase and a char as by-products [75,94–97]. The bio-oil fraction is mainly derived from lignin and contains more than half of the organic compounds of the raw material, so after being refined it can be used as biofuel or for chemicals production [97–99]. The compounds detected in the bio-oil include benzenoid aromatic compounds, phenols (H-type, mainly), aldehydes, ketones, esters, long-chain alkanes and heteroatomic compounds [97]. In this respect, the presence of organic solvents during the hydrothermal liquefaction of Kraft black liquor extends the variety of phenolic products in the resulting bio-oil and the range of their molecular weight distribution, as well as favouring the formation of acids and alcohols. Zhao et al. [97] reported that the best solvents for the production of phenolic compounds from Kraft black liquor were 50 wt% of ethanol or ethyl acetate, whereas the maximum bio-oil yield (53.3%) was achieved after hydrothermal liquefaction at 300 °C for 30 min and using 50 wt% ethyl acetate/water as a cosolvent.

Despite the little interest shown in this process in the past and the use of only small-scale reactors (see the review of Lappalainen et al. [98]), this alternative has recently been receiving more attention, as the simultaneous valorisation of by-products, either aqueous phase or char, together with bio-oil utilisation, makes the process more competitive and economically viable [94–96,98] (see preliminary techno-economic analyses in Ong et al. [96] and Lappalainen et al. [98]). The aqueous

phase contains either most of the inorganic compounds, which can be recirculated to the conventional Kraft process, or hydrophilic organic ones, which are mainly low-molecular-mass aliphatic carboxylic acids [97–99]. With regard to the valorisation of the hydrochar generated as a by-product, Zhao et al. [97] proposed its use as an adsorbent for Cr(VI) removal, indicating better adsorption performances with chars obtained by hydrothermal liquefaction of Kraft black liquor with water as compared to those formed using other solvents. As for the aqueous phase, the possible valorisation techniques would be the separation of value-added chemicals and biological or hydrothermal conversion [95].

Finally, apart from being used as feedstock, Kraft black liquor can be the alkaline catalyst during the liquefaction process, in the same way it was used for gasification. In this context, Ong et al. [96] evaluated the implementation of the hydrothermal liquefaction of the mixture of Radiata pine and Kraft black liquor in a pulp mill on the basis of a patent. With a mixture ratio of 1 kg of dry Radiata pine to 0.26 kg of dry black liquor solids, 23 wt% yield of bio-crude was reported. The scale-up and the economic analysis for the integration of this process in Kraft pulp mills had promising results, taking into account the upgrading stage of the bio-oil and a further SCWG of the aqueous phase.

Moving on to the process of hydrothermal carbonisation, this normally takes place at temperatures higher than 180 °C, but lower than those corresponding to liquefaction (around 250 °C), and above the saturation pressure (10–40 bar) [100,101]. Its main objective is usually the production of hydrochars for their use as solid fuels, although their interesting textural, morphological and physicochemical properties suggest other more valuable ways of valorisation for this material [94,102]. However, very few studies have focused on applying this treatment to Kraft black liquor for non-energetic purposes. Recently, Palanisamy et al. [101] produced an activated carbon from partially delignified Kraft black liquor (pH = 7) by hydrothermal carbonization at 200 °C for 24 h. The low equivalent series resistance (60 Ω), the porous structure and the oxygen doping characteristics make this material suitable for use as a supercapacitor electrode. Employing a hydrothermally carbonised black liquor, Wittmann and Richter [100] developed a method for recovering undissolved carbonised lignin (solid) by dewatering and washing the solid fraction, which had appropriate characteristics for it to be used as porous carbonaceous material in several fields.

Finally, thermal hydrolysis occurs under inert atmospheres at lower temperatures (between 100 and 200 °C), whereas wet oxidation takes place in presence of oxidising atmospheres at temperatures of up to 325 °C. As in the case of the previous treatments, the pressure has to be higher than the saturation: 1–16 bar for thermal hydrolysis or even higher than 120 bar for wet oxidation [12,103]. These treatments, in particular wet oxidation, are gaining in importance because they are more environmentally friendly than incineration, reduce odours and enable the production of high added-value products, such as carboxylic acids [104–106]. It should be noted that thermal hydrolysis has hardly been studied as a treatment for Kraft black liquor because the inert atmosphere leads to much more reduced degradation of organic matter than is found in wet oxidation, due to the absence of oxidation reactions [105]. In fact, long oxidation times have been shown to significantly reduce the toxicity of black liquor to both the environment in general and to microorganisms, an effect that is enhanced by the presence of homogeneous or heterogeneous catalysts, since they promote the degradation of refractory compounds [107–110]. However, when the objective is to obtain compounds of industrial interest, the best option is to carry out a partial oxidation in absence of a catalyst.

In this regard, several authors have studied the partial wet oxidation of Kraft black liquor as a renewable feedstock for carboxylic acids. During this treatment, the non-volatile hydroxy acids of higher molecular weight (malic, 2-OH-butyric, xyloisaccharinic and glucoisaccharinic acids) present in the raw black liquor are partially oxidised to shorter chain acids (oxalic, succinic, glycolic and lactic acids). On the other hand, short volatile fatty acids are degraded, with only acetic acid

concentration being increased, due to its refractory character, even with long reaction times [12,15,104]. The oxidation reactions involved in this mechanism are greatly influenced by temperature and reaction time. Thus, the formation of short-chain acids (formic, acetic and lactic acids) was favoured at higher temperatures, which was attributed to a greater degradation of organic matter due to the severe operating conditions, and short reaction times, when the formation rate of these acids exceeded their degradation [15,104]. The presence of some Fe-based catalysts, such as $(\text{Fe}_2(\text{SO}_4)_3)$, Fe in activated carbon and Fe in activated carbon with H_2O_2 , have also proved to accelerate these oxidation reactions, having a negative impact on the formation of organic acids due to the acceleration of the oxidation reaction they caused [104,111].

A more in-depth study of how wet oxidation affects the properties of black liquor was carried out by Pola et al. [106] with the aim of assessing its potential integration into the conventional Kraft process so as to simultaneously treat the black liquor and obtain organic acids. After testing different temperatures (170–210 °C) and pressures (55–85 bar), the authors reported that long oxidation times (>120 min) produced a slightly less concentrated but more purified stream of carboxylic acids, having a screening effect on their distribution due to the different evolution of each organic acid with time, with this facilitating their subsequent extraction. In contrast, short reaction times (around 60 min) increased the concentration of other high added-value compounds, such as sugars and phenolics. Additionally, partial wet oxidation was demonstrated to have a positive impact on odour reduction because sulphur and nitrogen compounds were retained in solution in inorganic form, and also on the handling of Kraft black liquor, due to the reduction in its viscosity and pH. Nevertheless, the partial oxidation of the organic matter also leads to a reduction in the gross calorific value, so the implementation of this stage would have to be optimised while regarding the specific interests of each mill [106].

The possibility of obtaining lignin and organic acids simultaneously has also been studied by separating the lignin using carbonation or acidification (Section 3.3) prior to applying wet oxidation to the remaining delignified black liquor [105,111]. In this regard, it has been found that lignin precipitation prior to oxidation had little impact on organic acid formation (formic, acetic and lactic + glycolic acids), when compared to that seen in direct partial wet oxidation [111]. If the sequence of treatments is reversed, the wet oxidation pre-treatment prior to the acidification stage improves the filterability of lignin, as explained in Section 3.3 for the Lignoforce systemTM [31]. Working with the first of these sequences, Pola et al. [105] studied the evolution of both volatile fatty (formic, acetic and propionic acids) and non-volatile hydroxy acids (oxalic, malic and lactic acids) during the hydrothermal treatment of delignified black liquor under different temperatures (170–210 °C) in presence of inert and oxidising atmospheres, reporting a maximum acid concentration (60 g/L) after 2 h of thermal hydrolysis at 190 °C and 70 bar. This was due to these compounds not being decomposed under an inert atmosphere, as occurred in the presence of oxidation reactions. However, wet oxidation produced a stream that was purer in organic acids, due to the degradation of organic matter [105].

7. Electrochemical treatments

By applying an electrical current to Kraft black liquor, high added-value products, such as lignin, hydrogen or carboxylic acids, can be recovered (Table 6). In fact, the intrinsic physicochemical properties of the Kraft black liquor, such as high pH, conductivity and lignin content, make it a suitable electrolytic medium [112,113].

For example, electrolysis of Kraft black liquor enables lignin to be obtained by electrodeposition at the anode and hydrogen at the cathode, but the lignin electrooxidation process is still poorly understood. To solve this, Oliveira et al. [112] studied this process by applying voltammetry, chronoamperometry and chronopotentiometry methods. Results showed that Pt was the best material for electrodes in terms of catalytic activity, overpotential and faradic efficiency, but Ni, being

cheaper and also showing good results, was a more competitive option.

In addition to the above, other electrochemical methods, such as electrodialysis, which is an electrochemical treatment involving the use of membranes, have been studied by several authors to acidify the black liquor and precipitate lignin. This alternative, compared to the conventional chemical acidification treatments, needs fewer chemicals and enables caustic soda to be obtained simultaneously. Nevertheless, these techniques are limited by the fouling of the ion exchange membranes [114–116]. In this respect, Jin et al. [113] performed an alternative acidification technique by electrodialysis with Ti/IrO₂-Ta₂O₅ and Hg/HgO electrodes as anode and cathode, respectively, separated by a proton exchange membrane (Nafion® N117), achieving pH values of up to 4.7 due to water electrolysis, accompanied by lignin precipitation and NaOH recovery. In this way, the chemical oxygen demand reduction was also greater than that achieved by the conventional acid precipitation (explained in Section 3.3). Haddad et al. [117] studied the electrodialysis acidification of black liquor as well, but using bipolar membranes (EDBM) and studying the roles of temperature (35 or 55 °C) and black liquor solids content (5–50 wt%) in the process. It was found that the higher the solids concentration and the lower the temperature, the higher and the faster the increase in the global system resistance. Moreover, the dynamic viscosity of Kraft black liquor increased exponentially with increasing the solids content, regardless of the temperature.

Not only lignin can be obtained from Kraft black liquor by

Table 6
Electrochemical treatments of Kraft black liquor.

Treatments	Main operational parameters	Products	Comments	References
Electrolysis	Electrodes: Pt, Ni, AISI 304	Lignin	Kraft black liquor is a suitable electrolytic medium due to its physicochemical properties	[112]
	Potential: 0.1–0.5 V	Hydrogen		
Electrodialysis	Electrodes: Ti/IrO ₂ -Ta ₂ O ₅ and Hg/HgO Membranes: ion exchange, bipolar	Lignin	Lignin electrodeposition at the anode	[113–120]
		Hydrogen	Hydrogen production at the cathode	
		NaOH	Ni is the most competitive electrode material	
		Carboxylic acids	Simultaneous lignin, hydrogen and NaOH production	
		H ₂ SO ₄	Technique limited by membrane fouling	
			Global resistance increased with solid concentration, but decreased with temperature	
			Recovery of sodium-free carboxylic acids and H ₂ SO ₄ using bipolar membranes	

electrochemical processes. Kumar and Alén [118] proposed an alternative treatment based on carrying out the electro dialysis of delignified Kraft black liquor by carbonation at pH = 8.5 to produce sodium hydroxide and aliphatic carboxylic acids at the same time. Nevertheless, to be used, the delignified Kraft black liquor required previous dilution with water, obtaining after electro dialysis sodium-free carboxylic acids and sodium hydroxide. These authors even proposed a more complex modification (see Fig. S.6 in the Supplementary Material): lignin precipitation from Kraft black liquor with carbon dioxide and sulphuric acid until pH = 2.5, the subsequent evaporation of the acidified liquor to separate volatile acids, followed by the precipitation of sodium sulphate from the residue with methanol and the distillation of the remaining liquid fraction to recover methanol and sodium-free hydroxy acids. Finally, sodium sulphate would be subjected to electro dialysis to obtain sodium hydroxide and recover sulphuric acid to be reused during the initial acidification stage. With these procedures, the authors claimed to simultaneously recover around 90% of the sodium as NaOH, 80% of the aliphatic acids as sodium-free and 76% of the lignin [118].

Finally, a mention should be made of the process proposed by Heinonen et al. [120] and Heinonen and Sainio [119], who suggested a combination of ion exchange and electro dialysis for the recovery of hydroxy acids from Kraft black liquor (see Fig. S.7 in the Supplementary Material). Their approach is based on an initial separation of lignin and NaOH from the Kraft black liquor by a weak cation exchange resin followed by a cellulose-based one. Afterwards, thiosulphate is also recovered using a strong anion exchange resin in SO_4^{2-} form, whereas the sodium forms of the hydroxy acids are subsequently converted into free acids by means of a strong cation exchange resin. Finally, an EDBM stage is used to treat the waste solutions from membrane regenerations, with the reagents being recirculated to the process.

8. Conclusions

Kraft black liquor constitutes a valuable renewable feedstock for chemicals, containing a large number of compounds, such as organic acids and aromatic compounds, that should be recovered instead of just being burned to produce energy, as is currently the case. This new approach has still received little study, as the heterogeneity of the Kraft black liquor hinders the design of standard extraction and purification stages, making it necessary to combine several unit operations.

Thus, the available studies dealing with the chemical valorisation of Kraft black liquor are scarce and only lignin separation is already implemented at an industrial scale, neglecting the rest of the compounds in the delignified solution. In this context, due to growing environmental concerns, some authors have already proposed methods for delignified Kraft black liquor valorisation with the aim of obtaining other high value-added compounds together with lignin. Another important area of study is the generation, by oxidation, and recovery, by extraction and/or filtration, of a mixed pool of organic acids. However, given their similar physicochemical properties, a higher degree of purification to obtain specific compounds is not efficient. For this reason, it would be necessary to search for applications in which the acids can be used as mixtures to be cost-effective.

A considerable effort is also being made to design environmentally friendly strategies by using waste acid solutions, co-treating the black liquor with other biomass feedstocks and/or new generation solvents. In this regard, many proposals also include the recirculation of the side streams obtained during and/or after the recovery of the different organic compounds, which are still rich in inorganic salts, to the conventional recovery stage of the Kraft process. However, the physicochemical changes in the black liquor produced by some of the proposed treatments would negatively affect this part of the process, and so some authors suggested the valorisation of only part of the total black liquor stream to mitigate the possible effects. Therefore, more research is needed in this area, seeking a suitable way to integrate the production of chemicals into the conventional Kraft process.

Finally, for pulp mills that cannot afford to implement the recovery process, methods using weak black liquor directly show great potential because the evaporation stage is avoided. In this regard, hydrothermal treatments would be adequate since they reduce toxicity, are environmentally friendly, promote the formation and purification of valuable compounds and can be coupled to lignin extraction.

Declaration of Competing Interest

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.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

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References

- [1] J. Hu, Q. Zhang, D.J. Lee, Kraft lignin biorefinery: A perspective, *Bioresour. Technol.* 247 (2018) 1181–1183, <https://doi.org/10.1016/j.biortech.2017.08.169>.
- [2] P. Bajpai, Pulp and paper industry. Chemical Recovery., Elsevier Inc., 2017.
- [3] A.K. Singh, R. Chandra, Pollutants released from the pulp paper industry: Aquatic toxicity and their health hazards, *Aquat. Toxicol.* 211 (2019) 202–216, <https://doi.org/10.1016/j.aquatox.2019.04.007>.
- [4] A.L. Woiciechowski, C.J. Dalmas, L. Porto de Souza, D.P. de Carvalho, A. C. Novak, L.A.J. Letti, S.G. Karp, L.A. Zevallos, C.R. Soccol, Lignocellulosic biomass: Acid and alkaline pretreatments and their effects on biomass recalcitrance – Conventional processing and recent advances, *Bioresour. Technol.* 304 (2020), 122848, <https://doi.org/10.1016/j.biortech.2020.122848>.
- [5] M. Cardoso, É.D. de Oliveira, M.L. Passos, Chemical composition and physical properties of black liquors and their effects on liquor recovery operation in Brazilian pulp mills, *Fuel*. 88 (2009) 756–763, <https://doi.org/10.1016/j.fuel.2008.10.016>.
- [6] R. Chandra, A. Abhishek, Bacterial decolorization of black liquor in axenic and mixed condition and characterization of metabolites, *Biodegradation*. 22 (2011) 603–611, <https://doi.org/10.1007/s10532-010-9433-1>.
- [7] N.S. Kevlich, M.L. Shofner, S. Nair, Membranes for Kraft black liquor concentration and chemical recovery: Current progress, challenges, and opportunities, *Sep. Sci. Technol.* 52 (2017) 1070–1094, <https://doi.org/10.1080/01496395.2017.1279180>.
- [8] Z. Al-Kaabi, R. Pradhan, N. Thevathasan, P. Arku, A. Gordon, A. Dutta, Beneficiation of renewable industrial wastes from paper and pulp processing, *AIMS Energy*. 6 (2018) 880–907, <https://doi.org/10.3934/ENERGY.2018.5.880>.
- [9] G. Ek, M.; Gellerstedt, G.; Henriksson, Pulp and Paper Chemistry and Technology, Walter de Gruyter GmbH & Co. KG, Berlin., 2009.
- [10] P. Bajpai, Kraft spent liquor recovery, *biermann's handb, Pulp Pap.* (2018) 425–451, <https://doi.org/10.1016/b978-0-12-814240-0.00017-3>.
- [11] P. Llamas, T. Domínguez, J.M. Vargas, J. Llamas, J.M. Franco, A. Llamas, A novel viscosity reducer for kraft process black liquors with a high dry solids content, *Chem. Eng. Process. Process Intensif.* 46 (2007) 193–197, <https://doi.org/10.1016/j.cep.2006.06.003>.
- [12] H. Debellefontaine, J.N. Foussard, Wet air oxidation for the treatment of industrial wastes Chemical aspects, reactor design and industrial applications in Europe, *Waste Manag.* 20 (2000) 15–25, [https://doi.org/10.1016/S0956-053X\(99\)00306-2](https://doi.org/10.1016/S0956-053X(99)00306-2).
- [13] E. Vakkilainen, E. Välimäki, Effect of lignin separation to black liquor and recovery boiler operation, in: TAPPI 's 2009 Eng. Pulping Environ. Conf., 2009. <https://doi.org/10.13140/2.1.2039.6485>.
- [14] S.H.F. da Silva, O. Gordobil, J. Labidi, Organic acids as a greener alternative for the precipitation of hardwood kraft lignins from the industrial black liquor, *Int. J. Biol. Macromol.* 142 (2020) 583–591, <https://doi.org/10.1016/j.ijbiomac.2019.09.133>.

- [15] H.R. Muddassar, K. Melin, S. Kuppa, J. Koskinen, M. Hurme, D. DE Kokkonen, J. Kallas, Novel treatment method for black liquor and biomass hydrolysate with partial wet oxidation, *Cellul. Chem. Technol. Cellul. Chem. Technol.* 49 (2015) 3–4.
- [16] T. Mehtiö, L. Nurmi, V. Rämö, A. Harlin, J. Ropponen, Copolymerization of glycolic, d, l-lactic and d, l-2-hydroxybutyric acid mixtures present in kraft black liquors, *Eur. Polym. J.* 48 (2012) 774–778, <https://doi.org/10.1016/j.eurpolymj.2012.01.010>.
- [17] H. Kumar, R. Alén, Recovery of aliphatic low-molecular-mass carboxylic acids from hardwood kraft black liquor, *Sep. Purif. Technol.* 142 (2015) 293–298, <https://doi.org/10.1016/j.seppur.2014.12.038>.
- [18] M. Kamali, Z. Khodaparast, Review on recent developments on pulp and paper mill wastewater treatment, *Ecotoxicol. Environ. Saf.* 114 (2015) 326–342, <https://doi.org/10.1016/j.ecoenv.2014.05.005>.
- [19] M. Benali, Z. Périn-Levasseur, L. Savulescu, L. Kouisni, N. Jemaa, T. Kudra, M. Paleologou, Implementation of lignin-based biorefinery into a Canadian softwood kraft pulp mill: Optimal resources integration and economic viability assessment, *Biomass and Bioenergy*. 67 (2014) 473–482, <https://doi.org/10.1016/j.biombioe.2013.08.022>.
- [20] S. Durmaz, E. Erisir, U.C. Yildiz, O.C. Kurtulus, Using Kraft Black Liquor as a Wood Preservative, *Procedia - Soc Behav. Sci.* 195 (2015) 2177–2180, <https://doi.org/10.1016/j.sbspro.2015.06.291>.
- [21] V.J. Ribeiro, E.M. Mattiello, D. De, J. Silva, L. Vergütz, Coating phosphorus fertilizer with renewable natural polymers, *Aust. J. Crop Sci.* 14 (2020) 782–787, <https://doi.org/10.21475/ajcs.20.14.05.p2180>.
- [22] T. Aro, P. Fatehi, Tall oil production from black liquor: Challenges and opportunities, *Sep. Purif. Technol.* 175 (2017) 469–480, <https://doi.org/10.1016/j.seppur.2016.10.027>.
- [23] Y. He, D.M. Bagley, K.T. Leung, S.N. Liss, B.Q. Liao, Recent advances in membrane technologies for biorefining and bioenergy production, *Biotechnol. Adv.* 30 (2012) 817–858, <https://doi.org/10.1016/j.biotechadv.2012.01.015>.
- [24] J. Fernández-Rodríguez, X. Erdocia, F. Hernández-Ramos, M.G. Alriols, J. Labid, Chapter 7. Lignin separation and fractionation by ultrafiltration, in: *Sep. Funct. Mol. Food by Membr. Technol.*, 2019: pp. 229–265. <https://doi.org/10.1016/B978-0-12-815056-6.00007-3>.
- [25] L.A. Zevallos Torres, A. Lorenci Woiciechowski, V.O. de Andrade Tanobe, S. G. Karp, L.C. Guimaraes Lorenci, C. Faulds, C.R. Soccol, Lignin as a potential source of high-added value compounds: A review, *J. Clean. Prod.* 263 (2020) 121499.
- [26] C.A.E. Costa, P.C.R. Pinto, A.E. Rodrigues, Lignin fractionation from E. Globulus kraft liquor by ultrafiltration in a three stage membrane sequence, *Sep. Purif. Technol.* 192 (2018) 140–151, <https://doi.org/10.1016/j.seppur.2017.09.066>.
- [27] M. Mänttari, J. Lahti, H. Hatakka, M. Louhi-Kultanen, M. Kallioinen, Separation phenomena in UF and NF in the recovery of organic acids from kraft black liquor, *J. Memb. Sci.* 490 (2015) 84–91, <https://doi.org/10.1016/j.memsci.2015.04.048>.
- [28] H. Niemi, J. Lahti, H. Hatakka, S. Kärki, S. Rovio, M. Kallioinen, M. Mänttari, M. Louhi-Kultanen, Fractionation of organic and inorganic compounds from black liquor by combining membrane separation and crystallization, *Chem. Eng. Technol.* 34 (2011) 593–598, <https://doi.org/10.1002/ceat.201000520>.
- [29] J. Lauwaert, I. Stals, C.S. Lancefield, W. Deschaumes, D. Dupuydt, B. Vanlerberghe, T. Devlamynck, P.C.A. Brujninckx, A. Verberckmoes, Pilot scale recovery of lignin from black liquor and advanced characterization of the final product, *Sep. Purif. Technol.* 221 (2019) 226–235, <https://doi.org/10.1016/j.seppur.2019.03.081>.
- [30] T.V. Lourençon, F.A. Hansel, T.A. Da Silva, L.P. Ramos, G.I.B. De Muniz, W.L. E. Magalhães, Hardwood and softwood kraft lignins fractionation by simple sequential acid precipitation, *Sep. Purif. Technol.* 154 (2015) 82–88, <https://doi.org/10.1016/j.seppur.2015.09.015>.
- [31] L. Kouisni, P. Holt-Hindle, K. Maki, M. Paleologou, The LignoForce System™, A new process for the production of high-quality lignin from black liquor, *J. Sci. Technol. For. Prod. Process.* 2 (2012) 6–10.
- [32] P.S.B. dos Santos, X. Erdocia, D.A. Gatto, J. Labidi, Characterisation of Kraft lignin separated by gradient acid precipitation, *Ind. Crops Prod.* 55 (2014) 149–154, <https://doi.org/10.1016/j.indcrop.2014.01.023>.
- [33] J.F. Howell, R.W. Thring, Hardwood lignin recovery using generator waste acid. Statistical analysis and simulation, *Ind. Eng. Chem. Res.* 39 (2000) 2534–2540, <https://doi.org/10.1021/ie990190q>.
- [34] P. Tomani, The lignoboost process, *Cellul. Chem. Technol.* 44 (2010) 53–58.
- [35] A. Tribot, G. Amer, M. Abdou Alio, H. de Baynast, C. Delattre, A. Pons, J. D. Mathias, J.M. Callois, C. Vial, P. Michaud, C.G. Dussap, Wood-lignin: Supply, extraction processes and use as bio-based material, *Eur. Polym. J.* 112 (2019) 228–240, <https://doi.org/10.1016/j.eurpolymj.2019.01.007>.
- [36] M.A. Lake, J.C. Blackburn, SLRP™. An innovative lignin-recovery technology, *Cellul. Chem. Technol.* 48 (2014) 799–804.
- [37] M. Namane, F.J. García-Mateos, B. Sithole, D. Ramjugernath, J. Rodríguez-Mirasol, T. Cordero, Characteristics of lignin precipitated with organic acids as a source for valorisation of carbon products, *Cellul. Chem. Technol.* 50 (2016) 355–360.
- [38] S.V. Kamble, Y.C. Bhattacharyulu, Selective separation of biomass from black liquor waste by inorganic and organic acids, *Int. J. Adv. Res.* 3 (2015) 684–692.
- [39] S. Sathawong, W. Sridach, K.A. Techato, Lignin: Isolation and preparing the lignin based hydrogel, *J. Environ. Chem. Eng.* 6 (2018) 5879–5888, <https://doi.org/10.1016/j.jece.2018.05.008>.
- [40] T. Pang, G. Wang, H. Sun, W. Sui, C. Si, Lignin fractionation: Effective strategy to reduce molecule weight dependent heterogeneity for upgraded lignin valorization, *Ind. Crops Prod.* 165 (2021), 113442, <https://doi.org/10.1016/j.indcrop.2021.113442>.
- [41] J. Velez, M.C. Thies, Solvated liquid-lignin fractions from a Kraft black liquor, *Bioresour. Technol.* 148 (2013) 586–590, <https://doi.org/10.1016/j.biortech.2013.08.097>.
- [42] M. Alekhina, O. Ershova, A. Ebert, S. Heikkinen, H. Sixta, Softwood kraft lignin for value-added applications: Fractionation and structural characterization, *Ind. Crops Prod.* 66 (2015) 220–228, <https://doi.org/10.1016/j.indcrop.2014.12.021>.
- [43] W. Zhu, H. Theliander, Precipitation of lignin from softwood black liquor: An investigation of the equilibrium and molecular properties of lignin, *Bioresour. Technol.* 10 (2015) 1696–1714, <https://doi.org/10.15376/biores.10.1.1696-1715>.
- [44] R.C. Andeme Ela, L. Spahn, N. Safaie, R.C. Ferrier, R.G. Ong, Understanding the effect of precipitation process variables on hardwood lignin characteristics and recovery from black liquor, *ACS Sustain. Chem. Eng.* 8 (37) (2020) 13997–14005.
- [45] J. Sundin, N. Hartler, Precipitation of kraft lignin by metal cations in alkaline solutions, *Nord. Pulp Pap. Res. J.* 15 (2000) 312–318, <https://doi.org/10.3183/npprj-2000-15-04-p306-312>.
- [46] S.A. Lisboa, D.V. Evtuguin, C.P. Neto, B.J. Goodfellow, Isolation and structural characterization of polysaccharides dissolved in Eucalyptus globulus kraft black liquors, *Carbohydr. Polym.* 60 (2005) 77–85, <https://doi.org/10.1016/j.carbpol.2004.11.024>.
- [47] L. Reyes, C. Nikitine, L. Vilcoq, P. Fongarland, Green is the new black-A review of technologies for carboxylic acid recovery from black liquor, *Green Chem.* 22 (2020) 8097–8115, <https://doi.org/10.1039/d0gc02627a>.
- [48] F. Kalu, J.M. Andresen, The potential black liquor has to improve the sustainability of Kraft process if used as feedstock for Kraft biorefinery, *J. Fundam. Renew. Energy Appl.* 7 (2017) 75, <https://doi.org/10.4172/2090-4541-c1-038>.
- [49] H.S. Kwon, B.H. Um, Optimization and evaluation of organic acid recovery from Kraft black liquor using liquid-liquid extraction, *Korean Chem. Eng. Res.* 54 (2016) 753–761, <https://doi.org/10.9713/kecr.2016.54.6.753>.
- [50] G.H. Kim, S.J. Park, B.H. Um, Response surface methodology for optimization of solvent extraction to recovery of acetic acid from black liquor derived from Typha latifolia pulping process, *Ind. Crops Prod.* 89 (2016) 34–44, <https://doi.org/10.1016/j.indcrop.2016.04.056>.
- [51] L.E. Navas, G. Dexter, J. Liu, D. Levy-Booth, M. Cho, S.-K. Jang, S.D. Mansfield, S. Renneckar, W.W. Mohn, L.D. Eltis, Bacterial transformation of aromatic monomers in softwood black liquor, *Front. Microbiol.* 12 (2021), 735000, <https://doi.org/10.3389/fmicb.2021.735000>.
- [52] D. Núñez, P. Oulego, S. Collado, F.A. Riera, M. Díaz, Recovery of organic acids from pre-treated Kraft black liquor using ultrafiltration and liquid-liquid extraction, *Sep. Purif. Technol.* 284 (2022), 120274, <https://doi.org/10.1016/j.seppur.2021.120274>.
- [53] J.M. Jardim, P.W. Hart, L. Lucia, H. Jameel, Insights into the potential of hardwood kraft lignin to be a green platform material for emergence of the biorefinery, *Polymers (Basel)*. 12 (2020) 1795, <https://doi.org/10.3390/polym12081795>.
- [54] E.C. Achinivu, Protic ionic liquids for lignin extraction—A lignin characterization study, *Int. J. Mol. Sci.* 19 (2018) 428, <https://doi.org/10.3390/ijms19020428>.
- [55] F. Saadat, Extraction of lignin from black liquor using protic ionic liquids and deep eutectic solvents, *Electron. Theses Diss.* 8571 (2021). <https://doi.org/https://scholar.uwindsor.ca/etd/8571>.
- [56] A. Foulet, M. Birot, R. Backov, G. Sonnemann, H. Deleuze, Preparation of hierarchical porous carbonaceous foams from Kraft black liquor, *Mater. Today Commun.* 7 (2016) 108–116, <https://doi.org/10.1016/j.mtcomm.2016.04.005>.
- [57] A. Foulet, M. Birot, G. Sonnemann, H. Deleuze, Life cycle assessment of producing emulsion-templated porous materials from Kraft black liquor - Comparison of a vegetable oil and a petrochemical solvent, *J. Clean. Prod.* 91 (2015) 180–186, <https://doi.org/10.1016/j.jclepro.2014.12.035>.
- [58] M. Jalalian, Q. Jiang, M. Birot, H. Deleuze, R.T. Woodward, A. Bismarck, Frothed black liquor as a renewable cost effective precursor to low-density lignin and carbon foams, *React. Funct. Polym.* 132 (2018) 145–151, <https://doi.org/10.1016/j.reactfunctpolym.2018.07.027>.
- [59] J. Merle, M. Birot, H. Deleuze, P. Trinsoutrot, H. Carré, Q. Huyette, F., Charrier-El Bouhtourt, Valorization of Kraft black liquor and tannins via porous material production, *Arab. J. Chem.* 12 (2019) 4731–4739, <https://doi.org/10.1016/j.arabjc.2016.09.006>.
- [60] G. Amaral-Labat, E. Leal da Silva, A. Cuña, C.F. Malfatti, J.S. Marcuzzo, M. R. Baldan, A. Celzard, V. Fierro, G.F.B. Lenze e Silva, A sustainable carbon material from kraft black liquor as nickel-based electrocatalyst support for ethanol electro-oxidation, *Waste and Biomass Valorization*. 12 (2021) 2507–2519, <https://doi.org/10.1007/s12649-020-01201-3>.
- [61] D. Hermosilla, N. Merayo, A. Gascó, Á. Blanco, The application of advanced oxidation technologies to the treatment of effluents from the pulp and paper industry: A review, *Environ. Sci. Pollut. Res.* 22 (2015) 168–191, <https://doi.org/10.1007/s11356-014-3516-1>.
- [62] Z. Al-Kaabi, R. Pradhan, N. Thevathasan, A. Gordon, Y.W. Chiang, P. Arku, A. Dutta, Ash removal from various spent liquors by oxidation process for bio-carbon production, *J. Environ. Chem. Eng.* 8 (2) (2020) 103520.
- [63] C.H. Ko, C.H. Tsai, J. Tu, B.Y. Yang, D.L. Hsieh, W.N. Jane, T.L. Shih, Identification of Paenibacillus sp. 2S–6 and application of its xylanase on biobleaching, *Int. Biodeterior. Biodegrad.* 65 (2011) 334–339, <https://doi.org/10.1016/j.ibiod.2010.12.006>.
- [64] C.H. Ko, W.L. Chen, C.H. Tsai, W.N. Jane, C.C. Liu, J. Tu, Paenibacillus campinasensis BL11: A wood material-utilizing bacterial strain isolated from

- black liquor, *Bioresour. Technol.* 98 (2007) 2727–2733, <https://doi.org/10.1016/j.biortech.2006.09.034>.
- [65] R. Morya, M. Kumar, I. Tyagi, A. Kumar Pandey, J. Park, T. Raj, R. Sirohi, V. Kumar, S.H. Kim, Recent advances in black liquor valorization, *Bioresour. Technol.* 350 (2022), 126916, <https://doi.org/10.1016/j.biortech.2022.126916>.
- [66] J. Potvin, M. Desrochers, Y. Arcand, Fermentation of Kraft black liquor for the production of citric acid by *Candida tropicalis*, *Appl. Microbiol. Biotechnol.* 28 (4–5) (1988) 350–355.
- [67] G. Singh, S.K. Arya, Utility of laccase in pulp and paper industry: A progressive step towards the green technology, *Int. J. Biol. Macromol.* 134 (2019) 1070–1084, <https://doi.org/10.1016/j.ijbiomac.2019.05.168>.
- [68] R. Paliwal, S. Uniyal, M. Verma, A. Kumar, J.P.N. Rai, Process optimization for biodegradation of black liquor by immobilized novel bacterial consortium, *Desalin. Water Treat.* 57 (2016) 18915–18926, <https://doi.org/10.1080/19443994.2015.1092892>.
- [69] H.J. Huang, S. Ramaswamy, W.W. Al-Dajani, U. Tschirner, Process modeling and analysis of pulp mill-based integrated biorefinery with hemicellulose pre-extraction for ethanol production: A comparative study, *Bioresour. Technol.* 101 (2010) 624–631, <https://doi.org/10.1016/j.biortech.2009.07.092>.
- [70] R.L. Kudahettige-Nilsson, J. Helmerius, R.T. Nilsson, M. Sjöblom, D.B. Hodge, U. Rova, Biobutanol production by *Clostridium acetobutylicum* using xylose recovered from birch Kraft black liquor, *Bioresour. Technol.* 176 (2015) 71–79, <https://doi.org/10.1016/j.biortech.2014.11.012>.
- [71] A. Faisal, M. Zhou, J. Hedlund, M. Grahn, Zeolite MFI adsorbent for recovery of butanol from ABE fermentation broths produced from an inexpensive black liquor-derived hydrolyzate, *Biomass Convers. Biorefinery.* 8 (2018) 679–687, <https://doi.org/10.1007/s13399-018-0315-9>.
- [72] V.S. Sikarwar, M. Zhao, P.S. Fennell, N. Shah, E.J. Anthony, Progress in biofuel production from gasification, *Prog. Energy Combust. Sci.* 61 (2017) 189–248, <https://doi.org/10.1016/j.peecs.2017.04.001>.
- [73] M. Naqvi, J. Yan, E. Dahlquist, Black liquor gasification integrated in pulp and paper mills: A critical review, *Bioresour. Technol.* 101 (2010) 8001–8015, <https://doi.org/10.1016/j.biortech.2010.05.013>.
- [74] D.T. Pio, L.A.C. Tarelho, P.C.R. Pinto, Gasification-based biorefinery integration in the pulp and paper industry: A critical review, *Renew. Sustain. Energy Rev.* 133 (2020), 110210, <https://doi.org/10.1016/j.rser.2020.110210>.
- [75] R. Alén, Chapter 3A. Pulp Mills and Wood-Based Biorefineries, in: *Ind. Biorefineries White Biotechnol.*, Elsevier B.V., 2015: pp. 91–126. <https://doi.org/10.1016/B978-0-444-63453-5.00003-3>.
- [76] C. Cao, Y. He, J. Chen, W. Cao, H. Jin, Evaluation of effect of evaporation on supercritical water gasification of black liquor by energy and exergy analysis, *Int. J. Hydrogen Energy.* 43 (2018) 13788–13797, <https://doi.org/10.1016/j.ijhydene.2017.11.158>.
- [77] A. Darmawan, M.W. Ajiwibowo, K. Tokimatsu, M. Aziz, Efficient co-production of power and ammonia from black liquor, *Int. J. Hydrogen Energy.* 45 (2020) 34437–34448, <https://doi.org/10.1016/j.ijhydene.2020.02.196>.
- [78] P. Casademont, J. Sánchez-Oneto, A.P.J. Scandellai, L. Cardozo-Filho, J.R. Portela, Hydrogen production by supercritical water gasification of black liquor: Use of high temperatures and short residence times in a continuous reactor, *J. Supercrit. Fluids.* 159 (2020), 104772, <https://doi.org/10.1016/j.supflu.2020.104772>.
- [79] T.V. Barros, J.d.C. Carregosa, A. Wisniewski Jr, A.C.D. Freitas, R. Guirardello, L. Ferreira-Pinto, L. Bonfim-Rocha, V. Jegatheesan, L. Cardozo-Filho, Assessment of black liquor hydrothermal treatment under sub- and supercritical conditions: Products distribution and economic perspectives, *Chemosphere.* 286 (2022) 131774.
- [80] I. Rönnlund, L. Myréen, K. Lundqvist, J. Ahlbeck, T. Westerlund, Waste to energy by industrially integrated supercritical water gasification - Effects of alkali salts in residual by-products from the pulp and paper industry, *Energy.* 36 (2011) 2151–2163, <https://doi.org/10.1016/j.energy.2010.03.027>.
- [81] M. Magdeldin, M. Järvinen, Supercritical water gasification of Kraft black liquor: Process design, analysis, pulp mill integration and economic evaluation, *Appl. Energy.* 262 (2020), 114558, <https://doi.org/10.1016/j.apenergy.2020.114558>.
- [82] K. Özdenkçi, M. Prestipino, M. Björklund-Sänkiäho, A. Galvagno, C. De Blasio, Alternative energy valorization routes of black liquor by stepwise supercritical water gasification: Effect of process parameters on hydrogen yield and energy efficiency, *Renew. Sustain. Energy Rev.* 134 (2020), 110146, <https://doi.org/10.1016/j.rser.2020.110146>.
- [83] O.N. Fedyayeva, A.A. Vostrikov, A.V. Shishkin, D.Y. Dubov, Conjugated processes of black liquor mineral and organic components conversion in supercritical water, *J. Supercrit. Fluids.* 143 (2019) 191–197, <https://doi.org/10.1016/j.supflu.2018.08.015>.
- [84] A. Darmawan, M.W. Ajiwibowo, M.K. Biddinika, K. Tokimatsu, M. Aziz, Black liquor-based hydrogen and power co-production: Combination of supercritical water gasification and syngas chemical looping, *Appl. Energy.* 252 (2019), 113446, <https://doi.org/10.1016/j.apenergy.2019.113446>.
- [85] C. De Blasio, S. De Gisi, A. Molino, M. Simonetti, M. Santarelli, M. Björklund-Sänkiäho, Concerning operational aspects in supercritical water gasification of kraft black liquor, *Renew. Energy.* 130 (2019) 891–901, <https://doi.org/10.1016/j.renene.2018.07.004>.
- [86] C. Peng, G. Zhang, J. Yue, G. Xu, Pyrolysis of black liquor for phenols and impact of its inherent alkali, *Fuel Process. Technol.* 127 (2014) 149–156, <https://doi.org/10.1016/j.fuproc.2014.06.020>.
- [87] A. Heeres, N. Schenk, I. Muizebelt, R. Blees, B. De Waele, A.J. Zeeuw, N. Meyer, R. Carr, E. Wilbers, H.J. Heeres, Synthesis of Bio-aromatics from Black Liquors Using Catalytic Pyrolysis, *ACS Sustain. Chem. Eng.* 6 (2018) 3472–3480, <https://doi.org/10.1021/acssuschemeng.7b03728>.
- [88] S. Chutia, R. Narzari, N. Bordoloi, R. Saikia, L. Gogoi, D. Sut, N. Bhuyan, R. Kataki, Pyrolysis of dried black liquor solids and characterization of the bio-char and bio-oil, *Mater. Today Proc.* 5 (2018) 23193–23202, <https://doi.org/10.1016/j.matpr.2018.11.050>.
- [89] Y. Wang, G. Yang, J. He, G. Sun, Z. Sun, Y. Sun, Preparation of biochar catalyst from black liquor by spray drying and fluidized bed carbonation for biodiesel synthesis, *Process Saf. Environ. Prot.* 141 (2020) 333–343, <https://doi.org/10.1016/j.psep.2020.04.050>.
- [90] J. Huang, W. Zhang, P. Yu, H. Dong, M. Zheng, Y. Xiao, H. Hu, Y. Liu, Y. Liang, Direct carbonization of black liquor powders into 3D honeycomb-like porous carbons with a tunable disordered degree for sodium-ion batteries, *New J. Chem.* 44 (2020) 10697–10702, <https://doi.org/10.1039/d0nj01228a>.
- [91] X.-Y. Zhao, J.-P. Cao, K. Sato, Y. Ogawa, T. Takarada, High surface area activated carbon prepared from black liquor in the presence of high alkali metal content, *J. Chem. Eng. Japan.* 43 (2010) 1029–1034, <https://doi.org/10.1252/jcej.10we170>.
- [92] O. Suárez-Iglesias, J.L. Urrea, P. Oulego, S. Collado, M. Díaz, Valuable compounds from sewage sludge by thermal hydrolysis and wet oxidation. A review, *Sci. Total Environ.* 584–585 (2017) 921–934, <https://doi.org/10.1016/j.scitotenv.2017.01.140>.
- [93] X. Zhao, L. Zhan, B. Xie, B. Gao, Products derived from waste plastics (PC, HIPS, ABS, PP and PA6) via hydrothermal treatment: Characterization and potential applications, *Chemosphere.* 207 (2018) 742–752, <https://doi.org/10.1016/j.chemosphere.2018.05.156>.
- [94] H. Boucard, E. Weiss-Hortala, F. Gueye, F. Espitalier, R. Barna, Insights in mechanisms of carbonaceous microparticles formation from black liquor hydrothermal conversion, *J. Supercrit. Fluids.* 161 (2020), 104817, <https://doi.org/10.1016/j.supflu.2020.104817>.
- [95] J. Watson, T. Wang, B. Si, W.T. Chen, A. Aierzhati, Y. Zhang, Valorization of hydrothermal liquefaction aqueous phase: pathways towards commercial viability, *Prog. Energy Combust. Sci.* 77 (2020), 100819, <https://doi.org/10.1016/j.peecs.2019.100819>.
- [96] B.H.Y. Ong, T.G. Walmsley, M.J. Atkins, M.R.W. Walmsley, A kraft mill-integrated hydrothermal liquefaction process for liquid fuel co-production, *Processes.* 8 (2020) 1–23, <https://doi.org/10.3390/pr8101216>.
- [97] Y. Zhao, Y. Tian, H. Zhou, Y. Tian, Hydrothermal conversion of black liquor to phenolics and hydrochar: Characterization, application and comparison with lignin, *Fuel.* 280 (2020), 118651, <https://doi.org/10.1016/j.fuel.2020.118651>.
- [98] J. Lappalainen, D. Baudouin, U. Hornung, J. Schuler, K. Melin, S. Bjelić, F. Vogel, J. Kontinen, T. Joronen, Sub- And supercritical water liquefaction of kraft lignin and black liquor derived lignin, *Energies.* 13 (2020) 3309, <https://doi.org/10.3390/en13133309>.
- [99] M. Huet, A. Roubaud, C. Chirat, D. Lachenal, Hydrothermal treatment of black liquor for energy and phenolic platform molecules recovery in a pulp mill, *Biomass and Bioenergy.* 89 (2016) 105–112, <https://doi.org/10.1016/j.biombioe.2016.03.023>.
- [100] T. Wittmann, I. Richter, Method for extracting lignin from black liquor and products produced thereby (US Patent 2016 / 0271610 A1), 2016.
- [101] S. Palanisamy, S.K. Kandasamy, S. Thangmuthu, D.K. Selvarasu, M. Panchanathan, P.V. Ramanai, B.S. Gevert, Synthesis of activated carbon from black liquor for the application of supercapacitor, *J. Mater. Sci. Mater. Electron.* 32 (2021) 25175–25187, <https://doi.org/10.1007/s10854-021-06974-4>.
- [102] S. Kang, X. Li, J. Fan, J. Chang, Solid fuel production by hydrothermal carbonization of black liquor, *Bioresour. Technol.* 110 (2012) 715–718, <https://doi.org/10.1016/j.biortech.2012.01.093>.
- [103] K. Hii, S. Baroutian, R. Parthasarathy, D.J. Gapes, N. Eshtiagi, A review of wet air oxidation and Thermal Hydrolysis technologies in sludge treatment, *Bioresour. Technol.* 155 (2014) 289–299, <https://doi.org/10.1016/j.biortech.2013.12.066>.
- [104] H.R. Muddassar, K. Melin, D. De Villalba Kokkonen, G.V. Riera, S. Golam, J. Koskinen, Green chemicals from pulp production black liquor by partial wet oxidation, *Waste Manag. Res.* 33 (2015) 1015–1021, <https://doi.org/10.1177/0734242X15602807>.
- [105] L. Pola, S. Collado, P. Oulego, M. Díaz, Production of carboxylic acids from the non-lignin residue of black liquor by hydrothermal treatments, *Bioresour. Technol.* 284 (2019) 105–114, <https://doi.org/10.1016/j.biortech.2019.03.066>.
- [106] L. Pola, S. Collado, P. Oulego, P. Calvo, M. Díaz, Characterisation of the wet oxidation of black liquor for its integration in Kraft paper mills, *Chem. Eng. J.* 405 (2021), 126610, <https://doi.org/10.1016/j.cej.2020.126610>.
- [107] A. Garg, I.M. Mishra, S. Chand, Catalytic wet oxidation of the pretreated synthetic pulp and paper mill effluent under moderate conditions, *Chemosphere.* 66 (2007) 1799–1805, <https://doi.org/10.1016/j.chemosphere.2006.07.038>.
- [108] Q. Zhang, K.T. Chuang, Alumina-supported noble metal catalysts for destructive oxidation of organic pollutants in effluent from a softwood kraft pulp mill, *Ind. Eng. Chem. Res.* 37 (1998) 3343–3349, <https://doi.org/10.1021/ie980111v>.
- [109] W. An, Q. Zhang, Y. Ma, K.T. Chuang, Pd-based catalysts for catalytic wet oxidation of combined Kraft pulp mill effluents in a trickle bed reactor, *Catal. Today.* 64 (2001) 289–296, [https://doi.org/10.1016/S0920-5861\(00\)00532-0](https://doi.org/10.1016/S0920-5861(00)00532-0).
- [110] Q. Zhang, K.T. Chuang, Kinetics of wet oxidation of black liquor over a Pt-Pd-Ce/alumina catalyst, *Appl. Catal. B Environ.* 17 (1998) 321–332, [https://doi.org/10.1016/S0926-3373\(98\)00016-2](https://doi.org/10.1016/S0926-3373(98)00016-2).
- [111] H.R. Muddassar, M.H. Sipponen, K. Melin, D. De Kokkonen, O. Pastinen, S. Golam, Effects of catalysts and pH on lignin in partial wet oxidation of wood and straw black liquors, *Ind. Eng. Chem. Res.* 54 (2015) 7833–7840, <https://doi.org/10.1021/acs.iecr.5b01764>.

- [112] R.C.P. Oliveira, M. Mateus, D.M.F. Santos, Chronoamperometric and chronopotentiometric investigation of Kraft black liquor, *Int. J. Hydrogen Energy*. 43 (2018) 16817–16823, <https://doi.org/10.1016/j.ijhydene.2018.01.046>.
- [113] W. Jin, R. Tolba, J. Wen, K. Li, A. Chen, Efficient extraction of lignin from black liquor via a novel membrane-assisted electrochemical approach, *Electrochim. Acta*. 107 (2013) 611–618, <https://doi.org/10.1016/j.electacta.2013.06.031>.
- [114] M. Haddad, S. Mikhaylin, L. Bazinet, O. Savadogo, J. Paris, Electrochemical acidification of Kraft black liquor by electro dialysis with bipolar membrane: Ion exchange membrane fouling identification and mechanisms, *J. Colloid Interface Sci.* 488 (2017) 39–47, <https://doi.org/10.1016/j.jcis.2016.10.015>.
- [115] M. Haddad, L. Bazinet, O. Savadogo, J. Paris, A feasibility study of a novel electro-membrane based process to acidify Kraft black liquor and extract lignin, *Process Saf. Environ. Prot.* 106 (2017) 68–75, <https://doi.org/10.1016/j.psep.2016.10.003>.
- [116] M. Haddad, L. Bazinet, O. Savadogo, J. Paris, Electrochemical acidification of Kraft black liquor: Impacts of pulsed electric field application on bipolar membrane colloidal fouling and process intensification, *J. Memb. Sci.* 524 (2017) 482–492, <https://doi.org/10.1016/j.memsci.2016.10.043>.
- [117] M. Haddad, R. Labrecque, L. Bazinet, O. Savadogo, J. Paris, Effect of process variables on the performance of electrochemical acidification of Kraft black liquor by electro dialysis with bipolar membrane, *Chem. Eng. J.* 304 (2016) 977–985, <https://doi.org/10.1016/j.cej.2016.07.030>.
- [118] H. Kumar, R. Alén, Partial recovery of aliphatic carboxylic acids and sodium hydroxide from hardwood black liquor by electro dialysis, *Ind. Eng. Chem. Res.* 53 (2014) 9464–9470, <https://doi.org/10.1021/ie5006004>.
- [119] J. Heinonen, T. Sainio, Novel chromatographic process for the recovery and purification of hydroxy acids from alkaline spent pulping liquors, *Chem. Eng. Sci.* 197 (2019) 87–97, <https://doi.org/10.1016/j.ces.2018.12.013>.
- [120] J. Heinonen, Y. Zhao, B. Van der Bruggen, A process combination of ion exchange and electro dialysis for the recovery and purification of hydroxy acids from secondary sources, *Sep. Purif. Technol.* 240 (2020), 116642, <https://doi.org/10.1016/j.seppur.2020.116642>.