Review

Beneficiation of renewable industrial wastes from paper and pulp processing

Zainab AL-Kaabi[1,2], Ranjan Pradhan[3], Naresh Thevathasan[1], Precious Arku[3], Andrew Gordon[1] and Animesh Dutta[3,*]

[1] School of Environmental Science, University of Guelph, N1G 2W1, Guelph, Ontario, Canada
[2] Al-Mustansiriyah University, Baghdad, Iraq
[3] School of Engineering, University of Guelph, N1G 2W1, Guelph, Ontario, Canada

* **Correspondence:** Email: adutta@uoguelph.ca; Tel: +15198244120 Ext. 52441.

Abstract: Black liquor (spent cooking liquor) is one of the major byproducts of pulp and paper manufacturing. Black liquor contains 10–50% lignin, which is the main organic matter found within that liquor. Different types of black liquors are obtained as per the type of feedstock, pulping process and cooking method adopted by industries. In recent years, industries have been required to accommodate newer varieties of feedstock such as non-wood and recycled fibers during the delignification process, which can save plenty of trees and hence reduce their carbon footprint. Therefore, the newer black liquors being generated differ in their physical characteristics, chemical composition, and energy content from that of traditional processes.

Currently, black liquor is seen as a platform for the production of many renewable materials for industrial applications that can be environmentally friendly with the potential to be used substitute for fuel and commercial materials. However, most of the published review articles focus on the kraft spent liquor and its derived kraft lignin that is obtained from kraft pulping process at the pulp and paper as a source of bio-fuel and biomaterials. Meanwhile, several other black liquors such as soda, and neutral sulfite spent (NSSC) liquor and their derived lignin are not highlighted as sources of biofuel and biomaterials. Therefore, this review highlights all the types of black liquors including soda, and neutral sulfite spent (NSSC) liquor in terms of their sources, physical and chemical characterization, purification processes, and the potential applications of black liquor and its derived lignin.

Keywords: bio-materials; bio-fuels; lignin; spent liquor; purification

1. Introduction

Climate change has urged researchers to discover green alternative fuel products to reduce fossil fuel dependency and improve the efficiency and the quality of these products in order to tackle environmental issues [1]. The world's total energy consumption is expected to increase by 26% between 2014 and 2040, therefore, the need to find a sustainable, reliable, environmentally friendly and cost-effective clean energy source commercial applications have increased [2]. Also, using green bio-base materials and bio-chemicals will effectively contribute in reducing environmental issues.

Biomass is one of the potential alternative resource to replace fossil fuel and petroleum-derived materials as it is carbon neutral and sustainable [3]. However, using biomass for the production of bio-energy and bio-base materials would perhaps create problems such as a competition with food production and deforestation that may impact the environment negatively [4]. Furthermore, the physical and chemical properties of biomass are another drawback for generating energy and production of bio-base materials for its direct application. Additionally, the bulk density is unfavorable for transportation, handling and storage, while high ash content, low alkali metals content, high oxygen content, and low higher heating value are major barriers preventing its use as an energy source [5]. Another drawback of using biomass as an energy source at existing power generation facilities is the possible need to change the design of the equipment to enable them to use biomass as an alternative fuel due to the major differences in the physicochemical properties between fossil fuels and biomass [6].

Bio-fuels and bio-materials production from bio-waste such as agricultural residue, food industry residue, and spent liquor from the pulp and paper industry are cheap and can add value to the waste stream. Therefore, they have become an attractive alternative to fossil fuel and petroleum chemicals. These exploited resources can attract more attention by pre-treating or converting them to high quality and reliable bio-materials for various purposes [7], such as bio-char that can be used in several applications such as carbon sequestration and soil amendment [8].

The pulp and paper industry uses forest biomass as a feedstock and produces a byproduct called black (spent) liquor which is one of the biomass resources. Spent liquor can be further used for the production of energy and bio-base materials [9]. Black liquor is composed mainly of water, organic, and inorganic matters [10]. It contains about 65–85% solid content [11] and 10–50% lignin by weight [12].

Spent liquor and its derived lignin have been used for energy and bio-base material production via bio-refinery technologies for an efficient biomass conversion. Kraft pulp mills are already applying this technology for the production of cellulose fibers as a bio-material, some bio-chemicals such as tall oil and turpentine, and bio-energy to become energy self-sufficient mills [13]. During this process, the delignification (cooking) step is first carried out that significantly degrades lignin and hemicellulose and produce black liquor as byproduct. This is followed by steps that include a recovery boiler unit where liquor is concentrated by evaporation, and then burned for recovery of up to 65.4% of the energy content of black liquor and 96.6% of its sodium [14].

Kraft pulping is the most popular process for the production of pulp and paper around the world, followed by soda pulping. However, many pulp and paper mills currently tend to use pulping processes of smaller daily production capacity in order to reduce the quantities of chemical products to obtain environmentally friendly products. Neutral Semi sulfite chemical (NSSC) pulping is one of the traditional pulping processes that has survived and can achieve that target. Therefore, many pulp and paper mills currently use that process for their production [15]. Using different processes for the

production of pulp and paper can produce a variety of black liquors as byproduct with different physicochemical characteristics that needs to be highlighted.

Most of the available literatures focus on Kraft spent liquor resulting from the Kraft pulping process, while there is absence of published literatures that involves all the other types of spent liquors, though in recent years, few other types of spent liquors from different processes have been reported. Therefore, the aim of this manuscript is to give a comparative account of all the types of spent liquors in terms of sources, physical and chemical characteristics, purification processes, and potential applications of spent liquor and its derived lignin. Also it provides a comparative potential application of these spent liquors. All types of spent liquors need an opportunity to be used as environmentally friendly substitutes of petroleum fuel and materials.

2.   Spent liquors

2.1. Sources and types of black (Spent) liquors

The pulp and paper industry is the main source of the spent liquor that results from different chemical pulping process under different operational conditions. Pulping chemicals and operation conditions vary depending on the feedstock used for the production. During the pulping, the separation of cellulose, lignin (delignification), and hemicellulose from the wood or any feedstock chips take place by treating them with chemicals. Several pulping processes are used in pulp and paper mills. Kraft (sulfate) and soda are the two main alkaline chemical pulping processes that have been used commercially [16], in addition to sulfite pulping processes such as neutral sulfite semi chemical (NSSC) that has also been used widely nowadays [17]. Based on the pulping processes spent liquors can be categorized into three main types. These types include kraft, soda, and NSSC spent liquors.

2.1.1.   Kraft spent liquor

Kraft (alkaline) pulping is the predominating procedure for the production of chemical pulp and its byproduct named kraft black liquor. Only minute changes have been made in terms of the practical performance of this process since its introduction in 1879 due to its simplicity, rapidity, and high quality of the resultant pulp. However, this process possesses several drawbacks such as incomplete delignification and high temperature requirements for sufficient and extensive delignification needed in order to avoid exposing the carbohydrates to the pulping conditions for a long time [18]. This process involves treating both hardwood and softwood with a sodium sulfide and sodium hydroxide solution within the temperature range from 160 to 180 °C at pH 9–13.5 [19] for the production of bleached-printing and writing papers, paperboard, unbleached-heavy packaging papers, paperboard. It also involves dissolving pulp to produce viscose rayon, cellophane, acetate fibers, and films [20] and the spent liquor resulting from this process has an alkaline pH value.

2.1.2.   Soda spent liquor

Soda pulping process was invented in 1851 in England by Burgess and Watts. It was used industrially starting from 1853, and then was transferred to the United State of America in 1854. The

first mill was started in 1866; however, many soda pulping mills were converted to kraft pulping mills once the kraft pulping was invented [21]. It was used traditionally for non-woody materials, and for obtaining high yields of hardwood pulps that are employed for the production of paper packaging and boards [22].

Soda pulping process includes heating lignocellulosic biomass in a pressurized reactor (140–170 ℃) in the presence of 13–16 wt% sodium hydroxide (alkaline hydrolysis), to produce lignin called Soda lignin. This process was replaced by kraft pulping, which now dominates the chemical pulping industry. The Soda pulping process has limited use for feedstock such as some hardwoods and straws that are easily pulped, therefore it only contributes to 5–10% of the total pulp production in the world [23]. This process involves treating feedstock which is mainly composed of agricultural wastes with sodium hydroxide (10–15 wt%) at a temperature range of 150–200 ℃ [24] and pH of 9.5–10.0 [25]. The main advantages of this process are the absence of sulfur [24] and the ability to be used for the production of pulp and paper from non-woody feedstock. Therefore, it is an environmentally friendly process [26]. Spent liquor resulting from this process is named soda spent liquor.

2.1.3. Neutral sulfite semi-chemical (NSSC) spent liquor

NSSC process is one of the sulfite pulping processes that is used currently for the production of hardwood corrugating medium [15]. Generally, sulfite pulping involves treating the feedstock species at temperatures between 120–180 ℃ for 1–5 hours [24]. Sulfite pulping can be categorized into three processes, which are acid sulfite, bisulfate, and neutral sulfite. The difference among these processes is the level of acidity or alkalinity of the delignification solutions [16]; hence they produce black liquors with pH that are identical to their corresponding pulping process. Acid sulfite pulping takes place in the pH range of 2–4, bisulfate sulfite pulping takes place in the pH range of 5–6 [27], and neutral semi-chemical sulfite (NSSC) process takes place in the pH range of 5–7 [19]. The feedstock for NSSC pulping can be a mix of virgin wood chips with 20–35% of recycled or re-pulped secondary fibers [17]. Current developments involve the use of NSSC as a partial kraft pulp substitute in linerboard and bag grades [28,29] and the bleached NSSC can be used for the production of printing and writing papers, cards and tissue paper [15] as it is more flexible than kraft pulping in terms of variety cooking chemicals that can be used as pulping medium, bleaching of NSSC pulp can be performed simply using less energy to be refined [30]. The main drawback of this process is that NSSC spent liquor drain to the water resources as effluents if not used for the production of energy and bio-materials. NSSC spent liquor contains high amounts of inorganic content (ash) compared to its organic content.

2.2. Physico-chemical characteristics of spent liquors

The characteristics and composition of spent liquors are different depending on the type of feedstock (such as softwood, hardwood, or fibrous plants), the type of pulping processes that represent the operational conditions, and the chemicals used in the pulp and paper production mills. However, for all the feedstock and pulping processes used, the spent liquor can be described as a complex aqueous mix. This mix is composed of organic substances of wood and fibrous plants such as lignin, polysaccharides and resinous compounds of low molar mass, as well as inorganic

compounds that come from soluble salts ions [31]. The composition of kraft spent liquor was assumed to be $C_{10}H_{12.5}O_7Na_{2.4}S_{0.36}$ with a molar S/Na_2 ratio of 0.3 [32]. However, different kraft liquor has different chemical formula based on their elemental analysis. Table 1 represents the physico-chemical and the energy content in black liquors obtained from different type of feedstock and different pulping processes.

Table 1. Physico-chemical and the energy content of spent liquors obtained from different type of feedstock and different pulping processes.

Pulping process	Feedstock	pH	Proximate analysis (%)			Ultimate analysis (%)						HHV (MJ/kg)	Refs.
			Ash	Volatile matter	Fixed Carbon	C	H	N	S	Na	K		
Kraft	Pine & Spruce	11.8	35.93	56.92	7.15	30.67	3.74	0.67	0.00	n.d.	n.d.	14.51	[33]
Kraft	Wood	n.d.	22.85	n.d.	n.d.	32.99	4.00	0.11	5.02	21.87	0.81	13.09	[34]
Kraft	Wood	n.d.	39.11	n.d.	n.d.	36.7	3.3	0.11	5.4	18.3	0.9	n.d.	[35]
Kraft	Straw	n.d.	20.63	65.98	13.39	39.05	4.54	1.00	0.78	8.83	4.10	n.d.	[35]
Kraft	n.d.	n.d.	n.d.	n.d.	n.d.	36.40	3.50	0.14	4.40	18.60	2.02	n.d.	[11]
Kraft	Reed	n.d.	24.39	50.00	25.61	33.76	4.15	0.38	0.95	17.64	1.92	13.35	[36]
Not mentioned	Spruce wood	n.d.	n.d.	n.d.	n.d.	34.2	4.1	0.2	4.0	18.6	0.07	n.d.	[37]
Kraft	Not mentioned	n.d.	16.58	n.d.	n.d.	32.00	4.70	0.00	1.28	26.66	n.d.	n.d.	[38]
Soda	Wheat straw	11.3	27.38	49.32	20.10	33.43	2.77	0.23	0.13	12.18	2.04	n.d.	[39]
Soda	Wheat straw	n.d.	26.74	54.43	11.65	39.84	3.03	0.31	0.64	n.d.	n.d.	9.70	[40]
Soda	Cotton Linter	13.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	11.4	[41]
Soda	Wheat straw	n.d.	20.63	65.98	13.39	39.05	4.54	1.00	0.78	8.83	4.10	14.43	[42]
NSSC	Broadleaf wood	n.d.	24.17	50.62	25.21	36.32	3.43	0.04	5.45	18.35	1.03	14.98	[43]
NSSC	Recycled paper and wood	7.1	23.27	66.19	10.54	38.30	4.74	0.39	0.00	12.71	0.61	15.71	[33]
Kraft	Wood	n.d.	7.2	11.0	0.4	31.8	3.7	n.d.	n.d.	21.5	n.d.	11.4	[44]
Kraft	Softwood	13.4	76.98	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	34.5	n.d.	n.d.	[45]
Kraft	Softwood	n.d.	28.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	18.1	n.d.	n.d.	[46]
Not mentioned	Not mentioned	n.d.	40.7	41.0	18.3	59.4	5.3	0.2	5.7	32.1	n.d.	n.d.	[47]
Soda	Wheat straw	12.1	25.41	51.07	17.56	34.43	3.12	0.86	0.84	n.d.	n.d.	n.d.	[48]

n.d= not done

2.3. Applications of spent liquors

Several processes are employed to use crude spent liquors for the production of a variety of

bio-products. Spent liquors undergo several pretreatment methods to produce a number of products that can be used industrially as potential environmentally friendly substitutions for their equivalent petroleum-based products.

2.3.1. Thermo-chemical conversion of spent liquor

2.3.1.1. Combustion

In conventional processes at pulp and paper mills, spent liquor with solid content 60–70% is burnt in the recovery boilers at temperature of 105–120 ℃. With high solid firing, the solid content may exceed 80% at firing temperature of 175 ℃ [49]. Spent liquor combustion is a technique that has being used for energy generation. This is achieved by burning the organic material in the spent liquor and makes the mills energy self sufficient, while eliminating the spent liquor as a danger to the environment. Meanwhile, this combustion process was being used to recover valuable pulping chemicals [50].

Spent liquor combustion involves three stages which are drying, devolatilization, and char burning. Drying process is relatively slow where the water is evaporated and the droplets of the spent liquor are slightly swelled at low temperatures of 150–300 ℃. Drying is followed by devolatilization that includes pyrolysis and gaseous combustion. Devolatilization is a rapid process where a visible yellow flame is generated and the spent liquor droplets are rapidly swelled. Char burning is the last stage of the combustion that is slow process controlled by the air rate, water vapor, and carbon dioxide supply. This reaction takes place at the spent liquor droplets with no clear flame generated [51].

Kraft pulping is the most popular chemical pulping method being used in the pulp and paper mill. This method generates high amounts of produced kraft spent liquor [52], where producing one ton of pulp is accompanied by about 10 tons of spent liquor [53]. Despite the common and wide used of the recovery boiler technology, the spent liquor is burnt to generate small amounts of electricity and steam and to recover the chemicals for reuse in the pulping unit [54,55]. However, it has several drawbacks which include the sedimentation of inorganic alkali salt in the upper furnace causing corrosion of materials and reduction of effectiveness of heat transfer, low electric power generation, and smelt water explosions severity [56,57]. Therefore, separating lignin from the spent liquors would reduce the load on the recovery boiler and generate valuable products [45].

It is worth mentioning that recovery boilers technology can only be used economically for conventional kraft pulping process of hardwoods or softwoods. Therefore, it cannot be employed in the other pulping processes where non-woody is used as a raw material [58]. Small pulp mills that use non-woody feedstock cannot afford the capital-intensive system in order to process the black liquor for energy production and recycling of pulping chemicals22. Therefore, many of these small non-woody mills are forced to discharge their effluents with no treatments into the downstream. Some of them try to treat these effluents with secondary biological treatment and then discharge them downstream. However, this type of treatment would not prevent water stream pollution. Furthermore, it leads to the loss of valuable chemicals that can be recovered with the use of an appropriate recovery system [58].

2.3.1.2. Pyrolysis

Pyrolysis refers to direct dry thermal degradation of organic matters in the absence of oxygen to produce solid, liquid, and gas. Fuels, chemicals, and other matters have been commercially produced by this process from biomass and other organic materials. Two categories of pyrolysis are classified based on the thermal reaction residence time. Slow pyrolysis which has a long residence time has been commercially used for the production of solid fuel which is char. On the other hand, short residence time pyrolysis which are fast, flash, rapid, and ultrapyrolysis have been used for the production of high yield liquid fuel at moderate temperatures [59].

A few studies have reported the behavior of black liquor during pyrolysis. Gea et al. [35] studied the behavior of alkaline black liquor during pyrolysis. Also, Fletcher et al. [60] developed a model which is chemical percolation devolatilization (CPD) to predict the light gas and tar yields from black liquor as a fuel. Furthermore, several studies were performed for the production of not only solid, liquid, and gas fuel but also, activated carbon. The alkali metals (Na, K, etc.) which exist in black liquor react as an activating agent in the process of activation [47]. Also, a few studies for the production of green chemicals from the black liquors using pyrolysis were performed as depicted in Table 2.

Table 2. Production of fuel and matters from spent liquors by pyrolysis.

Spent liquor type	feedstock	Reactor	Products	Objectives	Refs.
Kraft	Not mentioned	Batch	Activated carbon	Adsorbents	[47]
Kraft	Coir pith	Batch (slow pyrolysis)	Biochar	Energy	[61]
Soda	Wheat straw	Fixed bed	aromatic chemicals	Feedstock for chemical industry	[40]
Kraft	Not mentioned	Fixed-bed	Gas, liquid, solid	Energy	[38]
Kraft	Not mentioned	Batch	Soild, liquid, gas	Energy	[62]
Kraft	Reed	fluidized bed	Gas, liquid, solid	Energy	[63]

2.3.1.3. Hydrothermal conversion

Hydrothermal conversion process is employed to produce high quality solid, liquid and gaseous fuel and volatile matters with different characteristics from wet low grade agricultural and biomass waste. This process occurs in liquid water media at elevated temperatures and pressures above saturated pressure [64]. Hydrothermal carbonization (HTC) can be used for the production of a solid product, hydrochar. HTC requires low temperatures ranging from 160 to 250 °C [65] to increase the solid yield of the char [66,67]. A variety of feedstock can be converted to around 35–60% solid fuel mass yield with carbon content similar to lignite [68,69]. Temperature is the prominent factor in addition to the reaction residence time and solid to liquid load that determines the mass yield, carbon content, and energy content of the solid product (hydrochar) [70]. On the other hand, hydrothermal liquefaction (HTL) can be used for the production of liquid (biocrude). HTL requires 300–350 °C temperature range and 15–20 MPa of pressure. A particular application of hydrothermal liquefaction

is at the pulp and paper industry for separating lignin from lignocellulosic biomass under 400 ℃ during the pulping process. In addition to HTC and HTL, hydrothermal gasification (HTG) can be used for the production of methane or hydrogen from biomass-based feedstock [64].

Several studies on hydrothermal conversion of black liquor have been performed for the production of solid bio-fuel and gas adsorbents using hydrothermal carbonization. Also, hydrothermal liquefaction processes were performed for the production of phenolic molecules from the lignin inherent in spent liquor as depicted in Table 3.

Table 3. Hydrothermal conversion of black liquor for the production of energy and matter.

Spent liquor type	reactors	HT type	Catalysts with the HT media	product	objective	Refs.
Spent liquor solids	Batch	HT carbonization	Formaldehyde solution as a polymerization agent	Soild hydrochar	Energy or matter	[7]
Reed spent liquor	Batch	HT carbonization followed by fast carbonization at 350 ℃ in fluidized bed reactor	n.d.	Solid adsorbent	Adsorption for CO_2, CH_4 and N_2	[71]
NSSC Red Liquor	Batch	HT carbonization	Acetic acid	Solid hydrochar	Energy	[72]
Cotton linter Kraft liquor	Batch	HT carbonization	No addition	Solid hydrochar	Energy or matter	[41]
Caustic Soda sulfur free spent	Batch	HT liquefaction	No addition	Liquid and biocrude	Phenolic molecules and energy	[13]

n.d.= not done

2.3.1.4. Gasification

Spent liquor gasification technology is one of the main methods to avoid the challenges associated with the traditional recovery boilers in pulp and paper mills [73]. It has been proposed to convert the organic content of the spent liquor into clean gas fuel for gas turbine utilization to more value-added bath for spent liquor uses [74]. Several reports about spent liquor gasification using pyrolysis gasification [75,76], supercritical gasification [44,77], and steam gasification [3,42] are available.

Researchers are interested in designing an integrated system to combine the production of pulp and paper as main products, and use the black liquor to produce hydrogen by supercritical water gasification in addition to a low amount of carbohydrates and carbon dioxide [78]. This integrated system was designed for the potential production of pulp and paper and hydrogen for the mill energy purposes in a study by Cao et al. [48] to design an energy self-sufficient manufacturing mills. Therefore, spent liquor gasification can be a promising alternative or a complement to traditional recovery boilers as integrated gasification-combined-cycle power at pulp and paper industry.

Different gasification studies were performed for the production of gases for energy and materials using kraft and soda spent liquors as depicted in Table 4, while, no NSSC spent liquor gasification reports are available as the NSSC pulping process has only been in use as of recent times.

Table 4. Spent liquors gasification for the production of energy and matters.

Spent liquor type	Feed feedstock	Reactor	Products	Objective	Refs.
Soda	Wheat straw	Continuous reactor	H_2, CO, CO_2, low hydrocarbons	energy	[39]
Kraft	Not mentioned	Gas turbine	H_2S, CH_4	matter	[79]
Kraft	Not mentioned	Fluidized bed	H_2, CO, CO_2, low hydrocarbons	energy	[80]
Kraft	Not mentioned	Combined process	Methanol from syngas	matter	[81]
Kraft	Wood	Gasifier	CO_2, CO, and H_2	energy	[82]
Kraft	Not mentioned	Continuous reactor	H_2, CO, CO_2, low hydrocarbons	energy	[44]

2.4. Spent liquors purification processes

Purification is one of the necessary steps for beneficiation of the liquors and mainly refers to the ash removal process and lignin recovery from the spent liquors. Lignin is one of the most abundant aromatic materials in the world and pulp and paper manufacturing is the main source of the industrial lignin which is spent liquor lignin [83].

The amount of biomass derivatives such as lignin has attracted researchers to focus on how to purify the kraft spent liquor for the production of high value bio-fuel and bio-chemicals applications in addition to the pulp and paper production. This process is called integrated products biorefinery [58]. Several approaches have been used to purify the spent liquor for production of pure lignin. Acidification is the most prominent approach, but, lignoboost, lignoforce approaches have recently been commercialized [84]. Sequential liquid-lignin recovery and purification (SLPR) also has being used in a few mills [85].

2.4.1. Acidification

Acidification is the main efficient and economical approach that is being used for the kraft spent liquor purification to produce pure lignin [86]. Acidification relies on the precipitation of pure lignin using either CO_2 or sulfuric acid or a combination of both to reduce the pH of the spent liquor from more than 13 to around 9, filtering it using a filter belt, and then washing it with the water to obtain lignin, minimal amounts of carbohydrate and ash with trace of sulfur as shown in Figure 1 [87]. However, several drawbacks that can affect the efficiency of the process and the quality of the produced lignin were reported when using acidification for the purification of lignin. The first drawback is filtration problem that might be caused by rising temperatures during the acidification process hence, large particles of lignin can be generated and consequently impact the filtration rate negatively [88] by causing bulging in the filtration area. In addition, the impurities can accumulate within the precipitated lignin [89]. The second drawback is related to sulfur that may be released as a by-product at the low pH during the acidification hence, increasing the sulfur content of the resulting lignin [90]. The third drawback is that during the washing process of the precipitated

lignin, ionic strength gradients are created at pH of 9 in the lignin filter cake affecting the filtration process negatively [89].
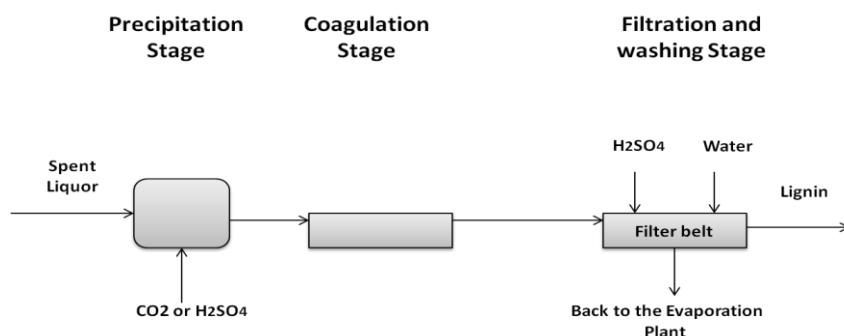
Figure 1. Acidification system for spent liquor lignin purification.

2.4.2. LignoBoost technology

Purification of lignin from kraft spent liquor can be performed using LignoBoost technology which was invented to develop the acidification process. Nowadays this technology is used on a commercial scale by Domtar Inc. in North Carolina, USA [91]. In this technology, kraft spent liquor that comes from evaporators of the recovery section of kraft pulping process would be acidified with carbon dioxide to reach a pH of 9 in order to precipitate lignin and then filter it. After this stage filtered lignin is re-dispersed and acidified again with sulfuric acid and then filtered and washed to obtain pure lignin as shown in Figure 2. The major advantage of this technology is that the pH and temperature of the liquid media of re-dispersed lignin are nearly equal to those of final washing liquid, leading to a reduced concentration gradient. Change in pH level, ionic strength, and lignin solubility occurs in the slurry during the washing stage. Also, the yield of lignin is higher [92] because of the low pH of the re-slurring water during this stage, which leads to an extra precipitation of extracted lignin. Moreover, the filtration area and the volume of the acid water can be reduced. These factors make this technology cost effective for pure lignin recovery [89].
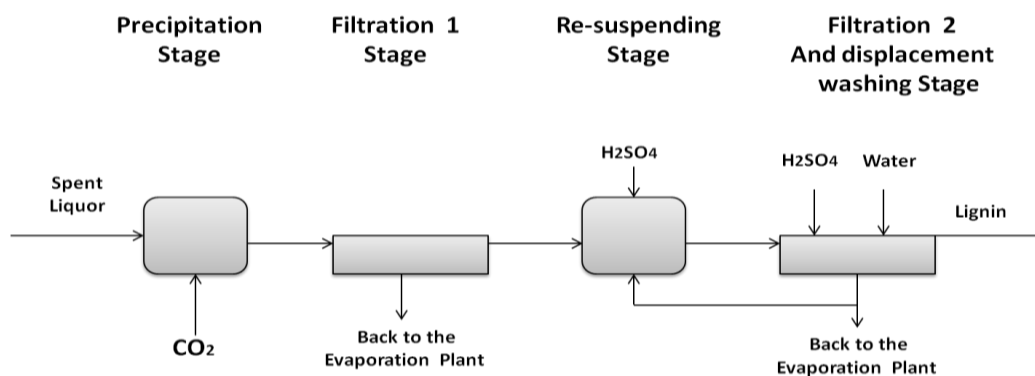
Figure 2. LignoBoost system for spent liquor lignin purification.

2.4.3. LignoForce technology

LignoForce technology is another process developed to obtain high quality lignin from the kraft spent liquor by FP Innovations. This technology was commercialized by West Fraser Inc. in Alberta, Canada in 2016. It includes several steps to purify the lignin as shown in Figure 3. The first step is the oxidation of black liquor by oxygen. The second step is the acidification of the oxidized spent liquor by spraying carbon dioxide into the spent liquor solution at temperature ranging from 70–75 °C to reach a pH of 9.5–10.0. The third step is the precipitation and filtration of the acidified spent liquor. This is followed by the washing of the filtered precipitated spent liquor cake with sulfuric acid and water. The fifth step is pressing, followed by the final step which is air drying of the produced lignin [88].
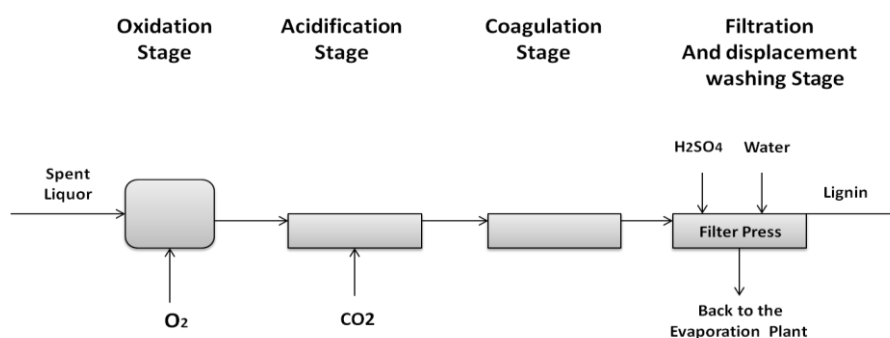

Figure 3. LignoForce system for spent liquor lignin purification.

2.4.4. Sequential liquid-lignin recovery and purification (SLPR) process

SLPR process involves three main stages which are carbonation, acidification, and filtration as shown in Figure 4 [93]. Carbonation is the process where carbon dioxide is bubbled near the bottom of spent liquor to reduce its pH to 9.5. This process leads to precipitation of lignin to a form of a highly solvated liquid at elevated temperature that can be over 90 °C [94]. Acidification process takes place where highly solvated liquid of lignin is pumped to a sulfuric acid reactor. After this process, precipitated lignin at pH of 2.5 would be in solid form. Solid lignin slurry will then be filtered by a filter press for the production of pure lignin with a solid content of 65% and 1% ash [24].
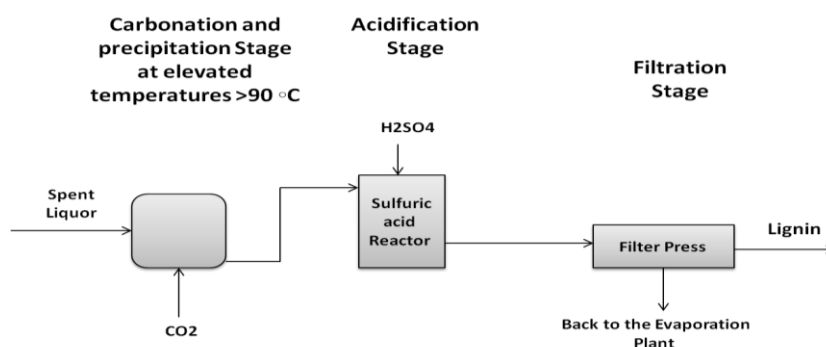

Figure 4. Sequential liquid-lignin recovery and purification (SLPR) system.

3. Spent liquor lignin derived from the pulp and paper industry

Industrial lignin is mainly obtained through paper and pulp industry from spent liquors resulted from the kraft process to produce a small percentage of energy [54]. In pulp and paper industry there are three main kinds of lignin which are kraft, soda, and sulfite (mainly NSSC) lignin.

3.1. Types of spent liquor lignin

3.1.1. Kraft lignin

Kraft lignin is one of the most predominant pulping operations which convert wood or non-wood material into pulp within paper industries around the world. Kraft pulp mills have evolved to integrate with the system requirements of high engineering to become large facilities in order to recover pulping chemicals and energy that rely on burning of the pulping liquor, which is spent liquor. Thus, the strategy of extraction and separation of lignin is to expand pulp capacity, as well as to find an economical and environmental balance within the paper manufacturing facilities to be exploited in the production of energy and chemicals [22].

Kraft or sulfate process is now the major traditional procedure for pulping to produce large amounts of lignin [95]. This process requires breaking down the linkage between lignin and cellulose by the treatment of wood chips with a mixture of sodium hydroxide and sodium sulfide under strong alkaline conditions. Delignification process takes place in three stages, first of which occurs at a temperature around 150 ℃ controlled by diffusion, second stage which is the biggest part of the delignification (90 wt%) occurring at temperatures ranging from 150 to 170 ℃ and the third stage which occurs at higher temperatures. The recovery of lignin can occur by lowering pH to values between 5 and 7.5 with either sulfuric acid or carbon dioxide of black liquor, which is the alkaline liquid remaining after pulp extraction [96]. The output lignin of this process with aliphatic thiol groups is called kraft lignin, which has sulfur content (1–2 wt%) and is hydrophobic. Therefore, it needs to be changed to improve its ability to react [97].

The major differences in physicochemical characteristics of kraft lignin mainly depend on the difference of the original feedstock used in the pulping process [98]. El Mansouri and Salvad'o [99] reported that kraft lignins obtained from softwood and calcium lignosulfonate have higher purity based on analysis of ash content, carbohydrate, molecular weight and functional group. It should, however, be noted that the purity level also depends on the purification method used.

3.1.2. Soda lignin

Lignin recovery process can be performed depending on the raw material used; therefore, lignin obtained from non-woody material is difficult to recover by filtration or centrifugation due to its high carboxylic acid content that emerging from oxidation of aliphatic hydroxy groups. One of the main features of soda lignin for use in specialized applications is that it contains no sulfur and little hemicelluloses or oxidized defect structures. Therefore, it has good potential uses in the production of high value product [97]. This type of lignin is insoluble lignin [98].

El Mansouri and Salvad'o [99] demonstrated that Soda-anthraquinone lignin, which is obtained from a mixture of long fiber plants, has low content of ash as kraft lignin. Therefore, it has high

purity compared with lignosulfonate (NSSC lignin) that has high content of ash. Also, based on its other characteristics such as carbohydrate, molecular weight and functional groups etc. soda lignin could be good as a crude material to produce adhesives. On the other hand, Schorr et al. [98] confirmed that soda lignin obtained from wheat straw has lower purity than kraft lignin.

3.1.3. NSSC lignin

The main commercial source of NSSC and other sulfite lignin at the present time is the pulp and paper industry. Sulfite pulping reactions are commonly implemented at temperatures ranging from 140 to 160 ℃ and pH of acid sulfite process ranging from 1.5 to 2.0, however pH of bisulfite process ranging from 4.0 to 5.0 [95]. Neutral sulfite process reaction temperatures are ranging from 160–180 ℃ and its pH ranging from 5–7. NSSC lignin has high ash content; therefore it needs to be purified by the reduction of its ash content [15] to be used in the generation of energy or bio-products. This lignin soluble in basic solution, acidic solution, and in highly polar organic solvents; however, reactions of hydrolysis and excessive sulfonations can take place [100].

3.2. Physico-chemical characteristics of purified spent liquor lignin

Lignin is composed of phenylpropane units that form a three-dimensional amorphous lignin macromolecule. Phenylpropane units come from the copolymerization of three primary sinapyl alcohol and *p*-coumaryl alcohol [83]. The energy content of lignin in terms of higher heating value (HHV) is 23.3–26.6 MJ/kg which is higher than the one of both cellulose 17–18 MJ/kg and hemicelluloses 17–18 MJ/kg [101].

The characteristics of spent lignin obtained from spent liquor vary based on the original feedstock and chemicals that are used in different pulping processes at pulp and paper mills as presented in Table 5. The chemical structure and content of natural lignin vary with and within the plants based on species, age, morphological position and growth environment of these plants. Softwood lignin is mainly composed of coniferyl alcohol (guaiacyl) units, while hardwood lignin is composed of various guaiacyl: syringil ratios [102,103].

Table 5. Physico-chemical characteristics of lignin derivate from spent liquors.

Purification process	Feedstock	Proximate analysis (%)			Ultimate analysis (%)				Refs.
		Ash	Volatile matter	Fixed carbon	C	H	N	S	
Acid precipitated kraft lignin	Eucalyptus	12.4	52.4	35.2	64.4	5.0	n.d.	1.2	[104]
Acid precipitated kraft lignin	Not mentioned	9.50	44.93	31.12	59.46	5.07	0.05	2.15	[105]
Acid precipitated kraft lignin	Eucalyptus hardwood	12.4	52.4	35.2	64.4	5.0	n.d.	1.2	[106]
Acid precipitated kraft lignin	Eucalyptus hardwood	2.1	n.d.	n.d.	60.4	5.3	0.2	3.5	[107]
Acid precipitated kraft lignin	Eucalyptus hardwood	2.1	n.d.	n.d.	71.4	8.6	n.d.	5.0	[90]

Continued on next page

Purification process	Feedstock	Proximate analysis (%)			Ultimate analysis (%)				Refs.
		Ash	Volatile matter	Fixed carbon	C	H	N	S	
Acid precipitated kraft lignin	Pinus softwood	4.5	n.d.	n.d.	43.8	4.5	n.d.	24.6	[90]
LignoBoost	Softwood	0.90	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	[108]
LignoBoost	Hardwood	0.75	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	[108]
Acid precipitated kraft	Softwood	n.d.	n.d.	n.d.	65.0	5.7	0.12	1.62	[109]
Acid precipitated soda lignin	Wheat straw	0.73	65.97	34.03	59.28	5.37	0.70	1.27	[40]

n.d.= not done

3.3. Spent liquor lignin modification methods

Spent liquor can be added as unchanged macromolecule directly to other materials in order to improve the properties of these materials to be used for many purposes. On the other hand, it can be modified to produce various compounds [110]. Modification of lignin can be performed by three methods which are depolymerization, modification of functional groups and modification of hydroxyl groups [111].

3.3.1. Lignin depolymerization

Spent liquor lignin is a potential source of small molar mass compounds that can be used as alternatives of fossil fuel compounds [110]. Several methods can be used to depolymerize that lignin into smaller fragments. Current lignin depolymerization processes are thermal depolymerization which includes pyrolysis and hydrothermal liquefaction to produce bio-crude, gasification of aromatic compounds to produce combustible gases, and direct combustion for oxidative energy generation. Also, chemical depolymerization includes basic/acidic catalysis and oxidation/reduction. Furthermore, biological depolymerization includes oxidative depolymerization or catabolizing lignin by enzymatic reactions and growing cells [112].

Oxidation is a chemical depolymerization method that has been used commercially for the production of significant amount of small molar mass compounds such as Vanillin, Syringic acid and 4-Hydroxybenzaldehyde. This process can be performed using different kinds of oxidants such as nitrobenzene, metallic oxides, air and oxygen. Pyrolysis depolymerization process can be used for the production of bio-oil, phenol and acetic acid from lignin. Also, gasification of lignin can be used to produce syngas. The other processes like hydrogenation, hydrolysis and microbial conversion are used to covert lignin into high-valued chemicals such as phenol, Vanillic acid, Ferulic acid and ρ-Coumaric acid [111]. Biological or microbial conversion of lignin can be performed by bacteria or fungi enzymes. The feasibility of biological valorization of lignin were proved by many studies, however this conversion method faced common limitations such as low productivity and yield that require to be solved in future [113].

3.3.2. Lignin functional groups modification

Lignin functional groups are hydroxyl, methoxyl, carbonyl and carboxyl groups. These

functional groups can be modified to improve and expand their potential application range [114]. Many modification methods have been investigated; however, the most common methods are alkylation or dealkylation. For example, formaldehyde-free wood adhesives have been developed using dealkylation processes [111].

Hydroxyl groups of lignin can be modified by only one method which is esterification to synthesize polyesters, elastomeric materials and epoxy resins from lignin. Phenolation is another process to modify lignin where it reacts with phenol in an acidic medium to synthesize phenol-formldehyde. By etherification, lignin can be converted into organic solvents soluble polyol that can be used to produce new materials such as lignopolyols [115,116].

Phenolic hydroxyl groups are the most effective groups on the material reactivity as they are the most reactive lignin's functional groups. Therefore, the modification of these groups is an important step to improve lignin's solubility [117].

3.4. Potential applications of the purified spent liquor lignin

Recently, lignin that comes as a byproduct from the paper and pulping industry and biorefineries has attracted wide attention for its valorization due to the necessity of environmentally friend bio-based industry [113]. Several high value organic compounds and inorganic compounds can be recovered from spent liquor by the purification processes [83]. Lignin is the commonly used name for the purified spent liquor as most of the organic material comes from lignin obtained from delignification (pulping process) in pulp and paper industry. Spent liquor lignin is significantly different than natural plant lignin in terms of purity and chemical structure. Spent liquor lignin contains a certain percentage of impurities as an ash that results from cooking process in pulp and paper mills. Also, during the cooking stage, a significant amount of C-O-C linkages between the propyl phenol units of lignin are decreased causing difficulties in the depolymeriztion of this lignin other than plant lignin [13]. Also, pulping stage and precipitation acidity in case of acid precipitation of lignin can affect its properties to those required for the final potential applications [118]. On the other hand, many studies have been performed to depolymerize spent liquor lignin into small phenolic molecules such as oxidative depolymerization, ionic liquid catalyzed depolymerization, heterogeneously catalyzed depolymerization, enzymatic depolymerization and thermal degradation [119]. Spent liquor lignin contains a high amount of carbohydrate functional groups such as carboxylic acids with low calorific value in comparison to lignin [120]. The recovery of this product prior to burning the spent liquor in the recovery boiler would add value to the waste stream and make the process more efficient [121]. Furthermore, the high content of aromatic units in lignin makes it a feedstock for the production of phenolic compounds [122].

Four main potential applications were applied for the utilization of lignin to replace petrochemical-based feedstock [123]. First application is the use of spent liquor lignin as fuel for generation of energy [124]. The second is utilizing lignin as bio-carbon material to prepare carbon-based materials such adsorbents as an activated carbon for waste water treatments, or carbon fibers [106,125]. The third application is using spent liquor as macromolecules such as polymer blends and adsorbents from lignin, hydrogels, and Phenol-formaldehyde resins. The final application is employing this lignin as source of aromatic compounds such as phenol, benzene, and vanillin [111].

3.4.1. Spent liquor lignin as bio-fuel

As spent liquor lignin possesses a high caloric value and high carbon content, it can be potential source of energy as bio-fuel [107]. Depolymerization and gasification are the main two different conversion pathways that can be used to produce combustible liquid, gaseous and solid bio-fuel from the spent liquor lignin. However, better process economy with higher yield can be accomplished by processes integration. For example, lignin depolymerization can be performed to produce aromatic chemicals; on the other hand the solid char can be received by a gasifier to obtain hydrogen for fuel upgrading. In addition to that, the light hydrocarbons can be catalytically reformed to obtain syngas and hydrogen [126].

Lignin can be a potential source of bio-oil using liquefaction process that depolymerize the lignin into bio-oil with low oxygen content to be blended with conventional fossil fuels for motor fuel applications [127]. Also, spent liquor lignin can be a potential source for solid bio-fuel production using the purified lignin directly for combustion, or by subjecting the lignin to thermal depolymerization such as pyrolysis or hydrothermal carbonization. Kim et al. [128] used hydrothermal carbonization (HTC) as depolymerization process to upgrade the thermal properties of lignin in terms of higher heating value and carbon content that were increased from 20.1 to 26.0 (MJ/kg) and from 51.8 to 58.0% respectively using HTC process at 280 ℃. Lignin pyrolysis conditions such as temperature range and residence time should be optimized for the type of lignin because lignin properties vary according to its original plants and chemical pulping that lignin subjected to at pulp and paper mills [126]. Thermogravimetric studies have conducted to show that lignin pyrolysis take place over a wider range of temperature that ranging from 160 to 900 ℃ compared to polysaccharides that range from 220 to 400 ℃ [129]. Also, the solid bio-fuel yield obtained from pyrolized lignin is higher than that obtained from the other lignocellulosic biomass components [126].

3.4.2. Spent liquor lignin as bio-carbon based materials

Lignin is a rich carbon resource which consists of 50–60% carbon therefore it can be great potential substitute of carbon-based materials such as activated carbon, carbon fiber, binders, carbon black.

Carbon-based materials can be used as activated carbon to remove compounds such as colors, odors, and organic materials from aqueous media. In addition, the adsorption of pharmaceutical compounds such as diclofenac [130] and removal of the antibiotics residue such as amoxicillin from water [131] can be performed using activated carbon. Feedstocks that can be used commercially to prepare the activated carbon include coal, peat, lignite, and lignocellulosic biomass such as some agricultural and woody wastes [132]. Also, black (spent) liquor which is a pulp and paper byproduct can be used to obtain low-cost lignin based activated carbon by steam activation for dye wastewater treatment such as methylene blue adsorption [133]. Activated carbon with a large surface area and porosity is efficient for adsorption of chemicals from gases and liquids. For example, a surface area ranging from 250 m^2/g to over 2000 m^2/g makes the activated carbon adaptable adsorbents for many applications such as water, waste water and gas treatment, removal of the undesirable compounds that impact color, odor, and taste in the food industry. The mining industry also uses activated carbon to remove metallic minerals from leached liquors [134].

The presence of high ash contents in the activated carbon causes several drawbacks because ash interferes with adsorption during the competitive adsorption process. Also, ash can cause blockages in the pores of the activated carbon and the catalysis of undesirable reactions during the adsorption process. Ash removal process reduces the harmful effect of pH on the activated carbon as Ahmedna et al. stated [135] therefore, spent liquor cannot be used directly as activated carbon; however, purified black liquor lignin can be excellent potential activated carbon. This lignin requires an activation process prior using it as activated carbon. The activation processes can be physical activation such as pyrolysis or chemical activation using different chemicals to increase the surface area and obtain activated carbon with high porosity. Table 6 indicates the possibility of production of activated carbon from activated purified spent liquor lignin.

Table 6. Production of activated carbon from spent liquors lignin.

Spent lignin used	Activation method	Surface area (m^2/g)	Micropore volume (cm^3/g)	Potential application of the product	Refs.
Kraft lignin	Physical Carbonization	1853	0.860	Removal of p-nitrophenol from aqueous solutions	[136]
Kraft lignin	Chemical: $ZnCl_2$	1800	1.039	removal of water pollutants	[137]
Kraft lignin	Chemical: H_3PO_4	1459	0.82	Removal of phenol, 2,4,5-trichlorophenol and Cr (VI) as representative of toxic contaminants found in industrial wastewaters	[138]
Kraft lignin	Chemical: ortho-phosphoric acid	1305	0.67	n.d.	[105]
Kraft lignin	Chemical: H_3PO_4	1370	0.78	n.d.	[139]
Kraft lignin	Physical: Carbonization	1613	0.47	n.d.	[140]
Kraft lignin	Physical: steam	289.21	0.222	Removal of methylene blue (MB) from aqueous solution	[133]
Kraft lignin	Chemical: KOH and Carbonization	2943	1.901	Ni (II) adsorption	[141]
Kraft lignin	Chemical: KOH and Carbonization	1199	0.97	potential sorbents of organic contaminants from polluted sediment or water	[108]

n.d.= not done

Lignin can be used as carbon fibers to replace polyacrylonitrile in civil engineering, automobile industry, aircrafts and sport goods applications therefore make the process economically viable [142]. Furthermore, spent liquor lignin plays a key role for the production of binders and resins such as phenol-formaldehyde resins that have unique heat and moisture resistance and strength. These binders can be fundamental materials in industries such as wood bonding, insulation, lamination or plywood adhesives [111].

3.4.3. Spent liquor lignin as macromolecules

Lignin of spent liquor can be used as polymer blends. Therefore, it can be blended with other synthetic or bio-based polymers as it is not native lignin and has some impurities that change its chemical and physical properties. This lignin is functionally fulfilled when blended with polyethylene, polystyrene, polypropylene or natural rubber within composites [98,111]. Also, this lignin can work as biopolymeric hydrogels that is able to absorb water or other solvents efficiently for biological, biomedical and environmental applications [111].

3.4.4. Spent liquor lignin as source of aromatic compounds

Aromatic compounds such as benzene, toluene, xylene, phenol, and vanillin can be produced from lignin as essential substances after breaking this lignin into its essential structural materials. Benzene, toluene, and xylene posse wide scale of applications in the chemical industry. They represent 60% of all aromatic compounds on market and 24% of the worldwide petrochemical compounds market [142]. Therefore, benzene, toluene, and xylene that are obtained from lignin can be great green substitutes for petroleum benzene, toluene, and xylene [111].

Also, phenols that obtained from lignin can be a great potential opportunity to replace phenols obtained from petroleum sources. Because the current prices of petroleum phenol depend on oil prices, lignin can be considered renewable material that has comparatively stable market price. Phenol is an important substance in the plastic and other industries [142]. Major phenol applications are phenol-formaldehyde resins production and polyurethane foams that is used in the vehicles manufacturing [111].

The other important aromatic petroleum substance obtained from lignin that can be replaced by a green substitute is vanillin. Nowadays, 20% of vanillin available on markets is produced from lignin but the other 80% is produced from the crude oil. However, vanillin prices from both resources are similar [142]. Furthermore, spent liquor lignin fractions can be functioned as antioxidants for different products [143] such as antioxidants derived from spent liquor lignin that proved to be used in thermoplastic industry [144]. Lignin can be a great platform for producing variety of green products as presented in Table 7.

Table 7. Production of high value compounds from black liquor lignin and their potential applications.

Spent liquor used	Feed stock	Method	Product	Potential application of the product	Refs.
Kraft	Softwood and hardwood	Lignoboost purification	Lignin fractions such as dichloromethane	Antioxidant	[143]
Soda	Alfa grass	Acid precipitation	Antioxidants	Antioxidants in thermoplastic industry	[144]

Spent liquor used	Feed stock	Method	Product	Potential application of the product	Refs.
Kraft	Soft and hardwood	Combining membrane filtration, acid precipitation and cooling crystallization	Hydroxy acids	Production of polymers, pharmaceuticals and food additives	[145]
Soda	Spruce	Acid precipitation and then washing with ether	Functional additive	UV stabilisers in polyethylene	[146]
Kraft	Pine and Spruce	Acid precipitation and then washing with ether	Functional additive	UV stabilisers in polyethylene	[146]
Kraft	Pin wood	Hydrolysis	Organic acids and small molecular aromatics	Lactic acid, and small molecular aromatics	[147]
Kraft	Soft wood	Fractionation by successive extraction	Wood adhesive	Binders	[148]
Soda	Sarkanda grass	Fractionation by successive extraction	Plywood adhesive	Binders	[148]
Kraft	pine	Acid precipitation	n.d.	Phenol (P) substitute in the synthesis of lignin-phenol-formaldehyde (LPF) resins	[149]
Kraft	Alfalfa	Acid precipitation and then Photodegradation By TiO2/UV Photo-catalytic process	Vanillin coniferylic alcohol and highly oxidized phenols	Feedstock for chemical industry	[12]
Soda	Softwood (pine)	Ultrafiltration	Hydroxy acids	Polymer feedstock for chemical industry	[150]
Soda	Hardwood (birch)	Ultrafiltration	Hydroxy acids	Feedstock for chemical industry	[150]
Sulphite	Hardwood (*Eucalyptus globules*)	HCl precipitation, ethyl acetate, and then liquid chromatography	Phenolic compounds	Antioxidants	[151]
Kraft	Softwood	Ultrafiltration and nanofiltration	Organic acids (e.g. hydroxy acids)	n.d.	[152]
Kraft	Hardwood and softwood	Ultrafiltration and nanofiltration	Organic acids (e.g. hydroxy acids)	n.d.	[152]

Spent liquor used	Feed stock	Method	Product	Potential application of the product	Refs.
Kraft	Not mentioned	Acidification/precipitation or LignoBoost purification and then oxidation of pure lignin	Vanillin	Food industry as a flavour agent and antioxidant additive, antifoaming agent, vulcanization inhibitor and chemical precursor for pharmaceutical and agrochemical industries	[83]
Soda	Birch wood	Acid-precipitation	Aliphatic low-molecular-mass carboxylic acids	Feedstock for chemical industry	[153]

n.d.= not done

4. Conclusion

All types of black (spent) liquor are promising sources of biofuel and biomaterials. However**,** most of the published literatures concentrate on the well-known black liquor and its derived lignin which is kraft black liquor. This study gives an insight into all the kinds of black liquor that are generated from various pulping processes which adopt newer raw materials with kraft, soda, and sulfite processes. The impacts of newer feedstock types were also highlighted. The characteristics of those different black liquor and their characteristics in terms of physical properties and chemical composition were summarized. Applicable purification processes, thermal, hydrothermal, and gasification of the black liquors were evaluated and analytical investigations were compared for the black liquors and the lignin derived by various researchers. Conclusive potential applications of these liquors and their derived lignin were tabulated for applicable categories as industrial products. Based on the information provided in this manuscript, a wide potential application can be added to the current applications of the pulp and paper byproduct. Spent liquor can be used either directly for example in combustion or after purification methods. A new stream of applications can be produced from byproduct of pulp and paper mills that use different feedstock such as virgin wood or recycled fibers or a mix of both.

Acknowledgements

Conflict of interest

All authors declare no conflicts of interest in this paper.

References

1. Thuijl E, Van Roos C, Beurskens L (2003) An overview of biofuel technologiesmarkets and policies in Europe,1–64.
2. ExxonMobil (2016) The Outlook for energy: a view to 2040, 1–16.
3. Naqvi M, Yan J, Dahlquist E (2010) Black liquor gasification integrated in pulp and paper mills: A critical review. *Bioresource Technol* 101: 8001–8015.
4. Field CB, Campbell JE, Lobell DB (2008) Biomass energy: The scale of the potential resource. *Trends Ecol Evol* 27: 761–767.
5. Demirbaş A (2005) Estimating of structural composition of wood and non-wood biomass samples. *Energ Source* 27: 761–767.
6. Kappejan J, Loo S, (2008) Biomass fuel properties and basic principles of biomass combustion, In: *The Handbook of Biomass Combustion and Co-Firing*, 2nd ed., Earthscan: London, UK, 1: 7–34.
7. Kang S, Li X, Fan J, et al. (2012) Solid fuel production by hydrothermal carbonization of black liquor. *Bioresource Technol* 110: 715–718.
9. Joelsson JM, Gustavsson L (2008) CO2 emission and oil use reduction through black liquor gasification and energy efficiency in pulp and paper industry. *Resour Conserv Recycl* 52: 747–763.
10. Marklund M, Tegman R, Gebart R (2007) CFD modelling of black liquor gasification: Identification of important model parameters. *Fuel* 86: 1918–1926.
11. Ramesh S, Chaurasia S, Mahalingam H, et al. (2013) Kinetics of Devolatilization of Black Liquor Droplets in Chemical Recovery Boilers—Pyrolysis of Dry Black Liquor Solids. *Int J Chem Eng Appl* 4: 1–5.
12. Ksibi M (2003) Photodegradation of lignin from black liquor using a UV/TiO2 system. *J Photochem Photobiol A* 154: 211–218.
13. Huet M, Roubaud A, Chirat C, et al. (2016) Hydrothermal treatment of black liquor for energy and phenolic platform molecules recovery in a pulp mill. *Biomass Bioenerg* 89: 105–112.
14. Adams TN, Frederick WJ, Grace TM, et al. (1997) Kraft Recovery Boilers. Tappi Press, Atlanta.
15. Area MC, Fernando FE, Venica A, et al. (1998) NSSC Process Optimization: I. Pulps Quality. Pulping Conference, Proceedings of the Technical Association of the Pulp and Paper Industry, 2: 671–81.
16. Andelin J, Robert W, Niblock JWC (1989) The Pulp and Paper Making Process. Technologies for Reducing Dioxin in the Manufacture of Bleached Wood Pulp.
17. Bajpai P (2014) Emissions from pulping, In: Biological Odour Treatment, *Springer Briefs in Environmental Science*, 9–17.
18. Gierer J (1980) Chemical Aspects of Kraft Pulping. *Wood Sci Technol* 14: 241–266.
19. Patt R, Kordsachia O, Süttinger R, et al. (2005) Paper and Pulp. Ullmann's Encyclopedia of Industrial Chemistry. Wiley-VCH Verlag GmbH and Co. KGaA. Available from: http://dx.doi.org/10.1002/14356007.a18_545.
20. Andelin J, Niblock R, Curlin J (1989) The pulp and paper making process, In: Technologies for Reducing Dioxin in the Manufacture of Bleached Wood Pulp. U.S. Congress, Office of Technology Assessment, Washington, DC, USA, 17–25.

21. Christopher B (1996) Handbook of Pulping and Papermaking. Second. California, United states of America: Academic Press, An imprint of Elsevier.

22. Lora J (2008) Monomers, Polymers and Composites from Renewable Resources: Industrial Commercial Lignins: Sources, Properties and Application, 225.

23. Patt R, Kordsachia O, Suttinger R (2011) Pulp, In: Ullmann's Encyclopedia of In-dustrial Chemistry, Wiley-VCH Verlag, 2011, 487–491.

24. Klett AS (2017) Purification, Fractionation, and Characterization of Lignin from Kraft Black Liquor for Use as a Renewable Biomaterial. Clemson University.

25. Ninawe S, Kuhad RC (2006) Bleaching of wheat straw-rich soda pulp with xylanase from a thermoalkalophilic Streptomyces cyaneus SN32. *Bioresource Technol* 97: 2291–2295.

26. González-García S, Moreira MT, Artal G, et al. (2010) Environmental impact assessment of non-wood-based pulp production by soda-anthraquinone pulping process. *J Cleaner Prod* 18: 137–145.

27. Gratzl JS, Chen CL (1999) Chemistry of Pulping: Lignin Reactions. *ACS Symp* 742: 392–421.

28. Von Koeppen A (1986) Chemimechanical Pulps from Hardwood Using the NSSC [Neutral Sulfite Semichemical] Process. *Paper Trade J* 170: 49–51.

29. Farrington A, Hickey BL (1989) Wood sources for the Port Huon Mill: NSSC pulping of some young eucalypt species. *Appita J* 42: 419–423.

30. Phillips FH, Logan AF, Balodis V, et al. (1991) Studies on pulpwood resources in southern tasmania. 2. Kraft-AQ, soda-AQ, and NSSC pulps. *Appita J* 44: 173–178.

31. Cardoso M, de Oliveira ÉD, Passos ML (2009) Chemical composition and physical properties of black liquors and their effects on liquor recovery operation in Brazilian pulp mills. *Fuel* 88: 756–763.

32. Demirbas A (2002) Pyrolysis and steam gasification processes of black liquor. *Energ Convers Manage* 43: 877–884.

33. Al-Kaabi Z, Pradhan RR, Thevathasan N, et al. (2017) Potential Value Added Applications of Black Liquor Generated at Paper Manufacturing Industry Using Recycled Fibers. *J Cleaner Prod* 149: 156–163.

34. Dickinson JA, Verrill CL, Kitto JB (1998) Development and Evaluation of a Low Temperature Gasification Process for Chemical Recovery from Kraft Black Liquor, In: International Chemical Recovery Conference, 1–17.

35. Gea G, Murillo MB, Arauzo J (2002) Thermal degradation of alkaline black liquor from straw. Thermogravimetric Study. *Ind Eng Chem Res* 41: 4714–4721.

36. Song X, Bie R, Ji X, et al. (2015) Kinetics of reed black liquor (RBL) pyrolysis from thermogravimetric data. *Bio-Resources* 10: 137–144.

37. Li J, Heiningen ARPV (1990) Kinetics of carbon dioxide gasification of fast pyrolysis black liquor char. *Ind Eng Chem Res* 29: 1776–1785.

38. Bhattacharya PK, Parthiban V, Kunzru D (1986) Pyrolysis of Black Liquor Solids. *Ind Eng Chem Process Des Dev* 25: 420–426.

39. Cao C, Guo L, Chen Y, et al. (2011) Hydrogen production by supercritical water gasification of alkaline wheat straw pulping black liquor in continuous flow system. *Int J Hydrogen Energ* 36: 13528–13535.

40. Peng C, Zhang G, Yue J, et al. (2014) Pyrolysis of black liquor for phenols and impact of its inherent alkali. *Fuel Process Technol* 127: 149–156.

41. Lu N, Yang G, Chen J, et al. (2017) Producing Hydrochar from Cotton Linter Black Liquor. *Bio-Resources* 12: 3666–3676.

42. S ánchez JL, Gonzalo A, Gea G, et al. (2005) Straw black liquor steam reforming in a fluidized bed reactor. Effect of temperature and bed substitution at pilot scale. *Energ Fuel* 19: 2140–2147.

43. Zhao Y, Bie R, Lu J, et al. (2010) Kinetic study of NSSC black liquor combustion using different kinetic models. *Energ Source* 32: 962–969.

44. Sricharoenchaikul V (2009) Assessment of black liquor gasification in supercritical water. *Bioresource Technol* 100: 638–643.

45. Arkell A, Olsson J, Wallberg O (2014) Process performance in lignin separation from softwood black liquor by membrane filtration. *Chem Eng Res Des* 92: 1792–1800.

46. Haddad M, Bazinet L, Savadogo O, et al. (2017) A feasibility study of a novel electro-membrane-based process to acidify Kraft black liquor and extract lignin. *Process Saf Environ* 106: 68–75.

47. Zhao XY, Cao JP, Sato K, et al. (2010) High Surface Area Activated Carbon Prepared from Black Liquor in the Presence of High Alkali Metal Content. *J Chem Eng Jap* 43: 1029–1034.

48. Cao C, Guo L, Jin H, et al. (2017) System analysis of pulping process coupled with supercritical water gasification of black liquor for combined hydrogen, heat and power production. *Energy* 132: 238–247.

49. Rasanen O, Alajarvi T (1990) Evaporation to ultra- high solids: Benefits and possibilities :1990 Kraft Recovery Operations Short Course Notes. TAPPI Press, Atlanta, 95–104.

50. Reza Fakhrai (2002) Black Liquor Combustion in Kraft Recovery Boilers-Numerical Modelling. Royal Institute of Technology.

51. Hupa M, Solin P, Hyoty P (1987) Combustion Behaviour of Black Liquor Droplets. *J Pulp Pap Sci* 13: 67–72.

52. Gellerstedt G (2015) Softwood kraft lignin: Raw material for the future. *Ind Crop Prod* 77: 845–854.

53. Tran H, Vakkilainnen EK (2012) The Kraft Chemical Recovery Process. TAPPI Kraft Recovery Course. TAPPI Press, 1–8.

54. Gosselink RJ, Ab ächerli A, Semke H, et al. (2004) Analytical protocols for characterisation of sulphur-free lignin. *Ind Crop Prod* 19: 271–281.

55. Santos PSBD, Erdocia X, Gatto DA, et al. (2014) Characterisation of Kraft lignin separated by gradient acid precipitation. *Ind Crop Prod* 55: 149–154.

56. Wessel R, Baxter L (2003) Comprehensive model of alkali-salt deposition in recovery boilers. *Tappi J* 2: 19–24.

57. Larson ED, Consonni S, Katofsky RE, et al. (2006) A Cost-Benefit Assessment of Gasification-Based Biorefining in the Kraft Pulp and Paper Industry. *Oper Res Decisions* 1: 17–28.

58. Nie ANS (2008) Characterization of Recovered Black Liquor and Isolated Lignin from Oil Palm Empty Fruit Bunch Soda Pulping. M.S. Thesis, Universiti Sains Malaysia.

59. Yaman S (2004) Pyrolysis of biomass to produce fuels and chemical feedstocks. *Energ Convers Manage* 45: 651–671.

60. Fletcher TH, Pond HR, Webster J, et al. (2012) Prediction of tar and light gas during pyrolysis of black liquor and biomass. *Energ Fuel* 26: 3381–3387.

61. Rojith G, Singh B (2012) Lignin recovery, biochar production and decolourisation of coir pith black liquor. *Res J Recent Sci* 1: 270–274.

62. Demirbaş A (2002) Utilization of urban and pulping wastes to produce synthetic fuel via pyrolysis. *Energ Source* 24: 205–213.

63. Song XF, Ji XY, Bie HP, et al. (2015) Characteristics of gas and char generation study from reed black liquor particles (RBLP) pyrolysis in fluidized bed. *Fuel* 159: 89–97.

64. Kruse A, Funke A, Titirici MM (2013) Hydrothermal conversion of biomass to fuels and energetic materials. *Curr Opin Chem Biol* 17: 515–521.

65. Falco C, Baccile N, Titirici MM (2011) Morphological and structural differences between glucose, cellulose and lignocellulosic biomass derived hydrothermal carbons. *Green Chem* 13: 3273–3281.

66. Kruse A, Badoux F, Grandl R, et al. (2012) Hydrothermale Karbonisierung: 2. Kinetik der Biertreber-Umwandlung. *Chem-Ing-Tech* 84: 509–512.

67. Möller M, Nilges P, Harnisch F, et al. (2011) Subcritical water as reaction environment: Fundamentals of hydrothermal biomass transformation. *Chemsuschem* 4: 566–579.

68. Berge ND, Ro KS, Mao J, et al. (2011) Hydrothermal Carbonization of Municipal Waste Streams. *Environ Sci Technol* 45: 5696–5703.

69. Dinjus E, Kruse A, Tröger N (2011) Hydrothermal carbonization-1. Influence of lignin in lignocelluloses. *Chem Eng Technol* 34: 2037–2043.

70. Kambo HS, Dutta A (2015) Comparative evaluation of torrefaction and hydrothermal carbonization of lignocellulosic biomass for the production of solid biofuel. *Energ Convers Manage* 105: 746–755.

71. Yang G (2015) A Fast Approach for Preparation of Adsorbent from Reed Black Liquor and Its Performance in Equilibrium and Kinetic Gas Separation. *Chem Biochem Eng Q* 29: 375–383.

72. Gamgoum R, Dutta A, Santos R, et al. (2016) Hydrothermal Conversion of Neutral Sulfite Semi-Chemical Red Liquor into Hydrochar. *Energies* 9: 435.

73. Naqvi M, Yan J, Dahlquist E (2012) Bio-refinery system in a pulp mill for methanol production with comparison of pressurized black liquor gasification and dry gasification using direct causticization. *Appl Energ* 90: 24–31.

74. Salmenoja K (1993) Black-Liquor Gasification: Theoretical and Experimental Studie. *Bioresource Technol* 46: 167–171.

75. Whitty K, Backman R, Hupa M (2008) Influence of pressure on pyrolysis of black liquor: 1. Swelling. *Bioresource Technol* 99: 663–670.

76. Whitty K, Kullberg M, Sorvari V, et al. (2008) Influence of pressure on pyrolysis of black liquor: 2. Char yields and component release. *Bioresource Technol* 99: 671–679.

77. Rönnlund I, Myrén L, Lundqvist K, et al. (2011) 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: 2151–2163.

78. Boucard H (2014) Contributions to the understanding of hydrothermal processes: Application to black liquor. Tohoku University.

79. Nong G, Wang S, Mu J, et al. (2012) Kinetics of Reaction between Dimethyl Sulfide and Hydrogen in Black Liquor Gasification Gas with ZnO Catalyst. *Asian J Chem* 24: 3118–3122.

80. Naqvi M, Yan J, Dahlquist E (2013) System analysis of dry black liquor gasification based synthetic gas production comparing oxygen and air blown gasification systems. *Appl Energ* 112: 1275–1282.

81. Häggström C, Öhrman O, Rownaghi AA, et al (2012) Catalytic methanol synthesis via black liquor gasification. *Fuel Process Technol* 94: 10–15.

82. Wiinikka H, Carlsson P, Marklund M, et al. (2012) Experimental investigation of an industrial scale black liquor gasifier. Part 2: Influence of quench operation on product gas composition. *Fuel* 93: 117–129.

83. Silva EAB, da Zabkova M, Araújo JD, et al. (2009) An integrated process to produce vanillin and lignin-based polyurethanes from Kraft lignin. *Chem Eng Res Des* 87: 1276–1292.

84. Bajpai P (2013) Biorefinery in the Pulp and Paper Industry. 1st Editio. ed. Academic Press, London, UK.

85. Fatehi P, Chen J (2016) Extraction of Technical Lignins from Pulping Spent Liquors, Challenges and Opportunities, In: *Production of Biofuels and Chemicals from Lignin*, 35–54.

86. Lake MA, Blackburn JC (2014) Slrp^TM an Innovative Lignin-Recovery Technology. Cellulose Chemistry and Technology. *Cellulose Chem Technol* 48: 799–804.

87. Mussatto SI, Fernandes M, Roberto IC (2007) Lignin recovery from brewer's spent grain black liquor. *Carbohyd Polym* 70: 218–223.

88. Kouisni L, Holt-Hindle P, Maki K (2012) The LignoForce System: A new process for the production of high-quality lignin from black liquor. *J Sci Technol Forest Prod Processes* 2: 6–10.

89. Tomani P (2010) The lignoboost process. *Cellul Chem Technol* 44: 53–58.

90. Lourençon TV, Hansel FA, Silva TAD, et al. (2015) Hardwood and softwood kraft lignins fractionation by simple sequential acid precipitation. *Sep Purif Technol* 154: 82–88.

91. Durruty J (2017) On the Local Filtration Properties of LignoBoost Lignin, Studies of the influence of xylan and ionic strength. Chalmers University of Technology, Gothenburg, Sweden.

92. Kong F, Wang S, Fatehi, P, et al. (2015) Water soluble kraft lignin-acrylic acid copolymer: Synthesis and characterization. *Green Chem* 17: 4355–4366.

93. Lake MA, Blackburn JC (2016) Process for recovering lignin. U.S. Patent, 9260464.

94. Velez J, Thies MC (2013) Solvated liquid-lignin fractions from a Kraft black liquor. *Bioresource Technol* 20: 586.

95. Smook GA (2002) Handbook for Pulp and Paper Technologies, 3rd ed. Angus Wilde Publications, Inc., Vancover, BC.

96. Koljonen K, Österberg M, Kleen M, et al. (2004) Precipitation of lignin and extractives on kraft pulp: Effect on surface chemistry, surface morphology and paper strength. *Cellulose* 11: 209–224.

97. Doherty WOS, Mousavioun P, Fellows CM (2011) Value-adding to cellulosic ethanol: Lignin polymers. *Ind Crop Prod* 33: 259–276.

98. Schorr D, Diouf PN, Stevanovic T (2014) Evaluation of industrial lignins for biocomposites production. *Ind Crop Prod* 52: 65–73.

99. EI Mansouri NE, Salvadó J (2006) Structural characterization of technical lignins for the production of adhesives: Application to lignosulfonate, kraft, soda-anthraquinone, organosolv and ethanol process lignins. *Ind Crop Prod* 24: 8–16.

100. Lange H, Decina S, Crestini C (2013) Oxidative upgrade of lignin—recent routes reviewed. *Eur Polym J* 49: 1151–1173.

101. Kambo H (2014) Energy Densification of Lignocellulosic Biomass via Hydrothermal Carbonization and Torrefaction. University of Guelph.

102. Adachi S, Tanimoto M, Tanaka M, et al. (1992) Kinetics of the alkaline nitrobenzene oxidation of lignin in rice straw. *Chem Eng J* 49: B17–B21.

103. Higuchi T, Kirk K, Higuchi T, et al. (1980) Lignin structure and morphological distribution in plant cell wall, In: *Lignin Biodegradation: Microbiology, Chemistry, and Potential Applications*, (eds) CRC Press, Boca Raton, 1–20.

104. Cordero T, Rodriguez J (1993) Activated Carbons from CO_2 Partial Gasification of Eucalyptus Kraft Lignin. *Energ Fuel* 7: 133–138.

105. Fierro V, Torné-Fernández V, Celzard A (2006) Kraft lignin as a precursor for microporous activated carbons prepared by impregnation with ortho-phosphoric acid: Synthesis and textural characterisation. *Micropor Mesopor Mat* 92: 243–250.

106. Rodriguez-Mirasol J, Cordero T, Rodriguez J (1993) Preparation and Characterisation of Activated Carbons from Eucalyptus Kraft Lignin. *Carbon* 31: 87–95.

107. Dieste A, Clavijo L, Torres AI, et al. (2016) Lignin from Eucalyptus spp. kraft black liquor as biofuel. *Energ Fuel* 30: 10494–10498.

108. Gustafsson Å, Hale S, Cornelissen G, et al. (2017) Activated carbon from kraft lignin: A sorbent for in situ remediation of contaminated sediments. *Environ Technol Innovat* 7: 160–168.

109. Jääskeläinen S, Liitiä T, Mikkelson A, et al. (2017) Aqueous organic solvent fractionation as means to improve lignin homogeneity and purity. *Ind Crop Prod* 103: 51–58.

110. Laurichesse L, Averous S (2014) Chemical modification of lignins: Towards biobased polymers. *Prog Polym Sci* 39: 1266–1290.

111. Hodásová L, Jablonsky M, Skulcova A (2015) Lignin, potential products and their market value. *Wood Res* 60: 973–986.

112. Li T, Takkellapati S (2018) The current and emerging sources of technical lignins and their applications. *Biofuels Bioprod Biorefin,* 1–32.

113. Chen Z, Wan C (2017) Biological valorization strategies for converting lignin into fuels and chemicals. *Renew Sust Energ Rev* 73: 610–621.

114. Jablonsky M, Kočiš J, Haz A, et al. (2014) The approach the isolation of lignins and its characterization. Power Engineering 2014. Renewable Energy Sources 2014, *In: Proceedings of 5th International scientific conference OZE 2014, Bratislava,* 27–32.

115. Thielemans W, Wool P (2005) Lignin esters for use in unsaturated thermosets: Lignin modification and solubility modelling. *Biomacromolecules* 6: 1895–1905.

116. Ahvazi B, Wojciechowicz O, Ton-That M, et al. (2011) Preparation of lignopolyols from wheat straw soda lignin. *J Agric Food Chem* 59: 10505–10516.

117. Bouajila J, Dole P, Joly C, et al. (2006) Some laws of a lignin plasticization. *J Appl Polym Sci* 102: 1445–1451.

118. Alekhina M, Ershova O, Ebert A, et al. (2015) Softwood kraft lignin for value-added applications: Fractionation and structural characterization. *Ind Crop Prod* 66: 220–228.

119. Xu C, Arancon D, Labidi J, et al. (2014) Lignin depolymerisation strategies: Towards valuable chemicals and fuels. *Chem Soc Rev* 43: 7485–7500.

120. Heiningen AV (2006) Converting a kraft pulp mill into an integrated forest biorefinery. *Pulp Pap Can* 107: 38–43.

121. Fitzpatrick M, Champagne P, Cunningham M, et al. (2010) A biorefinery processing perspective: Treatment of lignocellulosic materials for the production of value-added products. *Bioresource Technol* 101: 8915–8922.

122. Wahyudiono, Sasaki M, Goto M (2011) Thermal decomposition of guaiacol in sub- and supercritical water and its kinetic analysis. *J Mater Cycles Waste Manage* 13: 68–79.

123 Ragauskas A, Beckham G, Biddy M, et al. (2014) Lignin valorization: Improving lignin processing in the biorefinery. *Science* 344: 1246843.

124. Montané D, Torné-Fernández V, Fierro V (2005) Activated carbons from lignin: Kinetic modeling of the pyrolysis of Kraft lignin activated with phosphoric acid. *Chem Eng J* 106: 1–12.

125. Duval A, Lawoko M (2014) A review on lignin-based polymeric, micro- and nano-structured materials. *React Funct Polym* 85: 78–96.

126. Azadi P, Inderwildi R, Farnood R, et al. (2013) Liquid fuels, hydrogen and chemicals from lignin: A critical review. *Renew Sust Energ Rev* 21: 506–523.

127. Kleinert M, Barth T (2008) Towards a lignincellulosic biorefinery: Direct one-step conversion of lignin to hydrogen-enriched biofuel. *Energ Fuel* 22: 1371–1379.

128. Kim D, Lee K, Park Y (2016) Upgrading the characteristics of biochar from cellulose, lignin, and xylan for solid biofuel production from biomass by hydrothermal carbonization. *J Ind Eng Chem* 42: 95–100.

129. Yang H, Yan R, Chen H, et al. (2007) Characteristics of hemicellulose, cellulose and lignin pyrolysis. *Fuel* 86: 1781–1788.

130. Franco MAED, Carvalho CBD, Bonetto MM, et al. (2018) Diclofenac removal from water by adsorption using activated carbon in batch mode and fixed-bed column: Isotherms, thermodynamic study and breakthrough curves modeling. *J Cleaner Prod* 181: 145–154.

131. De Franco E, de Carvalho B, Bonetto M, et al. (2017) Removal of amoxicillin from water by adsorption onto activated carbon in batch process and fixed bed column: Kinetics, isotherms, experimental design and breakthrough curves modelling. *J Cleaner Prod* 161: 947–956.

132. Pollard T, Fowler D, Sollars J, et al. (1992) Low-cost adsorbents for waste and wastewater treatment: A review. *Sci Total Environ* 116: 31–52.

133. Fu K, Yue Q, Gao B, et al. (2013) Preparation, Characterization and Application of lignin-based activated carbon from black liquor lignin by steam activation. *Chem Eng J* 228: 1074–1082.

134. Ntuli V, Hapazari I (2013) Sustainable waste management by production of activated carbon from agroforestry residues. *S Afr J Sci* 109: 1–6.

135. Ahmedna M, Marshall W, Rao R (2000) Production of granular activated carbons from select agricultural by-products and evaluation of their physical, chemical and adsorption properties1Louisiana Agricultural Experiment Station manuscript 99-21-0066.1. *Bioresource Technol* 71: 113–123.

136. Cotoruelo M, Marqués D, Díaz J, et al. (2012) Adsorbent ability of lignin-based activated carbons for the removal of p-nitrophenol from aqueous solutions. *Chem Eng J* 184: 176–183.

137. Gonzalez-Serrano E, Cordero T, Rodriguez-Mirasol J, et al. (1997) Development of porosity upon chemical activation of kraft lignin with ZnCl2. *Ind Eng Chem Res* 36: 4832–4838.

138. Gonzalez-Serrano E, Cordero T, Rodriguez-Mirasol J, et al. (2004) Removal of water pollutants with activated carbons prepared from H 3PO4 activation of lignin from kraft black liquors. *Water Res* 38: 3043–3050.

139. Fierro V, Torne V, Montane´D, et al. (2003) Activated carbons prepared from kraft lignin by phosphoric acid impregnation. *In: Proc. Carbon* 2003, Oviedo, Spain.

140. Rodrı´guez-Miraso J, Cordero T, Rodrı´guez J (1993) Activated carbons from CO2 partial gasification of eucalyptus kraft lignin. *Energ Fuel* 7: 133–138.

141. Gao Y, Yue Q, Gao B, et al. (2013) Preparation of high surface area-activated carbon from lignin of papermaking black liquor by KOH activation for Ni(II) adsorption. *Chem Eng J* 217: 345–353.

142. Smolarski N (2012) High-value opportunities for lignin: Unlocking its potential. Frost and Sullivan, Paris, 1–15.

143. Niemi H, Lahti J, Hatakka H, et al. (2011) Fractionation of organic and inorganic compounds from black liquor by combining membrane separation and crystallization. *Chem Eng Technol* 34: 593–598.

144. Gosselink A, Snijder B, Kranenbarg A, et al. (2004) Characterisation and application of NovaFiber lignin. *Ind Crop Prod* 20: 191–203.

145. Zhu Z, Sun M, Su C, et al. (2013) One-pot quantitative hydrolysis of lignocelluloses mediated by black liquor. *Bioresource Technol* 128: 229–234.

146. Gosselink RJA, Dam JGEV, Jong ED, et al. (2010) Fractionation, analysis, and PCA modeling of properties of four technical lignins for prediction of their application potential in binders. *Holzforschung* 64: 193–200.

147. Nadji H, Diouf N, Benaboura A, et al. (2009) Comparative study of lignins isolated from Alfa grass (Stipa tenacissima L.). *Bioresource Technol* 100: 3585–3592.

148. Tejado A, Peña C, Labidi J (2007) Physico-chemical characterization of lignins from different sources for use in phenol-formaldehyde resin synthesis. *Bioresource Technol* 98: 1655–1663.

149. Hellstén S, Lahti J, Heinonen J, et al. (2013) Purification process for recovering hydroxy acids from soda black liquor. *Chem Eng Res Des* 91: 2765–2774.

150. Faustino H, Gil N, Baptista C, et al. (2010) Antioxidant activity of lignin phenolic compounds extracted from kraft and sulphite black liquors. *Molecules* 15: 9308–9322.

151. Mänttäri M, Lahti J, Hatakka H, et al. (2015) Separation phenomena in UF and NF in the recovery of organic acids from kraft black liquor. *J Membrane Sci* 490: 84–91.

152. Kumar H, Alén R (2015) Recovery of aliphatic low-molecular-mass carboxylic acids from hardwood kraft black liquor. *Sep Purif Technol* 142: 293–298.

153. Ponomarenko J, Dizhbite T, Lauberts M, et al. (2014) Characterization of Softwood and Hardwood Lignoboost Kraft Lignins with Emphasis on their Antioxidant Activity. *Bio-Resources* 9: 2051–2068.