

Small Phenolic Compounds Production from Kraft Black Liquor by Lignin Depolymerization with Different Catalytic Agents

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This work is aimed to produce small phenolic compounds from Kraft black liquor. For this purpose, depolymerization reaction is directly carried out over the liquor, without a previous isolation of lignin. In this sense, the intensification of lignin valorization is carried out by the reduction of the total stages of the whole process. Due to the alkali degree of Kraft liquors, base catalyzed depolymerization is proposed for the lignin cleaved reaction. In addition, two facilitating agents (phenol and hydrogen peroxide) were used to reduce the amount of undesirable reaction products, such as residual lignin and coke.

High yield of phenolic oil was recovered after treatment of the Kraft liquor in blank reaction (~30 %). However, high amount of undesirable products (residual lignin and coke) was also obtained (~65 % between both). The addition of phenol as capping agent reduced coke formation (almost to the half); and monomer phenolic compounds in oil were increased four times. The use of hydrogen peroxide reduces the phenolic oil yield (lower than 20 %). Catechol derivatives were the most plentiful products in the phenolic oil (92.44 % of total phenolic monomers) and a decreased of coke formation was similar to that in phenol. As summary it can be established that the intensification of the lignin depolymerization can be accomplished with high yields of phenolic oil production by avoiding the isolation of lignin and its further solubilization.

1. Introduction

Pulp and Paper industry is coping with a period of economical plateau due to different constraints, such as sale prizes or global market competition. New opportunities to define an enhanced and adapted business plan to the market conditions have to be identified to guarantee the viability of these mills (Lundberg et al., 2013).

The integrated forest biorefineries present a business model based on biomass processing from forest resources (wood, bark or other wastes) to produce biofuels and bioproducts, remaining their traditional portfolio of products from cellulose platform as main activity. Therefore, the approach of this concept is the transformation of current byproducts or wasted side-streams into value-added product, converting traditional mills into multiproduct innovative plants. In spite of the main efforts in new biorefinery industries are focused on the carbohydrate platform for chemical precursors as well as biofuel production, the platform of lignin is also essential for the economical sustainability of this industry (Fernández-Rodríguez et al., 2016).

Lignin is a three-dimensional amorphous polymer made up by the combination of three different phenylpropane monomer units: guaiacyl alcohol (G), *p*-coumaryl alcohol (H) and syringyl alcohol (S), linked mainly by (β -O-4) aryl ether bonds in a randomized way. Depending on the source of the raw material, the ratio between these monomers may vary significantly. G and S monomer units are present in different quantities in lignins from hardwood species, although roughly in similar quantities. In softwoods, G units are the most abundant while, in herbaceous lignin, all three units are usually present (Erdocia et al., 2012). The availability of lignin in the biosphere exceeds 300 billion tons and increases by around 20 billion tons every

year. Nevertheless, although lignin is produced worldwide in an amount of around 70 million tonnes, only 1-2% is intended as precursor for chemicals and materials (Laurichesse and Avérous, 2014).

The main process where lignin is produced is the Kraft pulping, with approximately 90 % of the world chemical pulp production. In Kraft process, an aqueous solution of sodium hydroxide and sodium sulfide, also known as white liquor, reacts with the wood chips in a large pressure unit called a digester. The white liquor and the chips are heated to a cooking temperature of about 170 °C and are allowed to cook at that temperature for about two hours. During this treatment, the hydroxide and hydrosulfide anions react with lignin, causing the polymer fragmentation into smaller water/alkali-soluble fragments.

Delignification in the Kraft cooking proceeds in three distinct phases: the initial phase, the bulk phase, and the final or residual phase. The initial phase of delignification takes place at a temperature of about 150 °C, and it is controlled by diffusion. The bulk phase includes the heating period from about 150-170 °C and the cooking treatment at 170 °C. The rate of delignification in the bulk phase is controlled by chemical reactions. Most of the lignin is removed in this phase. The residual or final phase, in which the rate of delignification is significantly decreased, begins when about 90% of the lignin has been removed and marks the end of the cooking (Chakar and Ragauskas, 2004). Black liquor contains typically 30-35% of lignin in dry solid weight basis. This stream is traditionally concentrated in evaporators and then burned for energy generation and chemicals recovery. However, the energy generated by burning the black liquor is greater than the process demand and as a consequence of that, this stage is considered the “bottleneck” of the pulping process (Da Silva et al., 2009). Hence, valorization of lignin as chemical precursor can be an option of sorting out this problem and obtaining an extra revenue in the process.

Amongst all possible applications for lignin, production of chemical precursors is gaining strength in recent years. A wide range of aromatic compounds can be obtained from lignin by means of its depolymerization reaction and cleavage into its more elemental structures. Base catalyzed depolymerization (BCD) has been widely used for small phenolic molecules production, in which the most common lignin linkage (β -O-4 bond) which represents around 60 % of the total lignin linkages (Azadi et al., 2013), is cleaved by the formation of a sodium phenolate derivative and a carbenium ion-like transition state, which is instantly neutralized by a hydroxide ion. The sodium cations catalyze the reaction by forming cation adducts with lignin and hence, polarizing the ether bond. This step increases the negative partial charge of the oxygen and, consequently, the energy necessary for heterolytic bond cleavage is reduced (Erdocia et al., 2015). Finally, an oil enriched in small phenolic compounds is obtained. The yield of this reaction is limited by the action of a repolymerization reaction that occurs when reactive phenolic and catechol derivative monomers undergo a polymerization reaction instead of remaining as monomeric products, generating residual lignin and coke as undesirable products (Roberts et al., 2011). Okuda et al. (2004), observed that the mixture of water-phenol as solvent of lignin reduces the cross-linking reactions to form high molecular weight compounds and avoids lignin repolymerization. Toledano et al. (2014) demonstrated that phenolic oil could be notably increased adding phenol as capping agent to an alkali medium in order to depolymerize lignin. On the other hand, the oxidative depolymerization of lignin could be considered as another option to depolymerize lignin from its initial structure to small molecules. Araujo et al. (2010) used this approach to obtain vanillin from lignin, using oxygen in alkali solution.

In this work, Kraft black liquor is directly depolymerized without previous isolation of lignin as it is done mostly in similar works. In this sense, the stage of lignin precipitation could be bypassed, reducing the costs by the intensification of the process flowsheet. As Kraft black liquor presents an alkali medium, BCD depolymerization of lignin is carried out to obtain small phenolic compounds. Furthermore, the influence of different capping agents is studied in order to maximize phenolic oil production as well as to reduce residual lignin and coke production, which are the undesirable products of the reaction.

2. Materials and methods

2.1 Raw material and equipment

In the present work, Kraft black liquor from “Papelera Guipuzcoana de Zicuñaga” (Spain), where *Eucalyptus Globulus* is the main raw material for pulp production, was used for the lignin depolymerization. This liquor was physico-chemically characterized.

The equipment used for lignin depolymerization was a batch reactor (5500 Parr reactor) with a 4848 Reactor controller. The volume of the reactor vessel is 100 mL.

2.2 Lignin depolymerization

The reaction was accomplished at 300 °C and 80 min, reaching a pressure inside the reactor of 9 MPa. Different catalytic agents (a capping and an oxidant ones) were used to increase the phenolic products yield and reduce the char formation. Phenol and hydrogen peroxide were used for this purpose in homogeneous phase reaction with a lignin:facilitating agent ratio of 1:0.5 (% wt.). Three main groups of products were

produced during the reaction: oil, enriched in phenolic monomers; residual lignin, resulted from the repolymerization reactions and coke.

2.3 Products separations

Once the depolymerization reaction was finished, downstream stages were necessary to separate the different products obtained after the reaction, following the method described by Erdocia et al. (2014a). In the first stage, the mixture was acidified with HCl (37 wt.%) dropping the pH = 2 to precipitate the residual lignin formed during the reaction. The solid phase, which combines residual lignin and coke, was separated from the mixture by filtration using MN 640w filters and washed with acidified water (pH = 2 with HCl as the acidic agent) to remove residual liquid. After that, the separation of residual lignin from the coke was carried out washing the solid content of the filters with tetrahydrofuran (THF), stirring the solution for 3 h, and filtrating again later. The non-solubilized solid (coke) remained in the filter, whereas the residual lignin goes throughout the filter due to its solubility in the THF, solvent which is finally evaporated under vacuum to recover the residual lignin.

On the other side, liquid phase produced after the filtration of residual lignin and coke was subjected to a liquid-liquid extraction to separate the phenolic-enriched oil from the aqueous phase using ethyl acetate as organic solvent. Residual aqueous phase was completely removed from the organic phase by an extraction process with sodium sulfate anhydrous. After a filtration step for the solid separation, the organic solvent was removed by evaporation, remaining the phenolic oil in a liquid phase. The yield of each product was calculated gravimetrically referring to the initial lignin weight introduced in the reactor.

2.4 Analytical methods

Kraft black liquor was characterized prior to its treatment at high temperature and pressures. Density was determined measuring the weight of the black liquor in a known volume previously weighed. Total dissolved solids (TDS) were determined using a method based on TAPPI T264 cm-97 to determinate the moisture content. Inorganic matter was determined after combustion of the sample at 525 °C using a method based on TAPPI T211 om-93 to calculate ash content. Organic matter was determined by the difference between total dissolved solids and inorganic matter. Lignin content was estimated by its precipitation, considering that all lignin is isolated. To this, a precipitation with H₂SO₄ (pH around 2) was carried out and then filtered through a 0.45 mm nylon filter. Finally the precipitated lignin was washed twice with acidified water (pH = 2) and then dried at 50 °C. Lignin content was calculated gravimetrically.

This precipitated lignin from black liquor was subjected to Gel Permeation Chromatography (GPC) to evaluate lignin average molecular weight (Mw), and molecular weight distribution (Mw/Mn) using a JASCO instrument equipped with an interface (LC-NetII/ADC) and a refractive index detector (RI-2031Plus). Two PolarGel-M columns (300 mm x 7.5 mm) and PolarGel-M guard (50 mm x 7.5 mm) were employed. The flow rate was 700 mm³ min⁻¹ and the analyses were carried out at 40 °C. Calibration was made using polystyrene standards (Sigma-Aldrich) ranging from 70,000 to 266 g/mol.

Phenolic oil was characterized in order to establish the nature of the monomeric phenolic compounds as well as to determine the molecular weight profile. The oil was dissolved in ethyl acetate (HPLC grade) in a metric flask. The solution was injected in a GC (7890A)-MS (5975C inert MSD with Triple-Axis Detector) Agilent equipped with a capillary column HP-5MS ((5%-Phenyl)-methylpolysiloxane, 30 m x 0.25 mm). The temperature program started at 50 °C then, the temperature was raised to 120 °C at 10 K min⁻¹, held 5 min, raised to 280 °C at 10 K min⁻¹, held 8 min, raised to 300 °C at 10 K min⁻¹ and held 2 min. Helium was used as carrier gas. Calibration was done using pure compounds (Sigma-Aldrich) phenol, *o*-cresol, *m*-cresol, *p*-cresol, guaiacol, catechol, 3-methylcatechol, 4-methylcatechol, 4-ethylcatechol, 3-methoxycatechol, syringol, 4-hydroxybenzaldehyde, acetovanillone, veratrol, 4-hydroxybenzoic acid, 4-hydroxy-3-methoxyphenylacetone, vanillin, vanillic acid, syringaldehyde, 3,5-dimethoxy-4-hydroxyacetophenone and syringic acid.

3. Results and discussion

As first step, characterization of the concentrated Kraft black liquor supplied directly from the mill was performed mainly to establish the concentration of lignin and its initial molecular weight as well as its distribution. These values are represented in Table 1.

Density and pH corresponds with typical values of concentrated Kraft black liquors. Organic matter is remarkably lower than inorganic matter due to the composition of the white liquor used for the Kraft cooking. However, lignin represents more than 85 % of this organic matter, highlighting the wealth of this stream to be valorized by transforming lignin in value-added bioproducts. Molecular weight of this lignin is also low in comparison with lignin obtained by others pulping methods as well as its molecular weight distribution (Vishtal and Kraslawski, 2011), what is a clear advantage to obtain high depolymerization yields.

Table 1: Physico-chemical characterization of Kraft black liquor.

Kraft Liquor Characterization	
Density (g/cm ³)	1.39 ± 0.84
pH	12.9 ± 0.12
Inorganic matter (%)	10.2 ± 0.06
Organic matter (%)	5.6 ± 1.89
Lignin content (g/L)	67.4 ± 5.21
Mw (g/mol)	2418 ± 461
Mw/Mn	3.21 ± 0.32

In this case, lignin from Kraft liquor was not isolated and then depolymerized as usual, the whole liquor was directly introduced to the reactor instead. In this way, the intensification of the common lignin depolymerization processes was also assessed.

Three main products were collected from the reaction after their separation by the methods described in Section 2.3. The yields of these products are shown in Table 2. First, a blank reaction without any additive was conducted as reference point to identify the action of the capping agent addition.

Table 2: Yields of recovered products after Kraft black liquor treatment.

Catalytic System	Phenolic Oil (% w/w) ¹	Residual lignin (% w/w) ¹	Coke (% w/w) ¹
Blank	30.09±1.03	39.43±1.57	24.52±0.98
Phenol	31.91±0.88	44.87±1.22	15.72±0.69
Hydrogen Peroxide	18.24±1.10	37.25±1.46	18.04±0.98

¹Yields are referred as weight of each product over the weight of organic content in the initial Kraft black liquor (% w/w).

The Kraft liquor depolymerization without any capping agent showed high yield of phenolic oil production in such harsh conditions. However, not only high yield of phenolic oil was produced, residual lignin as well as char (too). The repolymerization reaction of lignin was not avoided presenting 39.43 of yield, neither the char formation, the most undesirable product of the reaction with almost 25% of generation. The high yield of byproducts (residual lignin and char) justifies the use of capping agents in order to reduce the produced amount of these components.

The introduction of phenol leads to a similar phenolic oil generation. However, the residual lignin quantity was increased to almost 45%, which involves an increase of 13%. The most noticeable effect of phenol is the reduction of char in a really big quantity (35.9% of reduction). On the other hand, the hydrogen peroxide presented a big reduction in the phenolic oil (~40%) which is considered a serious negative effect due to the target of the reaction is maximizing this stream. The reason of this decrease is due to the action of hydrogen peroxide is cleaving the aromatic rings from initial lignin as well as from small phenolic compounds which are transformed into alkylic acids which cannot be quantified by this method since they would be wasted in the aqueous phase that remains after liquid-liquid extraction of phenolic oil accomplished with ethyl acetate. With regard to residual lignin, hydrogen peroxide addition had not any influence, presenting similar values than blank reactions. Referring to char formation, its influence was noticeable as well as phenol actions was. In this case, a reduction of 26.4% was achieved, slightly lower than the one obtained with phenol. Therefore, the more advantages have been found using phenol as capping agent than hydrogen peroxide in terms of product selectivity yields, since phenolic oil yield remains constant with a slight increase in residual lignin but decreasing hugely coke formation, insoluble product that could be considered as a recalcitrant component for its further valorization.

Besides the performance of reaction in terms of products yields, the chemical composition of phenolic oil was quantified. This characterization is necessary to find out the degree of lignin depolymerization indirectly, since phenolic oil not only combine different phenolic monomers but also phenolic molecules with more than one unit, which cannot be quantified by GC-MS. Hence, the higher phenolic monomers content is, the more lignin has been depolymerized into its most elemental structures. Furthermore, despite lignin is composed by repetitive units of guaiacol and syringol, other elemental compounds could be produced due to the harsh conditions lignin is cleavage at. These products were also measured and gathered in phenol or catechols and cresols derivatives, whose higher reactivity than guaiacol and syringol could be more interesting to valorize this stream as value-added chemical precursors (Montarezi and Eckelman, 2016). Hence, lignin cleavage undergoes different steps: first lignin can be depolymerized in small molecules compounds make up of some

repetitive units, then monomers (guaiacol and syringol) can be obtained if the reaction continues, and even these monomers can be degraded into more elemental compounds, such as phenol, catechols and cresols as it was demonstrated in a previous work (Erdocia et al., 2014b). In Table 3 the yield of phenolic monomers quantified in oil streams as well as the main components found in that stream are represented.

Table 3: Yields of phenolic monomers in final oil and their main components measured by GC-MS.

Catalytic System	Yield (% w/w)	Guaiacol (%)	Syringol (%)	Phenol (%)	Catechols (%)	Cresols (%)
Blank	7.81 ± 0.49	0.06 ± 0.01	0.05 ± 0.01	0.23 ± 0.005	7.22 ± 0.55	0.22 ± 0.11
Phenol	31.58 ± 2.74	0.01 ± 0.01	-	20.71 ± 0.36	2.85 ± 0.6	3.82 ± 0.75
Hydrogen Peroxide	12.33 ± 2.22	-	-	0.09 ± 0.05	12.13 ± 2.14	0.11 ± 0.02

Regarding phenolic monomers yield it can be seen the low yield of blank reaction with only 7.81%. This involves that without the action of a capping agent, Kraft lignin is difficult to be cleaved into its most elemental structures. This yield is clearly raised with phenol as capping agent (increasing more than 4 times its value) boosting the wealth of this stream considerably. In case of hydrogen peroxide, this yield is increased almost to the double. Once again, phenol showed the best results.

Guaiacol and syringol were only found in blank reaction (the amount measured in phenol reaction could be considered as neglected) and also in similar quantities, an expected fact since lignin in the black liquor comes from a hardwood species as eucalyptus is, being the common ration of G/S the unit. This fact verifies the reaction mechanism explained before, where a demethoxylation reaction of guaiacol and syringol is happening leading to phenol, catechol and cresols derivatives in such harsh conditions. Catechol is the main monomer component in phenolic oil in case of blank reaction. This change when phenol is used as capping agent, being phenol the richest component in the final oil. However, it is noticeable that cresols are produced in more amount than catechols when phenol is in excess during the reaction. In case of hydrogen peroxide as capping agent, also guaiacol and syringol are completely degraded to more elemental compounds, demonstrating that also this compound acts profitably in these reactions. Catechol is almost the unique product of the reaction, what can be explained as hydrogen peroxide provokes an excess of hydroxyl groups during the reaction, facilitating the pathway to form catechol derivatives. Therefore, a different mechanism of guaiacol and syringol degradation is happening when the capping agent is different.

4. Conclusions

Black liquor from a Kraft pulping process is valorized basis on its high lignin content. Depolymerization of lignin is directly accomplished to reduce the stages of the process, leading to a process intensification, which could notably decrease the operational cost of the final valorization process. High yield of phenolic oil was recovered after treatment of the Kraft liquor in blank reaction (~30 %), demonstrating that the alkali medium of black liquors could act as catalyst agent for the reaction. However, high amount of undesirable products (residual lignin and coke) was also obtained (~65 % between both). The addition of phenol as capping agent had its main influence on the reduction of coke formation (almost the half). The quality of phenolic oil was improved, increasing the monomer phenolic compounds four times in comparison with the reference reaction, fact that could hugely boost the valorization of lignin for chemical precursor production. Instead, hydrogen peroxide reduced the phenolic oil yield (lower than 20 %), showing that at such harsh conditions, aromatic rings of phenolic compounds are cleaved, leading to organic alkylic compounds which could not be measured. Although vanillin was not found in the phenolic oil, catechol derivatives were the (most plenty) products with the highest content in the phenolic oil (92.44 % of total phenolic monomers). A decrease of coke formation in similar amount than phenol was also reached. As summary, intensification of Kraft lignin valorization into small compounds by its base catalytic depolymerization has been demonstrated, obtaining high yields of phenolic derivatives compounds. However, the inclusion of facilitating agents presents a window to increase their effect in the reduction of undesirable products. To establish the economic feasibility of this process a simulation for cost estimation is proposed as future outlook. Additionally, the optimization of this reaction could be developed by the inclusion of other catalytic agents that contribute to the cleavage of the rest of lignin linkages (mostly C-C linkages), which require harsher conditions than the used in this work.

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