

# Lignin Depolymerization Process Intensification by Direct Treatment of Delignification Black Liquor

Xabier Erdocia\*, Javier Fernández-Rodríguez, Ane Sequeiros, María González Alriols, Jalel Labidi

Chemical and Environmental Engineering Department, University of the Basque Country (UPV/EHU), Plaza Europa 1, San Sebastian, Spain

[xabier.erdocia@ehu.eus](mailto:xabier.erdocia@ehu.eus)

In this study, lignin obtained from almond shell by soda delignification treatment was directly depolymerized to produce phenolic monomers without the need of isolating it after its extraction. Thus, the black liquor from the delignification treatment, where lignin is dissolved, was treated in a high pressure reactor at 300 °C for 80 minutes to depolymerize the dissolved lignin. In this way, the step of precipitating lignin from the liquor was suppressed intensifying the whole process of lignin valorization. On the other hand, in order to have a reference, lignin from black liquor was isolated using selective precipitation methods and was submitted to a depolymerization process with the same conditions applied to the black liquor, employing in this case sodium hydroxide dissolution (4 wt.%) in a solid:liquid ratio of 1:20. After both depolymerization treatments, three main products were obtained: oil, residual lignin and char. These products were quantified and analytically characterized by Gas chromatography/Mass spectroscopy (GC/MS) and gel permeation chromatography (GPC). The direct treatment of soda black liquor to depolymerize the lignin dissolved in there, gave better results regarding oil and char yields than depolymerizing the isolated solid lignin.

## 1. Introduction

Lignin is the second most abundant natural polymer made up by the combination of three different phenylpropane monomer units: guaiacyl alcohol, *p*-coumaryl alcohol and syringyl alcohol. These phenylpropane units form an amorphous three-dimensional structure and are linked mainly by aryl-aryl ether linkages (Chakar and Ragauskas, 2004). The traditional portfolio of pulp and paper industries is mainly focused on the cellulose platform neglecting, in large part, the options that both hemicelluloses and especially lignin could offer (Fernández-Rodríguez et al., 2016). Actually, the aromatic structure of lignin makes it a suitable candidate to be catalytically transformed into low molecular weight phenolic compounds, which may substitute petroleum based products (Cohen et al., 2009). Therefore, the valorization of lignin into high value-added compounds is fundamental for the profitability of any biomass conversion technology (Vardon et al., 2015).

Extraction of lignin can be carried out by several methods from lignocellulosic biomass. Nowadays, commercial lignin is obtained as by-product from lignocelluloses treatments performed in the pulp and paper (P&P) industry as lignosulfonates and kraft lignins with around 60 million metric tons of annual production (Zhang et al., 2011). In contrast to lignosulfonates or kraft lignins, sulfur-free delignification processes, like soda treatment, have received considerable attention as it allows obtaining a very rich in lignin black liquor without any sulfur contamination (Subhedar and Gogard, 2014). Production of high-added value phenolic compounds from black liquor involves the transformation of lignin into much smaller molecules. Alkaline lignin have been found to be suitable raw materials to produce low molecular weight compounds, such as vanillin, simple and hydroxylated aromatics, quinines, aldehydes, aliphatic acids and many others (González-Alriols et al., 2009). A number of thermochemical conversion methods have been proposed to depolymerize lignin into low-molecular weight compounds. Among them, pyrolysis (lignin to liquid, LtL), hydrogenolysis, oxidation or base-catalyzed hydrolysis have been deeply studied (Pandey and Kim, 2011). Lignin hydrolysis has many advantages comparing to other methods studied as it is performed at lower temperatures, it employs cheaper

reactants and favors higher yields of liquid including monomeric phenols (Da Silva et al., 2009). Nevertheless, in most of cases lignin is depolymerized after being isolated from the pulping black liquor, although in some works the direct dissolved lignin depolymerization has also been studied (Erdocia et al. 2012).

The aim of this work is to depolymerize the lignin contained in soda black liquor without precipitating it, making the process cheaper and more direct, as the reactants of the delignification of the biomass (NaOH and water) are employed as catalyst and solvent for the depolymerization reaction (Erdocia et al., 2015). In this sense, the intensification of the lignin valorization process by the removal of some stages was studied. For this purpose, soda black liquor from almond shell delignification processes was hydrolyzed without any previous conditioning and compared with a depolymerization of lignin previously isolated from the same black liquor. A wide range of monomeric phenols were recovered after the depolymerization processes being catechol and its derivatives the main products in all the cases. Otherwise, the main undesirable by-product was char formed during competitive repolymerization reaction.

## **2. Materials and methods**

### **2.1 Soda delignification treatment**

Almond shells (A), obtained from *Prunus Amygdalus* tree, used in this research were provided by “Eloy Castillo Fernandez” company located in Arnedo (La Rioja, Spain). After conditioning this raw material, it was subjected to a soda delignification process which was realized with a dissolution of NaOH 7.5 wt% at 121 °C, 90 min and a solid:liquid ratio of 1:6 (Urruzola et al., 2014).

After delignification process, the solid fractions were washed until neutral pH and the black liquor was stored. Part of this liquor was employed to precipitate the lignin dissolved in there adjusting the pH to 2 by adding concentrated sulfuric acid (96 %, w/w); the rest was used for further treatments.

### **2.2 Black liquor characterization**

Black liquor from delignification process of almond shell 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 determinate the ash content. Organic matter was determined by the difference between total dissolved solids and inorganic matter. Lignin content was quantified by precipitation from black liquor. Concentrated sulfuric acid (96 %, w/w) was added to a known volume of soda black liquor until pH = 2 to precipitate the lignin which was subsequently, filtered, dried and weighed.

### **2.3 Delignification process**

The black liquor was subjected to high temperatures and pressures in a batch reactor – 5500 Parr reactor – with a 4848 reactor controller. The reaction conditions were 300 °C and 80 minutes with constant stirring, and reaching pressure values of 90 bar.

The solid lignin precipitated from soda black liquor was also treated at the same conditions. In this case, the lignin:solvent (water) mass ratio was 1:20 and the catalyst (NaOH) concentration was set at 4 % wt. respect to all reaction system (water+lignin).

### **2.4 Products separation and characterization**

After the reaction time, the liquid solution in the batch microreactor from both processes (solid lignin and black liquor) was treated in order to separate the final products. Firstly, HCl at 37 % wt. was added until pH 1 was reached. In this way, residual lignin and char were precipitated and separated from liquid by filtration and washed with acidified water to remove residual liquid.

This liquid fraction was subjected to a liquid-liquid extraction process with ethyl acetate. Sodium sulfate anhydrous was added to the obtained organic phase to remove traces of water and then it was filtrated. Afterwards, this organic phase was vacuum evaporated to obtain an oil where the products of lignin depolymerization are dissolved.

On the other hand, solid phase was mixed with tetrahydrofuran (THF) and stirred for 3 hours in a beaker. Then, it was filtrated and the undissolved solid (char) was oven-dried at 50 °C. The THF solution was vacuum evaporated to recover the residual lignin (RL) dissolved in it.

Phenolic oil was characterized to establish the nature of the monomeric phenolic compounds. 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 is

raised to 120 °C at 10 K min<sup>-1</sup>, held 5 min, raised to 280 °C at 10 K min<sup>-1</sup>, held 8 min, raised to 300 °C at 10 K min<sup>-1</sup> and held 2 min. Helium was used as carrier gas. Calibration was performed employing the following 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.

Residual lignin was subjected to Gel Permeation Chromatography (GPC) to evaluate lignin average molecular weight (Mw), and polydispersity index (PI) 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 mm<sup>3</sup> min<sup>-1</sup> 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.

### 3. Results and discussion

#### 3.1 Black liquor characterization

The results of the characterization of the black liquor from soda process of almond shells are shown in table 1.

Table 1: Almond shell soda black liquor characterization

Soda black liquor	
Density (%)	1.07 ± 0.00
pH	13.89 ± 0.02
TDS (%)	14.99 ± 0.07
Organic matter (%)	5.39 ± 0.07
Inorganic matter (%)	9.60 ± 0.01
Lignin content (%)	4.57 ± 0.34

As it was expected, the pH of the black liquor was very high due to the load of NaOH in the delignification treatment while the density was slightly higher than water. In terms of composition, it has to be pointed out that from all the organic matter of the liquor the 84.79 % was lignin, which indicates the high selectivity of the process of delignification and the attractive properties of this stream for lignin valorization. It is also remarkable the high content of inorganic matter, basically composed of NaOH, which is crucial as it acts as catalyst in the following lignin depolymerization process step.

#### 3.2 Depolymerization process products yield

The yields of the three identified products are shown in Figure 1. These yields were calculated using the organic matter contained in black liquor as basis in case of soda black liquor treatment, and the loaded lignin content in the case of solid lignin treatment.

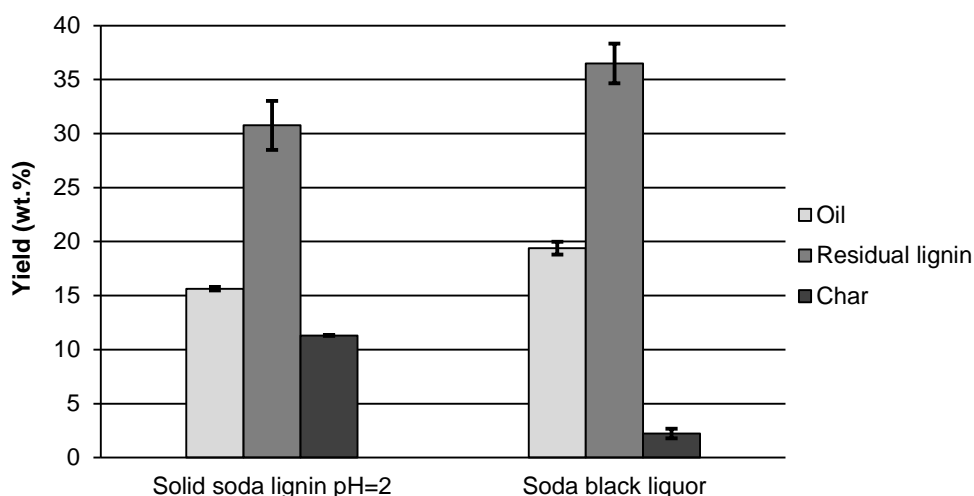


Figure 1: Yields of the different products obtained after lignin and black liquor depolymerization treatments.

It could be observed that in the case of soda black liquor direct treatment, the quantity of the target product (oil) was higher than in the case of solid lignin depolymerization treatment. In addition, the content of the most undesirable by-product (char) was also minimized. The increment in the phenolic oil was around 24 % while the production of char decreased in more than 80 %. This behavior could be explained due to the higher content of NaOH in the soda black liquor (7.5 %) than in the other case (4 %). The NaOH acts as a catalyst in the lignin depolymerization process helping to break the  $\beta$ -O-4 ether bonds and also inhibiting the formation of char (Toledano et al., 2012). This way, higher fraction of lignin was cleaved in the black liquor treatment forming smaller compounds which were recovered in the oil.

Regarding the residual lignin yield, it was higher in the case of soda black liquor treatment. In this case, as the production of char was inhibited by the higher load of NaOH in the reaction system and the oil yield is limited by oligomerization and polymerization reactions of the primary phenolic products formed in the process (Roberts et al. 2011), residual lignin yield had a considerable increment.

### 3.3 Phenolic monomers quantification

The phenolic oil isolated after the depolymerization processes was characterized by GC/MS to quantify the phenolic monomers dissolved in it. The results of the characterization are shown in table 2.

*Table 2: Monomers concentration in recovered phenolic oil (%wt.)*

Compound	Solid soda lignin	Soda black liquor
Phenol	0.23 $\pm$ 0.05	0.66 $\pm$ 0.07
Cresols	0.11 $\pm$ 0.02	0.30 $\pm$ 0.01
Guaiacol	0.02 $\pm$ 0.00	0.03 $\pm$ 0.01
Catechol	2.80 $\pm$ 0.54	1.63 $\pm$ 0.13
3-methylcatechol	1.03 $\pm$ 0.19	0.90 $\pm$ 0.03
4-methylcatechol	1.64 $\pm$ 0.38	1.85 $\pm$ 0.02
4-ethylcatechol	0.50 $\pm$ 0.10	0.89 $\pm$ 0.10

It can be observed that the nature of the recovered phenolic compounds is the same in both cases. As the reaction media had the same elements (lignin+water+NaOH) the mechanism of lignin depolymerization had been similar either with solid lignin or black liquor, which consequently leads to the same compounds production. In alkaline depolymerization processes, as aryl-alkyl ether bonds, including  $\beta$ -O-4 bonds, are the weakest bonds in lignin structure, cleavage of ether linkages is a dominant reaction (Li et al., 2015). This leads to the production of syringyl and guaiacyl intermediates. Afterwards, due to the presence of a strong base (NaOH), demethoxylation reactions of guaiacol and syringol took place to produce phenol, cresols and catechols (Toledano et al., 2012). Consequently, in all experiments the amount of guaiacol was very low and there was not presence of syringol which was in accordance with other works where it is stated that syringyl groups are more susceptible to BCD than guaiacyl groups (Sun et al., 2003).

Nevertheless, the quantity of the recovered compounds is slightly different in the studied cases. The concentration of the base is one of the key factors in the monomers production from lignin (Karagöz et al., 2006). Thus, as the NaOH concentration was higher in the soda black liquor treatment, the production of phenols and cresols (produced after guaiacol and syringol demethoxylation) was enhanced. Phenol and cresols quantity in the soda black liquor oil was almost three times higher than in the other oil which demonstrates the importance of the NaOH concentration in the demethoxylation reactions of lignin depolymerization intermediates.

### 3.4 Residual lignin molecular weight

The molecular size as well as the polydispersity index of the residual lignins recovered after depolymerization treatments were assessed by GPC analysis and compared with the initial lignin isolated from the soda black liquor.

*Table 3: Average molecular weight and polydispersity index of raw lignin from the black liquor and residual lignin isolated after depolymerization reactions.*

Sample	Mw(g/mol)	PI
Raw lignin	27322	12.33
Residual lignin from solid soda lignin	5031	6.07
Residual lignin from soda black liquor	2177	4.77

The Mw of all residual lignins was lower than its respective raw lignin present in the liquor. This descend was very significant in both studied cases proving that lignin depolymerization process was successful, in good agreement with previous studies where lignin had been treated under alkaline conditions (Kleinert and Barth, 2008).

It can be observed that the action of sodium hydroxide was very noticeable and enhanced the depolymerization of the lignins lowering the Mw of the obtained residual lignins since the base catalyst are said to prevent the repolymerization of monomeric products from lignin (Pineda and Lee, 2016). In addition, the PI also betrayed a significant decline. This behavior was even more significant in the case of the residual lignin from soda black liquor direct treatment. In this case, the Mw of the recovered residual lignin had a descent of 92 % with respect to the raw lignin while in the case of solid lignin depolymerization the decline was around 82 %. Thus, the higher load of NaOH improved the depolymerization of lignin as it was also demonstrated in the previous sections.

#### 4. Conclusions

Direct treatment of soda black liquor in order to depolymerize the lignin dissolved in there and compared to solid lignin depolymerization was studied in this work. The black liquor treatment gave better results regarding oil and char yields. The higher load of NaOH in the liquor not only enhanced depolymerization phenomena increasing the production of the phenolic oil but also inhibited the formation of char. In addition, the nature of monomeric phenols recovered in the oil was very similar in both cases and due to the higher concentration of the catalyst demethoxylation and demethylation reactions were enhanced increasing the production of more simple compounds like phenol and cresols.

Nevertheless, the main drawback of direct treatment of the soda black liquor was the increase in residual lignin yield. Despite it, the low Mw and PI of this lignin with regard to the raw lignin or the residual lignin recovered after solid lignin depolymerization treatment, makes it suitable for other applications like resins formulations.

As summary, the simpler and easier treatment of the black liquor proved to be appropriate for lignin depolymerization, justifying the proposed process intensification.

#### Acknowledgments

The authors would like to thank the Spanish Ministry of Economy and Competitiveness (CTQ2013-41246-R) and the University of the Basque Country (postdoctoral fellowship no. ESPDOC15/044) for supporting financially this work.

#### References

- Chakar F.S., Ragauskas A.J., 2004. Review of current and future softwood kraft lignin process chemistry, *Ind. Crops Prod.* 20, 131-141.
- Cohen S., Belinky P.A., Hadar Y., Dosoretz, C.G., 2009. Characterization of catechol derivative removal by lignin peroxidase in aqueous mixture, *Bioresour. Technol.* 100(7), 2247-2253.
- Da Silva E.A.B., Zabkova M., Araújo J.D., Cateto C.A., Barreiro M.F., Belgacem M.N., Rodrigues A.E., 2009. An integrated process to produce vanillin and lignin-based polyurethanes from Kraft lignin. *Chem.Eng. Res. Des.* 87(9), 1276-1292.
- Erdocia X, Toledano A., Corcuera M.A., Labidi J., 2012. Organosolv Black Liquor Hydrolysis to Obtain Low Molecular Weight Phenolic Compounds. *Chem. Eng. Trans.* 29, 535-540.
- Erdocia X., Corcuera M.A., Labidi J., 2015. Novel method for the depolymerisation of lignin. Patent nº: WO2015075290 A1
- Fernández-Rodríguez J., Garcia A., Coz A., Labidi J., Fractionation of Spent Sulphite Liquor into Monomeric Sugars and Lignosulphonates by an Ultrafiltration Series System. *Chem. Eng. Trans.* 45, 553-558.
- González Alriols M., Tejado A., Blanco M., Mondragon I., Labidi J., 2009. Agricultural palm oil tree residues as raw material for cellulose, lignin and hemicelluloses production by ethylene glycol pulping process. *Chem. Eng. J.* 148(1), 106-114.
- Karagöz S., Bhaskar T., Muto A., Sakata Y., 2006. Hydrothermal upgrading of biomass: Effect of K<sub>2</sub>CO<sub>3</sub> concentration and biomass/water ratio on products distribution. *Bioresour. Technol.* 97, 90-98.
- Kleinert M., Barth T., 2008. Phenols from lignin. *Chem. Eng. Technol.* 31(5), 736-745.
- Li C., Zhao X., Wang A., Huber G.W., Zhang T., 2015. Catalytic Transformation of Lignin for the Production of Chemicals and Fuels. *Chem Rev.* 115, 11559-11624.
- Pandey M.P., Kim C.S., 2011. Lignin Depolymerization and Conversion: A Review of Thermochemical Methods, *Chem. Eng. Technol.* 34(1), 29-41.

- Pineda A., Lee A.F., 2016. Heterogeneously catalyzed lignin depolymerisation. *Appl. Petrochem. Res.* 6(3), 243-256.
- Roberts V.M., Stein V., Reiner T., Lemonidou A., Li X., Lercher J.A., 2011. Towards Quantitative Catalytic Lignin Depolymerization. *Chem. Eur. J.* 17(21), 5939-5948.
- Subhedar P.B., Gogate P.R., 2014. Alkaline and ultrasound assisted alkaline pretreatment for intensification of delignification process from sustainable raw-material, *Ultrason. Sonochem.* 21, 216-225.
- Sun J.X., Sun X.F., Sun R.C., Fowler P., Baird M.S., 2003. Inhomogeneities in the chemical structure of sugarcane bagasse lignin. *J. Agric. Food Chem.* 51(23), 6719-6725.
- Toledano A., Serrano L., Labidi J., 2012. Organosolv lignin depolymerization with different base catalysts. *J. Chem. Technol. Biotechnol.* 87, 1593-1599.
- Urruzola I., Robles E., Serrano L., Labidi J., 2014. Nanopaper from almond (*Prunus dulcis*) shell. *Cellulose* 21(3), 1619-1629.
- Vardon D.R., Franden M.A., Johnson C.W., Karp E.M., Guarneri M.T., Linger J.G., Salm M.J., Strathmann T.J., Beckham G.T., 2015. Adipic acid production from lignin, *Energy Environ. Sci.* 8 (2), 617-628.
- Zhang X., Tu M., Paice M.G., 2011. Routes to Potential Bioproducts from Lignocellulosic Biomass Lignin and Hemicelluloses. *Bioenerg. Res.* 4(4), 246-257.