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Phenolic Monomers Production by the Direct Depolymerization of Lignin Contained in Kraft Black Liquor in the Presence of Metal Catalyst

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In this study, the influence of a metallic catalyst (Pt/C) on the direct depolymerization of the lignin contained in Kraft liquor (without its precipitation) has been studied. After the depolymerization reaction at the optimal conditions, three main products were obtained: oil (with phenolic monomers), residual lignin and char. The first one has been characterized by GC/MS to quantify the phenolic monomers present in the oil. An experimental response surface design was made using the Statgraphic Centurion version XV software to analyse the influence of the catalyst concentration and the reaction time in both oil yield and the phenolic monomers production from the lignin. The catalyst concentration and reaction time have been varied between 0 - 4 wt.% and 20 - 80 min. All the depolymerization processes have been carried out at 300 ºC of temperature and 90 bar of pressure. After the experimental design, an optimum point has been obtained where the yield of oil and monomeric products were maximum. The validation of the model has been carried out by performing the experiments at the optimal conditions and comparing them with the values predicted by the design.

1. Introduction

Nowadays oil is one of the main sources of raw material for the manufacture of many of the consumer goods and the main source of energy for the manufacturing and transport processes, despite being one of the major sources of pollution. For this reason, it is necessary to find new sources of raw materials, more sustainable and less polluting to replace oil. For this purpose, lignin appears as a good renewable alternative to chemical compounds derived from petroleum (Farag et al., 2014).

Lignin is the second most abundant polymer in nature after cellulose and is the most abundant renewable aromatic polymer on Earth (Kirk and Farrell, 1987). Lignin is one of the main components of the cell wall of vascular plants and constitutes between 15 – 30 % of the mass content depending on the species (Lindberg et al., 1988). It can be defined as a polyphenolic, amorphous material generated by the polymerization of three phenyl-propanoic monomers called p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol**.** These monomers are linked to each other by ether bonds, such as, α-O-4, β-O-4, 4-O-5 and carbon-carbon bonds forming a three-dimensional structure branched in the cell wall which acts as a resin, filling the gaps between cellulose and hemicelluloses. Lignins are complex molecules with a great heterogeneity that depend on the species of the plant, the separation process and the method used to recover the black liquor (Zinovyev et al., 2017). Therefore, the unique aromatic structure of lignin, makes it a candidate to transform it catalytically into low molecular weight phenolic compounds that replace the petroleum based compounds (Zakzeski et al., 2010).

Industrially, the main source of lignin is the pulp and paper (P&P) industry. In P&P industry the Kraft method is the most used one to generate chemical pulps. Through this process, about 50 Mt of a black liquor rich in lignin are generated as a byproduct (Mahmood et al., 2016), which are used as a fuel to satisfy part of the plant energy necessities (Bruijnincx et al., 2015). However, lignin can be used for other valuable purposes, like high-added value chemical precursor. In this sense, different depolymerization processes have been studied, such as depolymerization by acid catalysts, basic catalysts, ionic liquids, sub or supercritical fluids and metal catalysts to transform the isolated lignin from black liquor into monomeric compounds (Mahmood, 2016) such catechol

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and its derivatives (Fernández-Rodríguez et al., 2017) vanillin, aromatic compounds, aliphatic acids and many others (Alriols et al., 2009).

The aim of this work was to determinate de action of a metallic catalyst (Pt/C) in the depolymerization of the lignin contained in the Kraft liquor without precipitating it. For this purpose, an experimental design has been carried out using Statgraphic software. The selected catalyst was chosen based on a previous research (Kim et al., 2015). while the independent variables and their variation ranges were determined based on preliminary studies and other related studies (Erdocia et al., 2017).

2. Materials and methods

2.1 Black liquor and metal catalyst

The liquor used has been obtained as a byproduct of the delignification of *Eucalyptus Globulus* by Kraft process in the Papelera Guipuzcoana de Zikuñaga S.A. The catalyst used in this study was a metallic Pt 5 % wt. catalyst supported on activated carbon purchased from Sigma-Aldrich. The ethyl acetate, sodium sulfate anhydride and the tetrahydrofuran were also purchased from Sigma-Aldrich and used as received.

2.2 Black liquor characterization

Black liquor from delignification of *Eucalyptus Globulus* has been characterized before the delignification reaction. Density was calculated by weighing a sample of liquor in a known volume. Total dissolved solids (TDS) were determined using a method based on TAPPI T264 cm-97 to determinate the moisture content in wich the sample is dried for 24h at 105 °C. The inorganic matter (IM) has been determined after the combustion of the dried sample in an oven for 3h at 525 °C employing a method based on the TAPPI T211 om-93 standard used to determine the ash content. Organic matter (OM) has been determined by the difference between TDS and IM.

2.3 Depolymerization process

The depolymerization reaction of the lignin contained in the Kraft liquor has been carried out in a 100 mL batch reactor (5500 Parr) and a 4848 controller. The reaction conditions were 300 ºC and 90 bar in all experiments with constant stirring. 20 ± 0.1 g of Kraft liquor have been used and the catalyst has been added with respect to the organic matter.

2.4 Experimental design

A response surface methodology with a 3^2 design with three replicates in the central point was used for the experimental design and optimization. As it was mentioned in the introduction, the selected catalyst was chosen based on a previous research while the independent variables and their variation ranges were determined based on preliminary studies and other related studies . The experimental data obtained in the design have been adjusted using the regression analysis function of the data analysis of Microsoft Excel Add-In, USA. The determination of the optimum conditions has been estimated using the desirability function of the software Statgraphics Centurion version XV (StatPoint Technologies Inc., Warrenton, VA, USA). Model validation has been carried out by performing the experiments in the optimal conditions and comparing them with the values predicted by the model. The experimental variables involved in the study are shown in Table 1.

Table 1: Experimental variables involved in the study

Variable	Definition	Units	Nomenclature	Value
Fixed	Temperature	(ºC)		300
	Pressure	(bar)		90
Independent	Catalyst	(% wt respect OM)	X_1	0-4
	Time	min	X_2	20-80
Dependent	Oil	(% wt)	Y_A	
	Monomeric compounds	(% wt)	Y_C	

The experimental data were adjusted using a second-order polynomial described by the Eq(1):

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_{12} X_1 X_2 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \varepsilon \qquad (1)$$

Where Y are the dependent variables Y_A (% Oil) and Y_C (% Monomeric compounds); β_0, β_1 y β_2 are the regression coefficients calculated from the experimental results by the least-squares method and X_1 and X_2 are the normalized independent variables, time and catalyst, with variation ranges from -1 to 1.

2.5 Product separation and characterization

At the end of the reaction the method described by (Toledano et al., 2014) was used to separate the compounds. The liquor and the recovered solids, residual lignin and char, were acidified with HCl (37 % wt.) until pH1. In this way, the solids precipitate and are separated by filtration and washed with acidified water to remove the remains of the liquor. Two well-differentiated phases were obtained, a liquid phase rich in phenolic compounds and a solid phase composed of coke and residual lignin. To separate the monomeric compounds from the aqueous phase, a liquid-liquid extraction was carried out using ethyl acetate. Anhydrous sodium sulphate has been added to the organic fraction to remove traces of moisture and then it was filtrated and finally it was vacuum evaporated to obtain an oil where the depolymerization products are dissolved. The solid residue has been solubilized and stirred for 3 h in 30 mL of tetrahydrofuran (THF). Then it was filtrated to separate the insoluble char from the residual lignin that is dissolved in the THF. This THF solution was vacuum evaporated to recover the residual lignin.

The oil has been characterized to determine the nature of the monomeric compounds by GC/MS. For the analysis, the oil was dissolved in ethyl acetate (HPLC grade). 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 ºC then, the temperature was raised to 120 ºC at 10 K min^{-1}, held 5 min, raised to 280 ºC at 10 K min^{-1}, held 8 min, raised to 300 ºC at 10 K min^{-1} 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, veratrole, 4-hydroxybenzoic acid, 4-hydroxy-3-methoxyphenylacetone, vanillin, vanillic acid, syringaldehyde, 3,5-dimethoxy-4-hydroxyacetophenone and syringic acid.

3. Results and discussion

3.1 Black liquor characterization

The results of the characterization of the Kraft liquor are shown in Table 2.

Table 2: Kraft liquor characterization

	Kraft liquor
pH	13.03 ± 0.050
Density(g/mL)	1.06 ± 0.008
TDS (%)	11.78 ± 0.068
IM (%)	8.46 ± 0.082
OM (%)	3.32 ± 0.014

As it was expected, the pH of the liquor was high due to the use of NaOH during the delignification process. The content of inorganic matter is also elevated since in the Kraft process inorganic reagents are used, mainly NaOH and Na_2S, which remain dissolved in the liquor when the delignification process has finished. The organic matter was the expected for a Kraft liquor.

3.2 Optimization of the reaction conditions

In order to obtain the highest oil and monomeric compounds, the joint optimization of the most influential variables was addressed using a 3^2 experimental design combined with response surface methodology. Table 3 shows the set of experiments performed as well as the experimental results determined for the dependent variables, all of them in % wt. respect to the organic matter in the liquor: oil, monomeric compounds and the undesirable solid residue.

Table 3: Set of experiments and experimental results

Experiments	1	2	3	4	5	6	7	8	9	10	11
Catalyst (% wt respect OM)	0	2	2	2	0	4	2	2	4	0	4
Time (min)	50	50	50	50	20	50	20	80	80	80	80
X_1	-1	0	0	0	-1	1	0	0	1	-1	1
X_2	0	0	0	0	-1	0	-1	1	1	1	-1
Oil (% wt)	22.80	20.35	20.69	20.64	22.52	20.80	23.66	19.89	19.28	17.32	21.22
Monomeric compounds (% wt)	6.00	6.49	5.59	5.61	6.21	5.22	8.11	4.03	3.94	2.42	8.02
Solid residue (% wt)	41.18	39.48	41.38	40.46	39.85	40.22	40.56	38.70	41.03	34.90	39.84

As shown in the Table 3, experiment 7 had the higher percentaje of oil and monomeric compounds, 23.66 % wt. and 8.11 % wt. respectively. It can also be observed that the solid residue was elevated in all reactions, indicating that not only depolymerisation phenomena of the lignin took part in the process but also repolymerization of the different unstable reaction intermediates occurred.

Regarding the regression coefficients in Table 4, obtained for the models according to the second-order polynomial, Eq(1), only the independent variable that corresponds to time has a significant influence on the production of oil and monomeric compounds. This could be verified in Figure 1a and 1b where the interaction between time and catalyst for the production of oil and monomeric compounds respectively are shown.

In Figure 1a can be observed that the production of oil is favoured by short reaction times while the catalyst has little influence. On the other hand, it can be concluded that for higher reaction times the addition of the catalyst decreases the percentage of the oil. The obtaining of monomeric compounds is favoured by short reaction times as in the previous case, however in this case the addition of the catalyst has a greater influence and an increase in the concentration of catalyst improves the obtaining of the monomeric compounds, Figure 1b.

Table 4: Regression coefficients and statistical parameters of the model

Regression coefficients	Variables	
	Y_A	Y_C
β_0	21.18	6.03
β_1	-0.22	0.42
β_2	-1.84*	-1.99*
$\beta_1 \beta_2$	0.82	-0.07
$\beta_1 \beta_1$	-0.30	-0.62
$\beta_2 \beta_2$	-0.33	-0.16
R^2	0.76	0.90
F-exp	3.21	9.40
Significance level (%)	88.68	98.60

*Significant coefficients > 90% confidence level

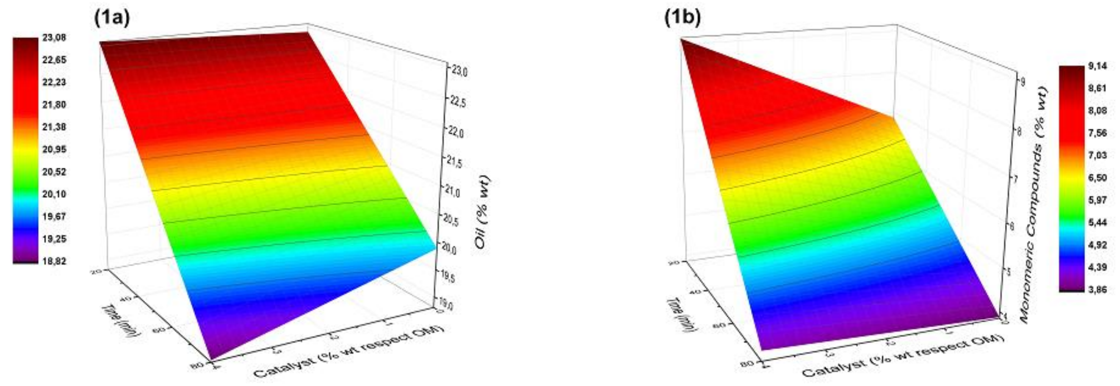

Figure 1: Response surface for Oil (% wt) (a) and Monomeric compounds (% wt) (b) in function of time(min) and catalyst (% wt respect OM)

Table 5 shows the combination of factors in which the optimum point of the system was obtained. This optimum point has been verified with a triplicate of the experiment. These conditions correspond to a catalyst concentration of 1.45 % with respect to the organic matter present in the Kraft liquor and a reaction time of 20 min. Under these conditions, the design foresees that 22.9 % of oil and 7.67 % of compounds will be obtained with respect to organic matter.

Table 5: Optimal point of the system

Factor	Low	High	Optimum
Catalyst (% wt respect OM)	-1	1	-0.2743
Time (min)	-1	1	-1

3.3 Oil characterization

The phenolic oil obtained after the depolymerization reaction was characterized by GC/MS to quantify the monomeric compounds. Table 6 shows these monomeric compounds obtained in each experiment (% wt. respect the OM) and Figure 2 shows syringol and guaiacol compared with catechol and its derivatives (4-Methylcatechol and 4-Ethylchatechol).

Table 6: Monomeric compounds (% wt. referred to OM)

	Experiments										
Compound	1	2	3	4	5	6	7	8	9	10	11
Phenol	0.167	0.166	0.146	0.142	0.083	0.121	0.185	0.116	0.119	0.103	0.142
o-cresol	0.048	0.051	0.050	0.046	0.019	0.036	0.039	0.040	0.036	0.032	0.035
m-p-cresol	0.062	0.067	0.073	0.063	0.022	0.046	0.043	0.060	0.058	0.056	0.038
Guaiacol	0.201	0.305	0.191	0.173	0.341	0.195	0.739	0.117	0.127	0.127	0.528
Catechol	2.241	1.768	1.507	1.820	2.483	1.518	3.010	0.675	0.770	0.392	2.681
3-Methylcatechol	0.402	0.481	0.438	0.400	0.246	0.375	0.270	0.379	0.372	0.196	0.390
3-Methoxycatechol	0.024	0.066	0.028	0.022	0.104	0.045	0.224	0.022	0.019	0.012	0.147
4-Methylcatechol	1.942	2.372	2.037	2.031	1.977	1.992	2.322	1.694	1.521	0.902	2.775
Syringol	0.089	0.238	0.152	0.140	0.186	0.138	0.445	0.095	0.115	0.096	0.334
4-Ethylcatechol	0.811	0.952	0.942	0.761	0.685	0.736	0.722	0.809	0.807	0.490	0.911
Vanillin	N.D.	0.003	0.003	N.D.	0.002	N.D.	0.004	N.D.	N.D.	N.D.	0.004
Acetovanillone	0.005	0.004	0.002	0.003	0.022	0.003	0.043	0.002	0.002	0.002	0.017
Veratrol	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Guaiacylacetone	0.011	0.016	0.022	N.D.	0.034	N.D.	0.035	0.023	0.019	N.D.	0.006
Vanillic acid	N.D.	N.D.	N.D.	0.008	N.D.	0.008	0.002	N.D.	N.D.	0.013	N.D.
Syringaldehyde	N.D.	N.D.	0.002	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Acetosyringone	0.004	0.004	0.005	N.D.	N.D.	N.D.	0.002	N.D.	N.D.	N.D.	0.008
Syringic acid	N.D.	N.D.	0.024	0.002	0.008	0.002	0.021	N.D.	N.D.	N.D.	N.D.

Table 6 shows that the major compounds in all reactions was catechol and its derivatives 4-Methylcatechol and 4-Ethylcatechol. These results were the expected for a base catalyzed depolymerization reaction (BCD) (Dos Santos et al., 2016). As it can be observed in Figure 2, syringol and guaiacol have appeared in low concentrations compared to catechol and its derivatives; this confirmed that the reaction was given via BCD reaction since syringol and guaiacol are susceptible to be converted into phenol, cresol, catechol and its derivatives by demethoxylation in BCD reactions (Wahyudiono et al., 2007). In addition, as would be expected in this type of reactions, syringol has appeared in lower concentration than guaiacol, since demethoxylation is more favorable in syringyl groups (Erdocia et al., 2014). This indicated that the addition of the Pt/C metal catalyst in the Kraft liquor for direct depolymerization has not favored the selectivity of the monomeric compounds.

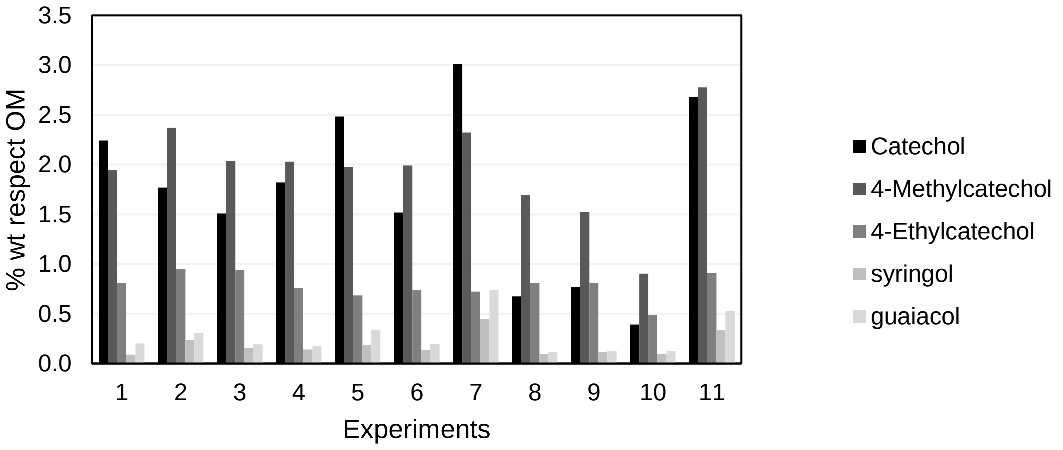

Figure 1: % wt. respect OM of the most significant monomeric compounds after depolymerization

3.4 Conclusions

In the direct depolymerization of the lignin contained in the Kraft liquor using a Pt/C as metal catalyst it has been observed that the most important variable was the reaction time. It has also been observed that with the addition of the catalyst less oil was obtained, however the addition of this has favoured the production of monomeric compounds at low reaction times. Nevertheless, the selectivity of these monomeric compounds was not improved and the same phenolic monomers were obtained when using the catalyst.

Through the experimental design it has been determined that the optimal reaction conditions have been established in 20 min and a catalyst concentration of 1.45 (% wt respect OM) at the temperature of 300 ºC and 90 bar of pressure.

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