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Title(s)

Analysis of the effect of temperature and reaction time on yields, compositions and oil quality in catalytic and non-catalytic lignin solvolysis with formic acid using experimental design.

Abstract

The catalytic solvolysis of Norway spruce lignin in a formic acid/water media using bifunctional Ru/Al_2O_3, Rh/Al_2O_3, Pd/Al_2O_3 catalysts was explored in a batch set-up at different temperatures and reaction times (283-397^oC and 21 min-11 h 40 min, respectively). Blank experiments using only gamma–alumina as catalysts and non-catalyzed experiments were also performed and compared with the supported catalysts results. Surface response methodology (RSM) and principal component analysis (PCA) were used to evaluate the influence of the reaction conditions and type of system on the oil yield, solid residue yield, oil quality and composition. The optimum reaction conditions were found to be around 340^oC and 6 h using Ru/Al_2O_3 as a catalyst; where nearly complete conversion of lignin into oil is achieved (83.8 %) while still having high H/C ratios (1.21) coupled with low O/C ratios (0.19) and M_w values (500 Da). No correlations between the oil yield and the quality of the oil has been found. The oil yield is strongly dependent on the presence of the catalyst, temperature and reaction time; while the oil quality is mainly dependent on reaction conditions. The recycling of the catalyst proves that the deactivation of the Ru/Al_2O_3 catalyst is negligible after two separate recycling tests. The results show the potential for improving the yields of oil by the use of catalysts which are easily recovered, and suggest a good potential for tuning the oil composition to specific composition depending on the requirements for the product.

Introduction

Global warming, volatile oil prices and world political instability point toward the necessity of new localized and environmentally friendly ways of producing fuels and oil derived products from non-alimentary sources [1, 2]. The development of economically feasible biomass-based bio-refineries is recognized as one of the best alternatives to meet all these ongoing challenges [3]. Among the biomass sources, lignocellulosic biomass (wood, grasses and agricultural residues) has been identified as a promising resource for this purpose [4], since unlike vegetable oil and sugar crops, the lignocellulose feedstocks avoid the negative side effect of intense farming [5] and ethical concerns about the use of food as fuel raw materials [6].

Extensive work has been done on the chemical and enzymatic fractionation of lignocellulose, and the subsequent conversion of the cellulose and hemicellulose fractions into bioethanol [6-10]. However, the third component, lignin, comprising between 10-30 % of the feedstock, is mostly considered to be a waste [11]. Several thermochemical processes have been explored as suitable for the conversion

of lignin-rich residual materials into fuels or phenols [4, 12-14]. A promising and relatively new lignin conversion approach, known as lignin-to liquids (LtL), involves the use of formic acid (FA) together with a solvent. The solvent can be either ethanol or water, though the latter is preferred due to its lower cost and more green nature. High oil yields, with high H/C and low O/C ratios are obtained, still retaining the phenol-type structure of the bio- oil components. Therefore this versatile process can be used for the production of both a bio-oil that can be blended with conventional fuels and to produce aromatic compounds such as phenol, catechol and guaiacol [15, 16].

One of the major research challenges of the LtL method is to obtain high oil yields and good quality while decreasing the temperature and the reaction time of the process. Good oil quality can be defined as a high energy content, stable, non-acidic and low viscous oils [17], with high H/C and low O/C ratios and low average molecular weight distribution (M_w). One alternative to address this challenge is the use of a catalyst in order to increase the lignin conversion rate[18]. Previously in our group, Ru/Al_2O_3 (Ru), Rh/Al_2O_3 (Rh) and Pd/Al_2O_3 (Pd) have been shown to be an active catalyst toward the conversion of lignin with formic acid in an aqueous media [19]. Among other aspects the activity of the alumina support and the influence of the type of noble metal in the oil quality and yield were discussed. However, the results found are not conclusive since those effects were mainly studied only at a specific reaction condition, i.e. 340^{o}C during 6 h.

A more systematic approach based on experimental design can be used, not only to confirm the effect of the alumina support and type of noble metal in the oil yield and quality in a wider experimental space, but also to address other aspects that could be interesting from an industrial perspective: (*i*) the optimal reaction conditions, (*ii*) possible correlations between the oil yield and the oil quality, (*iii*) the influence of reaction temperature and time in the composition of the oil, (*iv*) activity of the catalysts upon recycling.

Here, a step-wise approach based on experimental design will be presented. Initially the effect of the temperature (300-380^{o}C) and reaction time (2-10 h) for three different catalytic systems (Ru, Rh, Pd) will be evaluated using a full factorial design. Response surface methodology (RSM) and principal component analysis (PCA) [17, 20] will be used to evaluate the influence of the reaction conditions and type of catalyst on the oil yield, solid residue yield, oil quality and composition. An additional aim of this screening study is to assess the similarities and differences within the catalytic systems.

In a second step, the influence of temperature (283-397^{o}C) and reaction time (21 min-11h and 40 min) on three different reaction systems (non-catalyzed (NC), γ-Al_2O_3 (Al) and Ru catalyzed systems) will be studied based on a central composite design [21]. Again RSM and PCA will be used to evaluate the influence of the reaction conditions and type of system on the oil yield, solid residue yield, oil

quality and composition. In addition, the role of the noble metal and the γ-alumina support in the lignin de-polymerization and hydrodeoxygenation will be evaluated.

In a third step, the activity of one of the catalysts will be evaluated upon two recycling cycles in terms of oil yield and quality.

2. Materials and Methods

2.1 Chemicals

Formic acid (>98%), tetrahydrofuran (>99.9%) and ethyl acetate (99.8%) were purchased from Sigma Aldrich and used as supplied. Lignin from Norway spruce (*Picea abies L.*) from strong acid carbohydrate dissolution pre-treatment was received from Technical College of Bergen. The lignin was ground, sieved (<500µm) and dried at 80°C for 24 h prior to use.

2.2 Catalysts

Ruthenium on alumina (5 wt%), Rhodium on alumina (5wt%), and Palladium on alumina (10 wt%), were obtained from Sigma Aldrich, and gamma-alumina (97 wt%) was obtained from Strem Chemicals Inc. These were dried at 80°C for 24 h prior to use.

2.3 Catalyst characterization

The type of acidity (Lewis or Brønsted), the total acidity, the acidity retention and the active acidity of the Ru/Al_2O_3, Rh/Al_2O_3, Pd/Al_2O_3 and γ-alumina catalysts were analysed by NH_3-TPD and DRIFT of absorbed pyridine. The active acidity is defined as the fraction of total acidity that actually plays a significant role in the reaction (active acidity (T) = acidity retention (T) x total acidity).

Temperature-programmed desorption of ammonia, NH_3-TPD, was performed to determine the total acidity of the samples. The measurements were carried out in a chemisorption analyzer AutoChem II equipped with a thermal conductivity detector (Micromeritics, USA). A detailed description of the analysis procedure is given elsewhere by Oregui Bengoechea *et al.* [19].

Diffuse reflectance infrared Fourier transform, DRIFT, was used to distinguish Lewis and Brønsted acid sites of noble-metal containing catalysts and $\gamma\text{-}Al_2O_3$. The analyses were done using a VERTEX 70 spectrometer coupled with an external sample chamber that enables measurements under vacuum (Bruker, Germany). A detailed description on the analysis procedure is given elsewhere by Oregui Bengoechea *et al.* [19].

2.4 Experimental conditions

2.4.1 Experimental set-up

A detailed description is given elsewhere by Oregui Bengoechea *et al.* [19]. Briefly summarised, lignin (2g), formic acid (3.075g), water (5g) and the catalyst (0.2g) were added to a stainless steel reactor (Parr 4742 non-stirred reactor, 25 ml volume). The amounts of reactants are based on previous experiments for maximising oil yields. The reactor was closed and heated in a Carbolite LHT oven up to the desired conditions (283-397°C) for a given reaction time (21 min-11 h 40 min).

2.4.2 Sample work-up

A detailed description is given elsewhere by Oregui Bengoechea *et al.* [19]. Briefly summarized, after the reactor was cooled down to the ambient temperature the produced gas was vented and the gas quantity was determined. The reactor was opened and the liquid reaction mixture was extracted with a solution of ethyl acetate: tetrahydrofuran (90:10). The solid phase (unreacted lignin, reaction products and catalyst) was filtered and dried at ambient conditions for 2 days before weighing. Two well-separated liquid phases were obtained (organic top phase and aqueous bottom phase). The phases were separated by decantation and the organic phase was dried over Na_2SO_4 and concentrated at reduced pressure (ca. 250 mmbar) at 40°C. The final oil and solid yield was determined by weight (amount of oil/char (g.)/amount of introduced lignin (g.)). The solid yield for the catalyzed systems is calculated after subtracting the amount of catalyst introduced. Therefore the solid yield refers to the organic solids (char) and the inorganic lignin ashes.

2.4.3 Recycling of the catalyst

2.4.3.1 Ash content of lignin

Three crucibles were calcined at 575°C and weighted to the nearest 0.1 mg until constant weight (less than ±0,3 mg after one 1 h of heating at 575°C). Once the weight of each crucible is recorded, between 0.5 and 2.0 g. of lignin was weighed into each tared crucible. The lignin was calcined using the following temperature programme: hold the temperature at 105°C for 12 min, increase the temperature until 250°C at 10°C/min, hold the temperature at 250°C for 30 min, increase the temperature until 575°C at 20°C/min, and hold it at that temperature for 180 min. After cooling, the samples were weighed to the nearest of 0.1 mg weighted until constant weight. The final ash content is calculated as the mean of the three crucibles.

2.4.3.2 Recycling procedure

The residual solids recovered after the work-up described in Section 2.4.2, were subjected to a thermal treatment at 360°C for two hours with a heating ramp of 2°C/min to eliminate the organic (char) residues. After the thermal treatment the resulting solids, catalyst and ashes, were re-used at 340°C and 6 h following the experimental set-up described in Section 2.4.1. The oil and solid yields were calculated by weight and the oil was analysed. This procedure was repeated again to evaluate the activity of the catalyst upon two recycling-cycles.

2.5 Characterization of the oils

2.5.1 GC-FID analysis

A detailed description is given elsewhere by Oregui Bengoechea *et al.* [19]. Briefly, the samples were first silylated with BSTFA prior to the GC-FID analysis. The samples were analysed on a Thermo Finnigan TRACE GC Ultra with a FID-detector equipped with a chromatographic HP-ULTRA2 column from Agilent Technologies. The following heating programme was applied: 30°C for one minute, and then heating at 10°C/min up to 25°C. The injector temperature was 250°C, and the detector temperature was 320°C. Identification of the peaks was made by comparison with retention times of authentic commercially avail-able reference compounds that were also silylated prior to the analysis. The quantitative data was obtained using hexadecane as internal standard. Calibration curves were prepared for the following compounds: phenol (Ph), cresol (Cr), guaiacol (Gu), methyl-guaiacol (M-Gu), catechol (Ca) and syringol (Sy), and their concentrations were calculated as % weight in the oil.

2.5.2 Elemental analysis

All samples were analysed for their elemental composition in the CHNS mode with a Vario EL III instrument using helium as carrier gas. The amount of oxygen was calculated by difference.

2.5.3 GPC-SEC

The sample (1 mg) was dissolved in 1 mL of THF. The solution (20 µL) was injected into a GPC-SEC system equipped with a PLgel 3ìm Mini MIX-E column, and analysed at a flow rate of 0.5 mL/min of THF at 21.1◦C, and the detection was performed with UV at 254and 280 nm, as well as with RI. The set of columns was calibrated with a series of polystyrene standards covering a molecular-mass range of 162–2360 Da.

2.6 Data analysis

2.6.1 Screening Experiments

A two-level full-factorial design with three center points was used to evaluate the influence of the temperature (x_1) and reaction time (x_2) in each of the three different catalytic systems. The experimental design was done separately for each catalytic system and different responses were examined: oil and solid yield, H/C and O/C ratio, average molecular weight distribution (M_w) and oil composition (see Section 2.6.1). The selected control variables (temperature and reaction time) and their levels for each system are described in Table 1. The relation between the coded and the actual values is the following:

$$x_i = \frac{X_i - X_0}{\Delta X}$$

Where X_i is the actual value of the variable, X_0 is the actual value of X_i at the center point, and ΔX is the step change of the variable.

Table 1: experimental design for catalyst screening

Experiment	X_1 Temperature (°C)		X_2 Reaction time (h)	
	Actual	Coded	Actual	Coded
X[a]-1	300	-1	10	+1
X[a]-2	380	+1	10	+1
X[a]-3	300	-1	2	-1
X[a]-4	380	+1	2	-1
X[a]-5	340	0	6	0
X[a]-6	340	0	6	0
X[a]-7	340	0	6	0

a) X: refers to either Ru (Ru/Al_2O_3 catalyst), Rh (Rh/Al_2O_3 catalyst) or Pd (Pd/Al_2O_3 catalyst)

2.6.1.1 Response surface methodology (RSM) for the oil and solid yield

Response Surface Methodology (RSM) is a set of mathematical and statistical techniques that can be used to define the relationships between the response and the independent variables, and the objective is to maximize this response [17, 22]. In the present study oil and solid yields were selected as response variables and fitted in a linear regression model with an interaction factor in the form of a polynomial equation:

$$Y = \beta_0 + \sum \beta_i x_i + \sum \sum \beta_{ij} \; x_i x_j \quad (1)$$

Where Y is the predicted response variable (oil or solid yield); β_0, β_i, β_{ij} are constant regression coefficients of the model; and x_i, x_j (ij= 1,2; i ≠ j) represent the coded values of independent variables that are used in statistical calculations. For each system separate oil and solid regression models were calculated and their response surface model built. After the regression model was obtained, the significance of the regression model was evaluated by the analysis of variance (ANOVA) [23-25].

2.6.1.2 Principal component analysis (PCA) to evaluate the quality of the oil

Principal component analysis (PCA) is a commonly used technique in statistics for simplifying the data by reducing multivariable to a 2-D plot in order to characterise the results. The use of principal component analysis allows identifying the factors which influence the data so that relationship can be established on a qualitative analysis. PCA uses complex matrix transformation which does not impose fixed vectors, and is completely dependent on the data set [26]. PCA has been used in the past to discriminate the effect of reaction conditions and reactant compositions in the quality of the LtL oils [5] . In the present study, the variables studied to evaluate the quality of the oils are: reaction temperature, reaction time, type of catalyst, oil and solid yield, H/C and O/C ratio of the oil and

189 average molecular weight distribution (M_w). The variable named catalyst is added to visualize the
190 effect of the type of catalyst. This is a three level variable where Ru is represented by the coded level
191 +1, Rh by 0, and Pd by -1. No cross-term is considered in this analysis to maximize the explained
192 variance.

193 **2.6.1.3 Principal component analysis (PCA) to evaluate the oil composition**

194 Eight variables were submitted to PCA analysis. Three process variables, reaction temperature,
195 reaction time and type of catalyst; and five response variables, named concentration of phenol (Ph),
196 guaiacol (Gu), catechol (Ca), cresol (Cr) and methyl-guaiacol (M-Gu) in the oils. No cross-term is
197 considered in the analysis to maximize the explained variance.

198 **2.6.2 Optimization experiments**

199 A central composite design (CCD) with axial (α=1,41) and three centre points was used to evaluate
200 the influence of the temperature (x_1) and reaction time (x_2) in three different reaction systems (NC:
201 the non-catalysed system, Al: the γ-alumina system and the Ru system). The Ru system represents
202 the best catalytic system in terms of oil yield. CCD allows determining both linear and quadratic
203 models and is a good alternative of a three level full factorial design as it provides comparable results
204 with smaller number of experiments [27]. The experimental design was carried out separately for
205 each catalytic system and different responses were examined: oil and solid yield, H/C and O/C ratio,
206 and M_w and oil composition (see Section 2.6.1). The selected control variables (temperature and
207 reaction time) and their levels for each system are described in Table 2. The relation between the
208 coded and the actual values is the following:

209 $$x_i = \frac{X_i - X_0}{\Delta X}$$

210 Where X_i is the actual value of the variable, X_0 is the actual value of X_i at the centre point, and ΔX is
211 the step change of the variable. For each system separate oil and solid regression models were
212 calculated and their response surface model was built. After the regression model of experimental
213 data was obtained, the significance of the regression model was evaluated by the analysis of variance
214 (ANOVA) [23-25].

215 Table 2: experimental design for system optimization

Experiment	X_1 Temperature (°C)		X_2 Reaction time (h)	
	Actual	Coded	Actual	Coded
X-1	300	-1	10	+1
X-2	380	+1	10	+1
X-3	300	-1	2	-1

X-4	380	+1	2	-1
X-5	340	0	6	0
X-6	340	0	6	0
X-7	340	0	6	0
X-S1	397	+1.41	6	0
X-S2	283	-1.41	6	0
X-S3	340	0	21 min	-1.41
X-S4	340	0	11 h 40 min	+1.41

X: refers to either the Ru catalyzed system (Ru), γ-Al_2O_3 catalyzed system (Al) or the non-catalyzed system (NC) **S:** refers to the axial points were α=1,41

2.6.2.1 Response surface methodology (RSM) for the oil and solid yield

In the present study oil and solid yields were selected as response variables and fitted to a second-order (quadratic) model in the form of quadratic polynomial equation:

$$Y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \sum \beta_{ij} \; x_i x_j \qquad (2)$$

Where *Y* is the predicted response variable (either oil or solid yield); β_0, β_i, β_{ii} ,β_{ij} are constant regression coefficients of the model; and x_i, x_j (ij= 1,2; i ≠ j) represent the coded values of independent variables that are used in statistical calculations. For each system separate oil and solid second order regression models were calculated and their response surface model was built. After the regression model of experimental data was obtained, the significance of the regression model by analysis of variance (ANOVA).

2.6.2.2 Principal component analysis (PCA) to evaluate the quality of the oil

The variables studied to evaluate the quality of the oils are: reaction temperature, reaction time, type of system, oil and char yield, H/C and O/C ratio of the oil and average molecular weight distribution (M_w). The variable named system is added to visualize the effect of the type of system. This is a three level variable where Ru is represented by the coded level +1, NC by 0, and Al by -1. No cross or quadratic term is considered in the analysis to maximize the explained variance.

2.6.2.3 Principal component analysis (PCA) to evaluate the oil composition

Initially eight variables were submitted to PCA analysis. Three process variables, reaction temperature, reaction time and type of system; and five response variables, named concentration of Ph, Gu, Ca, Cr and M-Gu in the oils (see Section 2.5.1). No cross or quadratic term is considered in either analysis to maximize the explained variance.

3. Results and Discussion

3.1 Acidity Results of Ru/Al_2O_3, Rh/Al_2O_3, Pd/Al_2O_3 and γ-alumina

Table 3 summarizes the results obtained for the DRIFT and NH_3-TPD analysis. IR bands assigned to Brønsted acid sites (1545 and 1638 cm^{-1}) were not detected in any of the samples[28], suggesting that only Lewis acidity (1448 cm^{-1}) is present (see *Figure S1, Supplementary Information*).

The highest total acidity measured by NH_3-TPD was obtained for the γ-Al_2O_3 (1.51 mmol NH_3/g catalyst), with significantly lower acidities for the supported catalysts (Rh/Al_2O_3 > Ru/Al_2O_3 > Pd/Al_2O_3). Based on the IR band at 1445 cm^{-1}, acidity retention was also calculated as [peak area (T) / peak area (100°C)] x 100 (Table 3). Increasing the temperature did not influence the Lewis acid-bound pyridine in Al_2O_3 and Pd/Al_2O_3, but caused pyridine desorption in the case of Rh/Al_2O_3 and Ru/Al_2O_3. This suggests that the Lewis sites present in Rh/Al_2O_3 and Ru/Al_2O_3 samples are rather weak compared to the ones present in Al_2O_3 and Pd/Al_2O_3. Therefore the catalyst with the highest active acidity is γ- Al_2O_3 followed by Pd/Al_2O_3, Rh/Al_2O_3 and Ru/Al_2O_3.

Table 3: Total acidity, acidity retention and active acidity of γ-alumina, Rh/Al_2O_3, Ru/Al_2O_3 and Pd/Al_2O_3.

	Total acidity[a] (mmol NH_3/g cat.)	**Acidity retention[b] (%)**	**Active acidity (mmol NH3/g cat.)**
γ-alumina	1.51	100 (100°C) 92 (200°C) 92 (300°C)	1.51 (100°C) 1.39 (200°C) 1.39 (300°C)
Rh/Al_2O_3	1.34	100 (100 °C) 71 (200°C) 49 (300°C)	1.34 (100°C) 0.95 (200°C) 0.66 (300°C)
Ru/Al_2O_3	0.78	100 (100°C) 77 (200°C) 51 (300°C)	0.78 (100°C) 0.60 (200°C) 0.40 (300°C)
Pd/Al_2O_3	0.76	100 (100°C) 99 (200°C) 98 (300 °C)	0.76 (100°C) 0.75 (200°C) 0.74 (300°C)

a) Data obtained from NH3-TPD **b)** Data obtained from DRIFT

3.2. Screening experiments: effect of the type of catalyst

3.2.1 Effect of the catalyst, temperature and time on the oil and solid yield

The main goal of this experimental set was to determine which catalyst performs best in the terms of high oil and low solid yield. For this purpose three analogous experimental sets for the Pd, Rh and Ru catalysts were subjected to surface response modelling. The experiments were performed randomly to minimize the systematic error. The results obtained for the oil and solid yield are summarized in Table 4.

Table 4 Experimental design for screening experiments and oil and solid yields

Experiment	Oil Yield (%)	Solid Yield (%)	H/C	O/C	Mw	Ph*	Gu*	Ca*	Cr*	M-Gu*
Pd-1	86.1	12.8	1.19	0.21	444	2.6	4.2	1.1	5.8	3.8
Pd-2	57.1	6.2	1.18	0.1	305	2.8	3.3	0.7	5.3	3.7
Pd-3	38.2	60.3	1.24	0.26	538	2.3	3.7	0.3	0.0	3.4
Pd-4	78.5	7.5	1.15	0.16	404	2.0	2.9	1.7	4.3	2.8
Pd-5	81.7	2.8	1.21	0.14	323	2.5	3.4	2.0	5.2	3.4
Pd-6	85.4	2.4	1.19	0.17	332	1.9	2.8	2.0	3.9	2.6
Pd-7	81.6	2.9	1.21	0.18	340	2.2	3.1	2.0	4.6	3.0
Rh-1	83.0	16.5	1.22	0.22	556	2.0	3.4	1.1	4.6	3.1
Rh-2	58.9	5.7	1.18	0.1	187	2.0	2.6	0.6	4.3	2.9
Rh-3	38.4	56.4	1.25	0.26	561	3.4	5.3	0.3	0.0	5.0
Rh-4	74.0	5.2	1.15	0.16	296	1.7	2.5	1.1	3.6	2.4
Rh-5	81.0	4.8	1.21	0.14	344	1.4	2.0	1.3	2.9	1.9
Rh-6	83.9	4.0	1.2	0.16	388	1.3	1.9	1.7	2.8	1.8
Rh-7	76.6	5.0	1.2	0.16	420	1.4	2.0	1.5	2.9	1.9
Ru-1	91.8	10.1	1.23	0.18	688	2.4	4.0	1.3	5.2	3.5
Ru-2	60.7	5.0	1.19	0.09	359	2.5	2.7	0.4	4.4	0.0
Ru-3	37.0	61.9	1.25	0.26	721	2.1	3.4	0.3	4.7	3.1
Ru-4	83.9	8.2	1.17	0.17	497	1.5	2.3	1.7	3.2	2.1
Ru-5	90.0	5.1	1.21	0.19	490	1.6	4.5	2.4	6.7	4.4
Ru-6	84.2	3.3	1.21	0.19	522	1.3	3.9	2.1	5.5	1.7
Ru-7	86.2	3.2	1.21	0.19	487	2.0	3.2	1.9	4.3	2.8

Pd: Pd/Al_2O_3 was used as catalyst **Rh:** Rh/Al_2O_3 was used as catalyst **Ru:** Ru/Al_2O_3 was used as catalyst. The experimental conditions are given in Table 1. *: Phenol (Ph), cresol (Cr), guaiacol (Gu), methyl-guaiacol (M-Gu), catechol (Ca) and syringol (Sy) yields as %(weight) in the oil

Table S1, *Supplementary Information*, shows the results of the analysis of variance (ANOVA) of the fitted models for the oil and solids yields. The ANOVA results illustrate that none of the models are significant for a 90 % confidence interval. Nevertheless, the aim of this section is not to build

significant models but to evaluate the effect of the type of catalyst, temperature and reaction time in the response variables.

Figure 1 and Figure 2 show the surface response models for each catalyst system; the former describes the oil yields while the latter the solid yields. Note that the temperature and reaction time axes are in different position for the oil and solid yield. The fitted equations for the oil and char yield are presented in Table 5. From the results depicted one main conclusion is obtained: the Ru, Pd and Rh systems behave similarly for both the oil and solid yield, with regression coefficients that are of the same sign and comparable magnitude.

Table 5 Fitted equations for the oil and solid yield

System		Equation
Pd[a]	**Oil Yield (%)[d]**	$Y = 72.66 + 2.83X_1 + 6.63X_2 - 17.33X_1X_2$
Rh[b]		$Y = 70.83 + 2.88X_1 + 7.38X_2 - 14.93X_1X_2$
Ru[c]		$Y = 76.25 + 3.95X_1 + 7.9X_2 - 19.5X_1X_2$
Pd[a]	**Solid Yield (%)[e]**	$Y = 13.56 - 14.85X_1 - 12.2X_2 + 11.55X_1X_2$
Rh[b]		$Y = 13.94 - 15.5X_1 - 9.85X_2 + 10.1X_1X_2$
Ru[c]		$Y = 13.83 - 14.7X_1 - 13.75X_2 + 12.15X_1X_2$

Pd: Pd/Al_2O_3 system **Rh:** Rh/Al_2O_3 system **Ru:** Ru/Al_2O_3 system **Oil Yield (%):** regression model built for the oil yield (%) **Solid Yield:** regression model built for the solid yield (%)

According to the fitted equations, high temperatures or long reaction times increase the oil and decreases the solid yield; while the sign of the cross-term coefficient suggests that the maximum is found out of the experimental space, toward the corners. This is confirmed by the analysis of the surface response models in Figure 1, which showed that the highest oil yields are found at low temperatures and long reaction times and/or at high temperatures and short reaction times. When comparing the oil yields it is clear that the Ru system gives the highest values, followed by Pd and Rh system. Lesser differences are seen in terms of solid yield, with the best results being obtained for the Pd catalyst, followed by the Ru and Rh. Therefore, Ru is selected as the best catalyst overall in terms of oil and solid yield. The behavior of this catalyst in the experimental space, together with the Al and NC system, will be quantitatively analyzed in Section 3.3.1.

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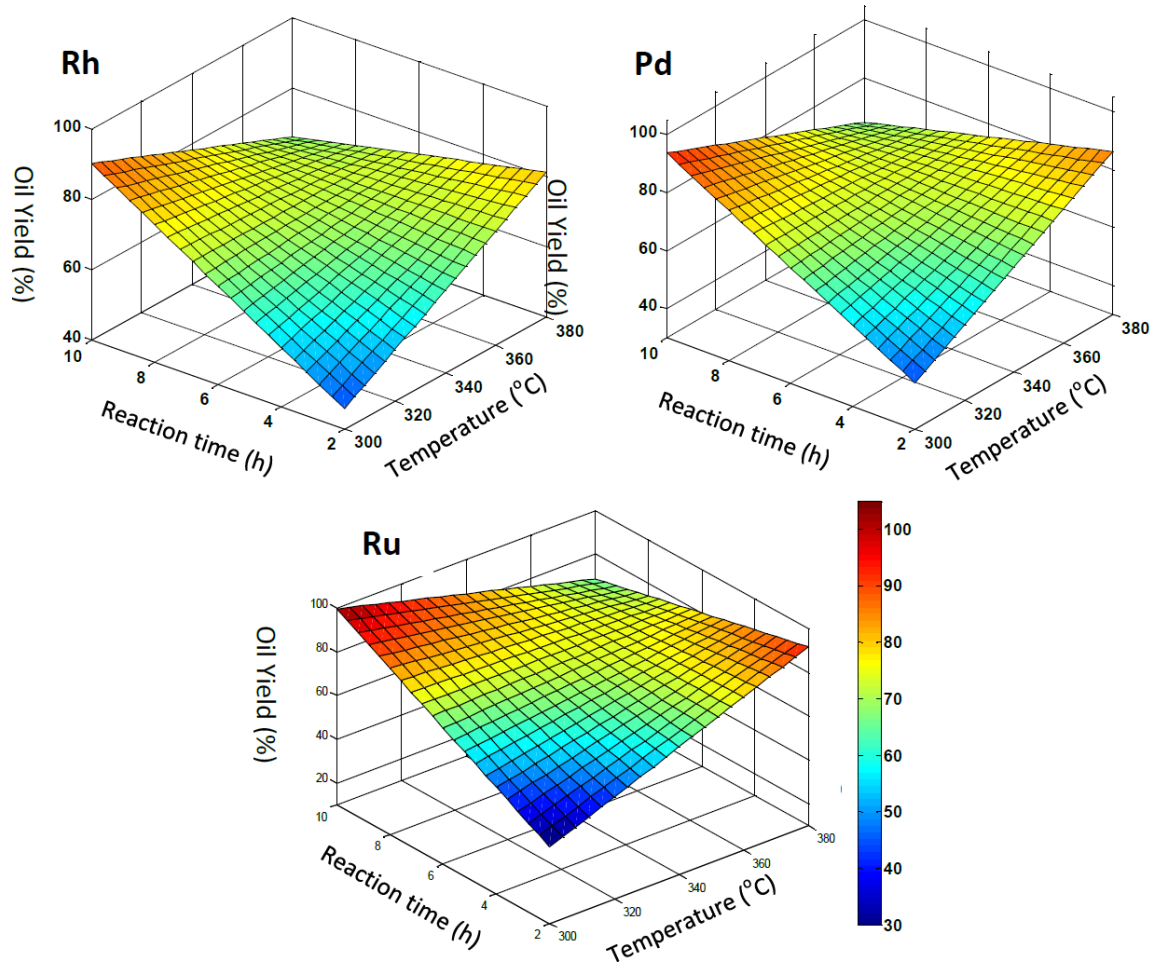

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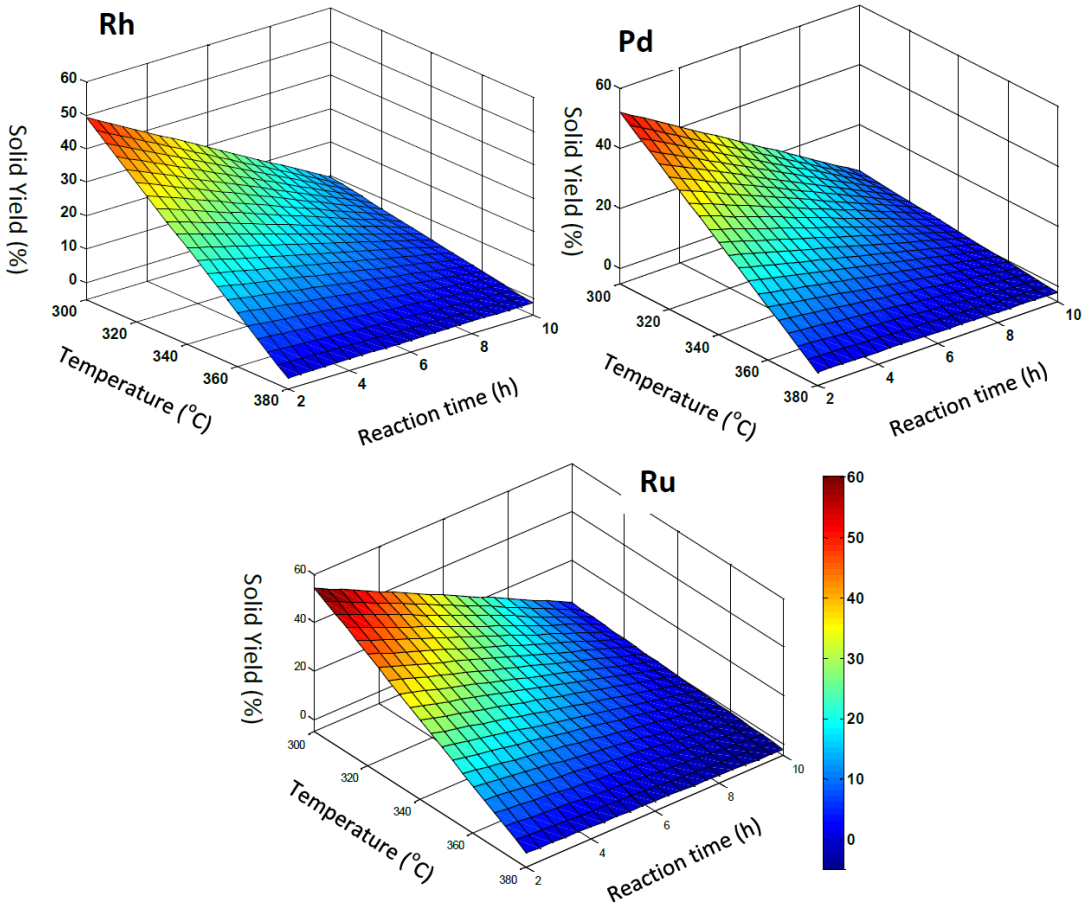
294 Figure 1: Response surface models for the oil yields. **Rh:** Rh/Al_2O_3 catalyzed system, **Pd:** Pd/Al_2O_3

295 catalyzed system , **Ru:** Ru/Al_2O_3 catalyzed system



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297 Figure 2: Response surface models for the solid yields. **Rh:** Rh/Al_2O_3 catalyzed system, **Pd:** Pd/Al_2O_3

298 catalyzed system , **Ru:** Ru/Al_2O_3 catalyzed system

3.2.2 Effect of type of catalyst, temperature and reaction time in the quality of the oil (PCA)

The aim of this section is mainly to establish the effect of the type of supported catalyst (Ru,Rh and Pd) on the quality of the oil, although correlations between time, temperature and oil quality will also be discussed. The values of the variables studied are summarized in Table 4. 85 % of the explained variance is described by three principal components (PCs). When analyzing the score plots (Figure 3a) it can be observed that the objects are somehow grouped together according to the type of catalyst (Ru in red, Rh in blue and Pd in green) and reaction conditions. Thus there is a correlation between the oil quality, oil and solid yield, the type of catalyst and the reaction conditions.

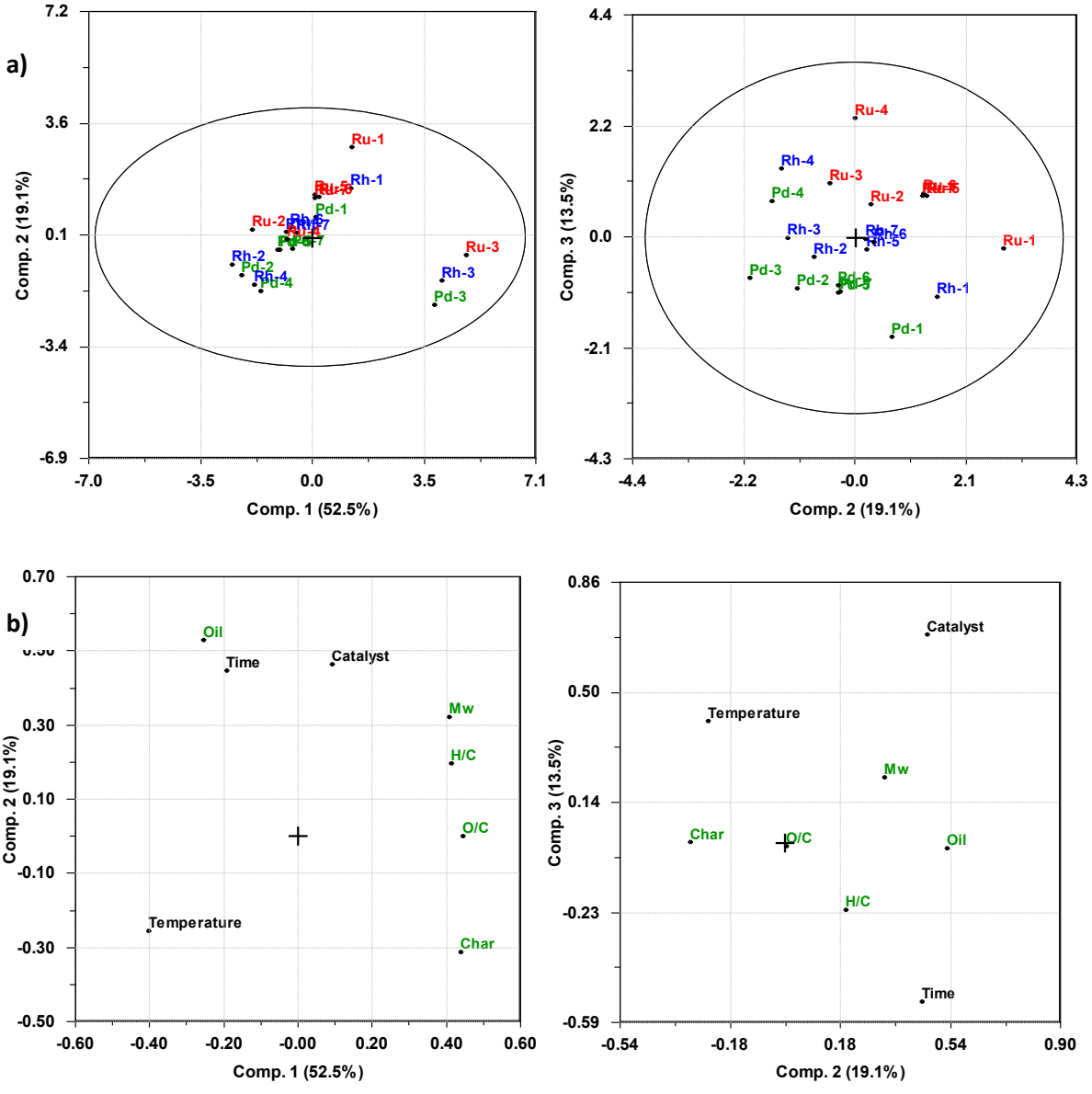


Figure 3: Score and loading plots for the quality of the oil. a) Score plots of the PCA analysis for the catalyst screening. Pd experiments in green, Rh experiments in blue, Ru experiments in red b) Loading plots of the PCA analysis for the catalyst screening. Factors describing the reaction

conditions in black, factors describing the oil yield (oil), solid yield (char) and quality of the oil (H/C, O/C and M_w) in green. Coding for the response variables is given in Table 1.

When analyzing the loading plots (Figure 3b), some correlations between the design variables and the oil quality variables can be observed. The most obvious observation is that the M_w is positively correlated to the catalyst variable in all cases. This means that the Ru catalyst gives the oils with the highest average molecular weight distributions followed by the Rh and Pd catalysts. Previous results obtained in our group [19]suggest that the average molecular weight is dependent on the active acidity of the alumina support (see Section 3.1), since lowering the active acidity resulted in an increase in the average molecular weight within the oils. This correlation is therefore confirmed by the data present in this study. M_w is negatively correlated to the temperature and reaction time on PC1, which explains up to 52.5 %. Further analysis of the data in Table 4 confirms this correlation; increasing the temperature and prolonging the reaction time resulted in oils with low molecular weight. For a given reaction temperature, lower M_w values are obtained at longer reaction times.

A strong negative correlation is found between the temperature and the H/C ratio, while no or weak correlations are found between the catalyst and the H/C ratio. When analyzing the data in Table 4 three trends can be identified: (*i*) at low temperatures the H/C ratio decreases with the reaction time, (*ii*) at high temperatures the H/C ratio increases with the reaction time, and (*iii*) slightly higher H/C ratios are obtained for the Ru system. In terms of O/C ratio, there is a clear negative correlation between this variable and the temperature and reaction time, while no correlation is found between the O/C ratio and the catalyst variable. This is confirmed when analyzing the raw data in Table 4, illustrating that high temperatures and long reaction times are the most beneficial conditions in terms of low O/C ratio. Hence the data shows two different behaviors in the elemental analysis of the oils depending on the temperature level. At low temperature both the O/C and H/C ratios decrease, while at high temperatures the O/C decrease and the H/C increases.

Another interesting result is the lack of correlation between the oil yield and the quality of the oil (H/C ratio, O/C ratio and M_w value). This is confirmed by both the loading plots and the analysis of the raw data. High H/C, O/C ratios and M_w values are obtained at low oil yields. Hence, the best reaction conditions are found around the center points: high oil yields coupled with relatively low Mw values and O/C ratios and relatively high H/C ratios.

3.2.3 Influence of the type of catalyst on the concentration of selected compounds

The values submitted to PCA are given in Table 4. In the data analysis 71.55 % of the variance is explained by three PCs. Figure 4 shows the score and loading plots. From the loading plots it can be observed that those compounds bearing methoxy-groups, such as Gu and M-Gu, show only a strong negative correlation with the temperature. Ca, a compound with two hydroxy-groups, is positively correlated to the catalyst variable and non-correlated with the temperature and reaction time. Coumpounds with only one hydroxy-group, such as Ph and Cr, are positively correlated with the reaction time. The former, Ph, is also negatively correlated to the catalyst, and whilst the latter, Cr, is positively correlated to the reaction time and catalyst variable.

These observations are in accordance with the behaviour of the elemental analysis of the oils presented in Section 3.2.2. At low temperatures the H/C and O/C ratio decreases with time suggesting that at this temperature level de-methoxylation and dehydration reactions of methoxy- and hydroxyl- bearing compound are the prevailing reactions. However, at high temperatures, low amount of methoxy- bearing compounds are found at low reaction times and the prevailing reaction seems to be the alkylation of the monomers; which would justify both the increase of the H/C ratio and the decrease of the O/C ratio.

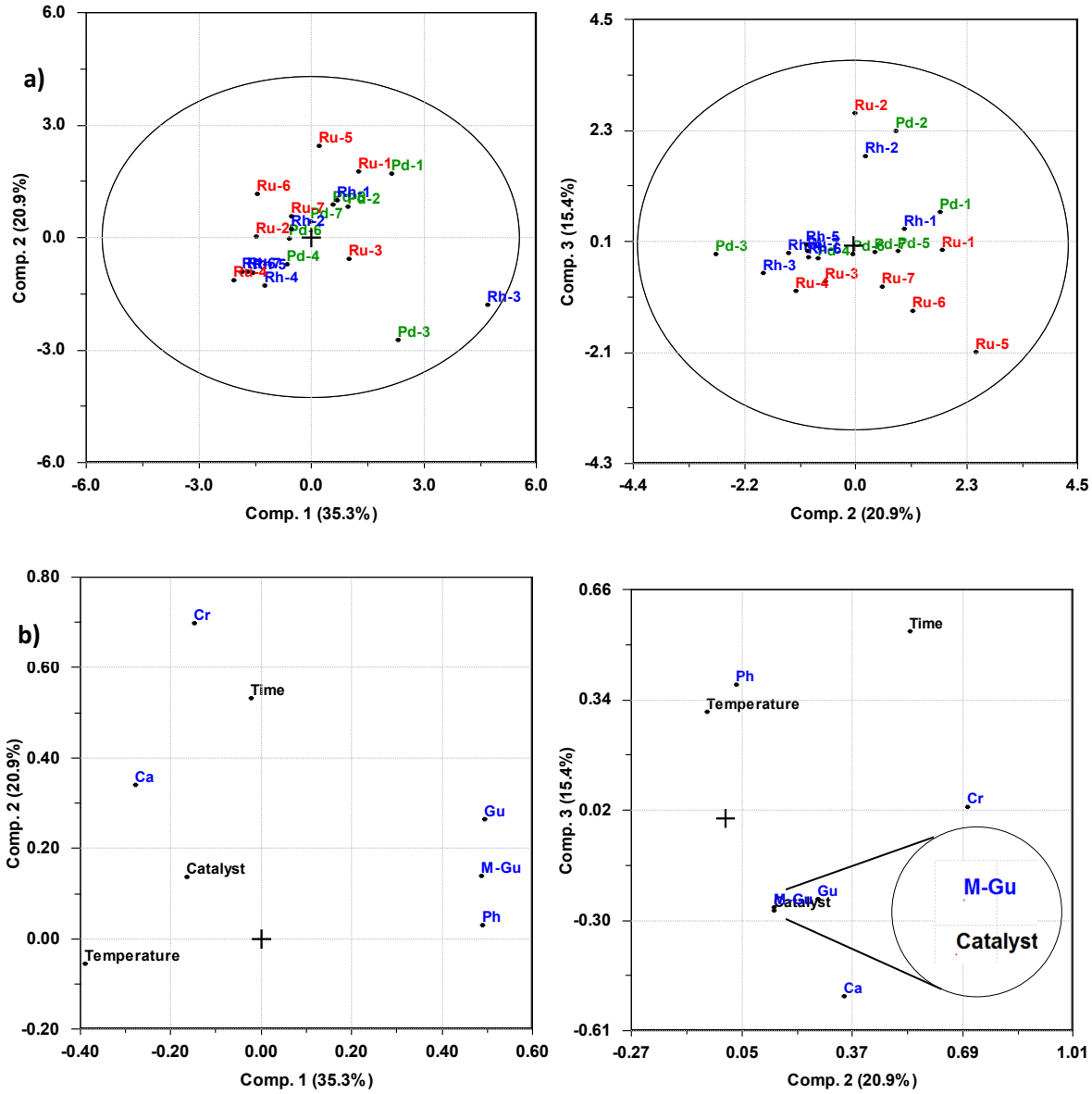


Figure 4: Score and loading plots for the composition of the oil. a) Score plots of the PCA analysis for the catalyst screening. Pd experiments in green, Rh experiments in blue, Ru experiments in red b) Loading plots of the PCA analysis for the catalyst screening. Factors describing the reaction conditions in black, factors describing the concentration of certain components in blue. Coding for the response variables is given in Table 1

Previous work [29, 30] proposed the following mechanism. Lignin is initially depolymerized into primary products bearing methoxy groups such as syringol and different guaiacols. These react further accompanied with an increase in the degree of demethoxylation and deoxygenation of the different substituted species to yield catechols and thereafter phenols as stable products. Unlike this kinetic study, our experimental set is held at different temperatures. This might have distorted the actual correlations, but the loading plots still support the mechanism. At low temperatures, when the conversion rate is slow, Gu and M-Gu are in high concentrations. Ca is not correlated with any of the

reaction conditions, which could indicate that the compound is an intermediate. Finally, at long reaction times the concentration of Ph and Cr is the highest which suggest them as the end products. In terms of type of catalyst, Ru seems to favor the abundance of both catechol and cresol, while Pd seems to be the most suitable catalyst when oils with a high concentration in phenol are preferred.

3.3 Optimization experiments: Effect of the type of system

3.3.1 Influence of the type of system, temperature and reaction time on the oil and solid yields

In Section 3.2 several first order response surface models were built to analyze the effect of the type of catalyst, temperature and time, but none of them were statistically significant. In this section, the best catalyst in terms of oil and solid yield, Ru, is compared to additional reaction systems NC (non-catalyzed) and Al (γ-alumina catalyst) to evaluate which is the effect of the alumina support and the noble metal (Ru) in the reaction in a central composite design with a wider experimental basis for the modelling. The results obtained for the oil and solid yield are summarized in Table 6.

Table 6: Experimental design for optimization experiments and oil and solid yields

Experiment	Oil Yield (%)	Solid Yield (%)	H/C	O/C	Mw	Ph*	Gu*	Ca*	Cr*	M-Gu*
NC-1	64.8	31.7	1.13	0.2	431	1.9	3.3	1.5	4.2	2.8
NC-2	50.2	16.2	1.17	0.08	206	2.9	3.7	0.5	5.9	4.3
NC-3	32.1	57.5	1.17	0.24	553	1.7	3.4	0.6	3.9	2.7
NC-4	54.0	26.3	1.11	0.17	294	2.7	4.2	3.7	5.9	3.9
NC-5	58.2	22.4	1.19	0.18	346	1.7	2.5	2.0	3.6	2.4
NC-6	62.3	23.0	1.21	0.21	327	1.8	2.6	2.9	3.6	2.4
NC-7	64.2	16.5	1.21	0.2	339	2.1	3.0	2.8	4.3	2.8
NC-S1	41.4	21.3	1.1	0.15	95	2.8	2.4	0.5	4.2	3.5
NC-S2	31.0	63.6	1.17	0.29	928	2.1	3.7	0.8	0.0	3.2
NC-S3	13.5	83.4	1.29	0.33	548	2.2	3.3	0.4	5.1	3.0
NC-S4	63.2	16.6	1.11	0.16	258	2.4	3.0	1.4	4.7	3.0
Ru-1	91.8	10.1	1.23	0.18	688	2.4	4.0	1.3	5.2	3.5
Ru-2	60.7	5.0	1.19	0.09	359	2.5	2.7	0.4	4.4	0.0
Ru-3	37.0	61.9	1.25	0.26	721	2.1	3.4	0.3	4.7	3.1
Ru-4	83.9	8.2	1.17	0.17	497	1.5	2.3	1.7	3.2	2.1
Ru-5	90.0	5.1	1.21	0.19	490	1.6	4.5	2.4	6.7	4.4
Ru-6	84.2	3.3	1.21	0.19	522	1.3	3.9	2.1	5.5	1.7
Ru-7	86.2	3.2	1.21	0.19	487	2.0	3.2	1.9	4.3	2.8
Ru-S1	59.3	5.5	1.11	0.11	91	2.7	4.5	0.6	6.2	2.2
Ru-S2	45.5	48.3	1.27	0.4	2150	1.5	2.6	0.2	3.6	0.0
Ru-S3	30.8	67.6	1.17	0.27	2049	2.5	4.7	0.4	5.9	3.9
Ru-S4	79.8	3.3	1.18	0.16	468	2.8	5.5	2.0	6.7	4.3
Al-1	84.8	16.1	1.18	0.23	276	1.2	2.3	1.2	2.8	2.3
Al-2	48.2	17.3	1.2	0.1	178	2.4	2.7	0.6	4.9	4.6

Al-3	36.8	61.8	1.22	0.27	318	2.3	4.2	0.5	0.0	4.0
Al-4	57.4	24.5	1.16	0.21	211	1.6	2.4	3.4	3.4	2.6
Al-5	63.1	22.0	1.2	0.21	215	1.4	2.2	3.1	3.2	2.3
Al-6	58.7	25.7	1.18	0.17	225	2.0	2.9	3.0	4.3	3.0
Al-7	66.5	17.1	1.19	0.19	210	2.5	3.6	2.9	5.5	3.8
Al-S1	43.3	21.0	1.12	0.12	108	2.8	3.0	0.5	5.6	4.5
Al-S2	49.8	52.1	1.19	0.25	1360	1.9	3.4	0.5	0.0	3.5
Al-S3	13.3	82.8	1.36	0.32	826	2.1	3.3	0.3	5.5	3.3
Al-S4	65.4	11.1	1.19	0.16	347	2.4	3.0	1.4	5.1	3.3

NC: non-catalysed experiments **Ru**: Ru/Al_2O_3 was used as catalyst **Al:** γ-Al_2O_3 was used as catalyst. **S:** refers to the axial points were α=1.41. The experimental conditions are given in Table 2. *: Phenol (Ph), cresol (Cr), guaiacol (Gu), methyl-guaiacol (M-Gu), catechol (Ca) and syringol (Sy) yields as %(weight) in the oil

The analysis of the variance (ANOVA) (Table S2, *Supplementary Information*), shows that all the models are significant for a confidence level of 90 %, which allows a quantitative analysis of the results. Table 7 displays the second order regression models for the oil and solid yield. The surface response models for the oil and solid yield are presented in Figures 5 and 6 respectively.

Ru gives higher oil and lower solid yields in the experimental space. The maximum oil and minimum solid yield is found around the center of the experimental space, and more precisely toward the area of low temperatures and long reaction times. This model differs from the one obtained in Section 3.2.1 where the maximum was not found within the experimental space. Hence, quadratic terms are important to provide significant models of the systems.

Table 7: Regression second order models for the oil yield and solid yield

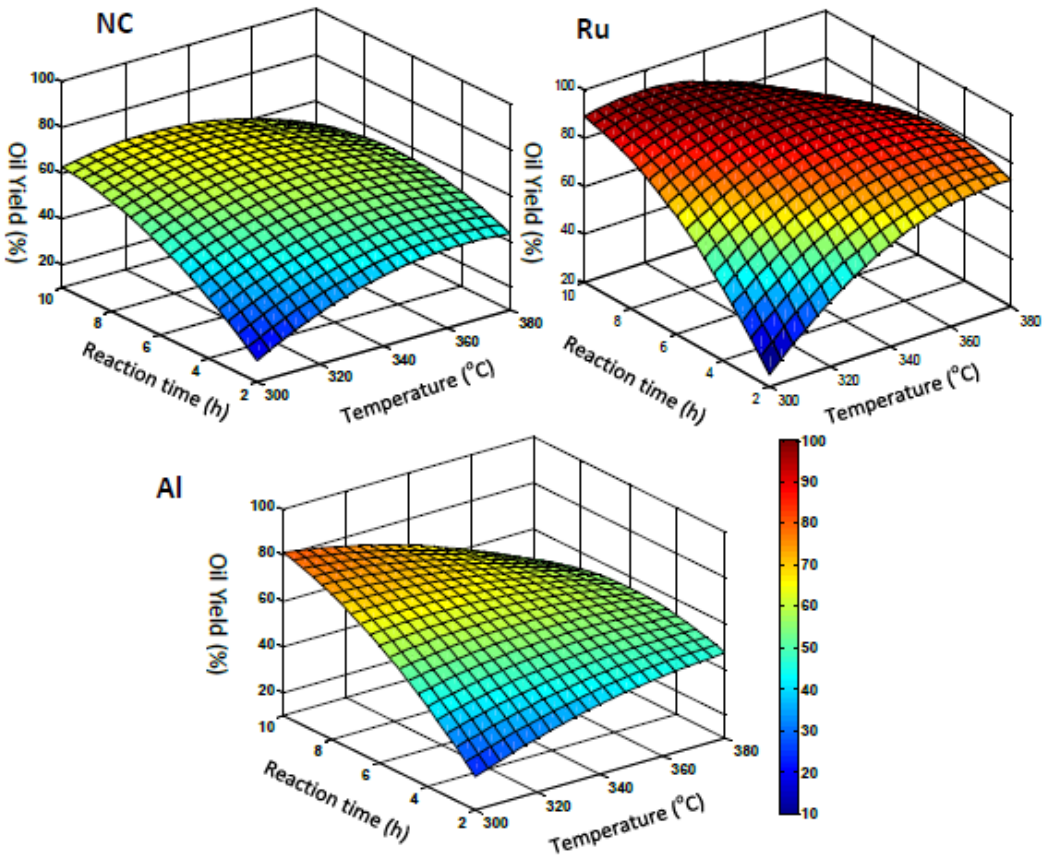
System		Equation
NC[a]	Oil Yield (%)[d]	$Y = 61.56 + 2.75X_1 + 12.40X_2 - 9.43X_1^2 - 8.36X_2^2 - 9.13X_1X_2$
Ru[b]		$Y = 86.79 + 4.41X_1 + 12.61X_2 - 19.5X_1^2 - 13.57X_2^2 - 12.12X_1X_2$
Al[c]		$Y = 62.76 - 3.15X_1 + 14.06X_2 - 4.64X_1^2 - 8.25X_2^2 - 14.3X_1X_2$
NC[a]	Solid Yield (%)[e]	$Y = 20.64 - 13.32X_1 - 16.30X_2 + 7.58X_1^2 + 11.36X_2^2 - 3.93X_1X_2$
Ru[b]		$Y = 3.87 - 14.92X_1 - 18.24X_2 + 12.15X_1^2 + 9.05X_2^2 + 12.32X_1X_2$
Al[c]		$Y = 21.6 - 10.01X_1 - 19.29X_2 + 4.52X_1^2 + 9.72X_2^2 + 9.63X_1X_2$

NC: non-catalysed reaction system **Ru:** Ru/Al_2O_3 was used as catalyst **Al:** γ-Al_2O_3 was used as catalyst **Oil Yield (%):** regression model built for the oil yield (%) **Solid Yield:** regression model built for the solid yield (%)

The NC systems give significantly lower oil yields than the Ru. However, the regression coefficients are of the same sign and the shape of the response surface is similar, and the maximum oil yield is found around the same area. On the other hand the oil yield maximum for the Al system is not found within the experimental space. This is because unlike Ru and NC, the Al system is negatively

correlated to the temperature, shifting the maximum towards the area of low temperatures and long reaction times.

The analysis of the solid yields (Figure 6 and Table 7), confirms the conclusions described above. Note that the axes regarding the temperature and reaction time are opposite the previous plot. NC and Ru systems behave analogously, although considerably lower solid values are obtained for the Ru system. However in the case of the Al system, the lowest solid yields are obtained in the areas of low temperatures and long reaction times. This confirms that the presence of γ-alumina increases the oil yield at low temperatures, while the presence of the noble metal Ru supported on the alumina increases the oil yield in the experimental space. This is in accordance with our previous results [19], suggesting that the alumina support can catalyze both the de-polymerization and re-polymerization reactions. Hence at low temperatures, where de-polymerization is favored, the oil yield for the Al systems increases, and while at high temperatures this effect is neutralized by the increase of the re-polymerization rate. It is noteworthy that at 380^{o}C the oil yield is slightly higher for the Al system (57.4 %) than that of the NC system (54.0 %) when the reaction time is 2 h, while the oil yield is slightly higher for the NC system (50.2 %) than for the Al system (48.2 %) when the reaction time is 10 h.



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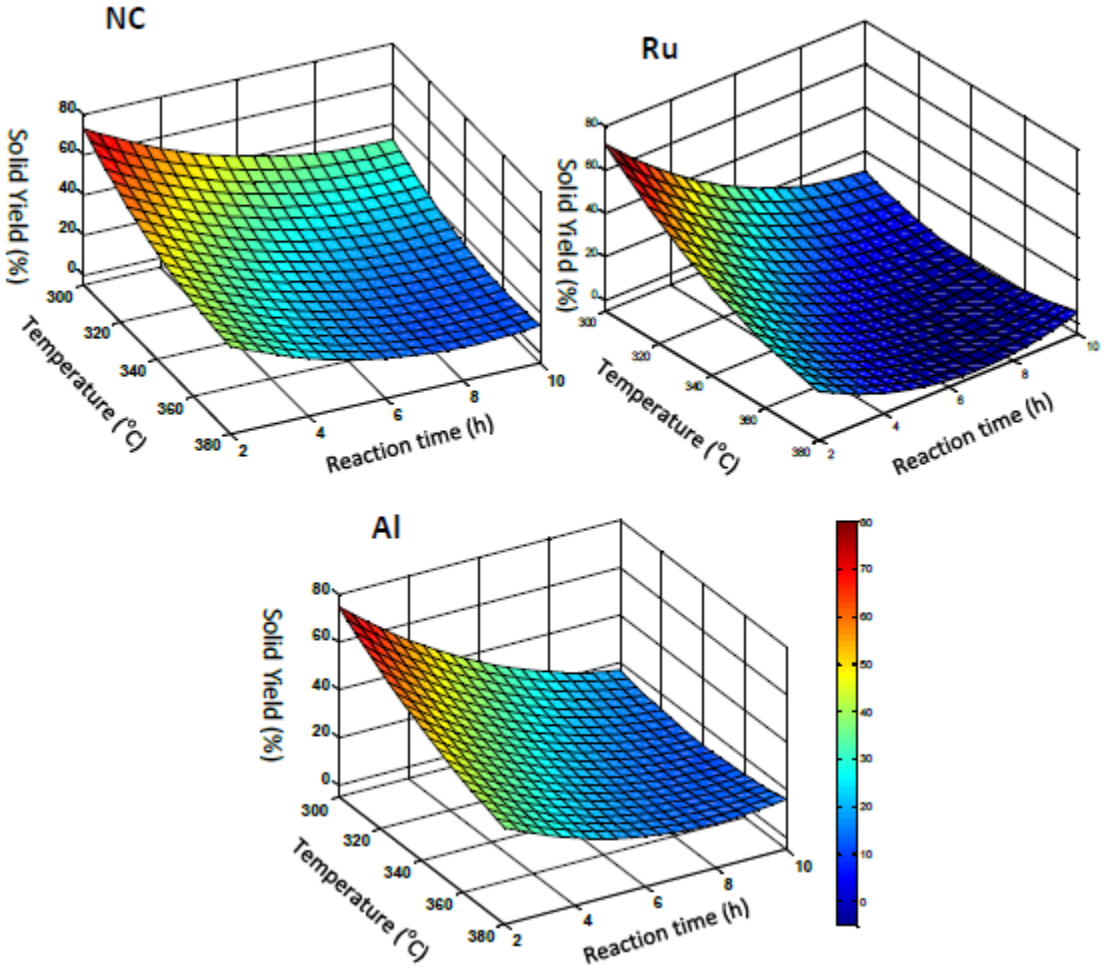
425 Figure 5: Response surface models for the oil yield. NC: non-catalyzed system, Ru: Ru/Al_2O_3 catalyzed

426 system, Al: γ-Al_2O_3 catalyzed system



427

428 Figure 6: Response surface models for the solid yield. NC: non-catalyzed system, Ru: Ru/Al_2O_3

429 catalyzed system, Al: γ-Al_2O_3 catalyzed system

430

3.3.2 Effect of type of system, temperature and reaction time in the quality of the oil

The system variable, accompanied by the temperature, reaction time, oil yield, solid yield and the oil-quality responses are submitted to an exploratory PCA. Table 6 describes the values of the different responses. 81.5 % of the variance is explained by three PC. The score plots depicted in Figure 7.a show that the objects are group in terms of system and reaction conditions, although this patterns is less clear than in Section 3.2.2. On the other hand, the loading plots in Figure 7.b significantly resemble the corresponding plots in Section 3.2.2.

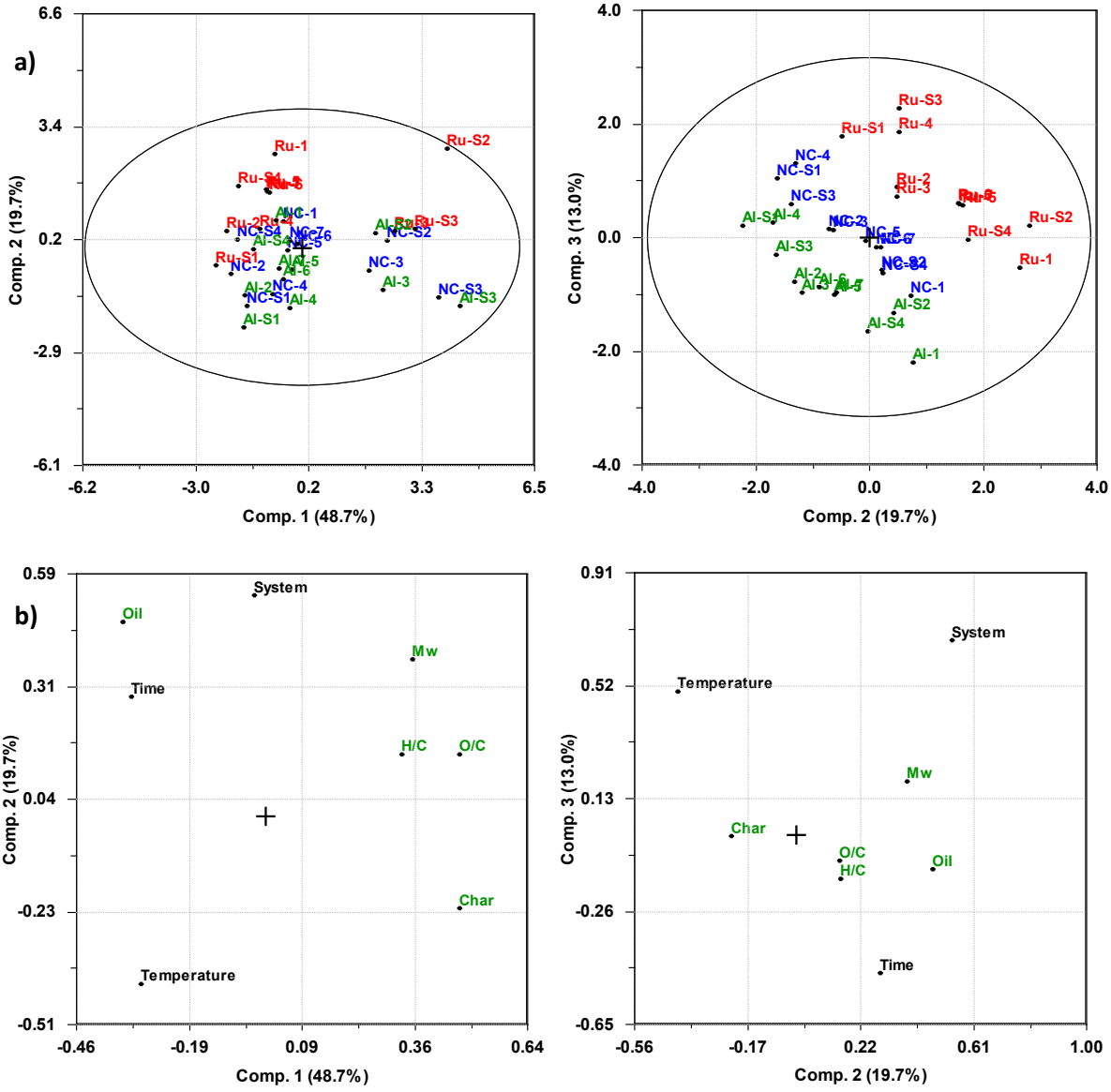


Figure 7: Score plots and loading plots for composition of the oil. a) Score plots of the PCA analysis for the catalyst optimization. Al experiments in green, NC experiments in blue, Ru experiments in red b) Loading plots of the PCA analysis for the optimization experiments. Factors describing the reaction conditions in black, factors describing the oil yield (oil), solid yield (char) and quality of the oil (H/C, O/C and M_w) in green. The coding for the response variables is given in Table 2.

445 The most obvious correlation is again the one between the system variables and the Mw. This means
446 that the Ru systems produce oils with higher average molecular weights, while the lowest Mw values
447 are obtained for the Al. In the absence of catalyst, the values of M_w are lower than the ones for the
448 Ru but higher than the ones for the Al systems. This phenomenon could be due the fact that the Ru
449 catalyst, the Ru active phase, can stabilize high M_w oligomers thought hydrodeoxygenation [31] and
450 alkylation reactions[32], while in the case of the Al and NC systems these compounds are re-
451 polymerized into solid. The lowest values of M_w obtained in the Al system could be due to the high
452 active acidity of the γ-alumina, a phenomenon already observed in Section 3.2.2. The loading plots
453 and the raw data in Figure 7.b suggest that the temperature and reaction time are negatively
454 correlated to the M_w, and support that high temperatures and long reaction times favor lignin de-
455 polymerization.

456 The behavior of the H/C ratio with respect to the temperature and reaction time is in accordance
457 with the results observed in Section 3.2.2. At low temperatures the H/C ratio decreases with the
458 reaction time while at high temperatures this values increases. From the loading plot (Figure 7a) no
459 or weak correlations are found between the system, reaction time and H/C variables. However, the
460 data in Table 6 clearly shows that the Ru (+1) system gives higher H/C ratio oils, followed by the Al (-
461 1) and the NC (0) system.

462 The O/C ratio is not considerably influenced by the type of system. Temperature is again negatively
463 correlated to the O/C ratio, while the correlation with the reaction time is not so clear when
464 analyzing the score plots. Nevertheless, the raw data again indicates that the higher the temperature
465 and the longer the reaction time, the lower the O/C ratio.

466 As in Section 3.2.2 there is a lack of correlation between the oil yield and the variables selected to
467 evaluate the quality of the oil. Some other aspects are also confirmed: (*i*) the active acidity of the
468 catalysts decreases the M_w value, (*ii*) the H/C ratio is negatively correlated to the temperature, (*iii*)
469 the O/C ratio is negatively correlated to temperature and reaction time, and (*iv*) the best results are
470 found in the center of the experimental space. An additional observation is that the presence of the
471 noble metal is positive for the H/C ratio, which can be explained by catalysis of the hydrogenation of
472 the end products, as expected.

473 **3.3.3 Analysis of the concentration of main compounds**

474 Table 6 describes the values of the variables submitted to exploratory PCA. As in Section 3.2.3, five
475 main components were selected (Ph, Gu, Ca, Cr, MGu). The first three PCs describe only 65.5 % of the
476 variance. From the analysis of the score plot in Figure 8.a, it can be observed that the objects are
477 mainly grouped by the type of the system. The loading plots in Figure 8.b show that the variance is

largely explained by the system variable, especially on PC2. All this indicates that there are significant differences on the kinetic or mechanistic pathways between the systems. When analyzing the correlations for each compound no clear patterns are observed. Each component is differently correlated to the temperature, reaction time and system variable depending on the PC. This shows that the significant difference in the reaction mechanisms prevent clear conclusions about how the experimental variables studied affect the composition of the oil using this multivariate approach.

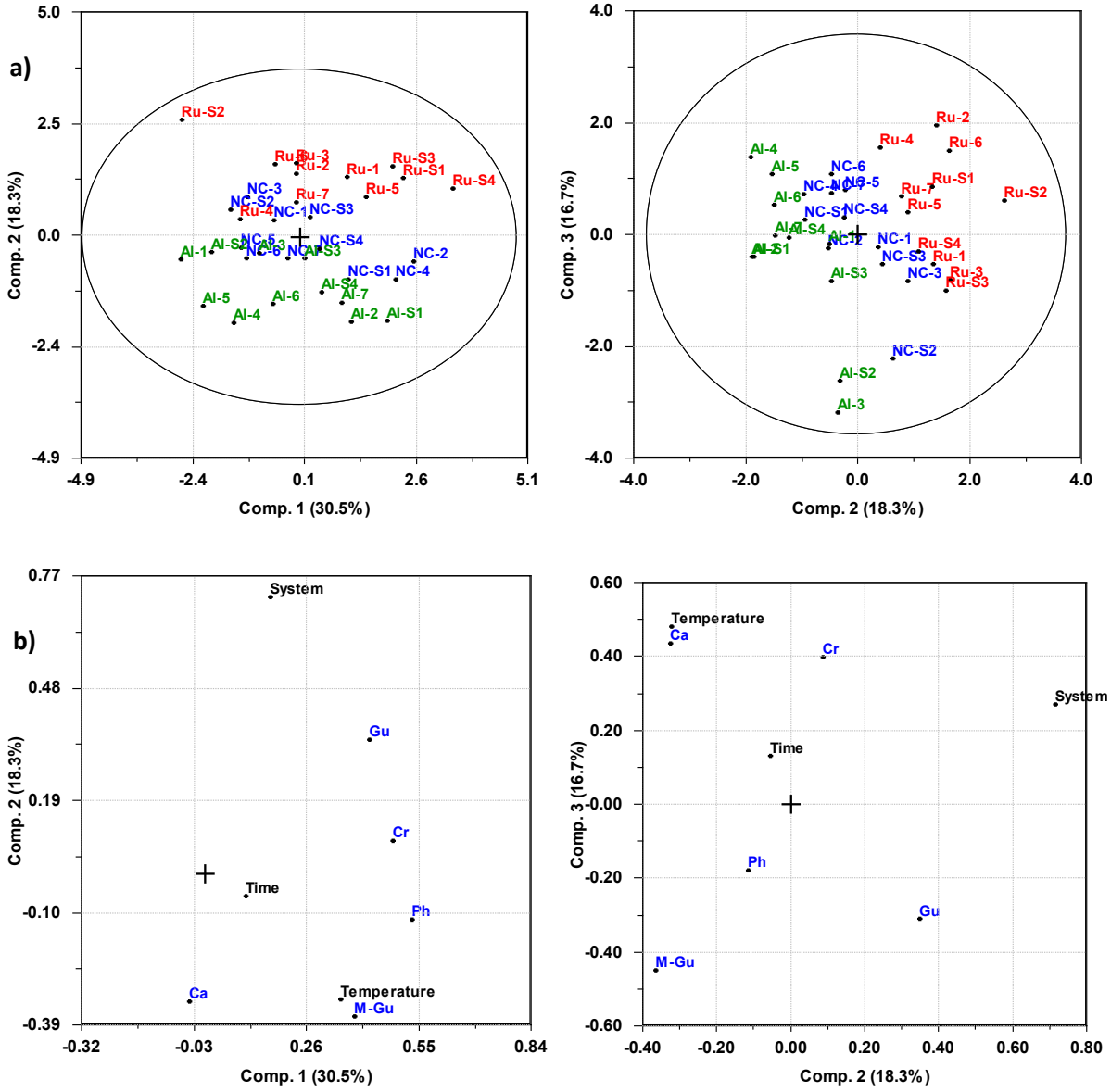


Figure 8: Score and loading plots of the composition of the oil. a) Score plots of the PCA analysis for the optimization experiments. Al experiments in green, NC experiments in blue, Ru experiments in red b) Loading plots of the PCA analysis for the optimization experiments. Factors describing the reaction conditions in black, factors describing the concentration of certain components in blue. The coding for the response variables is given in Table 2.

3.4 Recycling of the catalyst

The inorganic ash content of the lignin is 1.5 wt%. The average value of the recovered organic solids (char) and lignin-derived inorganic ashes for the Ru system, at 340°C and 6 hours, is 2.7 wt%. This means that the solids recovered after the reaction mainly comprises the catalyst. After the thermal treatment the organic matter was eliminated, giving a recovered catalyst with a small amount of inorganic impurities derived from the lignin (ashes).

The catalyst was recycled twice, and its activity was evaluated in terms of oil and solid yields. For the first cycle three replicates were made (Ru-A1, Ru-A2 and Ru-A3), while two replicates were carried out for the second recycling cycle (Ru-B1 and Ru-B2).

Table 11 shows the results obtained for both cycles. Surprisingly, the average values show that the oil yield is maintained or increased upon recycling. The solid yield is comparable for all the reaction cycles. The variation could be assigned to experimental uncertainty during the work-up procedure.

Table 11: Oil yield, H/C and O/C ration of the oil and solid yield for the recycling experiments

Experiment Name	Oil Yield (% on lignin)	Average Oil Yield (% on lignin)	(H/C)	(O/C)	Solid Yield (% on lignin)	Average Solid Yield (% on lignin)
Ru-5	90.0	86.8	1.21	0.19	5.1	3.9
Ru-6	84.2		1.21	0.19	3.3	
Ru-7	86.2		1.21	0.19	3.2	
Ru-A1	84.9	86.8	1.20	0.19	2.7	2.6
Ru-A2	88.7		1.18	0.18	2.5	
Ru-A3	86.7		1.16	0.18	2.5	
Ru-B1	88.9	91.6	1.22	0.20	4.7	4.6
Ru-B2	94.2		1.22	0.19	4.6	

A: refers to the replicates for first recycling cycle **B:** refers to the replicates for the second recycling cycle. Conditions: 340°C and 6 hours

Overall, the results show no deactivation of the catalyst in terms of oil and solid yield. The H/C and O/C ratio of the oils depicted in Table 11 confirm that there is no catalyst deactivation. The H/C ratios decrease slightly for some experiments in the first recycling cycle, but the results are comparable or higher for the second cycle. This means that the differences can be understood as a function of uncertainties during the work-up and/or the analytic procedures. The O/C ratio is also maintained within acceptable uncertainty limits.

4. Conclusion

Lignin from Norway spruce was successfully converted into aromatic based oil in the presence of several noble metal catalysts supported in alumina in a formic acid water media. Oils were produced over a range of reaction temperatures (283-397°C) and reaction times (2-10 h). Response surface methodology (RSM) has been proven to be a successful tool to build significant models for the oil and solid yield within the studied experimental space. Principal component analysis (PCA) is proven to be a successful tool to evaluate the effect of the reaction variables on the oil quality and composition, and to extract qualitative data on the reaction mechanism. The recycling of the catalyst shows that the Ru catalyst fully retains its activity in two separate recycling tests.

This systematic approach improved the quantitative understanding of the process and successfully confirmed features previously noted from less extensive investigations [19]. For the catalysts, both the noble metal and the γ-alumina are active in the LtL process. The former increases the oil yield while decreasing the solid yield. The latter is active in the lignin de-polymerization and in the re-polymerization of the lignin monomers, and therefore increases the oil yield at low temperatures, where re-polymerization is not favored. Among the noble metals studied Ru gives the highest oil yield in the whole experimental space. A strong dependency between the active acidity of the alumina support and the M_w of the oil has been also confirmed.

No correlations between the oil yield and the quality of the oil has been found. The oil yield is strongly dependent on the presence of the catalyst, temperature and reaction time; while the oil quality is mainly dependent on the temperature and reaction time. Therefore, the optimum reaction conditions were found to be around 340°C and 6 h; where nearly complete conversion of lignin into oil is achieved while still having high H/C ratios coupled with low O/C ratios and M_w values.

The study of the composition of the oil confirms that the reaction mechanism differs between the supported catalyst (Ru/Al_2O_3, Pd/Al_2O_3 and Rh/Al_2O_3) system, the γ-Al_2O_3 system and the non-catalyzed system. In the supported catalyst systems, the reaction comprises several steps. It starts with the de-polymerization of the lignin; followed by de-methoxylation, dehydration and alkylation of the monomers. At low temperatures de-methoxylation and dehydration reactions are predominant for the reaction times studied, while at high temperatures these reactions take place at short reaction times, followed by alkylation reactions. Thus, the final products obtained depend on the reaction temperature: at high temperature alkylated compounds such as cresol are favored, while at low temperatures non-alkylated compounds, such as phenol, are more abundant.

In an overall perspective, the results show the potential for improving the yields of oil by the use of catalysts which are easily recovered, and suggest a good potential for tuning the oil composition to

specific compositions depending on the requirements for the product. Such processing of lignin residues to phenol-type product compositions could be a complementary process to the carbohydrate conversion in the utilization of lignocellulosic biomass in a bio-based refinery.

5. Acknowledgement

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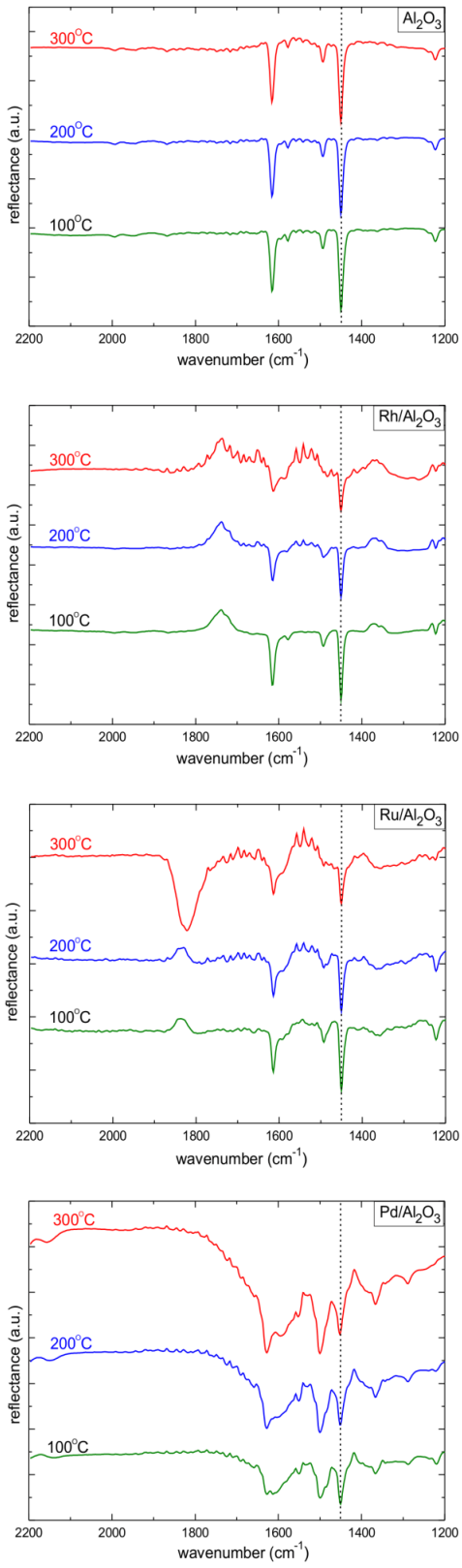

Figure S1: DRIFT spectra of pyridine adsorbed on Al_2O_3, Rh/Al_2O_3, Ru/Al_2O_3, and Pd/Al_2O_3.

Table S1: Analysis of the variance (ANOVA) of the built linear models

System-Product Yield (%)	Source of Variation	Degrees of Freedom	Summ of squares	Mean squares	F statistic	p-value
Pd[a]-Oil Yield (%)	Regression	3	1408.10	469.37	2.51	0.235
	Error	3	560.19	186.73		
	Total	6	1968.29			
Pd[a]-Solid Yield (%)	Regression	3	2011.10	670.35	3.25	0.180
	Error	3	619.00	206.33		
	Total	6	2630.10			
Rh[b]-Oil Yield (%)	Regression	3	1141.60	380.55	2.20	0.267
	Error	3	518.09	172.70		
	Total	6	1659.69			
Rh[b]-Solid Yield (%)	Regression	3	1757.10	585.71	3.83	0.150
	Error	3	458.83	152.94		
	Total	6	2215.93			
Ru[c]-Oil Yield (%)	Regression	3	1833.00	611.02	1.83	0.315
	Error	3	999.32	333.11		
	Total	6	2832.32			
Ru[c]-Solid Yield (%)	Regression	3	2211.10	737.03	4.41	0.127
	Error	3	501.17	167.06		
	Total	6	2712.27			

a) ANOVA analysis for the Pd/Al_2O_3 system **b)** ANOVA analysis for the Rh/Al_2O_3 system **c)** ANOVA analysis for the Ru/Al_2O_3 system

Table S2: ANOVA table for the second order regression models

System	Source of Variation	Degrees of Freedom	Summ of squares	Mean squares	F statistic	p-value
NC[a] Oil Yield (%)	**Regression**	5	2318.30	463.65	4.01	0.077
	Error	5	578.13	115.63		
	Total	10	2896.43			
NC[a] Solid Yield (%)	**Regression**	5	4443.80	888.77	5.35	0.045
	Error	5	830.38	166.08		
	Total	10	5274.18			
Ru[b] Oil Yield (%)	**Regression**	5	4398.00	879.60	7.12	0.025
	Error	5	617.79	123.56		
	Total	10	5015.79			
Ru[b] Solid Yield (%)	**Regression**	5	6197.10	1239.40	17.24	0.004
	Error	5	359.47	71.89		
	Total	10	6556.57			
Al[c] Oil Yield (%)	**Regression**	5	2892.90	578.59	5.05	0.050
	Error	5	572.39	114.48		
	Total	10	3465.29			
Al[c] Solid Yield (%)	**Regression**	5	4698.30	939.66	7.59	0.022
	Error	5	619.02	123.80		
	Total	10	5317.32			

a) ANOVA analysis for the non-catalysed system **b)** ANOVA analysis for the Ru/Al_2O_3 system **c)** ANOVA analysis for the γ-Al_2O_3 system