1 **Title page information**

2 **Title:** Simultaneous catalytic de-polymerization and hydrodeoxygenation of lignin in water/formic
3 acid media with Rh/Al_2O_3, Ru/Al_2O_3 and Pd/Al_2O_3 as bifunctional catalysts

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Abstract

The catalytic solvolysis of 3 lignins of different sources 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 (340°C-380°C and 2-6 hours respectively). Blank experiments using only gamma-alumina as catalysts and non-catalyzed experiments were also performed and compared with the supported catalysts results. All the supported catalysts significantly improved the oil yields on a lignin basis, with yields up to 91.5 wt% using the Ru catalyst. The main components phenol, cresol, guaiacol, methylguaiacol, catechol, ethylcatechol, syringol and o-vanillin are found in different concentrations depending on the catalytic system. The stable Lewis acidity in the alumina support has been found to be active in terms of de-polymerization of lignin, leading to lower average molecular weight oils. In addition, it was found that alumina plays a significant role in the re-polymerization mechanism of the monomers. The effect of the type of lignin on the final oil and solid yields was also established, demonstrating that lignins produced by basic pretreatment of biomass do not show significant increase in oil yield when catalysts on an acid support like alumina are used. The interpretation is that acid conditions are needed for efficient de-polymerisation of the lignin.

Keywords

Catalytic hydrotreatment; solvolysis; lignin; noble metals; alumina; bifunctional heterogeneous catalysis

1. Introduction

In the biofuel sector, the concept of a "biorefinery" describes all the processes and technologies involved in converting biomass to a range of fuels and value-added chemicals. Among the biomass sources, lignocellulosic biomass (wood, grasses and agricultural residues) has been identified as a promising alternative for this purpose [1], since unlike vegetable oil and sugar crops the lignocellulose feedstock avoid the negative side effect of intense farming [2] and ethical concerns about the use of food as fuel raw materials [3]. For lignocellulosic biomass conversion, most of the research has been focused on the conversion of cellulose and hemi-cellulose to biofuels and value added chemicals, and major breakthroughs have been achieved. However, valorization of lignin, an amorphous polymer that accounts for 15-30% of the feedstock by weight, and 40 % by energy [1], is still a challenge. Only approximately 2% of the lignin residues available from the pulp and paper industry are used commercially, with the remaining volumes burned as low value fuel [4]. Nevertheless, lignin has a significant potential as a feedstock for the sustainable production of fuels and bulk chemicals, and indeed lignin can be regarded as the major aromatic resource of the bio-based economy [1].

Various pathways have been explored for the conversion of lignin-rich residual material for fuels or phenols [1,5-7]. Among them, thermochemical conversion by fast pyrolysis is one of the central techniques, but the resulting "oil" has a high O/C and low of H/C ratio. These bio-oils are very acidic and corrosive and often chemically unstable, making it necessary to further upgrade them to produce motor fuels and chemicals to be used in the petrochemical industry [8-10]. In comparison to fast pyrolysis, solvolysis provides the advantages of milder conditions and a single phase environment due to the miscibility of the organic products in the (supercritical) solvent. Further advantages of solvolysis performed in polar solvents such as ethanol or iso-propanol [11] over fast pyrolysis are a less oxygenated oil fraction and almost no solid residue (< 5%) [12,13].A promising and relatively new lignin conversion methodology involves the use of a hydrogen donor solvent instead of molecular hydrogen [14]. A well-known hydrogen donor is formic acid (FA), which is converted *in situ*, either thermally or catalytically, to molecular hydrogen and CO/CO_2. Commonly used solvents are alcohols (methanol, ethanol) and water, the latter being a preferred system for biofuel conversion since it is a "green" solvent.

With temperatures typically of 350-400^{o}C and reaction times of typically 8-16 hours, lignin from spruce, pine, birch and aspen wood has been converted to a chemically stable bio-oil through a solvolysis process using formic acid as hydrogen donor. The molar H/C ratio of the product was between 1.3 and 1.8, and the O/C ratio between 0.05 and 0.1, indicative of a substantial reduction in

the oxygen content compared with the fast pyrolysis process [2,14,15]. However, in order to make this bio-oil fuel competitive with fuels and chemicals obtained from petroleum, some important process parameters need to be improved: i) shorter reaction times, ii)lower reaction temperatures and iii) the reduction of low-value side streams i.e. gas and solid residues.

One possibility to address these challenges is the use of catalysts in the process. Catalytic hydrotreatment of lignin has already been explored extensively and involves the reaction of lignin in the presence of a (heterogeneous) catalyst with molecular hydrogen at elevated temperatures. Several catalytic systems have been evaluated both with model compounds and lignin [5,6]. Catalysts such as Co-Mo/Al_2O_3 and Ni-Mo/Al_2O_3 and noble metals on different supports, Rh/C, Rh/Al_2O_3, Pd/C, Rh/ZrO_2, Ru/C [1] have extensively been evaluated for this purpose. Although very effective when using model compounds, only low levels of lignin conversion is achieved in such lignin based systems [5]. Recent research by Ligouri and Barth showed that the reaction time and temperature can be reduced dramatically when using heterogeneous (Pd/C) catalyst together with Nafion SAC-13 as solid superacid in a formic acid/water media (2011) [16]. The Pd/C catalyst increases the hydrogenation rate, while the Nafion SAC-13, a Brønsted acid, activates the lignin aryl ether sites (de-polymerization) and promotes their hydrogenolysis to phenols[17]. The lignin was converted at a reaction temperature of 300^{o}C and a reaction time of 2 h, and high conversions into oil were achieved. Nonetheless, the use of two types of catalyst presents some drawbacks from an industrial and economical point of view. In this perspective, the use of a bifuntional catalyst were a cheap acid support is used could have the potential to improve the industrial and economic performance without lowering the lignin conversion values. Alumina could be an adequate alternative, although the role of its Lewis acidity in the lignin de-polymerization and re-polymerization needs investigation.

In this study, several noble metals supported on alumina, Ru/Al_2O_3, Rh/Al_2O3 and Pd/Al_2O_3 are investigated as bifunctional catalyst in a formic acid/water media for the simultaneous de-polymerization and hydrodeoxygenation of three different types of lignins. The conversion of lignin to oil and solids (coke) and the effect of the alumina as a support with Lewis acid properties **a**re investigated at different temperatures (340-380^{o}C) and reaction times (2-6 h), in terms of bulk yields and chemical composition of the products.

2. Materials and Methods

2.1 Chemicals

N,O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA) with trimethylchlorosilane (TMCS) and pyridine (>99.5 %) was purchased from Fluka and used as bought. Pentane (>99%), formic acid (>98%), tetrahydrofuran (>99.9%) and ethyl acetate (99.8%) were purchase from Sigma Aldrich and used as bought.

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^{o}C for 24 h prior to use.

2.3. Acidity measurements (DRIFT and NH_3-TPD)

Temperature-programmed desorption of ammonia, NH_3-TPD, was performed to determine the total acidity of the samples. The measurements were carried out in chemisorption analyzer AutoChem II equipped with a thermal conductivity detector (Micromeritics, USA). The samples (50 mg) were flushed with helium at 650°C for 30 min, then cooled down to 40°C and loaded with ammonia for 30 min. Complete removal of physically adsorbed ammonia was carried out by purging the saturated samples with helium at 100°C until no further desorption was recorded. Under constant flow of helium, the samples were heated up from 100 to 650°C at a heating rate of 10°C/min, and the release of ammonia was recorded. The total acidity was determined by using calibration data.

Diffuse reflectance infrared Fourier transform, DRIFT, was used to distinguish Lewis and Brønsted acid sites of noble-metal containing catalysts and γ-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). The samples were dried *in situ* under vacuum for 1 h at 250°C and later cooled down to 40°C in order to record the background spectra. The main measurement features were a spectral range from 1650 to 1350 cm^{-1}, 200 scans, and a resolution of 4 cm^{-1}. Initially, the catalyst was brought in direct contact with pyridine at 40°C for 15 min. Analysis where obtained by heating the sample up to 100, 200, or 300°C for 15 min.

2.4 Type of lignins

Low sulfonate alkali lignin (KL lignin) was purchase from Sigma-Aldrich. Lignin from Norway spruce from strong acid carbohydrate dissolution pre-treatment (AL) was received from Technical College of Bergen, and lignin from Norway spruce from weak acid and enzymatic hydrolysis biomass pre-

treatment (EL) was received from the Norwegian University of Life Science in Ås. The two latter lignins were ground and sieved (<500µm). All the lignins were dried at 80°C for 24 h prior to use.

2.5 Experimental conditions

2.5.1 Experimental set-up

A detailed description is given elsewhere by Kleinert and Barth (2008) [14]. 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 to the desired conditions (340°C or 380°C) for a given reaction time (2 or 6 hours). The experimental conditions for all the experiments are summarized in Supplementary Material Table S1.

2.5.2 Sample work-up

After completed reaction time, the reactors were taken out of the oven and cooled in an air stream to ambient temperature. The amount of produced gases was determined by weighting the reactor before and after ventilating the gas. After opening the reaction container, the liquid reaction mixture was extracted with a solution of ethyl acetate: tetrahydrofuran (90:10) and the solid phase (unreacted lignin, reaction products and catalyst) were filtered. Two well-separated liquid phases were obtained (organic top phase and aqueous bottom phase). They were separated by decanting, and the pH and the weight of the aqueous phase was determined. The organic phase was dried over Na_2SO_4 and concentrated at reduced pressure (ca. 250 mmbar) at 40°C to yield a dark brown to black liquid. The yield was determined by weight. The solids were characterized by Fourier-Transformed Infrared Spectroscopy (FT-IR) and elemental analysis. The oil fraction was characterized by gas chromatography (GC-FID), gel permeation chromatography-size exclusion chromatography (GPC-SEC) and electrospray soft ionization mass spectroscopy (ESI-MS).

2.6 GC-FID analysis

The oil was sylilated with BSTFA prior to the GC-FID analysis. Typically 3 mg of oil was dissolved in 100 µL of pyridine and latter 100 µL of BSTFA with TMS was added. The samples were heated to 70°C for 20 min. After cooling the mixture was dissolved with pentane (3mg of oil/ml of pentane) and analysed by GC-FID.

The samples were analysed on a Thermo Finnigan TRACE GC Ultra with a FID- detector equipped with a chromatographic HP-ULTRA2 [(5%-phenyl-methylpolysiloxane], 25m, 0.200 ID column from Agilet Technologies. The following heating programme was applied: 30°C for one minute, and then heating

at 10°C/min up to 250°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 available reference compounds that were also sylilated prior to the analysis. The quantitative data was obtained using hexadecane as internal standard. Calibration curves were prepared for the following compounds: phenol, cresol, guiacol, methylguaiacol, catechol, ethylcatechol, syringol, o-vanillin.

2.7 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.

2.8 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 254 and 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.

2.9 FT-IR

The FTIR spectra were recorded by applying the sample to an attenuated total reflectance (ATR) crystal. The main measurement features were a spectral range from 4000 to 400 cm^{-1}, 16 scans, and a resolution of 4 cm^{-1}.

2.10 ESI-MS

Each sample (120 µg/ml) was dissolved in methanol and analysed by full-scan mass spectrometry (m/z range from 100 to 1000 with 1 scan/s) on an Agilent 6420 Triple Quad LC/MS system (Agilent Technologies, Inc., Palo Alto, CA). Samples of 2 µL were injected by direct injection into the ESI-MS. Both positive and negative electrospray ionization was used to detect different compounds.

2.11 Gas phase GC

Gas phase GC analysis was performed on a GC-FID/TCD (HP 7890A) and a 30 m Porapak Q Molsieve column equipped with a FID front detector and a TCD back detector, which was controlled by an HPChem laboratory data system. The heating programme was as follows: Initial temperature was 50°C for 22 min after which, the temperature was raised at a rate of 20°C/min up to 150°C. 15 min after reaching this temperature it was again raised at a rate of 50°C/min up to 220°C. This

temperature was held for 5 min. The injection port had a temperature of 250°C, the pressure was kept constant at 255 kPa and the FID was at 300°C.

2.12 Energy dispersive X-ray analysis (EDXA)

Compositional analysis of the reactor surface was carried out with an EDX spectrometer equipped with an SEM system (JEOL, JSM-5610LVS). The measurement duration of SEM-EDX analysis was set to 300 s. The energies of the obtained EDX spectra were calibrated by Cu·Lα and Kα lines of a copper (99.96%) plate.

3. Results

3.1 Acidity Results

Acidity measurements on the Ru/Al_2O_3, Rh/Al_2O_3, Pd/Al_2O_3 and γ-alumina were carried out to determine the type of acidity (Lewis or Brønsted), the acidity retention and total acidity of the samples. Table 1 shows the total acidity data recorded by NH_3-TPD in the 100-650°C temperature range. The highest acidity was obtained for the γ-Al_2O_3 (1.51 mmol NH_3/g cat.), with significantly lower acidities for the supported catalysts (Rh/Al_2O_3 > Ru/Al_2O_3 > Pd/Al_2O_3).

Table 1: Total acidity, acidity retention and active acidty of γ-alumina, Rh/Al_2O_3, Ru/Al_2O_3 and Pd/Al_2O_3.

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

The DRIFT spectra (see Supplementary Material Figure S1) of all the catalysts show sharp IR bands at 1445 and 1610 cm^{-1}, that are assigned to Lewis acid sites [18]**.** IR bands assigned to Brønsted acid sites (1545 and 1638 cm^{-1}) were not detected in any of the samples [18]. 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 1). Increasing the temperature did not influence the Lewis acid-bound pyridine in Al_2O_3 and Pd/Al_2O_3, as peak areas are not altered. In contrast, increased temperature causes pyridine desorption in Rh/Al_2O_3 and Ru/Al_2O_3 samples, which suggests that their acidity is rather weak. Given the reaction temperature, only the acidity obtained above 300°C could actively participate in the reaction, due to its capability to retain pyridine or similar molecules at the given reaction temperatures. Therefore the active acidity, define as the fraction of total acidity that actually plays a significant role in the reaction was calculated (active acidity (T) = acidity retention (T) x total acidity) and the results are shown in Table 1. The catalyst with the highest active acidity is γ- Al2O3 followed by Pd/Al_2O_3, Rh/Al_2O_3 and Ru/Al_2O_3.

3.2 Influence of the reaction surface

3.2.1 Analysis of the reactor surface

The composition of the reactor surface can affect the final results of our system. The reactor used is a T316 stainless steel Parr reactor. The metals present in the reactor surface could in principle catalyze the hydrodeoxygenation reactions and therefore affect the final product distribution [19]. Furthermore, when the reactor is used for repeated solvolysis reactions, alterations in the reactor surface are observed, and the metallic surface turns black. Previous experience in our group shows an improvement in the oil yields obtained after the reactor was submitted to 3-4 reaction cycles, suggesting that these alterations in the reactor surface are beneficial for the overall process.

To evaluate these changes and the possible metals that could have a catalytic effect in the reaction system, an EDXA analysis of the non-altered and the altered reactor surface was carried out. The results are shown in Table 2.

Table 2: Elemental composition of the altered and non-altered T316 stainless steel reactor surface

The composition of the non-altered surface is in accordance to the data provided by the producer, which confirms the suitability of this method to analyze the surface composition. When comparing both surfaces, several differences in the composition are observed. The content of Fe, Cr and Mn decreases significantly, while the O,C and Ni and Mo content increases.

3.2.2 Effect of the reactor surface in the non-catalyzed and catalyzed system

With the aim of evaluating the effect of the reactor surface, four experiments at a temperature of 340°C and 6 hours were performed. Two of the experiments, NC-Q and NC-1, were carried out without the catalyst, with and without a quartz insert to prevent contact between the system and the reactor surface. Subsequently, the equivalent experiments were carried out using Ruthenium on alumina (Ru/Al_2O_3) as catalyst (Ru-Q and RU-1).

Table 3 shows the results for these experiments. When the contact between the system and the reactor surface is reduced by using the quartz insert, the oil yield decreases by 11 wt% and the solid yield increases by 13 wt%. However, when the analogous experiments are done in the presence of the Ru catalyst, no significant difference is observed. Actually, when using the quartz liner, the oil yield is slightly higher and the solid yield is slightly lower.

Table 3: Mass balance of the selected experiments at 340°C

NC: non-catalyzed experiment. **A**: γ-alumina (0.2 g). **Rh:** rhodium on alumina (0.2 g). **Ru:** ruthenium on alumina (0.2 g). **Pd:** palladium on alumina (0.2 g). **Q:** A quartz insert was used to suppress the effect of the reactor wall **a) Reaction conditions:** 340°C and 6 h. 2 g of acid hydrolysis lignin, 5.0 g of water and 3.075 g of formic acid.

3.3 Screening of Rh (Rh/Al_2O_3), Ru (Ru/Al_2O_3) and Pd (Pd/Al_2O_3) on alumina

3.3.1 Reproducibility and mass balance

Table 3 shows the yields as a function of the inputs for the first replicate of each system. The lignin mass balance accounts for the amount of solids and oil (g) divided by the amount of lignin introduced, while the water recovery percentage accounts for the ratio of water phase recovered (g.) with respect to the water phase introduced (g.). All the experiments show a total mass balance of nearly a 100%, only the gamma-alumina (γ-Al_2O_3) system has a value around 94,8%, which can be assigned to the low water recovery percentage.

Table 3 shows that the solvolysis approach comprises of four major products: a gas phase, a solid phase, an aqueous liquid phase and an organic liquid phase (bio-oil). The amount of gas recovered after the reaction is very close to the values of the formic acid introduced, which supports that the main components of the gas phase are the decomposition products of the formic acid.

As mentioned above, the liquid phase obtained after the reaction can be divided into the clear water phase and the organic oil product. The water phase recovered mostly accounts for slightly higher amounts than the one introduced (see Table 3), which suggests that the water does not act as a reactant, but rather a solvent in the reaction media. Some water-soluble organics and water produced in deoxygenation reactions [20,21] could account for the increased amounts of water recovered, and also for the mass loss in the quantified products relative to the lignin input. The solid yield for the catalyzed systems is calculated after subtracting the amount of catalyst introduced. The sum of this value and the oil yield accounts for over 80 % of the lignin introduced for all experiments, and is even higher, 95 %, for the Ru catalyst. This supports that the solid and oil are the main products of the lignin de-polymerization and hydrodeoxygenation.

Table 4 shows a summary of the results for the three different replicates carried out for each system, the average of the oil and solid yield for each system, and the standard deviation from the average values. It can be observed the Ru system shows the highest standard deviation in terms of oil yield (6.3 wt%) while the alumina system shows the highest standard deviation in terms of solid yield (4.3 wt%).

Table 4: Average oil and solid yields for the selected replicates

NC: non-catalyzed experiment. **A**: γ-alumina (0.2 g). **Rh:** rhodium on alumina (0.2 g). **Ru:** ruthenium on alumina (0.2 g). **Pd:** palladium on alumina (0.2 g). **a) Reaction conditions:** 340°C and 6 h. 2 g of acid hydrolysis lignin, 5.0 g of water and 3.075 g of formic acid.

3.3.2 Effect of the catalyst on the oil and solid yields

From the results in Table 4 we can clearly see the effect of the catalysts in our reaction system. For the non-catalyzed system the average oil yield accounts for 61.6 ± 3.0 wt% and the solid for 20.6 ± 3.4 wt% of the lignin input. These results are comparable to the ones obtained in the gamma-alumina catalyzed system (62.8 ± 3.9 wt% oil yield and 21.6 ± 4.3 wt% solid yield). However, when comparing these systems with the supported catalyst systems, Rh/ Al_2O_3, Pd/ Al_2O_3, Ru/ Al_2O_3, a substantial increase in the oil yield together with a decrease in the solid yield is observed. The best result in terms of oil yield is obtained for the Ru catalyst with an increase of 29.9 wt%. Both the Pd and the Rh catalyst show comparable oil yield with 82.9 ± 2.2 wt% and 80.5 ± 3.7 wt% respectively. In terms of solid yield the best values are obtained for the Pd catalyst, where nearly no solid is found (2.7 ± 0.3 wt%). In the case of the Ru and Rh systems, slightly higher amounts of solids are obtained, with an average of 4.2 ± 1.0 wt% and 4.6 ± 0.5 wt% respectively.

3.3.3 Oil phase composition

The main components in the oil have been quantitatively analyzed by GC-FID as the tri-methyl silyl (TMS) derivatives. The results of the quantification are summarized in Table 5. The Ru-catalyzed system shows the higher abundance of highly hydrogenated and lower oxygenated compounds such as phenol (1.99 %) and cresol (4.27 %), followed by the Pd catalyst, the non-catalyzed system, the alumina catalyzed system and the Rh system. Less hydrogenated compounds such as catechol and ethyl-catechol are more abundant in the alumina system (3.15 and 3.24% respectively), followed by the palladium, non-catalyzed, ruthenium and Rh systems.

Table 5: Quantification of the main oil components by GC-FID and molecular weight distributions by GPC-SEC

NC: non-catalyzed experiment. **A**: γ-alumina (0.2 g). **Rh:** rhodium on alumina (0.2 g). **Ru:** ruthenium on alumina (0.2 g). **Pd:** palladium on alumina (0.2 g). **a) Reaction conditions:** 340°C and 6 h. 2 g of acid hydrolysis lignin, 5.0 g of water and 3.075 g of formic acid. **b) Reaction conditions:** 380°C and 2 h. 2 g of acid hydrolysis lignin, 5.0 g of water and 3.075 g of formic acid.

Table 6 gives the elemental composition of the oil. The H/C ratio is highest when using the Pd, Rh and γ-alumina catalyst, although comparable results are obtained for all the experiments. However when analyzing the O/C ratio, significant differences are observed. The Pd and Rh catalyzed oils clearly has the lowest O/C ratio (0.14), the Ru and the non-catalyzed systems have comparable values, and the highest value is obtained for the alumina catalyzed system.

Table 6: Results of the elemental analysis of the lignin, oils and solids

NC: non-catalyzed experiment. **A**: γ-alumina (0.2 g). **Rh:** rhodium on alumina (0.2 g). **Ru:** ruthenium on alumina (0.2 g). **Pd:** palladium on alumina (0.2 g). **AL:** acid hydrolysis lignin **a) Reaction conditions:** 340°C and 6 h. 2 g of acid hydrolysis lignin, 5.0 g of water and 3.075 g of formic acid. **b)** Elemental analysis of the oil. **c)** Elemental analysis of the recovered solids

According to the GPC-SEC analysis presented in Table 5, the γ-alumina catalyst generates the oil with the lowest average molecular weight (215 Da), followed by the Rh, Pd, non-catalyzed and Ru systems. When analyzing the GPC-SEC spectras in Figure 1, more information about the product distribution of the oils can be obtained. The shape of the peaks are narrower, nearly symmetric for the Rh and the non-catalyzed oils, but in the case of the Al and Pd the right side of the curve is less steep implying a higher concentration of lower molecular weight compounds.

Figure 1. GPC spectras of the oils for the NC-1, A-1, Ru-1, Rh-1 and Pd-1 experiments. Analytical conditions are given in section 2.8.

The ESI-MS spectra show a clear difference in the composition of the oils (see Supplementary Material Figure S2a-e). The alumina system shows the narrowest product distribution, with high intensity peaks in the low molecular range, 100-300 Da. The Ru, Pd and Rh catalyst show high intensity peaks in both low molecular range (100-300 Da) and medium molecular range (300-600 Da) which could explain the lower proportion of quantified compounds obtained by the GC-FID. In the case of the non-catalyzed system, a very wide product distribution is observed, with a high concentration of medium molecular range products (300-600 Da) and intense peaks even in the high molecular mass range.

Overall, the more hydrodeoxygenated oils are obtained in the case of the supported systems, as shown in the GC-FID and elemental analysis data, while lower average-molecular-weight oils are obtained in the γ-alumina and Pd systems. The reason for these results will be further discussed in section 4.

3.3.4 Solid phase composition

The amount of solid phase obtained in the Ru, Rh and Pd catalyst was insignificant, preventing any analysis. However, higher amounts of solid were recovered in the non-catalyzed and γ-alumina catalyzed systems. In Figure 2, the FT-IR spectras of the AL lignin, non-catalyzed solid phase products and gamma alumina solid phase products are compared with the aim of gaining insight into the nature of the solids, and the re-polymerization mechanism.

Two main observations can be made: i) the proportion of functional groups in the Al solids is much lower than in the non-catalyzed solid and the lignin; ii) there are significant differences between the solid obtained in the Al and the non-catalyzed system. It can be observed that the OH- stretching signal is broad (3500-3400 cm^{-1}) for both non-catalyzed and lignin spectra, while a much narrow signal is found in the alumina solid, suggesting that a lower abundance of intramolecular H-bonding in the latter. In addition, the CH- stretching signal for methyl and methylene peak (2940-2930 cm^{-1}) is not found in the Al experiment, which suggests an absence of these functional groups compared to the non-catalyzed system and the lignin. The same trend is seen for the carbonyl function above 1700 cm^{-1}, it is quite intense in the lignin with a peak at 1705 cm^{-1} which is typical for carboxylic acid. In the non-catalyzed oil there is a less intense peak at 1788 cm^{-1}, indicating ester groups and the carbonyl peak is inexistent in the alumina catalyzed solids. Some of the aromatic nature is retain in the alumina solid, as seen when analyzing the 1605-1600, 1515-1505 and the 1430-1425 cm^{-1} ranges, although this peaks are less intense than in the lignin and non-catalyzed solid [22]. The guaiacyl pattern is present in the lignin spectra, and the syringyl pattern in both the lignin and the non-catalyzed system. However, both the lignin and the alumina catalyzed solids spectra has a strong peak at around 1065 cm^{-1}, which can be assign to the C-O ether stretching (all band indexing is summarized in the Supplementary Material Table S2) .

Figure 2. FT-IR spectra for the AL lignin and the solids obtained in the A-1 and NC-1 experiments. For experimental conditions, see Table 1.

The results of the elemental analysis of the lignin and solid phases confirme the differences between these solids (Table 6). The non-catalyzed solids have a high content of carbon (73.63 wt%), followed by the lignin (61.27 wt%) and the alumina solids (42.6 wt%), while the content in O is higher for the alumina (53.82 wt%) and less than half for the non-catalyzed system (21.18 wt%).

3.3.5 Gas phase

The gas phase was analyzed for the non-catalyzed and the supported catalyzed systems, and the concentration of CO_2, CO, H_2 and some light alkanes (methane, ethane, propane and butane) were measured, see Table 7.

Table 7: Composition of the gas phase for the selected experiments

NC: non-catalyzed experiment. **A**: γ-alumina (0.2 g). **Rh:** rhodium on alumina (0.2 g). **Ru:** ruthenium on alumina (0.2 g). **Pd:** palladium on alumina (0.2 g). **a) Reaction conditions:** 340°C and 6 h. 2 g of acid hydrolysis lignin, 5.0 g of water and 3.075 g of formic acid.

No water was determined in the gas phase due to the inability to measure this by the selected method. Nevertheless, the analysis of the mass balance suggests that the water produced through the decomposition of the formic acid and the water-gas-shift-reaction (WGS) mainly condenses in the liquid water phase.

The main gas product in all cases is CO_2, produced mainly by the decomposition of the formic acid but also through decarboxylation and gasification reactions of the lignin and its monomers. The component with the second highest concentration is H_2, which can have a strong influence in the hydrogenation rate of the depolymerized lignin monomers. The hydrogen seen in these measurements does not account for all the hydrogen produced from decomposition of formic acid in the course of the reaction, since considerable quantities are used for the hydrogenation of the monomers, especially in the catalytic systems, as suggested by the higher oil yields (Table 3).

When comparing the different systems the following conclusion can be stated: i) the catalytic systems enhance the production of CO_2 (especially Pd and Rh), ii) the amount of hydrogen is higher in the Ru system, iii) the amount of CO is lower in all the catalytic systems (especially Ru) and the concentration of light hydrocarbons which are Fischer-Tropsch type reaction products are higher when using the Pd and Rh.

3.4 Influence of the type of lignin

Three different types of lignins were tested to evaluate the influence of the lignin type in the non-catalyzed and catalyzed systems. To ensure sufficient oil yields in all systems, the experiments were carried out at 380°C and 2 hours reaction time. In total nine experiments were done, one non-

413 catalyzed and two catalyzed (Rh and Ru) experiments for each lignin. The results obtained are
414 summarized in Table 8.

415

416 Table 8: Mass balance and aqueous pH of experiment with different lignins at 380°C

417 **NC:** non-catalyzed experiment. **A**: γ-alumina (0.2 g). **Rh:** rhodium on alumina (0.2 g). **Ru:** ruthenium on alumina (0.2 g). **Pd:** palladium on
418 alumina (0.2 g). **AL:** acid hydrolysis lignin. **KL:** kraft lignin. **EL:** enzymatic hydrolysis lignin **a) Reaction conditions:** 380°C and 2 h. 2 g of acid
419 hydrolysis lignin, 5.0 g of water and 3.075 g of formic acid.

420

421 The most obvious difference between the three lignins is in the pH of the recovered water phase.
422 While the KL lignin, which is a low sulfonate lignin derived from a kraft pretreatment process, yields a
423 water phase with a basic pH, the EL and the AL lignin yield acidic water phases. This is highly
424 correlated with the performance of the catalyst in the different lignin systems. For the KL lignin, with
425 final water phases pH from 8-9, there is no significant difference between the non-catalyzed and
426 catalyzed systems. The best results are obtained for the Rh catalyst, with an oil yield of 52.3 wt% and
427 a solid yield of 9.99 wt%, but these differences are not significant, and even lower oil yields are
428 obtained in the case of the Ru catalyst. In contrast, significant differences in the oil yield values are
429 observed for those lignins with a final water phase pH lower than 7. Here, the oil yield is increased
430 and the solid yield decreased when using the catalysts. In the case of the acid lignin there is an
431 increased of the oil yield in 30 wt% when using the Ru catalyst, while in the enzymatic lignin we
432 obtained an increase of 19 wt%. In both cases the solid yield were reduced.

433 To further evaluate the role of the alumina support in the AL and EL lignin, three additional
434 experiments using only the γ-alumina as catalyst where carried out at a temperature of 380°C and 2
435 hour reaction time (experiments A-4, A-KL and A-EL). These results are compared with the non-
436 catalyzed and Ru catalyzed results in Table 8. For both lignins, at this reaction conditions, there is
437 moderate increase in the oil yield when using the alumina compared to the non-catalyzed system,
438 with a 3.4 wt% increase for the AL lignin and a 13.7 wt% increase for the EL lignin.

439 To further confirm the effect of the alumina catalyst in the AL lignin, the oils obtained were
440 submitted to GPC-SEC and ESI-MS analysis (see Supplementary Material Figures S3a-c). As shown in
441 section 3.3.3, the average molecular weight of the oil is lower in the case of the alumina catalyzed
442 experiment than in the case of the non-catalyzed system (Table 5). Furthermore, when analyzing the
443 ESI-MS results, it can be observed that the Ru and alumina oil spectrograms show a narrower

product distribution of the oils, mostly below the 500 Da, while in the non-catalyzed experiments the product distribution goes up to over 800 Da.

Another aspect that can be evaluated in these results is the nature of the solids when using the supported catalysts. In the case of the El lignin, enough solids are recovered to analyze the non-catalyzed and the Ru supported catalyzed solid phase. In Figure 3 FT-IR spectrograms of the solids obtained in the Ru and non-catalyzed system are compared with the FT-IR spectra of the EL lignin. We can clearly see that the Ru solids shows the same reduced OH stretching peak, the lack of the methylene and methyl peak, the low intensity peaks in the aromatic region and the strong ether peak that appeared in the alumina solids FT-IR spectra in section 3.3.4. The non-catalyzed solids also show comparable spectra to the solids analyzed previously (see Figure 2).

Figure 3. FT-IR spectras for the EL lignin and the solids obtained in the Ru-EL and NC-EL experiments

3.5 Influence of the hydrogen partial pressure

Table 9: Gas, oil and solid yield for the high pressure and low pressure (LP) and reducted catalyst loading (LC) experiments

NC: non-catalyzed experiment. **Ru:** ruthenium on alumina (0.2 g). **LP:** low pressure. **LC:** low catalyst content. **a) Reaction conditions:** 340°C and 6 h. 2 g of acid hydrolysis lignin, 5.0 g of water and 3.075 g of formic acid. **b) Reaction conditions:** 340°C and 6 h. 1 g of acid hydrolysis lignin, 2.5 g of water and 1.5375 g of formic acid and 0,1 g of catalyst. **c)** 0.1 g of catalyst

To evaluate the influence of the total reaction pressure of the system in the final oil and solid yield two extra experiments were carried out, one without catalyst and one with the Ru/Al_2O_3 catalyst. The proportions of the reactants were held constant, but the amount of each reactant was reduced to half for the NC-LP and the Ru-LP experiments. A lower amount of reactant, specially a lower amount of formic acid, will generate less of gases when the reactor is heated. Since the reactor volume is constant, a lower total pressure will result, for the same temperature, in a lower hydrogen partial pressure.

In Table 9 we compare the results of the low pressure experiments with their higher pressure counterparts. For the non-catalyzed experiments, with reduced pressure, the oil yield is decreased to

nearly the half, from 58.2 wt% to 29.9 wt%. The solid yields is correspondingly higher, increasing from 22.4 wt% to 44.9 wt%. However when the supported Ru catalyst is used this effect is partially neutralized. The oil yield is lower, but the decrease is less than in previous case, from 90.0 wt% to 73.7 wt%. In the case of the solid yield, the increase is not significant, from 5.1 wt% to 6.6 wt%.

Another relevant result is the amount of gas obtained in the low-pressure experiments. Both for the NC-LP and the Ru-LP the gas percentage recovered is 3% higher than for their high pressure counterparts. This increase is observed together with a reduction in the values of the lignin mass balance percentage, suggesting that more lignin is gasified at these conditions.

3.6 Influence of the catalyst concentration

The amount of catalyst in the Ru system was reduced to 5 wt. % on lignin (Ru-LC) to evaluate the effect of the catalyst concentration. Even when the amount of catalyst was reduced to the half, the oil and solid yield does not vary significantly (Table 9). This suggests that the catalyst concentration could be reduced to 5 wt% on lignin without inducing major changes in the catalyst efficiencies.

4. Discussion

Replicate experiments in Table 4 show low standard deviation values, from 0.3 to 6% (n=3) for the oil and solid yields, which support that the reactions and workup are reproducible. The deviations that are observed can be caused by inhomogeneity in the lignins, evaporation of volatile compounds and experimental errors during the work-up procedure. The consistency of the reaction process and work-up procedure is further confirmed by mass balances shown in Table 3, with a total mass recovery above 95 wt% for all the cases, and higher than 98 wt % for the supported-catalyzed systems.

The effect of the selected catalysts (Ru/Al_2O_3, Rh/ Al_2O_3 and Pd/ Al_2O_3) is positive for all the experimental conditions tested, as described in section 3.3.2. This could be due to kinetic control of the lignin degradation mechanism by the catalysts. Gasson and Forchheim [22,23] suggest that the primary reaction in lignin solvolysis is a fast de-polymerization step, followed by competing reactions giving hydrodeoxygenation or repolymerisation of the de-polymerized monomers. The apparent activation energy values obtained for this kinetic model show that the probability of re-polymerisation of the lignin monomers is reduced when the monomers are hydrodeoxygenated and/or alkylated (see the simplified reaction scheme in Figure 4).

Figure 4. Simplified reaction scheme of lignin degradation

This effect is further confirmed by the results described in section 3.2.2, section 3.3.3 and section 3.5. Section 3.2.2 showed that the presence of a metalic reaction surface containing among other metals Ni and Mo, can increase the oil yield and reduce the solid yield. These metals are well known catalysts for hydrodeoxygenating reactions [19], and can also provide the kinetic enhancement discussed above. Nevertheless, the quantitative results indicate that the activity of the metallic reaction surface is significantly lower than the activity of the Ru/Al_2O_3 catalyst. Section 3.3.3 shows how the Ru, Rh and Pd systems have the highest H/C and lower O/C ratios in the oil phase products (Table 6) and the Ru and Pd systems the higher concentrations of highly hydrodeoxygenated compounds (Table 5). Finally, the results in section 3.5 also confirm this kinetic enhancement. The lower hydrogen partial pressure of the system lowers the hydrogenation rate, which significantly affects the oil and solid yield in the un-catalyzed system, while the Ru system is not as strongly affected. The oil yield is reduced to half in the case of the un-catalyzed system as opposed to only 17 wt % reduction in the case of the Ru system, and the solid yield is doubled in the un-catalyzed system while it remains nearly stable for the Ru system. All this suggests that the Ru, Pd and Rh active phases will catalyze the hydrodeoxygenation reactions (see Figure 4), increasing the oil yield and reducing the solid yield.

Another point for evaluation is to what degree the bifunctionality of the catalyst is important. The role of the hydrogenating active site (Ru, Rh and Pd) has already been discussed, but the support materials may also play an important role in the lignin degradation mechanism. Previous work suggests that acid heterogeneous catalysts are able to catalyzed the cleavage of ether bonds and cause de-polymerization of lignin[17,24], the polymerization of alcohols to ethers (re-polymerization) [25,26] and the deoxygenation of hydroxyl and methoxy aromatics [19,20]. Therefore an effect of the alumina support due to its acid nature could be expected. The results given in Table 4 show that alumina alone had no significant effect on the oil and solid yields, which may be due to the ability of alumina to catalyze both the de-polymerization and re-polymerization reactions. However, the composition of the oil shows a clear difference between the non-catalyzed and alumina catalyzed systems.

Table 5 indicates that the lowest values of average molecular weight are obtained for the oils from the γ-alumina and Pd systems. The ESI-MS analyses show that the γ-alumina has the highest concentration of low molecular weight compounds, followed by the Pd, Ru and Rh systems. The un-catalyzed system is the only one that shows high concentration of high molecular weight compounds. These results are in agreement with the acidity measurement in section 3.1. The γ-alumina sample

shows the highest stable acidity and consequently the oil obtained is the one with the lowest average molecular weight (215 Da). On the other hand, the oils in the noble metal containing catalysts have significantly higher average molecular weight in the following order: Pd/Al_2O_3 (323 Da) < Rh/Al_2O_3 (344 Da) < Ru/Al_2O_3 (397 Da). Since this order is inversely proportional to the active acidity of the catalysts, we can conclude that stable -strong Lewis acid sites play an important role in the de-polymerization of lignin into monomers.

The acid alumina support could also be able to catalyze the re-polymerization of the lignin monomers, which can be confirmed by comparing the FT-IR spectra for the AL lignin, the non-catalyzed and the alumina system. As described in section 3.3.4, the solid phase from the γ-aluna system has limited or no presence of methylene and carbonyl functionalities, very low concentration of intramolecular H-bonding of the hydroxyl groups, low intensity of aromatic bands and quite intense ether functionalities. In addition to this, the elemental composition data (Table 6) show that the solid phase has a high O/C ratio, which suggests that the O atoms have been retained in poly-phenolic or aryl ether dominated solids. On the other hand, the lack of ether functionalities and low O/C ratio in the un-catalyzed system suggest a more graphite like structure of the solid phase for this system. We can conclude that the alumina support directs the reactions towards an aryl ether type structure through acid-catalyzed condensation reactions of the hydroxyl groups present in the depolymerized lignin monomers. The same comparison was done for reactions with EL lignin, where solids from the Ru and the non-catalyzed system were compared. In Figure 3 the most intense IR peak for the Ru solid also corresponds to C-O stretching, again indicating a predominance of ether moieties in the solid products.

The importance of the acidity of the reaction system for the final oil and solid yield can also be evaluated by comparing experiments with different pH values in the reaction medium. As shown in section 3.4, when the recovered water phase pH is >7 (KL lignin), no significant effect of the catalyst on the oil or solid yield is observed. There are two possible explanations for this observation; either the acid sites of the solid are deactivated, or the influence of the basicity of the lignin is just through the pH of the reaction mixture. The increased oil yields obtained from the acidic AL and EL lignins in the catalyzed systems suggest that the latter mechanism is the main reason for the lack of effect of the catalyst. Furthermore, if the γ-alumina system is compared with the non-catalyzed system, we can clearly see that the presence of alumina at 380°C and 2 h icreases the amount of oil in acidic reaction media (marginally significant increase of 3.4 wt% for the A-4 experiment and a significant increase of 13.7 wt% for the A-EL experiment). This effect is higher for the EL lignin, which might be due to the higher pH of the reaction system. In the AL lignin, this increase is not so significant, but the GPC-SEC (Table 5) and the ESI-MS analysis confirms the higher amount of low molecular weight

compounds in the alumina system. All this implies that the properties of the selected lignin are a key factor when selecting the most efficient catalyst.

Finally, the effect of the catalysts in the composition of the gas phase should also be mentioned. The complexity of the reaction mechanisms producing the gas phase makes it complicated to analyze the reasons behind the disparity in the concentration of the components. It is clear that the lower CO values of the catalyzed systems (see section 3.3.5), can be caused by on the one hand, the displacement of the WGS equilibria towards the production of H_2, predominant in the Ru catalyst, and on the other hand to the Fishcer-Tropsch type reactions to low molecular weight hydrocarbons like methane, mainly in the Rh and Pd catalyst. The first mechanism is supported by the observation that higher H_2 amounts are found in the Ru system even though higher quantities of hydrogen are incorporated into the liquid products in the course of the reaction. The later mechanism is based on the observation that higher amounts of volatile alkanes are present in the Pd and Rh systems. Together, this indicates an effect of the catalyst in the final composition of the gas phase. In any case, the higher amount of hydrogen in the Ru system could be a reason for the highest oil yields obtanied in this system.

5. Conclusion

The simultaneous catalytic de-polymerization and hydrodeoxygenation of KL, EL and AL lignings was carried out in a formic acid/water media and their results were compared with the non-catalytized and a gamma-alumina support catalyzed system. Three bifunctional catalysts were screened, Rh, Pd and Ru on alumina, and evaluated in terms of the conversion of the lignin to oil and solids. A central focus of this paper was to identify the role of the alumina support and to evaluate its effect on the process. As a summary, the following conclusions can be made:

- The effect of the supported catalyst (Rh/Al_2O_3, Ru/Al_2O_3, Pd/Al_2O_3) is positive with regard to an increase on oil yield and a decrease on solid yield. The best result in terms of oil yield is for the Ru system, while the most effective one for the reduction of the solid yield was the Pd system.
- When analyzing the composition of the oils, 8 major components are identified and quantified: phenol, cresol, guaiacol, methyl guaiacol, catechol, ethylcathecol, syringol and o-vanilin. Ru shows the highest amount of highly hydrodeoxygenated monomers, followed by the Pd catalysts. However, when analyzing the average elemental composition of the oils, Pd and Rh show lower O/C and higher H/C ratios.
- The alumina support plays a vital role in the de-polymerization of lignin. This has been proved by analyzing the yields and composition of the oil and by changing the type of lignin

and consequently the pH of the reaction media. The presence of temperature-stable Lewis acid sites seems to increase the amount of low molecular weight compounds in the oils.

- The alumina support plays also a role in the re-polymerization of the lignin monomers. The elemental and FTIR analysis of the solids suggest an alternative re-polymerization mechanism when the alumina support is present in the system.
- The type of lignin is a key factor when analyzing the effect of the selected catalyst. Only lignins that provide acid reaction media are suitable for this type of bifunctional catalysts.
- The pressure has a strong influence in the final oil and solid yield. Under reduced pressure conditions, the oil yield is reduced while the solid yield is increased. This effect is partially neutralized when using a catalyst. In both cases the amount of lignin gasified increases.
- The reactor surface has a positive effect on the oil and solid yield. This is due to mainly its Ni and Mo content, which can catalyze hydrodeoxygenation reactions.
- The catalyst also affects the decomposition of the formic acid into molecular H_2 and CO/CO_2. The Ru catalyst is able to induce a higher production of H_2, while the Rh and Pd catalyst are responsible for a higher production of low molecular weight compounds.

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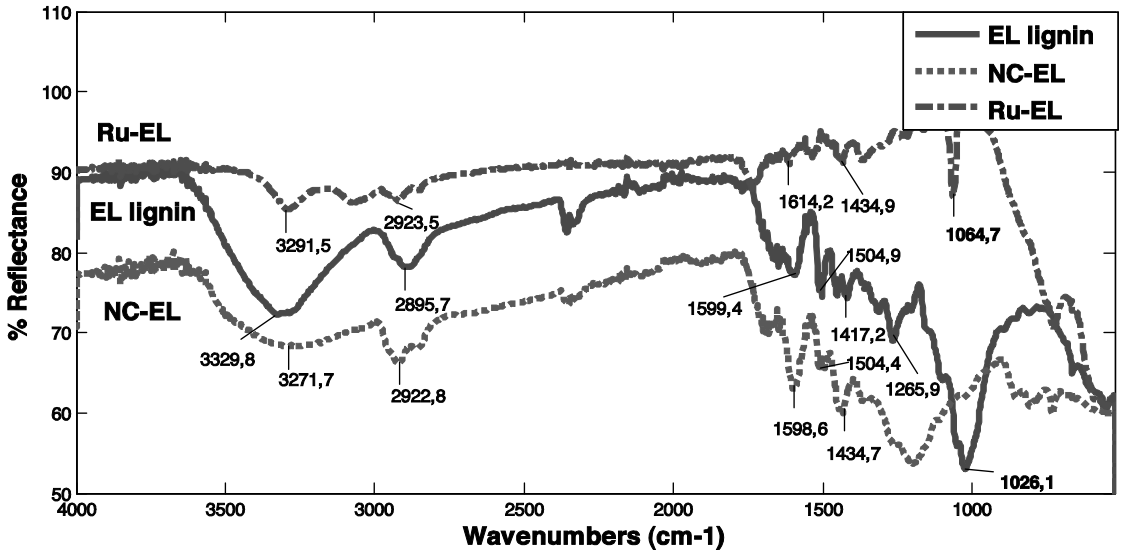

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668 Fig. 1

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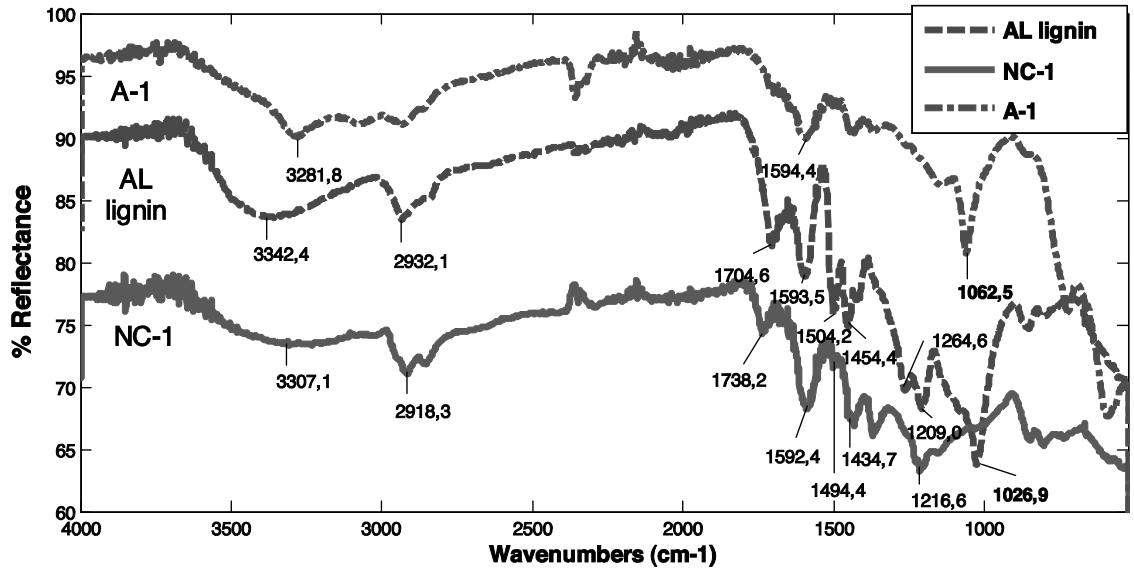

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673 Fig.2

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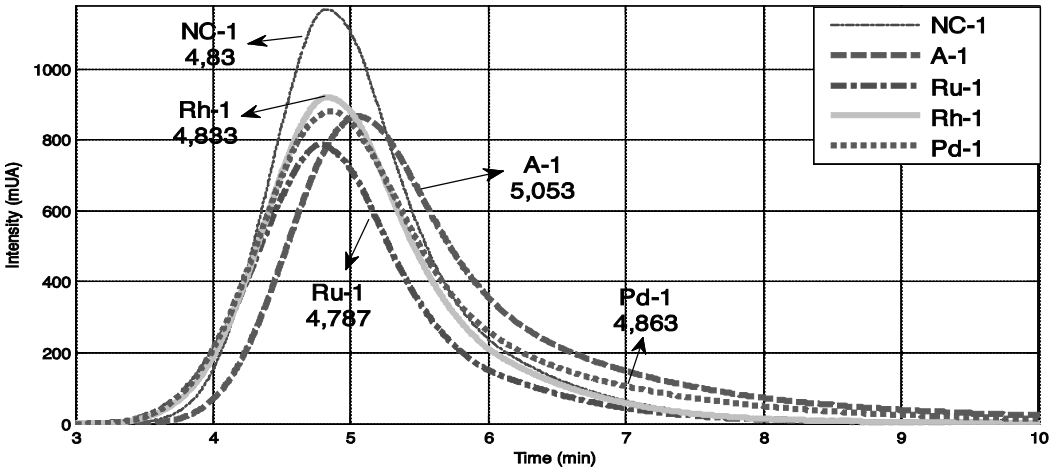

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680 Fig. 3

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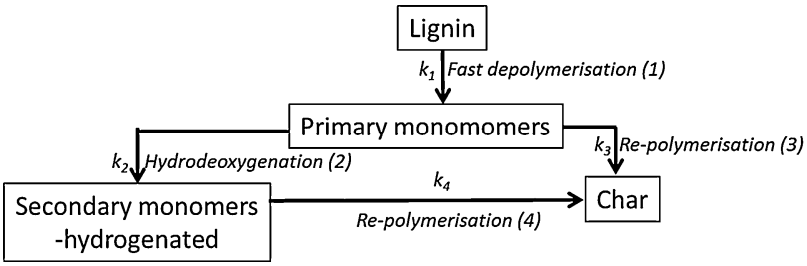

682

683 Fig. 4

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685 Table 1: Total acidity, acidityretention and active acidty of γ-alumina, Rh/Al_2O_3, Ru/Al_2O_3 and

686 Pd/Al_2O_3.

	Total acidity[a] (mmol NH_3/g cat.)	Acidityretention[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)

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

688

689 Table 2: Elemental composition of the altered and non-altered T316 stainless steel reactor surface

	Altered surface (%)	Non-altered surface (%)
C	32-45	0-4.8
O	28.5-32.5	0
Si	1.5-2.3	1
Fe	11-13	64-65
Cr	9.3-11.5	17
Ni	1.19-2.5	9-12
Mo	4.1-5.8	2.14-2.5
Mn	-	2-2.6

690

691 Table 3: Mass balance of the selected experiments at 340°C

Nameofexperiment	Oil Yield (% on lignin)	Solid Yield (% on lignin)	Gas phase (% total input)	Water Recovery(% inital input)	Lignin Mass Balance (%)	Total Mass Balance (%)
NC-Q[a]	49.5	35.0	29.5	103.7	84.5	97.3
NC-1[a]	58.2	22.4	30.5	103.6	80.6	97.9
Ru-Q[a]	91.2	3.5	29.9	88.2	94.7	93.3
Ru-1[a]	90.0	5.1	29.1	102.6	95.0	99.3
A-1[a]	63.1	22.0	30.0	94.8	85.1	94.8
Rh-1[a]	81.0	4.8	30.0	106.3	85.7	99.9
Pd-1[a]	81.7	2.8	30.8	101.1	84.4	98.1

692 **NC:** non-catalyzed experiment. **A**: γ-alumina (0.2 g). **Rh:** rhodium on alumina (0.2 g). **Ru:** ruthenium on alumina (0.2 g). **Pd:** palladium on
693 alumina (0.2 g). **Q:** A quartz insert was used to suppress the effect of the reactor wall **a) Reaction conditions:** 340°C and 6 h. 2 g of acid
694 hydrolysis lignin, 5.0 g of water and 3.075 g of formic acid.

695 Table 4: Average oil and solid yields for the selected replicates

Name of experiment	Oil Yield (% on lignin)	Average Oil Yield and Standard deviaton (%)	Solid Yield (% on lignin)	Average Solid Yield and Standard deviaton(%)
NC-1[a]	58.2	61.6±3.0	22.4	20.6±3.4
NC-2[a]	62.3		23.0	
NC-3[a]	64.2		16.5	
A-1[a]	63.1	62.8±3.9	22.0	21.6±4.3
A-2[a]	58.7		25.7	
A-3[a]	66.5		17.1	
Rh-1[a]	81.0	80.5±3.7	4.8	4.6±0.5
Rh-2[a]	83.9		4.0	

Rh-3[a]	76.6		5.0	
Ru-1[a]	90.0	91.5±6.3	5.1	4.2± 1.0
Ru-2[a]	98.4		4.4	
Ru-3[a]	86.2		3.2	
Pd-1[a]	81.7	82.9±2.2	2.8	2.7±0.3
Pd-2[a]	85.4		2.4	
Pd-3[a]	81.6		2.9	

NC: non-catalyzed experiment. **A**: γ-alumina (0.2 g). **Rh:** rhodium on alumina (0.2 g). **Ru:** ruthenium on alumina (0.2 g). **Pd:** palladium on alumina (0.2 g). **a) Reaction conditions:** 340°C and 6 h. 2 g of acid hydrolysis lignin, 5.0 g of water and 3.075 g of formic acid.

Table 5: Quantification of the main oil components by GC-FID and molecular weight distributions by GPC-SEC

GC-FID	**NC-1[a]**	**A-1[a]**	**Ru-1[a]**	**Rh-1[a]**	**Pd-1[a]**	**NC-4[b]**	**Ru-4[b]**	**A-4[b]**
Phenol (wt % oil)	1.68	1.44	1.99	1.41	2.47	2.70	1.52	1.56
Cresol (wt % oil)	3.62	3.16	4.27	2.94	5.22	5.90	3.17	3.41
Guaiacol (wt % oil)	2.53	2.18	3.21	2.03	3.44	4.22	2.28	2.42
Methylguaiacol (wt % oil)	2.38	2.29	2.80	1.91	3.38	3.92	2.13	2.58
Catechol (wt % oil)	2.00	3.15	1.91	1.35	2.05	3.68	1.70	3.35
Ethylcatechol (wt % oil)	1.36	3.24	1.44	0.99	1.69	2.33	1.36	3.76
Syringol (wt % oil)	0.19	0.20	0.22	0.12	0.23	0.47	0.19	0.26
o-Vanillin (wt % oil)	1.81	1.32	1.9	1.33	0	3.00	1.45	0
GPC-SEC	**NC-1[a]**	**A-1[a]**	**Ru-1[a]**	**Rh-1[a]**	**Pd-1[a]**	**NC-4[b]**	**Ru-4[b]**	**A-4[b]**
Average molecular weight (Da)	346	215	397	344	323	294	497	211

NC: non-catalyzed experiment. **A**: γ-alumina (0.2 g). **Rh:** rhodium on alumina (0.2 g). **Ru:** ruthenium on alumina (0.2 g). **Pd:** palladium on alumina (0.2 g). **a) Reaction conditions:** 340°C and 6 h. 2 g of acid hydrolysis lignin, 5.0 g of water and 3.075 g of formic acid.**b) Reaction conditions:** 380°C and 2 h. 2 g of acid hydrolysis lignin, 5.0 g of water and 3.075 g of formic acid.

Table 6: Results of the elemental analysis of the lignin, oils and solids

	C (%wt)	**H (%wt)**	**O (%wt)**	**N(%wt)**	**(O/C)**	**(H/C)**
AL lignin	61.27	5.74	32.82	0.16	0.40	1.12
NC-1 Oil[a,b]	73.78	7.37	18.09	0.76	0.18	1.19
A-1 Oil[a,b]	71.47	7.21	20.07	0.32	0.21	1.21
Ru-1Oil[a,b]	74.29	7.31	17.86	0.54	0.18	1.17
Rh-1Oil[a,b]	76.97	7.83	14.13	1.07	0.14	1.21
Pd-1Oil[a,b]	76.97	7.83	14.13	1.07	0.14	1.21
NC-1 Solid[a,c]	73.63	4.98	21.18	0.21	0.22	0.81

A-1Solid[a,c]	42.60	3.46	53.82	0.12	0.95	0.97

705 **NC:** non-catalyzed experiment. **A**: γ-alumina (0.2 g). **Rh:** rhodium on alumina (0.2 g). **Ru:** ruthenium on alumina (0.2 g). **Pd:** palladium on
706 alumina (0.2 g). **AL:** acid hydrolysis lignin **a) Reaction conditions:** 340°C and 6 h. 2 g of acid hydrolysis lignin, 5.0 g of water and 3.075 g of
707 formic acid. **b)** Elemental analysis of the oil. **c)** Elemental analysis of the recovered solids

708

709 Table 7: Composition of the gas phase for the selected experiments

	CO_2 (% mol)	CO (% mol)	H_2 (% mol)	CH_4 (% mol)	C_2H_6 (% mol)	C_3H_8 (% mol)	C_4H_{10} (% mol)
NC-1[a]	59.50	7.95	31.33	1.01	0.12	0.04	0.05
Ru-1[a]	60.69	2.97	34.74	1.35	0.13	0.06	0.06
Pd-1[a]	62.80	3.34	31.39	2.11	0.15	0.08	0.13
Rh-1[a]	63.99	3.67	29.88	2.10	0.16	0.09	0.12

710 **NC:** non-catalyzed experiment. **A**: γ-alumina (0.2 g). **Rh:** rhodium on alumina (0.2 g). **Ru:** ruthenium on alumina (0.2 g). **Pd:** palladium on
711 alumina (0.2 g). **a) Reaction conditions:** 340°C and 6 h. 2 g of acid hydrolysis lignin, 5.0 g of water and 3.075 g of formic acid.

712

713 Table 8: Mass balance and aqueous pH of experiment with different lignins at 380°C

Nameofexperiment	Type of lignin	pH (water phase)	Oil Yield (% on lignin)	Solid Yield (% on lignin)	Total Mass Balance (%)	Lignin Mass Balance (%)
NC-4[a]	AL	4-5	54.0	26.3	99.1	80.2
Rh-4[a]	AL	3-4	74.0	5.2	95.8	79.2
Ru-4[a]	AL	4	83.9	8.2	102.3	92.1
A-4[a]	AL	3-4	57.4	24.5	97.0	81.9
NC-KL[a]	KL	8-9	47.9	10.4	90.2	58.3
Rh-KL[a]	KL	8-9	52.3	10.0	92.8	52.3
Ru-KL[a]	KL	8-9	44.7	6.9	89.0	51.6
A-KL[a]	KL	8-9	47.0	11.7	92.8	58. 7
NC-EL[a]	EL	5	28.3	25.5	91.3	53.8
Rh-EL[a]	EL	5	45.3	2.9	90.1	48.2
Ru-EL[a]	EL	5	47.7	15.3	91.9	63.0
A-EL[a]	EL	5	42.0	27.1	91.3	69.1

714 **NC:** non-catalyzed experiment. **A**: γ-alumina (0.2 g). **Rh:** rhodium on alumina (0.2 g). **Ru:** ruthenium on alumina (0.2 g). **Pd:** palladium on
715 alumina (0.2 g). **AL:** acid hydrolysis lignin. **KL:**kraft lignin. **EL:** enzymatic hydrolysis lignin **a) Reaction conditions:** 380°C and 2 h. 2 g of acid
716 hydrolysis lignin, 5.0 g of water and 3.075 g of formic acid.

717

718 Table 9:Gas, oil and solid yield for the high pressure and low pressure (LP) and reducted catalyst
719 loading (LC)experiments

Name of experiment	Oil Yield (% on lignin)	Solid Yield (% on lignin)	Gas phase (% total)	Lignin Mass Balance (%)
NC-1[a]	58.2	22.4	30.5	80.6
NC-LP[b]	29.9	44.9	33.4	74.7
Ru-1[a]	90.0	5.1	29.1	95.0
Ru-LP[b]	73.7	6.6	32.4	80.3
Ru-LC[a,c]	85.2	4.5	30.0	89.7

720 **NC:** non-catalyzed experiment. **Ru:** ruthenium on alumina (0.2 g). **LP:** low pressure. **LC:** low catalyst content.**a) Reaction conditions:** 340°C
721 and 6 h. 2 g of acid hydrolysis lignin, 5.0 g of water and 3.075 g of formic acid.**b) Reaction conditions:** 340°C and 6 h. 1 g of acid hydrolysis
722 lignin, 2.5 g of water and 1.5375 g of formic acid and 0,1 g of catalyst.**c)** 0.1 g of catalyst

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