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Feature Article

Selective hydrogenolysis of α -O-4, β -O-4, 4-O-5 C-O bonds of ligninmodel compounds and lignin-containing stillage derived from cellulosic bioethanol processing



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ABSTRACT

Benzyl phenyl ether (BPE), phenethyl phenyl ether (PPE) and diphenyl ether (DPE) have been selected as model compounds of the most abundant and significant ether linkages found within the complex structure of lignin (e.g. α -O-4, β -O-4, and 4-O-5, respectively). The catalytic hydrogenolysis of these compounds has been carried out using several Ru, Pd and Ni catalysts supported over different metal oxides (e.g. Al₂O₃, ZrO₂, TiO₂) and carbon materials (e.g. active carbon, multiwall carbon nanotubes). The conversion of these compounds at relevant hydroprocessing conditions (150 °C, 25 bar-g in H₂ atmosphere) is much dependent on the labile nature of the relevant ether bonds of the selected model compounds. Conversion levels for the three compounds increases in the following order: DPE (4–O–5 linkage) < PPE (β –O–4) < BPE (α –O–4). Product distribution is also dependent on the chemical structure of the raw material subjected to catalytic hydroprocessing, with BPE and DPE mainly yielding aromatic monomers, whilst fully saturated monomers are the main reaction products when PPE is hydroprocessed. The reaction mechanisms upon hydroprocessing vary from one model compound to another, being hydrogenolysis the prevailing route in the catalytic hydroprocessing of BPE and DPE, whereas competing reaction pathways between dimer hydrogenation and hydrogenolysis of the C-O bond occur for the PPE molecule. The conversion and selectivity to relevant hydrogenolysis products are also dependent on the catalyst used. Ru-based catalysts are the most active followed by Pd - based and Ni-based, whereas selectivity to aromatic monomers increases in the reverse order (Ni > Pd > Ru). The catalytic systems with easier reducible species performes better in the conversion of the dimer models. Besides, a preliminary study on the catalytic depolymerization of a real lignin stream (lignin-containing 2G bioethanol plants stillage) has been carried out. Detailed characterization by ¹³C-¹H heteronuclear single-quantum correlation spectroscopy (HSQC) showed that on 5 wt.% Ru/C it is possible to achieve 50% desapearance of the most abundant lignin ether bond (i.e. β –O–4) and liquid yields above 50 wt.%.

1. Introduction

Mitigation of greenhouse emissions (GHE), energy independence, and rural development are the key drivers for biomass-conversion technologies. Moreover, according to reports from the International Energy Agency (IEA), between 2007 and 2030, global total primary energy demand is expected to increase by 40%, in which biomass conversion into liquid transportation fuels will play an important role. Hence, it is clear that biomass will be a critical part in the production of CO_2 -neutral fuels and chemicals [1,2]. This fact has stimulated the development of advanced biofuels such as cellulosic ethanol, which are now becoming a reality with the commissioning of large scale plants in Italy and USA [3–6]. This new generation of biofuels plants can convert agricultural wastes (*e.g.* wheat straw and corn stover) and organic fractions of municipal solid wastes into ethanol. These recalcitrant feedstocks require harsh chemical and thermal pretreatments that have been extensively optimized to increase accessibility and reactivity of the cellulose fibrils towards the enzymatic cocktail [7]. Likewise, intensive research has been focused on the development of recombinant enzymes and fermentation yeast by carefully tailoring genetics of

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enzyme-producing microorganisms and C₅-fermenting yeasts to maximize ethanol production [7,8]. A major challenge that remains unsolved, however, is the revalorization of lignin, the second most abundant naturally occurring polymer which accounts for 10–35% of biomass by weight and around 40% of its energy [9,10]. In second generation (2G) biorefineries, lignin can be produced at the pretreatment stage or at the stillage recovery, where the mixture is concentrated to ~40 wt.% total solids using press-filtration before entering a biomass-boiler to generate heat. Nonetheless, this approach has significant limitations, as lignin boilers are expensive and energy content of this material is significantly lower than natural gas. Additionally, the volume of lignin residue that will be produced readily exceeds the energy requirements of the biorefinery complicating its utilization as energy source, unless electricity is generated and transferred to the electrical grid [11].

Hence, economical conversion of this byproduct into valuable chemicals, fuels, polymers, and carbon-based structural materials is germane to guarantee the long-term profitability and sustainability of the biorefineries. Similarly, in the pulp and paper industry, black liquor produced after the purification of the cellulose pulp is used for energy recovery, in which the carbonaceous residues (i.e. lignin) are combusted and the mineral oxides are recovered for reuse in the caustic treatment of the lignocellulose. This process is also under significant political pressure as new caps of energy co-generation are imposed to pulp-manufacturers [12]. Thereby, it is clear that valorizing lignincontaining streams into added value products is highly desirable to improve economics of current 2G biofuels and pulping plants, and enhance CO2 abatement. In this context, different possibilities and approaches can be found in the scientific literature, targeting at breaking down the complex structure of lignin into simpler molecules that could further serve for producing valuable bio-based chemicals and fuels. Different processes, such as oxidation [13] or acid-base catalysis [14,15], have been studied as a means to catalytically depolymerize lignin, as thoroughly reviewed by several authors in recent times [16-20]. Thermochemical processing of lignin via fast pyrolysis for producing bio-oil, catalytic depolymerization, hydroprocessing and oxidation are different alternatives for lignin conversion, currently being intensively researched by many scientists [16]. Other routes include gasification and reforming processes, using steam or in liquid phase. Among these strategies, reductive lignin depolymerization, i.e. hydroprocessing, is one of the most widely studied routes nowadays to convert lignin and related model compounds. In this sense, approaches such as hydrodeoxygenation [21-23] or hydrogenolysis [24-31] under different solvent media have been studied to transform and/or remove functionality of lignin and model compounds to produce simpler but valuable chemicals [16,17].

Lignin polymeric structure is mainly based on aromatic rings linked to each other by means of C–O ether bonds and C–C bonds. Among them, β –O–4 linkages are the most abundant (up to 50% of total), followed by α –O–4 (12%) and 4–O–5 (8%) linkages (Fig. 1) [32,33].

Bearing in mind that C-C bonds are much more stable, and that upon dissociation of the C-O-C bonds the total amount of produced monomers will surpass that of dimers [18], selective depolymerization





of these linkages is of utmost importance for lignin valorization. In this sense, among the proposed alternatives to valorize lignin, catalytic depolymerization offers the possibility to cleave specific bonds in the lignin structure at high-rates. This process will generate oligomers and monomers, which can be further upgraded to fuels and chemical building blocks [17,34,35].

Since various factors can dramatically alter the structure and properties of lignin, including the source and isolation procedure for obtaining lignin, some recent studies have carried out hydrogenolysis of different types of lignin [36–44]. Moreover, in order to simplify the structural intricacy and variability of lignin, the use of lignin model compounds has been widely reported in the literature for hydroprocessing of lignin and lignin-derived streams. Phenol and phenolic compounds such as o-cresol (2-methylphenol) and guaiacol (2-methoxyphenol) have been widely selected as model compounds in studies related to thermal processing of lignin followed by catalytic upgrading via hydrodeoxygenation (HDO) [45–51]. Regarding hydrogenolysis, model compounds that have been typically selected to mimic characteristic linkages from lignin are aryl ethers, such as diphenyl ether (DPE), phenethyl phenyl ether (PPE), and benzyl phenyl ether (BPE) [32,52–58].³

In this scenario, it was considered of interest to study the performance of several catalytic materials using model compounds of relevant ether bonds in lignin structure (BPE, DPE and PPE). As commented before, the rupture of such bonds is crucial for lignin valorization, not only to reduce over-saturation of the aromatic ring, but also to increase the yield of depolymerization products. Thus, the present work investigates how product distribution and selectivity towards the cleavage of the different C–O bonds is affected by the characteristics of metal catalyst and support (*i.e.* metal oxides and carbon-based materials) together with the nature of the molecular structure of the selected model compounds. One of the most promising catalytic material (5 wt.% Ru/C) was tested as catalyst for the depolymerization of a real lignin stream (lignin-containing stillage obtained from 2G bioethanol plants).

2. Experimental

Materials and methods. Diphenyl Ether (DPE) was purchased from ACROS Organics (Phenyl Ether, 99%) whereas benzyl Phenyl Ether (BPE) was purchased from Sigma-Aldrich (Benzyl Phenyl Ether, 98%) and from ACROS Organics (Benzyl Phenyl Ether, 98%). Phenethyl Phenyl Ether (PPE) was synthesized according to the procedure detailed in the synthetic procedures subsection. Methanol used to prepare the stock solutions of the three model compounds was provided by VWR (Methanol GPR RECTAPUR, ≥99.5%). Ni precursor was purchased from ACROS Organics (Ni(NO₃)₂·6H₂O, 99%) and Ru and Pd precursors from Sigma Aldrich (RuCl₃, 45-55% Ru content and PdCl₂, Reagent plus[°], 99%). HCl used to prepare the solution to dissolve PdCl₂ was obtained from Sigma Aldrich (Hydrochloric acid, ACS reagent, 37%). In addition, the following supporting materials were used in this study without further purification: activated carbon (Activated Charcoal DARCO[°], ~100 mesh particle size, Sigma-Aldrich), titanium oxide (TiO₂-P25, Evonik), zirconium oxide (ZrO₂, Sigma-Aldrich), aluminum oxide (Al₂O₃, Martinswer (Albemarle), COMPALOX AN/V-813, provided by Sasol), purified multiwall carbon nanotubes (MWCNT-purified, kindly provided by SouthWest NanoTechnologies) and multiwall carbon nanotubes partially purified (MWCNT41, 41% content of SiO₂, also provided by SouthWest NanoTechnologies).

2.1. Experimental installation and procedures

Liquid-phase batch catalytic tests for hydroprocessing of BPE, PPE and DPE were carried out in a high-pressure stainless steel autoclave reactor (Berghof Highpreactor[™] High-Pressure Laboratory Reactor BR100), equipped with a 50-mL teflon liner, a pressure transducer or two manometers (one for pressures up to 10 bar, the other for pressures up to 250 bar), a stainless steel deposit for liquids, a thermocouple connected to a temperature controller, and a magnetic stirrer. Fig. S6 shows a scheme of the reaction system.

To carry out the catalytic runs, firstly, three stock solutions were prepared, one for each model compound, dissolving the necessary amount of BPE, DPE or PPE in methanol, in order to obtain solutions with a concentration of the corresponding model compound equal to 16 mM.

Prior to reaction, 70 mg of the desired catalyst were heated up to 250 °C (Ru catalysts), 400 °C (Ni-based catalysts except Ni/Al₂O₃), 650 °C (Ni/Al₂O₃), or 190 °C (Pd catalysts), for 1 h and under 15 mL/ min of H_2 in a tubular quartz reactor. Once the target temperature was reached for each case, the catalyst was reduced in situ at these conditions for 3 h. Then, the catalysts were passivated in an air flow (15 mL/min) at room temperature for 30 min. After this, 50 mg of the selected catalyst together with a magnetic stirrer were placed inside the 50 mL Teflon liner, the stainless-steel batch reactor was sealed, and a leak test was carried out at 50 bar-g in N2 atmosphere. Then the reactor was flushed 3 times with pure H2 in order to remove any remaining N2 from the leak test and after this the reactor was pressurized up to 7-8 bar-g using H₂. The reaction system was heated up to the desired temperature (150 °C) with a heating rate of approximately 1.5 °C/min and, once the target temperature was achieved, the system was maintained at this temperature and pressure for 30 min to activate the catalyst.

Afterwards, 20 mL of stock solution of the desired model compound were placed into the liquid's vessel of the reactor, which was subsequently pressurized to 25 bar-g using H₂. The discharge valve of the vessel was opened and the solution together with H₂ were introduced into the reactor. The latter procedure was repeated until the pressure inside the reactor vessel reached 25 bar-g and after this, a stirring speed of 750 rpm was set. At this moment, reaction time was set to zero. After two hours of reaction, the heating and stirring were stopped and the reactor was cooled down in an ice-cooled bath. When the reactor temperature was below 20 °C it was carefully depressurized.

Liquid products were filtered and analyzed using gas chromatography. The products obtained after reaction were analyzed by GC–MS for identification (Agilent 7890 GC-system, model G3440A, equipped with a 5975C mass spectrometer detector. Column: Agilent HP5-ms, 0.250 mm inner diameter, 30 m long, 0.25 μ m film thickness) and by GC-FID for quantification (Agilent 7890 GC-system, model G3440A, equipped with a 5975C flame ionization detector. Column: Agilent HP5, 0.320 mm inner diameter, 30 m long, 0.25 μ m film thickness).

After identification of the products, the sample was injected in the GC-FID system to quantify the obtained products with the aid of calibration curves previously prepared. Each curve contained eight concentration levels, from 1.2 mM to 50 mM, and response factors for each compound were obtained by adjusting the areas obtained at each concentration level, assuming that for concentration equal to 0 mM the response area will be 0 as well. Concentration levels were prepared by producing first a stock solution with a concentration 50 mM for each of the calibrated compounds in methanol, and diluting selected volumes of this solution to obtain the rest of concentrations. Each solution was injected three times, and the mean value of the obtained areas was calculated and used for fitting the curve.

Hydroprocessing of model compounds yielded some chemicals that could not be calibrated due to either their toxicity (*i. e.* benzene) or not being commercially available. In this sense, response factors for these non-calibrated compounds were approximated to those of the most similar compounds calibrated. Calibrated compounds included the three model compounds of ether bonds (BPE, PPE and DPE), toluene (99.9% purity, Sigma-Aldrich), ethyl benzene (99.8% purity, ACROS Organics), phenol (99% purity, ACROS Organics), benzyl alcohol (minimum purity 99.0%, Sigma-Aldrich), cyclohexane (minimum purity 99%, Sigma-Aldrich), methylcyclohexane (minimum purity 98.0%, Sigma-Aldrich), cyclohexanol (98% purity, ACROS Organics), 2-phenylethanol (minimum purity 99%, Sigma-Aldrich), cyclohexylphenyl ether (95% purity, Sigma-Aldrich), and cyclohexanone (minimum purity 99.5%, Sigma-Aldrich).

Once the concentration of each product before (in the case of the model compounds) and after reaction was calculated according to calibration curves, the yield to each product was determined. As several reactions were taking place at the same time (hydrogenation of the dimer, hydrogenolysis, etc.) conversion, selectivity and yields were calculated on a molar C basis. The defined equation for each parameter can be seen below (Eqs. (1)-(3)).

$$\% Conversion = \frac{mol \ C \ of \ Dimer_0 - mol \ C \ of \ Dimer_f}{mol \ C \ of \ Dimer_0} \cdot 100$$
(1)

$$S_A = \frac{mol \ C \ of \ product \ A}{Total \ mol \ C \ of \ products}$$
(2)

$$Y_A(\%) = S_A \cdot Conversion(\%) \tag{3}$$

where;

- mol C of dimer₀: the moles of carbons in the form of BPE, PPE or DPE in the solution before reaction.
- mol C of dimer: the moles of carbon in the form of BPE, PPE or DPE in the solution after reaction.
- SA: selectivity to product A, i. e. toluene.
- Total mol C of products: the sum of the moles of carbon of all the products detected by GC-FID.
- Y_A: yield to product A.

In addition, to ease comparison, some results were presented in the form of yield to four families of compounds: aromatic monomers, saturated monomers, partially saturated dimers and fully saturated dimers.

2.2. Catalyst preparation

Catalysts were prepared using aqueous solutions of Ru, Ni and Pd metal salt precursors for impregnation onto the selected supports. Materials acting as supports of the desired metals were either commercial supports or materials synthesized or modified in the laboratory. Commercial supports have been presented in the materials subsection. In addition, the following supports were prepared in the laboratory: titanium oxide, zirconium oxide, and TiO₂/C (see *Supplementary Information* for details on preparation methods).

Ru catalysts (supported on active carbon, Al_2O_3 , ZrO_2 commercial and from laboratory, TiO_2 commercial and from laboratory, and $TiO_2/$ C) were synthesized by excess impregnation. The necessary amounts of Ru precursor salt were weighed and dissolved in the corresponding volume of deionized water to produce a catalyst with a content of the active metal equal to 5 wt.% in the final solid, following the proportion of 500 mL of water for 0.54 g of RuCl₃. The solution of the precursor in water was stirred at room temperature using a magnetic stirrer, until complete dissolution of the salt. Once the solution of RuCl₃ was homogeneous, the desired amount of support was added to the solution and the mixture was maintained under stirring overnight. Afterwards, the solution was heated to evaporate the water, and the solid obtained was dried in an oven at 100 °C overnight.

Ru/MWCNT catalyst was synthesized by incipient wetness impregnation. A certain amount of the precursor salt (RuCl₃) was dissolved in a certain amount of a 1:1 (v/v) mixture of methanol and deionized water, in order to obtain a solution that allowed producing a catalyst with a 5 wt.% of the active metal in the final solid. The solution was impregnated into the desired support and then the catalyst was dried overnight at 100 °C in an oven.

Ni catalysts were synthesized by incipient wetness impregnation.

The precursor nitrate salt was dissolved in a certain amount of deionized water (approximately equal to the pore volume of the support (measured with water)), to obtain a solution that allowed producing a catalyst with a 5 wt.% of the active metal in the final solid. The solution was impregnated onto the desired support and then the catalyst was dried overnight at 100 $^{\circ}$ C in an oven.

Pd catalysts were also synthesized by incipient wetness impregnation. The precursor salt was dissolved in the necessary amount of deionized water to fill the pore volume of the support, though in this case, a few droplets (3–5) of a 0.2 M hydrochloric acid solution were added to the deionized water in order to facilitate the dissolution of the palladium salt. The resulting solution was impregnated onto the desired support and then the catalyst was dried overnight at 100 °C in an oven.

After impregnation and drying in an oven overnight, the catalysts were calcined as follows. In the case of samples including Al_2O_3 , ZrO_2 , and TiO_2 as supports, the prepared catalysts were calcined in a muffle furnace in air atmosphere, with a temperature ramp of 3 °C/min up to 400 °C, and maintained at such temperature for 4 h. On the other hand, when active carbon, MWCNT-purified, MWCNT41, or TiO_2/C were used as supports, the calcination of the catalysts was carried out in a tubular quartz reactor, with a vertical flow of nitrogen of 20 N mL/min. A temperature ramp of 3 °C/min was set to reach 400 °C and then the solid was maintained at this temperature for 4 h under nitrogen flux.

2.3. Catalyst characterization

Textural properties of some of these catalysts were analyzed by some of the following techniques: temperature programmed reduction (TPR), high resolution transmission electron microscopy (HRTEM), nitrogen adsorption isotherms, and X-ray photoelectron spectroscopy (XPS).

Temperature programmed reduction (TPR) analyses were carried out in a Micromeritics Chemisorption Analyzer (AutoChem II), equipped with TCD detectors. Samples were heated at 10 °C/min from room temperature to 800 °C or 900 °C, while a stream of 50 mL/min of 10% H₂-Ar mixture circulated through the system. High resolution TEM images were acquired in a Tecnai F30 (FEI company) high resolution Transmission Electron Microscope that can work in either TEM or STEM (Scanning-Transmission) modes. The working voltages in this microscope are 200 and 300 kV. Isotherms were determined in an ASAP 2020 system (Micromeritics). Prior to the analyses, samples were degasified under vacuum applying a temperature program (10 °C/min ramp from room temperature to 200 °C, holding the latter temperature during 360 min). N₂-adsorption was carried out at 77 K by dosing growing amounts of N2 to cover the whole relative pressures interval, until reaching a point close to saturation ($P/P_0 = 0.995$). Then vacuum was applied to progressively reduce pressure, producing desorption of the gas. Surface area was estimated using the Brunauer-Emmett-Teller (BET) model, applied to the adsorption branch at the selected partial pressures range for each catalyst, thus capillary condensation in mesopores was avoided. The samples analyzed by X-ray photoelectron spectroscopy (XPS) included 5% Ru/C, 5% Ru/Al₂O₃, 5% Ni/C, 5% Ni/ Al₂O₃, 5% Pd/C, and 5% Pd/Al₂O₃. All these powder materials needed to be compacted before being introduced in the XPS equipment. Given the impossibility of compacting active carbon-supported materials, they were mixed with calcined Al₂O₃ (the same used as support for the other catalysts), in a 1:1 proportion (C-based catalyst: Al₂O₃). XPS analyses were carried out in a PHOIBOS HSA3500 150 R6 spectrometer, with Al as source (250 W). Spectra were calibrated by using the C 1s peak at 284.6 eV. Analyses were first carried out on fresh samples, which were then treated under H₂ and temperature for 1 h, acquiring the corresponding spectra afterwards. Pd/C and Pd/Al₂O₃ were treated at 190 °C, Ru/C and Ru/Al₂O₃ at 250 °C, Ni/C at 400 °C and Ni/Al₂O₃ at 600 °C, as the latter was the maximum temperature allowed by the equipment. The binding energies of Ru $3p_{3/2}$, Ni $2p_{3/2}$, and Pd $3d_{5/2}$ have been studied and compared for the different catalysts before and

Table 1

Characterization results of particle size, metal dispersion, BET surface area and XPS binding energies (before and after reduction in hydrogen) of the selected catalysts.

Catalyst	BET surface area d dx(m ² /g)	HRTEM	
		d _{mean} (nm)	D(%)
5% Ru/C	814.4	4	21.6
5% Ru/MWCNT	300.9	2	46.1
5% Ru/Al ₂ O ₃	231.1	52	1.7
5% Pd/C	858.6	3	24.9
5% Pd/Al ₂ O ₃	217.3	8	9.7
5% Ni/C	861.1	5	18.7
5% Ni/MWCNT	259.8	n/a	n/a
5% Ni/Al ₂ O ₃	235.5	62	1.4

after the H₂ treatment (Table 1).

2.4. Synthetic procedures

PPE was synthesized in the laboratory according to the procedure described by Rensel et al. [59] Concisely, 4 g of phenol (99% purity, ACROS Organics) were added to a round bottom flask together with 6 g of K₂CO₃ (99% minimum purity, ACROS Organics) and 33 mL of anhydrous acetone (synthesis grade, Fisher Chemical). Then, after 1 h of reflux, 11 g of anhydrous (2-bromethyl)-benzene (Sigma Aldrich) were added to the mixture. After 24 h of reaction, 25 mL of ethyl ether and 25 mL of water were added. Ethyl acetate (99.8% purity, Sigma Aldrich) was used to extract the organic compounds, which were washed three times with a solution 1 M of sodium hydroxide (NaOH, reagent grade, 98% minimum purity, Sigma Aldrich) and another 1 M of sodium chloride (NaCl, 99.5%, ACROS Organics). Then, the ethyl acetate phase was evaporated in a rotary evaporator until only styrene, phenol and phenethyl phenyl ether were left. The desired compound (PPE) was separated by flash chromatography using a mixture of hexane and ethyl acetate as eluent.

2.5. Depolymerization of 2G lignin

Catalytic depolymerization of the stillage cake was carried out in the same installation described for hydrodeoxygenation of the lignin model compounds. The catalyst used for this preliminary test was 5% Ru/C, described in the *Catalyst preparation section*.

To carry out 2D NMR (HSQC-2D) analyses, ligninic samples were acetylated following this procedure: the acetylation process was carried out in an acetic anhydride/pyridine solution (1:1, v/v) stirred at room temperature for 48 h. 1 mL of solution was used for every 50 mg of ligninic sample. After acetylation, the reaction mixture was concentrated under vacuum, the crude residue was dissolved in dimethyl sulfoxide (DMSO, 99.5% minimum purity (GC), plant cell culture tested, Sigma-Aldrich), centrifuged and then the acetylated lignin dissolved in DMSO was recovered and finally lyophilized. The product obtained after lyophilization was dissolved in deuterated dimethyl sulfoxide (DMSO-d6, "100%", 99.96 atom% D, Sigma-Aldrich) to perform HSQC-2D analyses.

NMR spectra were run in DMSO-d6 on acetylated samples, to avoid fractionation of the material before NMR analysis and to increase both the solubility and the chemical shift dispersion of the side chain units. The inverse detected $^{1}H^{-13}C$ correlation spectra (HSQC) were measured at 25 °C on a Bruker AVANCE III 700 MHz instrument equipped with a cryogenically cooled 5mmTCI gradient probe with inverse geometry (proton coils closest to the sample). HSQC experiments used Bruker's "hsqcetgpsisp2.2" pulse program (adiabatic-pulsed version) with spectral widths of 5000 Hz (from 10 to 0 ppm) and 20,843 Hz (from 165 to 0 ppm) for the 1H- and 13C dimensions. The number of collected complex points was 2048 for the 1H-dimension with a recycle delay of 1.5 s. The number of transients was 64, and 256 time increments were



Fig. 2. Model compounds for ether bonds in lignin: BPE (α -O-4), PPE (β -O-4), and DPE (4-O-5).

always recorded in the 13C dimension. The 1JCH used was 145 Hz. Processing used typical matched Gaussian apodization in the 1H dimension and squared cosine-bell apodization in the 13C dimension. Prior to Fourier transformation, the data matrixes were zero-filled up to 1024 points in the 13C-dimension. The central solvent peak was used as an internal reference (δ C 39.5; δ H 2.49). Long range J-coupling evolution times of 66 and 80 ms were used in different heteronuclear multiple bond correlation (HMBC) acquisition experiments. As 2G lignin was obtained from the stillage of 2nd generation bioethanol production from corn stover, HSQC correlation peaks were assigned mainly by comparing with Min et al. [60] study on the structural changes of lignin and lignin-carbohydrate complexes in corn stover, though other references were also considered [61,62].

3. Results and discussion

BPE, DPE and PPE (Fig. 2) have been chosen as the model compounds of the most abundant lignin linkages, β –O–4, α –O–4 and 4–O–5, respectively, (Fig. 1) to perform the hydroprocessing studies over Ru, Ni and Pd catalysts.

3.1. Catalyst screening

Firstly, several catalysts were tested for the hydroprocessing of benzyl phenyl ether (BPE). BPE was selected as the benchmark model compound to test the catalytic activity of several materials for two main reasons: being commercially available (when compared to PPE) and having a lower energy of C–O bond dissociation [32] (when compared to PPE and DPE). A total of nineteen catalysts were tested for this purpose, with Ru, Ni and Pd selected as active metals. Supporting materials included: active carbon, multiwall carbon nanotubes, Al₂O₃, ZrO₂, TiO₂ and TiO₂/C. Reactions were carried out at the following conditions: 150 °C, 2 h of reaction, 25 bar-g of H₂, 20 mL of stock solution (16 mM, BPE in methanol) and 750 rpm (RCF = 4.55 ·g). After this screening, the most promising catalysts were selected to be further tested in the hydroprocessing of phenethyl phenyl ether (PPE) and diphenyl ether (DPE).

Fig. 3 shows the possible reaction pathways in the hydroprocessing of BPE in methanol. As it can be observed, the BPE molecule can undergo hydrogenation of one of the rings until the complete saturation of the dimer (steps 1, 2, 5 and 8); a cleavage of the partiallyhydrogenated dimers into the corresponding monomers (steps 6, 7, 9 and 10) and subsequent hydrogenation of those (steps 11 and 14-17); or the direct cleavage of the C-O-C bond to the corresponding monomers and subsequent hydrogenation of those (steps 3, 4 and 11-17). The main products observed after reaction of BPE (identified by GC-MS) are shown in Fig. S1. Compounds originated from both the hydrogenolysis of the C-O bonds and the hydrogenation of the dimer were observed. In addition, it was observed that, depending on the catalyst used, aromatic monomers produced from the hydrogenolysis of the C-O bonds underwent further hydrogenation. Regarding cyclohexanone, the currently discussed pathways [63] suggest that, using similar catalysts as the ones selected here and in the liquid phase, phenol hydrogenates sequentially. First, phenol hydrogenates to cyclohexanone, and then cyclohexanone is further hydrogenated to cyclohexanol, therefore explaining the presence of both products in the mixture after reaction [64]. In addition, methoxycyclohexane and 1,1dimethoxycyclohexane were also detected as products. They were generated due to the acetalyzation of cyclohexanone with methanol, which has been reported in the presence of a solid acid catalyst [48,65]. Consequently, both compounds have been considered as cyclohexanone in carbon mass balances and for yield calculations, *i.e.* 6 carbons instead of 7 or 8, as the extra carbons come from the reaction solvent (methanol).

Results for each tested catalyst are presented in Fig. 4 in terms of conversion of BPE and yield. To ease the comparison between catalysts, the different products were grouped in four families of molecules. These four families included: fully saturated dimers (FSD), partially saturated dimers (PSD), saturated monomers (SM), and aromatic monomers (AM). Taking as reference Fig. S1, the first line of compounds (toluene, phenol and phenylmethanol) was considered under the group of aromatic monomers (AM). The saturated monomers included cyclohexanone, cyclohexanol, methylcyclohexane, cyclohexane, Finally, (cyclohexylmethoxy)-benzene and [(cyclohexyloxy)methyl]benzene were the partially saturated dimers (PSD) and (cyclohexylmethoxy)-cyclohexane was the fully saturated dimer (FSD).

Based on the activity and product yield values obtained in this screening study, the following catalysts were selected to carry out further catalytic tests with PPE and DPE:

- 5% Pd/C, due to its high activity (100% conversion in 2 h) and also high selectivity to aromatics, as the yield to aromatic monomers was over 90%.
- 5% Ru/C. A high conversion value was also obtained with this catalyst, though the yield to aromatic monomers was lower than that obtained with 5% Pd/C. Nevertheless, the energy of C–O bond dissociation is greater for PPE and DPE and thus it was interesting to keep this catalyst as candidate to further evaluate its performance.
- 5% Ru/Al₂O₃ and 5% Ru/MWCNT. These two materials present similar conversion levels, but the yield to aromatics was greater with 5% Ru/Al₂O₃. Although the conversion achieved with them was lower than with the previous ones, they presented a notable ratio between AM and the rest of products.
- 5% Ni/C and 5% Pd/Al₂O₃. They attained a considerable level of conversion, bearing in mind the change of active metal from Ru, but more importantly, their selectivity to aromatic monomers was high. None or almost negligible yield to saturated products was observed, either to the saturated monomer family or to any of the saturated dimers.
- 5% Ni/MWCNT and 5% Ni/Al₂O₃, in order to compare the effect of changing the active metal while keeping the same support (Ni/ MWCNT versus Ru/MWCNT and Ni/Al₂O₃ versus Ru/Al₂O₃ or Pd/ Al₂O₃).

The rest of catalysts were discarded for further experiments with model compounds. For some of them, the observed conversions were significantly low (5% Ni/ZrO₂ comm, 5% Ni/TiO₂/C or Ru/TiO₂ lab). For others, better results regarding yield and/or conversion were observed when using the same active metal in a different support. Therefore, from the 19 catalysts screened in the hydroprocessing of BPE, 8 were finally selected to be tested with the model compounds of the other two ether bonds in lignin. These were: 5% Pd/C, 5% Ru/C, 5% Ru/Al₂O₃, 5% Ru/MWCNT, 5% Ni/C, 5% Pd/Al₂O₃, 5% Ni/MWCNT and 5% Ni/Al₂O₃.

3.2. Hydroprocessing of model compounds (BPE, PPE and DPE)

Fig. 5 presents the results obtained with each of the 8 selected catalysts after reaction with PPE and DPE. In addition, results obtained with the same catalysts in the hydroprocessing reaction of BPE are also included for comparison. The average mass balance closure for the presented experiments was 93 \pm 3%, which is assumed as acceptable.



Fig. 3. Proposed reaction network for hydroprocessing of BPE in methanol.



Fig. 4. Yields to families of compounds for the catalysts used in the initial screening. Reaction conditions: 150 °C, 2 h of reaction, 25 bar-g of H₂ and 16 mM of BPE. FSD: fully saturated dimers; PSD: partially saturated dimers, SM: saturated monomers; AM: aromatic monomers.

The calculated standard deviation of the experiments was bellow 5% for the model compounds studies.

Deviations may be a consequence of two factors: the presence of compounds which cannot be quantified due to their concentration being under the detection limit of the GC-FID system; or to errors in the calculations derived from the use of response factors estimated by correlating the structure of the unknown compound with commercially available standards [66].

Figs. 6 and 7 show the proposed reaction networks in the hydroprocessing of PPE and DPE, respectively. Figs. S2 and S3 show the products identified by GC–MS after catalytic reaction of PPE and DPE, respectively. Similar to the reported mechanism for BPE, observed products can be related to the hydrogenolysis of the C–O–Ar bonds (in the form of aromatic or saturated monomers) or to the hydrogenation of the dimer (PPE or DPE in this case). In addition, after reaction of PPE and DPE, cyclohexanone, methoxycyclohexane and 1,1-dimethoxycyclohexane were also observed. The same explanation applies as the one for the case of reaction with BPE for the presence of these compounds.

According to the results presented in Fig. 5, some general conclusions can be drawn regarding the effect of the type of ether linkage processed, the effect of the active metal and the effect of the support on the conversion levels and on the product distribution. When comparing the energy values of the bonds of the three selected model compounds (BPE, PPE and DPE), it can be noted that the most labile bond is the



Fig. 5. Conversion and yield to families of compounds after reaction of (a) BPE, (b) PPE and (c) DPE. Conditions: 150 °C, 2 h of reaction, 25 bar of H₂, 16 mM of model compound and RCF = 4.55 g.



Fig. 6. Proposed reaction network for hydroprocessing of PPE in methanol.



Fig. 7. Proposed reaction network for hydroprocessing of DPE in methanol.

 α –O–4 (BPE, 218 kJ/mol), as commented before, followed in terms of energy by β -O-4 and 4-O-5 linkages (PPE, and DPE, 289 and 314 kJ/mol, respectively) [32]. In general, it was observed that, for any given catalyst, the achieved conversion level (keeping constant the rest of operating parameters) decreases from BPE to PPE to DPE. Taking Pd/C as example, a conversion of ca. 100% was obtained in reaction with BPE. The conversion value decreased to approximately 50% for PPE, and finally the obtained conversion of DPE was 19.3%. In fact, the three catalysts selected from the screening that produced the lowest conversions of BPE, i.e. Pd/Al₂O₃, Ni/MWCNT and Ni/Al₂O₃, were not able to convert neither PPE nor DPE under the studied conditions. This can be clearly connected to the aforesaid bonding energy of the different model compounds. Thus, the dimer with the most labile linkage $(\alpha - O - 4)$ was the one to undergo the greatest conversion. Conversely, the conversion of the dimer with the strongest 4-O-5 bond was the lowest.

Regarding the product distribution, it can be observed that it differed from one model compound to another. Looking at the results obtained with Ru/C for the three model compounds, in the case of BPE

the yield to aromatic monomers was around 53%, leaving the rest of the products to fully saturated monomers (26% of yield) and partially saturated dimers (19% of yield). For PPE, though the conversion of the model compound was within the same range, the distribution to the product families was different: 59% of the obtained products corresponded to fully saturated monomers whereas aromatic monomers represented only 20% of the final products. The remaining products from PPE conversion were distributed as follows: 3% were partially saturated dimers and 18% were fully saturated dimers. Finally, in the case of carrying out the reaction with DPE as model compound, it can be seen that the main products obtained were aromatic monomers (37% of yield), followed by partially hydrogenated dimers (18%), fully hydrogenated monomers (4.8%) and fully hydrogenated dimers (1%). On one hand, the higher C-O energy bond dissociation for DPE may explain why the total yield to monomers, both aromatic and saturated, is lower (nearly 42%) than that obtained with BPE and PPE. On the other hand, the results also seem to indicate that the reaction mechanism varies from one compound to another, therefore changing the distribution of products. For example, for PPE it seems that hydrogenation of the dimer and hydrogenolysis of the C-O bond are competing pathways, whereas for BPE it seems that the hydrogenolysis of the α -O-4 ether bond is more important than dimer hydrogenation. It is also interesting to notice that if selectivity to fully and partially saturated dimers is calculated, an increase in the sum of both selectivities can be observed when changing from BPE to PPE and to DPE for some catalysts. Following the same Ru/C example, selectivity to fully or partially saturated dimers was 18% when the model compound was BPE. In contrast, selectivity to these families was 21% after PPE reaction, and increased up to 31% for DPE. The latter tendency was observed for reactions with all active carbon-supported catalysts. In addition, in the case of Ru/Al2O3 and Ru/MWCNT, selectivity to fully or partially saturated monomers increased from BPE to PPE, but then decreased from PPE to DPE, in contrast with the observed behavior in active carbon-supported catalysts.

These results seem to indicate that conversion and product distribution to the different families is dependent on the type of ether compound but also on the nature of the catalyst. In this sense, it was observed that, for any of the tested catalyst and under the same reaction conditions, achieved conversion of the model compounds decreased as follows: BPE > PPE > DPE. Interestingly, the energy necessary for scission of the C–O bond increases as BPE < PPE < DPE. In addition, for those catalysts with active carbon as support, the selectivity to saturated dimers increased in the order BPE < PPE < DPE. Thus, it can be said that, when the catalyst was not able to quickly break the C–O–C bond, saturation of the rings of the dimers gained importance. Nevertheless, the absence of the latter behavior when using Ru/Al₂O₃ or Ru/MWCNT as catalysts seems to indicate that product distribution is also affected by the nature of the selected support. A possible explanation might be that the way in which each dimer is absorbed on the catalyst surface varies, depending on the dimer itself, but also on the characteristics of the catalyst surface (metal particle size, support affinity, etc.), which will be discussed in depth later.

Regarding the effect of the active metal, when comparing the results obtained for the same model compound, operating conditions and catalyst support, it can be observed that conversion of dimers decreased from Ru to Pd and to Ni. Interestingly, this decrease in conversion caused also an increase in the selectivities to aromatic monomers. For example, if reaction results of PPE hydroprocessing over Ru/C, Pd/C and Ni/C were compared, it could be observed that conversion decreased in the order Ru/C (100%) > Pd/C (50%) > Ni/C (18%) while selectivity to aromatic monomers increased as Ru/C (20%) < Pd/C (30%) < Ni/C (75%). In this sense, Zhang et al. [67] reported the hydrogenolysis of 2-phenoxy-1-phenylethan-1-ol using unsupported NiM (M = Ru, Rh and Pd) catalysts. When studying the reaction on monometallic catalysts (Ru, Pd, and Ni) it was observed that noble metals (Ru and Pd) achieved higher conversions (ca. 100%) but with low selectivity to monomers (0.3 and 2.3% for Ru and Pd, respectively), whereas only 30% of conversion was obtained with monometallic Ni, but with a 57% of selectivity towards aromatic monomers.

3.3. Catalysts characterization

The results seem to indicate that the characteristics of the selected catalysts highly influenced the obtained product distributions. Different techniques, such as BET surface area, temperature programmed reduction (TPR), high-resolution transmission electron microscopy (HRTEM) and X-ray photoelectron spectroscopy (XPS) were used to characterize the catalysts.

3.3.1. N₂-physisorption

The surface topology of the different catalysts was characterized using nitrogen physisorption. The Brunauer–Emmett–Teller (BET) theory was employed to fit the N₂-physisorption isotherms obtained for the different catalysts and determine the surface area (see Table 1). As expected, catalysts supported on active carbon had the highest surface areas, with values around 800–860 m²/g, followed by those obtained using carbon nanotubes, that ranged between 200 and 300 m^2 /g. It is also remarkable the relatively high surface area obtained on the alumina-supported catalysts, which had surfaces areas around 215–230 m²/g in all the cases.

3.3.2. High-resolution transmission electron microscopy (HR-TEM)

Table 1 also summarizes the average particle size values of Ru, Ni and Pd in the analyzed catalysts by HRTEM, as well as the metal dispersion value. The procedure used for the metal dispersion calculation can be found in the *Supplementary Information* (Table S1). From the images of HRTEM of Ru catalysts (Fig. 8), it can be observed that Ru particles are homogeneously dispersed and present smaller particle size (2–4 nm) when they are supported in carbonaceous materials (active carbon and multiwall carbon nanotubes) than when the support is Al₂O₃ (~50 nm). When Ru is supported in the latter material, the average particle size is greater and particles tend to agglomerate in regions of the support, rather than being dispersed along the entire surface. In addition, it was observed that the active carbon selected as support contained other elements as impurities, such as Fe, Cu, S and Ca. From Fig. S4, a similar tendency can be noticed when comparing Ni and Pd catalysts supported on active carbon and Al₂O₃. Roughly, when Ni or Pd were supported on active carbon, particle size was smaller (3-5 nm, Table 1) than that observed for each metal on Al₂O₃ (~60 nm). Therefore, the metal dispersion highly decreases for the three metals when changing the support to Al₂O₃ (Table 1). The metal dispersion values for Al₂O₃ supported catalysts are lower than 2% for Ru and Ni, and almost 10% for Pd. However, when supported on active carbon, the dispersion increases to over 20%, and reaches a value of ~47% for Ru/MWCNT catalyst. Moreover, the tendency of metal particles to agglomerate when the support was Al₂O₃ could also be detected. Finally, HRTEM images for 5% Ni/Al₂O₃ where much more difficult to interpret than the rest. Ni particles were difficult to identify due to low contrast of the obtained images, which complicated the calculation of the mean particle size of this catalyst. This parameter was nevertheless calculated using the particles more clearly identified, to reasonably compare the value with those of the rest of the catalysts.

3.3.3. Temeprature programmed reduction (TPR)

Fig. 9 shows the TPR profiles of Ru and Ni catalysts supported on Al₂O₃, active carbon and MWCNT. Ru main reduction peaks were observed at varying temperatures depending on the support. For Ru/ Al₂O₃, the main reduction peak appeared at 208 °C and could be assigned to the reduction of Ru oxides [68]. A second peak was observed at ca. 532 °C, which could be the consequence of the reduction of bulk Ru atoms having stronger interaction with the Al₂O₃ support [69]. Ru/MWCNT profile showed a peak at 98 °C with a shoulder at 149 °C, and a wide peak at around 606 °C. The first two peaks might be matched to the reduction of ruthenium, as reported elsewhere [70,71]. Moreover, the reduction of surface oxygen complexes (incorporated as a consequence of the purification process of CNT) has been observed from 397 to 997 °C, thus explaining the wide peak observed with the maximum at 606 °C [72]. Finally, Ru/C presented a double peak with maximums at 171 and 244 °C which could be attributed to the reduction of RuO_v species and also to the reduction of bulk RuCl₃ [73]. The broad peak with maximum at 512 °C was attributed to the partial gasification of the carbonaceous support [74,75].

Likewise, the TPR profiles of Ni-based catalysts showed different reduction peaks depending on the supporting material. For the Ni/ Al₂O₃ sample, a small peak at 435 °C was observed, together with a wider peak with maximum at 651 °C and a shoulder at ca. 737 °C. The peak at the lowest temperature could be attributed to the reduction of NiO species with weak interaction with the support [76]. The peak at 651 °C could be connected to the reduction of non-stoichiometric nickel aluminate species [76], and the shoulder at 737 °C could be related to the reduction of NiO surface species with strong interaction with the support [77] and to the partial reduction of the NiAl₂O₄ spinel [78]. For the peak at 510 °C in the Ni/MWCNT sample, highly dispersed NiO particles with strong interaction with the support have been reported to produce peaks in the 420-560 °C range [79], but also peaks at around 550 °C have been related to partial methanation of CNT [80]. Thus, the observed peak at 510 °C can be a consequence of both contributions. In addition, the small peak observed at ca. 99 °C in the TPR profile of Ni/ MWCNT could be connected to water desorption. MWCNT were not dried before performing the TPR analysis, thus it is possible that some water adsorbed in the material could have been desorbed upon heating, producing the observed signal. Finally, Ni/C TPR profile presented a sharp peak at 398 °C and a wide peak with maximum at 552 °C. The former might be connected to the reduction of NiO species with weak interaction with the support, whereas the second can be attributed to a mixture of the reduction of NiO species with stronger interaction with the support together with partial gasification of the carbonaceous support as seen with the Ru/C catalyst.

Focusing on the Ni-based catalysts, it was observed that overall conversion of any of the dimers and product distribution to the different families of compounds were different when the support was changed (Fig. 5). In the results obtained using BPE as model compound, it was observed that conversion decreased as follows: Ni/C > Ni/MWCNT >



Fig. 8. HRTEM images for (a) 5% Ru/C, (b) 5% Ru/Al₂O₃, and (c) 5% Ru/MWCNT.

Ni/Al₂O₃. According to the temperature programmed reduction (TPR) characterization results (Fig. 9), Ni supported on active carbon presented the reducible NiO species at the lowest temperature (~400 °C), which seems to indicate that, under the selected activation conditions, most of the nickel in the catalyst was in its metallic reduced form. In fact, XPS analyses (Table 1) showed that treating Ni/C in H₂ atmosphere at 400 °C was enough to convert NiO in metallic Ni. Similarly, TPR profile of Ni/MWCNT showed reduction peaks at higher temperatures (\sim 550 °C) than those for Ni/C, and finally XPS and TPR characterization of Ni/Al₂O₃ showed the presence of nickel aluminate and NiAl₂O₄ spinel, which are species difficult to reduce. This indicates that as the reducibility of the catalyst increases the conversion of the dimer is favored. It is also worth noting that, according to HRTEM results, metal particle size increased from 5 to 62 nm when comparing Ni/C and Ni/Al₂O₃ (Table 1, Fig. S4), which may indicate also the importance of the effect of metal particle size. One can assert that the lower activity of the Ni/Al₂O₃ catalysts compared to the C could be associated to lower metal dispersions and the formation of partially unreduced $\mathrm{Ni}^{\,+\,\delta}$ species and nickel aluminates that have a lower catalytic activity.

3.3.4. X-ray photoelectron spectroscopy (XPS)

The samples analyzed by X-ray photoelectron spectroscopy (XPS)

included 5% Ru/C, 5% Ru/Al₂O₃, 5% Ni/C, 5% Ni/Al₂O₃, 5% Pd/C, and 5% Pd/Al₂O₃. Analyses were first carried out on fresh samples, which were then treated under H₂ and temperature for 1 h, acquiring the corresponding spectra afterwards. Pd/C and Pd/Al₂O₃ were treated at 190 °C, Ru/C and Ru/Al₂O₃ at 250 °C, Ni/C at 400 °C and Ni/Al₂O₃ at 600 °C, as the latter was the maximum temperature allowed by the equipment. Binding energies of Ru $3p_{3/2}$, Ni $2p_{3/2}$, and Pd $3d_{5/2}$ have been studied and compared for the different catalysts before and after the H₂ treatment.

3.3.4.1. *Ru-based catalysts*. The Ru $3p_{3/2}$ binding energies (BE) at which maxima of the primary peaks were found before and after H₂ activation in Ru/C and Ru/Al₂O₃ spectra are collected in Table 2. Values at 463.15 and 462.07 eV for the Ru/C catalyst were attributed to RuO₂ and metallic Ru, respectively, by comparison with literature [81]. Therefore, it can be said that, under the selected H₂ treatment, RuO₂ was reduced to metallic Ru, which was assumed to be the active phase for the hydroprocessing of the lignin model compounds. According to Shen et al. [82], increasing oxidation of a Ru wafer surface caused the presence of a second peak (after deconvolution of $3p_{3/2}$ spectrum) at higher binding energies that grew with increasing oxidizing treatment. Such peak, that appeared at 465.0 eV was observed on Ru/Al₂O₃ after reduction in H₂, was attributed to RuO_x/Ru species. Literature



Fig. 9. TPR profile of the Ru and Ni selected catalysts.

Table 2

Binding energies of the metal-species obtained from X-ray photoelectron spectroscopy (XPS) before and after reduction in hydrogen.

Catalyst	XPS Binding energies (eV) (Ru 3p _{3/2} , Ni 2p _{3/2} , & Pd 3d _{3/2})		
	Before	After	
5% Ru/C	463.2	462.1	
5% Ru/MWCNT	n/a	n/a	
5% Ru/Al ₂ O ₃	466.3	465.5	
5% Pd/C	335.2	335.1	
5% Pd/Al ₂ O ₃	339.6	338.6	
5% Ni/C	855.1	852.1	
5% Ni/MWCNT	n/a	n/a	
5% Ni/Al ₂ O ₃	859.2	861.9	

regarding XPS spectra for the ruthenium 3p level is scarce when compared to available data for 3d level, which is the primary XPS region for this metal. Nevertheless, the spectra for this level presents strong overlapping with C 1s level, and thus it was considered that, given one of the samples was supported on carbon, elucidation of spectra would be complicated. In turn, reported binding energies (BE) for $3p_{3/2}$ level are mostly in the 460–464 eV range and a match for the peak at 466.25 eV in Ru/Al₂O₃ could not be found in literature. Thus, following the aforesaid discussion by Shen et al. [82] it was proposed that this peak corresponded to a mixture of RuO_x/Ru species, with a higher degree of oxidation than the peak observed after the H₂ treatment of the sample. These results seem to indicate that, under the selected pretreatment conditions (H₂ at 250 °C), oxidized ruthenium particles could not be completely reduced.

3.3.4.2. Ni-based catalysts. In the case of the Ni/C catalyst, analyzing the Ni $2p_{3/2}$ spectra, the peak having a maximum at a BE of 855.14 eV before the H₂ treatment of the catalyst was attributed to Ni²⁺ of NiO [83]. After H₂ activation of the catalyst at 400 °C, the maximum of the primary peak in the Ni $2p_{3/2}$ spectrum shifted to a BE of 852.05 eV,

which could correspond to metallic Ni [84,85]. The shift of the primary peaks BE found on Ni indicated that, under the selected activation conditions for this catalyst, NiO is reduced to metallic Ni. Concerning the Ni/Al₂O₃ catalyst, the Ni 2p_{3/2} spectrum revealed a primary peak having a maximum before H₂ treatment at a BE of 859.15 eV, which was attributed to NiO [86]. Interestingly, after the H₂ treatment, the corresponding BE for the maximum of the main Ni $2p_{\rm 3/2}$ peak increased to 861.90 eV, instead of decreasing. This could be a consequence of the formation of nickel aluminates. Formation of nickel aluminates after calcination at 623–673 K has been reported in the literature [87], and as discussed by Salagre et al. [88], the presence of such irreducible species was connected to the presence of peaks in the Ni 2p_{3/2} spectra at ca. 863 eV. Moreover, the formation of structures that imply strong metal-support interactions such as nickel aluminates or nickel silicates have been reported to cause a shift of O 1s binding energy to higher values [89]. In this sense, the maximum of the primary peak of the O 1s spectra for Ni/Al₂O₃ increases from BE of 534.15-536.63 eV when the sample is subjected to the H₂ treatment at 600 °C.

3.3.4.3. Pd-based catalysts. Pd/C catalyst presented BE energies for the maxima at 335.23 eV before the H₂ treatment and 335.15 eV after it. Such peaks have been attributed to Pd [90] and bulk Pd metal [91], respectively. In addition, a secondary peak corresponding to the $3d_{3/2}$ level with a maximum at BE of 341.02 eV was found. The presence of such peak together with a primary peak at BE values of 335.8 eV has also been attributed to Pd⁰ [92]. Thus, it could be concluded that the Pd in the fresh Pd/C catalyst sample was already present in its metallic form (Pd⁰) without needing further activation. Regarding the Pd/Al₂O₃ catalyst, the maxima of the Pd $3d_{5/2}$ primary peak before and after H₂ treatment moved to higher BE when the support was changed from active carbon to Al₂O₃, as observed in the cases of Ru- and Ni-based catalysts. The presence of surface Pd(OH)₄ was proposed in previous studies of Pd-based materials by XPS, reporting BE for the maxima of the peaks at around 338.5 eV [93], whereas other authors endorsed maxima found at BE of 338 eV in Pd 3d_{5/2} spectra to PdO₂ [94]. On the other hand, similarly to what was discussed previously for Ru- and Nibased samples, the shift in the BE of the maxima of the primary and secondary peaks toward lower values (the latter, corresponding to the $3d_{3/2}$ level, shifting from *ca*. 345.29 to *ca*. 343.70 eV) was observed for the Pd/Al₂O₃ sample after the H₂ treatment. This could be connected to the fact that surface Pd species would have less degree of interaction with the support because of the H₂ treatment, probably due to partial reduction of the surface Pd species. Considering the acidic nature of the medium in which the Pd/Al₂O₃ catalyst was prepared and the rather oxidizing conditions of the calcination carried out during its preparation, it could be concluded that the BE values of the maxima of the peaks obtained for the samples analyzed before and after the H₂ treatment could probably correspond to surface PdO₂ with certain degree of interaction with the Al₂O₃ support.

A more in-depth analysis of both spectra (including deconvolution of the secondary Pd 3d_{3/2} peaks at 345.29 and ca. 343.70 eV) revealed that this peak could actually be the sum of two peaks, one at lower BE values that could correspond to Pd⁰ and the other having the maximum at greater BEs, that could be attributed to Pd²⁺ species, in agreement with similar results found for other impregnated Pd/Al₂O₃ catalysts, which also reported the coexistence of surface Pd species with both electronic states [92]. Despite the use of different metal precursor and calcination conditions, the fraction of metallic Pd to Pd²⁺ was also low here, though the differences in the BE values of the different peak maxima, greater in this study, could be attributed to a stronger interaction of the Pd species with the support (Pd-Al₂O₃). Also, when analyzing the spectra of the Pd/Al₂O₃ sample before the hydrogen treatment it should also be noted that maxima of primary peaks at 339.2 and 339.9 eV have been previously reported for the presence of surface Pd(CN)₂ and K₂(PdCl₆) species [95]. Although it is not likely that these specific structures were present in the sample, it could also be

possible that the observed peak for $3d_{5/2}$ at 339.63 might be connected to some PdCl₂-related structures in the sample, as a consequence of the metallic precursor used to prepare the catalyst. It should also be noticed the presence in both reduced samples (Pd/C and Pd/Al₂O₃) of a secondary peak with a maximum at BE around 560 eV, corresponding to another region of the spectrum attributed to the Pd $3d_{3/2}$ level, which had previously been assigned to the existence of surface Pd⁰ [90].

XPS analyses for Ru/C and Ru/Al₂O₃ indicated that Ru was more easily reducible when supported on active carbon, in agreement with TPR results (Fig. 9). On the other hand, the TPR profile of Ru/MWCNT showed that reduction peaks were obtained at slightly lower temperatures than with Ru/C. In this case, the decrease in conversion from Ru/ C to Ru/MWCNT could have been caused by a fraction of the Ru particles being deposited inside of the MWCNT tubes and thus being less accessible to the dimers to react. Regarding Pd catalyst, XPS analyses (Table 1) revealed again that Pd was more difficult to reduce when supported on Al_2O_3 than on active carbon, shifting Pd $3d_{5/2}$ signal to higher binding energies. In the case of supporting Ru and Pd, differences in particle size were also observed when changing the supporting material. HRTEM images of Ru catalysts (Fig. 8) showed that Ru particle size (Table 1) increased from Ru/MWCNT (2 nm) to Ru/C (4 nm) and Ru/Al₂O₃ (52 nm). For Pd, when it was supported on C mean particle size was 3 nm, whereas this value increased to 8 nm when the supporting material was Al₂O₃ (Table 1, Fig. S4). Therefore, one could infer that, according to XPS, TPR and HRTEM characterization, Ru, Pd and Ni were more difficult to reduce when Al2O3 was selected as support than with carbonaceous materials due to the larger particle size and stronger metal-support interactions between the metals and Al₂O₃. This may explain the differences observed in product distribution when changing from one support to another.

3.4. Comparative analysis of the catalysts performance

To evaluate the overall performance of each catalyst considering the three model compounds, a weighting factor was defined. For each model compound, the catalyst that provided the highest AM/(SM + PSD + FSD) ratio was assigned with a 5, the one that provided the following ratio with 4 and then sequentially down to 1 for the catalyst yielding the lowest ratio. Then the three values assigned to each catalyst (one for each model compound) were added, obtaining the weighting values shown in Fig. 10. In this way, it is possible to identify the best catalyst for the three different types of C–O bonds. It was observed that the catalyst that provided the highest value of this factor was Ru/Al₂O₃, due to achieving medium values of production of aromatic monomers from the three dimers when compared to other catalysts. The following catalyst with the highest weighting factor was

(4)

Ni/C, as it provided an elevated concentration of aromatic monomers in the hydrogenolysis of BPE and PPE, but aromatic monomers were not observed when DPE was the model compound. Moreover, Pd/C also provided a high weighting factor, mostly due to the high selectivity to aromatic monomers achieved for BPE. In the case of Ru/C and Ru/ MWCNT, the lower values of this ratio were mainly related to a greater value of saturated monomers and partially saturated dimers.

On the other hand, both BPE and PPE present two different C–O linkages to be theoretically broken, whereas the two DPE C–O linkages are equivalent. Subsequently, the preference of rupture of the C–O bond with the C belonging to the aromatic ring (C_{ar} –O) versus that of the C–O bond with the C in the aliphatic chain (C_{ali} –O) was also calculated according to Eq. (4). The results obtained are presented in Fig. 11.

$$R = \frac{mol \ C \ of \ compounds \ produced \ through \ specific \ Cxx - O \ rupture}{mol \ C \ of \ compounds \ produced \ through \ any \ C - O \ rupture}$$

It was observed that, with BPE as model compound, Cali-O scission occurred preferentially, with only a minor rupture of the Car-O bond when the catalysts were Pd/C, Ru/Al₂O₃ or Ru/MWCNT. The preferential rupture of the Cali-O bond was an expected result, due to its bonding energy being 96 kJ/mol lower when compared to that of the Car-O bond. For instance, He et al. showed that Ni/SiO2 catalyst preferentially depolymerize the Cali-O bond of the BPE in aqueous and organic (e.g. hexadecane) environments [32]. The high selectivity observed was attributed to the differences in bonding strengths of the two bonds. Similar results were reported by Z. Luo and C. Zhao using Ru and Pd catalysts supported on activated carbon and sulfated zirconia for the selective hydrogenolysis of BPE [96]. In this kinetic study they showed that the rate on metal surfaces, in the absence of acid sites, is the cleavage of the C-O bond. Therefore, the stronger the C-O bond energy the higher the activation barrier. In contrast, when studying this phenomenon with PPE as model compound, it was observed that while Cali-O scission was still majoritarian in most cases, an increment of products obtained from the rupture of the C_{ar}-O bond is produced. It should be noticed that, in this case, the bonding energy of the Cali-O bond is only 25 kJ/mol lower than that of the C_{ar} –O bond, which may explain the greater competence between the rupture of both. Interestingly, whereas with Ni/C no products from Car-O scission of PPE were observed, when using Pd/C products from such rupture exceeded those obtained from the hydrogenolysis of the Cali-O bond. This seems to indicate, as commented previously, that product distribution is affected both from the strength of the C-O bond but also from the specific characteristics of the catalyst employed.

To rationalize these results first the possible surface reaction mechanism must be taken into account. Recently, He et al. [57] showed



Fig. 10. Ratio of production of aromatic monomers versus the rest of products.



Fig. 11. Observed selectivity for the rupture of C_{ar}–O or C_{ali}–O bonds. (a) BPE as model compound, (b) PPE as model compound.

through kinetic studies and Density Functional Theory (DFT) that on Ni (111) catalyst the hydrogenolysis of Car-O bonds of 4-4'-dihydroxydiphenyl ether starts with the non-dissociative chemisorption of the molecule in a co-planar configuration. Then, the C_{ar}-O bond cleavage takes place leading to the formation of $HOC_6H_4^*$ and $OC_6H_4OH^*$. The latter intermediate latter undergoes a second Car-O hydrogenolysis step leading to the formation of HOC₆H₄* and O* surface species. Finally, the two surface HOC₆H₄* undergo hydrogenation to generate phenol. In the case of the present study, it could be proposed that hydrogenolysis of the Car-O ether bond of the BPE will require the coplanar adsorption of the aromatic ring containing the sp carbon bonded to the oxygen. On the contrary, the cleavage of the Cali-O bond will require the binding of the carbonyl carbon of the aliphatic chain and the oxygen. Therefore, it is possible to interpret the differences in selectivity observed on BPE hydrogenolysis in terms of the interaction of the aromatic ring C_6H_6 and C_{ali} -O to the metal surface. The interaction of benzene and CO with metal surfaces has been studied in detailed using experimental [97-99] and theoretical methods [100–102]. While, quantitatively, the accuracy of first principle calculations is significantly sensitive to the proper description of the surface, Van der Waals interactions, crystalline structure of the surface, and orientation of the molecule, the qualitative information can be used to obtain a deeper understanding of the underplaying phenomena [100,101]. Aromatic molecules tend to adsorb flat-lying onto the metal surface via covalent bonding of π orbitals of the aromatic ring with d states of the metal. When comparing the theoretically calculated adsorption energies of benzene adsorption on ferromagnetic Ni (111) with platinum group metals such as Ru(0001) and Pd (111) significant differences arise. While on Ni (111) the adsorption energy of benzene varies between 0.91 and 1.00 eV (20.98 kcal/mol) [103,104], which are not far from experimentally obtained adsorption energies of 0.78 eV [105], the binding to Ru(0001) and Pd(111) is higher with approximate values of 1.31 eV (30.21 kcal/mol) [106] and 1.03-1.19 eV (23.75-27.44 kcal/mol) [107,108], respectively. Thus, the C₆H₆-metal interaction increases as follows; Ru > Pd > Ni. In contrast, the adsorption energy of CO on Ni, Pd, and Ru follows a completely different trend. Theoretical and experimental data show that among the three metals Ru (001) has the higher adsorption interaction with CO with values of approximate 48.6 [109] and 41.8 kcal/mol [110], respectively. On Ni (111) the calculated adsorption energy of CO varies between 34.0 and 51.3 kcal/mol depending on the cluster size [109], while the experimental value is around 36.6 kcal/mol [111]. Notably, calculated adsorption energies of CO on Pd decreased to values ranging from 25.5 to 37.7 Kcal/mol [109], which were similar to experimental adsorption heats obtained by temperature programmed desorption (30 kcal/mol) [112]. Therefore, the CO-metal surface chemisorption energy decreases as follows; Ru > Ni > Pd. In consequence, the differences in selectivity observed on BPE and PPE may be attributed to both the lower bond strength of C_{ali} –O compared to C_{ar} –O and to the affinity of the metal surface to the aromatic ring and carbonyl moiety.

The latter effect becomes more pronounced when the differences in bond energies of C-O are smaller, like the one observed on BPE. For instance, when the reaction is performed on Ni/C the ratio of C_{ali} –O to total is nearly one. In this case the interaction of the aromatic ring and the surface is significantly lower than that of the C_{ali} -O with surface and as result the sp carbon of the aromatic ring bonded to the ether oxygen is not activated. The opposite occurs on Ru/C and Pd/C where the ratios of Car-O to the total were 0.35 and 0.55, respectively. Here, the interaction of the aromatic ring with the Ru and Pd surfaces facilitated the activation of the aromatic ring. Notably, on Pd the lower interaction with CO could explain the higher selectivity to Car-O hydrogenolysis observed when compared to Ru and Ni. These observations will be in line with the previously reported results. For instance, S. Sitthisa and D. E. Resasco studied that the hydrodeoxygenation of furfural over Pd, Cu, and Ni [113]. In that case, the authors observed that on Ni catalyst the ring-opening reaction (i.e. C-O hydrogenolysis) was favored, while on the Pd catalyst decarbonylation and hydrogenation reactions were predominant. The authors found that while the aromaticity of the furan makes the furural more stable the activity for ring-opening is much higher with furan than with tetrahydrofuran. They attributed this enhancement to the strong interaction of the π electrons of the furan aromatic ring with the metal surface [114].

3.5. Hydroprocessing of lignin-containing 2G stillage

A preliminary study on the influence of the presence of a catalyst in the depolimerization of lignin-containing 2G stillage (named as 2G lignin) was carried out. Several tests were undertaken to determine more clearly the actual influence of the catalyst on the reaction. For this purpose, experiments 1, 2, and 3 were carried out (see Table 3 for operating conditions), each of them having a total running time equal to 4 h. Experiments 1–3 were carried out in the laboratory-scale set-up described in the experimental section. The catalyst used in reaction 3 was 5 wt.% Ru/C. Fig. 12 shows the overall results in terms of yield to solid and liquid products for these experiments.

Mass balance closures were in the 90–100 wt.% range, as can be seen in Fig. 12. Variations were attributed to experimental deviations in the quantification of solid and liquid products. It was observed that, even from just heating 2G lignin in methanol at atmospheric pressure (Blank), some yield to liquid products was obtained (30 wt.%). Most likely, these products may have originated from small molecules

Table 3Reaction conditions for experiments 1–3.

Experiment	1	2	3
Catalyst Pressure (bar-g) Gas atmosphere Temperature (°C)	No 50 N ₂ 200	No 50 H ₂ 200	Yes 50 H ₂ 200



Fig. 12. Yields to solid and liquid products after 2G lignin depolymerization. Experiments 1–3.

contained within the stillage cake, that under heating and stirring were dissolved into the methanol used as solvent. The source of such molecules can be found in the process from which 2G lignin was recovered from the raw stillage sample. As 2G lignin was the cake obtained after filtration, it is plausible that during filtration small molecules dissolved in the liquid fraction of stillage could be retained in the cake, thus being dissolved afterward when heated in methanol. Moreover, it was observed that, when 2G lignin was heated in N₂ atmosphere and 200 °C (Experiment 1), the recovered liquid fraction increased from 30 to 37 wt.%.

Regarding Experiment 2, when the reaction was carried out in the presence of hydrogen, it was observed that liquid fraction accounted for up to 48 wt.% of the recovered products, which clearly indicates the cracking ability of H₂ in the studied conditions. Finally, when a catalyst (5% Ru/C) was included in the process (Experiment 3), the highest yield to liquid products (*ca.* 56 wt.%) was observed.

To have a deeper insight in the depolymerization effect of each of the studied factors, solid samples after experiments 2, and 3 were analyzed by HSQC-2D. Fig. 13 shows the HSQC-2D spectra of acetylated 2G lignin, together with the identification of relevant regions attributed to several substructures and types of linkages in lignin. In this sense, regions corresponding to guaiacyl, syringyl and hydroxyphenyl units can be observed. Also, p-coumarate and ferulate structures were identified in the spectra of 2G lignin. Regions denoting the presence of methyl and methoxy groups can also be observed, the latter coming from the lignin structure itself and from the acetylation process. Deuterated dimethyl sulfoxide (DMSO-d6), the solvent for the HSQC analysis, was also detected. Moreover, some of the types of linkages that bond these units were identified such as β - β or β -5, as well as β -O-4 ether linkages. For analysis of the samples after catalytic depolymerization of 2G lignin, the regions corresponding to guaiacyl and syringyl units (Fig. 14), together with β -O-4 linkages are of particular relevance.

 β –O–4 linkages were selected as the target bonds for depolymerization of 2G lignin, since they are the most abundant ether bonds in lignin, accounting from 40 to 60% [115–117]. Thus, the determination of their abundance in the native sample, as well as in the samples after reaction, is necessary. Several quantitative and semi-quantitative methods have been proposed to determine the abundance of relevant units and inter-unit linkages in different lignin samples [61,118–120]. Most of them are based on the integration of the areas corresponding to the C9-units (hydroxyphenyl (H), guaiacyl (G) and syringyl (S) structures presented in Fig. 14) and the relative abundance of the desired inter-unit linkage was calculated referring it to the total integrated area of C9-units. Differences between methods are mostly in connection with the relative weight of each C9-unit in the total integrated area. In some cases, S2/6 (syringyl) regions are corrected by a factor of 0.5388 whereas in some others all the areas are added without further correction [60]. Given the characteristics of the material, it was proposed to calculate the proportion of β –O–4 linkages by adding the total areas of G and S subunits identified in Fig. 13 and assume them to stand for 100% (100% of C9). The selection of these two subunits alone was justified by being the most easily identifiable and abundant in the obtained spectrum. Then, the area corresponding to the H_α in β –O–4 linkage was integrated and related to that of total C9, thus calculating the percentage of this linkage in the sample. Fig. 15 shows the relevant regions integrated for the determination of the share of β –O–4 linkages in 2G lignin.

Following the procedure described above, it was calculated that the raw material used in catalytic depolymerization studies contained *ca.* 46.6% of β –O–4 bonds. The latter value is within the range reported by Min et al.[60], who observed that β –O–4 were the most abundant linkages, with a share between 40% and 60%. The same calculation procedure was followed with the HSQC spectra of the acetylated samples after reaction, obtaining the percentage of β –O–4 linkages in each sample. Then, by comparison with the initial results for acetylated 2G lignin, the percentage of disappearance of such bond was calculated. This value was selected as the factor to describe lignin depolymerization achieved after each reaction. Fig. 16 shows the integrated HSQC spectra from acetylated lignin after Experiment 3.

Based on the results observed in HSQC-2D, it was possible to quantify the degree of depolymerization of the β –O–4 linkages after the different reactions performed. The reported results (Table 4) indicate that disappearance of β –O–4 linkages increases from 7% to 10% when comparing the blank experiment and Experiment 2, but more importantly, this percentage rises to 53.1% when using 25 bar of H₂ combined with a catalyst (Experiment 3). Therefore, the effect of a catalyst was proven to be positive for the depolymerization of β –O–4 bonds in 2G lignin. In addition, to further analyze the effect of the different conditions applied in experiments 1–4, liquid products from these experiments were analyzed by GC–MS. The corresponding chromatograms (together with a blank) are depicted in Fig. S5.

As a first appreciation, it can be observed that GC-MS analyses of the liquid samples corresponding to experiments 1-3 presented their main peaks at almost equal retention times, which indicated that the most important compounds for each sample were the same. Nevertheless, some differences can be observed between the four chromatograms. Firstly, the number of detected compounds grew in the following order: Experiment 1 < Experiment 2 < Experiment 3. This is in accordance with the already observed behavior of increasing liquid yield and depolymerization of the β -O-4 linkage. Therefore, it seems that even though some compounds were extracted or dissolved by only heating the cake in methanol (blank), an increase in temperature (experiment 1) but most importantly, the use of H₂ and H₂ plus a catalyst (experiments 2 and 3, respectively), improve all the parameters that indicate a higher degree of depolymerization of the sample. In this sense, it is significant the increase of compounds detected with retention times above 19 min, which present higher molecular weights. This indicates that lignin structure is being attacked yielding aromatic species such as 1-methoxy-2-(methoxymethyl)benzene or methyl (E)-3-(4-hydroxy-3-methoxyphenyl)acrylate. In addition, the most important detected compounds of the samples in Fig. S5 are presented in Table S2.

The tabulated compounds (Table S2) can be grouped into four main families: short-chain linear compounds, nitrogen-containing compounds, benzene-based monomers, and esters of fatty acids. Benzene-based monomers, which represented the greatest share of detected compounds (> 66 wt.% of GC-FID-detectable compounds in all the cases), were clearly derived from the polyphenolic structure of lignin. Monomers presenting syringylic, ferulic, hydroxyphenolic and coumaric structures were detected and such monomers can be matched to the



Fig. 13. HSQC-2D spectra of acetylated 2G lignin.



Fig. 14. Lignin Syringyl (S), Guaiacyl (G) and Hydroxyphenyl (H) subunits.

already identified sub-structures in 2G lignin by HSOC. Several studies have reported similar aromatic monomers after lignin depolymerization reactions [16,24,44,121,122]. For example, Barta et al. [44] reported C9 catechols as major products after depolymerization of organosolv lignin in methanol media using a Cu-PMO catalyst. On the other hand, Parsell et al. [122] observed 2-methoxy-4-propylphenol and 3-(3methoxy-4-hydroxyphenyl)-1-propanol as major products after depolymerization of a synthetic lignin polymer which comprises only the β –O–4 ether linkage. Such reaction was carried out in methanol at 150 °C and 20 bar H₂ using a bimetallic catalyst system based on metallic Pd nanoparticles on carbon and Zn (II) Lewis acid. It should be pointed out that, regarding this family of compounds, no saturated compounds derived from this type of structures were detected. Therefore, lignin structure was depolymerized during reaction, but saturation of aromatic rings did not take place to such extent to fall beyond the detection limits of the GC-MS, and thus saturation could be considered as negligible.

While the results using Ru supported on activated carbon showed significant improvement over the control experiments, it is clear that a significant fraction of the lignin is transformed to liquids in the presence of methanol. The use of microporous catalytic materials like activated carbon to perform depolymerization of a macromolecule like lignin is inevitably hindered by mass transport limitations. While this point has been avoided in the literature, here we see that a significant fraction of the lignin is depolymerize in the homogeneous phase, and the catalyst helps to increase this fraction considerably. For this reason, additional studies using heterogeneous catalysts for lignin depolymerization with an enhanced catalyst/lignin contact are required to reduce those limitations.

4. Conclusions

Several catalysts have been studied for the hydrogenolysis of three model compounds of ether linkages in lignin: benzyl phenyl ether (BPE), phenethyl phenyl ether (PPE), and diphenyl ether (DPE). Firstly, up to 19 catalysts based on different active metals and supports were screened using BPE as model compound, due to its commercial availability and lower dissociation energy for the C-O bond. From these tests, 8 catalysts including; Pd/C, Ni/C, Ru/C, Ru/MWCNT, and Ru/Al₂O₃ were selected to further study the hydrogenolysis of DPE and PPE. The results indicated that as the energy necessary for the scission of the C-O bond increased (BPE < PPE < DPE), the conversion of such dimer for the same catalyst decreased (BPE > PPE > DPE). In addition, for a given model compound, supporting different metals on the same support caused also differences in the products obtained. In general, the activity of such metals decreased from Ru to Pd to Ni, which in turn increased the selectivity to aromatic monomers in most cases from Ru to Pd to Ni. Finally, the selected support also influenced the performance of the catalyst. From the HRTEM and TPR characterization results it was observed that Ru, Pd and Ni were more difficult to



Fig. 15. Integration of relevant regions for the determination of β -O-4 linkages in acetylated 2G lignin.

reduce and presented greater values of metal particle size when they were supported in Al_2O_3 than in carbonaceous materials, which seemed to affect the performance of the catalysts. Those with easier reducible species tended to perform better in terms of conversion of the dimer models.

When comparing the ratio of aromatic monomers to the rest of

products obtained with several catalysts, results observed for Ru/Al_2O_3 were interesting as it achieved a medium value of such ratio for the three model compounds studied. If the model compound with the greatest bonding energy (DPE) was not considered, Pd/C and Ni/C also provided interesting results, mainly due to the significant yield of aromatic monomers obtained when studying the hydrogenolysis of BPE.



Fig. 16. Integrated HSQC spectra from acetylated solid after Experiment 3.

Table 4

Calculation of $\beta-O-4$ depolymerization (% Dep.) degree. $S_{2/6}$ and $S'_{2/6}$ correspond to syringyl units, G_2 and G_{5+6} to gualacyl units, and A_α to the H_α in $\beta-O-4$ linkages.

Area					% Dep.
S _{2/6}	S' _{2/6}	G_2	G_{5+6}	A _α (%)	
23.2	4.1	20.1	52.6 77.3	46.6	-
16.1	6.5	10.8	66.6	41.8	10.3%
	Area S _{2/6} 23.2 8.5 16.1 12.4	Area $S_{2/6}$ $S'_{2/6}$ 23.2 4.1 8.5 2.9 16.1 6.5 12.4 4.0	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	$\begin{tabular}{ c c c c c c c c c c c c c c c } \hline Area \\ \hline $S_{2/6}$ & $S'_{2/6}$ & G_2 & G_{5+6} & A_{α} (\%) \\ \hline 23.2 & 4.1 & 20.1 & 52.6 & 46.6 \\ \hline 8.5 & 2.9 & 11.3 & 77.3 & 43.2 \\ \hline 16.1 & 6.5 & 10.8 & 66.6 & 41.8 \\ \hline 12.4 & 4.0 & 39.5 & 44.1 & 21.9 \\ \hline \end{tabular}$

Finally, the preference of rupture of the C–O bond with the C belonging to the aromatic ring (C_{ar}–O) versus that of the C–O bond with the C in the aliphatic chain (Cali-O) for BPE and PPE was studied. It was observed that, as expected, in the case of BPE hydrogenolysis the rupture of the Cali-O bond was preferential due to its lower binding energy, with only minor rupture of the C_{ar}–O. In contrast, competence in the hydrogenolysis of both linkages was observed when PPE was used as model compound. Although C_{ali} –O scission was still more important, Car-O was also present, varying the proportion between them depending on the catalyst employed: with Ni/C as catalysts C_{ar}-O rupture was not detected, but with Pd/C C_{ar}-O rupture exceeded that of C_{ali}-O bond. Thus it was concluded that, in addition to binding energy of the C–O bond, the specific characteristics of the catalyst also affected the preferential rupture of one of the bonds. Further studies will be necessary to establish the specific characteristics of the catalyst surface affecting product distribution.

When using real lignin, it was observed that the presence of hydrogen, and foremost, hydrogen plus a catalyst is crucial to improve the depolymerization of the lignin. Very promising results of over 50% of depolymerization degree of the $\beta-O-4$ linkages were obtained when using a Ru/C catalyst. Further studies with this real residue must be carried out to analyze the effect of different parameters, such as temperature, pressure, type of metal and catalyst support, and metal loading.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2017.04.022.

References

- J.E. Holladay, J.J. Bozell, J.F. White, D. Johnson, Top value added chemicals from biomass volume I — Results of screening for potential candidates from sugars and synthesis gas, 2004.
- [2] J.C. Serrano-Ruiz, J.A. Dumesic, Energy Environ. Sci. 4 (2011) 83–99.
- [3] A. Bioenergy, 2014. Project Hugoton. http://www.abengoabioenergy.com/web/ en/2g_hugoton_project/general_information/.
- B. Magazine, 2014. Commercial-scale cellulosic ethanol refinery opens in Italy http://biomassmagazine.com/articles/9540/commercial-scale-cellulosic-ethanolrefinery-opens-in-italy/.
- [5] POET-DSM, Project Liberty, (2014) http://poetdsm.com/liberty.
- [6] DuPont, DuPont Nevada Site Cellulosic Ethanol Facility, (2014) http://biofuels. dupont.com/cellulosic-ethanol/nevada-site-ce-facility/.
- [7] W. Kricka, J. Fitzpatrick, U. Bond, Front. Microbiol. 5 (2014) 174.
- [8] D. Yuan, K. Rao, P. Relue, S. Varanasi, Bioresour. Technol. 102 (2011) 3246–3253.
- [9] D.E. Resasco, S. Sitthisa, J. Faria, T. Prasomsri, M.P. Ruiz, Heterogeneous Catalysis
- in Biomass to Chemicals and Fuels, in: D. Kubicka, I. Kubicková (Eds.), Research Signpost, Kerala, 2011.

- [10] A. Rico Campos, PhD Thesis. University of Seville (Spain), 2014.
- [11] F.F. Furlan, R.T. Filho, F.H.P.B. Pinto, C.B.B. Costa, A.J.G. Cruz, R.L.C. Giordano, R.C. Giordano, Biotech. Biofuels 6 (2013) 142.
 [12] E. Hyvärinen, Unasylva 56 (2005) 39–41.
- [13] W. Deng, H. Zhang, X. Wu, R. Li, Q. Zhang, Y. Wang, Green Chem. 17 (2015) 5009–5018.
- [14] A. Toledano, L. Serrano, J. Labidi, Fuel 116 (2014) 617–624.
- [15] X. Erdocia, R. Prado, M.A. Corcuera, J. Labidi, Front. Energy Res. 2 (2014) 1–7.
 [16] C. Li, X. Zhao, A. Wang, G.W. Huber, T. Zhang, Chem. Rev. 115 (2015)
- 11559–11624.
- [17] J. Zakzeski, P.C.A. Bruijnincx, A.L. Jongerius, B.M. Weckhuysen, Chem. Rev. 110 (2010) 3552–3599.
- [18] P. Azadi, O.R. Inderwildi, R. Farnood, D.A. King, Renew. Sustain. Energy Rev. 21 (2013) 506–523.
- [19] M.D. Kärkäs, B.S. Matsuura, T.M. Monos, G. Magallanes, C.R.J. Stephenson, Org. Biomol. Chem. 14 (2016) 1853–1914.
- [20] C. Xu, R.A.D. Arancon, J. Labidi, R. Luque, Chem. Soc. Rev. 43 (2014) 7485–7500.
 [21] J. Kong, B. Li, C. Zhao, RSC Adv. 6 (2016) 71940–71951.
- [22] D.D. Laskar, M.P. Tucker, X. Chen, G.L. Helms, B. Yang, Green Chem. 16 (2014)
- 897-910. [23] S. Kasakov, H. Shi, D.M. Camaioni, C. Zhao, E. Baráth, A. Jentys, J.A. Lercher,
- [20] O. Katakovi, H. Shi, China Gaman, G. Jando, E. Barduli, H. Schryb, S. H. Ercher, Green Chem. 17 (2015) 5079–5090.
 [24] O. Song, F. Wang, J. Cai, Y. Wang, J. Zhang, W. Yu, J. Xu, Energy Environ. Sci. 6
- [24] Q. Song, F. Wang, J. Cai, Y. Wang, J. Znang, W. Yu, J. Xu, Energy Environ. Sci. 6 (2013) 994–1007.
 [25] K. Barta, T. D. Matson, M.L. Fettig, S.L. Scott, A.V. Iretskii, P.C. Ford, Green Chem.
- [25] K. Barta, T.D. Matson, M.L. Fettig, S.L. Scott, A.V. Iretskii, P.C. Ford, Green Chem. 12 (2010) 1640–1647.
- [26] J.A. Onwudili, P.T. Williams, Green Chem. 16 (2014) 4740-4748.
- [27] A. Toledano, L. Serrano, A. Pineda, A.A. Romero, R. Luque, J. Labidi, Appl. Catal. B Environ. 145 (2014) 43–55.
- [28] H. Wang, L. Zhang, T. Deng, H. Ruan, X. Hou, J.R. Cort, B. Yang, Green Chem. 18 (2016) 2802–2810.
- [29] X. Huang, T.I. Korányi, M.D. Boot, E.J.M. Hensen, Green Chem. 17 (2015) 4941–4950.
- [30] Z. Luo, Y. Wang, M. He, C. Zhao, Green Chem. 18 (2016) 433-441.
- [31] S. Nanayakkara, A.F. Patti, K. Saito, Green Chem. 16 (2014) 1897–1903.
- [32] J. He, C. Zhao, J.A. Lercher, J. Am. Chem. Soc. 134 (2012) 20768-20775.
- [33] G. Zhu, X. Ouyang, Y. Yang, T. Ruan, X. Qiu, RSC Adv. 6 (2016) 17880–17887.
 [34] A.J. Ragauskas, G.T. Beckham, M.J. Biddy, R. Chandra, F. Chen, M.F. Davis, B.H. Davison, R. a Dixon, P. Gilna, M. Keller, P. Langan, A.K. Naskar, J.N. Saddler, T.J. Tschaplinski, G. a Tuskan, C.E. Wyman, Science 344 (1–10) (2014) 1246843.
- [35] H. Wang, M. Tucker, Y. Ji, J. Appl. Chem. 2013 (2013) 1–9.
 [36] H. Wang, M. Tucker, Y. Ji, J. Appl. Chem. 2013 (2013) 1–9.
- [36] R. Shu, J. Long, Z. Yuan, Q. Zhang, T. Wang, C. Wang, L. Ma, Bioresour. Technol. 179 (2015) 84–90.
- [37] R. Shu, J. Long, Y. Xu, L. Ma, Q. Zhang, T. Wang, C. Wang, Z. Yuan, Q. Wu, Bioresour. Technol. 200 (2016) 14–22.
- [38] F. Liu, Q. Liu, A. Wang, T. Zhang, ACS Sustain. Chem. Eng. (2016) acssuschemeng.6b00620.
- [39] J. Long, Y. Xu, T. Wang, Z. Yuan, R. Shu, Q. Zhang, L. Ma, Appl. Energy 141 (2015) 70–79.
- [40] T. Klamrassamee, N. Laosiripojana, D. Cronin, L. Moghaddam, Z. Zhang, W.O.S. Doherty, Bioresour. Technol. 180 (2015) 222–229.
- [41] J. Zhang, H. Asakura, J. van Rijn, J. Yang, P. Duchesne, B. Zhang, X. Chen, P. Zhang, M. Saeys, N. Yan, Green Chem. 16 (2014) 2432–2437.
- [42] X. Erdocia, R. Prado, M.A. Corcuera, J. Labidi, Biomass Bioenergy 66 (2014) 379–386.
- [43] F.P. Bouxin, A. McVeigh, F. Tran, N.J. Westwood, M.C. Jarvis, S.D. Jackson, Green Chem. 17 (2015) 1235–1242.
- [44] K. Barta, G.R. Warner, E.S. Beach, P.T. Anastas, Green Chem. 16 (2014) 191–196.
 [45] S. Boullosa-Eiras, R. Lødeng, H. Bergem, M. Stöcker, L. Hannevold, E.A. Blekkan,
- Catal. Today 223 (2014) 44–53.
- [46] C. Zhao, J. He, A.A. Lemonidou, X. Li, J.A. Lercher, J. Catal. 280 (2011) 8–16.
- [47] Y.-B. Huang, L. Yan, M.-Y. Chen, Q.-X. Guo, Y. Fu, Green Chem. 17 (2015) 3010–3017.
- [48] J. He, C. Zhao, J.A. Lercher, J. Catal. 309 (2014) 362-375.
- [49] R.C. Runnebaum, T. Nimmanwudipong, D.E. Block, B.C. Gates, Catal. Sci. Technol. 2 (2012) 113.
- [50] M. Saidi, F. Samimi, D. Karimipourfard, T. Nimmanwudipong, B.C. Gates, M.R. Rahimpour, Energy Environ. Sci. 7 (2014) 103–129.
- [51] Q. Bu, H. Lei, A.H. Zacher, L. Wang, S. Ren, J. Liang, Y. Wei, Y. Liu, J. Tang, Q. Zhang, R. Ruan, Bioresour. Technol. 124 (2012) 470–477.
- [52] A.G. Sergeev, J.F. Hartwig, Science 332 (2011) 439–443.
- [53] S. Jia, B.J. Cox, X. Guo, Z.C. Zhang, J.G. Ekerdt, Holzforschung 64 (2010) 577–580.
 [54] A.G. Generary, J.D. Wahk, J.D. Warnin, J. An. Cham. Comput. Action 10, 1001 (2010).
- [54] A.G. Sergeev, J.D. Webb, J.F. Hartwig, J. Am. Chem. Soc. 134 (2012) 20226–20229.
 [55] A. Wu, B.O. Patrick, E. Chung, B.R. James, Dalton Trans. 41 (2012) 1109
- [55] A. Wu, B.O. Patrick, E. Chung, B.R. James, Dalton Trans. 41 (2012) 11093–11106.
 [56] V. Roberts, S. Fendt, A.A. Lemonidou, X. Li, J.A. Lercher, Appl. Catal. B Environ. 95 (2010) 71–77.
- [57] J. He, C. Zhao, D. Mei, J.A. Lercher, J. Catal. 309 (2014) 280–290.
- [58] C.M. Bernt, G. Bottari, J.A. Barrett, S.L. Scott, K. Barta, P.C. Ford, Catal. Sci. Technol. 6 (2016) 2984–2994.
- [59] D.J. Rensel, S. Rouvimov, M.E. Gin, J.C. Hicks, J. Catal. 305 (2013) 256-263.
- [60] D.Y. Min, H. Jameel, H.M. Chang, L. Lucia, Z.G. Wang, Y.C. Jin, RSC Adv. 4 (2014) 10845–10850.
- [61] J.L. Wen, S.L. Sun, B.L. Xue, R.C. Sun, Materials (Basel) 6 (2013) 359–391.
- [62] T.Q. Yuan, F. Xu, R.C. Sun, J. Chem. Technol. Biotechnol. 88 (2013) 346-352.

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- [63] Y. Yoon, R. Rousseau, R.S. Weber, D. Mei, J.A. Lercher, J. Am. Chem. Soc. 136 (2014) 10287–10298.
- [64] C. Zhao, Y. Kou, A.A. Lemonidou, X. Li, J.A. Lercher, Angew. Chem. Int. Ed. 48 (2009) 3987–3990.
- [65] B. Thomas, S. Prathapan, S. Sugunan, Microporous Mesoporous Mater. 80 (2005) 65–72.
- [66] P. Zapata, J. Faria, M.P. Ruiz, D.E. Resasco, Topic Catal. 55 (2012) 38-52.
- [67] J. Zhang, J. Teo, X. Chen, H. Asakura, ACS Catal. 4 (2014) 1574–1583.
- [68] V. Mazzieri, F. Coloma-Pascual, A. Arcoya, P.C. L'Argentière, N.S. Fígoli, Appl. Surf. Sci. 210 (2003) 222–230.
- [69] S. Gaur, D. Pakhare, H. Wu, D.J. Haynes, J.J. Spivey, Energy Fuel 26 (2012) 1989–1998.
- [70] W. Deng, X. Tan, W. Fang, Q. Zhang, Y. Wang, Catal. Letters 133 (2009) 167–174.
- [71] A.K. Hill, L. Torrente-Murciano, Int. J. Hydrogen Energy 39 (2014) 7646–7654.
- [72] A.K. Hill, L. Torrente-Murciano, Appl. Catal. B Environ. 172–173 (2015) 129–135.
 [73] C. Liang, Z. Wei, M. Luo, P. Ying, Q. Xin, C. Li, Hydrogen spillover effect in the reduction of barium nitrate of Ru- Ba(NO₃)₂/AC catalysts for ammonia synthesis, in: A. Guerrero-Ruiz, I. Rodriguez-Ramons (Eds.), Studies in Surface Science and Catalysis, vol. 138, Elsevier Masson SAS, 2001, 2017, pp. 283–290.
- [74] L. Hu, S. Yin, Q. Yin, H. Wang, S. Wang, Energy Sci. Eng. 3 (2015) 126–134.
- [75] J. Xiong, X. Dong, L. Li, J. Nat. Gas Chem. 21 (2012) 445–451.
- [76] M.H. Youn, J.G. Seo, K.M. Cho, J.C. Jung, H. Kim, K.W. La, D.R. Park, S. Park, S.H. Lee, I.K. Song, Korean J. Chem. Eng. 25 (2008) 236–238.
- [77] G. García, A. Monzon, F. Bimbela, J.L. Sanchez, J. Abrego, Energy Fuel 27 (2013) 2846–2856.
- [78] J. Remón, J. Medrano, F. Bimbela, L. García, J. Arauzo, J. Appl. Catal. B Environ. 132–133 (2013) 433–444.
- [79] M. Zhou, L. Tian, L. Niu, C. Li, G. Xiao, R.U. Xiao, Fuel Process. Technol. 126 (2014) 12–18.
- [80] S. Wang, Q. Yin, J. Guo, L. Zhu, Energy Fuel 27 (2013) 3961–3968.
- [81] B. Folkesson, Acta Chem. Scand. 27 (1973) 287-302.
- [82] J.Y. Shen, A. Adnot, S. Kaliaguine, Appl. Surf. Sci. 51 (1991) 47-60.
- [83] F. Bimbela, D. Chen, J. Ruiz, L. García, J. Arauzo, Appl. Catal. B Environ. 119–120 (119) (2012) 1–12.
- [84] A.M. Beccaria, G. Poggi, G. Castello, Br. Corros. J. 30 (1995) 283-287.
- [85] C.D. Wagner, W.M. Riggs, L.E. Davis, J.F. Moulder, Handbook of X-ray Photoelectron Spectroscopy, in: G.E. Muilenberg (Ed.), 1st ed., Perkin-Elmer Corporation (Physical Electronics), 1979, 2017.
- [86] D.P. Upare, S. Yoon, C.W. Lee, J. Porous Mater. 20 (2013) 1129–1136.
- [87] K. Ahmed, P. Mistry, Collect. Czech. Chem. Commun. 57 (1992) 2073–2077.
 [88] P. Salagre, J.L.G. Fierro, F. Medina, J.E. Sueiras, J. Mol. Catal. A Chem. 106 (1996)
- [88] P. Salagre, J.L.G. Fierro, F. Medina, J.E. Sueiras, J. Mol. Catal. A Chem. 106 (1996) 125–134.
 [89] R.B. Shalvoy, P.J. Reucroft, B.H. Davis, J. Catal. 56 (1979) 336–348.
- [69] R.B. Sharvoy, P.J. Reucroit, B.H. Davis, J. Catal. 56 (1979) 536–548.
 [90] S. Hüfner, G.K. Wertheim, J.H. Wernick, Solid State Commun, 17 (1975) 417–422.
- [91] T.J. Sarapatka, Chem. Phys. Lett. 212 (1993) 37–42.

- [92] S. Hinokuma, K. Murakami, K. Uemura, M. Matsuda, K. Ikeue, N. Tsukahara, M. MacHida, Top. Catal. 52 (2009) 2108–2111.
- [93] T.L. Barr, T.L. Barr, J. Phys. Chem. 82 (1978) 1801-1810.
- [94] A.L. Guimaraes, L.C. Dieguez, M. Schmal, An. Acad. Bras. Cienc. 76 (2004) 825–832.
- [95] G. Kumar, J.R. Blackburn, M.M. Jones, R.G. Albridge, W.E. Moddeman, Inorg. Chem. 11 (1972) 296–300.
- [96] Z. Luo, C. Zhao, Catal. Sci. Technol. 6 (2016) 3476-3484.
- [97] M.A. Filler, S.F. Bent, Prog. Surf. Sci. 73 (2003) 1–56.
- [98] H. Search, C. Journals, A. Contact, M. Iopscience, J. Physics. Condens. Matter 15 (2003) R1501–R1516.
- [99] F. Zaera, Chem. Rev (1995) 2651–2693.
- [100] S.J. Jenkins, Proc. R. Soc. A (2009) 2949-2976.
- [101] H. Yildirim, T. Greber, A. Kara, J. Phys. Chem. C 2057 (2013) 2-2058 (3).
- [102] C. Chiu, A. Genest, A. Borgna, N. Ro, ACS Catal. (2014) 4178–4188.
- [103] S. Yamagishi, S.J. Jenkins, D.A. King, J. Chem. Phys. 114 (2001) 5765-5773.
- [104] F. Mittendorfer, J. Hafner, Surf. Sci. 472 (2001) 133–153.
 [105] A.K. Myers, G.R. Schoofs, J.B. Benziger, J. Phys. Chem. (1987) 2230–2232.
- [106] Firk myes, ene ochoos, on beinager, or First, enem (1997) 2250-2252.
 [106] G. Held, W. Braun, H. Steinrück, S. Yanagishi, S.J. Jenkins, D.A. King, Phys. Rev. Lett. 87 (2001) 216102-1-216102-4.
- [107] C. Morin, D. Simon, P. Sautet, J. Phys. Chem. 108 (2004) 5653-5665.
- [108] H. Orita, N. Itoh, Appl. Catal. A Gen. 258 (2004) 17-23.
- [109] C.D. Zeinalipour-Yazdi, A.L. Cooksy, A.M. Efstathiou, Surf. Sci. (2008) 1858–1862.
- [110] O. Dulaurent, M. Nawdali, A. Bourane, D. Bianchi, Appl. Catal. A Gen. 201 (2000) 271–279.
- [111] S. Derrouiche, D. Bianchi, Appl. Catal. A Gen. 313 (2006) 208-217.
- [112] J. Szanyi, W.K. Kuhn, D.W. Goodman, J. Szanyi, W.K. Kuhn, D.W. Goodman, J. Vac. Sci. Technol. A 11 (1993) 1969–1974.
- [113] S. Sitthisa, D.E. Resasco, Catal. Lett. 141 (2011) 784-791.
- [114] M.K. Bradley, J. Robinson, D.P. Woodruff, Surf. Sci. 604 (2010) 920–925.
 [115] C. Zhang, J. Lu, X. Zhang, K. MacArthur, M. Heggen, H. Li, F. Wang, Green Chem.
- [113] C. Zhang, J. Li, X. Zhang, K. MacArinut, M. Feggei, H. Li, F. Wang, Green Chem. 19 (2016) 702–706, http://dx.doi.org/10.1039/C6GC01456A.
 [116] S. Dabral, J. Mottweiler, T. Rinesch, C. Bolm, Green Chem. 17 (2015) 4908–4912.
- [110] S. Dabrai, J. Mottweiter, T. Rinesch, C. Bolin, Green Chem. 17 (2015) 4908–4912 [117] Z. Strassberger, A.H. Alberts, M.J. Louwerse, S. Tanase, G. Rothenberg, Green
- Chem. 15 (2013) 768–774. [118] A.T. Martínez, J. Rencoret, G. Marques, A. Gutiérrez, D. Ibarra, J. Jiménez-
- Barbero, J.C. del Río, Phytochemistry 69 (2008) 2831–2843. [119] J.L. Wen, Z. Sun, Y.C. Sun, S.N. Sun, F. Xu, B.C. Sun, Biobased Mater, Bioene
- [119] J.L. Wen, Z. Sun, Y.C. Sun, S.N. Sun, F. Xu, R.C. Sun, Biobased Mater. Bioenergy 4 (2010) 408–425.
- [120] M. Sette, R. Wechselberger, C. Crestini, Chem. Eur. J. 17 (2011) 9529–9535.
- [121] W. Xu, S.J. Miller, P.K. Agrawal, C.W. Jones, ChemSusChem 5 (2012) 667-675.
- [122] T.H. Parsell, B.C. Owen, I. Klein, T.M. Jarrell, C.L. Marcum, L.J. Haupert, L.M. Amundson, H.I. Kenttämaa, F. Ribeiro, J.T. Miller, M.M. Abu-Omar, Chem. Sci. 4 (2013) 806–813.