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Towards a sustainable bio-fuels production from lignocellulosic bio-oils: Influence of operating conditions on the hydrodeoxygenation of guaiacol over a Mo_2C/CNF catalyst

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Abstract:

This work firstly provides a thorough insight into the effects of the operating conditions (catalyst loading, initial H_2 pressure temperature, reaction time, H_2/guaiacol ratio and liquid reaction volume) on the hydrodeoxygenation (HDO) of guaiacol over a Mo_2C/CNF catalyst. Under the operating condition tested, gas and solid formation was negligible and guaiacol was primary converted to different liquid products, including non-deoxygenated (0-oxy), mono-deoxygenated (1-oxy) and fully deoxygenated (2-oxy) compounds, together with high molecular weight soluble oligomers. An increase in the catalyst loading increased the guaiacol conversion and HDO efficiency, augmenting the proportions of HDO products. Among these species, the progressive transformation of 1-oxy compounds into 2-oxy species was kinetically and thermodynamically controlled by the catalyst loading and the amount of H_2 dissolved in the liquid medium, respectively. Augmenting the H_2 pressure increased the H_2 availability in the liquid, which led to increases over time in the guaiacol conversion and HDO efficiency, thus promoting the production of HDO products and facilitating the transformation of guaiacol into fully de-oxygenated products. This increase depended on the reaction volume, with more pronounced variations occurring for a

small than for a large volume due to the greater variations occurring in the H_2/guaiacol ratio for the former than the latter. The temperature exerted a kinetic promoting effect together with a thermodynamic inhibitory influence, as some of the reactions involved were not thermodynamically favoured at high temperature. Therefore, the detailed analysis included in this work brings novel information on guaiacol HDO, which can help to establish the basis for catalysts development and reactors design to achieve a sustainable bio-fuels production from lignocellulosic bio-oils.

Keywords: guaiacol, bio-oil, bio-fuels, hydrodeoxygenation, Mo_2C/CNF catalysts

1. Introduction

As a result of the world new policies to decrease the current over dependency of crude oil and mitigate environmental pollution, a lot of effort has been devoted to seeking new processes, renewable materials and sustainable strategies to produce fuels and chemicals [1]. As part of this, the use of lignocellulosic biomass to produce these commodities is gaining increasing attention [2]; hydrothermal liquefaction and fast pyrolysis being regarded as two promising processes to this end, as they allow the transformation of biomass into a liquid-energy carrier called bio-oil [3-6].

Bio-oil is a dark brown liquid with a higher energy density than the original biomass [7], it is easy to transport and store, has a relatively high calorific value (HHV around 17 MJ/kg) [8-10] and offers several environmental advantages over fossil fuels [11-13]. However, the high oxygen content and elevated viscosity, acidity and corrosiveness of bio-oil hinder its use as a liquid biofuel [14] and some upgrading treatments such as hydrodeoxygenation, hydrocracking, hydrotreating [10] and/or the use of supercritical water [8, 11-13, 15] are necessary. Among these, hydrodeoxygenation (HDO) is

considered an up-and-coming methodology to improve the physicochemical properties of bio-oils [16]. This process consists of the total or partial removal of the bio-oil oxygen content under a hydrogen atmosphere at moderate temperature (250-450 ºC) and elevated pressure (40-100 bar) in the presence of a hydrogenation catalyst [17].

The catalysts generally used for HDO include conventional metal-sulphide hydrotreating catalysts (NiMoS and CoMoS) [18] as well as noble (Rh, Pt, Pd and Ru) and transition (Ni, Cu and W) metal supported catalysts [19]. However, these catalysts have some disadvantages when used for HDO reactions. In particular, metal-sulphides suffer from deactivation as the sulphur content of the catalyst can be replaced by oxygen during the HDO reaction, noble metal catalysts require high hydrogen pressures and may deactivate in the presence of water at high temperatures, while transition metals deactivate by coking and may also leach to the solution. The supports for these catalysts include metal oxides (Al_2O_3, SiO_2, ZrO_2, CeO_2 and TiO_2), zeolites (HZSM-5) and carbon-based materials. Al_2O_3 is the most widely used support, although it can be transformed into bohemite at common HDO conditions and its high acidity promotes the development of side reactions leading to catalyst deactivation [20-22]. Alternative oxide supports (SiO_2, ZrO_2, CeO_2 and TiO_2) might be also a plausible option, even though they are more expensive and have low surface area, while Zeolites are quite acidic and can only be used at relatively low temperatures [20-22].

Aiming to overcome these drawbacks, the development of novel, active and resistant catalysts is gaining increasing attention. On this subject, metal-carbides are regarded as suitable catalytic materials for liquid phase reactions [23-25]. These carbides have a better stability than sulphides together with similar catalytic properties than noble

metals [25, 26]. Among the different metal carbides, Mo_2C has recently appeared as a promising material to be used as the catalyst for HDO reactions. Although Mo_2C might be less active than noble metals under some reaction conditions, it is indeed more efficient in terms of O-removal with a minimal hydrogen consumption [23], thus intensely increasing the hydrogen efficiency of the HDO process. The supports commonly used for metal carbides include metal oxides (Al_2O_3, SiO_2, ZrO_2) [18, 27, 28], zeolites (HZSM-5) [18, 23, 29], active carbon [25, 30-33] and bio-char [34]. However, these supports also have the shortcomings described above, and novel supports need to be tested and developed for the synthesis of active, selective and resistant Mo_2C supported catalysts.

On this matter, carbonaceous materials are considered appropriate catalytic supports for the synthesis and development of catalysts based on Mo_2C. In the midst of the different carbon materials, carbon nanofibres (CNF) are regarded as excellent catalyst supports for liquid phase reactions due to their high chemical stability in non-oxidising environments, their tuneable chemical nature and their outstanding textural properties [33, 35]. In addition, since one of the most common methodologies to synthesise Mo_2C is the temperature programmed reaction, in which a molybdenum precursor is heated up in the presence of a carburising gas [36], CNF themselves can be used as the carbon source during the carburisation process by simply employing H_2 as the carburising agent. This strategy dispense with the need of using hydrocarbons in the carburisation process, thus preventing the counterproductive formation of coke on the Mo_2C surface [37]. Despite these outstanding properties, to the best of the authors' knowledge, the work conducted addressing the use of Mo_2C/CNF catalysts for the hydrodeogygenation (HDO) of lignocellulosic bio-oil is very scarce and all the publications reported to date

have used guaiacol (2-methoxyphenol) as a bio-oil model compound. Guaiacol, found in large quantities in bio-oils produced from lignocellulosic biomass [23, 38, 39], is a good representative of the phenolic compounds derived from the thermal decomposition of lignin [40]. Moreover, this chemical owns the most typical functionalities found in lignin derived phenolic monomers, which allows establishing a reliable comparison between the removal of oxygen from the hydroxylic (-OH) and methoxy ($-OCH_3$) groups and the hydrogenation of the phenyl group [39, 41-45]. In addition, it must be borne in mind that it is thermodynamically more difficult to remove oxygen from the phenolic-derived bio-oil compounds than from those obtained from the biomass carbohydrate content (cellulose and hemicellulose) [42]. Therefore, the efficiency of the catalysts will be determined by their capacity to upgrade lignin derived bio-oil constituents, thus making guaiacol a suitable chemical to test not only the behaviour of different HDO catalysts, but also the effects of the operating conditions on the process. Likewise, from a global perspective, it is also more attractive to produce alternative bio-fuels from the lignin fraction than from the carbohydrate (cellulose and hemicellulose) biomass fraction due to the lower O/C ratio of the former than the latter [39, 42].

The publications addressing the use of Mo_2C/CNF catalysts for the HDO of guaiacol have largely focused on catalyst development (catalyst synthesis and properties, testing the catalysts at only some HDO common conditions), rather than on the evaluation of the influence of all the operating conditions during the HDO process. Ochoa et al. [44] evaluated the effect of the carburisation temperature (550-750 ºC) and heating rate (1-10 ºC/min) on the properties and performance of a Mo_2C/CNF catalyst during the HDO of guaiacol in a batch reactor operated at 300 ºC, 20 bar initial H_2 pressure for 2 h. They found that high carburisation temperatures and low heating rates improved the catalytic

activity of the catalyst under the HDO conditions tested. Moreira et al. [46] used a Mo_2C catalyst supported on commercial CNF for the HDO of guaiacol, evaluating the effect of the temperature (300 and 350 ºC), initial H_2 pressure (20 and 30 bar) and reaction time (2 and 4 h). Increasing the temperature and/or reaction time increased the guaiacol conversion, but also augmented the proportion of high molecular weight compounds in the reaction mixture, while augmenting the H_2 pressure led to increases in the guaiacol conversion and phenol selectivity. Jongerius et al. [47] evaluated the performance of a Mo_2C/CNF catalyst during the HDO of guaiacol at different temperatures (300-350 ºC) and reaction times (0-6 h) using a H_2 pressure of 55 bar. They reported that long reaction times and high temperatures increased the guaiacol conversion and the production of benzene and toluene. Liu et al. [23] analysed the effects of the temperature (330-375 º) and reaction time (0-300 min) in a 300 mL batch reactor using an initial H_2 pressure of 34 bar, achieving a complete guaiacol conversion in 250 min at 300 ºC. Increasing the temperature and reaction time increased the guaiacol conversion. As a result, a complete conversion was achieved in 120 min at 375 ºC. In addition, they reported that the HDO of guaiacol over Mo_2C/CNF catalysts occurred by the direct demethoxylation of guaiacol yielding phenol, followed by Ar-OH bond cleavage to produce benzene at high temperatures, as Mo_2C is very efficient in terms of O-removal with minimal H_2 consumption [48].

These publications provide useful information about the synthesis, characterisation and performance of several Mo_2C/CNF catalysts. Nonetheless, since different reactors, operating conditions and catalyst types were used, the comparison between the different data available in the literature in unreliable. Therefore, new insights must be gained into the effects of the operating conditions during the HDO of guaiacol over Mo_2C/CNF

catalysts. Given this scenario, this work firstly evaluates the effects of the temperature (270-330 ºC), reaction time (0-180 min), catalyst loading (0-0.15 g cat/g guaiacol), initial H_2 pressure (20-60 bar), H_2/guaiacol ratio (1.5-13.6 mol/mol) and liquid reaction volume (120-200 mL) on the HDO of guaiacol using a Mo_2C/CNF catalyst. This includes the analyses of the effects of these operating conditions on the reaction pathway, guaiacol conversion, HDO efficiency and chemical composition of the liquid fraction produced during the experiments. Therefore, the rigorous parametric study conducted, together with the limited amount of experimental data available in the literature carefully evaluating the effects of the operating conditions over Mo_2C/CNF catalysts, demonstrate that this work represents a novel and challenging investigation in this field.

2. Experimental

2.1 Catalyst preparation and characterisation

A Mo_2C supported on CNF catalyst was used for the experiments. The catalyst preparation comprises two consecutive steps: the synthesis of the support; i.e. the carbon nanofibres (CNF), and the subsequent incorporation of Mo_2C on the fibres. The CNF were produced by means of a synthetic biogas (CH_4:CO_2; 50:50 vol/vol) decomposition over a Ni:Co:Al (33.5:33.5:33; wt.%) catalyst using a rotatory bed reactor at 650 ºC. Then, the CNF were functionalised in a two-step process: sonicated in HCl at 60 ºC (aimed to remove the possible metal content derived from the catalyst used in the decomposition reaction) followed by HNO_3 treatment at boiling point in order to create oxygen groups on their surface, as these groups facilitate the dispersion of the active phase when the catalyst precursor is deposited onto the fibres. More details about the CNF synthesis and characterisation can be found elsewhere [44]. The Mo_2C was

187 incorporated on the CNF by incipient wetness impregnation using a
188 $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ aqueous solution. The solution was prepared to obtain a catalyst
189 with a MoO_3 content of 15 wt.%. After the impregnation, a carbothermal hydrogen
190 reduction (CHR) was conducted, using a temperature program optimised in a previous
191 work [44]. Briefly, the CHR was carried out in a fixed-bed tubular quartz reactor (75 cm
192 in length and 15 mm of internal diameter) using 100 mL STP/min of H_2 at 750 ºC and
193 atmospheric pressure. This temperature was reached in two steps: a first increase up to
194 350 ºC at a rate of 10ºC/min, followed by a second increase up to 750 ºC at a rate of 1
195 ºC/min up and a third 1 h isothermal period. Finally, the reactor was cooled down under
196 a N_2 atmosphere and the active catalyst was passivated with an O_2/N_2 (1/99 vol.%)
197 mixture using a flow rate of 24 mL STP/min at 25 ºC for 2 h.
198
199 The characterisation of the catalyst revealed that the prepared Mo_2C/CNF catalyst has a
200 Mo content of 12.9 wt.% (measured by ICP, Inductive Couple Plasma, analysis)
201 supported on a CNF resembling a fishbone-type structure (observed by Transmission
202 Electron Microscopy, TEM). The crystallinity of the catalyst determined by XRD (X-
203 Ray Diffraction) and the crystal size of the Mo phases were calculated by using the
204 diffractometry suite TOPAS. In these analyses three phases were observed: graphitic
205 carbon from CNF, Mo_2C peaks related to the hexagonal close packing structure (β-
206 Mo_2C) of 10.9 nm and small crystals of less than 2 nm of MoO_2 as a consequence of
207 CHR process. The XPS (X-ray Photoelectron Spectroscopy) spectra revealed the
208 coexistence of Mo^{2+}, related to Mo_2C, and $Mo^{\delta+}$ ($2+ < \delta+ < 4+$), commonly named
209 molybdenum oxycarbides (Mo-C-O), corresponding to an intermediate state between
210 Mo_2O and β-Mo_2C. The catalyst showed a BET (Brunauer–Emmett–Teller) surface area
211 of 64.2 m^2/g and a total pore volume of 0.398 cm^3/g. The porous were largely

mesoporous (40-70 nm) with a small volume of micropores (1-1.5 nm) according to the DFT (Discrete Fourier Transform) analysis. More information about the characterisation of the catalyst can be found elsewhere [44].

2.2 Experimental reaction system

A 300 mL autoclave batch reactor (Parker Autoclave Engineers) connected to a liquid sampler was used for the HDO experiments. The reactor is heated up by an external heating jacket and the reaction temperature is monitored and controlled by means of a thermocouple connected to a PID control. A stirrer bar, controlled by a magnetic rotor (Magnedrive), was used to homogenise the reaction mixture, while a coil tube and a baffle helped to create a turbulent regime in order to facilitate the diffusion of H_2 in the liquid. To analyse the evolution over time of the HDO reaction, several aliquots were withdrawn by means of a liquid sampler, containing a solid filter on its tip to prevent solid loss, connected to the reactor.

2.3 Experimental procedure, operating conditions and data analysis

The experiments to assess the effect of the operating conditions on the process were conducted with a 3 vol.% guaiacol/n-decane solution (both chemicals, guaiacol used as the reactant and n-decane as the solvent, with a purity greater than 99%). The guaiacol concentration and the solvent were chosen having regard to previous works addressing the HDO of guaiacol [20, 22, 44, 46, 47]. For the experiments, the reactor was loaded with 120 or 200 mL of the 3 vol.% guaiacol/n-decane solution and different amounts of catalyst depending on the process conditions. Then, it was closed and two leak tests, one with N_2 and other with H_2, were conducted using a similar pressure to that achieved at reaction conditions. Afterwards, the reactor was purged with 300 mL STP/min of H_2 for

15 min in order to remove all the air and N_2 from the vessel, creating a H_2 atmosphere. Then, the reactor was pressurised with more H_2 and heated up to the reaction temperature. In these steps, a stirring rate of 300 rpm was used in order to minimise the turbulence to prevent any significant reaction. Once the reaction temperature was achieved, the rotation speed was increased up to 1000 rpm.

The progress of the reaction was analysed with time by withdrawing different aliquots during the reaction process, purging the sampling line before collecting each aliquot. Once the reaction time was complete, the stirring speed was diminished down to 300 rpm and the reactor let cool to room temperature. Then, the pressure was released, the gas phase analysed and the reaction vessel opened to recover the catalyst and the liquid reaction mixture. After the HDO experiments, three fractions were obtained. A liquid fraction, comprising the unreacted guaiacol and the reaction liquid products dissolved in decane as the solvent; the spent gas phase and a solid fraction consisting of the spent catalyst. The gas phase was analysed using a micro gas chromatograph (micro GC Varian CP4900) equipped with two packed columns, molecular sieve and porapack, coupled to a TCD detector. The liquid product recovered after the experiment was separated from the spent solid by filtration using a filtration funnel. All the liquid samples, including the liquid product recovered from the reactor at the end of the experiment and all the aliquots collected over the course of the reaction were filtered using a 20 µm filter syringe prior to their analysis. In the sampling step, less than 0.05% of the catalyst loaded in the reactor was recovered in the filter; thus indicating a negligible catalyst loss during the sampling process. The solid fraction, consisting of the spent catalyst, was rinsed with ethanol and dried overnight at 60 ºC in an oven. Then the liquid and solid fractions were stored for further analyses. The mass balance conducted

at the end of the experiment confirmed that 99% of the catalyst initially loaded in the reactor was recovered. All the liquid samples collected, i.e. the aliquots obtained during the course of the reaction together with the liquid recovered after the experiment, were analysed in a Gas Chromatographer (CLASUS 5080 Perkim Elmer) coupled with a FID detector. The identification and quantification of the unreacted guaiacol and liquid products were performed as described elsewhere [44, 46].

The parametric analysis comprises the effects of the temperature (270-330 ºC), reaction time (0-180 min), catalyst loading (0-0.15 g cat/g guaiacol), initial H_2 pressure (20-60 bar), H_2/guaiacol ratio (1.5-13.3 mol/mol) and liquid reaction volume (120-200 mL) on the process. The effects of the temperature, initial H_2 pressure and reaction time were evaluated using a total liquid volume of 200 mL. The influences of the H_2/guaiacol ratio and total liquid volume were evaluated using two liquid volumes: 120 and 200 mL, which varied the free volume between 180 and 100 mL (considering the total volume of the reactor, 300 mL), respectively. This variation in the free volume allows the analyses of the effects on the process of the H_2/guaiacol ratio using the same initial H_2 pressure. Likewise, the same H_2/guaiacol ratio can be achieved using different liquid volumes and initial H_2 pressures. These effects were evaluated on the guaiacol conversion, HDO efficiency and liquid product composition (solvent and un-reacted guaiacol free), which were calculated according to Eq. 1-3, respectively.

$$Conversion\ (\%) = \frac{initial\ guaiacol\ (g) - final\ guaicol\ (g)}{initial\ guaiacol\ (g)} \quad \text{(Eq. 1)}$$

$$Product\ composition\ (wt.\%) = \frac{amount\ of\ product\ (solvent\ and\ guaiacol\ free)\ (g)}{total\ reaction\ products\ (solvent\ and\ guaiacol\ free)\ (g)} \quad \text{(Eq. 2)}$$

$$HDO\ efficiency\ (\%) = \frac{oxygen\ in\ the\ feed\ (g) - oxygen\ in\ the\ quantified\ products\ (guaiacol\ free)\ (g)}{oxygen\ in\ the\ feed\ (g)} \quad \text{(Eq. 3)}$$

3. Results and discussion

3.1 Possible reaction pathway during the HDO of guaiacol

Three different fractions were recovered after the HDO experiments: gas, solid and liquid. The gas phase is largely made up of the H_2 initially loaded in the reactor, while the solid fraction recovered after the experiment consists of the spent Mo_2C/CNF catalyst. The liquid phase comprises unreacted guaiacol together with different reaction products dissolved in decane. Attending to the number of oxygen atoms removed from the original guaiacol structure, these species can be classified into three categories [23]: 2 oxygen atoms removed (2-oxy), 1 oxygen atom removed (1-oxy) and non-oxygen removed (0-oxy). 2-oxy compounds include toluene, benzene and cyclohexane; 1-oxy compounds comprise phenol, anisole, o-cresol, 2,3-xylenol and 3-methyl-ciclohexanol; while 0-oxy compounds contain catechol. In addition, the mass balance conducted revealed the formation via condensation reactions of soluble, high molecular weight species, namely high molecular weight oligomers, which could not be detected by Gas Chromatography [23, 44, 47].

Figure 1 shows a possible reaction pathway for the HDO of guaiacol over the Mo_2C/CNF catalyst based on the liquid reaction products distribution obtained in the experiments. The HDO of guaiacol largely comprises demethylation, demethoxylation, deoxygenation, transalkylation, methylation and dehydrogenation reactions [23, 42, 44-46, 49, 50]. At early reaction stages, guaiacol can decompose into 0-oxy compounds (catechol), via a demethylation reaction and 1-oxy compounds through demethoxylation and deoxygenation reactions. Guaiacol demethoxylation leads to the production of phenol, while its deoxygenation yields anisole and o-cresol [23, 43-46], this latter via a

first deoxygenation reaction followed by subsequent rearrangements [46]. Subsequently, catechol and anisole can be deoxygenated and demethylated, respectively, to produce phenol [43-46]. In addition, o-cresol can also be produced from anisole via a transalkilation reaction, while toluene can also be obtained from anisole and o-cresol via deoxygenation and dehydration reactions, respectively [41, 44-46]. O-cresol can undergo a subsequent methylation reaction to produce 2,3-xylenol or a hydrogenation reaction to give 3-methyl-cyclohexanol. Afterwards, benzene, which can be latterly hydrogenated to cyclohexane, can be produced from the deoxygenation of phenol and/or demethylation of toluene. In addition, cyclohexane can also be produced from 3-methyl-cyclohexanol through a hydration/demethylation reaction [41, 44-46].

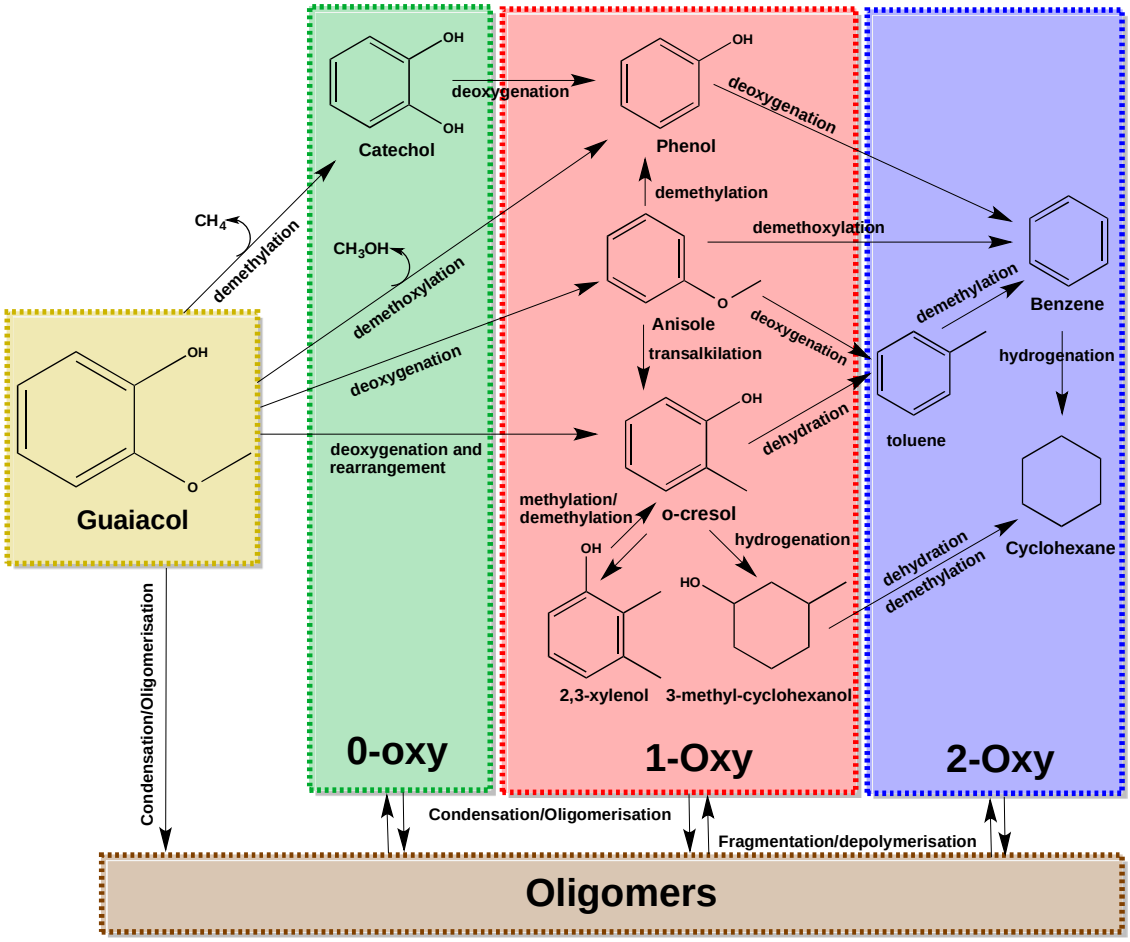

Figure 1. Possible reaction pathway during the hydrodeoxygenation of guaiacol over a Mo_2C/CNF catalyst.

In addition, condensation, polymerisation and oligomerisation reactions occur during the HDO of guaiacol, especially in the absence of a catalyst [23, 44, 46, 47]; these reactions leading to the formation of high molecular weight species, namely oligomers. These molecules can also undergo cracking, depolymerisation and fragmentation reactions leading to the formation of low molecular weight species and contributing to the formation of 0-oxy, 1-oxy and 2-oxy compounds.

3.2 Effects of the operating conditions during the HDO of guaiacol

Regardless of the operating conditions, gas and solid formation was negligible; the gas phase largely consisting of the H_2 initially loaded in the reactor (97-99 vol.%), with small amounts of CO_2 (0-1 vol.%) and CH_4 (0.5-2 vol.%) and the solid fraction comprising the spent Mo_2C/CNF catalyst. This indicates a negligible formation of gases and solid species such as humins, char and/or coke at the operating conditions used in this work. The liquid phase consists of unreacted guaiacol together with different reaction products dissolved in decane, whose precise chemical composition strongly depends on the HDO conditions. Given these results, the effects of the operating conditions during the HDO of guaiacol have been assessed analysing the guaiacol conversion (%), liquid product composition (solvent and un-reacted guaiacol free, wt.%) and HDO efficiency (un-reacted guaiacol and oligomers free) (%). In particular, the effects of the catalyst loading, initial H_2 pressure, reaction temperature, initial H_2/guaiacol ratio and liquid reaction volume are discussed next. The detailed liquid compositions obtained in the experiments are provided in the supplementary information.

3.2.1 Catalyst loading

Figure 2 shows the effects of the catalyst loading on the HDO of guaiacol at 300 ºC, using an initial H_2 pressure of 20 bar (60 bar at reaction conditions) and a liquid reaction mixture of 200 mL. Two non-catalytic experiments were conducted: a pure non-catalytic experiment (blank test) without any catalyst and semi-blank test, using 0.15 g of carbon nanofibres (CNF) to test the possible catalytic activity of the support. Figures 2 a and b plot the evolution over time of the guaiacol conversion, HDO efficiency and liquid product composition in the absence of a catalyst (0 g catalyst/ g guaiacol) and using the prepared CNF (prior to Mo_2C incorporation) as the catalyst, respectively. In addition, Figures 2 c-e show these effects for catalyst/guaiacol ratios of 0.06, 0.09 and 0.15 g catalyst/guaiacol. Tables S1a-e list the detailed liquid product composition.

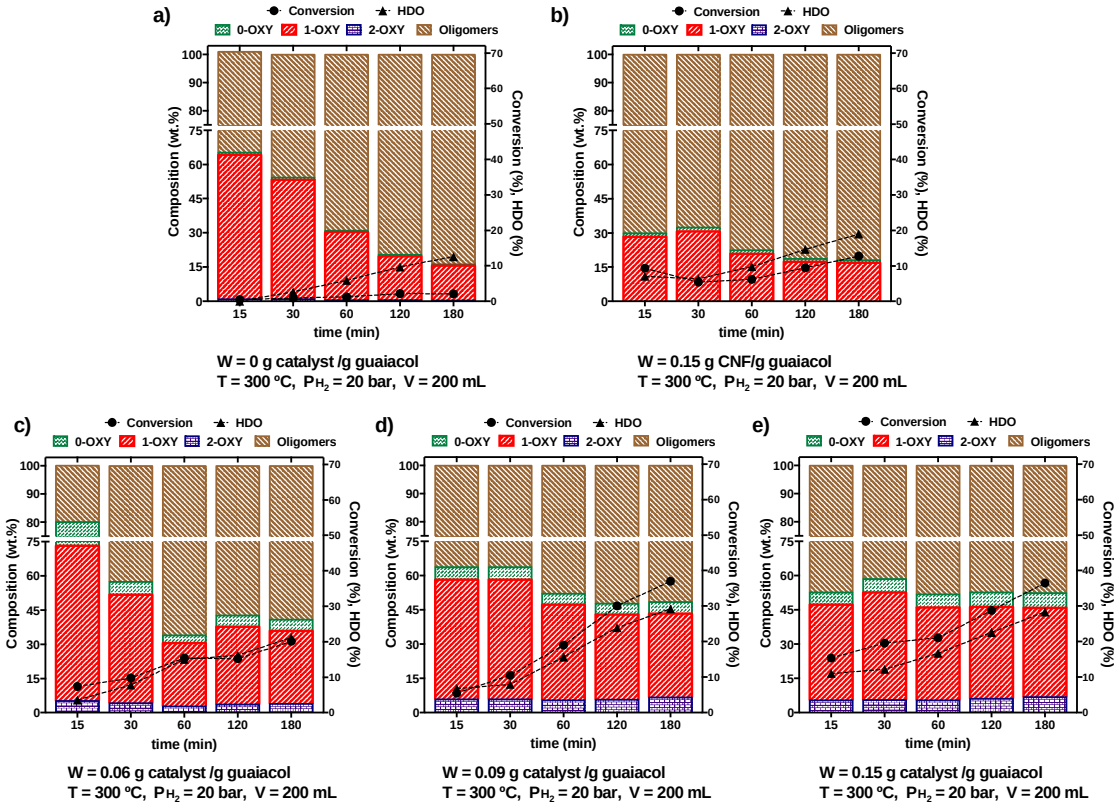

Figure 2. Evolution over time of the guaiacol conversion, HDO efficiency and liquid product distribution (un-reacted guaiacol and solvent free) using different catalyst loadings.

In the absence of a catalyst, the guaiacol conversion and HDO efficiency are very low regardless of the reaction time (0-180 min). The liquid phase is largely made up of 1-oxy products and high molecular weight soluble oligomers. The large proportion of this latter species in the liquid product is accounted for by the great spread of condensation, polymerisation and oligomerisation reactions occurring during the HDO of guaiacol in the absence of a catalyst [23, 44, 46, 47]. Increasing the reaction time leads to a small increase in the guaiacol conversion and HDO efficiency together with a substantial increase in the relative amount of high molecular weight species in the liquid product, due the progressive extension of condensation and oligomerisation reactions with the course of the reaction [46, 47, 51].

Using the CNF as the catalyst for the HDO of guaiacol leads to an increase in the guaiacol conversion and HDO efficiency in comparison to the results obtained without a catalyst, which indicates that the fibres on their own (without Mo_2C) possess some catalytic activity. These differences are notably marked at early reaction stages, as the positive catalytic effect of the fibres allows achieving the same degree of conversion obtained in the absence of a catalyst using a much shorter reaction time. The liquid product largely comprises high molecular weight oligomers together with small amounts of 0-oxy and 1-oxy compounds. In addition, the reaction time exerts a significant influence. While an initial increase in the reaction time between 0 and 60 min does not substantially increase the guaiacol conversion, HDO efficiency or liquid product distribution, a further increase up to 180 min not only does lead to increases in the guaiacol conversion and HDO efficiency, but also it modifies the composition of the liquid product. In particular, the proportion of 1-oxy compounds decreases and the relative amount of high molecular weight species increases. This is believed to be the

392 consequence of the greater extension of condensation and oligomerisation reactions of
393 guaiacol occurring in the absence of a selective hydrodeoxygenation catalyst, which
394 increases the guaiacol conversion but decreases the selectivity towards desired HDO
395 products [44, 46, 47, 51].
396
397 The catalyst loading has a significant influence on the HDO of guaiacol at the operating
398 conditions tested in this work. Regardless of the reaction time, an initial increase in the
399 amount of catalyst from 0 to 0.09 g catalyst/g guaiacol (Figures 2 a, c and d)
400 significantly increases the guaiacol conversion and HDO efficiency due to the positive
401 effect of the catalyst on demethylation, demethoxylation, deoxygenation,
402 transalkylation, methylation and hydrogenation reactions [23, 42, 44-46]. In addition,
403 this increase in the catalyst amount also modifies the composition of the liquid product.
404 In particular, the proportion of oligomers decreases at expense of the increase in the
405 relative amount of HDO products (2-oxy, 1-oxy and 0-oxy compounds) due to the
406 positive catalytic effect of the catalyst on the process [23, 45, 46]. Increasing the
407 guaiacol conversion decreases the proportion of oligomers in the liquid product, as
408 some intermediate 1-oxy products, such as phenol and cresol, are more stable against
409 self-condensation than guaiacol, thus decreasing the formation of these macromolecular
410 species [47, 51]. In addition, it might be also possible that the oligomers produced can
411 be transformed into low molecular weight compounds via fragmentation,
412 depolymerisation and cracking reactions. Among the HDO products, the relative
413 amounts of 0-oxy and 2-oxy compounds increase, while the concentration of 1-oxy
414 compounds remains relatively steady for the first 60 min of reaction and increases
415 afterwards (60-180 min). At early reaction stages, the proportion of 1-oxy compounds is
416 not greatly affected by the catalyst loading due to the compensation of two

developments: the decrease in the relative amount of oligomers and the increase in the proportion of 2-oxy species produced from 1-oxy compounds. Conversely, when a longer reaction time is used (60-180 min), increasing the catalyst amount also leads to an increase in the guaiacol conversion; however, the amount of catalyst and/or H_2 in the reactor is not sufficient to transform 1-oxy compounds into 2-oxy compounds; and consequently, 1-oxy compounds accumulate.

A further increase in the catalyst amount from 0.09 to 0.15 g catalyst/g guaiacol results in two different outcomes depending on the reaction time. On the one hand, when a short reaction time (0-30 min) is used, increasing the catalyst loading leads to small increases in the guaiacol conversion and HDO efficiency. On the other, between 60 and 180 min, this same increase in the catalyst loading does not exert a significant influence on the guaiacol conversion or HDO efficiency. In addition, the overall composition of the liquid phase is not substantially modified with increasing the catalyst loading from 0.09 to 0.15 g catalyst/g guaiacol. Specifically, while at early reaction stages (between 0 and 30 min), moderate increases and decreases take place for the proportions of oligomers and 1-oxy compounds, respectively, non-significant variations are observed in the composition of the liquid product between 60 and 180 min. However, this increase in the catalyst loading does significantly modify the composition of 1-oxy compounds. In particular, the proportion of phenol decreases, while the relative amount of 2,3-xylenol increases, thus suggesting the progressive transformation of the former in the latter due to the greater amount of catalyst in the reactor (Table S1e).

These developments are believed to be a consequence of a possible H_2 limitation; i.e. a limited amount of H_2 dissolved in the reaction medium (decane) under some conditions.

Under the operating conditions tested (200 mL of a 3 vol.% guaiacol solution, 300 ºC, 60 bar of H_2 and a liquid reaction mixture of 200 mL), the maximum H_2/guaiacol ratio that could be achieved in the experiment (if all the H_2 initially loaded in the reactor was effectively dissolved in the decane solution) is 1.51 mol H_2/mol guaicol. Taking into account the thermodynamic solubility of H_2 in decane at reaction conditions (0.63 mol H_2/kg decane [52]), the maximum thermodynamic H_2/guaiacol ratio that can be achieved is 2.61 mol H_2/mol guaiacol, which is higher than the experimental H_2/guaiacol ratio loaded in the reactor. Therefore, the activity of the catalyst might be limited by the H_2 availability in the reaction medium, this phenomenon also being controlled by the diffusion of H_2 from the gas to the liquid. Thus, this limited amount of H_2 in comparison to the amount of guaiacol in the liquid hinders the transformation of 1-oxy into 2-oxy compounds. However, despite this H_2 limitation, a greater amount of catalyst in the reactor might promote other reactions, such as transalkylation and methylation, which modifies the reaction pathway. This prevents phenol deoxygenation due to the limited amount of H_2 in the reaction medium, favouring its transformation into 2,3-xylenol instead, via a first transalkylation to o-creosol followed by a methylation reaction. As a result, non-significant variations are observed for the total proportions of 1-oxy and 2-oxy compounds with increasing the catalyst loading, especially from 0.09 to 0.15 g catalyst/g guaiacol at long reaction times.

3.2.2 Initial H_2 pressure

Figure 3 shows the effects of the initial H_2 pressure on the HDO of guaiacol at 300 ºC using a catalyst loading of 0.15 g catalyst/g guaiacol and a liquid reaction volume of 200 mL. In particular, Figures 3 a, b and c plot the evolution over time of the guaiacol conversion, HDO efficiency and liquid product composition using an initial H_2 pressure

of 20, 30 and 60 bar (60, 80 and 120 bar at reaction conditions). Tables S2a-c list the detailed liquid product composition.

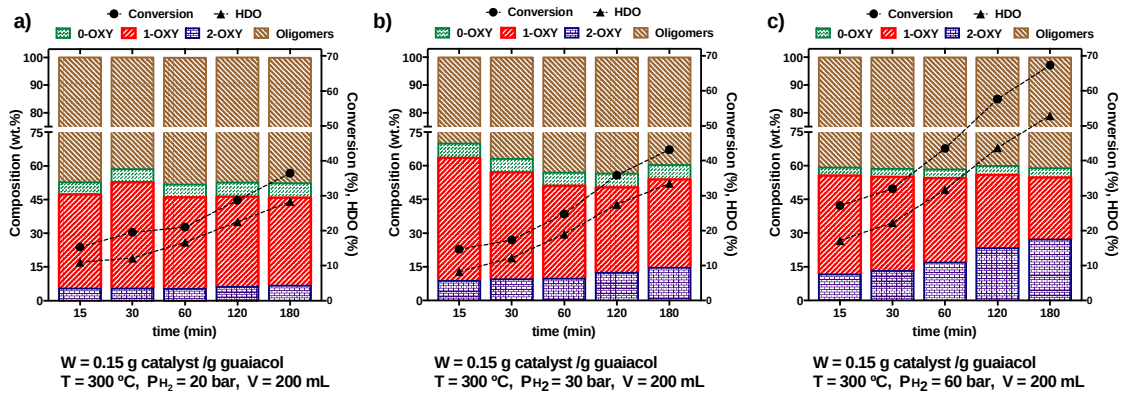

Figure 3. Evolution over time of the guaiacol conversion, HDO efficiency and liquid product distribution (un-reacted guaiacol and solvent free) using different initial H_2 pressures.

Figure 3 shows the significant effect of the H_2 pressure on the HDO of guaiacol. An increase in the initial H_2 pressure from 20 to 60 bar increases the guaiacol conversion and HDO efficiency and modifies the liquid product distribution. In particular, this increase in the H_2 pressure leads to an increase in the proportion of HDO products together with a decrease in the relative amount of high molecular weight oligomers. This is believed to be the result of the greater spread of HDO reactions in comparison to condensation reactions due to the greater amount of H_2 dissolved in the reaction medium [23, 45, 46]. Increasing the H_2 pressure not only does upsurge the initial H_2/guaiacol ratio (1.51, 2.28 and 4.55 mol H_2/mol guaiacol at 20, 30 and 60 bar initial H_2 pressure, respectively) but also it increases the thermodynamic H_2/guaiacol ratio (2.61, 3.43 and 5.10 mol H_2/mol guaiacol at 60, 80 and 120 bar of H_2 at reaction conditions, respectively). This increase in the initial H_2 pressure upsurges both the initial and thermodynamic H_2/guaiacol ratios, decreasing the difference between them. This improves the solubility of H_2 in the reaction medium, which might allow reaching

experimental H_2/guaiacol ratios much closer to the thermodynamic values. Therefore, augmenting the H_2 pressure increases the proportion of 2-oxy compounds, leading to reductions in the relative amounts of 0-oxy and 1-oxy compounds. This promotes the progressive conversion of 0-oxy compounds into 1-oxy compounds; this latter species being subsequently transformed into 2-oxy compounds [23, 45-47]. These variations are notably more marked when the initial H_2 pressure increases from 30 to 60 bar due to the greater increase achieved in the H_2/guaiacol ratio as described above.

Regardless of the initial H_2 pressure, both the guaiacol conversion and HDO efficiency increase over time due to the positive effect of the reaction time on the process, leading to a progressive guaiacol decomposition into less oxygenated products, thus increasing the conversion and HDO efficiency over time. However, these increases depend on the initial H_2 pressure; the higher the initial H_2 pressure, the sharper are the increases observed for the guaiacol conversion and HDO efficiency. In addition, the evolution over time for the liquid product distribution also depends on the initial H_2 pressure with different variations taking place. On the one hand, when a low initial H_2 pressure is used, the liquid composition remains relatively steady over the 3 h reaction. Only minor decreases and increases over time are observed for the relative amounts of 1-oxy and 2-oxy compounds, respectively; these variations leading to a soft increase in the HDO efficiency. On the other hand, increasing the initial H_2 pressure boosts the effect of the reaction time on the liquid product composition. In particular, sharper increases and decreases over time are observed with increasing the H_2 pressure for the proportions of 2-oxy and 1-oxy compounds, respectively. The different evolution of these variables over time might be accounted for by the variations in the experimental H_2/guaiacol ratio of the solutions. For a low initial H_2 pressure, the experimental H_2/guaiacol ratio is quite

low and decreases over the course of the reaction due to the progressive H_2 consumption, thus impeding the progress of the reaction and hampering the conversion of 1-oxy compounds into 2-oxy species. Conversely, increasing the H_2 pressure augments both the initial maximum H_2/guaiacol ratio and the thermodynamic H_2/guaiacol ratio dissolved in decane at reaction conditions; thus the process is less affected by the experimental decrease in the H_2/guaiacol ratio over the course of the reaction.

3.2.3 Reaction temperature

Figure 4 shows the effects of the reaction temperature on the HDO of guaiacol using a catalyst loading of 0.15 g catalyst/g guaiacol, an initial H_2 pressure of 30 bar and a liquid reaction volume of 200 mL. In particular, Figures 4 a, b and c plot the evolution over time of the guaiacol conversion, HDO efficiency and liquid product composition using a reaction temperature of 270, 300 and 330 ºC, respectively. Tables S3a-c list the detailed liquid product composition.

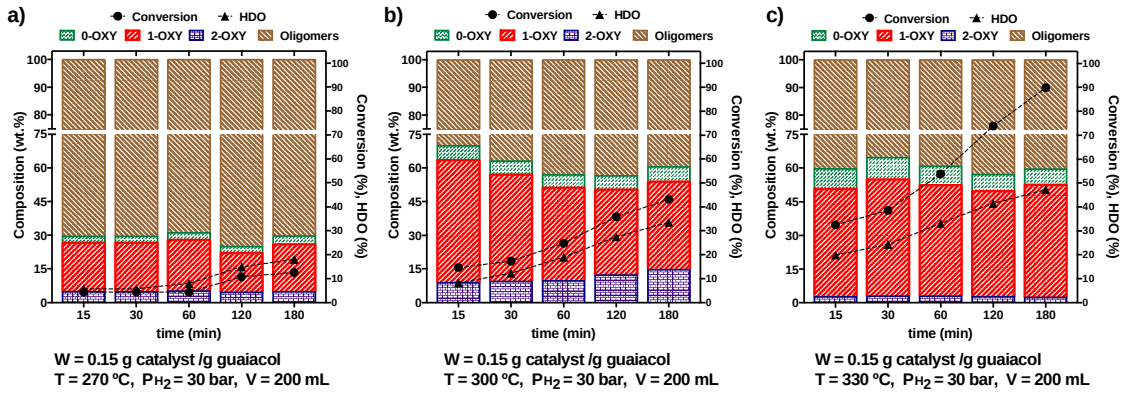

Figure 4. Evolution over time of the reaction temperature on the guaiacol conversion, HDO efficiency and liquid product distribution (un-reacted guaiacol and solvent free) using different reaction temperatures.

The temperature exerts a significant influence on the guaiacol conversion, HDO efficiency, liquid product distribution and the evolution of these variables over time. When a low temperature (270 ºC) is used, the guaiacol conversion and the HDO efficiency are very low, especially during the first 60 min of reaction. In addition, the liquid product largely comprises high molecular weight oligomers; the proportion of HDO products in the reaction mixture being lower than 30 wt.% regardless of the reaction time. An increase in the reaction temperature from 270 to 300 ºC substantially increases the guaiacol conversion and HDO efficiency. In addition, this increase in temperature leads to a significant decrease in the relative amount of oligomers together with an increase in the concentration of HDO products. This also results in a greater amount of 0-oxy, 1-oxy and 2-oxy compounds in the liquid product. A subsequent increase from 300 to 330 ºC leads to a sharp increase in the guaiacol conversion, augmenting the HDO efficiency very slightly. Although these variations take place without substantially modifying the proportions of oligomers in the liquid reaction product, some variations in the distribution of HDO products occur. In particular, augmenting the temperature from 300 to 330 ºC leads to increases in the relative amounts of 0-oxy and 1-oxy species along with a decrease in the proportions of 2-oxy compounds; thus explaining the small increase observed in the HDO efficiency.

It is believed that thermodynamic and kinetic phenomena account for these variations. At low temperature (270 ºC) the catalysts might not be active enough and as a result, low conversions and HDO efficiencies are observed. In these cases, the liquid product is largely made up of high molecular weight oligomers resulted from the non-catalytic decomposition of guaiacol. An initial increase in the temperature from 270 to 300 ºC increases the guaiacol conversion, HDO efficiency and the presence of HDO species in

the liquid product mixture due to the positive kinetic effect of the temperature on the process, thus increasing the activity of the catalyst as well as the reaction rate of the HDO reactions [47]. A further increase in the temperature also leads to a significant increase in the guaiacol conversion due to the positive effect of the temperature on some reactions. However, the composition of the liquid product is controlled thermodynamically. In particular, deoxygenation and dehydration reactions are exothermic [53], and therefore, increasing the temperature prevents the development of these reactions, thus hampering the initial transformation of 0-oxy compounds into 1-oxy species as well as the subsequent conversion of these latter compounds into 2-oxy products. In addition, it must be borne in mind that H_2 adsorption on the catalyst surface is also an exothermic process and an increase in the reaction temperature changes the H_2 sorption equilibrium [54]. Thus, the decreases in H_2 adsorption and surface coverage with the increase in the temperature hinder hydrogenation reactions [54].

As a result of these developments, the proportions of 0-oxy and 1-oxy compounds in the liquid product increase as the expense of the reduction in the relative amount of 2-oxy compounds. These variations are clearly observed analysing the detailed liquid product compositions (Tables S3b and c), as increasing the temperature from 300 to 330 ºC substantially increases the proportion of phenol and decreases the relative amount of 2,3-xylenol. Furthermore, the initial H_2/guaiacol ratio is 2.28 mol H_2/mol guaiacol regardless of the reaction temperature, while the thermodynamic value depends on the temperature and pressure achieved in the experiment; i.e. 2.61, 3.43 and 3.51 mol H_2/mol guaiacol for the experiments conducted at 270, 300 and 330 ºC, respectively. Therefore, the small variations occurring in the H_2/guaiacol ratio when the temperature

584 of the experiment increases from 300 to 330 ºC supports the thermodynamic limitation
585 hypothesis.
586
587 With regard to the evolution over time of these variables, Figure 4 shows how such
588 variations depend on the reaction temperature. At 270 ºC, small variations over time are
589 observed for the guaiacol conversion and HDO efficiency due to the low guaiacol
590 catalytic conversion achieved at low temperature [47]. In addition, the composition of
591 the liquid product does not depend on the reaction time, and largely the same product
592 composition is observed within the 180 min of reaction. Conversely, increasing the
593 temperature modifies the effect of the reaction time on the process. At medium
594 temperature (300 ºC), sharp increases in the guaiacol conversion and HDO efficiency
595 take place with the course of the reaction. In addition, the composition of the liquid
596 product also depends on the reaction time. In particular, even though the relative
597 amount of high molecular oligomers does not depend on the reaction time, and the same
598 proportion for these species is observed in the reaction mixture, several variations in the
599 relative amount of HDO products take place.
600
601 In particular, the proportion of 1-oxy compounds decreases and the relative amount of
602 2-oxy compounds increases due to the progressive transformation of the former into the
603 latter compounds over the course of the reaction. This transformation is the
604 consequence of the positive kinetic effect of the reaction time on the process. In
605 addition, two counteracting effects might account for the steady value observed in the
606 relative amount of oligomers. On the one hand, an increase in the reaction time
607 promotes the formation of oligomers via condensation and radical-induced
608 rearrangement reactions, thus increasing the proportions of oligomers over time. On the

other, increasing the reaction time also reduces the amount of guaiacol available to undergo condensation and radical-induced rearrangement reactions due to the formation of 1-oxy and 2-oxy species, which are less reactive towards these reactions. In addition, oligomers can also be transformed into low molecular weight compounds via depolymerisation, fragmentation and cracking reactions. As a result of this compensatory effect, the proportion of oligomers remains steady over time. A further increase in the temperature from 300 to 330 ºC modifies the effect of the reaction time on the process. While the guaiacol conversion displays a substantial increase over time, the HDO efficiency does not evolve accordingly, and a soft increase is observed for this variable. In addition, the liquid product distribution is not greatly influenced by the reaction time. This is the result of the thermodynamic inhibitory effect of the pressure hindering the transformation of 1-oxy compounds into 2-oxy species [53, 54]. Therefore, although the guaiacol conversion and the production of oligomers and 1-oxy compounds increase over time, their relative amount in the product mixture remains constant.

3.2.4 Initial H_2/guaiacol ratio and liquid reaction volume

Figure 5 shows the effects of the H_2/guaiacol ratio and the liquid reaction volume on the HDO of guaiacol using a catalyst loading of 0.15 g catalyst/g guaiacol at 300 ºC for 120 min. Figure 5 shows the effects of the initial H_2 pressure (20, 30 and 60 bar) using two reaction liquid volumes: 200 and 120 mL, which allowed varying the initial H_2/guaiacol ratio from 1.51 to 4.55 mol H_2/mol guaiacol and from 4.55 to 13.60 mol H_2/mol guaiacol using the large and the small liquid reaction volume, respectively. The H_2 pressure achieved at reaction conditions (300 ºC) using an initial H_2 pressure of 20, 30 and 60 bar is as follows: 60, 80 and 120 bar, using a reaction liquid volume of 200 mL

and 34, 50 and 80 bar using a liquid volume of 120 mL. Table S4 lists the detailed liquid product composition.

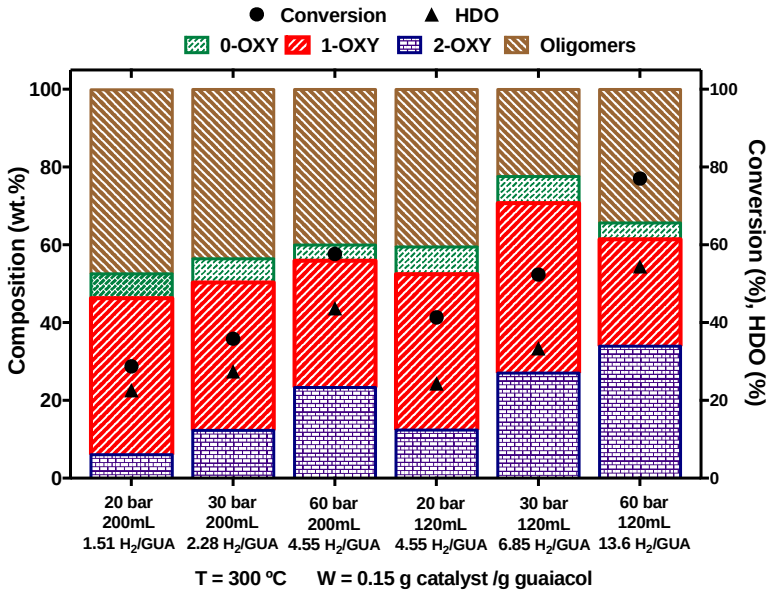

Figure 5. Effect of the H_2/guaiacol ratio and liquid reaction volume on the guaiacol conversion, HDO efficiency and liquid product distribution (un-reacted guaiacol and solvent free).

The effect of the H_2 pressure on the HDO of guaiacol depends on the liquid reaction volume and vice versa. Regardless of the liquid volume, an increase in the initial H_2 pressure from 20 to 60 bar leads to an increase in the guaiacol conversion and HDO efficiency. However, these increases depend on the reaction volume, with more pronounced variations occurring for a small (120 mL) than for a large (200 mL) liquid volume. These differences are accounted for by the greater variation occurring in the H_2/guaiacol ratio for the small (120 mL) than for the large (200 mL) liquid volume. A 300 mL reactor was used in both cases, thus allowing a greater amount of H_2 to be loaded in the reactor when using 120 mL than 200 mL at the same initial H_2 pressure.

In addition, the composition of the liquid phase is also influenced by the initial H_2/guaiacol ratio and liquid reaction volume. When a large reaction volume is used

(200 mL), increasing the H_2 pressure leads to an increase in the relative amount of 2-oxy compounds together with decreases in the proportions of oligomers, 0-oxy and 1-oxy compounds. This increase in the initial H_2 pressure increases the H_2/guaiacol ratio, thus favouring HDO reactions over oligomerisation and condensation reactions [23, 45, 46]. This leads to a decrease in the relative amount of oligomers together with an increase in the proportions of HDO products in the liquid [46, 47]. Among these, the proportions of 0-oxy and 1-oxy compounds decrease, while the relative amount of 2-oxy species increases due to the progressive transformation of 0-oxy and 1-oxy compounds into fully deoxygenated products [23, 45-47]. Conversely, for a small liquid reaction volume (120 mL), an initial increase in the initial H_2 pressure from 20 to 30 bar results in a similar liquid product evolution; i.e. a decrease in the proportions of oligomers together with an increase in the relative amount of 2-oxy compounds with minimal variations in the proportions of 0-oxy and 1-oxy compounds. While a further increase from 30 to 60 bar also increases the relative amount of 2-oxy compounds, the proportion of oligomers and 1-oxy compounds increases and decreases, respectively. This suggests the transformation of 1-oxy and 2-oxy compounds into high molecular weight oligomers via polymerisation and oligomerisation reactions at high guaiacol conversion levels. As a result, the relative amount of 1-oxy compounds decreases and the increase in the proportion of 2-oxy compounds is not as pronounced as it could have been expected attending the increase observed in the guaiacol conversion.

The comparison between the experiments conducted with the same experimental H_2/guiacol ratio (4.45 mol/mol) using a H_2 pressure and a reaction volume of 60 bar and 200 mL, and 30 bar and 120 mL reveals the relationship between the H_2 pressure and liquid volume during the HDO of guaiacol. Despite the fact that the same experimental

H_2/guaiacol ratio is used, different results are observed. In particular, a higher guaiacol conversion and HDO efficiency take place at 60 bar than at 20 bar. In addition, the liquid product has a higher amount of 2-oxy compounds together with a lower proportion of 1-oxy species when a high H_2 pressure is used. These differences are accounted for by the higher thermodynamic H_2/guaiacol ratio achieved at 60 bar and 200 mL of liquid (5.1 mol H_2/mol guaiacol) than at 30 bar and 120 mL of liquid (1.25 mol H_2/mol guaiacol) [52]; thus increasing the H_2 availability in the reaction medium. This higher amount of H_2 increases the guaiacol conversion and shifts the liquid product distribution towards the formation of more deoxygenated species (2-oxy compounds), augmenting the HDO efficiency of the process [23, 45-47].

4. Conclusions

This work firstly addresses the effects of the catalyst loading (0-0.15 g cat/g guaiacol), initial H_2 pressure (20-60 bar), temperature (270-330 ºC), reaction time (0-180 min), H_2/guaiacol ratio (1.5-13.6 mol/mol) and liquid reaction volume (120-200 mL) on the hydrodeoxygenation (HDO) of guaiacol, a common lignocellulisic bio-oil representative molecule, using a Mo_2C/CNF catalyst. The most important conclusions are summarised as follows.

1. The Mo_2C/CNF catalyst displayed a positive effect on the HDO of guaiacol. Very low guaiacol conversions and HDO efficiencies were obtained in the absence of a catalyst. Conversely, increases over time were observed for the guaiacol conversion and HDO efficiency in the presence of the Mo_2C/CNF catalyst. Furthermore, an increase in the catalyst loading increased the guaiacol conversion and HDO efficiency as well as the proportions of HDO products in the liquid phase.

2. Augmenting the initial H_2 pressure rose the experimental and thermodynamic H_2/guaiacol ratios, thus augmenting the H_2 availability in the reaction medium and therefore, increasing the guaiacol conversion and HDO efficiency. Regardless of the H_2 pressure, the guaiacol conversion and HDO efficiency increased over time; these variations being notably marked at elevated H_2 pressure, which promoted the transformation over time of 1-oxy compounds into fully deoxygenated products.

3. The temperature exerted a kinetic promoting effect together with a thermodynamic inhibitory influence. An initial increase in the temperature increased the guaiacol conversion, HDO efficiency as well as the proportion of HDO products in the liquid. Conversely, a subsequent temperature increase hindered the conversion of partially deoxygenated species into fully deoxygenated products due to the exothermic nature of some of the chemical reactions involved in such transformations.

4. The increases observed in the guaiacol conversion and HDO efficiency as well as the presence of less oxygenated compounds in the liquid product with increasing the H_2 pressure depended on the reaction volume, with more pronounced variations occurring for a small than for a large liquid volume; these differences being the consequence of the greater variation occurring in the H_2/guaiacol ratio for former than the latter volume. In addition, when the same experimental H_2/guiacol ratio was attained with two different initial H_2 pressures and reaction volumes, higher guaiacol conversions, HDO efficiencies and proportions of fully deoxygenated products were achieved using the higher initial H_2 pressure and larger volume due to the greater thermodynamic H_2/guaiacol ratio achieved.

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