Sustainable production of liquid biofuels and value-added platform chemicals by hydrodeoxygenation of lignocellulosic bio-oil over a carbon-neutral Mo_2C/CNF catalyst

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Abstract:

For the first time, this work addresses the hydrodeoxygenation (HDO) of lignocellulosic bio-oil over a carbon-neutral Mo_2C/CNF catalyst for the production of liquid biofuels and value-added chemicals, thoroughly examining the effect of the temperature, initial H_2 pressure, reaction time and catalyst/bio-oil ratio. These variables had a significant influence on the process, allowing the transformation of the original bio-oil into different fractions in varying yields, including an upgraded bio-oil (17-72%), a solid product (4-44%), an aqueous phase (5-39%) and a gaseous stream (1-15%). The upgraded bio-oil comprised a mix of phenols (56-78%), cyclic ketones (7-30%), carboxylic acids (2-8%), esters (0-9%) and aromatic compounds (0-20%). The relative amounts of C, H and O of this product shifted by 34-78 wt.%, 3-8 wt.% and 13-62 wt.%, while its HHV ranged between 9 and 35 MJ/kg. Process optimisation revealed that using a temperature of 350 ºC, an initial H_2 pressure of 40 bar and 0.19 g cat/g bio-oil for 1 h, it was possible to convert 65% of the organic content of the bio-oil into a liquid bio-fuel with a HHV of 30 MJ/kg (twice the value of the original feedstock), which represents a deoxygenation degree of 70% and an energy efficiency of 62%. Besides, all the bio-oil organic content can be converted into a liquid product with a high proportion of phenols (79%) at 250 ºC, applying an initial H_2 pressure of 20 bar and 0.14 g cat/g bio-oil for around 0.5 h. This liquid can be used as a sustainable phenolic-rich antioxidant additive as well as a bio-based source of aromatic compounds. Therefore, these results are a step forward in the biomass conversion over carbon-neutral catalysts.

Keywords: bio-oil, hydrodeoxygenation, molybdenum carbides, carbon nanofibres, biofuels.

1. Introduction

Dwelling resources, global megatrends, planetary boundaries, together with environmental concerns, have led researches to investigate carbon-neutral and sustainable strategies to satisfy the energy requirements and well-being of present and future generations. Amongst the different approaches reported to date to achieve this goal, the use of biomass is seen as an up-and-coming option, as its conversion provides the possibility to furnish a broad range of clean fuels and high-value chemicals [1, 2]. In particular, fast pyrolysis and/or hydrothermal liquefaction of biomass allows its transformation into a high energy-dense liquid product termed bio-oil [3-6]. This product is a brownish, viscous liquid with a superior energy density in comparison to the original biomass [7]. Despite offering many environmental advantages over fossil fuels [8-10] and having a rather elevated Higher Heating Value (HHV≈17 MJ/kg) [11-13], it is not possible to use this liquid as a 'drop-in' transportation bio-fuel. This is the consequence of its high O/C ratio and elevated viscosity, acidity and corrosiveness [14]. These unfavourable characteristics are related to the reactive O functionalities present in bio-oils, them all have been directly inherited from the original biomass from which bio-oils are produced. As a result of these drawbacks, it is compulsory to subject bio-oil to an upgrading process, such as hydrotreating, hydrocracking, hydrodeoxygenation [13] and/or the applications of fluids at the supercritical state [8-11, 15], to arise with a bio-liquid compatible with the actual fuel infrastructure. Amongst these, hydrodeoxygenation (HDO) is seen as one of the most promising technologies for the production of biofuels and chemicals from lignocellulosic bio-oils in sufficient quantity and quality [16].

HDO involves the catalytic reduction of the O/C ratio of the bio-oil under a H_2-rich atmosphere at mid temperature (250-450ºC) and pressure (40-100 bar H_2) [17]. This H_2 addition must be conducted efficiently, as HDO not only is expected to increase the bio-oil H content but also decrease the relative amount of O of this liquid. Some of the most critical reactions include: i.) H_2 dissociation into the catalyst active sites to produce highly reactive H radicals; ii.) their interaction with C-O bonds in bio-oil, leading to the production of -OH groups or water on the one hand, and/or alkanes on the other. Besides, C=O groups in bio-oil can be reduced to C-O by H_2 and undergo the same route described above. The catalysts most commonly synthesised for HDO involve metal-sulphide (NiMoS and CoMoS) catalysts [18] together with noble (Pd, Pt, Ru and Rh) or transition (Cu, Ni and W) metals [19] supported over metal

oxides (Al_2O_3, SiO_2, ZrO_2, CeO_2 and TiO_2), zeolites and/or carbon-based materials. However, these catalysts suffer from different types of deactivation and have some intrinsic physicochemical properties that hamper their use for bio-oil HDO [20-22].

Therefore, to surpass these catalytic weaknesses, it is necessary to develop new, active, selective and deactivation resistant catalysts. In this regard, metal carbides have recently arisen as favourable catalytic materials for the HDO of lignocellulosic bio-oil. Among these, molybdenum carbide (Mo_2C) is seen as an auspicious material to this end. This carbide has better stability in comparison to sulphides [23, 24] and displays a noble metal catalytic behaviour [23, 25, 26]. Besides, it is more effective in maximising the O-removal and minimising the consumption of hydrogen [25]. Nonetheless, these carbides have commonly been supported over metal oxides (Al_2O_3, SiO_2, ZrO_2) [18, 27, 28] and zeolites (largely HZSM-5) [18, 25, 29], which result into the same disadvantages as traditional catalysts. As such, more work is still needed on this matter, with substantial emphasis to be placed on the development of adequate supports for Mo_2C. In this respect, carbon nanofibres (CNF) own excellent physicochemical properties to be used as the support for catalysts preparation. These include extraordinary chemical steadiness in non-oxidising media, an extremely tuneable chemical nature, accompanied by stupendous textural properties [30, 31]. Besides, they can be produced using environmentally friendly and carbon-neutral processes, thus clearly contributing to the development of future bio-refineries. It must be borne in mind that Mo_2C is usually synthesised by a carbothermal reaction, in which a molybdenum precursor is heated along with a carburising gas [32]. Therefore, CNF themselves can serve as the source of carbon if H_2, which can also be renewable, is used as the reducing agent. This process, termed 'carbothermal hydrogen reduction' (CHR), avoids using hydrocarbons during the catalyst preparation procedure, which helps not only to inhibit coke formation on the Mo_2C surface [33] but also improve the sustainability and renewable nature of the catalyst. This is in line with the new bio-refinery models and circular economy principles, wherein not only the feedstocks, reagents and procedures but also the catalysts used must be renewable and environmentally friendly.

Regarding the use of Mo_2C/CNF as a catalyst for bio-oil HDO, all work reported to date has focused on upgrading guaiacol (2-methoxy phenol), a bio-oil model compound. Jongerius et al. [34] used a

Mo_2C/CNF catalyst for guiacol HDO, studying the impact of the temperature (300-350 ºC) and reaction time (0-6 h) at 55 bar of H_2 pressure. They reported that the guaiacol conversion and benzene and toluene selectivities increased with augmenting the temperature and/or prolonging the reaction time. Liu et al. [25] used a 300 mL batch reactor to address the influence of the reaction temperature (330-375 ºC) and process duration (0-300 min) at 34 bar of initial H_2 pressure. Augmenting the reaction time or temperature improved the guaiacol conversion, which led to complete conversion in 120 min at 375 ºC. Moreira et al. [35] used a Mo_2C/commercial CNF catalyst to study the influences of the temperature (300-350 ºC), initial H_2 pressure (20-30 bar) and time (2-4 h) during the HDO of guaiacol. They found that the use of elevated temperatures and prolonged reaction times aided to the guaiacol conversion, but such spreads also promoted the formation of high molecular weight undesirable compounds. Ochoa et al. [36] studied the influences of the temperature (550-750 ºC) and rate (1-10 ºC/min) of carburisation on the catalytic properties and activity of a Mo_2C/CNF catalyst with a 15 wt.% Mo loading. The catalyst was tested in the HDO of guaiacol at 300 ºC, 20 bar initial H_2 pressure for 2 h. Elevated temperatures coupled with low heating carburisation rates were fundamental to achieve an adequate catalyst for this reaction. In a parallel work [37], these authors examined the effects of the carburisation time (1-18 h) at 750 ºC on both, the physicochemical and catalytic properties of a Mo_2C/CNF catalyst, under the same reaction conditions described above. Augmenting the carburisation time from 1 to 18 h enlarged the β-Mo_2C crystal size from 6 to 18 nm, resulting in substantial gasification of the CNF, which overall decreased the catalytic activity of the material. In another work [38], these authors used a Mo_2C/CNF catalyst prepared at optimum conditions to analyse the influences of the processing parameters. They reported that the progressive transformation of guaiacol into less oxygenated species substantially depended on the catalyst/guiacol ratio and the quantity of H_2 dissolved in the reaction medium. They indicated that a careful selection of these variables is fundamental to achieve an efficient HDO process.

These publications provide valuable data on the most important physicochemical properties and catalytic behaviour of Mo_2C/CNF catalysts in the HDO of guaiacol, a bio-oil model compound, at different operating conditions. However, the reactivity of a certain species is commonly different when being in a complex mixture (bio-oil) in comparison to its own conversion, since several interactions between bio-oil constituents may occur in the upgrading process [39]. Therefore, novel insights still

need to be gained into the use of Mo_2C/CNF catalysts for the HDO of real bio-oil to study their activity in a real case scenario. Besides, the significance of design, process control and optimisation in the early-stage technology development is emphasised as crucial to the commercial and sustainable feasibility of future bio-refineries. As such, not only it is vital to study the catalytic behaviour of Mo_2C/CNF catalysts using real bio-oil, but also it becomes crucial to carefully understand the influences of the operating reaction parameters on the process.

However, to the best of the authors' knowledge, Mo_2C/CNF catalysts have never been used for the HDO of real bio-oil, while the publications addressing the effects of the processing variables and/or catalyst type on the HDO of real bio-oils are also extremely scarce. Zhang et al. [40] scrutinised the HDO of bio-oil over a sulphided CoMo-P/Al_2O_3 catalyst with tetralin as a solvent. At optimum conditions (360 ºC, 20 bar initial H_2 and 30 min), 76% of the bio-oil was converted into a hydrocarbon-rich product (60 wt.%), with a HHV of 42 MJ/Kg (twice as high as that of the original bio-oil 21 MJ/kg). Churin et al. [41] upgraded a pyrolysis bio-oil over a CoMo and a NiMo catalyst, reporting the influences of the H_2 pressure (50-120 bar) and reaction temperature (270-400 ºC) in a continuous reactor. After the reaction, the proportion of phenols decreased from 40 to 18 wt.%, while the relative amount of hydrocarbons increased from 10 to 70 wt.%. Shu et al. [42] developed a Pt/TiO_2 catalyst for the HDO of bio-oil, derived from the pyrolysis of cotton straw, at 280 ºC, 1 MPa of H_2 for 4 h. After the treatment, the hydrocarbon content increased from 11 to 34%, while the proportion of alkylphenols augmented from 28 to 51%. Cheng et al. [43] investigated the HDO upgrading of bio-oil produced from pyrolyzed pine sawdust using different Fe-Co/SiO_2 (monometallic and bi-metallic) catalysts in a batch reactor at 300 °C and 3.45 MPa. Bimetallic Fe-Co/SiO_2 catalysts were more active to transform the bio-oil oxygenates into hydrocarbons. Among these, the bimetallic, equimolar, Fe-Co/SiO_2 catalyst was the most efficient for bio-oil upgrading, as it allowed transforming the raw bio-oil into a product with a hydrocarbon content of 23%. Hita et al. [44] developed a series of Pt-Pd and Ni-W catalysts supported on a phosphorus-containing activated carbon (ACP), mixed with HZSM-5 zeolites for the HDO of bio-oil. The experiments were performed at 450 °C and 65 bar using a space-time of 0.15 g cat h^{-1} g bio-oil with 90 mL min^{-1} of H_2 during 6 h. The Ni-W catalyst provided the best catalytic results. Alone, it achieved an upgraded bio-oil yield of 42%, with 5 wt.% of phenolic compounds and 12 wt.% of aromatic

products. Mixed with a HZSM-5 zeolite (Si/Al ratio of 140) the catalyst converted 47% of the bio-oil into an upgraded product with a yield of phenolic compounds and aromatic species of 7 and 16 wt.%, respectively. Cordero-Lanzac et al. [45] developed a kinetic model describing the HDO of bio-oil over a Co-Mo bifunctional catalyst supported on activated carbon, using a continuous packed bed reactor operated between 425 and 475 °C. The model described HDO reactions using seven lumps and eleven reaction steps with a high degree of accuracy.

Given this background, for the first time, this work addresses the use of a carbon-neutral Mo_2C/CNF catalyst for the HDO of bio-oil produced from the fast pyrolysis of pine wood biomass, carefully evaluating the effects of the temperature (250-350 ºC), initial H_2 pressure (20-40 bar), reaction time (0-60 min) and catalyst/bio-oil ratio (0-0.25 g cat/g bio-oil) on the processes. This includes the full effects of these conditions on the distribution of the overall reaction products (gas, upgraded bio-oil, residual aqueous fraction and solid residue) and key physicochemical properties (elemental and chemical compositions and HHV) of the upgraded bio-oil. After this analysis, the process was optimised for the selective production of liquid biofuels and value-added platform chemicals. Given the lack of works utilising Mo_2C/CNF as a catalyst for the HDO of bio-oil, along with the negligible information in the literature, thoroughly investigating the full effects of the processing conditions during the HDO of bio-oil, this work exemplifies a step forward in this field, thus helping to the development of greener processes to convert biomass into fuels and chemicals.

2. Experimental

2.1 Catalyst used in the HDO experiments

A carbon-neutral Mo_2C supported on CNF (Mo_2C/CNF) catalyst was employed for the bio-oil HDO, using synthetic bio-gas as the carbon source. This catalyst was previously developed and tested for the HDO of guaiacol, a bio-oil representative compound [36]. It contains a total Mo loading of 14 wt.% (determined by Inductive Coupled Plasma), consisting on Mo^{2+} and Mo_2O/β-Mo_2C species (observed by X-ray Photoelectron Spectroscopy), with a diameter of 10.3 nm and 1.7 nm (determined by X-Ray Diffraction and Transmission Electron Microscopy), respectively, supported on fishbone-type CNF (observed by Transmission Electron Microscopy). The bulk solid has a BET (Brunauer–Emmett–Teller)

surface area of 69.5 m^2/g and a total pore volume of 0.44 cm^3/g. The preparation of the catalysts includes two main steps: the preparation of the support (CNF) and the successive inclusion of Mo_2C using a Mo precursor by impregnation. In a first step, CNF were produced by catalytic decomposition of synthetic biogas (an equimolar CH_4/CO_2 gas mixture) in a rotary bed reactor operated at 650 ºC using a Ni:Co:Al (33.5:33.5:33 wt.%) catalyst. Subsequently, the CNF were functionalised, firstly, with HCl at 60 ºC, intended to eliminate the possible remaining metal content, and then with HNO_3 at its boiling point to generate surface oxygen groups to aid to the Mo precursor impregnation on the fibres [36]. In a second step, the precursor was integrated on the CNF by incipient wetness impregnation, using a $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ aqueous solution with a 10 wt.% Mo content. Then, a carbothermal hydrogen reduction (CHR) process was conducted [36] in the rotary bed reactor operated in a fixed bed position, using 50 mL STP $H_2\cdot min^{-1}\cdot g^{-1}$ CNF. In this process, the catalyst precursor is heated using H_2 as the carburising gas [32], while the CNF serve as the source of carbon. The temperature was increased at a rate of 10 ºC/min from 25 to 750 ºC, after which an isothermal step at 750 ºC was applied for 2 h. As the final, step, the reactor was chilled using a N_2 stream and subjected to passivation employing an O_2/N_2 (1/99 vol.%) gas mix with 545 mL STP $min^{-1}\cdot g^{-1}$ CNF at 25 ºC for 2 h. Complete information about the catalyst synthesis and characterisation can be found elsewhere [36, 37].

2.2 HDO reaction set-up and procedure

Bio-oil HDO experiments were conducted in a 100 mL autoclave reactor made of stainless steel, designed and constructed by Parker Autoclave Engineers. The reaction vessel was heated through a heating jacket controlled by a PID control, monitoring the reaction temperature with a thermocouple internally positioned. Agitation was provided by a stirrer bar, mechanically moved by a magnetic rotor. Besides, a baffle and a coiled tube, located inside the reactor, helped create a turbulent regime and facilitated the intimate hydrogen, bio-oil, catalyst contact. More information about this set-up can be found elsewhere [36-38].

For each run, the reactor was loaded with 30 mL of bio-oil together with different catalyst amounts and H_2 initial pressures, following the experimental design employed in this work. Before the reaction, the reactor was pressurised with N_2 up to a pressure higher than that achieved at reaction conditions to

validate that the reactor is airtight. Subsequently, it was purged with H_2 and pressurised up to the pressure of the experiment. A ramp time (time to reach reaction conditions from room temperature, i.e., 25 ºC) of around 25-35 minutes (depending on the temperature of the HDO reaction) was employed. As such, the reaction time used in the HDO process varied between 0 and 1 h. Therefore, a 0 h experiment only comprises the initial heating and cooling steps, with this latter being the same for all runs. After the reaction, the reactor was quenched with cold water to achieve room temperature conditions as quickly as possible. Once chilled, a gas sample was collected and analysed. Then, the reactor was opened and its content, primarily consisting of a solid (char and spent catalyst)/liquid (bio-oil and water) mixture, was recovered. Besides, the stirrer bar and the reaction vessel were rinsed with chloroform to recover all the reaction products. Subsequently, a solid-liquid extraction was performed in a funnel. The solid was dried at 105 ºC for 24 h and quantified gravimetrically. The liquid, consisting of an aqueous product and the upgraded bio-oil, was subjected to a liquid-liquid separation using chloroform as a solvent. The former fraction was weighted and stored, while the latter was subjected to a two-step separation: first in a rotary evaporator to considerably remove the chloroform and, secondly, in a N_2 drier to completely evaporate the remaining solvent. Finally, the upgraded bio-oil was weighted and stored for analysis.

2.3 Response variables and analytical methods

The distribution of the overall reaction products (gas, aqueous phase, upgraded bio-oil and solid) yields, as well as the HHV and elemental and chemical compositions of the upgraded bio-oil, were used as the response variables to study the influence of the processing conditions. Table 1 shows these variables and the analytical methodologies employed in their determination. The gas-phase composition was determined using a micro gas chromatograph (μGC, Varian CP4900) equipped with a molecular sieve and a Porapack packed columns, coupled to a thermal conductivity detector (TCD). A Varian CP-3800 gas chromatograph (GC) connected to a Saturn 2200 ion trap mass spectrometer (MS) coupled with a low-bleed capillary column (CP-Sil 8 CB: Phenyl 5%, dimethylpolysiloxane 95%, 60 m in length with 0.25 mm of inner diameter and a film thickness of 0.25 μm) was used for the characterisation of the original and upgraded bio-oil. For this, an aliquot was prepared by dissolving the bio-oil (1:25 vol.) in an equivolumetric dichloromethane/ethanol solution. Then, 1 μL of this solution was injected with a

split ratio 25:1. The MS detector operated in electronic ionization mode with a range of 35–550 *m*/*z*. For the analyses, the temperatures of the injector, detector and transfer line were 300 °C, 220 °C and 300 °C, respectively, using He (BIP grade) as the carrier gas at a constant column flow of 1 mL STP/min. In the analyses, an initial oven temperature of 40 °C was used and maintained for 4 min. This isothermal period was followed by a 4 °C/ min ramp increase up to a final temperature of 300 °C, which was kept for 16 min. The NIST 2011 library was used for the individual identification of the compounds. A semi-quantitative approach was used by determining the relative area percentage of all the identified compounds according to a specific m/z ion (base peak) and classifying them into different chemical families (phenols, cyclic ketones, carboxylic acids, esters, aromatic compounds, furans, sugars and others). The elemental analyses were conducted using a Carlo Erba EA1108 Elemental Analyser.

Table 1. Response variables and methods

Product	Response variable	Method
Gas	$\text{Gas yield (\%)} = \frac{\text{mass of gas (g)}}{\text{mass of raw bio} - \text{oil (g)}} 100$	µGC-TCD
	$\text{Composition (vol.\%)} = \frac{\text{mol of each gas}}{\text{total mol of gas}} 100$	µGC-TCD
Bio-oil	$\text{Bio} - \text{oil yield (\%)} = \frac{\text{upgraded bio} - \text{oil (g)}}{\text{raw bio} - \text{oil (g)}} 100$	Gravimetric
	$\text{C, H, O, N, S (wt.\%)} = \frac{\text{mass of C, H, O, N (g)}}{\text{mass of upgraded bio} - \text{oil (g)}} 100$	Elemental Analysis
	HHV (MJ/kg) = 0.3491 C (wt.%) + 1.1783 H (wt.%) – 0.1034 O (wt.%) – 0.015 N (wt.%) + 0.1005 S (wt.%)	Estimated
	$\text{Composition (Area \%)} = \frac{Area\ of\ each\ compound}{\text{Total area of compounds}} 100$	GC-MS
	$\text{Deoxygenation degree (\%)} = \frac{\left(\frac{O}{C}\ bio - oil\right) - \left(\frac{O}{C}\ Upgraded\ bio - oil\right)}{\left(\frac{O}{C}\ bio - oil\right)} 100$	Calculated
	$\text{Energy Efficiency (\%)} = \frac{Upgraded\ Bio - oil\ yield \cdot HHV\ upgraded\ bio - oil}{HHV\ bio - oil} 100$	Calculated
Aqueous phase	$\text{Aqueous yield (\%)} = \frac{\text{mass of water liquid product (g)}}{\text{mass of raw bio} - \text{oil (g)}} 100$	Gravimetric
Solid	$\text{Solid yield (\%)} = \frac{\text{mass of solid (g)}}{\text{mass of raw bio} - \text{oil (g)}} 100$	Gravimetric

2.4 Experimental design and statistical analyses

A statistical 2 level 4 factor Box-Wilson Central Composite Face Centred (CCF, α: ±1) design was used to plan the HDO experiments for the analysis of the temperature, initial H_2 pressure, reaction time and catalyst to bio-oil mass ratio. This design comprises 16 experiments to study linear effects and first-order interaction, 4 repeats conducted at medium conditions to determine the variance of the system, and 8 star runs to address the possible influence of quadratic effects and second-order interactions (Table 4). The experimental HDO data were statistically analysed, utilising a 95% confidence ANOVA

combined with a cause-effect Pareto test. These analyses aided to detect the operating variables and interactions, exerting a significant influence on the process (overall distribution of products and physicochemical properties of the bio-oil). In these analyses, codec variables (varying between -1 and +1) were used, so that all the factors vary within the same interval and are directly comparable. Interaction plots were developed, making use of the results obtained with the ANOVA of all the experiments, in order to carefully explain the effects of the conditions and interactions on the process. To describe graphically and discuss the effects of the processing conditions and interactions between them, their variations were graphically represented in the interaction plots, making use of the formulae obtained in the ANOVA analysis of the 28 experiments performed. In these plots, some experimental points were also included, when possible, to visually demonstrate that the lack of fit is not significant. Overall, this thorough analysis allows conducting a detailed and accurate analysis of the experimental data [46].

2.5 Raw bio-oil characterisation

The bio-oil used in this work was supplied by the Dutch company Biomass Technology Group (BTG). It was produced from the fast pyrolysis of pine sawdust in a rotating cone reactor. The bio-oil was characterised through proximate and ultimate analyses (standard methods ISO-18134:2016, ISO-18122:2016 and ISO-18123:2016) elemental and chemical analyses, calorific value, pH, density, viscosity and water and total acid contents. An Ika Werke C2000 calorimeter was used to determine the HHV of the original bio-oil, while the elemental and chemical analyses were performed using the apparatus described above. The water and total acid contents were determined in a Karl-Fischer titration (Crison Titromatic) according to ASTM E203-96. The pH was determined in a Mettler Toledo T50 pH meter and a Cannon-Fenske routine viscometer (Cannon Instrument 150 T845) at 40 ºC, EN ISO 3104) was used to calculate the viscosity. The most important physicochemical properties of the bio-oil are listed in Table 2.

Table 2. Bio-oil characterisation

Composition	
Organics (wt.%)	60.95
Ash (wt.%)	<0.001
Water content (wt.%)	39.05±0.39
Elemental analysis (raw basis)	
C (wt.%)	44.52±0.34
H (wt.%)	7.43±0.12
O (wt.%)	46.99±0.82
N (wt.%)	1.06±0.12
S (wt.%)	<0.001
Physical properties	
pH	2.69±0.02
Density (g/mL)	1.16±0.01
Viscosity (mPa·s)	10.44±0.48
Tan (mg KOH/g)	111.93±9.72
HHV (MJ/kg) calorimetric	19.54±0.28
HHV (MJ/kg) correlation	19.42
Chemical composition (Area %)	
Phenols	36.39±0.82
Cyclic ketones	3.492±0.28
Carboxylic acids	2.24±0.41
Esters	1.35±0.01
Furans	37.32±3.77
Sugars	19.22±3.07

*O was determined by difference. Results are presented as mean ± standard deviation of three repeats.
Phenols: Phenol, 2-methyl- phenol, 3-methyl- phenol, 2,3-dimethyl- phenol, 2-methoxy- phenol, 4-ethyl-2-methoxy- phenol, 2-methoxy-4-propyl- phenol, creosol and vanillin. **Cyclic ketones:** 2-cyclopenten-1-one, 3-methyl-1,2-cyclopentanedione and 3-ethyl-2-hydroxy-2-cyclopenten-1-one. **Carboxylic acids:** acetic acid, trans-2-Dodecenoic acid and homovanillic acid. **Esters:** 7-oxodehydroabietic acid, methyl ester and hexanoic acid, 3-hydroxy-5-methyl-, methyl ester. **Furans:** 1,4,3,6-Dianhydro-.alpha.-d-glucopyranose, 3,4-Anhydro-d-galactosan, 2,3-Anhydro-d-mannosan and 2,3-Anhydro-d-galactosan. **Sugars:** Levoglucosan.

3. Results and discussion

The experimental reaction conditions used for the bio-oil HDO experiments together with the experimental results are summarised in Table 3. These results include the yields to gas, upgraded bio-oil, aqueous fraction and solid residue as well as the most important physicochemical properties of the upgraded bio-oil, including its HHV and elemental and chemical compositions. The full effects of the processing HDO conditions on the experimental results according to the ANOVA and cause-effect Pareto principle analyses, considering the 28 runs conducted, are summarised in Table 4.

3.1 Overall distributions of the reaction products

The HDO of bio-oil leads to the formation of four main products, whose yields depend on the processing conditions, and vary as follows: gas (2-15%), upgraded bio-oil (17-72%), aqueous fraction (5-39%) and solid (4-44%). The cause-effect Pareto analysis (Table 4) reveals that the temperature is the variable exerting the most considerable influence on the distribution of these products. The positive or negative

influence of a variable can be gathered from the coefficients in the codec formulae obtained from the ANOVA. As such, in general, augmenting the temperature upsurges the gas, solid and aqueous fraction yields (positive term) and the expenses of the upgraded bio-oil yield (negative term). Reforming, cracking, thermal decomposition [47-50] and free-radical [49, 51] reactions are endorsed with temperature, thus promoting bio-oil transformation into other fractions. Besides, the catalyst/bio-oil ratio significantly impacts the solid and aqueous yields, and incrementing the catalyst amount leads to decreases in both variables (negative term). These changes are the outcome of the beneficial influence of the temperature and catalyst on HDO reactions, including hydrogenation, deoxygenation, dehydration, decarbonylation and decarboxylation, which are responsible for bio-oil upgrading and its transformation into gas and aqueous products [43, 52, 53]. This analysis also reveals that the impact of the initial H_2 pressure and reaction time on the overall product distribution is less critical. Furthermore, the reaction time (linear, quadratic or interactions) does not influence the solid yield, which indicates that the vast amount of the solid (principally char) is produced during the heat up step, from the thermal decomposition of non-volatile species in the bio-oil [48]. This finding was already reported during the upgrading of bio-oil derived from biomass and accounted for its high thermal instability [11, 46, 54].

Apart from these single effects, different interactions between variables also significantly affect the distribution of the main reaction products. These interactions are summarised in Figure 1. Notably, as the reaction time does not influence the solid formation, Figure 1 a and b shows the effect of the temperature in the absence and with the highest amount of catalyst (catalyst/bio-oil ratio = 0 and 0.25 g cat/g bio-oil), for a low (20 bar) and high (40 bar) initial H_2 pressure, respectively. Besides, as the gas, upgraded bio-oil and aqueous fraction are influenced by the reaction time, Figure 1 c/d and e/f shows the effect of the temperature, using a reaction time of 0/1 h, on the gas yield, for a catalyst/bio-oil ratio of 0 and 0.25 g cat/g bio-oil, at 20 and 40 bar of initial H_2, respectively. These trends are plot for the upgraded bio-oil and aqueous fraction yields in Figure 1 g-j and k-n, respectively.

Table 3. Bio-oil HDO conditions and experimental results.

Run	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17-20	21	22	23	24	25	26	27	28
T (°C)	250	350	250	350	250	350	250	350	250	350	250	350	250	350	250	350	300	250	350	300	300	300	300	300	300
P (bar)	20	20	40	40	20	20	40	40	20	20	40	40	20	20	40	40	30	30	30	20	40	30	30	30	30
t (h)	0	0	0	0	1	1	1	1	0	0	0	0	1	1	1	1	0.5	0.5	0.5	0.5	0.5	0	1	0.5	0.5
catalyst/bio-oil (g/g)	0	0	0	0	0	0	0	0	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.125	0.125	0.125	0.125	0.125	0.125	0.125	0	0.25
Products distribution																									
Gas yield (%)	2.69	7.85	4.26	8.31	3.91	13.89	3.99	9.52	3.25	11.08	2.59	9.29	3.9	15.43	4.83	14.74	4.77±0.51	3.47	9.24	5.9	5.26	4.91	4.92	4.78	4.68
Solid yield (%)	18.57	41.33	18.89	23.06	18.41	43.65	25.25	32.5	15.91	30.62	6.03	24.48	8.76	32.22	11.54	24.66	5.70±2.14	7.48	30.22	13.57	4.28	5.03	4.95	25.14	8.05
Bio-oil yield (%)	55.05	20.46	71.58	39.33	50.34	19.43	49.9	45.79	58.27	27.33	61.76	28.58	53.56	17.32	56.73	22.1	64.44±1.30	63.96	21.86	60.82	52.51	65.05	64.61	34.94	62.28
Aqueous yield (%)	23.69	30.36	5.27	29.29	27.35	23.02	20.86	12.19	22.56	30.97	29.61	37.64	33.78	35.03	26.89	38.5	25.10±0.99	25.09	38.67	19.71	37.96	25.02	25.51	35.14	24.99
Gas composition (vol.%, H_2 Free)																									
CO_2	99.38	95.67	100	99.37	100	84.12	100	86.82	100	100	100	82.33	100	76.02	100	73.61	99.99±0.01	100	84.68	100	98.95	100	100	98.72	99.65
CH_4	0.62	4.33	0	0.63	0	15.88	0	13.18	0	0	0	17.67	0	23.98	0	26.39	0.01±0.01	0	15.32	0	0.02	0	0	1.28	0.35
Bio-oil elemental composition and HHV																									
C (wt.%)	46.3	54.1	34.05	52.05	43.8	65.65	43.75	50.68	43.4	65.67	47.7	66.93	46.33	75.25	52.15	78.4	48.76±1.06	52.35	73.1	43.73	47.75	48.53	47.75	46.6	50.42
H (wt.%)	4.33	5.81	3.16	5.1	4.11	6.76	4.17	5.19	4.02	6.66	4.8	6.96	4.48	7.67	5.25	7.83	4.72±0.32	5.21	7.54	4.32	4.63	4.66	4.63	4.51	4.88
O (wt.%)	48.84	39.66	62.44	42.21	51.89	27.1	51.54	43.55	52.14	26.92	46.51	25.35	48.66	16.81	42.05	12.79	46.06±1.34	41.94	18.67	51.31	46.93	45.96	46.93	41.94	44.08
N (wt.%)	0.53	0.44	0.36	0.65	0.21	0.5	0.55	0.59	0.45	0.75	0.99	0.75	0.53	0.28	0.56	0.98	0..46±0.12	0.51	0.68	0.63	0.69	0.84	0.69	0.15	0.63
HHV (MJ/Kg)	16.2	21.63	9.15	19.81	14.77	28.07	14.84	19.29	14.49	27.98	17.48	28.94	16.41	33.57	20.03	35.25	17.86±0.76	20.06	32.47	15.05	17.26	17.67	17.26	20.06	18.78
Bio-oil chemical composition (Area %)																									
Phenols	70.69	69.96	74.12	71.62	74.35	65.97	71.59	55.83	76.25	64.23	68.25	66.08	70.53	70.63	72.43	77.83	73.17±0.51	68.23	65.87	67.09	71.37	67.18	68.17	75.66	71.42
Cyclic ketones	11.83	13.19	18.25	12.66	12.07	9.25	15.90	7.71	13.10	13.49	19.84	14.67	16.51	13.90	14.64	7.13	15.04±0.73	19.02	13.63	20.79	14.44	20.81	21.68	10.94	14.91
Carboxylic acids	4.83	2.52	4.12	3.10	3.93	4.48	5.61	6.08	2.67	2.65	4.23	2.31	5.77	3.21	5.15	4.44	3.43±0.17	5.45	2.60	5.59	4.92	4.47	2.65	4.63	5.00
Esters	9.16	8.21	1.26	5.64	2.15	4.20	2.00	5.20	2.14	7.94	2.73	4.25	1.74	2.81	2.53	3.02	3.25±1.03	2.04	3.92	1.38	2.77	2.19	1.73	2.85	2.06
Aromatics	0.00	1.95	0.00	2.28	1.06	10.70	0.43	20.27	1.22	6.28	0.23	6.78	0.35	5.85	0.21	2.96	0.76±0.13	0.19	7.90	0.19	0.77	0.38	0.67	1.45	0.93
Furans	0.43	0.74	0.00	0.91	0.00	0.66	0.45	0.33	0.52	0.70	0.59	0.70	0.62	0.16	0.51	0.07	0.60±0.07	0.76	0.83	0.79	0.75	0.67	0.76	0.66	0.71
Others	3.06	3.44	2.24	3.80	6.44	4.74	4.01	4.58	4.10	4.72	4.13	5.21	4.48	3.43	4.54	4.54	4.26±0.26	4.32	5.25	4.17	4.99	4.32	4.34	3.82	4.97

Phenols: phenol, 2-methyl- phenol, 3-methyl- phenol, 2,3-dimethyl- phenol, 2-methoxy- phenol, 4-ethyl-2-methoxy- phenol, 2-methoxy-4-propyl- phenol, vanillin and creosol**. Cyclic ketones:** 2-methyl-2-Cyclopenten-1-one, 2,3-dimethyl-2-Cyclopenten-1-one, 2-hydroxy-3-methyl-2-Cyclopenten-1-one and 2,3-dimethyl-2-cyclopenten-1-one. **Carboxylic acids:** acetic acid, butanoic acid, homovanillic acid, bicyclo (2.2.1) heptane-1,2-dicarboxylic acid, 3-(2-Methylallyl) salicylic acid and primaric acid. **Esters:** 2-propenoic acid, hexyl ester, 9-octadecenoic acid (Z)- phenyl methylester, 5,8,11-Heptadecatriynoic acid, methyl ester, methyl dehydroabietate and 7-oxodehydroabietic acid, methyl ester. **Aromatics:** 10,18-Bisnorabieta-5,7,9(10),11,13-pentaene and retene. **Furans:** 2,4-dimethylfuran. **Others:** 1,2,5,6-Dianhydrogalactitol, 2-Hexenal, (E)-, 3-Methyl-2-hexene, 2,4-Pentadien-1-ol, 3-ethyl-, (2Z)-, 2,4-Pentadien-1-ol, 3-propyl-, (2Z)-, 4-hydroxy- benzaldehyde, and retinol.

Table 4. Relative influence of operating conditions and interaction on the HDO results obtained from analysis of variance (ANOVA) and cause-effect Pareto principle.

Response variables	R^2	Ind.	T	P	t	C	TP	Tt	TC	Pt	PC	tC	T^2	P^2	t^2	C^2	TPt	TPC	TtC	PtC	T^2P	T^2t	T^2C	TP^2	TPtC	T^2P^2
Overall products distribution																										
Gas yield (%)	0.99	4.76	2.89 (33)	-0.28 (3)	n.s.	n.s.	-0.52 (4)	0.83 (7)	0.70 (6)	-0.23 (2)	n.s.	0.28 (2)	1.73 (13)	0.96 (4)	n.s.	n.s.	-0.24 (2)	n.s.	n.s.	0.56 (5)	n.s.	1.31 (11)	0.67 (6)	0.91 (3)	n.s.	n.s.
Solid yield (%)	0.94	6.92	8.44 (26)	-2.91 (9)	n.s.	-4.70 (15)	-2.70 (8)	n.s.	n.s.	n.s.	n.s.	n.s.	9.56 (27)	n.s.	n.s.	7.31 (10)	n.s.	1.87 (5)	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.
Bio-oil yield (%)	0.99	64.57	-21.05 (24)	-4.16 (6)	n.s.	13.67 (0)	1.78 (3)	1.57 (2)	-2.07 (3)	n.s.	-3.04 (4)	n.s.	-21.66 (16)	-7.90 (1)	n.s.	-15.96 (4)	1.77 (3)	-1.86 (3)	-2.41 (3)	0.79 (1)	8.78 (4)	-2.95 (4)	-15.31 (7)	6.25 (3)	-1.29 (2)	23.29 (6)
Aqueous yield (%)	0.99	25.15	6.79 (10)	9.13 (1)	0.48 (1)	-5.08 (12)	1.44 (4)	-2.95 (8)	0.73 (2)	-0.94 (3)	2.94 (8)	1.16 (3)	6.73 (1)	3.68 (2)	n.s.	4.91 (0)	-0.68 (2)	n.s.	2.51 (7)	-1.21 (3)	-10.78 (10)	n.s.	10.26 (9)	-3.85 (3)	2.03 (5)	-13.79 (6)
Bio-oil elemental composition and HHV																										
C (wt.%)	0.97	49.15	9.56 (30)	n.s.	n.s.	n.s.	n.s.	n.s.	2.63 (8)	n.s.	2.74 (8)	n.s.	11.14 (13)	-5.85 (8)	n.s.	n.s.	-1.55 (5)	n.s.	n.s.	n.s.	n.s.	2.86 (8)	5.34 (16)	n.s.	1.59 (5)	n.s.
H (wt.%)	0.94	4.78	1.11 (36)	n.s.	0.26 (8)	0.52 (17)	n.s.	n.s.	0.22 (7)	n.s.	0.34 (10)	n.s.	1.28 (18)	-0.62 (5)	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.
O (wt.%)	0.99	46.19	-10.72 (26)	-2.19 (1)	n.s.	n.s.	0.78 (2)	-1.13 (3)	-2.83 (6)	n.s.	-3.13 (7)	-0.72 (2)	-15.89 (10)	2.93 (7)	n.s.	-3.18 (0)	1.65 (4)	n.s.	-0.71 (2)	n.s.	3.09 (2)	-3.11 (7)	-6.00 (13)	n.s.	-1.83 (4)	9.85 (4)
N (wt.%)	0.80	0.55	0.05 (9)	0.10 (17)	-0.05 (8)	0.11 (18)	n.s.	n.s.	n.s.	n.s.	0.05 (8)	n.s.	n.s.	n.s.	0.20 (8)	-0.17 (13)	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	0.12 (18)	n.s.
HHV (MJ/kg)	0.99	27.54	-0.98 (7)	0.46 (3)	n.s.	n.s.	0.53 (4)	n.s.	-0.51 (4)	-1.45 (10)	-1.14 (8)	-2.23 (16)	-1.70 (13)	-1.74 (6)	n.s.	n.s.	0.49 (3)	1.83 (13)	1.43 (10)	n.s.	n.s.	0.53 (4)	n.s.	n.s.	n.s.	n.s.
Bio-oil chemical composition (Area %)																										
Phenols	0.99	73.29	-1.18 (11)	2.14 (1)	n.s.	-2.12 (2)	0.38 (2)	n.s.	1.17 (6)	n.s.	0.67 (3)	2.20 (11)	-6.24 (5)	-4.06 (1)	-5.62 (2)	n.s.	-0.64 (3)	1.52 (8)	2.54 (13)	2.08 (11)	-2.44 (4)	n.s.	2.88 (5)	-1.07 (2)	n.s.	12.65 (11)
Cyclic ketones	0.99	15.04	-1.97 (12)	-3.18 (0)	n.s.	1.99 (6)	-1.42 (8)	-0.76 (5)	n.s.	-1.26 (7)	-0.56 (3)	n.s.	1.29 (10)	2.58 (2)	6.21 (5)	-2.12 (12)	n.s.	n.s.	n.s.	-0.81 (5)	3.64 (7)	-1.25 (7)	-1.21 (2)	n.s.	n.s.	-9.61 (7)
Carboxylic acids	0.98	3.48	-1.43 (15)	-0.34 (6)	-0.91 (15)	n.s.	n.s.	0.19 (5)	-0.18 (4)	0.18 (4)	n.s.	n.s.	0.55 (1)	1.78 (8)	n.s.	1.34 (2)	0.15 (4)	n.s.	-0.36 (9)	-0.25 (6)	0.65 (5)	1.68 (13)	-0.27 (6)	0.96 (8)	0.32 (8)	-3.08 (12)
Esters	0.74	2.60	1.08 (19)	-0.57 (10)	-1.01 (18)	-0.64 (11)	n.s.	n.s.	n.s.	0.96 (16)	n.s.	n.s.	1.35 (14)	n.s.	n.s.	n.s.	n.s.	-0.71 (12)	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.
Aromatic compounds	0.99	0.79	3.86 (19)	0.35 (2)	n.s.	-0.26 (4)	0.58 (3)	1.37 (7)	-0.87 (4)	0.38 (2)	-0.80 (4)	-2.09 (11)	3.24 (10)	-0.33 (1)	-0.28 (0)	0.38 (1)	0.35 (2)	-0.74 (4)	-1.79 (9)	-0.70 (4)	n.s.	1.44 (7)	-0.54 (1)	-0.51 (1)	-0.88 (5)	n.s.
Furans	0.98	0.60	0.07 (7)	n.s.	n.s.	0.02 (2)	n.s.	-0.12 (11)	-0.15 (13)	n.s.	n.s.	-0.03 (3)	0.19 (10)	0.17 (5)	0.11 (5)	0.08 (4)	-0.08 (7)	n.s.	-0.03 (3)	-0.04 (4)	n.s.	-0.11 (10)	n.s.	n.s.	0.09 (8)	-0.70 (8)
Others	0.78	4.31	n.s.	n.s.	0.34 (17)	0.22 (11)	0.31 (15)	-0.36 (17)	n.s.	n.s.	0.30 (14)	-0.53 (25)	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.

T= temperature, P=pressure, t= time, C= catalyst/bio-oil ratio. R_2: regression coefficient. n.s: Non significant with 95% confidence. Response = Ind. + Coeficient T·T + Coeficient P·P + Coeficient t·t + Coeficient C·C + Coeficient Tt·T·t + Coeficient TC·T·C+ Coeficient Pt·P·t + Coeficient PC·P·C + Coeficient tC·t·C + Coeficient T^2·T^2 + Coeficient P^2·P^2 + Coeficient t^2·t^2 + Coeficient C^2·C^2 + Coeficient TPt·T·P·t+ Coeficient TPC·T·P·C + Coeficient TtC·T·t·C + Coeficient PtC·P·t·C + Coeficient T^2P·T^2·P + Coeficient T^2C·T^2·C+ Coeficient TP^2·T·P^2 + Coeficient TPtC·T·P·t·C. Standardised codec formula: all operating variables vary between -1 and +1. Numbers in brackets show the relative influence (%) of each factor on the response variable. These values show the orthogonal estimated total value (%). The higher the Pareto value is, the greater the influence of the parameter in the response.

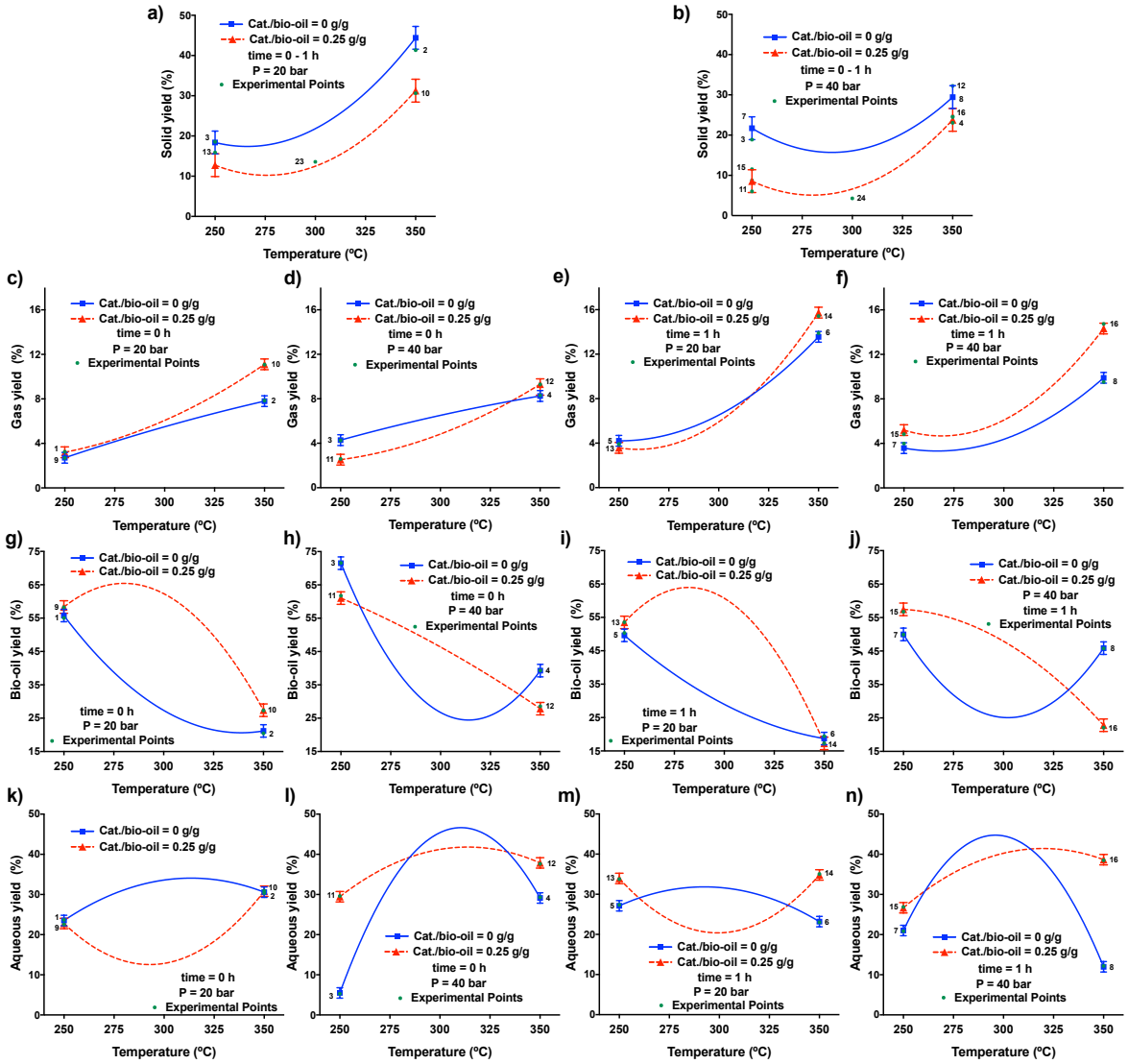

Figure 1. Effects of the operating conditions and interactions on the solid (a and b), gas (c-f), upgraded bio-oil (g-j) and aqueous fraction (k-n) yields. Bars depict 95% confidence LSD intervals.

3.1.1 Solid yield

Regarding solid formation, the impact of the temperature on this fraction is influenced by the catalyst/bio-oil ratio and initial H_2 pressure. At low pressure (20 bar), regardless of the catalyst loading, augmenting the temperature between 250 and 300 does not noticeably increase the solid yield. Conversely, a consequent increase up to 350 ºC leads to a sharp augment in the formation of solid, as bio-oil repolymerisation and poly-condensation reactions are enhanced at high temperature [43, 55]. In particular, the repolymerisation of lignin oligomers and phenols are promoted by the reaction temperature, thus contributing to char formation [56]. Besides, the raw bio-oil contains a high amount of sugars, which are unstable upon heating and can evolve towards the formation of solid species, largely char [11, 46, 57-61]. Increasing the H_2 pressure (Figure 1 a vs b) from 20 to 40 bar drops the solid

formation as H_2 adds to bio-oil stabilisation, thus preventing its transformation into char by thermal decomposition [10, 46]. At high pressure (40 bar), the temperature exerts a similar influence on solid formation as that described at low pressure (20 bar), i.e., the solid yield depicts a steady evolution between 250 and 350 ºC and a subsequent rise when the temperature increases up to 350 ºC. This upturn is less pronounced for a high than for a low pressure due to the significant impact of H_2 on bio-oil stabilisation. Regardless of the temperature or initial H_2 pressure, increasing the catalyst/bio-oil ratio from 0 (without catalyst) to 0.25 g cat/g bio-oil substantially inhibits solid formation. This suggests that the Mo_2C/CNF catalyst helps stabilise the bio-oil during the heating up step, avoiding repolymerisation and oligomerisation reactions, thus preventing bio-oil decomposition into solid species, principally char. This positive inhibitory influence is especially notorious using a H_2 rich atmosphere, as this gas contributes to stabilising the bio-oil reactive species during the heating up step [10, 46]. Besides, the presence of a catalyst not only might inhibit the formation of char but also it favours char gasification, which overall adds to decrease the solid yield [62].

3.1.2 Gas yield

The gas recovered after the HDO reactions is composed of H_2 (principally non-reacted, although some also can have been produced) along with small quantities of CO_2 and CH_4. The presence of CO_2 indicates that some small oxygenates in the bio-oil, such as ketones and carboxylic acids underwent decarboxylation, decarbonylation, reforming and thermal cracking during the upgrading process [43, 63, 64], while CH_4 formation suggests the thermal cracking and hydro-cracking of alkyl groups [43, 56]. The gas yield depends primarily on the temperature and reaction time. When a short time (0 min) is applied, increasing the temperature linearly enlarges the gas formation independently of the amount of catalyst or pressure of H_2. Besides, the impact of the catalyst loading for such a short reaction time is determined by the H_2 pressure. At 20 H_2 bar, the catalyst only exerts a significant impact at high temperature (320-350 ºC), wherein increasing the catalyst/bio-oil ratio enlarges the formation of gases. Cracking and reforming reactions can be promoted at high temperature in the presence of an active catalyst; thus, these reactions are thought to be responsible for the greater gas yield attained at elevated temperature [47-50].

However, strengthening the H_2 accessibility helps inhibit these reactions, especially at low temperature (between 250 and 325 ºC). The gas formation can be delayed by the creation of a solvent cage surrounding the species of solute (cage effect). This phenomenon hampers fission-type reactions by delaying the emerging species within the cage so that they are more likely to react between themselves and revive the reagents, thus diminishing the formation of gas and augmenting the yield to upgraded bio-oil [50, 65]. As the cage effect is more efficient as the pressure increases [50, 65], it can be sufficient to inhibit gas formation at low temperature if a high H_2 pressure is applied, conditions at which the formation of gas is not promoted. Also, the consequences taking place when the initial H_2 pressure is augmented from 20 to 40 bar depend on the catalyst/bio-oil ratio. Without a catalyst, the effect of the H_2 pressure is not detrimental. On the contrary, for a catalyst/bio-oil ratio of 0.25 g cat/g bio-oil, such increase drops the gas yield. A H_2 rich atmosphere, in the presence of a sufficient catalyst amount, promotes hydrogenation reactions. These reactions occur to a greater extent at low temperature, since hydrogen solubility decreases with increasing the reaction temperature [66] and hydrogenation reactions are exothermic [43, 63, 64], so that they are not thermodynamically promoted at elevated temperature. As a consequence, for an initial H_2 pressure of 40 bar, augmenting the catalyst loading decreases the gas formation between 250 and 325 ºC, due to the cage effect and the positive impact of H_2 on bio-oil stabilisation and hydrogenation [10, 46].

Prolonging the time of reaction from 0 to 1 h (Figure 1 c/d vs e/f) modifies the influence of the temperature on the gas yield, especially at high temperature. Regardless of the H_2 pressure, when a temperature between 300 and 350 ºC is used, prolonging the reaction time increases the gas yield. Besides, for a 1 h reaction, uprising the temperature between 300 and 350 ºC extends the production of gas. Thermal decomposition, cracking and reforming of the lights oxygenates in bio-oil, resulting in the formation of gases, might be responsible for such variations, as these transformations are enlarged at elevated temperatures and using lengthy reaction times [43, 63, 64]. Furthermore, when a reaction time of 1 h is used, increasing the catalyst/bio-oil ratio also upsurges the gas yield. This is particularly noticeable at high temperature (325-350 ºC) when an initial H_2 pressure of 20 bar is used or at 40 bar of H_2 irrespective of the temperature. At low pressure (20 bar), the beneficial catalytic impact of the catalyst on cracking and reforming reactions might be responsible for the increase in the gas yield, while O

removal in the form of CO_2 can explain the increase observed in gas formation when a H_2 rich atmosphere (40 bar) is used. This latter hypothesis can be confirmed by comparing the gas yield at low (20 bar) and high (40 bar) initial H_2 pressure for a 1 h reaction. For a non-catalytic reaction, increasing the H_2 pressure helps inhibit bio-oil thermal decomposition reactions into gas and solid [50, 65], and bio-oil HDO reactions prevail. As a result, the gas yield decreases when the initial H_2 pressure is incremented from 20 to 40 bar (Figure 1 e vs f). On the contrary, for the highest catalyst/bio-oil ratio (0.25 g cat/g bio-oil), such spread in the pressure does not markedly modify the gas yield, and only a small decrease in the gas formation happens at high temperature (325-350 ºC). This might be the consequence of the competitiveness and compensation between two different phenomena. On the one hand, a H_2 rich atmosphere helps inhibit bio-oil thermal decomposition as H_2 endorses bio-oil stabilisation, thus diminishing the formation of gas via thermal cracking as described earlier. On the other, the combination of an elevated H_2 pressure together with a high amount of catalyst intensifies the efficiency of bio-oil HDO reactions [67], which promotes O removal in the form of CO_2, thus increasing the gas yield [43].

3.1.3 Upgraded bio-oil and aqueous fraction yields

The liquid produced after the experiments comprise the upgraded bio-oil together with a yellowish aqueous phase, primarily consisting of water together with a few organic compounds. In the scope of this paper, the amounts of these species in the aqueous phase was not determined. The upgraded bio-oil and aqueous fraction yields are intensely affected by the reaction temperature, with distinctive developments occurring, subjected to the initial H_2 pressure and catalyst loading. At 20 bar, different evolutions are detected for the upgraded bio-oil and aqueous fraction yields related to the catalyst/bio-oil ratio. Irrespective of the reaction time, for a non-catalytic reaction (Figure 1 g and i), increasing the temperature diminishes the bio-oil yield and upsurges the aqueous fraction yield between 250 and 325 ºC. In the absence of an efficient hydrogenating catalyst, the temperature promotes bio-oil decomposition into gas and solid species by cracking, demethoxylation, dehydroxylation, dehydration, decarbonylation and decarboxylation reactions, which remove O from the bio-oil in the form of H_2O and CO_2 [43, 52, 53]. An additional temperature increment up to 350 ºC results in a levelling-off for both fractions, which might indicate that most reactive species in the bio-oil, which are more prone to

be transformed to gas, are removed between 250 and 325 ºC. Augmenting the catalyst amount from 0 to 0.25 g catalyst/g bio-oil markedly rises the yield to upgraded bio-oil and drops the aqueous fraction yield. These evolutions are accounted for by the positive impact of the catalyst on HDO reactions [43, 52, 53], thus not only preventing bio-oil decomposition into gas and solid, but also decreasing the formation of water by condensation and/or low molecular weight water-soluble products via thermal cracking [43]. As a result, when the highest amount of catalyst is used (0.25 g cat/g bio-oil), the yield to upgraded bio-oil and aqueous fraction respectively increases and decreases slightly between 250 and 280 ºC. A further increase in the temperature up to 350 ºC leads to a progressive decrease in the bio-oil yield and an increase in the aqueous fraction yield due to the conversion of the bio-oil into solid and gaseous species via repolymerisation, reforming and HDO reactions as described earlier [43, 55]. Besides, the yields to upgraded bio-oil and aqueous fraction are not substantially induced by the reaction time (Figure 1 g/k vs i/m). In particular, in the absence of a catalyst, the bio-oil and aqueous fraction yields decrease very slightly, possibly due to the increase taking place in the production of gases.

Augmenting the initial H_2 pressure leads to diverse outcomes for the upgraded bio-oil and aqueous fraction yields depending on the reaction time and catalysts amount (Figure 1 h/i and j/n). For a non-catalytic upgrading, irrespective of the reaction time, increasing the initial H_2 pressure from 20 to 40 bar, surges the upgraded bio-oil yield and drops the aqueous fraction yield between 250 and 300 ºC (Figure 1 h/k vs i/m). These variations are accounted for by the greater H_2 readiness in the reaction medium, which helps bio-oil stabilisation and avoids its degradation into solid (char) and gaseous species [10, 46]. As a result, when an initial H_2 pressure of 40 bar is used, the effect of the temperature does not substantially depend on the reaction time due to the beneficial impact of H_2 [10, 46]. For a non-catalytic upgrading, between 250 and 325 ºC, the yield to upgraded bio-oil decreases and the aqueous fraction yield increases due to the beneficial influence of the temperature. This promotes reforming, cracking and HDO, including demethoxylation, dehydroxylation, dehydration, decarbonylation and decarboxylation, reactions [43, 52, 53]. Besides, an additional temperature increment up to 350 ºC enlarges the yield to upgraded bio-oil and diminishes the aqueous fraction yield. The increase in gas formation might be responsible for the decrease occurring in the aqueous phase yield at an elevated temperature, as part of the water can be consumed in reforming reactions leading to the formation of

gaseous species. In general, an increase in the catalyst/bio-oil ratio increases the upgraded bio-oil and the aqueous fraction yields, as the catalyst prevents bio-oil degradation [10, 46]. However, regardless of the reaction time, for 0.25 g cat/g bio-oil, increasing the temperature leads to a decrease in the bio-oil yield together with a moderate increase in the aqueous fraction yield, especially between 250 and 325 ºC due to the greater spread of HDO reactions, removing O from the bio-oil in the form of water [67].

The impact of the reaction time depends on the catalyst/bio-oil ratio. In the absence of a catalyst, prolonging the time of reaction from 0 to 1 h leads to a decrease in the bio-oil yield along with an increase in the aqueous fraction yield only at low temperature (250-300 ºC) due to the beneficial effect of the reaction time on the HDO of the bio-oil. On the contrary, when the HDO upgrading is conducted employing the greatest catalyst loading (0.25 g cat/g bio-oil), the influence of the reaction duration is less significant, as the presence of a catalyst can mask the impact of the reaction time. This allow achieving the same deoxygenation degree using shorter reaction times. As such, prolonging the reaction duration from 0 to 1 h does not extensively alter the upgraded bio-oil or aqueous fraction yield. This might be the result of the beneficial outcome of the catalyst when a H_2 rich atmosphere is used, which helps stabilise the bio-oil, thus preventing its decomposition into gaseous and solid species [10, 46].

3.2 Properties of the upgraded bio-oil

3.2.1 Elemental composition and HHV

The elemental composition and HHV of the upgraded bio-oil depend on the HDO processing conditions. The proportions of C, H, N and O in the upgraded bio-oil vary between 34-78 wt.%, 3-8 wt.%, 0-1 wt.% and 13-62 wt.%, while its HHV shifts between 9 and 35 MJ/kg. The cause-effect Pareto principle denotes that the temperature, followed by the catalyst/bio-oil ratio, are the operating variables having the most considerable impact on these properties. Likewise, the HHV is also influenced by the reaction time, while the concentration of N in the upgraded bio-oil is meagre, and the influence of the operating conditions is not essential practically. Besides, the codec models imply that in general, augments in the temperature or the catalyst/bio-oil ratio upsurge the proportions of C and H (positive terms) and decline the relative amount of O (negative terms) in the bio-oil; these developments leading to an increase

(positive terms) in the HHV. These variations can be attributed to bio-oil hydrodeoxygenation, deoxygenation, decarbonylation and decarboxylation reactions, which decrease the oxygen content and increase the carbon content in the upgraded bio-oil [43, 63, 64]. Besides, significant interactions between the operating variables also take place. Figure 2 a/c and b/d shows the effect of the temperature, using a reaction time of 0/1 h, on the relative amount of C in the upgraded bio-oil, for a catalyst/bio-oil ratio of 0 and 0.25 g cat/g bio-oil, at 20 and 40 bar of initial H_2, respectively. These effects are plot for the proportions of H and O and the HHV of the bio-oil in Figure 2 e/g, i/k and m/o at 20 bar and f/h, j/l and n/p, at 40 bar of initial H_2.

The effect of the temperature on the elemental composition and HHV of the upgraded bio-oil primarily depends on the initial H_2 pressure and catalyst loading. For a low initial H_2 pressure (20 bar), irrespective of the reaction time, the effect of the temperature predominantly depends on the catalyst/bio-oil ratio (Figure 2 a/e/i/m and c/g/k/o). Regardless of the reaction time, in the absence of a catalyst, the temperature does not exert an essential effect between 250 and 300 ºC. Within this temperature range, the relative amounts of C and O respectively increases and decreases marginally, which moderately improves the HHV of the upgraded bio-oil. Conversely, a further increase up to 350 ºC increases the relative amounts of C and H and decreases the proportion of O, which increase the HHV of the upgraded bio-oil. These differences are notably more discernible as the reaction time is prolonged from 0 to 1 h (Figure 2 a/e/i/m vs c/g/k/o). These changes are accounted for by the increases in the solid and gas yields with rising the temperature and reaction time at low pressure in the absence of a catalyst. Such developments remove C from the bio-oil in the form of char and CO_2, respectively [43, 63, 64]. The effect of the catalyst/bio-oil ratio is induced by the reaction temperature. At low temperature (250-300 ºC), augmenting the catalyst amount from 0 to 0.25 g cat/g bio-oil leads to a small decrease in the C content of the upgraded bio-oil along with a moderate increase in the proportion of O, without substantially modifying the concentration of H in the upgraded bio-oil, which produce a soft decrease in its HHV. These variants take place along with an increase in the upgraded bio-oil yield, as described above, which might indicate that the amount of H_2 used (20 bar initial pressure) is sufficient to stabilise the bio-oil in the presence of a catalyst, thus preventing its decomposition into solid and gaseous species; however, it is not high enough for HDO reactions to take place to a significant extent. Conversely, at

high temperature (325-350 ºC), this same increase in the catalyst/bio-oil ratio increases the proportions of C and H and decreases the relative amount of O, thus augmenting the HHV of the upgraded bio-oil. These variations account for the increase observed in the gas yield under these conditions [43, 63, 64]. As a result, for 0.25 g cat/g bio-oil, the effect of the reaction time is not very important as the effect of the reaction time can be masked by the positive effect of the catalyst. In general, similar changes with the temperature are observed as those described in the absence of a catalyst, i.e., between 250 and 300 ºC, the temperature does not greatly influence the chemical composition or HHV of the upgraded bio-oil. In contrast, a further increase in the temperature up to 350 ºC leads to increases in the relative amounts of C and H and a decrease in the proportion of O, which increases the HHV of the upgraded bio-oil. These differences are particularly more pronounced when the reaction time increases due to the advantageous influence of the catalyst on chemical reactions leading to gas production as described earlier.

A spread in the initial H_2 pressure from 20 to 40 bar slightly modifies the effect of the other processing conditions, which leads to different outcomes depending on the catalyst/bio-oil ratio (Figure 2 a/e/i/m vs b/f/j/n and c/g/k/o vs d/h/l/p). On the one hand, for a non-catalytic upgrading and irrespective of the reaction time, such increase in pressure declines the relative amounts of C and H and augments the proportion of O and HHV of the upgraded bio-oil. Under these conditions, an increase in the H_2 pressure helps bio-oil stabilisation, thus preventing its decomposition into gas and solid species. Therefore, O removal by cracking and reforming reactions is inhibited, which results in an increase in the relative amount of O in the upgraded bio-oil in comparison to the results obtained at low H_2 pressure, conditions at which these reactions ensue to a greater extent. On the other hand, when the highest catalyst/bio-oil ratio is used (0.25 g cat/g bio-oil), the same increase in the pressure leads to a reverse outcome, i.e., the relative amounts of C and H increase, while the proportion of O and HHV decrease. These changes are the consequence of the catalytic impact of the catalyst on the HDO of bio-oil, as it promotes hydrodeoxygenation, deoxygenation, decarbonylation and decarboxylation reactions, which decrease the O content and increase the C concentration in the upgraded bio-oil [43, 63, 64].

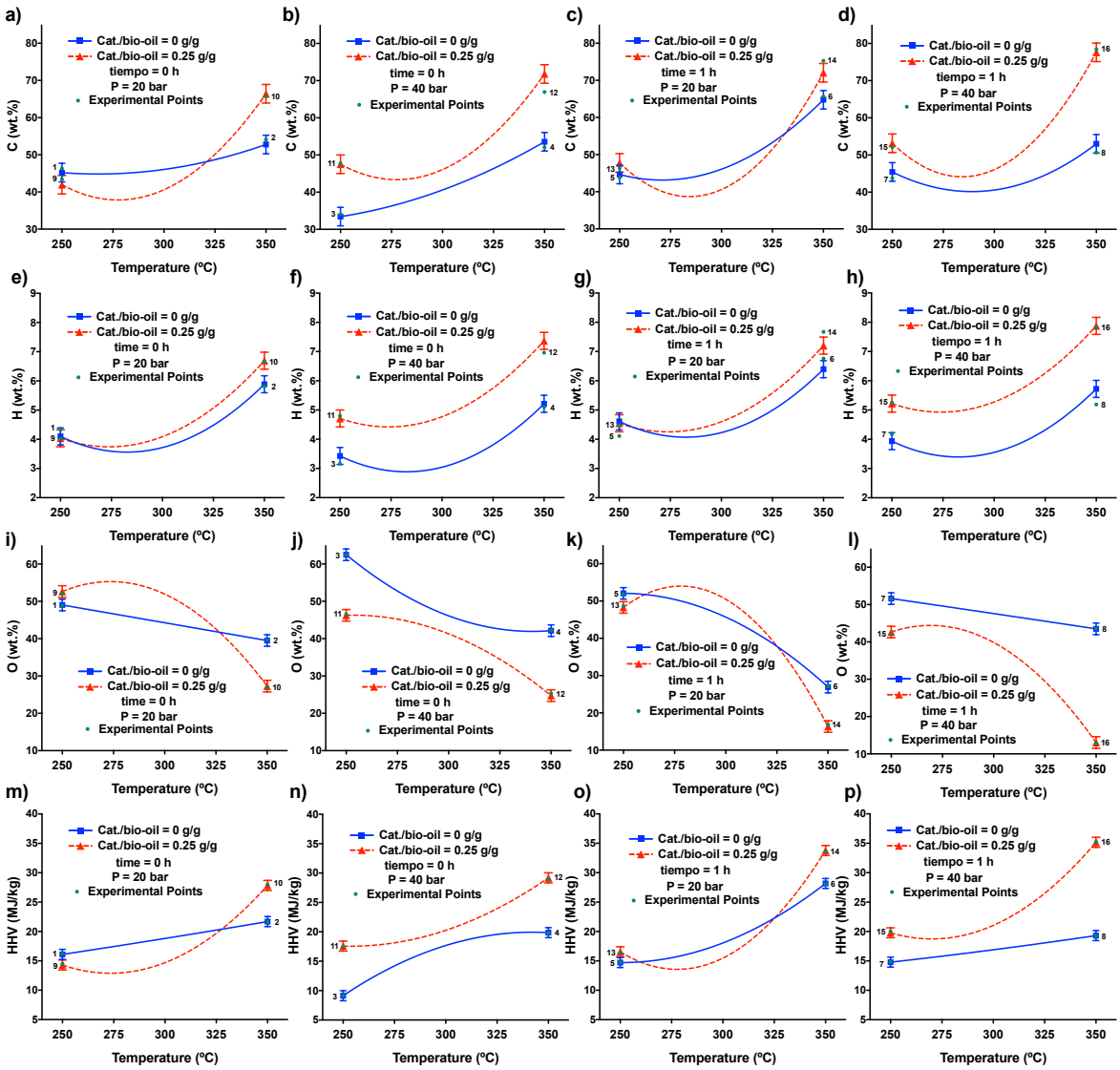

Figure 2. Effects of the operating conditions and interactions on the relative amounts of C (a-d), H (e-h) and O (i-j) and the HHV (m-p) of the upgraded bio-oil. Bars depict 95% confidence LSD intervals.

In general, the same evolutions with the temperature as those described at low pressure take place irrespective of the amount of catalyst employed. However, when the highest catalyst loading (0.25 g cat/g bio-oil) is used at 40 bar, the variations observed are more pronounced, especially at high temperature. In particular, augmenting the temperature from 300 to 350 ºC sharpeners the increases occurring in the concentrations of C and H and the HHV as well as the decreases in the proportion of O. The greater spread of HDO and reforming and thermal cracking reactions taking place at high temperature in the presence of a catalyst can explain these variations. Besides, extending the reaction duration up to 1 h promotes these reactions to occur in a greater extent.

3.2.2 Chemical composition

The upgraded bio-oil is made up of a mix of phenols, cyclic ketones, carboxylic acids, esters, aromatic compounds and furans, whose proportions, determined as a relative chromatographic area, vary as follows: 56-78%, 7-30%, 2-8%, 0-9%, 0-20% and 0-1%, respectively. The upgraded bio-oil contains a negligible amount of saccharides, which indicates they are converted into other species during the upgrading process. These sugars are unstable upon heating and can evolve towards the formation of solid species, largely char [11, 46, 57-61]. As such, sugar decomposition into char can partially account for the solid formation occurring in this work. The cause-effect Pareto principle (Table 4) reveals that the chemical composition of the upgraded bio-oil is principally influenced by the reaction temperature (linearly and quadratically). Besides, other variables also exert a significant influence on the chemical composition of the upgraded bio-oil. In particular, the relative amounts of carboxylic acids and esters are also influenced by the reaction time. At the same time, the proportions of phenols and aromatics are influenced by several linear and quadratic interactions taking place between the reaction time and catalyst loading. Figure 3 plots the effects of the processing variables and interactions on the relative amount of the most abundant species identified in the upgraded bio-oil. Specifically, Figure 3 a/c and b/d shows the effect of the temperature, using a reaction time of 0/1 h, on the relative amount of phenols in the upgraded bio-oil, for a catalyst/bio-oil ratio of 0 and 0.25 g cat/g bio-oil, at 20 and 40 bar of initial H_2, respectively. These effects are plot for the proportions of cyclic ketones, carboxylic acids, esters and aromatic compounds in Figure 3 e/g, i/k, m/o, and q/s at 20 bar and f/h, j/l, n/p, and r/t at 40 bar of initial H_2.

The effect of the temperature on the chemical composition of the upgraded bio-oil primarily depends on the initial H_2 pressure and reaction time. For a low initial H_2 pressure (20 bar) and a short reaction time (0 h), irrespectivelof the catalyst amount (Figure 3 a/e/i/m/q), rising the temperature between 250 and 300 ºC drops the relative amount of phenols and enlarges the proportions of cyclic ketones and carboxylic acids. These variations might be accounted for by the hydrogenation of phenols resulting in the formation of cyclic ketones [68], transformations that can be promoted when a high catalyst/bio-oil ratio (0.25 g cat/g bio-oil) is used. Besides, the proportion of furans in the upgraded bio-oil is much lower than that of the original liquid, while the upgraded bio-oil is enriched in cyclic ketones, thus

suggesting the transformation of the former into the latter by hydrogenation [56, 69]. A posterior augment in the temperature up to 350 ºC increases the relative amount of phenols in the upgraded bio-oil and decreases the proportions of cyclic ketones and carboxylic acids. Such changes might be the outcome of two different phenomena. On the one hand, the progressive decomposition and depolymerisation of lignin oligomers into phenolic compounds, as these reactions are promoted at high temperature, thus leading to an increase in the relative amount of phenolic compounds in the upgraded bio-oil [56]. These oligomers are produced from the biomass lignin fraction during the pyrolysis step and are not detectable by gas chromatography due to their high molecular masses. On the other hand, phenols hydrogenation, leading to the formation of carboxylic acids and cyclic ketones, might be inhibited due to the lower solubility of H_2 at high temperature [66] and the exothermic nature of hydrogenation reactions [43, 63, 64].

Lengthening the reaction time up to 1 h does not substantially alter the impact of the other conditions on the upgraded bio-oil chemical formulation (Figure 3 c/g/k/o/s), and similar evolutions are observed predominantly for a non-catalytic upgrading. However, the variations occurring for the relative amount of phenols and carboxylic acids when the temperature is modified are less marked, especially between 300 and 350 ºC, probably due to the positive effect of the reaction time which can mask the effect of the temperature. As a result, prolonging the reaction time in the absence of a catalyst upsurges the proportion of phenols and drops the relative amount of cyclic ketones at low temperature (250-300 ºC). These variations might account for the positive effect of the temperature on decomposition and depolymerisation of lignin oligomers into phenolic compounds [56]. Besides, between 300 and 350 ºC this same increase in the reaction time declines the proportions of phenols and carboxylic acids at the expenses of the relative amount of aromatic compounds, whose formation might be favoured from the repolymerisation of phenolic compounds and depolymerisation of lignin oligomers using long reaction times [56, 69]. On the contrary, more significant variations are observed when the greatest amount of catalyst (0.25 g cat/g bio-oil) is used. Between 250 and 300 ºC, this increase in time decreases the relative amount of phenols and increases the proportion of carboxylic acids and cyclic ketones. Hydrogenation reactions might be promoted within this temperature range using large catalyst quantities and, therefore, these transformations could be responsible for such variations. Also, between 300 and 350 ºC, the

relative amount of phenols increases, while the proportion of carboxylic acids decreases; with the relative quantity of cyclic ketones remaining practically unaffected. The use of long reaction times with the highest catalyst/bio-oil ratio promotes ligno-oligomers depolymerisation, favouring the transformation of part of the upgraded bio-oil into gaseous species [43, 56, 69]. These developments are in line with the variations observed in the relative amount of phenols and carboxylic acids.

An increment in the initial H_2 pressure from 20 to 40 bar modifies the effect of the temperature on the chemical composition of the upgraded bio-oil. In the absence of a catalyst, the chemical composition of the upgraded bio-oil is not much affected by the temperature. The proportions of phenols and cyclic ketones decrease at the expenses of the relative amount of esters. In contrast, the relative quantity of carboxylic acids upsurges between 250 and 300 and drops with a further temperature increment. At high temperature, carboxylic acids can be converted to esters by transesterification [43] and/or decomposed to gases [43, 56, 69], which connects well with the increase observed in the gas yield at high temperature. However, these variations are not relevant on a practical matter, probably as the greater H_2 availability can mask the effect of the temperature for non-catalytic reactions. Increasing the catalyst amount from 0 to 0.25 g cat/g bio-oil declines the proportion of phenols and upturns the proportion of cyclic ketones due to the positive effect of the catalyst in a H_2 rich reaction medium, thus enhancing the transformation of the former into the latter. These reaction conditions also favour the hydrogenation of the furan compounds of the original bio-oil yielding cyclic ketones [56, 69]. Additionally, this increase in the catalyst amount also diminishes the relative amount of esters and enlarges the proportion of aromatic compounds. These aromatic species can be produced from phenols by condensation reactions, which are catalytically promoted at high temperature [56, 69]. As a result of these changes, the effect of the temperature on the chemical composition of the upgraded bio-oil is more critical. In particular, an increase in the temperature between 250 and 300 ºC decreases the relative amount of phenols and increases the proportion of cyclic ketones and carboxylic acids due to the transformation of the former into the latter species [68]. A further upsurge up to 350 ºC increases the proportion of phenols and decreases the relative amounts of cyclic ketones and carboxylic acids. Increasing the temperature decreases the efficiency of hydrogenation reactions due to the lower H_2 solubility in the reaction medium [66] and the exothermicity nature of these transformations [43, 63, 64]. Besides, the temperature exerts

a positive influence on depolymerisation and gas formation by reforming and thermal cracking, thus favouring the bio-oil degradation into gaseous products.

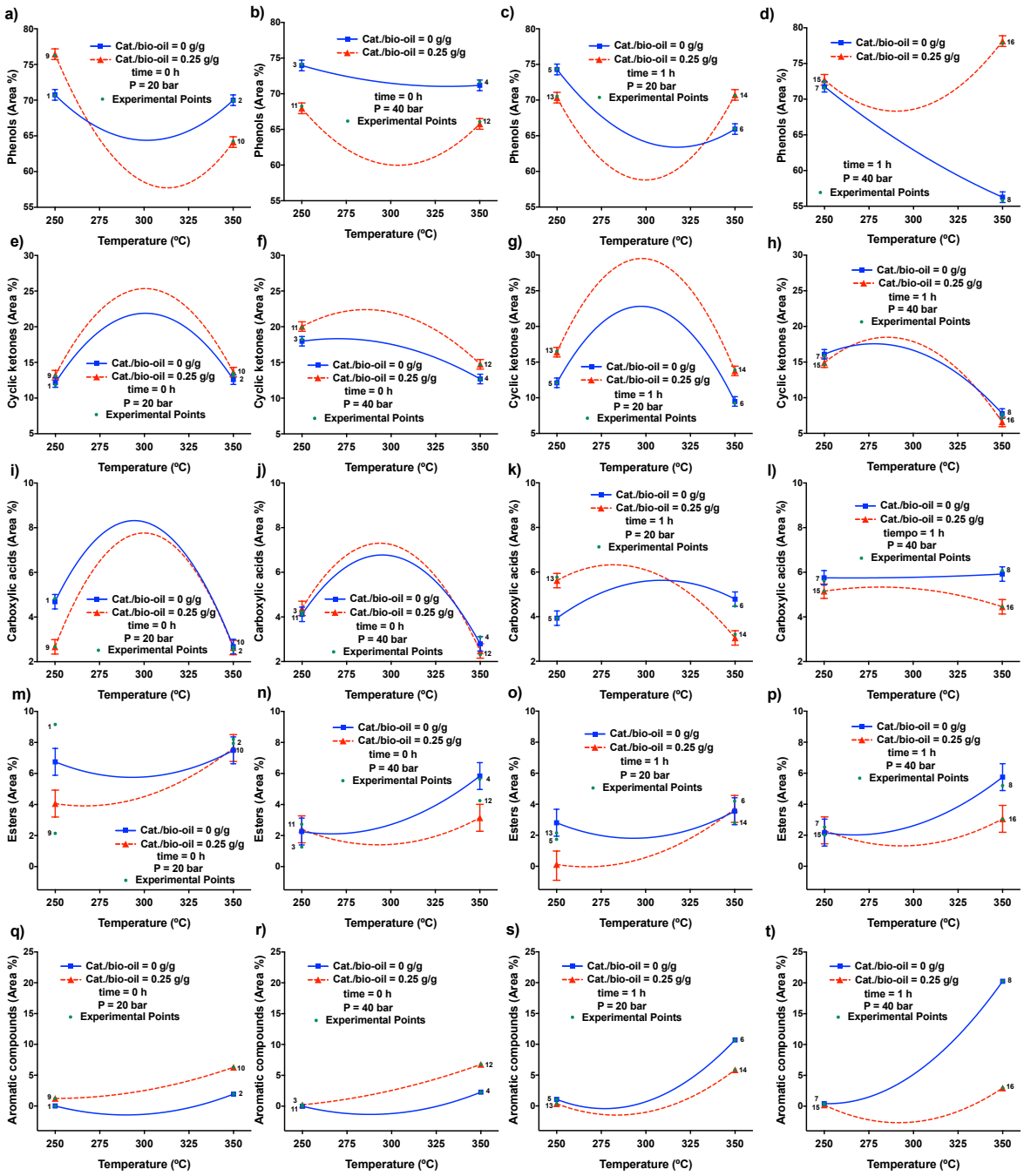

Figure 3. Effects of the operating conditions and interactions on the relative amounts of phenols (a-d), cyclic ketones (e-h) carboxylic acids O (i-j), esters (m-p) and aromatic compounds (q-t) in the upgraded bio-oil. Bars depict 95% confidence LSD intervals.

The effect of the reaction time depends on the catalyst amount (Figure 3 b/f/j/n/r vs d/h/l/p/t). When the upgrading process is conducted without a catalyst, lengthening the reaction time from 0 to 1 h diminishes the relative amount of phenols and augments the proportion of aromatic compounds, probably due to

the more significant extension of condensation reactions [56, 69], which are favoured using long reaction times, together with the positive effect of H_2, helping bio-oil stabilisation and preventing its decomposition into gaseous species. When the highest amount of catalyst is used (0.25 g cat/g bio-oil), this same increase in time leads to a substantial increase in the proportion of phenols along with decreases mainly in the relative amounts of cyclic ketones and aromatic compounds. These differences are thought to be the consequence of the positive catalytic impact of the catalyst on ligno-oligomers depolymerisation when a high H_2 pressure is used for long reaction times. As a result of these variations, in the absence of a catalyst, increasing the temperature between 250 and 350 ºC leads to a considerable decrease in the proportion of phenols along with an increase in the relative amount of aromatic compounds, as condensation reactions are promoted using long reaction time at high temperature in the absence of a hydrogenation catalyst [56, 69]. Increasing the catalyst loading from 0 to 0.25 g cat/g bio-oil increases the relative amount of phenols at the expenses of the proportion of aromatic compounds. In this case, depolymerisation and HDO reactions prevail over condensations due to the significant influence of the catalyst on the depolymerisation of lignin oligomers when elevated temperatures are applied for long reaction times. As such, increasing the temperature under these conditions leads to an increase in the proportion of phenols along with a decrease in the relative amount of cyclic ketones. These variations are the result of a progressive depolymerisation of bio-oil lignin oligomers along with the transformation of some bio-oil small oxygenates into gases by thermal cracking and reforming as described above.

Given the above information, Figure 4 depicts a schematic reaction pathway summarising the most important chemical transformations occurring during the HDO process for the most abundant chemical families found in the bio-oil used in this work. These chemical reactions provide evidence for the composition of the upgraded bio-oil as well as the formation of solids (principally char) gaseous and an aqueous species during the upgrading process.

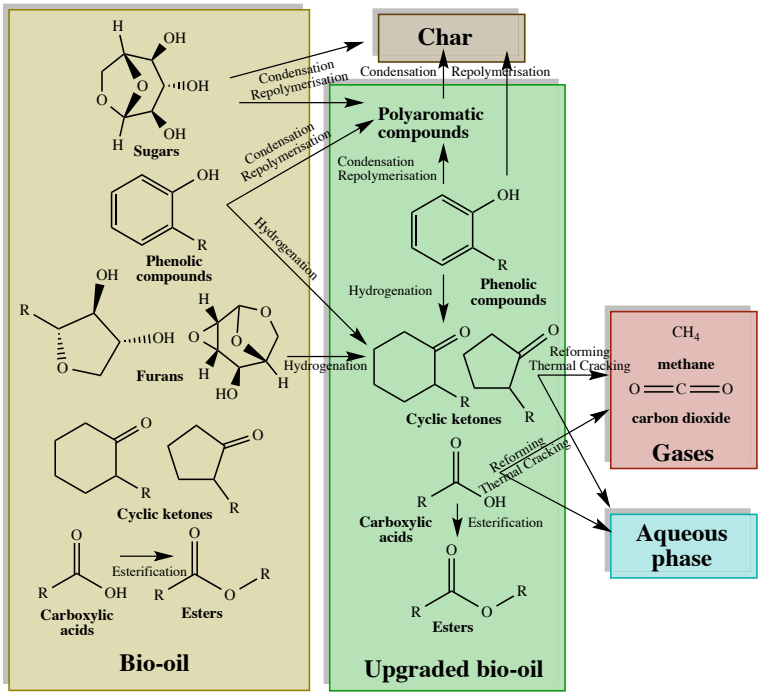

Figure 4. Schematic reaction pathway showing the chemical transformations of the bio-oil during the HDO process.

3.3 Theoretical process optimisation, scale-up and industrial implementation

Three possible different optimisation scenarios were sought for the transformation of the original bio-oil into liquid biofuels and value-added chemicals, using the formulae developed from the ANOVA analysis of the experimental results (Table 5). To this end, for all the scenarios considered, the gas and solid yields were minimised, while the upgraded bio-oil yield was maximised. The first optimisation comprises the transformation of the bio-oil into an upgraded liquid with adequate fuel properties. Consequently, the HHV of the upgraded bio-oil was maximised. Also, the relative amount of carboxylic acids was minimised as these species increases the instability of the liquid and are responsible for the oxidation of the combustion engines. The second optimisation aims to obtain an upgraded liquid with a high proportion of phenols and aromatic compounds, as these species can be used as precursors for fine chemicals production. The third optimisation includes the maximisation of the relative quantity of phenols in the upgraded bio-oil to produce a liquid that could be used as a renewable and natural oxidation additive. For all these case scenarios, each constraint has been assigned with a relative importance (from least important, 1, to most important, 5) to obtain processing conditions that satisfy all the optimisation criteria.

Table 5. Process optimisation: restrictions and optimum conditions using the model formulae produced during the ANOVA of the results.

Optimisation	1		2		3	
	Objective	Solution	Objective	Solution	Objective	Solution
Temperature (ºC)		350		350		250
H_2 pressure (bar)		40		40		20
Time (h)		1		0.98		0.45
Catalyst (g cat/g bio-oil)		0.19		0		0.14
Overall producs distribution						
Gas yield (%)	Minimise (2)	13.3±0.4	Minimise (2)	9.9±0.4	Minimise (2)	3.4±0.4
Solid yield (%)	Minimise (2)	19.8±3.4	Minimise (2)	29.3±3.4	Minimise (2)	8.0±3.4
Bio-oil yield (%)	Maximise (2)	40.1±1.2	Maximise (2)	45.9±1.2	Maximise (2)	65.5±1.2
Aqueous yield (%)		28.6±0.8		12.3±0.8		23.1±0.8
Upgraded bio-oil chemical composition (% Area)						
Phenols		72.8±0.5	Maximise (5)	56.9±0.5	Maximise (5)	78.7±0.5
Cyclic ketones		8.4±0.6	Minimise (5)	7.5±0.6	Minimise (5)	9.5±0.6
Carboxylic acids	Minimise (5)	3.8±0.2	Minimise (5)	5.8±0.2	Minimise (5)	2.8±0.2
Esters		3.7±1.2	Minimise (5)	5.7±1.2	Minimise (5)	3.5±1.2
Aromatic compounds		6.9±0.1	Maximise (5)	19.9±0.1	Minimise (5)	0.6±0.1
Furans		0.1±0.1	Minimise (5)	0.4±0.1	Minimise (5)	0.2±0.1
Others		4.6±0.4	Minimise (5)	4.6±0.4	Minimise (5)	4.5±0.4
Upgraded bio-oil elemental composition and HHV						
C (wt.%)		71.7±2.4		53.1±2.4		44.7±2.4
H (wt.%)		7.4±0.4		5.7±0.4		4.3±0.4
O (wt.%)		22.7±1.1		44.4±1.1		53.7±1.1
N (wt.%)		0.9±0.1		0.4±0.1		0.4±0.1
HHV (MJ/kg)	Maximise (5)	30.1±0.6		19.4±0.6		13.7±0.6

Results are expressed as mean ± 95% confidence interval.

Opt. 1 reveals that an upgraded bio-oil with an elevated HHV (30 MJ/kg) can be obtained in high yield (40%) from the HDO of the original bio-oil at 350 ºC, 40 bar initial H_2, using a catalyst loading of 0.19 g cat/g bio-oil for 1 h. Taking into account the organic content of the original bio-oil (61 wt.%) and its HHV (19 MJ/Kg), these conditions allow transforming 65% of the bio-oil organic compounds into an upgraded liquid product with a HHV almost twice as high as that of the original feedstock. Besides, these results represent a deoxygenation degree of 70% and an energy efficiency of 62%. This biofuel has comparable fuel characteristics than diesel (C = 85 wt.%, H = 15 wt.%, 44 MJ/kg) and biodiesel (C=75 wt.%, H =12 wt.%, O= 11 wt.%, 40 MJ/kg) [70] and therefore, it may be combusted in current engines, either alone and/or blended [71]. This could aid to dismiss the net emissions of CO_2 without adapting the fleet infrastructure, thus being a fine solution in the medium term. Opt. 2 indicates that when a temperature of 350 ºC, an initial H_2 pressure of 40 bar in the absence of a catalyst is used for 1 h, it is possible to convert around 46% (75% of the organic content) of the bio-oil into a liquid product with high proportions of phenols and aromatics (77%). Besides, Opt. 3 shows that 79% of the bio-oil (which correspond to a complete organic conversion) can be converted into a liquid with a high

proportion of phenols (79%) during its HDO at 250 ºC, using an initial H_2 pressure of 20 bar and a catalyst/bio-oil ratio of 0.14 g cat/g bio-oil for around 0.5 h. Run 8 was conducted using comparable operating conditions (350 ºC, 40 bar H_2, 1 h and 0 g cat/g bio-oil) as the optimum predicted in Opt. 2 and non-significantly different results were experimentally attained, which can prove validation for the theoretical predictions. Table 6 summarises the results reported in the literature addressing the HDO of lignocellulosic bio-oil over different catalysts. Although data are not directly comparable, as the feedstock (raw bio-oil) exerts a significant influence on the process, the experimental results obtained in this work highlight the excellent performance of the Mo_2C/CNF catalyst for the production of biofuels and value-added chemicals from bio-oil.

Table 6. Overview of the results reported in the literature testing the HDO of bio-oil over different catalysts.

Authors	Catalyst	Conditions	Yield (%)	Calorific Value	Composition
Zhang et al. [40]	Sulphided CoMo-P/Al_2O_3	360 ºC, 20 bar initial H_2 and 30 min. Batch Reactor	76	From 21 MJ/kg to 42 MJ/Kg	Hydrocarbons increased up to 60%
Churin et al. [41]	CoMo and a NiMo	270-400 ºC and 50-120 bar H_2. Flow Reactor			Hydrocarbons from 10 to 70%, Phenols from 40 to 18%
Shu et al. [42]	Pt/TiO_2	280 ºC, 1 MPa of H_2 for 4 h. Batch Reactor.			Hydrocarbons from 11 to 34%, Phenols from 28 to 51%
Cheng et al. [43]	Fe-Co/SiO_2	300 °C and 3.45 MPa of H_2 for 5 h. Batch Reactor.	20-30	From 22 MJ/kg to 31 MJ/Kg	Hydrocarbons from 11 to 22%, Phenols from 22 to 6%
Hita et al. [44]	Pt-Pd/ACP and Ni-W/ACP	450 °C and 65 bar, 0.15 g cat h^{-1} g bio-oil, 90 mL min^{-1} H_2 for 6 h. Flow Reactor.	42-47		Phenols and aromatics increased up to 7 and 16%, respectively

Regarding the industrial implementation of this process, possible mass transfer limitations should be considered. These could be due to a relatively low efficient mixing when a batch reactor is used. However, such problems are typically solved for hydrogenation reactions, conducted in batch reactors, adopting a combined gassing system (Ekato type stirrers specifically developed for hydrogenation reactors). These issues are particularly important for the potential scale-up and commercialisation of this process, as these can make the performance of the lab-scale process not comparable to that of the industrial plant. Such stirrers significantly improve the hydrogen mass transfer into the liquid phase,

through a jet gas disperser in the bottom of the reactor. A suitable designed impeller disperses the hydrogen fed into very fine gas bubbles with a consequent increase in the gas-liquid surface. A self-aspirating turbine swallows the non-converted gas from the head space of the reactor into the liquid phase through a hollow shaft system, thus providing an effective internal hydrogen recycle. In this way, hydrogenation reactions take place under non mass-transfer-limited conditions.

Prior to the scale-up, at the laboratory scale, the role of the mass transfer limitations can be easily assessed performing reaction runs at different stirring speeds: if the reactor behaviour in terms of, for example, heat removal rate, does not change, this means that the increase in the mass transfer surface exerts a minor impact and that the process is performed under kinetically controlled conditions. If instead, the increase in the mass transfer surface related to the increased stirring speed plays a relevant role on the reactor performance, this means that the process is performed under mass transfer limited conditions and that a more efficient stirring of the reaction phase must be adopted in order to minimise mass transfer resistances. Besides, other important issues are the reutilisation of the catalyst to analyse whether or not catalyst deactivation takes place to a significant extent, and the use of a continuous flow reactor avoiding solid formation. Given this, future work should address these aspects to assess the possible of scale-up and commercialisation of bio-oil HDO over carbon neutral Mo_2C/CNF catalysts.

4. Conclusions

This work addresses the hydrodeoxygenation of a lignocellulosic bio-oil over a carbon-neutral Mo_2C/CNF catalyst, examining the effect of the temperature, H_2 pressure, reaction time and catalyst loading. The statistical analysis of the results revealed that these variables exerted a significant influence on the process so that they must be carefully controlled to strike a right balance between the quantity and quality of the upgraded bio-oil produced. During the HDO process, four different fractions were obtained: an upgraded bio-oil (17-72%), a solid product (4-44%), an aqueous fraction (5-39%) and a gaseous stream (1-15%). The upgraded bio-oil principally consisted of a mix of phenols (56-78%), cyclic ketones (7-30%), carboxylic acids (2-8%), esters (0-9%) and aromatic compounds (0-20%). The relative amounts of C, H, O of this product shifted by 34-78 wt.%, 3-8 wt.% and 13-62 wt.%, while its HHV ranged between 9 and 35 MJ/kg. Rising the temperature and/or prolonging the reaction time

enlarged gas and solid formation, which decreased the yield to upgraded bio-oil, as reforming and thermal decomposition are enlarged with temperature. However, these variations also increased the proportions of C and H. They also decreased in the relative amount of O in the upgraded bio-oil, which led to increases in its HHV, since hydrogenation, deoxygenation, decarbonylation and decarboxylation reactions took place in a greater extent. Augmenting the catalyst loading and/or H_2 pressure helped stabilise the bio-oil, thus decreasing its transformation into gas and solid species. These increments also promoted hydrodeoxygenation reactions up to a specific limit, as hydrogenation reactions are limited by the amount of H_2 available and the thermodynamics of the hydrogenation reactions. These beneficial features not only enlarged the yield to upgraded bio-oil but also helped produce an upgraded bio-oil with more C and less O, which increased the HHV of the upgraded bio-oil in comparison to that of the original feedstock. The optimisation of the process revealed that HDO over a Mo_2C/CNF catalyst is an excellent route for the production of liquid-energy carriers and platform chemicals from bio-oil. Using a temperature of 350 ºC, an initial H_2 pressure of 40 bar with a catalyst loading of 0.19 g cat/g bio-oil for 1 h, it is possible to convert 65% of the organic content of the bio-oil into an upgraded liquid with a HHV of 30 MJ/kg, achieving a deoxygenation degree of 70% with an energy efficiency of 62%. Besides, all the bio-oil organic content can be converted into a liquid with a high proportion of phenols (79%) during its HDO at 250 ºC, using an initial H_2 pressure of 20 bar and a catalyst amount of 0.14 g cat/g bio-oil for around 0.5 h.

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