



Research paper

Influence of feedstock, catalyst, pyrolysis and hydrotreatment temperature on the composition of upgraded oils from intermediate pyrolysis



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ABSTRACT

Hydrodeoxygenation (HDO) of bio-oils obtained from intermediate pyrolysis with hot vapor filtration was investigated over Ru/C and NiCu/Al₂O₃ catalysts as a function of several parameters: feedstock (beech wood, wheat straw), pyrolysis temperature, catalyst and hydrotreatment temperature. Beech wood was found to be a suitable feedstock for HDO due to its low heteroatom content, whereas the high sulfur content in the wheat straw bio-oil caused irreversible poisoning of the catalysts. Ru/C generally consumed more hydrogen than NiCu/Al₂O₃, showing higher hydrogenation/HDO activity with higher selectivity towards alcohols and hydrocarbons, whereas NiCu/Al₂O₃ resulted in a higher concentration of ketones. The pyrolysis temperature affected the fragmentation degree; higher temperatures resulted in a higher quality pyrolysis oil with low oxygen mass fraction, but with decreased mass yield. By varying the hydrotreatment temperature (80, 150, 250, 350 °C), different classes of compounds were converted and different deoxygenation degrees were achieved. Overall the results indicate that intermediate pyrolysis with hot vapor filtration is a valid alternative to the more commonly used fast pyrolysis for decentralized (or small-scale) applications, especially for heterogeneous feedstocks with high ash content.

1. Introduction

Biomass represents the main renewable carbon resource and biomass conversion into higher value products has been the subject of much research in recent years [1]. However, this subject still constitutes a significant challenge due to the highly complex chemical structure of biomass. Among several conversion technologies, fast pyrolysis followed by upgrading is considered an economical and energetically valuable route to produce transport fuels and eventually chemicals [2]. Besides fast pyrolysis, intermediate pyrolysis in screw reactors is an emerging technology [3–5], which can also be used for bio-oil production. Intermediate pyrolysis shows longer vapor residence times than fast pyrolysis (order of minutes vs seconds), and usually two condensates are obtained (an aqueous phase and an organic phase defined as bio-oil). Although the yield of bio-oil is lower compared to fast pyrolysis, the bio-oils produced from intermediate pyrolysis are more stable, contain less oxygen ([6]) and exhibit lower molecular weight substances. The process is easier to control [4] and can be a valid alternative to fast pyrolysis in a decentral to central biomass-to-fuels

framework, especially for heterogeneous feedstock with high ash content [6]. However, the technology is relatively new and therefore requires deeper understanding of the process and evaluation of the feasibility of upgrading the bio-oils produced. According to the authors' knowledge, no studies have been previously performed related to the upgrading of intermediate pyrolysis oils, which is necessary for the subsequent production of transportation fuels and chemicals due to their higher oxygen mass fraction [2]. Hydrodeoxygenation (HDO), which can be also indicated as hydrotreatment in this context, offers a potential strategy to decrease the oxygen content, since it can provide higher upgraded oil yield, with higher carbon recovery and better quality in comparison to alternative methods such as zeolite cracking [2,7–9].

In this work, a systematic analysis on intermediate pyrolysis and HDO was carried out in order to understand the influence of different parameters on the composition of the upgraded oils, including: biomass feedstock [10,11], catalyst type, pyrolysis temperature and hydrotreatment temperature. Experiments related to intermediate pyrolysis were carried out in the screw reactor STYX (Institute for Technical

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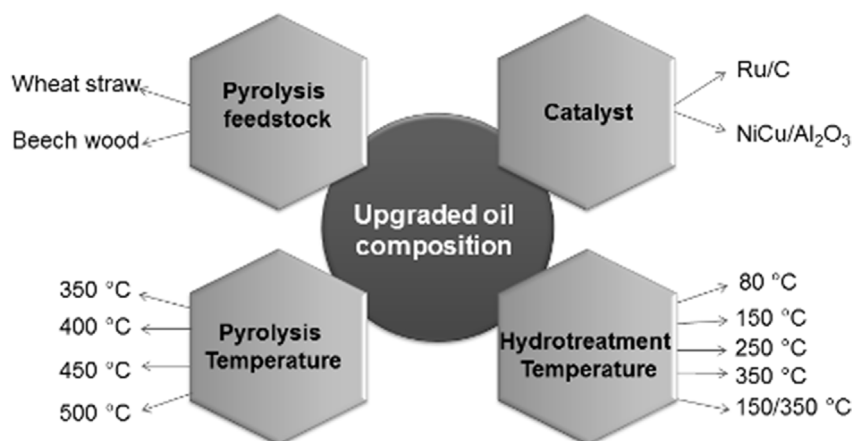


Fig. 1. Different parameters affecting the composition of the upgraded oils and conditions tested in this study.

Chemistry, Karlsruhe Institute of Technology), which implements hot vapor filters integrated with the pyrolysis unit for removal of solids, heavy tar substances and minerals [5]. A summary of the experimental parameters of interest to evaluate the potential of intermediate pyrolysis with integrated hot vapor filtration as basis for fuels/chemical production is shown in Fig. 1. The chosen biomass feedstock influences the bio-oil composition, which in turn can affect the upgraded oil composition and the catalyst performance. Herein beech wood and wheat straw were chosen as feeds for intermediate pyrolysis, as representative of hard wood and herbaceous species respectively. Concerning the upgrading process, Ru/C was chosen as a noble metal catalyst and NiCu/Al₂O₃ as an alternative HDO nickel-based catalyst, whereby differences in activity and product selectivity are expected [12,13]. The pyrolysis temperature has a known influence on the fragmentation degree of the molecules, producing oils with different composition and molecular weight. Four bio-oils were therefore produced using beech wood and different pyrolysis temperatures: 350, 400, 450 and 500 °C. The hydrotreating temperature was investigated using the bio-oils from beech wood and wheat straw produced at 450 °C, which optimizes the mass and carbon yields of the oils. Four HDO temperatures (80, 150, 250 and 350 °C) were used in order to see the reactivity of different functional groups and the deoxygenation degree (DOD) over NiCu/Al₂O₃ and Ru/C. The influence of the stabilization step at 150 °C was also studied for HDO at 350 °C. A detailed analysis of the products by the combination of GC-MS, ¹H NMR, elemental analysis and Karl Fischer titration was chosen to provide more detailed on understanding the reaction pathways and elaborate a general reactivity scale of bio-oil components over Ru/C and NiCu/Al₂O₃ catalysts. Finally, analysis of the spent catalysts is presented to obtain information about deactivation processes on the catalysts surface.

2. Materials and methods

2.1. Production of the bio-oils

Four bio-oils derived from beech wood and one from wheat straw were produced in the so-called STYX reactor. The beech wood was bark-free with chips particle size between 2.0 and 4.5 mm (*Fagus Sylvatica*, Räuhergold® delicatessen from J. Rettenmaier und Söhne GmbH & Co. in Rosenberg, Germany). More information about elemental composition is reported in Ref. [5]. The wheat straw derived from winter straw (*triticum aestivum*, cultivar “Tommi”) sown in October 2012 on fields near “Urspring” in Germany (latitude 48.546764 °N, longitude 9.896208 °E), harvested in August 2013 and stored as rectangular bales in an open storage shed and delivered to the pyrolysis plant in July 2014. It was stored in a closed storage in KIT Campus North until being used in 2016.

The intermediate pyrolysis bench scale reactor (STYX) was developed by the Institute for Technical Chemistry (ITC) at Karlsruhe Institute of Technology (KIT) and was previously described by Tomasi Morgano et al. [5]. STYX consists of a screw reactor with an integrated hot gas filtration, i.e. ceramic filter candles displaced within the vessel of the reactor. Hot gas or vapor filtration enables the elimination of char particles and minerals from the final bio-oil, producing a feed more suitable for HDO. Two-step condensation was employed: the first at 80 °C and the second at 15 °C, including an electrostatic precipitator for the removal of organic aerosols. The feedstock materials were continuously fed to the reactor with a mass flow rate of 2 kg h⁻¹. The bio-oils from beech wood were produced at temperatures of 350, 400, 450 and 500 °C (denoted in this study beech 350 °C – beech 500 °C), and the one derived from wheat straw at 450 °C (named straw 450 °C). The

Table 1

Bio-oil yield from the intermediate pyrolysis process as mass fraction and chemical compositions of the bio-oils used in this study.

	beech 350 °C	beech 400 °C	beech 450 °C	beech 500 °C	straw 450 °C
Bio-oil yield from pyrolysis process (%)	9.1	12.8	14.3	12.9	13.1
pH	2.5	2.6	2.7	3.0	3.8
Water mass fraction (%)	17.8	14.6	12.4	11.5	23.7
Element mass fractions, as received; water free (%)					
C	49.3; 60.0	52.2; 61.1	55.4; 63.2	58.9; 66.6	49.7; 65.1
H	7.7; 7.0	7.6; 7.0	7.1; 6.5	7.2; 6.7	8.5; 7.6
O	43.0; 33.1	40.2; 31.9	37.5; 30.2	33.9; 26.8	40.6; 25.6
N	< 0.3; < 0.3	< 0.3; < 0.3	< 0.3; < 0.3	< 0.3; < 0.3	1.2; 1.5
S	< 0.005; < 0.005	< 0.005; < 0.005	< 0.005; < 0.005	< 0.005; < 0.005	0.3; 0.4
Higher heating value (HHV) as received; water free (MJ/kg)	21.1; 25.7	22.5; 26.3	23.4; 26.7	25.1; 28.4	22.2; 29.1

residence time of the solids was set to 10 min. The resulting residence time of the vapors, which decreases with the increase of the off-set temperature of the reactor was in the range of 20–40 s. After filtration, the pyrolysis vapors were quenched in the condensation unit. The pyrolysis condensate was separated mechanically into an oil phase (bio-oil) and an aqueous phase. The yield of bio-oil and other physical-chemical characteristics are reported in Table 1.

2.2. Hydrotreatment experiments

The catalysts used during hydrotreatment were a commercial Ru/C catalyst (Sigma Aldrich n. 206180, nominal loading 5% mass fraction of Ru) and NiCu/Al₂O₃ (17.8% mass fraction of Ni, 2.1% mass fraction of Cu) prepared by wet impregnation as described in Boscagli et al. [12]. The Al₂O₃ support was provided by Saint Gobain NorPro (SA31145, mainly theta alumina), Ni(NO₃)₂·6H₂O (Alfa Aesar n. A15540) and Cu(NO₃)₂·2.5H₂O (Alfa Aesar n.12523) were used as metal salt precursors. The BET surface area was 66 m² g⁻¹ and the particle size used was less than 100 μm. The catalyst was activated at 500 °C in an atmosphere of 25% H₂ in N₂ (total flow 1.6 L min⁻¹ for normal condition) for 4 h prior to hydrotreatment.

Hydrotreatment experiments were carried out in a batch autoclave reactor (Institute of Catalysis Research and Technology, KIT). The 200 cm³ volume autoclave is made of Inconel alloy 625 and designed to work up to 400 °C and 36 MPa. It is equipped with a magnetically-coupled stirrer (Premex AG, torque 80 N cm) and a gas injector stirrer in order to facilitate H₂ mass transfer from gas to liquid phase. The autoclave was inserted in a brass mantle containing electrical cartridges to heat the reactor. The power supply was controlled by a program based on Labview (National Instruments). For each experiment approximately 50 g of bio-oil together with 2.5 g of pre-reduced catalyst were inserted in the autoclave, which was first purged with nitrogen, then pressurized with H₂ (6.0 Air Liquide) to 14 MPa at room temperature. The stirrer speed was set at 16.7 Hz (1000 rpm) and the reactor was heated to the final temperature with a heating rate of 15 K min⁻¹. The HDO reaction began already during the heating ramp, providing the stabilization for the bio-oil, as also reported by de Miguel Mercader et al. [14]. To monitor the influence of pyrolysis temperature on the upgraded oils derived from beech wood, the different bio-oils were treated over Ru/C and NiCu/Al₂O₃ at 150 °C for 1 h and subsequently at 350 °C for 2 h (time at which no more significant hydrogen consumption was observed). To monitor the influence of hydrotreatment temperature, different HDO temperatures were investigated for the beech 450 °C and straw 450 °C bio-oils: 80, 150, 250 and 350 °C. For the reaction at 80, 150 and 250 °C the reaction time was 1 h at the final temperature. Two experiments were performed at 350 °C, with and without performing a previous stabilization step at 150 °C for 1 h. In both cases the temperature 350 °C was held for 2 h to ensure complete H₂ consumption (not completed after 1 h). The above experiments were carried out for both Ru/C and NiCu/Al₂O₃. Once the reaction was complete, the autoclave was cooled first with compressed air, then in an ice/water bath. The experiments were repeated only once due to limited availability of pyrolysis oil, but similar previous experiments showed a standard deviation on average around 3 L kg⁻¹ (normal condition: 0 °C, 101.325 kPa) in terms of H₂ consumption (in general less than 5% of the total hydrogen consumption [13]).

Gaseous products were sampled and analyzed by gas chromatography (GC) (see Section 2.3). The remaining products (solid and liquids) were collected from the autoclave and centrifuged at 7240 RCF for 30 min (Thermo Scientific Heräus Biofuge Stratos, fixed angle rotor 26 n.75003014). The different liquid phases were separated and weighed. Depending on the temperature and the catalyst used, either one phase, two phases (upgraded oil and aqueous phase) or three phases (low density upgraded oil, aqueous phase and high density upgraded oil) were separated. The residue in the reactor interior consisting of catalyst, solid and tar-like components, was collected by

washing with acetone. This fraction, together with the solids separated by centrifugation, was washed with acetone, filtered with a Whatman filter (Grade 589/3 blue ribbon) and the resulting solids dried under vacuum. In general, the concentrations or yields presented in this paper are reported as mass fraction, if not else specified.

The H₂ consumption during each experiment was determined from the difference of the number of hydrogen moles before and after the reaction at room temperature. The starting moles of H₂ and the final total moles of gas were calculated using the Soave-Redlich-Kwong equation [15] for real gases. The final moles of H₂ were calculated by multiplying the final total moles of gas per the H₂ mol fraction calculated by GC. The hydrogen consumption is expressed as normal liter (normal condition: 0 °C, 101.325 kPa) of hydrogen per kg of pyrolysis oil (L kg⁻¹).

Since in some experiments the weight loss by mass balance could be around 10–20% (due to losses of the liquid products on the reactor wall and on the catalyst), the mass balance of the liquid products was calculated using the elemental composition of each phase and the principle that the mass of carbon and oxygen should be conserved during the reaction.

$$\text{Tot C} = (\%wp \cdot C_w + \%oil \cdot C_{oil})/100 \quad (1)$$

$$\text{Tot O} = (\%wp \cdot O_w + \%oil \cdot O_{oil})/100 \quad (2)$$

In the equation system (1, 2), *Tot C* and *Tot O* are the quantity of carbon and oxygen theoretically recovered in the upgraded oil and aqueous phase. These quantities were calculated by subtracting the carbon and oxygen contained in the gas and solids from the amount of the feed. GC analysis was used to determine the mass and elemental composition of the gas phase. The carbon mass fraction of the solid was determined by elemental analysis (Section 2.4), while oxygen was considered negligible. *%wp* and *%oil* are defined as the respective quantity (mass percent) of aqueous phase and upgraded oil produced from the reaction. *C_w* and *C_{oil}* are the carbon mass fraction (%) measured in the aqueous and the oil phase. *O_w*, *O_{oil}* are the analogous oxygen mass fractions (%). Solving the system (1, 2) for *%wp* and *%oil* permits closing the mass balance with less than 3% error, minimizing the losses and giving a more precise result. However, equation (1) was not applicable if multiple organic and aqueous phase were present.

2.3. Characterization of the bio-oils and HDO products

The hydrotreatment of the bio-oils formed several product phases: a gas phase, one/two upgraded oils with different densities, an aqueous phase and solids. Different analytical techniques were employed for product characterization. The gas phase was analyzed by GC using a 7890 A Agilent instrument equipped with two columns (Restek 57096 Hayesep Q and Restek Molsieve 5 A) and connected to a TCD and a FID detector. 100 mm³ of gas was injected (injector temperature 250 °C) and a split ratio 28:1 was used (carrier gas helium). The oven temperature program for the analysis was: 50 °C for 10 min, heating at 3 K min⁻¹ until 90 °C, 20 K min⁻¹ until 150 °C (hold for 16 min), 50 K min⁻¹ until 230 °C (hold for 10 min). A system of switching valves between the two columns during the measurement and a catalyst for the conversion of CO and CO₂ to methane were used.

The liquid products and the bio-oil were analyzed by Karl Fischer titration, elemental analysis, GC and quantitative ¹H NMR. The water content was determined by Karl Fischer titration using a Titrando 841, Metrohm. HYDRANAL-Methanol dry and HYDRANAL-Composite 5 (Sigma Aldrich) were used as solvent and reagent for the titration. C, H, N content was measured by an elemental analyser CHN628 (Leco). Oxygen was calculated by the difference. The Higher Heating Value (HHV) of bio-oils and upgraded oils was calculated by elemental analysis using Channiwala's equation [16]. GC with mass spectrometry (GC-MS, HP G1800A, GCD system equipped with Stabilwax column) was employed for qualitative liquid phase product analysis. Samples

were prepared by dilution in methanol (1:10 or 1:20) and filtrated by a PTFE filter 0.250 mm 1 mm^3 volume of the sample was injected with a split ratio 20:1 (injector temperature 250 °C). The following heating program was used: 5 min at 40 °C, heating with 8 K min^{-1} until 250 °C, hold for 10 min at 250 °C. ^1H NMR spectroscopy was performed in a Bruker Biospin spectrometer with ^1H frequency 250 MHz (5.47 T magnet). The sample (circa 100 mg) was dissolved in 1 cm^3 of CD_3OD containing TMS- d_4 (sodium 3-trimethylsilyl-2,2',3,3-tetradeuterio-propionate, circa 2 g L^{-1}) as internal standard. In case the sample was not completely soluble in methanol, like for the upgraded oil derived from wheat straw, deuterated dichloromethane was added to the sample in a volume ratio of 1:1 with respect to methanol. The samples were then centrifuged and measured at 25 °C. ^1H NMR spectra were measured with the following parameters: 90° pulse program (4.95 μs), acquisition time 10 s, relaxation delay 1.0 s, number of scans 24, spectral width 3255.2 Hz and time domain 32 k. ^1H NMR data were processed using MestReNova (version 9.0). The use of an internal standard allowed the conversion of the integrated signal into moles of protons [17]. The spectra were integrated in different regions typical for specific functional groups [18], as reported in Boscagli et al. [12]: aldehydes (10.1–9.2 ppm); (hetero) aromatics (8.5–6.0 ppm); carbohydrates, water, -OH exchanging groups (6.0–4.3 ppm); alcohols, ethers, alkenes (4.3–3.0 ppm); alpha to unsaturated groups (3.0–1.5 ppm); alkanes (1.5–0.5 ppm). In addition, the original bio-oils were analyzed by ICP-OES (Agilent 725 Inductively Coupled Plasma Optical Emission Spectrometry) to determine the sulfur and metal content. Solvent fractionation was also performed for the original bio-oils in order to gain information about the compound nature present in the bio-oil. The procedure adopted took inspiration from Oasmaa et al. [19], but some modifications were made as reported in Ref. [12]. In Table 2 the classes derived from the solvent fractionation are reported. More information about the fractionation procedure can be found in Ref. [12]. The molecular weight distribution of the different pyrolysis oils was estimated by gel permeation chromatography (GPC), performed in a Column-Thermostat T 6300 from Merck provided with a pre-column PSS SDV 5 $\mu\text{m} \times 50\text{ mm}$, two columns PSS SDV 5 $\mu\text{m} 1000\text{ A} \times 300\text{ mm}$ and PSS SDV 5 $\mu\text{m} 100\text{ A} \times 300\text{ mm}$ and a RI-Detector L-7490. 10 mg of sample was dissolved in 5 ml of THF with internal standard toluene.

2.4. Characterization of the spent catalysts

The catalysts were analyzed by elemental analysis, scanning electron microscopy - energy dispersive X-ray spectroscopy (SEM-EDX), X-ray diffraction (XRD) and ICP-OES. Carbon deposition, sulfur and nitrogen mass fraction were mainly monitored by elemental analysis of the spent catalysts measured on Elemental Vario el Cube. This method was not suitable for carbon-supported catalysts and due to the low difference in weight it was not possible to determine the carbon deposition on Ru/C. SEM-EDX was employed in order to gain an overview of the elements present on the catalyst. The field emission SEM (FE-SEM) used was a DSM 982 Gemini microscope, Carl Zeiss Ltd. (Oberkochen, Germany) equipped with secondary ion, backscattered and transmission detectors. The EDX unit was equipped with a Si(Li) X-ray detector (type INCA Penta FET; 30 mm^2 crystal size; Oxford

Instruments UK). The approximate superficial concentration detected by SEM-EDX is reported as an average of ROIs (Region of Interest) of circa 1 mm^2 . Powder XRD was measured using an X'Pert PRO MPD instrument (PANalytical GmbH) equipped with a copper anode (Cu $K\alpha$ 1.54060 Å). The XRD patterns were recorded for some samples in a 2θ range between 20 and 80° (30 min, step size 0.017°) and for others between 5 and 120° (1 h, step size 0.017°). The average crystallite size was estimated using the Scherrer equation (shape factor $K = 0.9$) after correction of the instrumental line broadening and if necessary after subtracting the contribution of the support signal. Leaching of the catalyst was monitored by analyzing the aqueous phase by ICP-OES (Agilent 725 ICP-OES Spectrometer).

3. Results and discussion

3.1. Characterization of the bio-oils

The chemical composition of the different pyrolysis oils varied depending on the pyrolysis temperature and the feedstock (Table 1). The pyrolysis temperature had a gradual effect on the composition of the bio-oil produced from beech wood. For example, at higher pyrolysis temperatures the pH increased gradually, while the water and oxygen content decreased. The lower water content was attributed to a different phase separation equilibrium established during the vapor condensation phase. This is due probably to the different polarity of the products, as confirmed by the lower oxygen mass fraction recorded for the pyrolysis oils produced at higher temperatures. As a result, the HHV increased with the pyrolysis temperature, reaching a maximum value at 500 °C. However, pyrolysis at 500 °C favored fragmentation reactions, resulting in higher gas yield and decreased yield of bio-oil (Table 1) [5]. For this reason, 450 °C was considered as a suitable compromise between reduced oxygen mass fraction and maximum bio-oil yield. The concentration of heteroatoms was below the detection limit for the bio-oils from beech wood. On the other hand, pyrolysis oil produced from wheat straw showed a higher pH and a higher water content compared to the beech wood bio-oil produced at the same temperature. On dry basis the oxygen mass fraction was lower than the respective beech wood bio-oil, but the content of heteroatoms like N and S was relatively high, and this could represent an issue in terms of catalyst poisoning during hydrotreatment [20] (see Section 3.5). In addition, the straw 450 °C bio-oil was received as one phase, but displayed a tendency to separate in two phases if centrifuged (7240 RCF, 30 min, same condition for the separation of HDO products): 25% of the original mass was recovered as a light fraction containing 60.6% water and 75% as a heavy fraction containing 14.4% water. The beech wood bio-oils showed no phase separation at this stage. Generally, the oxygen mass fraction was lower for bio-oils produced by intermediate pyrolysis compared to those by fast pyrolysis. Note that a direct comparison with other works in literature is difficult due to different setups, pyrolysis conditions and biomass characteristics, therefore the following values should be used only as a qualitative indication. For example, for beech wood an oxygen mass fraction of 38% on dry basis was reported for fast pyrolysis at 512 °C [21], whereas in case of intermediate pyrolysis at 500 °C we obtained a bio-oil with 26.8%. For wheat straw, previous

Table 2
Fractionation of pyrolysis oil by solvent extraction (according to Ref. [12]).

Extracted-fraction notation	Characteristic of the extracted fraction	Main components extracted
WS-DDS	Water soluble- dichloromethane diethylether soluble	Aldehyde, ketones, furans, lignin monomers, volatile acids
WSDDIS*	Water soluble- dichloromethane diethylether insoluble without water	Sugars derivatives, hydroxyacids, additives of bioliq process, etc.
WIS-DS#	Water insoluble-dichloromethane soluble without extractives	Low-molecular mass lignin, aging product
WIS-DIS + Extractives	Water insoluble-dichloromethane insoluble without solids n-hexane soluble	High-molecular mass lignin, aging products Apolar components
Solids	Not soluble in methanol	char
Water	Determined by Karl Fisher titration	Water

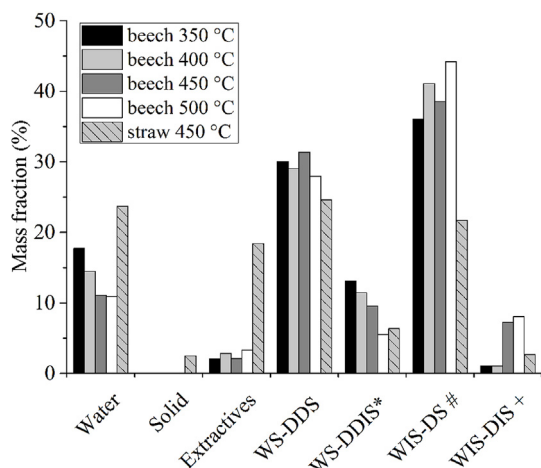


Fig. 2. Solvent fractionation of the bio-oils produced from beech wood and wheat straw. extraction classes given in Table 2).

experiments in KIT showed that intermediate pyrolysis at 450 °C in STYX produced a bio-oil with 25.6% oxygen mass fraction, while the bio-oil produced at 500 °C in bioliq® 30.4%. For wheat straw further comparison could be found in Ref. [6].

Solvent fractionation also showed a trend with pyrolysis temperature used for the beech wood feedstock (Fig. 2, see fractionation scheme in Boscagli et al. [12]). With increasing pyrolysis temperature, the content of sugar derivatives (WS-DDIS) decreased, while the non-soluble fraction in water (WIS-DS and WIS-DIS, mainly constituting of pyrolytic lignin with different molecular weight) increased. This can be explained by considering the degradation temperature of lignin, cellulose and hemicellulose [22]. Since lignin degrades at higher temperature than hemicellulose and cellulose, more pyrolytic lignin (lower molecular mass and higher molecular mass) was released at higher temperature. At the same time sugar-derived components can undergo further degradation forming low molecular weight compounds, which are recovered in other fractions or in the gas phase. WIS-DS was the main fraction obtained for all the beech wood bio-oils, consisting of low molecular-weight pyrolytic lignin. High molecular weight lignin derivatives (WIS-DIS) appeared only for higher temperatures (450 and 500 °C), resulting from the further decomposition of components that otherwise would be recovered as char. The results obtained by the solvent fractionation of straw 450 °C bio-oil showed a different composition compared to beech 450 °C. The straw 450 °C bio-oil had a lower content of the fraction containing pyrolytic lignin (WIS) and of the sugar derived fraction (WS-DDS), but a higher content of extractives. This high content of extractives is difficult to explain, but probably could be justified by the presence of compounds less polar and therefore more soluble in n-hexane (long chain molecules C₁₄-C₂₀ with different functionalities were detected by GC-MS). This could also have influenced the polarity of straw 450 °C bio-oil, which in fact was not completely soluble in methanol (see solids content, Fig. 2), but in acetone. As supplementary information, Fig. S1 reports the GC-MS chromatograms, showing the main differences in composition among the intermediate pyrolysis oil from wheat straw and beech wood and a fast pyrolysis oil produced in bioliq® [23]. Similar compounds in different concentrations were detected among the three bio-oils.

The molecular mass distribution was estimated for each bio-oil by GPC (Fig. 3). Note that this can be considered only as a qualitative measurement. Concerning the beech wood bio-oils, higher pyrolysis temperatures produced higher molecular weight compounds (Fig. 3a), in line with the observations from solvent fractionation. The main peaks observed were indicatively at 130, 250, 370 g mol⁻¹, which can be attributed to monomers, dimers and trimers of phenol derivatives, respectively (for example the molecular mass of guaiacol is 124 g mol⁻¹).

Similar peak positions were observed also in the case of straw 450 °C bio-oil: approximately 120, 230, 380 and 780 g mol⁻¹. In comparison to beech 450 °C, straw 450 °C bio-oil had qualitatively slightly lower content of high molecular compounds.

In order to better understand the chemical composition, GC-MS was employed and similar low molecular weight compounds were detected in the beech bio-oils (see Supporting Information, Fig. S2). Beech 350 °C and 400 °C bio-oil had similar compositions, also beech 450 °C and beech 500 °C bio-oils were comparable, showing that over specific temperature ranges other fragmentation reactions take place during pyrolysis and also more material is released from the solid phase to the gas phase. The main differences were related to aromatic compounds. At higher temperatures, aromatic molecules with fewer or shorter-chain substitutions were produced. In this specific case, higher amounts of phenol were detected at higher temperatures instead of guaiacol and syringol, probably as a result of demethoxylation/demethylation processes. Alkyl-phenols were also detected in higher concentrations at higher temperatures, indicating alkylation of the aromatic ring (probably due to radical rearrangement) or a different kind of fragmentation pathway [24,25]. At the retention time 28–30 min, partially identified molecules consisting of a phenolic unit with substitutions (molecular mass between 160 and 200 g mol⁻¹) were detected with relatively high concentrations at low temperatures, but they disappeared at 500 °C, confirming higher levels of fragmentation at elevated temperatures. Xylene isomers were detected at the retention time between 8 and 9 min in higher concentrations for higher temperatures. Straw 450 °C bio-oil contains analogous compounds, some of them in similar concentrations and some of them in different concentrations (Fig. S1, Supporting Information).

¹H NMR was a useful complementary technique to detect trends in the beech wood bio-oils depending on the pyrolysis temperature (Fig. 4). With increasing temperature, the concentration of protons in the (hetero-)aromatics (8.5–6.0 ppm) and the protons alpha to carboxylic/carbonylic/unsaturated groups (3.0–1.5 ppm) increased. At the same time, those related to alcohols and ethers (4.3–3.0 ppm) decreased, probably due to methoxylation/methylation reactions as also observed by GC. The concentration of protons belonging to alkane groups was similar for 350–400 °C and 450–500 °C. The straw 450 °C bio-oil was found to contain more water (6.0–4.3 ppm) and alkane protons (1.5–0.5 ppm) compared to the beech 450 °C bio-oil. On the other hand, protons in aromatics (8.5–6.0 ppm), alpha to carboxylic/carbonylic/unsaturated groups (3.0–1.5 ppm) and alcohols/etheric bonds (4.3–3.0 ppm) were less concentrated. These observations are in line with the results obtained by GC-MS, elemental composition and Karl Fischer titration.

3.2. Influence of the pyrolysis temperature and of the catalyst on the upgraded oil composition

Similar behavior was observed during hydrotreatment of the four pyrolysis oils produced at 350, 400, 450, 500 °C from beech wood. The hydrotreatment carried out at 350 °C (2 h) with previous stabilization at 150 °C (1 h) resulted in similar H₂ consumption for all bio-oils, exhibiting a slightly lower value only for the bio-oil produced at 500 °C (Fig. 5 a, c). This was probably due to its lower original oxygen mass fraction, which supposes a theoretically lower H₂ need. In general, the use of NiCu/Al₂O₃ resulted in a lower H₂ consumption in comparison to Ru/C (in the range of 198–232 L kg⁻¹ and 284–317 L kg⁻¹, respectively). These values were slightly higher of those reported by Ardiyanti et al. [26] for fast pyrolysis oil (147 normal L kg⁻¹ for Ni₁₆Cu₂/Al₂O₃ and 272 normal L kg⁻¹ for Ru/C). Ru/C was more active for hydrogenation/HDO, but it was considered less convenient from a H₂ economy point of view. CO₂ and methane were the main gases produced on both catalysts (Fig. 5 b, d). Higher gas quantities and especially methane were formed on Ru/C, particularly at 350 °C and 400 °C (Fig. 5 b,d). As reported in Section 3.1, more methoxy-groups were

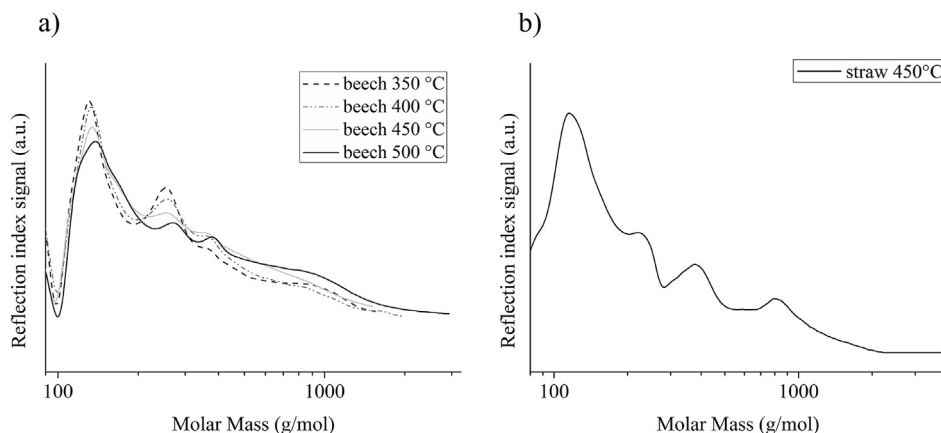


Fig. 3. Gel permeation chromatography of the bio-oils produced from beech wood at different pyrolysis temperatures (a) and wheat straw (b).

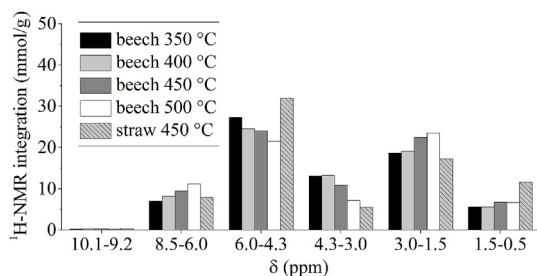


Fig. 4. ¹H NMR spectra integration of the bio-oils produced from beech wood at different pyrolysis temperature and wheat straw.

present in the bio-oils produced at lower pyrolysis temperatures, therefore the higher production of methane could be justified from their HDO activity [27], favored mainly over Ru/C.

The yield of the upgraded oils increased with pyrolysis temperature on both catalysts (mass balance reported in Table 3). Compared to fast pyrolysis studies [26], the yield of upgraded oil acquired from HDO is considerable higher for bio-oils derived from intermediate pyrolysis (35–42% vs 60–77%). However, conversely it should be considered also that the original yield of bio-oil obtained from intermediate pyrolysis is lower compared to fast pyrolysis. The carbon recovery in the upgraded oil increased as well for higher temperatures, with values in the range of 87.9%–94.6%. Therefore, hydrotreatment was considered to be a suitable upgrading method, permitting deoxygenation with low loss of

carbon via by-products. The upgraded oils produced on NiCu/Al₂O₃ and Ru/C showed a different composition (Table 3). Generally, the upgraded oils produced at higher pyrolysis temperature exhibited a lower oxygen mass fraction, which was dependent mainly on the original bio-oil composition (more oxygen at lower pyrolysis temperature) and by the DOD, the latter which did not followed a defined trend in correlation to the pyrolysis temperature. Ru/C provided an upgraded oil that had a lower oxygen mass fraction (15–17% dry basis) than NiCu/Al₂O₃ (16–21% dry basis), which was similar to values reported for fast pyrolysis (12.0% for Ru/C and 17.1% for Ni₁₆Cu₂/Al₂O₃ in Ref. [26]). In addition, upgraded oil produced with Ru/C had a lower density than water, while the oil produced over the nickel catalyst had a density higher than the aqueous phase. Contrary to bio-oil yield, the yield of the aqueous phase decreased for higher pyrolysis temperatures (Table 3). The aqueous phases consisted mainly of water, between 71% and 82% (higher mass fraction at higher temperatures), with a carbon mass fraction between 4% and 9% (lower mass fraction at higher temperatures). Ru/C enhanced more the production of the aqueous phase as a result of its higher hydrogenation/HDO activity (higher production of water and alcohols) compared to NiCu/Al₂O₃ (see also DOD Table 3).

The van Krevelen plot (Fig. 6) shows the differences in composition between the original bio-oils and the upgraded oils following hydro-treatment. The O/C and H/C ratios were gradually smaller for bio-oils produced at higher pyrolysis temperature, although the initial composition of the bio-oils was reflected also in the upgraded oils. However,

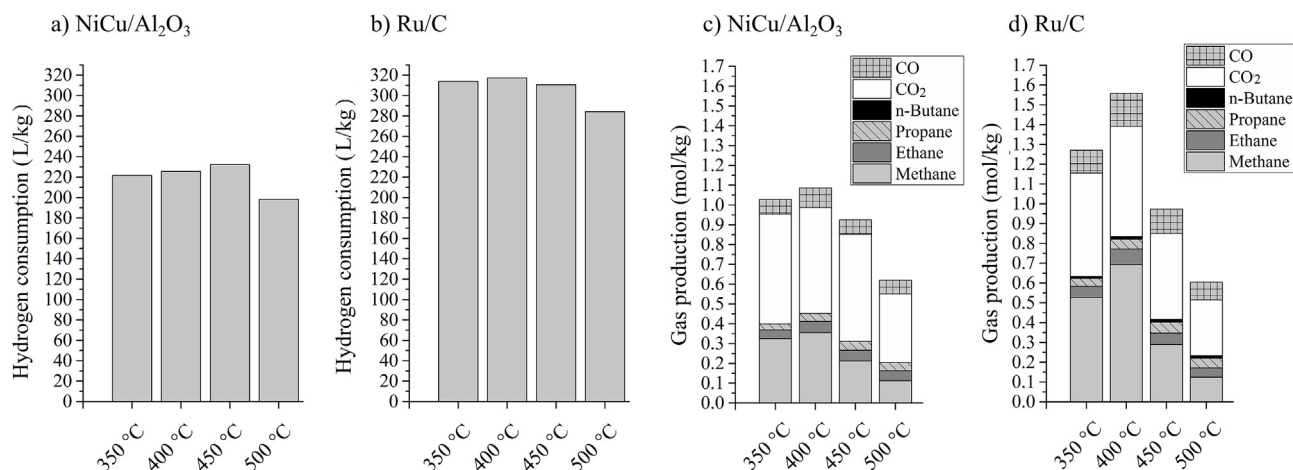


Fig. 5. Hydrogen consumption during hydrotreatment (150 °C 1 h, 350 °C 2 h, 14.0 MPa H₂ at room temperature) of bio-oils produced at different pyrolysis temperatures (350, 400, 450, 500 °C) from beech wood on NiCu/Al₂O₃ (a) and Ru/C (b). The gas production during the reaction is reported in (c) for NiCu/Al₂O₃ and in (d) for Ru/C.

Table 3

Mass yield of upgraded oil, aqueous phase and gas, with element and water mass fraction (as received), carbon recovery and deoxygenation degree for the hydrotreatment of the beech 350, 400, 450, 500 °C bio-oils.

Catalyst	Pyrolysis temperature (°C)	Aqueous phase (%)	Upgraded oil (%)	Gas (%)	C (%)	H (%)	O (%)	Water (%)	Carbon recovery in oil (%)	DOD %
Original bio-oil	350	–	–	–	49.3	7.7	43.0	17.8	–	–
Original bio-oil	400	–	–	–	52.2	7.6	40.2	14.6	–	–
Original bio-oil	450	–	–	–	55.4	7.1	37.5	12.4	–	–
Original bio-oil	500	–	–	–	58.9	7.2	33.9	11.5	–	–
Upgraded bio-oil	NiCu/Al ₂ O ₃ 350	32.2	66.0	3.5	65.8	8.9	25.3	6.2	88.1	36.2
Upgraded bio-oil	NiCu/Al ₂ O ₃ 400	25.8	72.4	3.6	65.4	9.0	25.6	6.5	90.7	33.5
Upgraded bio-oil	NiCu/Al ₂ O ₃ 450	25.4	73.6	3.3	69.8	8.8	21.4	5.6	92.7	42.4
Upgraded bio-oil	NiCu/Al ₂ O ₃ 500	21.9	77.4	2.6	71.9	8.7	19.4	4.5	94.5	39.8
Upgraded bio-oil	Ru/C 350	37.6	60.9	3.9	71.1	9.6	19.3	3.3	87.9	48.8
Upgraded bio-oil	Ru/C 400	31.3	66.4	4.5	70.6	9.4	20.0	3.9	89.8	46.0
Upgraded bio-oil	Ru/C 450	27.3	72.4	3.2	70.8	9.5	19.7	4.0	92.5	44.4
Upgraded bio-oil	Ru/C 500	24.4	75.9	2.1	73.4	9.3	17.3	3.4	94.6	44.8

Hydrotreatment performed over NiCu/Al₂O₃ and over Ru/C (150 °C 1 h, 350 °C 2 h, 14.0 MPa H₂ at room temperature). Yield is indicated in wet basis.

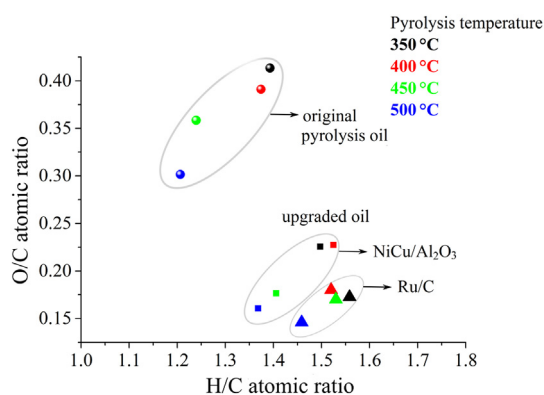


Fig. 6. Van Krevelen plot of the upgraded oils (dry basis) produced from HDO (stabilization at 150 °C for 1 h and at the final temperature 350 °C for 2 h, 14.0 MPa H₂ at room temperature) of intermediate pyrolysis of beech wood at different pyrolysis temperatures.

the differences were much less pronounced, especially for Ru/C. This meant that the pyrolysis temperature had an influence on the bio-oil composition, but the hydrotreatment attenuated these differences among the upgraded oils. Higher DOD was recorded over Ru/C, while the bio-oil produced at 500 °C showed the lowest oxygen mass fraction (Fig. 6). The original bio-oils had HHV in the range of 25–28 MJ kg⁻¹ and after hydrotreatment these values increased to 32–36 MJ kg⁻¹. A typical behavior observed for intermediate pyrolysis in contrast to fast pyrolysis oil is related to the increase of H/C ratio of the upgraded oil. In the case of fast pyrolysis under similar conditions a decrease of H/C ratio was usually reported [26,28,29]. This could be explained since the H/C ratio and O/C ratio of the intermediate pyrolysis oils is generally lower than for fast pyrolysis oil, due to more dehydration reactions favored by longer vapor residence times. Therefore, in relation to the initial bio-oil composition, reactions like hydrogenation could be enhanced more than HDO in the case of intermediate pyrolysis oils. To the authors' knowledge, no studies about HDO of intermediate pyrolysis oils and the influence of pyrolysis temperature were reported previously in the literature, therefore no comparative datasets are available.

The composition of the upgraded oils and aqueous phases produced over the two catalysts was investigated by ¹H NMR (Fig. 7). Some trends due to the influence of the pyrolysis temperature (visible in the composition of the original bio-oil) were observed in both phases. This could be found in the aromatic proton concentration (8.5–6.0 ppm), which increased with pyrolysis temperature as a result of the higher content of lignin-derivatives contained in the bio-oil (comparison in

Section 3.1). On the other hand, protons alpha to alcohols/etheric bonds (4.3–3.0 ppm) decreased, due to the lower concentration of methoxy-groups at higher pyrolysis temperatures. Protons alpha to carboxylic/carbonylic and unsaturated groups (3.0–1.5 ppm) had the highest concentration in the upgraded oils, but the same trend of the original oil was observed only for Ru/C. Alkane groups (1.5–0.5 ppm) were mainly produced over Ru/C, confirming its higher hydrogenation/HDO activity. Only few organic compounds were present in the aqueous phase, containing mainly protons alpha to carboxylic/carbonylic/unsaturated groups and to alcohols/ethers. Similar compounds were detected by GC-MS in upgraded oils hydrotreated over the same catalyst (Fig. S3–S4 Supplementary Information). Over NiCu/Al₂O₃ a significant amount of cyclic and linear ketones was produced, while over Ru/C alcohols and hydrocarbons were predominant. The effect of pyrolysis temperature could be observed for the composition of aromatic compounds over both catalysts. For instance, syringol and guaiacol were detected at lower temperature, while demethylated forms like phenol and o-cresol were favored at higher temperatures. The concentration of alkyl-phenols increased for higher temperatures, as also observed in the original bio-oils (Section 3.1), confirming the influence of pyrolysis temperature also on the upgraded oils.

3.3. Influence of hydrotreatment temperature on the upgraded oil composition from beech wood bio-oil

The influence of hydrotreatment temperature was investigated for the set of bio-oils produced from beech wood, in order to determine characteristics of the oil and product composition. At higher hydrotreatment temperatures, H₂ consumption was more pronounced as expected [7], and was higher for Ru/C than for NiCu/Al₂O₃ (Fig. 8 a, b). The use of a previous stabilization step at 150 °C resulted in a higher H₂ consumption at 350 °C. At 80 and 150 °C, the H₂ consumed was relatively low and the bio-oils were not subject to phase separation, while two phases were formed at 250 °C and at 350 °C regardless of whether a stabilization step was performed. At 250 °C the density of the upgraded oils was higher than the one of the aqueous phase for both catalysts. The same was observed at 350 °C for NiCu/Al₂O₃, while for Ru/C at 350 °C the density was lower than the one of water. Gases were already formed at low hydrotreatment temperature (Fig. 8 c, d) and mainly in the form of CO₂, which could be attributed to the decomposition of formic acid that acted as reducing agent (verified by ¹H NMR). The main gaseous product at higher temperature was also CO₂. Methane was formed only above 250 °C for the nickel catalyst and above 150 °C for Ru/C. In general, the amount of gas produced on Ru/C was higher, probably by favoring cracking reactions. The influence of the stabilization step at 150 °C for the reaction at 350 °C on the gas production

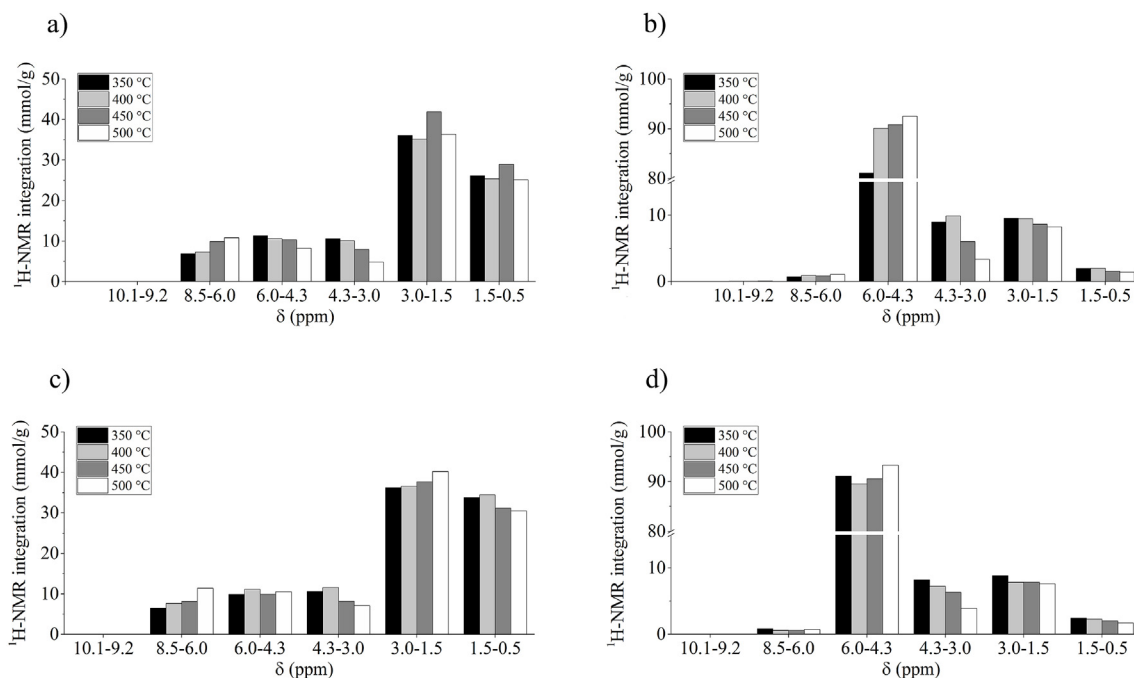


Fig. 7. ^1H NMR spectra integration of the upgraded oils produced from beech wood at different pyrolysis temperatures on NiCu/Al₂O₃ (a) and the respective aqueous phases (b), and of the upgraded oils on Ru/C (c) and the respective aqueous phases (d). Hydrotreatment performed at 350 °C for 2 h with previous stabilization at 150 °C for 1 h, 14.0 MPa H₂ at room temperature (details, cf. text).

was not clear, since gas formation was enhanced over NiCu/Al₂O₃ and reduced over Ru/C.

Regarding the mass balance, the aqueous phase production increased with temperature and less upgraded oil was recovered (Table 4). In all cases the carbon recovery in the upgraded oil was more than 90% for both Ru/C and NiCu/Al₂O₃. Higher temperature resulted in upgraded oils with lower water content. Solids were negligible in the mass balance, less than 0.3% for NiCu/Al₂O₃ and not calculable for Ru/C. Higher D.O.D were recorded at higher temperatures, reaching 40%.

According to the van Krevelen plot (Fig. 9), the O/C ratio of the upgraded oil was comparable between the experiments carried out on NiCu/Al₂O₃ and Ru/C, showing only a deviation for the reaction at 350 °C without stabilization. However, the H/C ratio was higher for Ru/C indicating a higher hydrogenation activity, as confirmed by the H₂ consumption values. Hydrogenation was predominant at low

temperatures (80 and 150 °C), where the oxygen mass fraction remained almost constant, but the H₂ content increased. Deoxygenation, together with an increase of the H₂ content, took place only at higher temperatures when phase separation occurred. The HHV increased after hydrotreatment reaching the maximum value at 350 °C with stabilization at 150 °C: 34 MJ kg⁻¹ for NiCu/Al₂O₃ and 35 MJ kg⁻¹ for Ru/C.

The results obtained by the integration of the ^1H NMR spectra are shown in Fig. 10. Aldehydes (10.1–9.2 ppm) were partially consumed at 80 °C and were no longer detected at 150 °C. The aromatic proton content (8.5–6.0 ppm) decreased slightly until 250 °C, before increasing again at 350 °C. Protons associated with water (or exchanging with water, 6.0–4.3 ppm) and protons alpha to alcohols/etheric bonds (4.3–3.0 ppm) increased in concentration until 150 °C, and after phase separation they were detected mainly in the aqueous phase. Hydrogenation of aldehydes contributed to this signal at low temperatures.

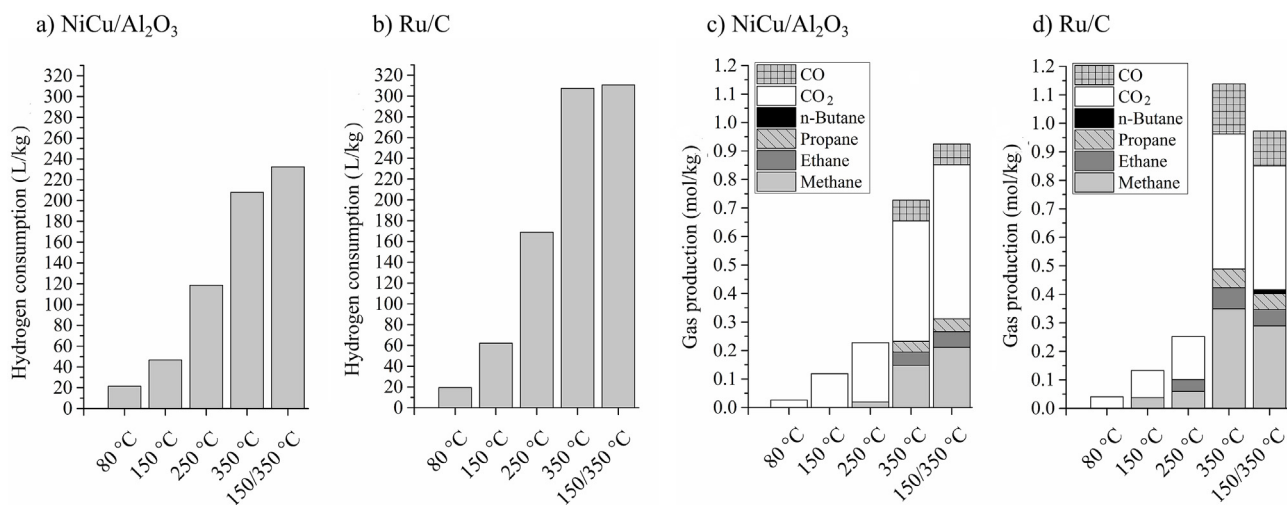


Fig. 8. Hydrogen consumption of hydrotreatment of beech 450 °C bio-oil at different temperatures (80, 150, 250, 350 and 150/350 °C, 14.0 MPa H₂ at room temperature) on NiCu/Al₂O₃ (a) and Ru/C (b). The gas production during the reaction is shown in (c) for NiCu/Al₂O₃ and in (d) for Ru/C.

Table 4

Mass yield in upgraded oil, aqueous phase and gas, with element water mass fraction (as received), carbon recovery and deoxygenation degree for the hydro-treatment of beech 450 °C bio-oil.

	Temp. (°C)	Aqueous phase (%)	Upgraded oil (%)	Gas (%)	C (%)	H (%)	O (%)	Water (%)	Carbon recovery in oil (%)	DOD (%)
beech 450 °C	–	–	–	–	55.4	7.1	37.5	12.4	–	–
NiCu/Al ₂ O ₃	80	no separation	–	0.1	55.5	7.5	37.0	12.1	99.9	1.2
NiCu/Al ₂ O ₃	150	no separation	–	0.5	55.1	7.7	37.2	13.5	99.7	3.6
NiCu/Al ₂ O ₃	250	14.1	86.1	0.9	60.4	8.1	31.5	10.7	93.9	18.5
NiCu/Al ₂ O ₃	350	22.7	76.4	2.6	67.3	8.5	24.2	6.0	92.9	33.6
NiCu/Al ₂ O ₃	150; 350	25.4	73.6	3.3	69.8	8.8	21.4	5.6	92.7	42.4
Ru/C	80	no separation	–	0.2	55.1	7.6	37.3	12.4	99.9	0.8
Ru/C	150	no separation	–	0.5	54.7	7.7	37.6	13.8	99.7	2.8
Ru/C	250	14.8	85.8	0.9	59.6	8.4	32.0	11.5	92.3	18.6
Ru/C	350	26.7	72.2	3.7	70.8	9.2	20.0	4.4	92.3	44.3
Ru/C	150; 350	27.3	72.4	3.2	70.8	9.5	19.7	4.0	92.5	44.4

Hydrotreatment performed over NiCu/Al₂O₃ and over Ru/C (80, 150, 250, 350 and 150/350 °C, 14.0 MPa H₂ at room temperature). Yield is indicated in wet basis.

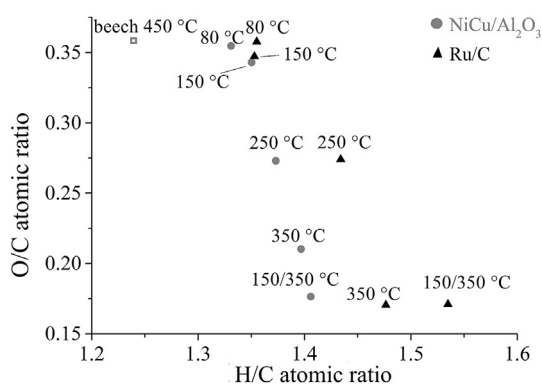


Fig. 9. Van Krevelen plot of the upgraded oils (dry basis) produced at different hydrotreating temperatures (80, 150, 250, 350 and 150/350 °C, 14.0 MPa H₂ at room temperature) of beech 450 °C bio-oil on NiCu/Al₂O₃ and Ru/C.

Protons alpha to carbonyl/carboxylic and unsaturated groups (3.0–1.5 ppm) were unchanged for NiCu/Al₂O₃ until 150 °C, after this point increasing to a maximum at 350 °C. Over Ru/C, the increase in the previous signal was noted already at low temperature, again showing a

maximum at 350 °C without stabilization. Alkane protons (1.5–0.5 ppm) also increased at low temperature, probably due to hydrogenation of unsaturated groups (more reactive than aldehyde, in agreement with [10]), and reached a maximum at 350 °C. The concentration of alkane protons in the products over Ru/C was higher, confirming higher hydrogenation/HDO activity for this catalyst.

GC-MS (Fig. S5-S6, Supplementary Information) was used to establish the reactivity of various compounds at different temperatures under hydrotreating conditions (summary in Fig. 11). Alkane formation was observed at 250 °C with low amounts of methyl-cyclopentane, and was enhanced at 350 °C with the production of other hydrocarbons. The original feed contained signals from cyclopentene and cyclopentenone derived analogues, but these disappeared already at 80 °C, with selective hydrogenation of unsaturated bonds forming cyclopentanones. The formation of 2-methyl-cyclopentanone (probably from sugar derived components) coincided with the conversion of furfural at 150 °C. At 250 °C cyclopentanones were converted mainly to cyclopentanol over Ru/C and at 350 °C to cyclopentanes. On the contrary, NiCu/Al₂O₃ was found to be selective for ketone production, as the concentration of cyclopentanones increased until 350 °C and only a low quantity of cyclopentanes were formed. Therefore, the increase in ketone concentration for NiCu/Al₂O₃ could be associated to an accumulation of

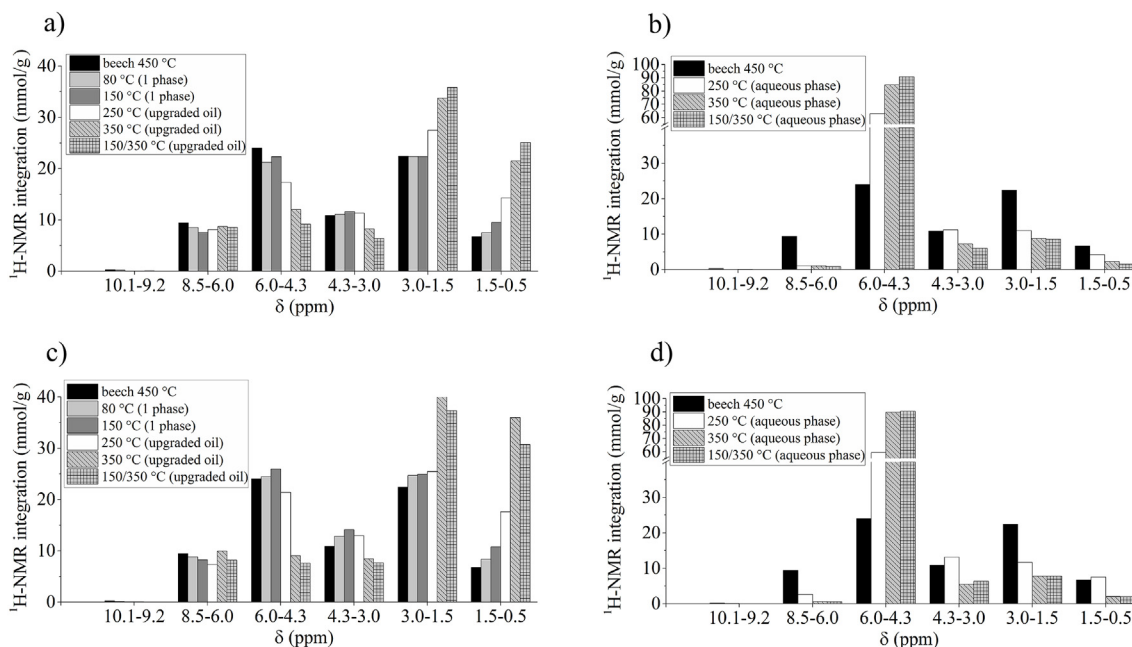


Fig. 10. ¹H-NMR spectra integration of the upgraded oils on NiCu/Al₂O₃ (a) and Ru/C (c) and the respective aqueous phases (b, d) produced from the HDO of beech 450 °C bio-oil. Hydrotreatment at 80, 150, 250, 350 and 150/350 °C, 14.0 MPa H₂ at room temperature.

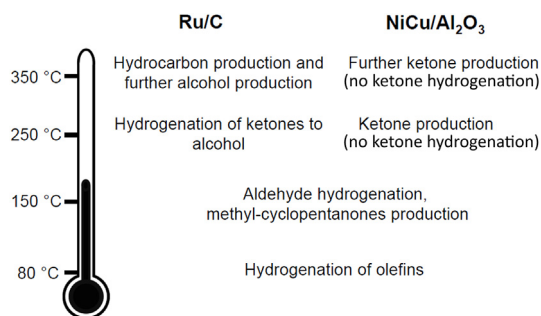


Fig. 11. Reactivity of some functional groups over Ru/C and NiCu/Al₂O₃ at different temperature using beech 450 °C bio-oil.

ketones, which were not further converted under these reaction conditions. As described later in Section 3.5, this is probably due to a structural modification of the catalyst. At 350 °C Ru/C favored the production of alcohols (some linear alcohols were detected) and hydrocarbons. Propionic, butyric and pentanoic acid were produced at higher concentrations with increasing temperature. Both Ru/C and NiCu/Al₂O₃ resulted in a similar range of aromatic compounds, indicating that both catalysts were inactive for the conversion of aromatics. Higher quantities of phenol were detected at higher temperature, due to two effects: the concentration of this molecule in the upgraded oil after phase separation, and HDO or other kind of cleavage of higher molecular weight components. The acid environment and high temperature could result in the formation of alkyl phenols with substitution in ortho and para positions, as detected at higher temperature. Guaiacol and syringol were mainly not converted at 350 °C. Compounds with higher molecular weight (retention time 28–30 min) composed of substituted phenolic rings (not easily identifiable) were converted at 350 °C.

The reactivity of some classes of compounds on NiCu/Al₂O₃ and Ru/C was delineated as a function of the hydrotreatment temperature (Fig. 11). In comparison to the reactivity reported in Refs. [30,31] for a sulfided NiMo catalyst, some differences were observed. Olefins and aldehydes were converted at lower temperatures over NiCu/Al₂O₃ and Ru/C, but carboxylic groups and phenols were more resistant to HDO.

3.4. Influence of the hydrotreatment temperature on the upgraded oil composition from wheat straw bio-oil and influence of the feedstock

The influence of hydrotreatment temperature was also tested for the intermediate pyrolysis oil produced from wheat straw at 450 °C. H₂ consumption of wheat 450 °C bio-oil was inferior compared to that of beech 450 °C bio-oil and was only observed at temperatures of 150 °C and above (Fig. 12). Higher H₂ consumption was recorded at higher temperatures, with similar values for the reactions at 350 °C with and without stabilization (e.g. 147 L kg⁻¹ for NiCu/Al₂O₃ versus 238 L kg⁻¹ for Ru/C at 350 °C with stabilization). Wheat 450 °C bio-oil produced limited amounts of gaseous products in comparison to beech 450 °C bio-oil, indicating lower catalytic cracking activity with wheat straw as a feedstock. The main gaseous products were CO₂ and methane, the latter mainly produced on Ru/C.

The liquid phase products recovered from hydrotreatment of the straw 450 °C bio-oil showed a different phase behavior at various temperatures. It should be mentioned that the original bio-oil was present as one phase, but a phase separation could be induced by centrifugation forming a light aqueous phase and heavy organic phase. At HDO temperatures in the range between 80 °C and 250 °C a light aqueous phase and a heavier upgraded oil were formed. At 350 °C three phases were observed: a light upgraded oil, an aqueous phase and a heavier upgraded oil. No trends in mass balance of the upgraded oils were observed as function of the hydrotreatment temperature (Table 5). Note that at 350 °C the mass balance was not closed due to the high

percentage of material losses. Since three liquid phases were produced, it was not possible to calculate the mass balance from elemental analysis and the collected products are reported instead. Due to the elemental composition of the different phases, the correlation of aqueous phase and upgraded oil yields with temperature was not so easy as in the case of beech wood bio-oils. Water content in the products was variable and showed no correlation with temperature. The phase separation behavior is challenging to explain, but it could be dependent on the complex phase equilibria established at a determined temperature. Gas and solids were negligible amounts for the mass balance, and the main percentage of carbon was recovered in the upgraded oils. The elemental composition, H/C and O/C ratios of the light and heavy upgraded oils are reported in Table 6. Since the original pyrolysis oil is separated during centrifugation, the heavy phase with a H/C ratio of 1.34 and O/C 0.22 should first be considered. The general trend observed was an increasing H/C and a decreasing O/C ratio at higher temperature, producing an oil with lower oxygen mass fraction and better quality. Also in the heavier organic phase at 350 °C, the content of oxygen decreased in a similar way to the lighter phase. Oxygen mass fraction in the upgraded oils was generally inferior than in the case of beech wood, probably due to the different oxygen content in the original bio-oils. In addition, the starting phase separation helped decreasing the oxygen mass fraction to 21%. The DOD is reported in relation to the original bio-oil and to its heavy phase in Table 6. Considering the heavy phase, the D.O.D is comparable or slightly higher than those of the beech wood experiments, but it was much higher compared to the original oil the DOD. Ru/C was the more active catalyst at higher temperatures, forming products with higher H/C ratio. In summary, hydrotreatment of straw 450 °C bio-oil allowed the production of an upgraded oil with lower oxygen mass fraction, but the products were more viscous and thus more difficult to recover compared to the beech wood bio-oil.

The ¹H NMR spectra integration of the upgraded oils (light and heavy phase) and aqueous phase are shown in Fig. 13. In agreement with the previous observations by elemental analysis, the heavy upgraded oil had different characteristics compared to the light upgraded oil, due to variable water content and composition. On the contrary, some trends are visible for the light upgraded oil. Both the alkane region (1.5–0.5 ppm) and protons alpha to carbonylic/carboxylic or unsaturated groups (3.0–1.5 ppm) increased with temperature to a maximum at 350 °C (similar results with and without stabilization). The protons alpha to alcohols/etheric bonds (4.3–3.0 ppm) decreased with temperature, as also observed by beech wood. The aromatic protons (8.5–6.0 ppm) also slightly decreased with temperature. In the aqueous phase, soluble compounds decreased with temperature and were constituted mainly by alpha to carbonylic/carboxylic/unsaturated and alpha to alcohols/etheric bonds. Alkane groups were more concentrated in the light upgraded oil of the wheat straw than in the upgraded oil of the beech wood, but this was probably a consequence of the phase separation rather than higher deoxygenation activity.

GC-MS results (Figs. S7–S8, Supplementary Information) indicate that the lower H₂ consumption for straw-derived bio-oil was associated with a lower reactivity of the compounds. In contrast to beech wood, cyclopentanones were resistant to hydrogenation at 80 °C. In the case of NiCu/Al₂O₃, cyclopentanones reacted at 150 °C and were converted to cyclopentanones, while in Ru/C methyl-cyclopentanone was converted mainly at 350 °C. This may be associated with catalyst poisoning already at low temperature and may also explain the similar elemental composition of the upgraded oil over Ru/C at 80–150 °C and 250 °C. Furfural reacted at 150 °C as observed in the beech wood products. Alkanes were formed, but qualitatively in lower amounts, while toluene and ethyl-benzene were detected only in the products from wheat straw. At higher temperatures, phenol and alkyl-phenol were predominant, while guaiacol and syringol were completely converted. Similar compounds were detected in both the light and the heavy upgraded oils, but generally the concentration was lower in the former

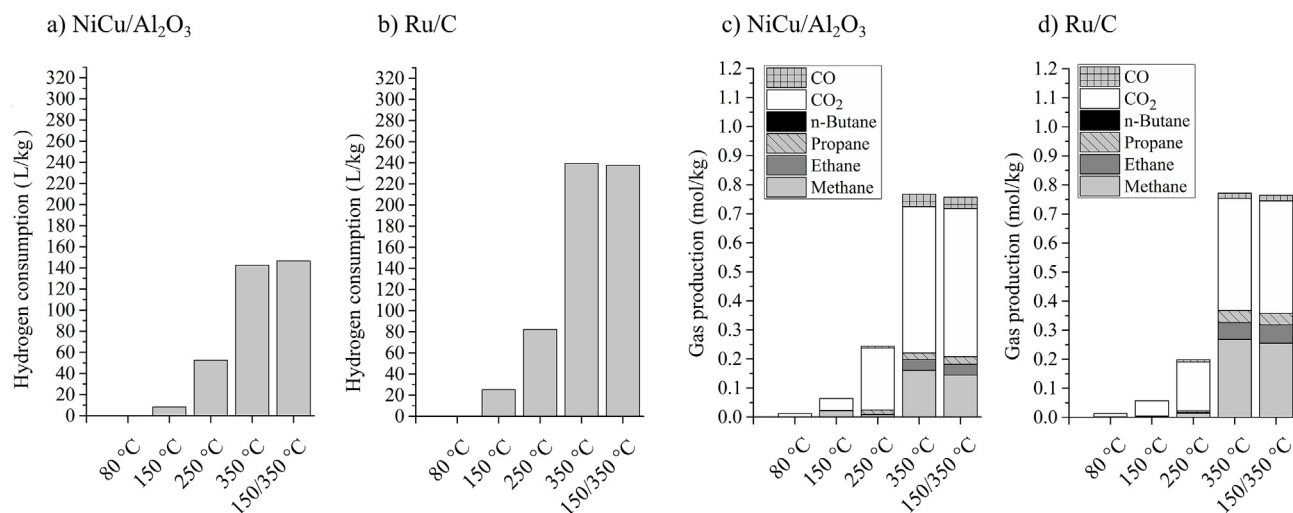


Fig. 12. Hydrogen consumption of hydrotreatment of straw 450 °C bio-oil at different temperature (80, 150, 250, 350 and 150/350 °C, 14.0 MPa H₂ at room temperature) on NiCu/Al₂O₃ (a) and Ru/C (b). The gas production during the reaction is reported in (c) for NiCu/Al₂O₃ and in (d) for Ru/C.

Table 5

Mass balance (yield in aqueous phase, upgraded oil, gas) of the hydrotreatment products of straw 450 °C bio-oil and carbon recovery in the upgraded oil for different hydrotreatment temperature.

Temp. (°C)	Catalyst	Light organic (%)	Aqueous phase (%)	Heavy organic (%)	Gas (%)	Losses (%)	Carbon recovery (%)
80	NiCu/Al ₂ O ₃	–	34.1	66.5	0.1	–0.7	86.0
150	NiCu/Al ₂ O ₃	–	21.4	78.8	0.2	–0.4	91.8
250	NiCu/Al ₂ O ₃	–	31.8	67.9	1.0	–0.7	91.2
350	NiCu/Al ₂ O ₃	16.4	26.2	32.2	2.8	22.4	56.1
150; 350	NiCu/Al ₂ O ₃	19.9	32.9	28.9	3.0	15.2	69.7
80	Ru/C	–	36.3	63.6	0.1	0.1	84.8
150	Ru/C	–	28.9	71.1	0.2	–0.2	88.8
250	Ru/C	–	19.7	79.9	0.8	–0.3	93.8
350	Ru/C	17.1	29.7	28.9	2.6	21.8	61.2
150; 350	Ru/C	16.2	25.7	28.5	2.6	27.0	53.4

Hydrotreatment performed over NiCu/Al₂O₃ and over Ru/C (80, 150, 250, 350, 150/350 °C, 14.0 MPa H₂ at room temperature).

Table 6

Water and element mass fractions of the bio-oil and hydrogenation reaction products from 450 °C straw bio-oil at different hydrotreatment temperatures.

Temp (°C)	Catalyst	phase	C (%)	H (%)	O (%)	N (%)	Water (%)	H/C	O/C	DOD (%)	DOD* (%)
		s. 450 ^a	49.7	8.5	40.6	1.2	23.7	1.42	0.3	–	–
		s.h.p. ^b	60.1	8.3	30.2	1.4	14.4	1.34	0.22	21	–
		s.l.p. ^c	21.0	9.6	68.4	1.0	60.6	1.64	0.52	–	–
80	NiCu/Al ₂ O ₃		62.1	7.8	28.5	1.6	10.3	1.29	0.23	16	0
150	NiCu/Al ₂ O ₃		57.9	8.6	32.0	1.5	17.4	1.38	0.21	22	1
250	NiCu/Al ₂ O ₃		66.8	8.7	22.8	1.7	8.6	1.39	0.17	35	18
350	NiCu/Al ₂ O ₃	light	75.6	9.4	13.7	1.3	2.9	1.44	0.11	55	44
150; 350	NiCu/Al ₂ O ₃	light	75.5	9.6	13.1	1.8	2.6	1.48	0.11	57	45
350	NiCu/Al ₂ O ₃	heavy	48.1	9.7	41.0	1.2	35.5	1.44	0.15	43	28
150; 350	NiCu/Al ₂ O ₃	heavy	67.8	9.6	21.0	1.6	10.1	1.5	0.13	48	34
80	Ru/C		63.0	7.9	27.4	1.7	9.2	1.31	0.23	17	0
150	Ru/C		62.1	8.3	28.1	1.6	12.7	1.33	0.20	25	5
250	Ru/C		58.4	8.2	31.8	1.6	17.5	1.28	0.21	23	3
350	Ru/C	light	77.4	10.3	10.6	1.8	1.7	1.56	0.09	64	55
150; 350	Ru/C	light	77.0	10.4	11.0	1.6	1.8	1.59	0.09	62	52
350	Ru/C	heavy	59.6	10.8	27.7	2.0	20.8	1.71	0.12	55	43
150; 350	Ru/C	heavy	49.3	10.2	39.1	1.4	39.5	1.42	0.06	75	68

Hydrotreatment performed over NiCu/Al₂O₃ and over Ru/C (80, 150, 250, 350, 150/350 °C, 14.0 MPa H₂ at room temperature). H/C and O/C ratio are calculated on dry basis. The deoxygenation degree (DOD) is reported considering the original bio-oil (s.450) or the heavy phase after centrifugation (s.h.p.).

^a s.450 = original bio-oil.

^b s.h.p. = straw bio-oil heavy phase.

^c s.l.p. = straw bio-oil light phase.

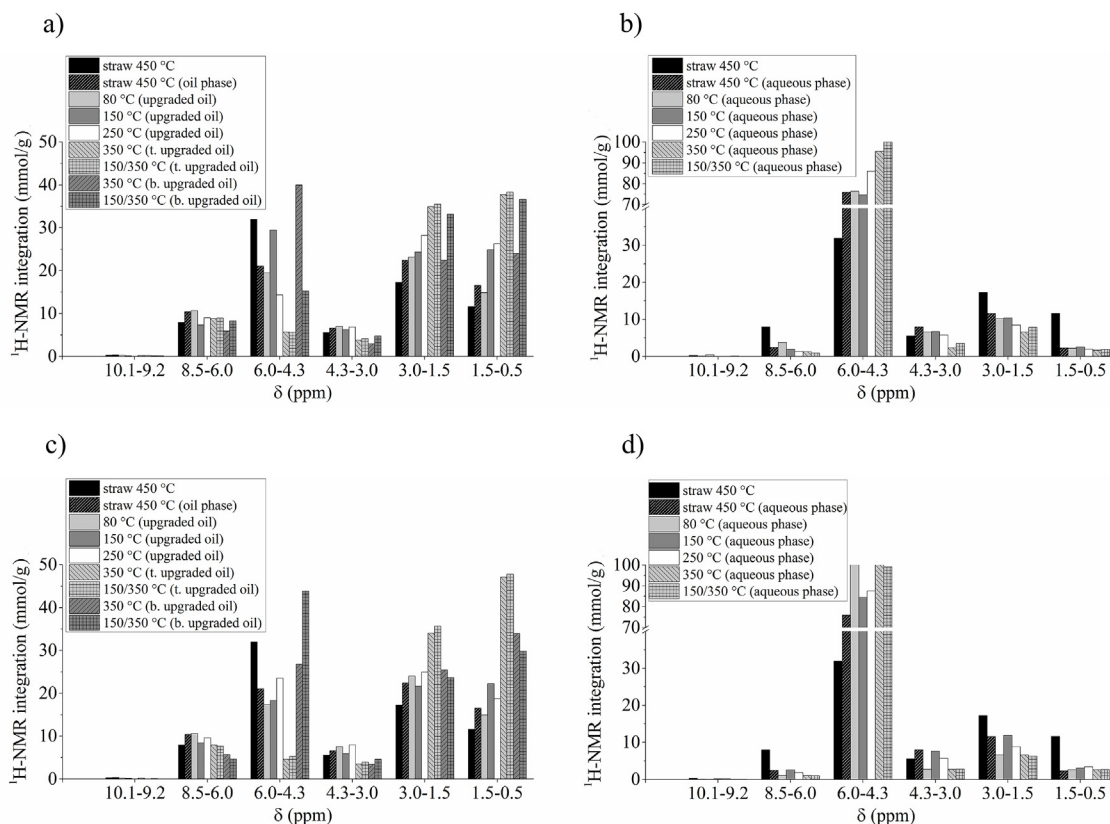


Fig. 13. ^1H NMR spectra integration of the upgraded oils on $\text{NiCu}/\text{Al}_2\text{O}_3$ (a) and the respective aqueous phases (b), and of the upgraded oils on Ru/C (c) and the respective aqueous phases (d) produced from HDO of straw 450 °C bio-oil.

The hydrotreatment was performed at 80, 150, 250, 350, 150/350 °C, 14.0 MPa H_2 pressurized at room temperature. “b.” in the legend indicates the bottom organic phase (heavier than water) of the upgraded oil and “t.” the top organic phase (lighter than water) of the upgraded oil.

case, probably due to the higher water content.

In general, $\text{NiCu}/\text{Al}_2\text{O}_3$ showed selectivity towards production of ketones, while Ru/C predominantly formed alcohols and alkanes. The conversion of aromatics was limited over both catalysts. However, the catalytic activity associated to the intermediate pyrolysis oil from straw was reduced in comparison to the beech wood, which may result from heteroatoms poisoning the catalysts and therefore lowering their activities. The influence of the pyrolysis feedstock on HDO has not been widely reported in literature, except a few works of Elliott et al. [10] and Elkasabi et al. [11]. Elliott et al. [10] referred mostly to various woody biomass feedstock and did not report significant differences in the upgraded oils, justified by notable similarities in the original bio-oil composition. On the other hand, Elkasabi et al. [11] investigated switchgrass (herbaceous biomass) and eucalyptus (hard wood). Higher H_2 consumption was associated to eucalyptus, but switchgrass led to an upgraded oil with lower oxygen mass fraction, although the original bio-oils had similar oxygen content. This result is analogous to those reported here regarding beech wood and wheat straw, indicating that the bio-oil composition could favour hydrogenation (more probable in hard wood) compared to HDO (more probable in herbaceous biomass).

3.5. Analysis of the spent catalysts

Analysis of the spent catalysts offered insights into the possible deactivation processes which occurred. Carbon deposition was only recorded for $\text{NiCu}/\text{Al}_2\text{O}_3$, since the ruthenium catalyst was supported on carbon and the weight of the recovered catalyst was similar to the original. The carbon deposits on the $\text{NiCu}/\text{Al}_2\text{O}_3$ varied from 2.7 to 6.3% of the catalyst weight for the beech wood feedstock to 8.4–16.3% for wheat straw (Table S1 Supplementary Information). The

dependency on the temperature was not clear, but a minimum was observed at 250 °C. Nitrogen was found in limited quantities on the catalyst surface for experiments with beech wood, but higher quantities were reported for straw 450 °C bio-oil with a decreasing tendency at higher temperatures.

Sulfur was observed on the catalyst surface for both feedstocks and for both catalysts, with higher concentrations at higher temperatures (Table S1 Supplementary Information). Beech wood pyrolysis oil had a sulfur concentration less than 0.005%, but mainly concentrated on the catalyst surface (0.2–0.4%). In XRD (Fig. S9, Supplementary Information) no reflections of Ni_3S_2 were observed, indicating probably that the adsorption was limited to an external layer. The pyrolysis oil from wheat straw had higher sulfur concentration, which led to the formation of bulk Ni_3S_2 (especially above 250 °C), observed in the XRD patterns (Fig. S10, Supplementary Information). The formation of this phase may also result in sintering of the nanoparticles, as observed by SEM-EDX. XRD further showed that the alumina support was converted into boehmite when in contact with the bio-oil produced from wheat straw. This was not observed in the beech wood pyrolysis oil.

For further developments, other supports with a greater water resistance should be used for HDO. Leaching was a phenomenon important only at 80 °C in the case of $\text{NiCu}/\text{Al}_2\text{O}_3$ (circa 20% of the active metal in the case of straw bio-oil), while it was generally negligible in comparison to other deactivation processes observed (less than 1%).

4. Conclusions

HDO of several bio-oils produced from intermediate pyrolysis with integrated hot gas filtration was systematically investigated. Although the pyrolysis temperature influenced the oil composition, leading to

lower oxygen mass fraction and higher molecular weights for higher temperatures, HDO mitigated the differences between the upgraded oils. Therefore, the most favorable conditions of the two processes should be chosen in terms of upgraded bio-oil yield or energy invested. In our case, the combination of pyrolysis of beech wood at 450 °C and hydrotreatment at 350 °C gave the best results in terms of upgraded bio-oil yield. The choice of catalyst plays a fundamental role in the conversion and selectivity of the products: NiCu/Al₂O₃ mainly accumulated ketones, while Ru/C was more active in hydrogenation/HDO producing more alcohols and alkanes. This indicates that the HDO process may be tuned towards e.g. synthesis of ketones, alcohols, or hydrocarbons as desired by careful selection of the appropriate catalyst and experimental conditions. Aromatics were hardly converted over both catalysts and they could be separated in future and used as fine chemicals. The choice of the HDO temperature also affected the product composition, with lower temperatures promoting stabilization of the bio-oil, and higher temperatures increasing hydrocarbon production and DOD. Hot vapor filtration has the advantage to deliver a bio-oil with low inorganic content, but sulfur is still present especially in wheat straw bio-oil. The upgrading of this kind of bio-oils requires further studies in order to prevent catalyst poisoning. Furthermore, future studies should systematically evaluate the advantages of fast and intermediate pyrolysis using hot vapor filtration.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.biombioe.2018.06.022>.

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