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Abstract

Fast pyrolysis followed by catalytic hydroconversion is a value chain aimed to transform lignocellulosic biomass into biofuel or chemicals. During hydroconversion, desired catalytic deoxygenation reactions are in competition with thermal side reactions like condensation or oligomerization. These undesired pathways lead to high molecular weight compounds (i.e. macromolecules) that are responsible for catalyst deactivation and severe plugging of the reactor. We investigate here the impact of a phenolic compound on the formation of these macromolecules. Catalytic hydroconversion of a fast pyrolysis bio-oil and a bio-oil/guaiacol (50/50 wt%) mixture were carried out in a batch reactor using a NiMo/alumina catalyst. An extended analytical strategy has been developed involving size-exclusion chromatography (SEC) and liquid state ^{13}C NMR dedicated to the in depth characterization of effluents as well as physicochemical analysis of the fresh and used catalyst (XRD, Hg porosimetry, N_2 physisorption, STEM). This strategy allowed bringing new insights on aromatic structures larger than 1,000 $g.mol^{-1}$ and their formation mechanism. This formation can be chemically inhibited by the introduction of organic component such as guaiacol. This stabilization was mainly observed and explained at low temperature and short reaction time.

Keywords: Biofuel • Oligomers • Humins • SEC • Guaiacol • Hydrodeoxygenation

1. Introduction

Fast pyrolysis is a thermochemical liquefaction process that can be used to transform solid biomass into liquids [1, 2]. However, the obtained bio-oils (BO) have limited application due to their lower heating value compared to fossil fuels (respectively 16-17 against 42-44 MJ/kg), their acidity (Total Acid Number between 70 and 120 mg $KOH.g^{-1}$), their immiscibility with hydrocarbons and their thermal instability resulting from high oxygen content [3]. Oxygen is present not only in organic compounds but also as free water (up to 30 wt% of the pyrolytic BO). Therefore, catalytic deoxygenation or co-processing upgrading [4] must be performed to convert the BO into valuable fuels. To promote these reactions, micro/mesoporous catalysts based on various mono/bi-metallic or sulfide active phases were screened [5,6]. Despite the better performances of noble metals (such as Pt, Pd or Ru), Ni/Alumina-based catalysts [7,8] are often preferred because of quite good performances, resistance to poisons [9,10] and their much lower cost which make them suitable for an industrial process.

Nevertheless, due to the high reactivity of pyrolytic BO compounds such as carbonyls and carbohydrates, deoxygenation reactions are in competition with condensation and oligomerization reactions [4, 11]. For instance, using a continuous reactor, Venderbosch et al. [11, 12] and Elliott et al. [13] evidenced the competition between the hydroconversion (HDC) pathways and the production of macromolecules which are readily observed from 175°C. Wang et al. even observed heavy components during hydrogenation of woody bio-oil over Ru/TiO_2 catalyst at even lower temperature (120°C-160°C) [14]. These side reactions are favored in absence of catalyst and hydrogen. Nevertheless, the targeted HDC reactions require such temperatures ranges. The production of high molecular weight compounds is detrimental to the process because it leads to an extensive plugging of the reactor and catalyst deactivation in addition to lower yields into valuable deoxygenated compounds. This is a process limitation which still needs an in-depth comprehension before any industrial scale-up. Due to the BO complexity, the presence and growth of macromolecules is not easily characterized but SEC (or GPC) [37 = 15] and NMR/HSQC analyses [16-18] are sometimes used to reveal the macromolecule aromatic structures. Nevertheless, from a chemical point of view, the increase of the BO molecular weight is better described during storage conditions (BO aging). Then, periodic tracking [19-21] of either some macroscopic properties (such as pH or viscosity) or the

molecular composition (such as the carbonyl and sugar titrations) bring the identification [22, 23] of reactions like esterification, aromatic condensation or acetylation leading to macroscopic precursors.
To limit those undesirable reactions, the BO can be stored below 0°C (preferably below -15°C) [21] or diluted in a solvent [24]. Some studies tried to mimic the positive effect of non-polar [25, 26] or polar [27-29] (oxygenated) solvents during the BO upgrading to dilute or convert macromolecules precursors. Another strategy is the multi-steps hydroconversion [29, 30] which converts macromolecules precursors at low temperatures (from 100 to 200°C) and is followed by a deep deoxygenation at higher temperatures (up to 350°C). Nevertheless, the involved reactions are not fully described and literature is largely lacking of rationalization of the chemical mechanisms leading to these macromolecules.
Numerous studies deal with representative model molecules of BO composition which result from lignocellulose degradation during the pyrolysis step. Because of the high diversity and chemical complexity of oxygenated compounds in a BO, it is mandatory to consider at least a mixture of representative compounds even if very few studies were proposed in the literature. During previous works performed by our group [31, 32], the catalytic hydroconversion of D-glucose and furfural was investigated and evidenced a fast and large production of macromolecules even at 200°C. Those structures were proven to arise from furanic (e.g. furfural, 5-HMF) and aromatic (e.g. 1,2-benzenediol) compounds that were extensively produced by D-glucose dehydration and furfural hydrolysis. The conversion of single and mixed model molecules was studied using a multi-technique characterization strategy of liquid effluents (SEC, ^{13}C NMR, GC and HPLC) allowing the description of reaction pathways. By this mean, the beneficial effect of guaiacol for preventing macromolecules formation was demonstrated. Besides those studies, the description of the macromolecules production during a real BO hydroconversion is still needed. Therefore, in the present work, the catalytic hydroconversion of two feeds is investigated: the first one involves only a wood residues pyrolytic BO while the second one includes an addition of 50% of guaiacol in the same BO feed. This ratio was chosen after being compared with a 25% guaiacol/BO ratio which revealed the same trends that are exacerbated during the hydroconversion of bio-oil/guaiacol (50/50 wt%) mixture (SI, Fig. S4 & S5).

2. Experimental Section

2.1. Experimental set-up

The bio-oil (BO) under investigation was produced from the fast pyrolysis of solid residues at 480°C by VTT research center in 2013 on their industrial-representative pilot plant. Table 1 compares some macroscopic analysis of BOs from the literature with the characteristics of the one used in this study. The BO characteristics are well within the typical range of fast pyrolysis bio-oils which was stored at -20°C for limiting the aging effects [21, 22]. Guaiacol (GUA) was purchased from Acros Organics (99+% purity) and was used as received. Finally, a proprietary NiMo/γ-Al_2O_3 catalyst displaying hydrothermal resistance was supplied by Axens. Before each reaction, fresh catalyst was crushed and sieved to particle size from 1 to 2 mm and was reduced using a hydrogen flow (0.30 $m^3.h^{-1}$) at atmospheric pressure and 400°C during 2 h. This catalyst develops 0.33 and 0.1 $cm^3.g^{-1}$ of mesoporous and macroporous volumes respectively.
All catalytic reactions were carried out in an isothermal 500 cm^3 stainless steel autoclave equipped with an electromagnetic driven stirrer (Rushton impeller). For each run (schematized experimental procedure is reported in Figures S1), 150 g of feed was introduced followed by 15 g of freshly reduced catalyst transferred in an argon vessel avoiding any post-oxidation. Two feeds will be considered: either 150 g of BO or 75 g of BO plus 75 g of GUA (mixture referred to BO+GUA). Considering non-catalytic reactions (investigated in SI, section 3.3.), 30 g of glass balls were introduced (2 mm diameter) representing the same volume than the NiMo catalyst. The reactor was hermetically closed and purged by substituting air by N_2 and finally by H_2 (during hydroconversion tests). The initial pressure of hydrogen or nitrogen was set to 3.0 MPa before temperature increase.
The reaction temperatures ranged from 200 to 300°C. In order to limit the catalytic reactions during the heating ramp (15 min to reach 250°C), the feed was vigorously stirred (1,200 $tr.min^{-1}$) only once the reaction temperature was reached. Stirring was maintained during cooling down. Hydrogen addition was set to maintain a constant total pressure of 13 MPa during the run. Considering those stirring rates and catalyst beads size, no external hydrodynamic limitations have been observed [31].

Once the reaction time was reached, H_2 introduction was stopped and the reactor was quickly cooled down to room temperature (10 min to cool down from 300 to 100°C). Then, gaseous, liquid and solid products were totally recovered and separately analyzed. Gases were collected using an auxiliary vessel and sampled in vacuum TEDLAR® bags for subsequent off-line gas chromatography

(GC-FID/TCD) analysis. While the reactor was purged by nitrogen and unlocked, the catalytic basket was removed. The liquid phases and the solid residues were separated by centrifugation at 4,000 tr.min^{-1} during 20 min. Subsequently, aqueous and organic phases were placed in a separator funnel referred respectively as “aqueous phase” and “organic phase”. The recovered catalyst was washed using a Thermo Scientific™ Dionex™ (ASE 150) extractor heated at 60°C and under a 10 MPa acetone pressure. The catalyst and the solid residues were dried at 70°C under atmospheric pressure during 12 h. Acetone was used as a washing solvent also to recover remaining products in the reactor and the impeller and was further removed by a vacuum rotary evaporator. The obtained liquid phase will be referred as “washed phase”. The low experimental losses and the good repeatability contribute to reliability of our study (SI, Fig. S2 and S3).

2.2. Analysis

In order to determine the carbon balance, a Thermo Scientific™ FLASH 2000 was used to analyze the elemental carbon deposition (CHONS). Grinded solid samples were injected twice in an oven set at 950°C where CO_2 was formed. An on-line TCD detector quantified this component and calculated the sample corresponding carbon equivalent. Every six samples, the analyzer was controlled by a BBOT (2,5-Bis(5-tert-butyl-benzoxazol-2-yl)thiophene) standard.

Gases were analyzed by GC (Agilent 7890A) equipped with a Flame Ionization Detector (FID) and two Thermal Conductivity Detectors (TCD). Three parallel columns were used: HP-Plot Q (30 m x 0.32 mm i.d x 20 µm), HP-Plot 5A (30 m x 0.32 mm i.d x 1 µm) and PONA (50 m x 0.2 mm i.d x 0.5 µm) to get a complete analysis of all the gases. The carrier gas was helium. Standards were periodically injected for alkanes (C1 to C6), CO, CO_2, N_2 and H_2 quantification. The oven temperature program ranged from 30 to 200°C at a rate of 20°C.min^{-1}.

Liquid effluents were analyzed by GC (AGILENT-6890N) with a Flame Ionization Detector (FID) and a PONA (50 m x 0.2 mm i.d x 5 µm) column. The vaporization temperature was 280°C, the oven temperature program ranged from 100 to 250°C at a rate of 5°C.min^{-1}. For each identified compounds, quantification was performed with guaiacol as an external standard and Effective Carbon Number method (ECN) was used to estimate FID response factors for oxygenates [33]. The GC/MS analysis was conducted with a Thermo Trace GC/MS equipped with the same columns and program than the GC/FID analysis. The mass analyzer is a simple quadrupole with an electron ionization ion source at 70 eV. The products were identified using the NIST library (2009).

Water content in liquid effluents was measured by a Karl Fischer (KF) Mettler Toledo V20. For every sequence, a calibration procedure with a Fluka Hydranal water standard 1.0 in methanol was performed. Each value indicated in this study corresponds to average of three measurements.

Soluble macromolecules contained in liquid effluents were analyzed by size exclusion chromatography (SEC) by a Waters system (Alliance). The system was constituted by four columns in series (7.8 × 300 mm) containing 5 µm-particle size with porosity ranging from 10 to 1,000 nm. During a typical analysis, 50 mg of sample was diluted in 10 ml of THF and injected into the column. Run were performed at 30°C (columns temperature) during 49 min. Two detectors were used: a refractive index-detector and a UV-detector (set to three wavelengths: 214, 254 and 280 nm). Tetrahydrofuran was used as mobile phase (1 cm^3.min^{-1}). Standard polystyrene mixtures having various molecular weights were used for calibration at the beginning of each new sequence and correspond to a Polystyrene (PS) molecular weight range from 160 to 5,000 g.mol^{-1}. All signals were normalized following Equation 5 further presented.

In addition, liquid state quantitative ^{13}C NMR analysis were performed at 20°C on an AVANCE III Bruker 600 MHz (14.1 T) equipped with a 5 mm Z-gradient BBI probe and using inverse gated decoupling pulse sequence (zgig) with Spectral width: 42 kHz; Sweep Width O1 (center): 15 kHz; FID size: 65 K; time between pulses (D1+AQ: 5.76 s; All spectra were obtained after 1024 scans (acquisition time 1h30) and were referenced to deuterated tetrahydrofuran (THF-d8). For each analysis, 0.05 mL of sample was diluted in 0.45 mL of THF-d8 without any relaxant. Quantification of the functional groups present in each sample was determined after baseline correction by integrating over characteristic regions using TopSpin 3.0 software. Intensities over defined chemical shift windows were integrated to quantify selected C structures; 10-55 ppm (C-C_{alkyl}), 55-60 ppm (C-methoxyl), 60-90 ppm (C_{alkyl}-O

including carbohydrates), 90-165 ppm (C-aromatic), 165-220 ppm (C-carbonyl in carboxylic acids, esters, amides, ketones and aldehydes). Aromatic carbons will be discriminated between 90-142 ppm (Car-C and Car-H) and 142-165 ppm (Car-O). The peaks corresponding to guaiacol were not integrated. An example of ^{13}C spectrum for the starting bio-oil and bio-oil with 50% guaiacol after conversion are given in supplementary material (SI Fig. S24 & S25).

Textural analyses of the fresh and used catalyst were performed by nitrogen physisorption Autopore4 and Hg porosimetry Micromeritics ASAP2420 equipment using ASTM D3663-03 method. The catalysts were additionally analyzed by X-Ray diffraction (XRD) using a PANalytical XPert pro endowed with a copper anode (Kα1 = 1.5406 Å). The XRD patterns were measured for the catalyst powder in a range of 2θ between 5 à 72° (step size 0.033°, 500 s). The detector was set to scanning mode at 2.122°. Scherrer's equation was used in order to calculate the size of Ni^0 crystallites prior and after reaction. Finally, TEM analyses were performed with a JEOL 2010F microscope in STEM-HAADF mode (probe size 0.7 nm). Samples were grinded and dispersed in ethanol with ultra sound. A drop of solution was deposited on a holey carbon copper grid. Further drying, the grid was introduced into the TEM.

2.3. Calculation of the mass balance, carbon balance, guaiacol conversion and normalized SEC-signals

Equation 1: mass balance

$$\text{Experimental mass loss (expressed in weight \%)} = \frac{\left(m_{liquid}+m_{gases}+m_{catalyst}\right)_{in}-\left(m_{liquid}+m_{gases}+m_{catalyst}+m_{residues}\right)_{out}}{\left(m_{liquid}+m_{gases}+m_{catalyst}\right)_{in}} \times 100$$

Equation 2: guaiacol conversion

$$X_{gua} = \frac{n_{gua,0} - n_{gua}}{n_{gua,0}}$$

With:

- Xgua : guaiacol conversion rate
- $n_{gua,0}$ and n_{gua} : guaiacol molar amount respectively at the beginning and the end of the reaction [mol]

Equation 3: carbon equivalent mass balance during guaiacol conversion

$$m_{C,gua} = (n_{gua,0} - n_{gua}) \times Wgua \times \text{wt\%Cgua}$$

With:

- $m_{C,gua}$: mass of carbon equivalent from the guaiacol conversion [g]
- W_{gua} : guaiacol molecular mass = 124.1 $g.mol^{-1}$
- $wt\%C_{gua}$: weight carbon content in guaiacol = 67.7 wt%

Equation 4: guaiacol products' selectivity

$$Y_j = \frac{m_{Cj}}{m_{C,gua}} \times 100$$

With:

- Y_j : selectivity to the "j" guaiacol product
- $m_{C,j}$: mass of carbon equivalent in the compound j [g]

In order to compare SEC analyses with various water content liquid phases, raw signals will take into account the water dilution. Thus, signals will be presented as:

Equation 5: $$\text{Nomalized SEC signal} = \frac{\text{Raw signal}}{100\text{mg}} \times \frac{1}{1 - \text{Water content} - \text{Guaiacol content}}$$

$$= \frac{\text{Raw signal}}{100\text{mg}} \times \frac{1}{\text{Organic content}}$$

With:

- Raw signal / 100: Raw signal (RI or UV 254 nm) normalized to a 100 mg sample [mg^{-1}].

- Water content: weight water content in the liquid phase [-].
- Guaiacol content: weight guaiacol content remaining in the liquid phase (for BO+GUA experiments) [-].
- Organic content: weight organic content in the liquid phase [-].

- To facilitate the following discussion, Fig. S17 in SI gives an overview of the main analytical results and conclusions.

3. Results and Discussion

3.1. Effect of the reaction time on the bio-oil and bio-oil/guaiacol catalytic hydroconversion

In this part, the effect of reaction time on the catalytic hydroconversion of BO is investigated concurrently with BO+GUA. Reaction temperature was set at 250°C and various reaction times were used ranging from t_0 (just reaching 250°C) to 180 min.
Mass balances are reported in supporting information (SI, Fig. S6.). As observed by others [5, 6], two liquid phases were recovered in addition of the gas phase. The analysis of this gaseous fraction shows mainly CO_2 and CO; CO_2 decreased in favor of CH_4 and CO for BO+GUA mixture (SI, Fig. S7). No extensive solid production was observed but a progressive and significant coke deposit in the catalyst porosity was noticed, with a maximum coke deposition reaching 13.1 wt% after a 3 h BO conversion in absence of guaiacol. For both BO and BO+GUA, a heavy organic phase has been obtained representing up to 74.9 wt% of the mass balances (from the BO+GUA hydroconversion during 3 h). When guaiacol was added, the viscosity of the organic phase was significantly decreased, enabling a better experimental mass balance (loss lower than 5 wt% for all cases). It is interesting to note that BO released an extensive quantity of gas mainly composed by CO and CO_2 suggesting the importance of decarbonylation and decarboxylation reactions contrary to BO+GUA feed. Gas phase analysis provided the remaining amount of hydrogen. By difference with the amount of introduced hydrogen during the test, the consumption is calculated and reported in Figure 1 [A] for both BO and BO+GUA hydroconversion experiments. During the first hour, the consumption was multiplied by 2.7 and 1.8 respectively (corresponding to a consumption of 16.7 and 20.9 mol% of the introduced hydrogen). Further, only a 12.1 mol% growth was observed during the BO hydroconversion confirming the importance of the first minutes of the process. The H_2 consumption significantly increased in the presence of guaiacol even after 1 h of reaction. This growth could be explained by the conversion of guaiacol, nevertheless, after 3 h, only 3 mol.% of the H_2 consumption can be directly ascribed to the production of 1,2-benzenediol. In our operating conditions, only this product was detected from the guaiacol hydroconversion (SI, Fig. S9.). This indicates that the increase of H_2 consumption after 1 h of reaction is not only due to guaiacol conversion.
Concerning the BO+GUA feed, the evolution of the guaiacol conversion (quantified by GC-FID) is illustrated by Figure 1 [B]. This Figure also reports the ratio between GC-quantified 1,2-benzenediol carbon equivalent and carbon equivalent released from guaiacol conversion (Eq. (3) and (4)). During the reactor heating ramp, 38.9 % of the guaiacol was converted, nevertheless, only 0.3 wt% of the released carbon was actually transformed into 1,2-benzenediol. From t0 to 30 min, more than 47.3 % of guaiacol was converted but less than 0.4 wt% was ascribed to 1,2-benzenediol. Finally, above 30 min reaction, the guaiacol conversion significantly decreased (as shown by a higher GC-FID quantification of guaiacol) while 1,2-benzenediol production increased. This is consistent with the higher production of CH_4 above 30 min of reaction as methane comes mainly from demethylation of guaiacol to benzenediol (SI, Fig. S7.). This trend has already been described by Patil *et al.* [34] and also observed during our previous study [32] dealing with the catalytic HDC of BO model compounds mixtures for instance D-glucose and guaiacol. Under the same operating conditions, we concluded that guaiacol was readily reacting with sugar type macromolecules but was converted through HDO pathways after 30 min of reaction. The reactions between guaiacol and macromolecules until 30 min did not consume hydrogen as shown in Figure 1. In addition, due to the moderated temperature (250°C), the conversion of guaiacol by cracking reactions was not considered [35]. Thus, the carbon balance is an efficient tool to assess the conversion of guaiacol between well-known HDC conversion pathways [36, 37] (i.e. GC-quantified products) and macromolecules precursors stabilization pathways [32]. This macroscopic analysis will be herein completed by SEC and ^{13}C NMR analysis.
Figure 2 represents the normalized SEC analysis (following eq. (5)) of the raw BO and the recovered liquid effluents. Graphs [A] and [B] correspond to the BO conversion respectively analyzed with RI and UV-254 nm detectors. These two analyses are also reported in Graphs [C] and [D] for the conversion of the BO+GUA mixture. Thus, the BO was initially constituted by heavy compounds not larger than 3,000 $g.mol^{-1}$ PS eq.. Thanks to the UV-254 nm detector (Figure 2 [B]), the contribution of unsaturated compounds like aromatic and carbonyl functions can be assessed as a significant part of those heavy structures. Nevertheless, due to the difference

between profiles of BO continuum shape and of the effluents ones, it is impossible to directly compare their compositions. Regarding the BO HDC (Figure 2, Graphs [A] and [B]), the signals confirm the presence of macromolecules that spread the molecular weight domain up to 8,000 $g.mol^{-1}$ PS eq.. This suggests the importance of the first minutes of reaction where homogeneous catalyzed reactions (refer to t0) such as dehydration, aldolization/crotonization [31, 32] are favored in acidic medium (See SI section 3.5 dedicated to the effect of the catalyst). In the same way, UV-254 nm detector did not only indicate the presence of aromatic and carbonyl compounds constituting the macromolecules but also the formation of compounds with molecular weight higher than 400 $g.mol^{-1}$ PS eq. above 30 min of reaction. Aqueous phases (dotted lines) presented signals which did not involve macromolecules greater than 1,000 $g.mol^{-1}$ PS eq.. In addition, SEC clearly indicated a decrease of the normalized signals suggesting the conversion or the migration of some lighter macromolecules from the aqueous to the organic phase. The fast production and the stability of macromolecules at this temperature is also observed during the HDC of BO+GUA. SEC-RI analysis (Figure 2 [C] and [D]) confirms the production of 1,2-benzenediol (160 $g.mol^{-1}$ PS eq.) previously detected by GC (Figure 1 [B]) after 1 h of reaction. Regarding Figure 2 [A] and [B], those macromolecules were obviously quite different (but still stable at this temperature) since their higher molecular weight did not go beyond 3,000 $g.mol^{-1}$ PS eq. According to the previous model molecule conversion study [32], guaiacol limited the macromolecules growth, not only by a dilution effect, but also by reacting with the precursors coming from glucose and furfural. To go further on the effect of guaiacol addition and to evaluate the chemical reaction effect versus the physical dilution effect, additional experiments were performed with six different molecules (SI, Figure S10). The use of oxygenated compounds like anisole, phenol, heptanol or 1,2-benzenediol led, as guaiacol, to decrease macromolecules formation while tetralin performed the worst limitation. This results suggest that, as expected, tetralin interferes differently with macromolecules precursors but also points out the weaker solvating properties towards oxygenated organic compounds in our conditions (1h, 250°C). All the molecules used were more or less converted during the experiments but it can be noted that phenolics ones and especially guaiacol, and 1,2-benzenediol, were the most converted.

The beneficial effect of guaiacol had also consequences on the textual properties of used catalysts. Figure 2 [E] reports the evolution of the pore size distribution and volumes of used catalysts respectively from BO and BO+GUA HDC. In absence of guaiacol, the predominance of macromolecules observed in Figure 2 [A] and [B] resulted in the deposition of carbon from 4.2 to 8.4 wt% between t_0 and 30 min of reaction. This value rose up to 13.1 wt% after 3 h of reaction, with a coke preferentially located into the mesopores (pore diameters ranging from 2 to 50 nm) which lose half of their initial volume. The bimodal pore size distribution presented in SI (Fig. S11) illustrates the impact of the first 30 min of the reaction. In parallel to the macromolecule production decrease, the guaiacol addition lowers the carbon deposition to 10.9 wt% after 3 h of reaction. In this case, the volume of the macropores only decreased from 0.21 to 0.15 $cm^3.g^{-1}$ (-28.6 %) for BO HDC. With both feeds, XRD analysis did not allow the detection of boehmite (AlOOH) crystallites suggesting the protection [32] of alumina carrier against carrier acidic species and water. XRD and STEEM-HAADF (SI, Fig. S12 and S13) analyses also revealed the presence of Ni and Mo sintered crystallites (about 20 nm after 1 h after BO and BO+GUA conversion). Nevertheless, those crystallites were too scattered to be statistically representative of the metal dispersion of the used catalysts.

Finally, to better understand the chemical reaction occurring during the hydroconversion, liquid state ^{13}C NMR analysis has been performed and compared to initial BO (SI, Fig. S24). Figure 3 [A] and [B] report carbon distributions in the liquid products (organic and aqueous phases) obtained after BO and BO+GUA HDC at different reaction times. For BO HDC, the organic phase compositions were function of the reaction time and revealed the increase of aromatic carbons contribution (especially C-C and C-H). This observation suggests the occurrence of deoxygenating (demethoxylation, dehydroxylation) and cyclization reactions. Overall, the aromatic carbons represented more than 60 at.% after 3 h of reaction concomitantly to aromatic compound observed by SEC-UV 254 nm results (Figure 2 [B]). This composition is also in accordance with the elemental ratios reported in the Van Krevelen Diagram (SI, Fig. S8) where organic phases were located in the lignin area. In parallel, the aqueous phases analysis revealed an increase of the aliphatic carbons (C-C and C-O). Moreover, the high concentration of carbonyls species suggests the formation of polar compounds more soluble in water than aromatic compounds.

Considering BO+GUA products analysis (Figure 3 [B]), ^{13}C NMR spectral contributions belonging to remaining guaiacol (at 55.8, 110.9, 114.7, 120.2, 121.5, 145.7, 146.7 ppm) have been subtracted from the different integrated area (SI, Fig. S25). As discussed previously, the production of guaiacol derivatives such as 1,2-benzenediol in the organic effluent (Figure 1 [B]) led to an increase of the $C_{aromatic}$-O contribution which represents 8.9 atomic% (or at.%) after 3 h of reaction. This observation is also true for the C-OMe carbons including guaiacol derivatives (such as anisole groups). As observed by the H_2 consumption (Figure 1 [A]), the aliphatic carbons significantly increased up to 29.4 at.% suggesting an improvement of HDO reactions compared to the BO HDC. While the

organic phases were composed by aromatic compounds, the aqueous phases contained mainly low molecular mass compounds with aliphatic carbons (C-C and C-O) shaping the low molecular mass compounds (Figure 2 [C] and [D]).
During the hydroconversion involving D-glucose, furfural and guaiacol, we observed reactions between guaiacol and macromolecules precursors which effectively avoid the macromolecules formation [32]. This study confirms the role of guaiacol reactivity while converted with BO macromolecules precursors including carbohydrates type components [18, 38]. This phenomena was mainly observed before 1 h and below 250°C as regard to the fast reaction kinetics involved on the macromolecules production (Fig. 2 [A] and [B]). To compare this trend, the second part of this paper deals with the effect of the temperature following the same methodology.

3.2. Effect of the reaction temperature on the bio-oil and bio-oil/guaiacol catalytic hydroconversion

Following the previous analytical strategy, the 1 h conversion of both feeds (BO and BO+GUA) at 200, 250 and 300°C will be presented herein. As previously shown at 250°C, those experiments led mainly to the production of liquid in the 200 - 300°C range. Mass balances (SI, Fig. S14) confirmed that BO conversion produced a larger quantity of gas phase detrimentally to liquid phase when temperature increased. Gas phase analysis (SI, Fig. S15) showed a slight increase of CO and CH_4, detrimental to CO_2, by increasing the temperature; this increase is more pronounced in the case of the presence of guaiacol. H_2 consumption has been calculated from the gas analysis (Figure 4 [A]). While temperature increases, H_2 consumption decreases. As an autoclave reactor is used, H_2 partial pressure varies according to the temperature, nevertheless, the H_2 consumed/introduced ratio increases except for BO HDC at 300°C. This phenomena is due to production of macromolecules and coke formation on the catalyst evidenced by the decrease of the porosity (Fig. 5). The decrease was significantly lower in the case of the mixture conversion (BO+GUA). At 300°C, 8 % of the H_2 consumption can be directly ascribed to the production of 1,2-benzenediol. As discussed previously for the effect of reaction time, guaiacol addition in the reactant mixture enhances catalyst reactivity, and its conversion into HDO products is favored [31, 32]. Once again, the guaiacol conversion and the ratio between GC-quantified guaiacol products (1,2-benzenediol) expressed in carbon equivalent (Eq. (4)) is reported herein in Figure 4 [B]. While the conversion of guaiacol was quite constant in function of the HDC temperature, 1,2-benzenediol production (following CH_4 reported in SI, Figure S13) grew up to 6.0 wt% of the converted guaiacol at 300°C. This H_2 consuming reaction was previously observed [32] during the conversion of the model molecules mixture at this temperature. Although guaiacol readily reacted with macromolecules coming from D-glucose and furfural, we also observed that guaiacol HDO was promoted at 300°C as it was expected thanks to the published works [36, 37].
As observed at 250°C in Figure 2, up to 8,000 $g.mol^{-1}$ PS eq. macromolecules were formed in the organic phases by SEC-RI/UV analysis (Figure 5 [A] and [B]). From 200 to 300°C, an increase of the signal ranging from 300 to 2,000 $g.mol^{-1}$ PS eq. and a decrease of higher components was noticed. In that molecular weight range, the UV-254 nm detector (Figure 5 [B]) highlighted the growth of the normalized signal intensity suggesting the production of smaller aromatic macromolecules. Considering the decrease of the H_2 consumption with temperature (Figure 4), the production of smaller macromolecules suggests the importance of hydrolysis reactions instead of hydrogenolysis reactions. Indeed, hydrolysis reactions were observed during the conversion of carbohydrates and derivatives conversion in acid-hydrothermal medium [31]. Again, those detrimental reactions were arising from the homogenous phase (SI section 3.5) and strongly affected the textural properties of the NiMo catalyst. The conversion of BO+GUA with temperature exhibits a similar behavior as the one observed at 250°C. Despite the modification of the guaiacol conversion pathway observed at 300°C (Figure 4 [B]), the production of macromolecules was still limited to 2,000 $g.mol^{-1}$ PS eq. (Figure 5 [C] and [D]). This observation is also confirmed in the aqueous phases where no compound has been observed above 600 $g.mol^{-1}$ PS eq..
The hydroconversion temperature has an impact on the reactivity (further described by ^{13}C NMR and SEC analysis) and thus the textural properties of catalysts are also modified regarding the evolution of BET and porous volumes of the used catalysts (Figure 5 [E]). The BO conversion led to an extensive coke deposition which mainly decreased the mesoporous volume of the catalyst and consequently H_2 consumption stagnancy from 200 to 300°C. In the case of the BO+GUA mixture hydroconversion, the textural properties are kept which is in line with the lower macromolecule production. Effectively, mesoporous volumes were quite preserved at 0.21 $cm^3.g^{-1}$ (decrease of 36 % of the mesopores volume compared to the fresh catalyst) and did not depend on the reaction temperature. This effect, ascribed to the guaiacol presence, follows the enhancement of the H_2 consumption (Figure 4 [A]) and the low coke deposition even at 300°C. Indeed, at this temperature, 12.8 and 10.5 wt% of coke was analyzed on the used catalysts after conversion of BO and BO+GUA respectively. While XRD analysis did not reveal any boehmite formation, sintering of Ni^0 crystallites

was observed (size up to 30 nm) during BO and BO+GUA conversions at 300°C/1 h. Moreover, no large crystallites were observed by STEM afterwards.

To go further in the molecular description, liquid state ^{13}C NMR analysis was performed for both organic and aqueous effluents arising from BO (Figure 6 [A]) and BO+GUA (Figure 6 [B]). Increasing the temperature during BO conversion enhances the concentration of aromatic carbons in the organic phase (Figure 6 [A]). Cyclisation reactions (without H_2 consumption) into oxygenated aromatic compounds such as 1,2,3-benzenetriol has been previously reported during the dehydration of D-glucose into 5-HMF in the same operating conditions [30]. This observation is in agreement with the decrease of carbonyls compounds into the organic phase, as shown in Boscagli's study [7]. As observed during the model molecule conversion [30, 31] at 300°C, the organic phase deoxygenation proceeds mainly by dehydration and cyclization reactions. Then H_2 consumption remained low (Figure 4 [A]) and the organic phase tends to form a lignin-like structure (see Van Krevelen Diagram in Figure S16). For BO, we mainly observed aliphatic and carbonylic carbons in aqueous phase (Figure 6 [A]), suggesting the presence of water-soluble oxygenated compounds such as esters or carboxylic acids. In the same aqueous fraction, aliphatic C-O decreased with the temperature increase.

Considering ^{13}C NMR analysis of organic phases arising from BO+ GUA (Figure 6 [B]), the evolution of the organic composition between 200 and 250°C was not significant. The large proportion of $C_{aliphatic}$-O carbon at 200°C (38.8 at.%) confirms their low tendency to produce macromolecules (Figure 5 [C]). At 300°C, $C_{aromatic}$-O contribution increased possibly due to the production of 1,2-benzenediol from guaiacol while the aliphatic C-O decreased strongly compared to lower temperature. These results are in agreement with the H_2 consumed to produce GC-quantified guaiacol products (Figure 4 [B]) and the SEC-UV 254 nm analysis (Figure 5 [D]). This also confirms the production of 1,2-benzenediol which can further participate, as guaiacol, to the limitation of the macromolecule production [31]. This latter component is also solubilized into the aqueous phase (solubility: 0.44 $g.g^{-1}$ of water at 20°C) as indicated in SEC-UV 254 nm analysis (Figure 5 [D]). The global disappearance of carbonyls at high temperature is concomitant with the production of CO and CO_2 from decarbonylation and decarboxylation reactions (SI, Fig. S15). As reported in our previous studies, those two gaseous compounds were mainly produced during the conversion of D-glucose under hydrothermal operating conditions into humins/macromolecules components.

These results bring new insights in regards to Venderbosch et al. [11,12] and Elliott et al. [13] studies on BO instability during the hydroconversion, as well as about solvent role in pilot scale. Processing BO at high temperature favored uncontrolled dehydration and cyclisation reactions from carbonyls and carbohydrates leading to macromolecules with aromatic structures [30]. Thanks to this systematic methodology and considering a representative BO model molecules mixture [32], we described the macromolecules formation by the fast reaction of guaiacol and/or its products, especially 1,2-benzenediol, with carbohydrates at low temperature. From ^{13}C NMR, SEC and elemental analysis, those macromolecules are supposed to be linked by C_{ar}-O ethers bonds (lignin-like) which are stable at low temperature but converted at higher temperature (see Figures 5 [A - B] and Figure 6 [A]).

4. Conclusions

Despite the extended literature dealing with the catalytic hydroconversion of fast pyrolysis bio-oil (BO), the undesired macromolecule production depending on the process parameters still needs to be clarified. Because of the chemical complexity of the BO, we applied an analytical strategy characterizing both organic and aqueous effluents. The influence of the residence time and of the temperature on the nature of the products have also been investigated with a reliable experimental procedure.

While gaseous chromatographic analyses are not able to characterize macromolecules production arising during the BO conversion, SEC analysis highlight structures beyond 5,000 $g.mol^{-1}$ PS eq.. For the BO hydroconversion at 250°C, macromolecules were produced in homogeneous phase and were further recovered in the organic phases. Those structures were particularly stable with reaction time since no conversion has been observed by SEC analysis. Nevertheless, elemental analysis and quantitative liquid state ^{13}C NMR indicated the production of deoxygenated species mostly composed of aromatic rings as well as deoxygenated aliphatic compounds. Those catalyzed reactions were enhanced at higher temperature despite the low hydrogen consumption. Thanks to the textural analysis of used catalysts, it was demonstrated that mesopores were particularly affected by this production unlike the experiments carried out in presence of guaiacol.

Effectively, the BO+GUA mixture hydroconversion showed enhanced hydrogen consumption that was consistent with the lower coking of the catalyst compared to the BO hydroconversion. As shown by SEC and GC analyses, guaiacol reacted with the macromolecules precursors and limited their production of high molecular mass molecules (up to 3,000 $g.mol^{-1}$ PS eq. into the organic phases). This phenomenon was mainly observed at low temperature and short reaction time as guaiacol was not converted

into its light usual hydroconversion products (1,2-benzenediol, phenol). At high temperature and/or long reaction time guaiacol was mainly converted into light aromatic compounds and contributed in a lesser extent to the macromolecule solubilization. As already demonstrated with model molecules, the positive role of guaiacol or some other oxygenated compounds like phenol, 1,2-benzenediol, anisole or heptanol for preventing the formation of undesired macromolecules is now confirmed in the case of a bio-oil hydroconversion. Therefore, in this case, the recycling of a fraction of the products into the reactor or the recycling of a well-chosen solvent would be highly desirable to improve the process.

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Appendix A. Supplementary information

Supplementary information (referred to SI) related to this article can be found at …

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	In this study BO	In the literature[1,3] bio-oils
Water (wt%)	26.4	20 – 35
C (wt%)	56.4	48 – 60
H (wt%)	6.4	5.9 – 7.2
O (wt%)	36.7	34 – 45
N (wt%)	0.0042	< 0.3
Viscosity (cSt)	14.9 (40°C)	10 – 80 (50°C)
Total Acid Number ($mgKOH.g^{-1}$)	91	70 – 120
Ash (wt%)	0.2	0.02 – 1.2
Density at 20°C ($kg.m^{-3}$)	1,200	1,100 – 1,300

Table 1. Macroscopic analyses of the studied bio-oil (BO) compared to the average data for bio-oils in literature