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## Co-pyrolysis of beech wood and polyamide-6: Impact of plastic concentration and wood/plastic synergistic effects

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## 31 1. Introduction

32 Co-pyrolysis of wood and plastics could be considered in the near future to recycle waste  
33 biomass, in particular municipal waste and construction wood, which generally also contain  
34 plastics. Among these plastics, N- or Cl-containing plastics such as polyamide or  
35 polyvinylchloride have been little studied and should also be considered, given their wide use in  
36 many applications, but also because waste biomass contains various types of plastics that cannot  
37 be easily sorted and separated according to their composition. In a previous study [1], the co-  
38 pyrolysis of beech wood (BW) and polyamide-6 (PA6) chips was investigated and the effect of  
39 ex-situ treatment of the pyrolysis vapors using a HZSM-5 catalyst was assessed. However, the  
40 biomass/plastic ratio is also an important parameter that affects the pyrolysis process and the  
41 products quality [2], through interactions between the wood chips and the plastic particles, or  
42 among their degradation products, that can lead to synergistic effects.

43 Most of the studies dealing with synergistic effects in co-pyrolysis were carried out using  
44 polyolefin-based polymers like PP and PE, or polyaromatics like PS, which do not contain  
45 heteroatoms (Cl, N) that could affect the pyrolysis process and impair the catalyst performances,  
46 when a catalytic treatment is applied. For instance, aiming to identify the mechanisms responsible  
47 for this synergistic effect, Cheng and Huber [3] studied the conversion of furanic compounds  
48 (furan, 2-methylfuran, furfural, and furfuryl alcohol) and olefins (ethylene and propylene) over  
49 ZSM-5 in a fixed-bed reactor operating between 450°C and 600°C. An increase in aromatics  
50 selectivity was observed when propylene was added to the feed, due to the occurrence of Diels-  
51 Alder reactions. The authors also reported that furfural and furfuryl alcohol underwent  
52 decarbonylation to produce furan and CO. Finally, a decrease in coke and CO<sub>2</sub> yields was  
53 observed, suggesting that the presence of hydrogen-rich reactants such as olefins modified the  
54 reaction pathways for oxygen removal, shifting from decarbonylation and decarboxylation to  
55 dehydration.

56 Liu and coworkers [4] also evaluated the synergistic effects observed during co-pyrolysis of  
57 pinewood and polypropylene carried out without a catalyst in a fixed-bed reactor at 900°C. The  
58 authors reported an increase in syngas (H<sub>2</sub> and CO) production and a decrease in the formation of  
59 non-condensable hydrocarbons and in chars. These effects were assigned to the interaction  
60 between oxygen-containing radicals in the volatiles evolved from pinewood with hydrogen-rich

61 radicals from the polymer that act as H-donor species, which promoted pinewood volatilization  
62 and inhibited the condensation and repolymerization reactions, hence reducing the char formation.

63 Li et al.[5] studied the catalytic fast pyrolysis (CFP) of cellulose and low-density polyethylene  
64 (LDPE), polypropylene (PP) and polystyrene (PS) employing HZSM-5 as catalyst. Among the  
65 plastics studied, LDPE showed a higher synergistic effect, with a significant increase in aromatic  
66 yield and a reduction in coke formation. These effects were ascribed to interactions between  
67 volatiles from plastic and biomass, as discussed previously. However, when the reaction was  
68 performed with PP, the synergistic effect was smaller than that observed with LDPE. The  
69 explanation relies on the higher concentration of branched olefins obtained with PP when  
70 compared to LDPE. The electronic phenomena and steric hindrance of their branching prevented  
71 the Diels-Alder reactions essential to the formation of aromatic compounds. Finally, the co-  
72 pyrolysis with PS showed the lowest synergistic effect, with insignificant interactions between PS  
73 and cellulose; however, an increase in aromatics yield was observed, mainly due to the aromatic  
74 nature of PS itself that depolymerizes into styrene and polyaromatic species.

75 Ghorbannezhad et al.[6] evaluated the co-pyrolysis of sugarcane bagasse pith and polyethylene  
76 terephthalate (PET) in a tandem micro-reactor at 700 °C using HZSM-5 and sodium carbonate/ $\gamma$ -  
77 alumina as catalysts. The main results were an increase in aromatics formation (especially benzene,  
78 toluene, xylene, and ethylbenzene - BTXE) and a reduction in coke deposition in the presence of  
79 the plastic. The hypothesis proposed for these observations was the occurrence of H-transfer from  
80 PET-derived aliphatics towards lignin-derived oxygenated compounds, contributing to the  
81 hydrocarbon pool pathway and avoiding cross-linking reactions that result in char formation.  
82 However, the decomposition of PET also resulted in the formation of benzoic acid, which is  
83 detrimental to bio-oil quality [7].

84 As our current situation stands, the concentrations of polyamide-based plastics in municipal  
85 solid waste (MSW) are expected to increase in the next years due to the COVID-19 pandemic and  
86 the massive utilization of personal protective equipment, notably disposable masks that are made  
87 from woven polyamide tissues. Therefore, this study focuses on co-pyrolysis of beech wood (BW)  
88 and polyamide-6 (PA6) at concentrations between 5 and 20 wt.% (close to those found in  
89 municipal solid waste [8, 9], aiming at understanding the synergistic effects between them and the  
90 chemical processes involved. All co-pyrolysis experiments were carried out using HZSM-5 as

91 catalyst for ex-situ treatment of the pyrolysis vapors. In combination with a previous publication  
92 on this topic [1] that assessed more specifically the role of the HZSM-5 catalyst, the present study  
93 covers the most important aspects related to the co-pyrolysis of lignocellulosic biomass and  
94 polyamide, which are scarce in the literature. In addition, this work presents an extensive range of  
95 characterizations of the liquid, gaseous and solid products obtained by co-pyrolysis, as well as the  
96 characterization of fresh and spent catalysts.

97

## 98 2. Experimental section

### 99 2.1. Feedstocks

100 The lignocellulosic biomass used consists of beech wood chips supplied by J. Rettenmaier &  
101 Söhne; they were sieved to obtain particle sizes I, the range from 0.75 to 1.7 mm. Polyamide-6  
102 (BASF - Ultramid® B) was supplied as pellets, which were crushed and sieved before use to obtain  
103 particle sizes in the same range as the wood chips. BW chips were mechanically mixed with 5, 10  
104 and 20 wt.% of PA6 (on dry basis). All feedstock samples were dried in an oven at 110°C for 1h  
105 before each pyrolysis experiment and stored in airtight flasks.

### 106 2.2. Catalyst

107 Zeolite HZSM-5 with a molar Si/Al ratio of 40 was supplied by Céramiques Techniques  
108 Industrielles (CTI) Salindres, France. The catalyst characterization has been described previously  
109 [10] and its main properties are summarized in Table 1.

110 Table 1 - Properties of HZSM-5 catalyst

Property	Value
Particle size ( $\mu\text{m}$ )	100-300
Water content <sup>a</sup> (% wt.)	3.9
Si/Al atomic ratio <sup>b</sup> (SAR)	40.5
Total SSA <sup>c</sup> ( $\text{m}^2\text{g}^{-1}$ )	423
Microporous surface ( $\text{m}^2\text{g}^{-1}$ )	363
External surface ( $\text{m}^2\text{g}^{-1}$ )	60
Average pore diameter <sup>d</sup> (nm)	0.55

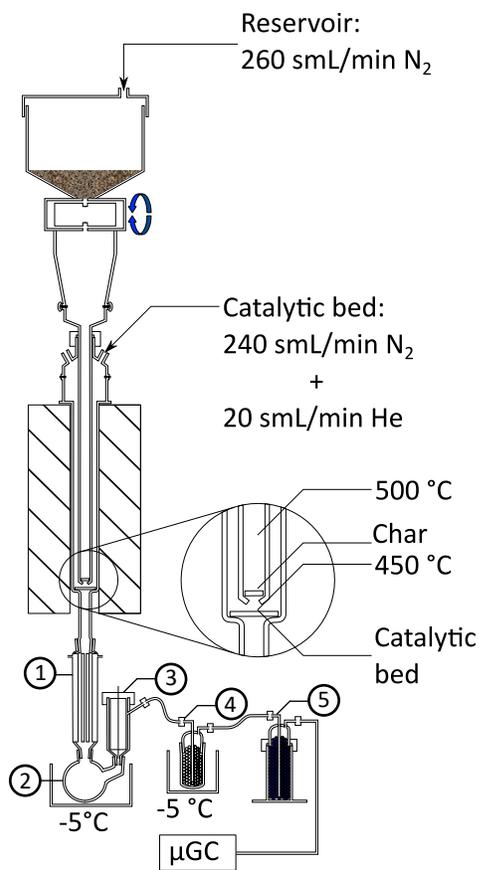
Total pore volume (cm <sup>3</sup> g <sup>-1</sup> )	0.18
Brønsted acid sites <sup>c</sup> (μmol/g)	127
Lewis acid sites <sup>c</sup> (μmol/g)	45

111 <sup>a</sup> measured by TGA; <sup>b</sup> measured by ICP; <sup>c</sup> BET method; <sup>d</sup> from International Zeolite Association  
 112 database; <sup>e</sup> measured by FT-IR of pyridine adsorbed at 150°C.

### 113 2.3. Pyrolysis set-up

114 Co-pyrolysis of beech wood and PA6 was carried-out in a lab-scale pyrolytic bench already  
 115 described [11], with a few modifications to adapt the system to the mixed wood/plastic feedstocks  
 116 (Figure 1). The jacketed reactor has an internal zone where the thermal pyrolysis is carried out and  
 117 a bed of catalyst can be placed (or not) just below to treat the vapors which come out of the  
 118 pyrolysis zone. The BW chips or BW+PA6 blends were previously dried at 110°C for 1.5 h before  
 119 being placed in the gas-tight hopper and kept under N<sub>2</sub> atmosphere.

120 Unlike the previous description [11], the new inner reactor (pyrolysis zone) was a straight  
 121 quartz tube, in which the solid chips were fed semi-continuously from the top for 1 h, by small  
 122 increments of ≈0.045 g every 10 s, and fell down by gravity onto a quartz porous frit at the bottom  
 123 of this section, where the chars and solid residues were retained. The total mass of solid chips fed  
 124 in the reactor was ≈16 g in 1 h of experiment. The temperature in the pyrolysis zone was 450-  
 125 500°C along the tube and 480°C on the porous frit where the wood chips were stopped. The  
 126 pyrolysis vapors (formed by thermal pyrolysis) were entrained downstream by a nitrogen flow of  
 127 260 smL/min (flow rate standardized at 0°C and 1 atm) and passed through the catalyst bed placed  
 128 just below the pyrolysis zone on a second quartz frit. All pyrolysis experiments were carried out  
 129 with *ex-situ* catalytic treatment of the vapors using the HZSM-5 catalyst described previously. The  
 130 temperature of the catalyst bed was 453 ± 2°C. In this external part of the reactor, an additional  
 131 gas flow composed of 240 smL/min N<sub>2</sub> and 20 smL/min He (used as internal standard for GC  
 132 analysis) was added to prevent retro-diffusion of the vapors and to adjust the total gas flow rate.  
 133 The residence time of the vapors in the pyrolysis zone was estimated at 41 s, while the contact  
 134 time with the catalyst (when present) was around 2 s. The pressure in the reactor was continuously  
 135 monitored by a pressure sensor connected to a safety device which cuts off the experiment  
 136 automatically if the pressure exceeds 1.3 bars. The pressure measured during the experiments was  
 137 around 1.1 bar.



138

139 Figure 1 - Pyrolysis setup scheme

140 The vapors were condensed downstream the reactor and collected in a series of traps including  
 141 a condenser (1) and a round bottom flask (2) both cooled at  $-5^{\circ}\text{C}$ , an electrostatic precipitator (3),  
 142 a trap filled with glass beads at  $-5^{\circ}\text{C}$  (4) and a trap at ambient temperature filled with silica gel  
 143 beads (5), that prevented any condensable compound from being introduced in the micro-GC for  
 144 online gas phase analysis. The total mass of bio-oils formed in the experiments was assessed by  
 145 mass difference, by weighing the different glassware parts before and after the experiments.

146 Prior to starting the reaction, the reactor was loaded with 2 g of catalyst and heated to  $500^{\circ}\text{C}$   
 147 under a  $\text{N}_2$  flow for 2 h to ensure fully stabilized temperatures in the whole system (reactor and  
 148 cold traps) and to desorb the water adsorbed on the catalyst.

149

150 2.4. Products recovery

151 Non-condensable gaseous products (hereinafter called “gas phase”) were analyzed and  
152 quantified online using a micro-GC.

153 The fractions called “aqueous phase” and “organic phase” were recovered directly in the round  
154 bottom flask and simply separated by centrifugation; thus, they constituted the most representative  
155 share of the bio-oil produced in the process. Other fractions of bio-oils were also deposited in the  
156 downstream traps and remained stuck on the glassware parts. In order to obtain a detailed mass  
157 balance, these fractions were recovered by washing the glassware with methanol, followed by  
158 evaporation of the methanol at 50°C under a pressure of 400 mbar, yielding the “recovered organic  
159 phase”. However, the evaporation step was found to modify the composition of this bio-oil fraction  
160 due to simultaneous evaporation of volatile components. In addition, <sup>13</sup>C-NMR analysis showed  
161 the presence of residual methanol in this fraction. Therefore, it was decided not to mix the  
162 “recovered organic phase” with the native “organic phase”. Finally, a part of the bio-oil could not  
163 be recovered because it was adsorbed on the silicagel beads or lost during the different steps of  
164 recovering the other fractions. This fraction was called “organic not recovered” and was quantified  
165 by weighing the glassware parts before and after experiment.

166 The chars were recovered from the first quartz frit, weighed and are hereinafter called “solid  
167 phase”.

## 168 2.5. Product characterization

169 Gaseous products were analyzed online using a micro gas chromatograph Inficon 3000 (SRA  
170 instruments) equipped with three analytical modules and TCD detectors, calibrated with  
171 appropriate compound mixtures. A MolSieve column equipped with a Plot U pre-column was used  
172 to analyze He, H<sub>2</sub> and CO; a Plot U column was used to analyze CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>; an alumina  
173 column was used to analyze the remaining hydrocarbons (C<sub>3</sub>-C<sub>5</sub>). The duration of each analysis  
174 was 6 minutes and the analyses were repeated over 90 minutes. Helium was used as internal  
175 standard to account for the variations of total gas flow rates at the reactor inlet and outlet.

176 Elemental compositions (CHNS) were obtained with a Flash2000 (Thermo Scientific)  
177 equipment. For each analysis, a known mass of sample (1-3 mg) was placed in a tin crucible and  
178 each measurement was repeated three times to determine the measurement uncertainty.

179 The HHV was calculated from the elemental analysis using the equation proposed by  
180 Channiwala and Parikh [12].

$$181 \quad \text{HHV} = 0.3491[\text{C}] + 1.1783[\text{H}] - 0.1034[\text{O}] - 0.0151[\text{N}]$$

182 In this equation the HHV is expressed in MJ/kg and [C], [H], [N] and [O] in mass percentages  
183 on dry basis.

184 The water content of bio-oils was determined by Karl-Fischer (KF) titration using a Metrohm  
185 Titrando 852 analyzer. The samples were diluted in THF at a concentration of 10 wt.% and the  
186 volumetric method was employed. To avoid side reactions of aldehydes and ketones with  
187 traditional KF reagents, which produce water, specific reagents for samples containing these  
188 organic compounds were chosen: Karl Fischer ROTI hydroquant C5K (5 mg of water/mL of  
189 solution) and Karl Fischer ROTI hydroquant working medium K. The calibration was carried out  
190 using a solution of 10 wt.% of H<sub>2</sub>O in THF.

191 Molar mass distributions were obtained by gel permeation chromatography (GPC) using an  
192 Agilent equipment (1200 series) equipped with two PL gel columns with different pore sizes (500  
193 and 50 Å) using THF as the mobile phase (1 mL/min). Two detectors were used, a refractive index  
194 detector (RID) and diode-array detector (DAD), collecting data each 0.4 s in the range of 200-450  
195 nm with a resolution of 2 nm. The samples were prepared with concentration of 1 wt.% in THF  
196 and filtered before analysis (PTFE – 0.45µm). The measurements were carried out at 35°C and the  
197 calibration was performed using hydrocarbons standards (molecular weight between 86 and 1000  
198 g/mol).

199 <sup>13</sup>C nuclear magnetic resonance (<sup>13</sup>C-NMR) spectra were recorded using a Bruker AVANCE  
200 400 MHz spectrometer and the spectra were analyzed with the TopSpin 3.0 software. The analyses  
201 were carried out at room temperature with an accumulation of 4500 scans. Trioxane was used as  
202 internal standard, diluted in DMSO-D<sub>6</sub> in a coaxial tube configuration that prevented the contact  
203 of the solvent with the bio-oil samples.

204 Gas chromatography coupled with a mass spectrometer was performed with a GCMS-QP2010  
205 SE apparatus (Shimadzu) equipped with a Zebron ZB Wax-Plus column (length 60 m, internal  
206 diameter 0.25 mm, film thickness 0.25 µm). The samples were diluted in methanol (20 wt.% for  
207 organic phase and 30 wt.% for aqueous phase) and filtered before the analysis (Cellulose acetate

208 – 0.45 $\mu$ m). The oven temperature program started at 70 °C (held for 10 min), then was heated at a  
209 rate of 5°C/min up to 150 °C. At this point the heating rate changed to 3°C/min up to 250 °C (held  
210 for 15 min).

211 Two-dimensional gas chromatography coupled with mass spectrometry (GCxGC-MS) was  
212 carried out with an Agilent GC 6890N apparatus. The first separation was performed by a polar  
213 column VF-1701 MS (I.D 0.25 mm; film thickness 0.25  $\mu$ m; length 30 m) followed by a second  
214 apolar column DB1 (I.D 0.25 mm; film thickness 0.25 $\mu$ m; length 1.5m) for the second dimension  
215 of separation. The modulation was performed by a cryogenic modulator (Zoex Corporation USA)  
216 each 12s. The compounds were identified by the coupled MS detector (5975B). The use of a first  
217 polar column followed by a less polar column favored the separation of oxygen and nitrogen-  
218 containing compounds, widely present in bio-oils [13]. The temperature program was set as  
219 follows: first column from at 50°C to 300 °C with a ramp of 1.75 °C/min, then to 320°C with a  
220 ramp of 1.8 °C/min. The second column went from 50 °C to 320°C at 1.8 °C/min. The samples  
221 concentration was the same as described for GC-MS analyses.

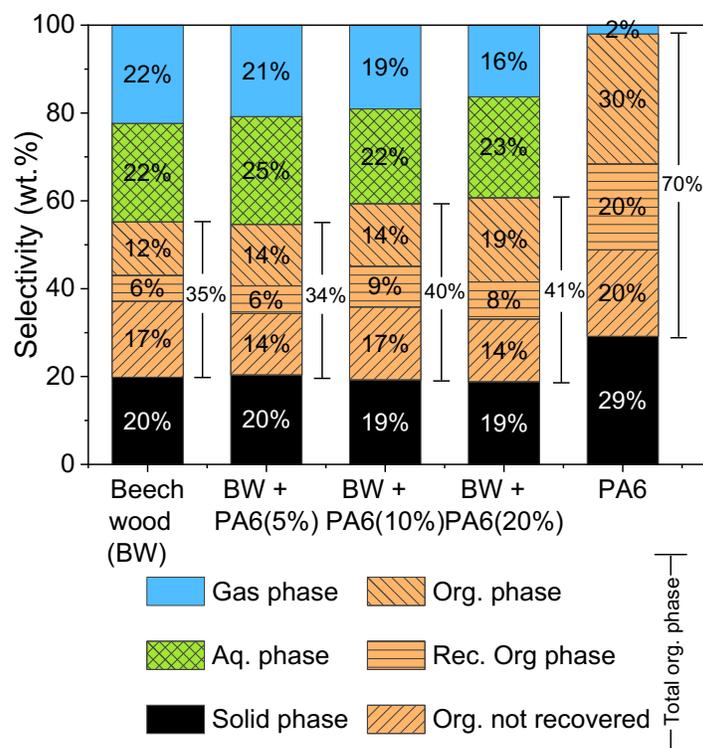
222 The spent catalyst (recovered after reaction) was analyzed by thermogravimetric analysis  
223 (TGA) under air (40 mL/min) using a TGA/DSC-1- Star<sup>e</sup> system (Mettler Toledo) equipped with  
224 a gas controller GC200. The temperature was initially held at 25°C for 5 minutes, then increased  
225 up to 900°C with a heat-up ramp of 10°C/min.

226

### 227 **3. Results and discussion**

#### 228 **3.1. Co-pyrolysis of BW and PA6 and products characterization**

229 The selectivity for gas, liquid and solid products is displayed in Figure 2. The mass balance  
230 obtained for all reactions was  $\geq 95\%$  and generally close to 100%, and the liquid products were  
231 the main fraction collected, including when pure PA6 was used.

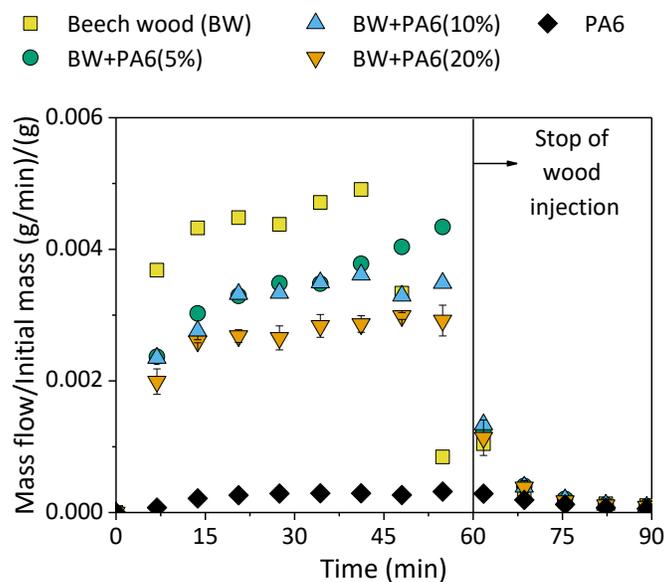


232

233 Figure 2 - Product selectivity in experiments with different concentrations of PA6

234 The increase in PA6 concentration led to a decrease in the production of gaseous products  
 235 associated with an increase in the selectivity in liquid products, essentially the organic phase. With  
 236 pure PA6 there was no phase separation of the liquid fraction, which consists only of an organic  
 237 phase. Since PA6 does not contain any water or hydroxyl groups its degradation is less likely to  
 238 yield water than that of biomass. PA6 also yielded more solid products than BW+PA6 blends, but  
 239 the solid residues included a significant part of white polymer particles, collected downstream the  
 240 reactor, probably formed by re-condensation of PA6-derived monomers or oligomers.

241 Figure 3 shows the cumulative production of all non-condensable products, normalized by unit  
 242 mass of feedstock. Increasing the concentration of PA6 in BW+PA6 blends led to a decrease in  
 243 the production of gases, and the pyrolysis of pure PA6 produced the fewest gaseous products,  
 244 indicating that, unlike wood, PA6 and its pyrolysis products cracked only marginally into light  
 245 compounds.



246

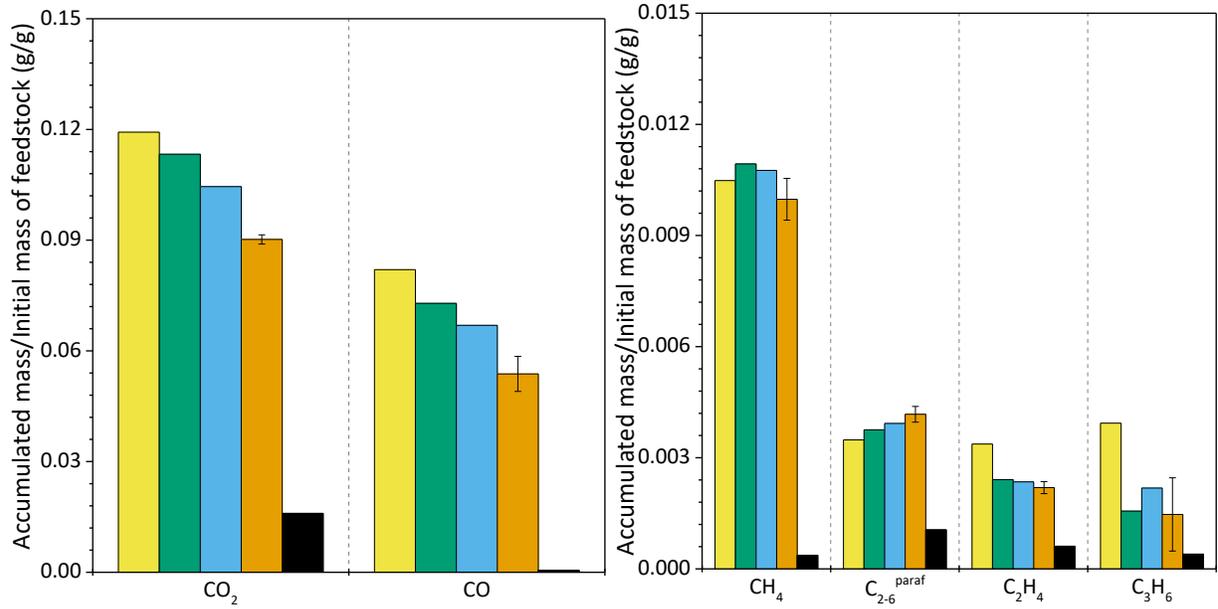
247 Figure 3 - Total mass flow of gaseous products normalized by the initial mass of feedstock

248

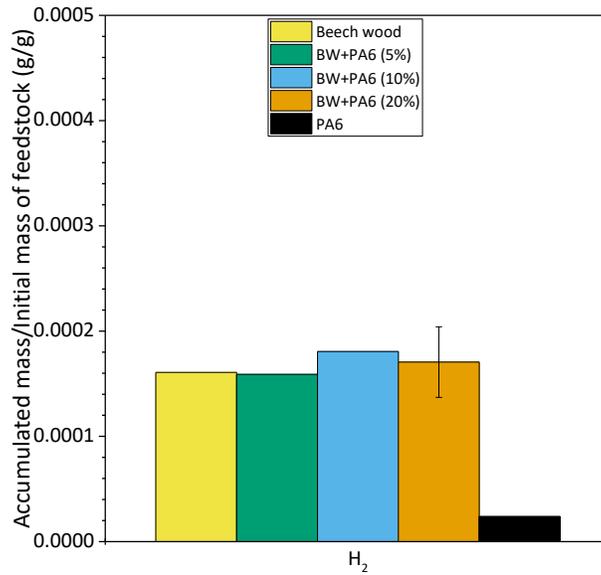
249 The composition of the gas phase is detailed in Figure 4. The increase in plastic concentration  
 250 led to a decrease in CO<sub>x</sub> and C<sub>2</sub>-C<sub>3</sub> olefins production, and to a small but significant increase in  
 251 light paraffins production (C<sub>2-6</sub><sup>paraf</sup>), while less olefins (ethylene and propene) are formed. The  
 252 changes in CH<sub>4</sub> and H<sub>2</sub> production from BW and BW+PA6 were statistically insignificant, but  
 253 pure PA6 produced almost no methane or hydrogen, which suggests that they are essentially  
 254 produced from the wood. Finally, H<sub>2</sub> was a minor product in all experiments in terms of mass, but  
 255 also in terms of moles.

256

257



258



259 Figure 4 - Cumulative mass of non-condensable gases, normalized by unit mass of feedstock

260

261 Table 2 shows the water content, the ultimate analysis and the calculated higher heating value  
262 (HHV) of the two liquid phases obtained in the experiments. The CHNO analyses were calculated  
263 on dry basis, therefore they represent the composition of what is not water, in both types of liquid  
264 phases.

265

266 Table 2 - Water content, ultimate analysis and HHV of the liquid fractions.

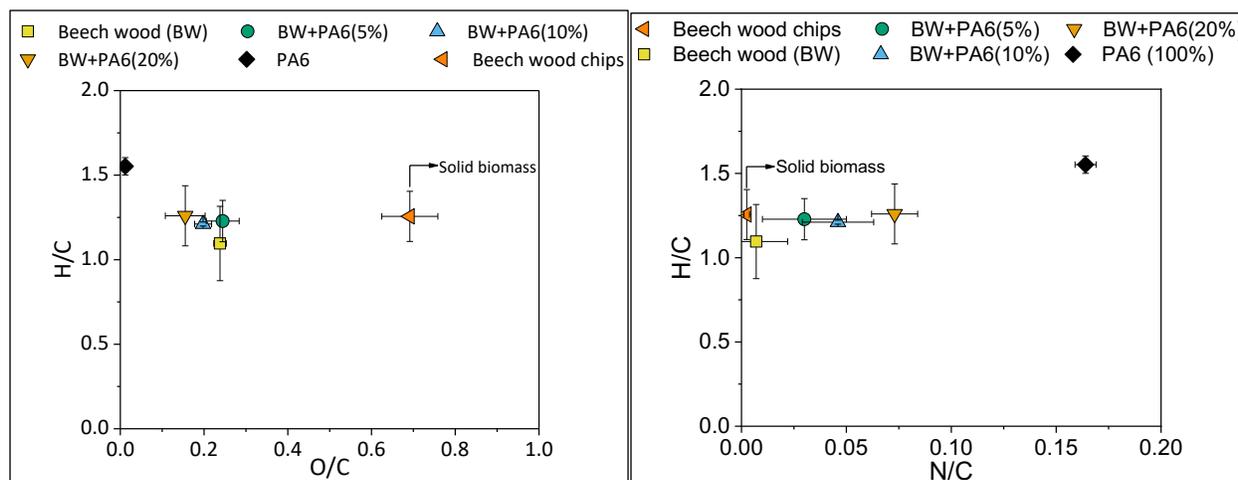
Feedstock	%H <sub>2</sub> O	Ultimate analysis (wt.% on dry basis)				HHV (MJ/kg)
		C	H	N	O*	
<b>Organic phase</b>						
Beech wood	11.9±1.8	70.6±1.2	6.4±0.6	0.5±0.6	22.4±0.6	29.9±0.8
BW+PA6 (5%)	12.5±1.1	68.3±1.3	7.0±0.3	2.4±0.8	22.3±1.7	29.8±0.2
BW+PA6 (10%)	13.4±0.8	70.5±0.3	7.11±0.02	3.8±0.7	18.6±1.0	31.0±0.2
BW+PA6 (20%)	13.8±1.4	71.6±2.4	7.5±0.5	6.1±0.4	14.8±2.2	32.2±0.7
PA6	15.2±1.0	74.8±0.7	9.7±0.1	14.3±0.2	1.2±0.5	37.2±0.2
<b>Aqueous phase</b>						
Beech wood	78.9±1.3	61.3±1.6	3.9±3.2	2.1±1.3	32.7±2.2	23.5±2.6
BW+PA6 (5%)	74.3±0.7	62.0±3.3	6.2±0.4	3.6±0.7	28.2±2.9	26.0±1.9
BW+PA6 (10%)	76.2±6.2	66.4±2.5	4.6±1.6	5.8±2.2	23.3±5.0	26.1±2.7
BW+PA6 (20%)	65.8±2.3	54.5±1.8	6.2±7.2	8.7±1.8	30.6±5.3	23.1±8.9

267 \* by difference.

268 The increase in PA6 concentration resulted in an increase in the water content in the organic  
 269 phase, and to the opposite in the aqueous phase (not present with pure PA6). This could be related  
 270 to the fact that caprolactam, which is the main product of PA6 degradation as will be shown later,  
 271 is hygroscopic [14]: when the content of PA6 increased, there was more caprolactam in the organic  
 272 phase, which could promote water solubility in this phase. The organic phase obtained from pure  
 273 BW contained ≈0.5 wt.% N and the aqueous phase ≈2 wt.%. Using BW/PA6 blends, the N-content  
 274 in both phases increased regularly with PA6 concentration, which suggests that N-containing  
 275 compounds derived from PA6 are shared out in both organic and aqueous phases. PA6 also  
 276 contains oxygen in the form of a carbonyl group and oxygen accounts for ≈14 wt.% of its molar  
 277 mass, while beech wood contains ≈44 wt.% O. Therefore, the oxygen content in the liquid fractions  
 278 originated predominantly from the biomass. Accordingly, reducing the BW fraction in the

279 feedstock led to a lower oxygen content in the organic phase (Table 2), the HHV increased with  
280 the percentage of PA6 and the organic phase obtained from pure PA6 showed the highest HHV.

281 A number of studies reviewed by Ansari et al. [15] reported that the co-pyrolysis of biomass  
282 with various types of plastics results in bio-oils with higher H/C ratios, the plastic behaving as  
283 hydrogen-donor for intermolecular H-transfer. In the present study, the Van Krevelen diagram  
284 (Figure 5) indeed showed a slight increase in the H/C ratio for organic phases produced from  
285 BW+PA6 blends, but the difference was within the margin of error.

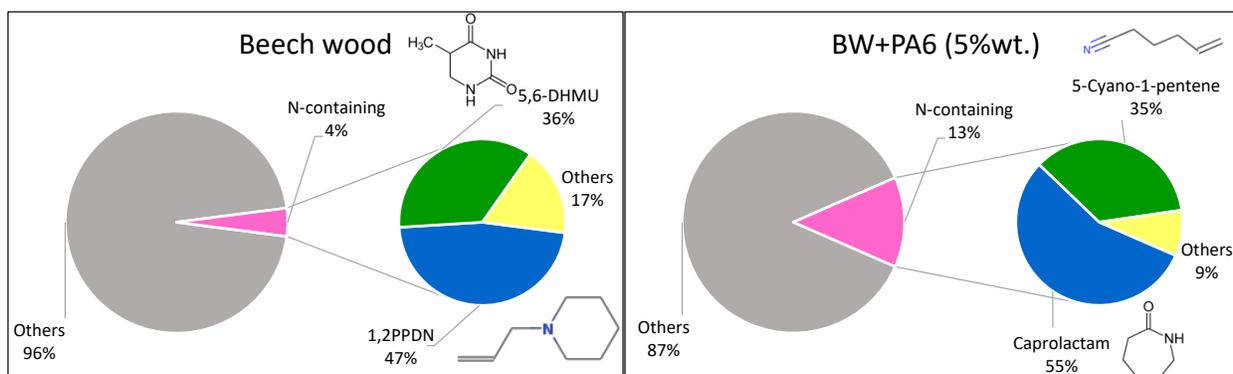


286  
287 Figure 5 - Van Krevelen diagrams of liquid organic phases compared to solid beech wood

288 The N/C ratio increased strongly with PA6 concentration, but this increase was not  
289 proportional to the concentration of PA6 in the BW+PA6 blends. This trend will be discussed in  
290 paragraph 3.3.

291  
292 Figure 6 specifically shows the distribution of N-containing compounds identified by GC-MS  
293 in both organic and aqueous phases. The percentages are expressed relative to the total peaks area.

294



295

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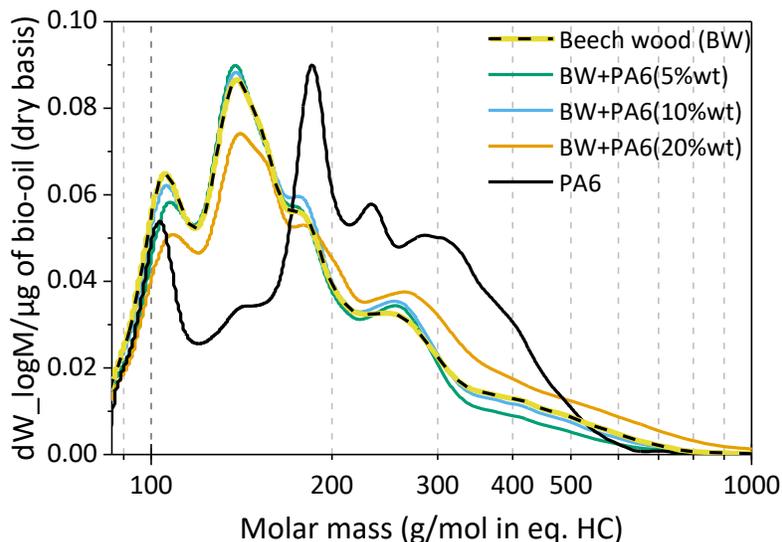
298

Figure 6 - N-containing products distribution in the organic phases and 5-cyano-1-pentene/caprolactam ratio as a function of PA6 concentration

299 For experiments with pure BW, 4% of the total peaks area corresponded to N-containing  
 300 compounds. This fraction consisted mainly of 1-(2-propenyl)piperidine (1,2PPDN – 47%) and 5,6-  
 301 dihydro-5-methyluracil (5,6-DHMU – 36%). These compounds are related to biological functions  
 302 and metabolic processes in biomass. Adding 5 wt.% of PA6 to BW led to 13 % of N-containing  
 303 compounds (relative to the total peaks area), and within these 55% was caprolactam, 35% 5-cyano-  
 304 1-pentene and the remaining 9% other N-containing compounds. The complete list of analyzed  
 305 compounds can be found in the supplementary information.

306 In all experiments in the presence of PA6, the main N-products were caprolactam and 5-cyano-  
 307 1-pentene. However, the 5-cyano-1-pentene/caprolactam ratio decreased non-linearly with the  
 308 PA6 concentration, suggesting a competition between the reaction pathways leading to their  
 309 formation.  
 310

311 GPC analyses with RI detector provided the molar mass distribution of the compounds present  
 312 in the different organic phases (Figure 7).



313  
 314 Figure 7 - MW distribution of the organic phase normalized by unit mass of dry bio-oil

315 At low PA6 concentrations (5 and 10 wt.%), the GPC profiles were very similar to the one  
 316 obtained with pure BW, with a maximum intensity at  $\approx 140$  g/mol, and the MWs below 300 g/mol  
 317 represented  $\approx 70\%$  of the total area. The organic phase obtained from pure PA6 exhibited a very  
 318 different profile, with a maximum intensity found at 185 g/mol and the area in the 160-500 g/mol  
 319 range representing 86% of the total area. With the BW+ 20% PA6 blend, the GPC profile was a  
 320 combination of the two previous profiles and the formation of heavier compounds was clearly  
 321 revealed. These modifications are translated in the average molar mass variations reported in Table  
 322 3.

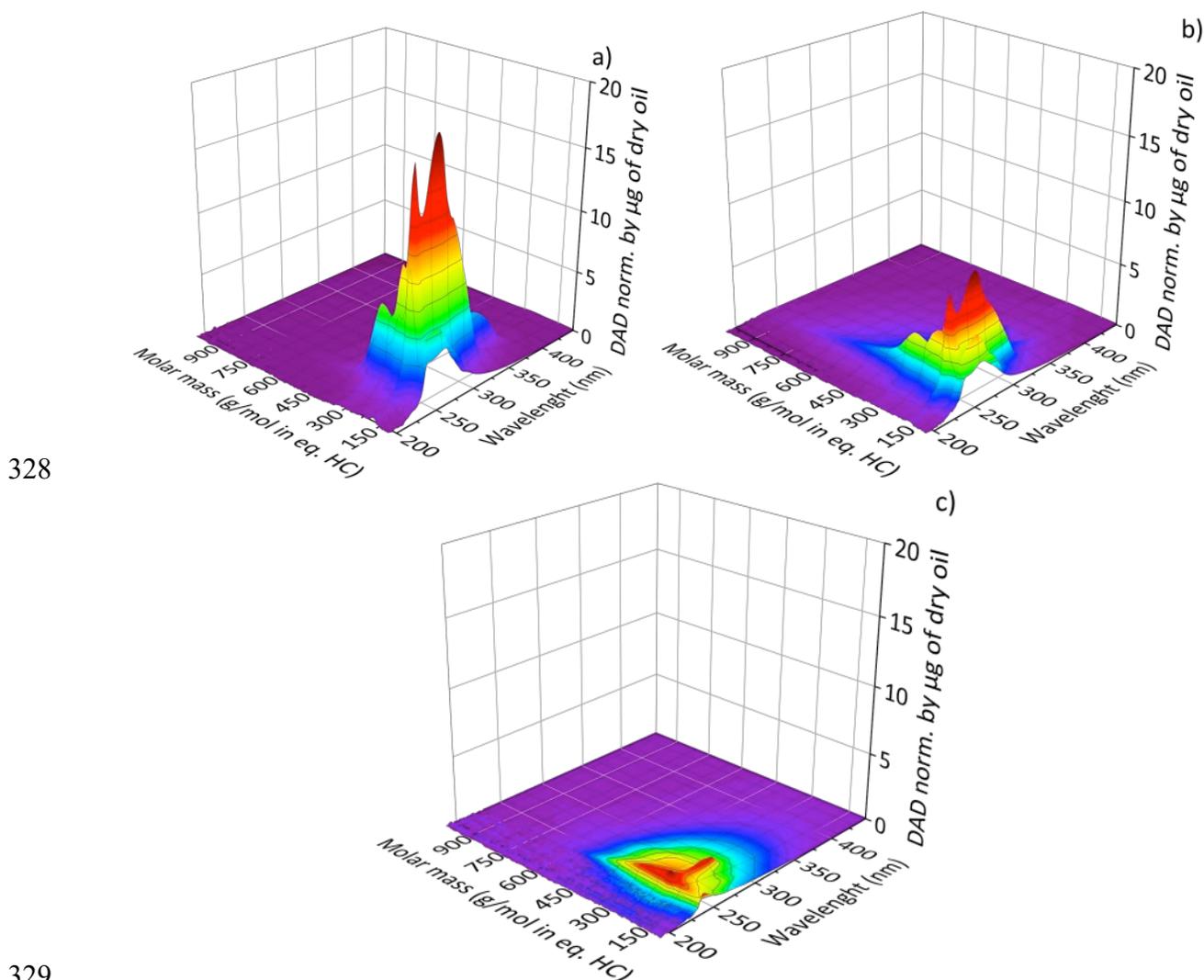
323 Table 3 - Average molar mass of organic fractions

Feedstock	MW (g/mol, in eq. HC)
Beech wood	191
BW+5 % PA6	179

BW+ 10% PA6	185
BW+ 20% PA6	219
PA6	228

324

325 GPC analyses were also carried out using UV/DAD in order to obtain specific information  
 326 regarding the unsaturated compounds present in the bio-oils (Figure 8). For comparison, only the  
 327 results obtained with 100% BW, with BW +20 % PA6 and with 100 % PA6 are shown.



329

330

331 Figure 8 - GPC- DAD chromatograms of organic fraction obtained from (a) BW, (b) BW+ 20%  
 332 PA6 and (c) PA6

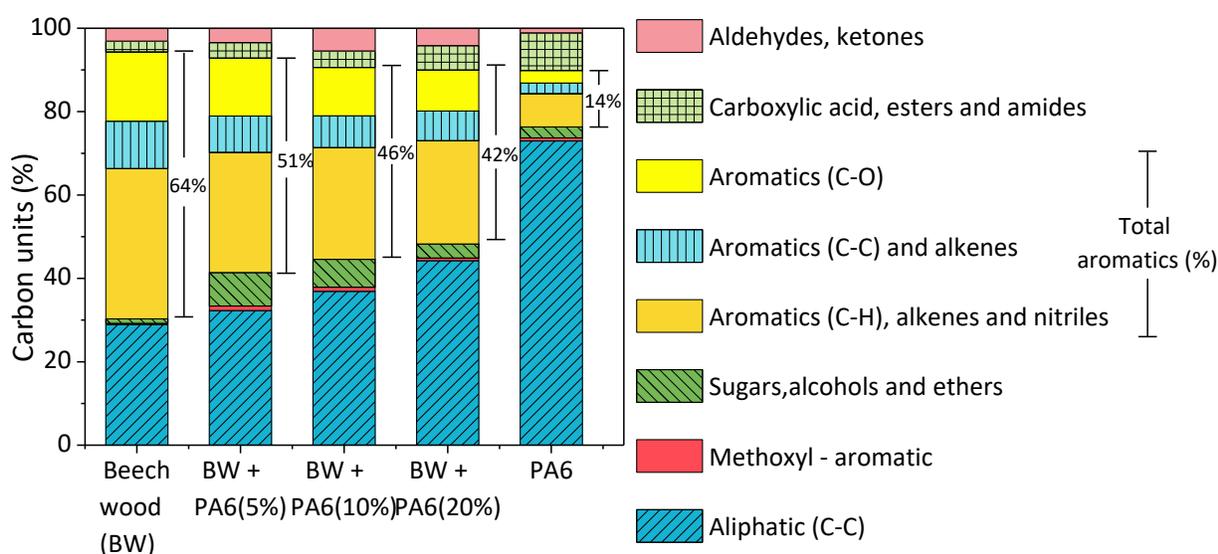
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334

In all cases, the profiles were centered at MWs in the range of 150–200 g/mol and a wavelength close to 267 nm. Absorption in this region is assigned to compounds with conjugated double bond systems such as aromatics, and the peak shifts towards larger wavelengths when the size of the

335 conjugated system increases (e.g. benzene – peak at 255 nm; naphthalene – 286 nm; anthracene –  
 336 375 nm) [16]. The pyrolysis of lignocellulosic biomass produces many aromatic compounds such  
 337 as guaiacols, syringols, phenols and aromatic ethers. This production was marginal using pure  
 338 PA6, as evidenced by the intensity close to zero. It was also strongly reduced using the BW+20%  
 339 PA6 blend, but not proportionally to the concentration of PA6 since the maximum peak intensity  
 340 decreased by more than 50%.

341 <sup>13</sup>C-NMR analyses depicted in Figure 9 show the different functional groups present in the  
 342 organic phases.

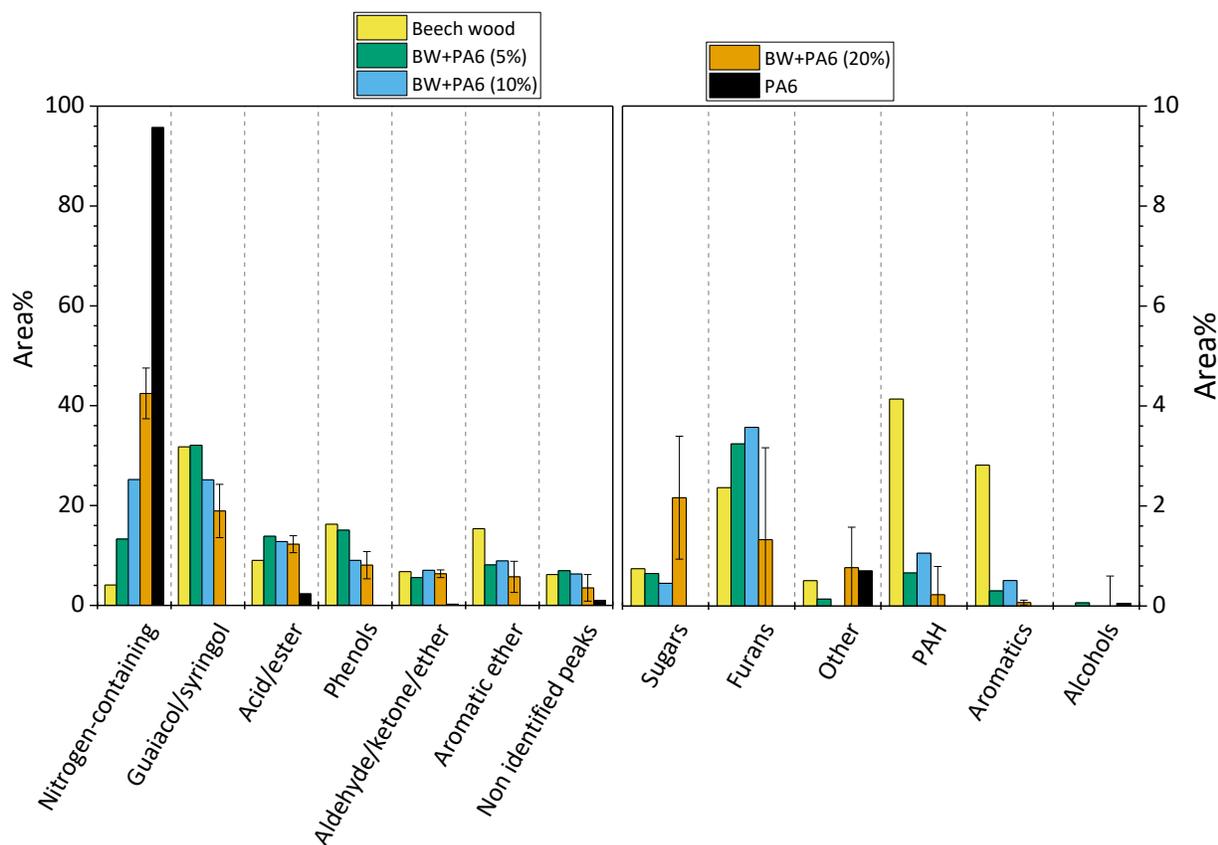


343

344 Figure 9 - <sup>13</sup>C-NMR - Functional group distribution in the different organic phases

345 The content of aromatic compounds decreased when the concentration of PA6 increased, in  
 346 agreement with the GPC-DAD analyses shown previously. It should be mentioned that the  
 347 chemical shift assigned to nitriles (range 110-130 ppm, e.g.: 5-cyano-1-pentene) is similar to that  
 348 assigned to aromatic C-H (dark yellow). Therefore, the reduction in aromatic groups was probably  
 349 underestimated in this analysis. Another case of superposition of chemical shifts is related to the  
 350 carboxylic acid and amide groups (green with squares): in this case, this concentration growth  
 351 should be associated mainly to the presence of caprolactam, which was the main degradation  
 352 product of PA6. Consistently, the amount of aliphatic carbon units increased with the concentration  
 353 of PA6.

354 More detailed information about the composition of the organic phases is given by the GC-MS  
 355 analyses presented in Figure 10.



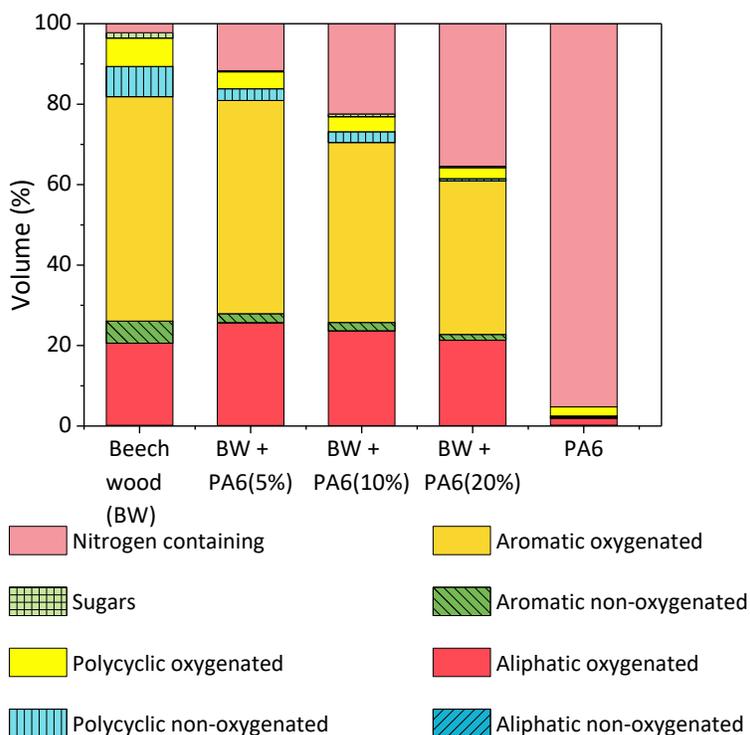
356  
 357 Figure 10 - Relative areas of compounds families identified by GC-MS for the different organic  
 358 phases

359 As expected, the concentration of nitrogen-containing compounds grew with the increase in  
 360 plastic concentration, from 4% with pure beech wood to 96% with pure plastic. Concurrently, there  
 361 was a progressive reduction in the production of aromatic compounds originating from the  
 362 biomass, such as guaiacol, syringol and phenols. Moreover, the presence of PA6, even at low  
 363 concentration (5 wt.%), resulted in a significant drop in the amount of deoxygenated aromatic  
 364 compounds (i.e. PAH and aromatics). These results confirmed that the catalytic activity was  
 365 impaired in its oxygen-removal function in the presence of PA6. This was corroborated by the  
 366 sharp increase in sugar concentration together with a decrease in furans (product of sugars  
 367 dehydration) when the plastic concentration reached 20 %.

368

369

Figure 11 shows the group of compounds obtained with GCxGC-MS analyses.



370

371

372

Figure 11 - Relative blob volumes of compound families identified by GCxGC-MS in the organic phases

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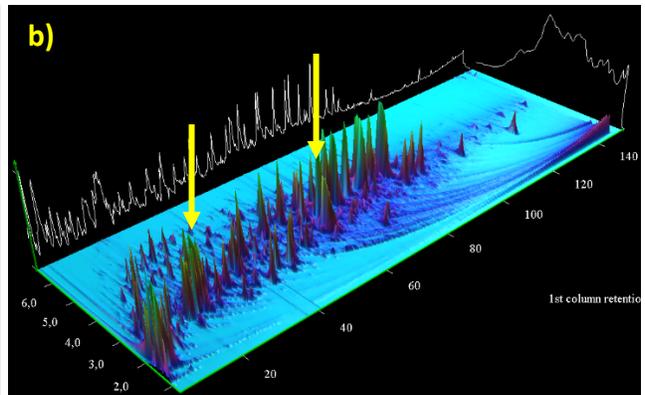
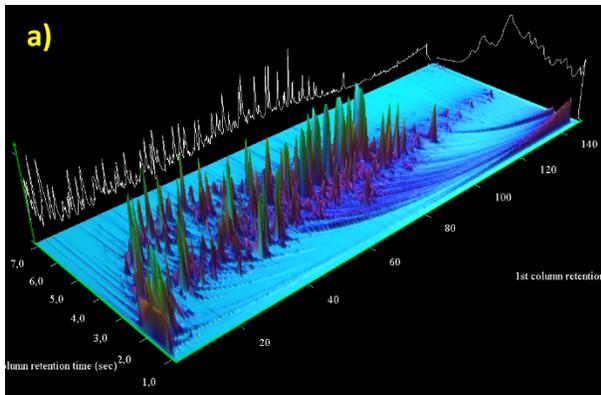
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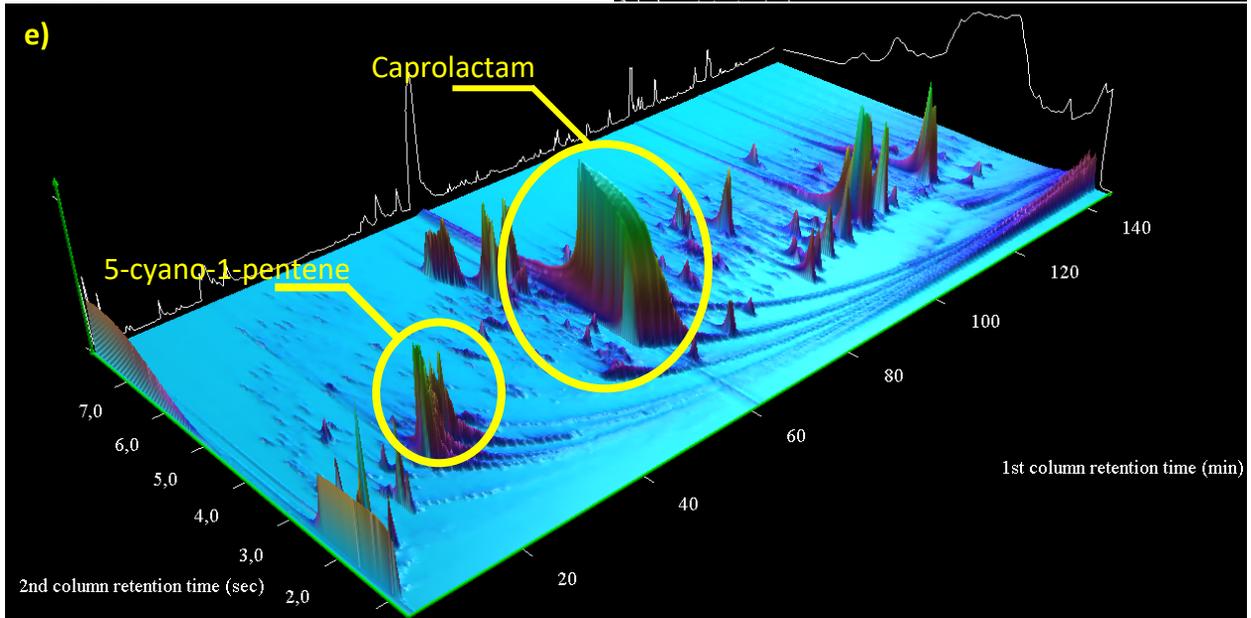
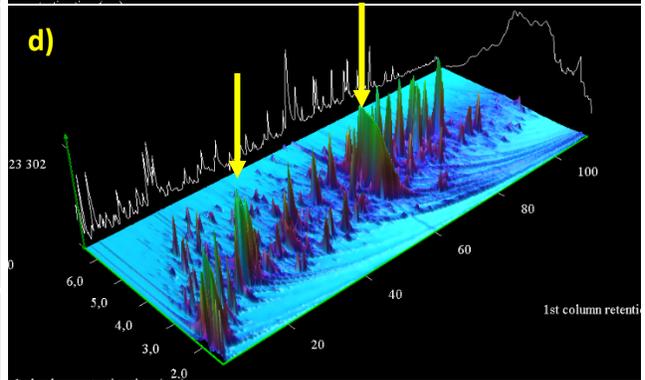
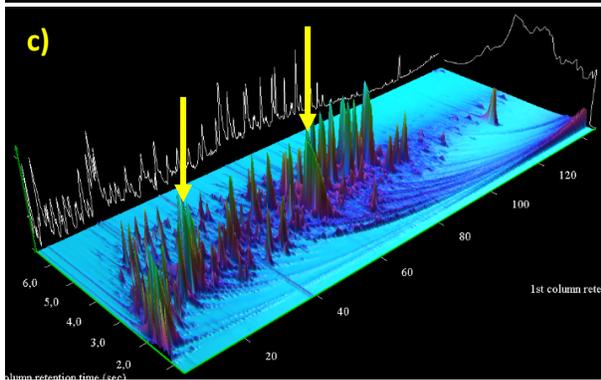
379

These results fully support the trends observed with the previous techniques. The selectivity for nitrogen-containing compounds increased proportionally with the concentration of plastic, whereas that for aromatic oxygenated compounds (i.e. guaiacols, syringols, phenols...) decreased. Finally, the groups of fully deoxygenated compounds (non-oxygenated aromatics and polycyclics) were strongly reduced in the presence of plastic. The evolution of peaks assigned to caprolactam and 5-cyano-1-pentene were evidenced in the 3D projections of chromatograms shown in Figure 12.

380



381



382

383 Figure 12 - 3D projections of chromatograms obtained with GCxGC-MS for the organic phases.

384 a) BW; b) BW + PA6 (5%); c) BW + PA6 (10%); d) BW + PA6 (20%); e) PA6.

385

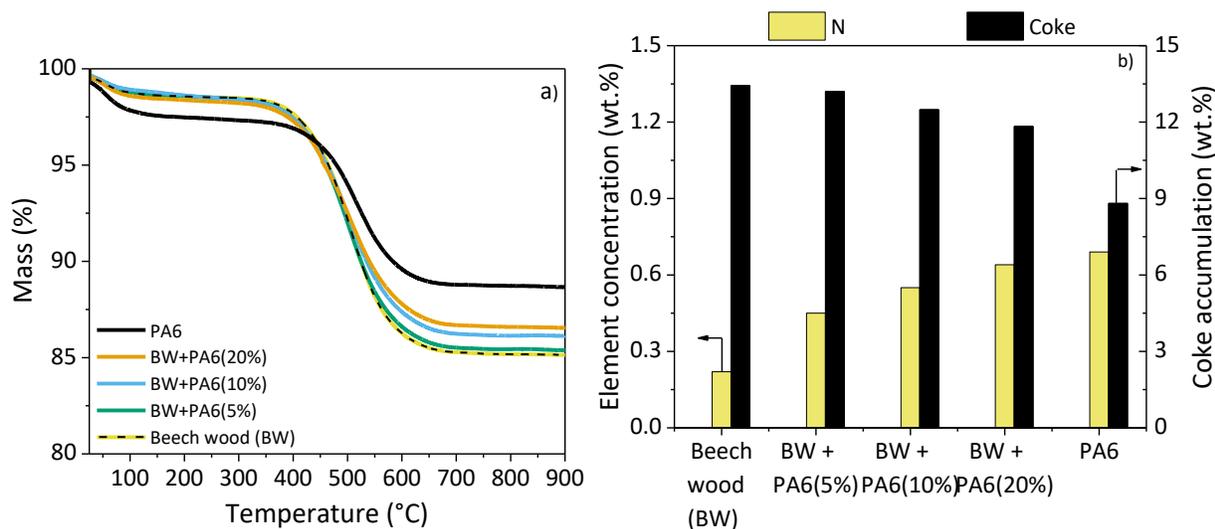
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388

### 389 3.2. Characterization of spent catalysts

390 The spent catalysts were analyzed to determine the coke composition (CHN) and the amounts  
391 of deposited coke were quantified using thermogravimetric analysis (TGA) performed under air  
392 to burn the carbon deposits. The results are presented in Figure 13.



393

394 Figure 13 - Mass loss profiles for catalysts after reaction (a); amounts of coke removed from  
395 spent catalysts and N content of the coke (b)

396 For experiments performed in the presence of BW and BW+PA6 blends, an initial mass loss  
397 around 1.5 wt.% was observed between 25 and 200°C. It can be attributed to the desorption of  
398 water or light compounds adsorbed in the catalyst pores, since the solids were not pre-heated before  
399 TGA. The catalyst obtained after the pyrolysis of pure PA6 showed a more significant mass loss  
400 in this region (2.5%). This could indicate that N-containing compounds were also adsorbed on the  
401 catalytic sites, corroborating the hypothesis of a partial deactivation of HZSM-5. This is also  
402 consistent with the increase in liquid products and decrease in gas products with the amount of  
403 PA6, shown in Fig. 2, which could indicate a lower cracking activity of the catalyst. The  
404 deactivation of acid catalytic sites by nitrogen poisoning is well documented [17–19] and even at  
405 low concentration (<0.1%), the presence of N-containing compounds may cause a deactivation of  
406 zeolites, as reported by Caeiro et al. [20].

407 The mass loss between 300 and 900°C was assigned to coke combustion, which took place in  
408 a simple one-step profile at similar temperatures, indicating that the carbon deposits were rather

409 homogeneous in their structure. The amount of coke deposited on the catalyst decreased when the  
410 PA6 concentration increased; however, the experiment using pure PA6 yielded almost 9 wt.% of  
411 coke on the catalyst. The increase in the PA6 amount in the blend also led to a steady rise in the N  
412 content in the spent catalyst, although not proportional to PA6 concentration.

413 Several studies reported the beneficial effect of co-pyrolysis with some plastics (notably olefin-  
414 derived plastics such as polyethylene and polypropylene) in reducing the catalyst deactivation by  
415 coke [6, 17–21]. The explanation relies on the high H content in the plastics that promotes the  
416 formation of liquid products, and on the low amounts of aromatic compounds formed during their  
417 degradation, which limits the condensation/polymerization reactions of these species. The effect  
418 of plastic, however, should be assessed by comparing the effective coke yields with the calculated  
419 arithmetic sum of coke yields expected on the basis of a proportional contribution of coke  
420 originating from BW and PA6, respectively. This will be described in the next section.

421

### 422 3.3. Synergistic effects

423 The effect of adding PA6 to BW on the pyrolysis products yields and properties has been  
424 assessed by comparing the calculated value of each property, based on an arithmetic contribution  
425 of the values obtained using pure BW and pure PA6 (in wt. %), with the value of this property  
426 effectively measured, using the following equation [26]:

$$427 \quad Y_{estimated(BW+\alpha PA6)} = \alpha Y_{exp(BW)} + (1 - \alpha) Y_{exp(PA6)} \quad (1)$$

428 where  $Y_{exp(BW)}$  is the experimental value of the parameter evaluated (e.g. phase selectivity, N  
429 concentration, coke content...) obtained with pure BW,  $Y_{exp(PA6)}$  is the experimental value  
430 obtained with pure PA6 and  $\alpha$  is the concentration of plastic in the blend.

431 The synergistic impact ( $\Delta Y$ ) was evaluated using the following equation [27]:

$$432 \quad \Delta Y = \frac{Y_{exp(BW+\alpha PA6)} - Y_{estimated(BW+\alpha PA6)}}{Y_{estimated(BW+\alpha PA6)}} \times 100\% \quad (2)$$

433 where  $Y_{exp(BW+\alpha PA6)}$  is the experimental value obtained from the co-pyrolysis of feedstock  
434 containing  $\alpha\%$  of plastic and  $Y_{estimated(BW+\alpha PA6)}$  was calculated using Eq.(1). The evaluation of  
435 the synergistic impact for different parameters of the pyrolysis process is presented in Table 4.

436

437 Table 4 - Synergistic impact between BW and PA6 for different parameters

Parameter	Experimental			Calculated BW+20%PA6	$\Delta Y$
	100% BW	BW+20%PA6	100% PA6		
Gas products (%)	22	16	2	18	-11%
Liquid products (%)	57	64	70	60	+8%
Solid products (%)	20	19	29	22	-14%
Coke on catalyst (wt.%)	13.43	11.83	8.81	12.50	-5%
N (wt.%) in organic phase	0.5	6.1	14.3	3.3	+87%
H/C organic phase	1.1	1.3	1.6	1.2	+6%
O/C organic phase	0.24	0.16	0.01	0.19	-19%

438

439 The co-pyrolysis of PA6 and BW resulted in a gas phase selectivity below what was expected.  
 440 According to the literature [24, 25], the melting temperature of PA6 is between 170°C and 260°C.  
 441 At the inlet of the heated zone, the plastic starts to melt and it may partially cover the wood  
 442 particles, which could hinder the evolution of gaseous products from the wood. Besides, it can  
 443 modify the heat conductivity of wood chips and delay the evolution of gases [4].

444 Conversely, the production of liquid products benefited from a positive synergistic effect, with  
 445 the experimental selectivity for condensable products higher than the calculated value. The blend  
 446 of BW with PA6 chips could have prevented the premature agglomeration of the melted polymer,  
 447 as observed in the experiment with pure PA6, and which interferes with heat transfer and with the  
 448 cracking of the polymeric chain. Another evidence of this agglomeration was provided by the  
 449 aspect and consistency of the chars obtained after pyrolysis: using pure BW, the char consisted of  
 450 blackened but well separated wood particles, while the chars obtained from co-pyrolysis of  
 451 BW+PA6 blends consisted of aggregated particles, with a certain mechanical resistance. The same  
 452 phenomenon also explains the synergy effect on the solid product selectivity, BW contributing to  
 453 improve the cracking of PA6, which led to lesser amounts of solid products.

454 The nitrogen content in the organic phase also exhibited a strong positive synergistic effect,  
455 with an experimental value 85% higher than the calculated value. This could be due to the  
456 promotion of PA6 cracking by water, present at high concentration, and by oxygen-containing  
457 radicals originating from the biomass, which could attack the polymer chain [30].

458 The impact of PA6 on the H/C atomic ratio of bio-oils was modest (+6%). In contrast, the  
459 BW+20 wt.% PA6 blend showed a synergistic effect of -19% on the O/C atomic ratio of the  
460 organic phase, indicating that the overall deoxygenation was improved in the presence of PA6,  
461 although fewer totally deoxygenated compounds were formed, as shown previously. During the  
462 initial stages of co-pyrolysis, the degradation of biomass released highly reactive oxygen-  
463 containing species. These species may attack the polymer, subtracting hydrogen from its structure  
464 and favoring the chain scission, as mentioned before. In return, this hydrogen transfer from the  
465 polymer contributed to the stabilization of the biomass-derived compounds, reducing the coke  
466 formation through polymerization and condensation reactions [27, 28]. This effect on coke  
467 formation was confirmed by the synergistic impact that showed a coke deposition 5% lower than  
468 the calculated value.

469 The reactions leading to deoxygenation (dehydration, decarbonylation, decarboxylation) occur  
470 mainly inside the zeolite pores and, as regards HZSM-5 (pore diameter – 0.55 nm), many  
471 compounds were too large to be able to enter the pores. For example, levoglucosan first needs to  
472 be converted into furan, by dehydration on acid sites of the external catalyst surface, which can  
473 then diffuse into the pores to complete the deoxygenation [33]. Therefore, coke deposition at the  
474 entrance or inside the pores reduces the deoxygenation activity. As co-pyrolysis with PA6  
475 decreased the rate of coke deposition, the deoxygenation activity was maintained for a longer  
476 period, contributing to the reduction in the O/C ratio.

#### 477 **4. Conclusion**

478 The co-pyrolysis of beech wood (BW) and polyamide-6 (PA6) combined with *ex situ* catalytic  
479 treatment of the pyrolysis vapors was investigated at different BW/PA6 ratios. The presence of  
480 PA6 resulted in a decrease in the gaseous product selectivity and in the coke deposition on the  
481 catalyst. N-containing compounds derived from PA6 were found in the liquid phase (mainly as  
482 caprolactam) and in the solid products, but no N-containing gaseous product was formed. The

483 production of aromatic compounds derived from the wood was also reduced in the presence of  
484 PA6.

485 This work showed that the properties of the co-pyrolysis products were not the simple  
486 arithmetic addition of the properties of the products obtained by pyrolysis of pure BW or pure  
487 PA6: positive or negative synergistic effects were observed depending on the property considered.  
488 The most important synergistic effect was observed on the concentration of nitrogen in the organic  
489 phase (+87 %). It was attributed to a higher depolymerization of PA6 promoted by reactive  
490 oxygenated species originating from the wood, and probably associated to the negative synergistic  
491 effects observed on coke deposition (-5 %) and on the O/C ratio (-19 %) of the co-pyrolysis oil.

492

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498

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