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# Co-processing of Wood and Wheat Straw Derived Pyrolysis Oils with FCC Feed—Product Distribution and Effect of Deoxygenation

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## Abstract

The behavior of bio-oils when co-processed with conventional fossil feed in a fluid catalytic cracking (FCC) unit is suitably tested using a microactivity testing unit (MAT). In the present study, non-catalytic fast pyrolysis oils originating from wood and wheat straw were co-processed in a MAT at a 20/80 weight blend (bio-oil/FCC feed). In addition, bio-oil obtained from deoxygenating the straw derived vapors over a steamed HZSM-5/Al<sub>2</sub>O<sub>3</sub> extrudate catalyst was tested. The bio-oils were characterized for elemental composition and moisture content to calculate energy recoveries, amounting to 35% and 30% for the non-catalytically obtained wood and straw oils, while it was 19% for the partly deoxygenated straw oil. Wood oil showed higher acidity (61 mg KOH/g) and molar O/C ratio (0.35) compared to straw oil (54 mg KOH/g and O/C = 0.24). The acidity and O/C ratio was reduced for the straw-derived bio-oil from catalytic vapor treatment (3 mg KOH/g, O/C = 0.08). At constant conversion

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(77.5%) at the MAT, the wood pyrolysis oil showed a product distribution quite similar to the reference oil while the wheat straw pyrolysis oil gave a 1.6% points higher coke yield and a 1.2% points lower liquid petroleum gas (LPG) yield. For the catalytically treated wheat straw pyrolysis oil, an even higher coke yield (2.6% points) and 1.9% points lower LPG yield resulted. The observations are attributed to the higher content of aromatics, phenolics, and nitrogen containing compounds of the catalytically upgraded straw fast pyrolysis oil.

*Keywords:* FCC, Co-processing, Deoxygenation, Straw, Pyrolysis oil, HZSM-5

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## 1 Introduction

Co-feeding of biomass-derived fast pyrolysis (FP) oils with fossil oil in oil refineries can attenuate our dependence on crude oil. Advantageously, FP processes are generally flexible with respect to biomass feedstocks [1–8]. However, raw pyrolysis oil is comprised of hundreds of oxygenated species which makes the oil acidic, instable, and capable of dissolving high amounts of water compared to the mostly aliphatic and hydrophobic refinery feedstock [9–12]. In order to improve the miscibility of fossil oils with biomass FP oils, the pyrolysis vapors can be (partly) deoxygenated under atmospheric conditions over solid acid catalysts [13]. In this way, the renewable oils could be upgraded using existing refinery infrastructure [14]. The refineries' acceptance for co-processing biomass-derived oils is crucial, especially since the bio-oil properties may fluctuate due to the heterogeneity and variety of the feedstock. It is noted that due to the high acidity of raw bio-oils, separate feed lines and tanks with stainless steel cladding would be necessary for bio-oil co-processing to minimize corrosion [15, 16]. Recently, Stefanidis et al. [17] reviewed studies [15, 18–21] that investigated co-feeding of raw FP bio-oils and the resulting shift in product distribution. Reduced gasoline and light cycle oil (LCO) yields were attributed to increased coke formation and the dilution of the reactant stream with water from the raw bio-oil feed. Most studies reported reduced hydrogen yields, which was attributed to the introduction of the hydrogen-deficit bio-oil. The shifts in

22 gasoline, LCO, and coke yield were not consistent across all studies, which may  
23 be related to the difficulty in blending and feeding raw bio-oil with fossil oil and  
24 the different experimental conditions [17]. Pinho et al. [22] conducted tests in  
25 a demonstration-scale FCC unit using 450 kg catalyst and feeding 150 kg/h of  
26 10/90 and 20/80 weight ratios of bio-oil/vacuum gas oil (VGO). In both cases,  
27 approximately 30% by weight of the renewable carbon present in the bio-oil  
28 was preserved in the liquid effluent. In a later study [15] at similar scale (oil  
29 feeding rate 200 kg/h), 5/95 and 10/90 bio-oil/VGO blends were tested. The  
30 pine wood derived bio-oil contained 31.9 wt % moisture and 32.8 wt% O on  
31 dry basis (d.b.). Liquid product streams of gasoline and LCO contained 1 wt%  
32 of renewable carbon respectively for the 5/95 bio-oil/VGO blend. Interestingly,  
33 the coke yield decreased when co-processing 5 wt% bio-oil while no benefits with  
34 respect to coking resulted when blending 10 wt% bio-oil.

35 Since the majority of the laboratory and pilot-scale FCC co-processing tests  
36 resulted in higher coke production when introducing raw bio-oil (especially at  
37 high blending ratios), some authors have investigated co-feeding of stabilized  
38 bio-oils with reduced oxygen content that were obtained by catalytic deoxy-  
39 genation of the pyrolysis vapors prior to condensation. Catalytic deoxygenation  
40 of FP oils not only reduces the extent of oil aging and plant corrosion, but it  
41 also improves the evaporation properties and the miscibility with fossil feed-  
42 stock [4, 10–12, 23, 24]. This has the potential to increase the fraction of bio-oil  
43 being co-processed and thus increase the proportion of renewable carbon in  
44 the desired refinery products. Compared to studies co-processing partly deoxy-  
45 genated oils obtained by hydrodeoxygenation (HDO) of raw FP oils [17], studies  
46 on co-processing of catalytic fast pyrolysis (CFP) oils are fewer and more re-  
47 search is needed to properly evaluate this approach. Table 1 summarizes studies  
48 in which bio-oils (all wood derived) obtained by CFP over HZSM-5 were tested  
49 for blending with fossil feed. Agblevor et al. [25] carried out catalytic cracking  
50 of a CFP oil blended with 85 wt% standard gas oil over an equilibrated FCC  
51 catalyst (E-cat) in a laboratory catalyst evaluation unit. The CFP oil was pro-  
52 duced via HZSM-5 catalytic pyrolysis of poplar wood in a fluidized-bed reactor

53 at 450 °C. Only the fraction that was collected from the electrostatic precipita-  
54 tor was used for co-processing, which accounted for 50 wt% of the total bio-oil  
55 and had relatively low moisture (8.9 wt%) and oxygen content (22 wt% on dry  
56 basis), a total acid number (TAN) of 41 mg KOH/g oil and a carbon content  
57 of 71 wt% (dry basis). The CFP oil was shown to be stable since only minimal  
58 increase in viscosity after long-term storage at ambient conditions was observed  
59 and high temperature simulated distillation to ~600 °C could be carried out with  
60 only minor char formation. Co-processing standard gas oil with CFP oil did not  
61 have any obvious adverse effects on the yield of the various product fractions,  
62 especially gasoline. However, the blend produced less hydrogen and slightly less  
63 coke than standard gas oil, which was attributed to the presence of steam and in  
64 situ generated hydrogen that moderated coke formation. Radiocarbon analysis  
65 showed that the bio-carbon content of the cracked liquid products was 3 wt%.  
66 Thegarid et al. [26] reported almost two fold higher coke yields and enhanced  
67 dry gas and CO<sub>2</sub> yields when co-feeding 10 wt% CFP oil (beech wood, 27 wt%  
68 O) with VGO. These researchers found enhanced gasoline and decreased LCO  
69 oil yields upon co-processing. Lindfors et al. [19] tested CFP oil (pine wood, 22  
70 wt% O d.b.) at a blending ratio of 20/80 with VGO and observed a doubling in  
71 coke yield from 5 to 10 wt% and an increase in both gasoline, LCO, and dry gas,  
72 while the heavy cycle oil and slurry oil (>370 °C (HCO) decreased. This is in  
73 agreement with Marker et al. [16] who found that the acidic bio-oils increased  
74 the cracking of the VGO and shifted the yields toward increased light ends,  
75 which is an economically attractive outcome. Wang et al. [4] obtained CFP oil  
76 with 73 wt% C, 5.6 wt% H and 19.5 wt% O using Fe/HZSM-5 and reported  
77 7 wt% (bio)carbon recovery in the gasoline fraction when 10 wt% bio-oil was  
78 added to VGO. The results indicate that increased C/O ratios of upgraded oils  
79 can increase the (bio)carbon recovery in the gasoline product fraction, and the  
80 lower C recovery reported by Agblevor et al.[25] may be reasoned by the higher  
81 blending ratio and lower C/O ratio compared to Wang et al. [4].

**Table 1.** Shift in gasoline, light cycle oil (LCO), coke, and hydrogen yields [wt%] when co-processing catalytic pyrolysis oil (CPO) with vacuum gas oil. Adapted from Stefanidis et al.[17] and amended by the oxygen and carbon content of the upgraded bio-oils used for co-feeding.

| Ref. | Reactor                            | O wt% <sub>d.b.</sub><br>bio-oil | C wt% <sub>d.b.</sub><br>bio-oil | bio-oil/VGO | Change Gasoline<br>(wt%) | Change LCO<br>(wt%) | Change Coke<br>(wt%) | Change Hydrogen<br>(wt%) |
|------|------------------------------------|----------------------------------|----------------------------------|-------------|--------------------------|---------------------|----------------------|--------------------------|
| [25] | Lab-scale<br>fluidized-bed reactor | 21.9                             | 71.2                             | 15/85       | +0.4                     | +0.1                | -0.3                 | -0.05                    |
| [26] | Lab-scale<br>fixed-bed reactor     | 27.0                             | 66.0                             | 10/90       | +1.7-+15.1               | -13.0-0.0           | +1.6-+1.9            | -0.3-0.1                 |
| [19] | Lab-scale<br>fixed-bed reactor     | 22.0                             | 71.5                             | 20/80       | +3.0                     | +2.0                | +5.0                 | Not reported             |
| [4]  | Pilot-scale<br>circulating riser   | 19.5                             | 73.1                             | 10/90       | -0.1                     | +0.5                | -0.1                 | -0.04                    |

82 The objective of this work was to compare the cracking performance of blends  
 83 of regular FCC feed with pyrolysis oils from different feeds (pine and wheat  
 84 straw). In addition, a catalytically deoxygenated oil obtained from wheat straw  
 85 was included in the FCC blending tests. While the potential of wheat straw as  
 86 a renewable source of fuels and chemicals via FP has been recognized by others  
 87 [7, 8, 27–30], to the best of our knowledge wheat straw derived pyrolysis oils  
 88 (raw or deoxygenated) have not yet been tested for FCC co-feeding.

89 At fixed blending ratios between bio-oil and the FCC reference feed (20/80 by  
 90 weight), the blend was tested at a MAT unit at different catalyst-to-oil ratios  
 91 (cat/oil) in order to obtain complete yield curves and assess the impact of the  
 92 addition of bio-oils on the product distribution.

## 93 2. Experimental section

### 94 2.1. Bio-oil generation

#### 95 2.1.1. Pyrolysis

96 The experimental set-up, procedure, and the characteristics of the wood (pine)  
 97 and wheat straw feedstock are described elsewhere[31]. Briefly, biomass was  
 98 fed at  $\sim 200$  g/h to an ablative FP unit, operated at  $500^\circ\text{C}$  using pine and  
 99 at  $530^\circ\text{C}$  using wheat straw as feedstock. Char separation was achieved by  
 100 cyclones ( $450^\circ\text{C}$ ) and hot gas filtration using a ceramic filter candle  $350^\circ\text{C}$  up-  
 101 stream the ex-situ located catalytic fixed bed. Vapors were condensed in three

102 stages: At 4 °C, a series of metal impingers was used, followed by an electro-  
103 static precipitator (ESP) operated at room temperature, and a series of glass  
104 impingers cooled to -60 °C. Noncondensable gases (NCG) were analyzed us-  
105 ing NDIR and GC-TCD/FID. For both pine and straw feedstock, non-catalytic  
106 thermal reference oils were obtained by filling the catalytic reactor with 95 g  
107 SiC. To obtain partly deoxygenated wheat straw FP oil, 260 g HZSM-5/Al<sub>2</sub>O<sub>3</sub>  
108 extrudates (Extr) consisting of 65% HZSM-5 and 35% Al<sub>2</sub>O<sub>3</sub> binder were pro-  
109 vided by Haldor Topsøe A/S and steamed prior to its use by injecting water (2  
110 ml/min) into a preheated nitrogen stream (4 Nl/min) and passing the steam  
111 (~30 vol-%) for 5 h through the catalyst bed kept at 500 °C under atmospheric  
112 pressure conditions. The steamed extrudates were crushed, screened, and the  
113 fraction between 250–850 µm was used for the catalytic runs. Oil was collected  
114 first over the freshly steamed extrudate (Extr-st) after feeding a ratio of dry,  
115 ash free (daf) biomass-to-catalyst ratio (w/w, B:C) of 1.9. Subsequently, oil  
116 was collected over the pre-coked extrudate (Extr-st-u) during continued biomass  
117 feeding at B:C = 1.9–5.6. Coke combustion after the second upgrading interval  
118 was conducted according to the conditions described by Eschenbacher et al.[31]  
119 and allowed closing the mass balance to ~94%. Only the latter oil was used in  
120 the MAT experiments.

### 121 **2.1.2. Oil characterization.**

122 The oil characterization methodology was reported earlier[31, 32]. Karl Fis-  
123 cher titration, elemental analysis and GC-MS/FID was conducted for the mix-  
124 ture of oil fractions (mix OF) obtained at the 4 °C, the ESP, and the -60 °C  
125 condensation stage. The mixtures were prepared gravimetrically according to  
126 the oil’s yield at each condensation stage. The organics contained in the phase  
127 separated oil and water fractions are referred to as liquid-range organics. Since  
128 the sulfur concentration was below the detection limit of the elemental analyzer,  
129 the oil fractions (OF) were subjected to total sulfur analysis according to ASTM  
130 method D5453. In addition, analysis of the TAN, basic nitrogen content and  
131 evaporation characteristics was conducted, and the oils were analyzed using <sup>1</sup>H,

132  $^{13}\text{C}$ , and 2D HSQC NMR. For the investigation of the oils' evaporation behavior  
133 in a thermogravimetric analyzer (TGA simulated distillation), about 20 mg of  
134 oil were prepared into a Pt crucible with lid shortly before start of the heating.  
135 The temperature was ramped to 650 °C at 10 °C/min under  $\text{N}_2$  atmosphere.  
136 For details regarding the GPC system used for size exclusion chromatography  
137 of the oils, the reader is referred to our earlier work[31]. It should be noted that  
138 for mixtures of chemically similar compounds, the components with higher MW  
139 elute at lower retention volumes.

## 140 **2.2. MAT experiments**

### 141 **2.2.1. FCC catalyst pre-deactivation**

142 A commercial resid FCC catalyst was used in the study. The FCC catalyst  
143 was first impregnated with nickel and vanadium naphthenates according to the  
144 Mitchell method [34]. The target metals level after impregnation were 2500 ppm  
145 V, 1667 ppm Ni, *i.e.* a target V:Ni ratio of 3:2. Then the FCC catalyst was  
146 deactivated by Cyclic Propylene Steaming (CPS) [35]. The CPS deactivation  
147 was performed as recommended by Wallenstein et al.[36], but with some minor  
148 modifications: The deactivation temperature was 795 °C, and the number of de-  
149 activation cycles was 40. In addition, two deactivation cycles were run during the  
150 last part of heating of the deactivation unit. After CPS deactivation, the FCC  
151 catalyst had a zeolite surface area of 147  $\text{m}^2/\text{g}$  (micropores) and a matrix surface  
152 area of 36  $\text{m}^2/\text{g}$  (mesopores), resulting in a total surface area of 183  $\text{m}^2/\text{g}$ .

### 153 **2.2.2. FCC feed properties**

154 A North Sea Atmospheric Resid with properties as shown in Table 2 was used  
155 as reference feed in the MAT experiments. The boiling point distribution of the  
156 reference feed based on high-temperature simulated distillation (Fig. S1) shows  
157 that the feed mostly (85%) contained heavy cycle oil (HCO), boiling above  
158 350 °C, but it also contained approximately 15 wt% with a boiling point below  
159 350 °C, corresponding to light cycle oil (LCO) with a defined boiling point range  
160 of 225–350 °C. Three different pyrolysis oils were tested and their properties are  
161 described in more detail in Section 3.1 and Table 3. The oxygen content of



162 the reference oil is assumed to be close to zero and the TAN is expected to be  
163  $\sim 1$  mg KOH/g based on TAN-numbers for other North Sea atmospheric resids.  
164 The bio-oils tested in the MAT unit were blended with the reference feed in the  
ratio 20/80 by weight.

**Table 2.** Properties of FCC reference feed

|                                |        |
|--------------------------------|--------|
| Density (kg/l)                 | 0.9342 |
| Conradson Carbon Content (wt%) | 3.78   |
| Sulphur (wt%)                  | 0.46   |
| Vanadium (ppm)                 | 2.6    |
| Ni (ppm)                       | 4      |
| Na (ppm)                       | 2.8    |
| Fe (ppm)                       | 3.4    |
| Basic Nitrogen (ppm)           | 620    |

165

### 166 **2.3. MAT Testing**

The MAT experiments were done in a fully automated MAT unit, as described by Myrstad and Engan[33], with an oil injection time of 30 s and a reaction temperature of 525 °C. The catalyst/oil ratio in the experiments was varied by varying the amount of feed injected over a bed containing 3 g catalyst. For the catalytic cracking, the conversion [%] was defined as

$$\text{Conversion} = 100 - (\text{light cycle oil (LCO)} + \text{heavy cycle oil (HCO)}). \quad (1)$$

167 Besides light gases and coke formed on the catalyst, liquefied petroleum gas  
168 (LPG) was defined as  $C_3+C_4$  compounds and naphtha was defined as  $C_5+$   
169 compounds up to a boiling point of 221 °C.

170 As will be shown in Section 3.1, the bio-oils—especially the catalytically  
171 treated one—contained some components in the naphtha range. Since the  
172 biomass derived components are more reactive, it is likely that they are con-  
173 verted to both heavier and lighter product components during the cracking and  
174 the calculation of conversion was not adjusted for this aspect.

175 All results were normalized against the mass balance. Thus, the differences  
176 in the mass balances are the largest source of uncertainty in the experiments.

177 To reduce the uncertainty, only experiments with mass balances of  $100 \pm 2.5$  %  
178 were accepted. The standard deviation (SD) was not calculated in this paper  
179 but has earlier been reported to 0.51 wt% for 20 replicates[33]. The different  
180 yield curves are drawn by using linear, logarithmic, or exponential regression.  
181 The regression coefficient  $R^2$  can be used as an indication on the quality of  
182 the results. For the conversion vs. catalyst/oil curves and most yields  $R^2$  was  
183  $>0.95$ .  $R^2$  for the coke and naphtha yield curve were lower ( $\sim 0.8$ ).

### 184 **3. Results**

#### 185 **3.1. Bio-oil Generation & Characterization**

##### 186 **3.1.1. Product Distribution Bio-Oil**

187 Fig. S3 shows the product distributions from bio-oil generation (yields based  
188 on dry, ash-free biomass; reaction water excludes biomass induced moisture). As  
189 was noted earlier [31], compared to oil collected with an empty catalytic reactor,  
190 passing the vapors over a SiC bed slightly decreased the oil yields and its oxygen  
191 content. The coke yield amounted to  $\sim 0.1$  wt% of fed biomass when using the  
192 SiC bed, and to 4.2 wt% using the steamed HZSM-5/ $\text{Al}_2\text{O}_3$  extrudate after  
193 feeding of biomass corresponding to B:C = 0–5.6. Higher char and gas yields  
194 resulted when using wheat straw compared to wood, which led to a significantly  
195 lower yield of liquid-range organics, see Fig. S3. This can be attributed to the  
196 high ash content of straw (5.9%) compared to wood (0.2%), which is known to  
197 promote cracking and char formation[2, 5]. The upgrading of the vapors over the  
198 catalyst severely decreased the yield of liquid-range organics at B:C = 1.9 (at  
199 enhanced gas formation), while for B:C = 1.9–5.6 the losses to gas decreased and  
200 higher yields of liquid-range organics were obtained, yet only  $\sim 50\%$  compared  
201 to SiC (see Fig. S3).

##### 202 **3.1.2. Catalyst characterization**

203 Catalyst characterization of the HZSM-5/ $\text{Al}_2\text{O}_3$  extrudate has been reported  
204 in earlier work[32]. Table S1 and adjacent section in the supporting informa-  
205 tion summarize the physicochemical characterization of the catalyst used for  
206 deoxygenation of the wheat straw FP vapors.

### 207 3.1.3. Oil Properties

208 Table 3 provides an overview of important properties of the bio-oils tested for  
209 co-processing in the MAT. Each oil was prepared as a mixture of oil fractions  
210 obtained at three different condensation stages, and the analysis of these single  
211 oils (4 °C OF, ESP OF, -60 °C OF) is provided in Table S2–S4. A comparison of  
212 the straw oils shows that a higher fraction of the organics content was recovered  
213 in the water fraction (mix WF) for oils with higher oxygen content (Tables  
214 S3–S4). Along with the oils’ yield, moisture and oxygen content (wt% d.b.),  
215 Table 3 lists the oils’ TAN content and char remains upon TGA simulated  
216 distillation, with both the solid remains of the dry organics content at 300 °C  
217 and 500 °C indicated. The weight loss curves during TGA simulated distillation  
218 are shown in Fig. 1a. The TAN content refers to the “wet” oil samples, *i.e.* the  
219 oil fraction including the dissolved water. In addition, Table 3 includes sulphur  
220 analysis and density of the oils. Wood FP oil has 29.7 wt% O (d.b.), which  
221 shows some reduction compared to the feedstock (41.9 wt% O d.b.). Straw FP  
222 oil has a lower oxygen content and TAN compared to the wood oil (Table 3),  
223 however a slightly higher sulfur content (0.07 wt%) which agrees with the ~10  
224 fold higher S concentration in the feedstock. While a deep deoxygenation (2.9  
225 wt% O) was obtained for the catalytically upgraded oil at B:C = 1.9, the yield  
226 of the oil fraction was only 3.5 wt% of daf straw. Over the coked catalyst with  
227 reduced activity (B:C = 1.9–5.6), oil with 8.8 wt% O was obtained at almost  
228 three times higher oil yield (10 wt%).

229 When oxygen is released as water during the cracking of oxygenates over  
230 acidic catalysts, hydrogen is depleted which leads to enriched aromatics content  
231 in the products but also rapid coke formation. In view of this, the effective  
232 hydrogen to carbon ratio (EHI) as defined by Chen et al.[34] can be used to  
233 assess the coking propensity of the product mixture. EHI is defined as  $(H - 2O$   
234  $- 3N - 2S)/C$ , where H, C, O, N, and S are atoms per unit weight of sample of  
235 hydrogen, carbon, oxygen, nitrogen and sulfur, respectively. All three bio-oils  
236 have  $EHI < 1$ , which is indicative of their hydrogen deficiency. Pine-derived oil

237 showed the lowest EHI of 0.5 and lowest heating value (26.8 MJ/kg) due to its  
 238 higher oxygen content, while EHI and HHV were higher for the wheat straw  
 239 derived bio-oils, especially for the catalytically treated one.

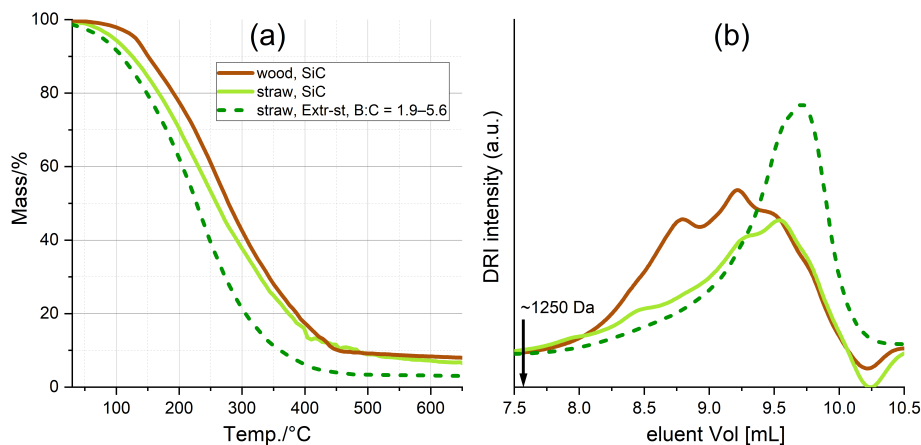
**Table 3.** Overview of properties of bio-oil: Oils yield (not including C<sub>4</sub>+ measured in gas), density, moisture, elemental composition (d.b.), TAN, basic nitrogen content, and mass remaining with respect to dry organics content upon heating to 500 °C in a TGA (Pt crucible with lid, 10 °C/min heating rate, 150 mL/min flowrate N<sub>2</sub>).

|   | Pine, SiC | Straw, SiC | Straw, Extr-st-u |
|---|-----------|------------|------------------|
| B:C                                       | 0–4.2     | 0–11.0     | 1.9–5.6          |
| Yield of oil phase (OF) [wt% of daf feed] | 25.5      | 19.4       | 10               |
| Density at 25 °C [g/ml]                   | 1.1752    | 1.105      | 1.0162           |
| H <sub>2</sub> O [%]                      | 7.8       | 14.7       | 2.3              |
| wt% C (d.b.)                              | 63.7      | 69.9       | 79.8             |
| wt% H (d.b.)                              | 6.5       | 7.1        | 7.9              |
| wt% N (d.b.)                              | 0.2       | 1.6        | 3.6              |
| wt% O (d.b.)                              | 29.7      | 21.4       | 8.8              |
| wt% S (d.b.)                              | 0.01      | 0.07       | 0.14             |
| Higher heating value (HHV) [MJ/kg]*       | 26.8      | 30.50      | 36.2             |
| Effective hydrogen index (EHI)*           | 0.50      | 0.69       | 0.90             |
| TAN [mg KOH/g]                            | 60.8      | 54.4       | 3.4              |
| Basic nitrogen content [ppm]              | 30        | 3920       | 5670             |
| Solid remains (w-% d.b.) at 300 °C/500 °C | 44.0/17.2 | 44.5/16.9  | 17.7/5.9         |

\*HHV was calculated based on the elemental composition of the oil according to correlations reported by Channiwala et al.[35], and the EHI parameter was defined by Chen et al.[34].

240 Despite different O content and MW distribution, the evaporation of straw  
 241 and pine oils obtained over SiC did not differ much (Fig. 1a, Table 3). The evap-  
 242 oration characteristics and TAN of the wheat straw derived FP oil improved by  
 243 the catalytic treatment (Table 3). Analysis by size exclusion chromatography  
 244 (SEC) shows several discernable components for the oils (Fig. 1b). For chem-  
 245 ically similar compounds, a higher retention volume indicates a shift to lower  
 246 molecular weight. Based on the elution of a dodecastyrene standard with MW

247 = 1250 Da at 7.57 mL, the oils contain compounds with MW <1000 Da. The  
 248 catalytically obtained straw derived oils show reduced contributions of high MW  
 249 compounds and a more intense refractive index (RI) response of low MW com-  
 250 pounds, especially the oil obtained at B:C = 0–1.9. While the wood and straw  
 251 derived oils show a similar distribution of low MW compounds eluting >9.5  
 252 mL, wood oil obtained over SiC contains a higher amount of compounds with  
 253 higher MW. The lower MW of the straw SiC oil is attributed to the additional  
 254 cracking effect induced by the alkaline ashes (especially K) during pyrolysis and  
 255 possibly upon contact of the vapors with the chars collected at the hot gas  
 256 filter[11, 36–38].



**Fig. 1.** (a) TGA simulated distillation curves of bio-oils. 20 mg of oil heated at 10 °C/min to 650 °C in 150 mL/min N<sub>2</sub>. (b) Differential refractive index (DRI) output for SEC chromatograms of bio-oils.

257 The quality of the condensed oils was further compared by their molar H/C  
 258 and O/C ratios (see Fig. S4). The thermochemical conversion of both wood  
 259 and straw produced oils with lower O/C and H/C ratio compared to the feed-  
 260 stock composition. Oil obtained from straw FP had a significantly lower O/C  
 261 ratio (0.24) compared to wood oil (0.35), while the H/C ratio of the two oils  
 262 was about the same (1.2). The energy recovery as phase separated oil fraction  
 263 amounted to 35.2% and 30.4% for wood and straw oils obtained over the ex-situ  
 264 SiC bed. For catalytically upgraded oils obtained from straw at B:C = 1.9–5.6,

265 the energy recovery was 18.6%. Table 4 shows an overview of the proton NMR  
266 analysis of the oils, and the corresponding spectra are provided in Fig. S5. For  
267 straw derived oils, the most pronounced change upon catalytic upgrading of the  
268 vapors is the clearly enhanced proton concentration of aromatics and conjugated  
269 alkenes from 12% for SiC to 31.9% for oil obtained at B:C = 1.9–5.6. The H%  
270 of oxygenates and aliphatics (6–2 ppm) shows an inversely related trend and  
271 decreases from 62.7% (SiC) to 47.30% for B:C = 1.9–5.6. The H% of pine oil  
272 (from SiC bed) shows a higher contribution of carboxyl-groups compared to the  
273 straw oil, in agreement with a higher TAN of the former. In addition, carbonyl  
274 groups, phenols and aromatics show higher H% compared to the wheat straw-  
275 derived oil, which is likely the result of the elevated lignin content of wood (31.1  
276  $\pm 0.8$  wt%) compared to straw (20.2  $\pm 1.5$  wt%). Table 5 provides the overview  
277 of the  $^{13}\text{C}$  NMR characterization of the oils and the corresponding  $^{13}\text{C}$  NMR  
278 spectra are provided in Fig. S6 and S7. It is noted that the C% of the wood  
279 FP oil was calculated based on the  $^{13}\text{C}$  NMR analysis of the three oils collected  
280 at the different condensation stages and their weight yields on dry basis. The  
281 pine derived SiC oil shows a higher C contribution of aldehydes, ketones, lev-  
282 oglucosan, anhydrosugars, alcohols, ethers, and lignin derived methoxyl-groups  
283 compared to the straw oil, which agrees with the higher oxygen content of the  
284 former. In agreement with the  $^1\text{H}$  NMR results for the straw derived oils, the C  
285 content of aromatics (including olefins and phenols) increases from 36% (SiC) to  
286 56.9% for B:C = 1.9–5.6. Enhanced phenol yields besides aromatics for HZSM-5  
287 based catalysts were also observed by others[39–41] and agrees with our GC-  
288 MS/FID results, especially for oil obtained at B:C = 1.9–5.6 (Table S5). Phenols  
289 were pointed out to have low reactivity and may strongly adsorb to the active  
290 sites on HZSM-5 and contribute to coke formation[42, 43]. The C content of  
291 the oils associated with oxygenates (220–160 ppm and 105–55 ppm) decreased  
292 from 27.6% to 9.3% for B:C = 1.9–5.6. This observation is further confirmed  
293 by 2D HSQC NMR (see Fig. S8), which shows that especially sugars and -CH-  
294 O- groups are still effectively converted over the pre-coked HZSM-5 extrudates  
295 (B:C = 1.9–5.6).

**Table 4.** Hydrogen percentage based on the  $^1\text{H}$  NMR analysis of the bio-oils.

| Assignment                                   | Chemical shift range (ppm) | Pine, SiC | Straw, SiC | Straw, Extr-st-u, B:C = 1.9–5.6 |
|--|----------------------------|-----------|------------|---------------------------------|
| -COOH  | 12.5–11.0                  | 1.0%      | 0.2%       | 0.1%                            |
| -CHO, ArOH                                   | 11–8.2                     | 6.2%      | 0.7%       | 3.5%                            |
| Aromatics and conjugated alkene H            | 8.2–6                      | 17.6%     | 12.0%      | 31.9%                           |
| Aliphatic OH, -CH=CH-, ArCH <sub>2</sub> -OR | 6–4.2                      | 11.8%     | 4.7%       | 1.2%                            |
| RCH <sub>2</sub> O-R, CH <sub>3</sub> OR     | 4.2–3                      | 21.2%     | 9.6%       | 2.2%                            |
| Aliphatic H, -CHR-C=O, -CHR-C=C              | 3.0–2.0                    | 20.8%     | 48.4%      | 43.9%                           |
| Aliphatic H                                  | 2.0–0                      | 21.4%     | 24.6%      | 17.2%                           |

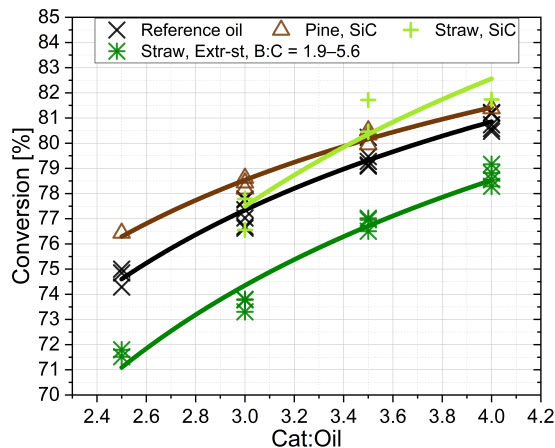
**Table 5.** Carbon percentage based on the  $^{13}\text{C}$  NMR analysis of the bio-oils.

| Assignment                                    | Chemical shift range (ppm) | Pine, SiC | Straw, SiC | Straw, Extr-st-u, B:C = 1.9–5.6 |
|---|----------------------------|-----------|------------|---------------------------------|
| Aldehydes, ketones                            | 220–180                    | 8.4%      | 7.8%       | 4.2%                            |
| CO groups (carboxylic acids and derivatives)  | 180–160                    | 6.6%      | 7.6%       | 2.2%                            |
| Total Ar including olefins and phenolics      | 160–105                    | 40.1%     | 36.0%      | 56.9%                           |
| Carbons in aromatic HC further from an O atom | 140–125                    | 8.9%      | 9.1%       | 28.6%                           |
| Levoglucosan, anhydrosugars, alcohols, ethers | 105–60                     | 15.4%     | 8.3%       | 2.5%                            |
| Methoxyl-group in lignin                      | 57– 55                     | 4.4%      | 3.9%       | 0.4%                            |
| Aliphatic hydrocarbons                        | 55–0                       | 25.1%     | 36.4%      | 33.7%                           |

296 **3.2. Results Co-processing Bio-oils with FCC Feed**

297 Fig. 2 shows the conversion of the different bio-oils mixed with the reference  
 298 feed at increasing cat/oil ratios. The conversion for co-processing of the catalyt-

299 ically upgraded pyrolysis oil was significantly lower than when the reference oil  
 300 was processed alone. Without catalytic upgrading, the conversion was higher  
 301 than or similar to the reference oil, and the pyrolysis oil originating from wheat  
 302 straw and pine wood showed similar conversion behavior.



**Fig. 2.** Conversion from co-processing of bio-oil at different catalyst/oil ratios.

303 Table 6 compares the product yields from co-processing of the different bio-  
 304 oils in the MAT at a fixed conversion of 77.5%. The pine pyrolysis oil showed  
 305 similar yields to the reference oil. Compared with the reference oil, the wheat  
 306 straw pyrolysis oil without catalytic treatment gave a higher coke yield and  
 307 correspondingly a lower LPG yield. For the catalytically treated wheat straw  
 308 pyrolysis oil, this effect was even higher, resulting in an even higher coke yield  
 309 and lower LPG yield (Table 6). This result seems surprising at first considering  
 310 the lower MW, higher volatility, reduced oxygen content, and higher EHI of  
 311 the upgraded oil compared to the raw wheat straw oil. However, the observa-  
 312 tions can be reasoned based on the higher concentration of aromatics, phenolics  
 313 and nitrogen containing compounds for the partly deoxygenated oil obtained  
 314 derived from using HZSM-5 based catalyst for vapor deoxygenation, as will be  
 315 elaborated in the discussion (Section 4).



**Table 6.** Yield comparison from MAT at constant conversion of 77.5%.

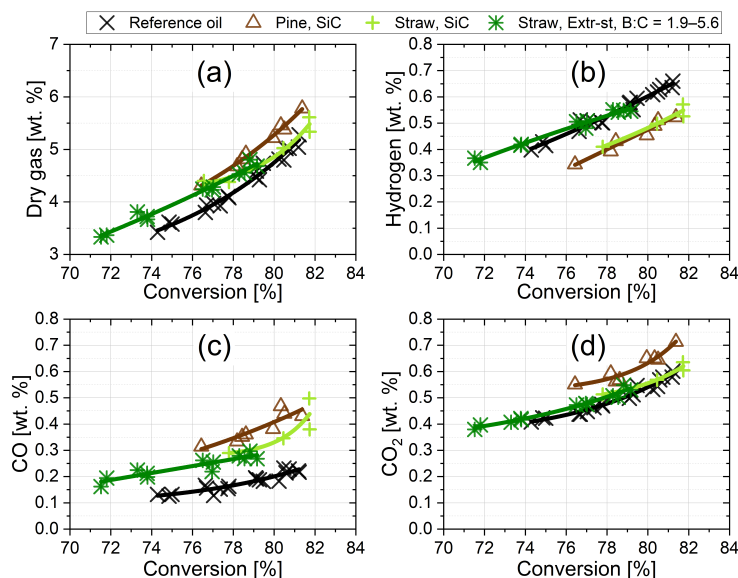
|                                | Reference oil | Pine, SiC | Straw, SiC | Straw, Extr-st-u,<br>B:C = 1.9-5.6 |
|--------------------------------|---------------|-----------|------------|------------------------------------|
| Catalyst/oil                   | 3.1           | 2.7       | 2.6        | 3.7                                |
| Yields (wt%)                   |               |           |            |                                    |
| CO                             | 0.16          | 0.38      | 0.27       | 0.25                               |
| CO <sub>2</sub>                | 0.47          | 0.54      | 0.51       | 0.49                               |
| Hydrogen                       | 0.51          | 0.38      | 0.4        | 0.51                               |
| C <sub>1</sub> +C <sub>2</sub> | 3.6           | 3.9       | 4          | 3.9                                |
| LPG                            | 16            | 16        | 14.8       | 14.1                               |
| Naphtha                        | 45.1          | 45.2      | 44.2       | 44                                 |
| LCO                            | 14.2          | 14.3      | 14.3       | 14.3                               |
| HCO                            | 8.3           | 8.2       | 8.2        | 8.2                                |
| Coke                           | 11.7          | 11.1      | 13.3       | 14.3                               |

316 Commercially, FCC units are often operated at constant coke generation and a  
317 comparison of the MAT results at constant coke yield thus can be more realistic.  
318 Compared with the reference oil at constant coke yield (11.7 wt%), the wheat  
319 straw pyrolysis oil without catalytic treatment gave a lower conversion and thus  
320 higher yields of LCO and HCO, and a corresponding lower LPG yield (see  
321 Table 7). For the catalytically treated wheat straw FP oils, this effect was even  
322 higher, *i.e.* an even lower conversion and higher yields of LCO and HCO, and  
323 lower LPG yields. Fig. 3a shows the yield of dry gas, which is defined as the  
324 sum of C<sub>1</sub>+C<sub>2</sub> hydrocarbons and hydrogen. All pyrolysis oils gave higher dry  
325 gas yields than the reference oil. The pine pyrolysis oil gave a higher dry gas  
326 yield than the wheat straw pyrolysis oils, and there was no significant effect of  
327 the catalytic treatment of the wheat straw pyrolysis oil on the total dry gas  
328 yield. Considering the hydrogen yields (Fig. 3b), the two pyrolysis oils without  
329 catalytic treating gave similar hydrogen yields, lower than the reference oil. The  
330 catalytically treated wheat straw pyrolysis oil gave similar hydrogen yields as

**Table 7.** Yield comparison from MAT at fixed coke yield of 11.7 wt%.

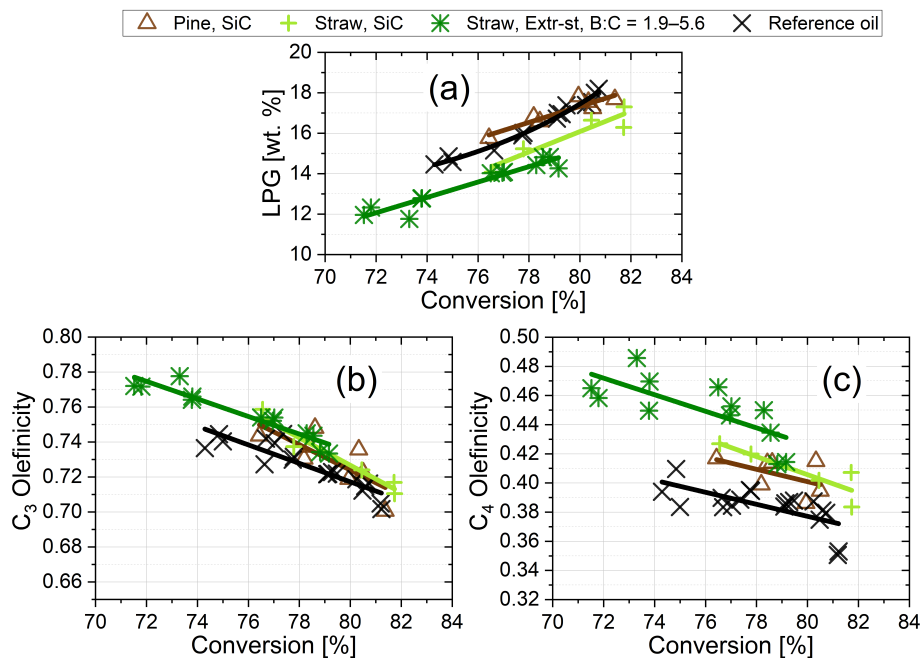
|                                | Reference oil | Pine, SiC | Straw, SiC | Straw, Extr-st-u,<br>B:C = 1.9-5.6 |
|--------------------------------|---------------|-----------|------------|------------------------------------|
| Conversion                     | 77.5          | 77.9      | 75.1       | 74.2                               |
| catalyst/oil                   | 3.1           | 2.9       | 2          | 3                                  |
| Yields (wt%)                   |               |           |            |                                    |
| CO                             | 0.16          | 0.33      | 0.18       | 0.2                                |
| CO <sub>2</sub>                | 0.47          | 0.57      | 0.46       | 0.43                               |
| Hydrogen                       | 0.51          | 0.4       | 0.34       | 0.43                               |
| C <sub>1</sub> +C <sub>2</sub> | 3.6           | 4.2       | 3.6        | 3.3                                |
| LPG                            | 16            | 16.4      | 13.7       | 12.9                               |
| Naphtha                        | 45.1          | 44.3      | 45.1       | 45.1                               |
| LCO                            | 14.2          | 14.2      | 15.7       | 16.1                               |
| HCO                            | 8.3           | 7.9       | 9.2        | 9.7                                |

331 the reference oil. This agrees with higher values of H/C and EHI of the partly  
332 deoxygenated oil compared to the raw FP oils. All the pyrolysis oils tested  
333 gave significantly higher yields of CO than the reference oil (Fig. 3c). The  
334 pine pyrolysis oil gave higher CO yield than the wheat straw pyrolysis oils, as  
335 expected from its higher O-content. The same effect could also be observed for  
336 CO<sub>2</sub>, but less pronounced (Fig. 3d).



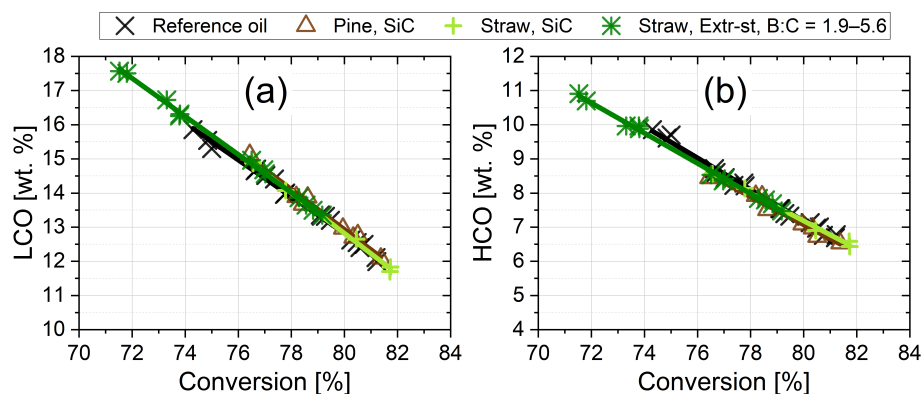
**Fig. 3.** Yields of gas species for reference oil and 80/20 blend with different bio-oils. (a) Yields of dry gas, that is  $C_1+C_2$  hydrocarbons plus hydrogen, (b) Hydrogen yields, (c) CO yields, and (d)  $CO_2$  yields.

337 The pine pyrolysis oil gave similar LPG-yields as the reference oil. The wheat  
 338 straw pyrolysis oils gave lower LPG yields, whereas the catalytically  
 339 wheat straw pyrolysis oil gave the lowest LPG-yield (see Fig. 4a). The  $C_3$  and  
 340  $C_4$  olefinicity of LPG is defined as the ratio of propene to total  $C_3$  and the ratio of  
 341 butene to total  $C_4$ , respectively. The pyrolysis oils gave higher LPG olefinicity  
 342 than the reference oil. (Fig. 4b+c). The effect was especially pronounced in  
 343 the  $C_4$  fraction (Fig. 4c). No significant difference between the wheat straw  
 344 pyrolysis oil and the pine pyrolysis oil could be observed, but the catalytically  
 345 treated wheat straw pyrolysis oil gave an even higher LPG olefinicity.

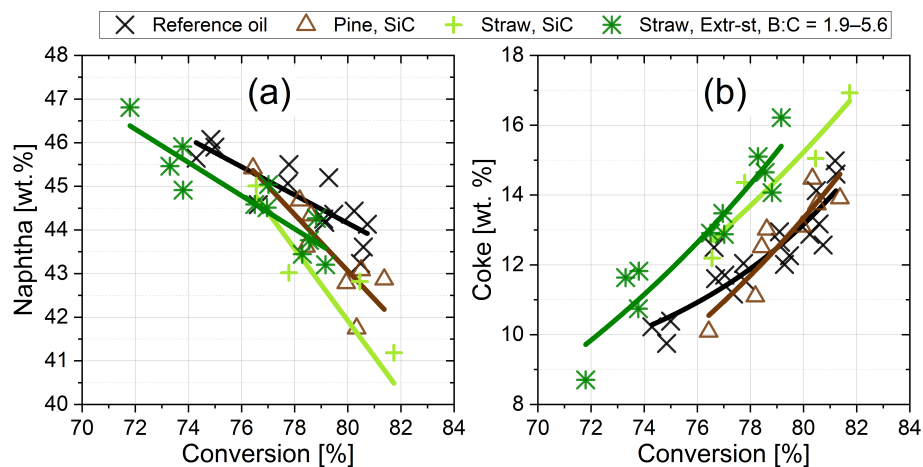


**Fig. 4.** (a) Yields of LPG ( $C_3+C_4$ ) when processing reference oil and 80/20 blends of reference oil with different bio-oils. (b) and (c) show the LPG olefinicity for  $C_3$  and  $C_4$  (b), which is defined as the ratio of propene to total  $C_3$  and the ratio of butene to total  $C_4$ , respectively.

346 Only small differences could be observed for LCO (221-350 °C) and HCO  
 347 (350 °C+) for the different oils tested (see Fig. 5). The processing of blends  
 348 of pyrolysis oil and reference oil resulted in lower naphtha yields ( $C_5-221$  °C)  
 349 compared to processing of 100% reference oil (see Fig. 6a). The pine pyrolysis  
 350 oil gave a slightly higher naphtha yield than the wheat straw pyrolysis oils, and  
 351 there was no significant effect of the catalytic treatment of the wheat straw  
 352 pyrolysis oil on the naphtha yield during co-processing. Note that the exper-  
 353 imental points were obtained in the over-cracking region, where the naphtha  
 354 yield decreases with increasing conversion. Fig. 6b shows a comparison of the  
 355 coke yields. The wheat straw pyrolysis oils with and without catalytic treat-  
 356 ment gave higher coke yields than the reference oil. The pine pyrolysis oil gave  
 357 similar coke yield as the reference oil.



**Fig. 5.** (a) Yields of LCO (221-350 °C) and (b) Yields of HCO (350 °C+) for the different oils tested.



**Fig. 6.** Yields of naphtha (a) and coke (b) when processing reference oil and 80/20 blends of reference oil with different bio-oils in the MAT.

#### 358 4. Discussion

359 A rough calculation indicates that at 80 % conversion, the coke yield was  
 360 about 28 wt% from the wheat straw bio-oils, indicating that a significant amount  
 361 of biogenic carbon was lost to coke on the FCC catalyst.

362 While water was not analyzed for in the products from these tests, the blend-  
363 ing of the FCC reference feed with bio-oil introduced water in the feed and  
364 additional water may be formed during catalytic cracking of pyrolysis oils. In  
365 general, the influence of this on the results is minor compared to the mass bal-  
366 ances uncertainty, as discussed in detail in the SI, Tables S6 and S7. However,  
367 the corrected yield for naphtha could be about 6 percentage points lower for the  
368 blends with raw FP oils due to their higher moisture content and possibly higher  
369 yield of cracking water by oxygen removal via dehydration, while it could only  
370 be about 2 percentage points lower for the blends with catalytic fast pyrolysis  
371 oil. Taking into account these considerations, it can be concluded that for the  
372 interpretation of the naphtha yields (Fig. 6a) all blends with bio-oils resulted in  
373 lower naphtha yields compared to processing of 100% reference oil. In addition,  
374 it is possible that the blends with untreated wood and straw FP oils produced  
375 less naphtha compared to the catalytically treated FP oil.

376 Untreated pyrolysis oils have a very high TAN number ( $>50$  mg KOH/g),  
377 which can cause severe corrosion in commercial operation[44]. The TAN of  
378 pyrolysis oils is effectively reduced by catalytic upgrading of the vapors prior  
379 to condensation, however, the oil yield decreases with the severity of the vapor  
380 deoxygenation. Mild deoxygenation of the pyrolysis vapor over a pre-coked  
381 HZSM-5/ $\text{Al}_2\text{O}_3$  catalyst, as applied in this work, obtained higher bio-oil yields  
382 compared to upgrading over a fresh catalyst due to the reduced carbon losses  
383 to gas and coke, while the TAN of the obtained oil (3.4 mg KOH/g) was still  
384 considerably lowered compared to the raw FP oil[31, 32]. The TAN-number  
385 for the reference feed used in this study was not measured, but based on TAN-  
386 numbers for other North Sea atmospheric resids, the value is assumed to be close  
387 to 1 mg KOH/g. Assuming a maximum allowable TAN for the blended feed  
388 of  $\sim 2$  mg KOH/g in order to prevent corrosion of the FCC plant, the residual  
389 acidity of the pyrolysis oil could then be accommodated by diluting with crude  
390 oil or an internal refinery stream (naphtha, gas oil, etc.)[12]. Thus, for untreated  
391 wood and straw bio-oils the blend ratio would have to be limited to 1–2 wt%  
392 bio-oil, while up to  $\sim 40$  wt% could be blended in the case of the catalytically  
393 upgraded oil.

394 On the other hand, 39% of the energy of the wheat straw FP oil was lost by  
395 the pre-cracking, and the conversion of the blend with deoxygenated oil in the  
396 subsequent MAT tests was lower compared to the raw bio-oil. This indicates  
397 that HZSM-5 based catalysts may not be the optimal choice for this application.  
398 HZSM-5 is well known for its high aromatization activity and lower coke yields  
399 compared to other zeolites. However, besides monoaromatics also higher con-  
400 centrations of phenols and nitrogen-containing compounds were observed in the  
401 product mixture, and all three product groups may negatively affect the con-  
402 version when added to an FCC feedstock [45]. Once the deoxygenation activity  
403 of HZSM-5 decreases, more oxygen and nitrogen appears to be retained in the  
404 hydrocarbon pool, leading to the formation of hetero-aromatics with nitrogen  
405 and oxygen[46]. In catalytic cracking, aromatic rings are difficult to crack and  
406 tend to polymerize and form coke. In addition, phenolic molecules can have  
407 a detrimental impact on the zeolite component of FCC catalysts[47, 48]. The  
408 deoxygenated oil contained higher concentrations of aromatics (1-3 rings) and  
409 the concentration of phenolics determined by GC-MS/FID was 6.5 times higher  
410 compared to oil obtained over SiC[32]. Since the deoxygenated oil was collected  
411 at B:C = 1.9–5.6, it is very likely that the production of phenolics was partic-  
412 ularly favored in this range as opposed to B:C <1.9 or operation to very high  
413 B:C ratios which would approach the composition of the SiC oil.

414 Basic nitrogen is a well-known catalyst poison in catalytic cracking[49–51].  
415 Decreased gasoline yields and increased hydrogen yields (compared at constant  
416 conversion) were observed by Caeiro et al.[50] for increasing feedstock basic ni-  
417 trogen content. For conventional refinery feedstock, the content of basic nitrogen  
418 is usually about one third of the total nitrogen[51–53]. The basic nitrogen con-  
419 tent of the wheat straw oils obtained with SiC and HZSM-5/Al<sub>2</sub>O<sub>3</sub> was 3920  
420 and 5670 ppm, which is less than one third of the total nitrogen content of the  
421 oils (see Table 3) but still considerably higher compared to the basic nitrogen  
422 content of the reference feed (620 ppm). Basic nitrogen compounds may reduce  
423 the cracking activity by (i) site competition due to their reversible adsorption  
424 to Brønsted and Lewis acid sites, and (ii) acting as coke precursors due to their  
425 size and aromatic nature. The nitrogen content of the severely deoxygenated

oil collected at B:C = 1.9 with 2.9 wt% O and 6.6 wt% C recovery was only 1.5 wt%, while the oil collected at B:C = 1.9–5.6 had increased carbon recovery of 17.1 wt% but contained 3.6 wt% N. Analysis by GC-MS/FID indicated that methyl- and dimethyl-pyridine, as well as dimethyl-indazole are amongst the highest concentrated nitrogen compounds in the oil collected at B:C=1.9–5.6 and the concentration of N containing compounds was about twice as high compared to the non-catalytically treated wheat straw oil and the oil collected at B:C = 0–1.9 over HZSM-5/Al<sub>2</sub>O<sub>3</sub>. With increasing catalyst deactivation, a shift to higher MW compounds occurred which lie outside the identification range of the applied gas chromatography method. While non-basic nitrogen compounds and condensed aromatics contribute to coke formation on the external surface of zeolite crystallites and pore blockage[54], the poisoning ability of bulkier nitrogen bases is even higher[52, 55]. Xu et al.[56–60] demonstrated that N-heterocycles (pyridines, pyrroles, anilines and indoles) can be produced via reaction of biomass derived oxygenates and ammonia. Even though not measured directly, some ammonia may be produced from the FP of wheat straw containing ~1 wt% N (d.b.) and lead to the formation of N-heterocycles.

The present results agree with Stefanidis et al.’s review[17] indicating that most studies that investigated co-processing of bio-oil found decreased naphtha yields. Lower hydrogen yields compared to the reference feed upon co-feeding of untreated pyrolysis oils were also observed by others[4, 15, 22, 25, 61]. Increased coke yields upon co-feeding of both raw and CFP oils agrees with Lindfors et al.s work[19], who tested CFP oil (22 wt% O) at the same blending ratio as this study (20/80), however at lower conversions (30–41%). It should be noted that lab scale co-processing of bio-oils to FCC units may overestimate the coke yields[15, 62]. In contrast to larger operation scale, a thermal shock between the hot catalyst and the bio-oil is not possible at laboratory scale and the non-vaporized fraction of the bio-oil will yield more char/coke upon reheating[22]. The thermal shock allows to break high MW compounds in larger scale units and improves the accessibility to the micropores of the catalyst[26]. This was confirmed by Wang et al.[4] who attributed their good results in terms of almost complete oxygen removal during FCC co-processing to the larger operating scale and the



458 benefits of thermal shock effect in their pilot-scale unit. Several researchers  
459 have investigated FCC of upgraded FP oils mixed with crude oil distillates in  
460 MAT units[26, 63–65]. While co-refining may lead to severe changes in product  
461 quality, such as a higher aromaticity and residual oxygenates in the hybrid fuels  
462 that are produced, it was concluded that a compromise can be reached between  
463 bio-oil upgrading severity and FCC product yields and quality.

464 To allow processing in FCC, the oils oxygen and nitrogen content has to be  
465 taken into account as they affect plant corrosion and FCC catalyst deactivation.  
466 While the reduced TAN and polarity of the deoxygenated oil will allow higher  
467 blend ratios compared to untreated bio-oil considering corrosion and miscibility,  
468 the current study shows that the basic nitrogen content has to be taken into  
469 account as well since it affects FCC catalyst deactivation. Thus, catalytically  
470 treated wheat straw oil obtained with HZSM-5 based catalysts may require  
471 further hydrotreating prior to FCC in order to saturate condensed aromatics,  
472 remove phenols and reduce the content of basic nitrogen[51, 66]. While it is  
473 desirable to develop a nitrogen-resistant FCC catalyst[50, 67–69], the nitrogen  
474 poisoning is reversible, as the nitrogen components are burned in the FCC  
475 regenerator (see Peng *et al.*[45], and references therein).

476 Mild upgrading by cracking increases the energy recovery of bio-oil compared  
477 to deep deoxygenation[32]. Higher coke yields upon co-feeding of bio-oil may  
478 be tolerable to some extent as the oxidative regeneration generates the energy  
479 required to run the endothermic cracking process[70]; however, increased coke  
480 yields in combination with lower conversion as was observed for blends with  
481 catalytically deoxygenated wheat straw oil indicates a less desirable FCC per-  
482 formance.

## 483 5. Conclusion

484 Two untreated fast pyrolysis oils from pine and wheat straw and a catalyti-  
485 cally treated wheat straw fast pyrolysis oil were blended in a 20/80 ratio with  
486 FCC reference feed oil and tested in a MAT containing a partly deactivated

487 FCC catalyst. Fast pyrolysis oil from pine performed best as it resulted in sim-  
488 ilar product and coke yields compared to the reference oil. The conversion of  
489 blends with untreated oils from pine and wheat straw was higher compared to  
490 the reference oil, however, blends with the wheat straw oil resulted in higher  
491 coke and lower LPG yields. Catalytically upgraded straw pyrolysis oil gave an  
492 even higher coke yield and lower LPG yield and resulted in lower conversions  
493 compared to the reference oil. All the pyrolysis oils gave lower naphtha yield  
494 than the reference oil and the pine pyrolysis oil gave a slightly higher naphtha  
495 yield compared to the straw oils. The study shows that not only wood derived  
496 pyrolysis oils but also pyrolysis oils obtained from agricultural residues such as  
497 wheat straw could contribute to the refinery input stream. However, the reduc-  
498 tion of the TAN via deoxygenation of wheat straw fast pyrolysis vapors over  
499 HZSM-5/Al<sub>2</sub>O<sub>3</sub> increased the nitrogen concentration of the stabilized oil, which  
500 in turn had a poisoning effect on the FCC catalyst. The basic nitrogen content  
501 of fast pyrolysis oils produced from agricultural residues with elevated nitrogen  
502 content shall thus be taken into account during the catalyst optimization for  
503 deoxygenation of fast pyrolysis vapors.

## 504 **ASSOCIATED CONTENT**

### 505 **Supporting Information**

506 NH<sub>3</sub>-TPD of HZSM-5 extrudate; Moisture content, HHV and elemental anal-  
507 ysis of oil and aqueous fractions; TGA simulated distillation curves; Size exclu-  
508 sion chromatograms; molar H/C ratio and O/C ratio of oils; <sup>1</sup>H NMR and <sup>13</sup>C  
509 NMR spectra; HSQC NMR spectra; yields obtained by GC-MS/FID analysis.

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523 **ABBREVIATIONS**

524 BET, Brunauer-Emmett-Teller; CFP, catalytic fast pyrolysis; CPS, cyclic  
525 propylene steaming; daf, dry and ash-free basis; d.b., dry basis; HCO; heavy  
526 cycle oil; FCC, Fluid Catalytic Cracking; GC-MS/FID, gas chromatography  
527 mass spectrometry with flame ionization detection; HHV, higher heating value;  
528 LCO, light cycle oil; LPG, liquid petroleum gas; MW, molecular weight; NMR,  
529 nuclear magnetic resonance; SEC, size exclusion chromatography; TAN, total  
530 acid number; TGA, thermogravimetric analysis; OF, oil fraction; VGO, vacuum  
531 gas oil; WF, water fraction;

532 **References**

- 533 [1] G. W. Huber, A. Corma, Synergies between bio- and oil refineries for the  
534 production of fuels from biomass, *Angewandte Chemie - International Edi-*  
535 *tion* 46 (38) (2007) 7184–7201. doi:10.1002/anie.200604504.
- 536 [2] N. Tröger, D. Richter, R. Stahl, Effect of feedstock composition on product  
537 yields and energy recovery rates of fast pyrolysis products from different  
538 straw types, *J. Anal. Appl. Pyrolysis* 100 (2013) 158–165. doi:10.1016/  
539 j.jaap.2012.12.012.
- 540 [3] C. W. Edmunds, E. A. R. Molina, N. Andre, C. Hamilton, S. Park,  
541 O. Fasina, S. Adhikari, S. S. Kelley, J. S. Tumuluru, T. G. Rials, N. Labbe,  
542 Blended Feedstocks for Thermochemical Conversion: Biomass Character-  
543 ization and Bio-Oil Production From Switchgrass-Pine Residues Blends,  
544 *Front. Energy Res.* 6 (August) (2018) 16. doi:10.3389/fenrg.2018.

545

00079.

546 [4] C. Wang, M. Li, Y. Fang, Coprocessing of Catalytic-Pyrolysis-Derived Bio-  
547 Oil with VGO in a Pilot-Scale FCC Riser, *Ind. Eng. Chem. Res.* 55 (12)  
548 (2016) 3525–3534. doi:10.1021/acs.iecr.5b03008.

549 [5] D. L. Carpenter, T. L. Westover, S. Czernik, W. Jablonski, Biomass feed-  
550 stocks for renewable fuel production: a review of the impacts of feed-  
551 stock and pretreatment on the yield and product distribution of fast py-  
552 rolysis bio-oils and vapors, *Green Chem.* 16 (2) (2014) 384–406. doi:  
553 10.1039/C3GC41631C.

554 [6] B. Rejai, S. C. S. C. Engineer, R. J. Evans, S. Chemist, P. Chemist, J. P.  
555 Diebold, P. C. Engineer, J. W. Scahill, S. C. S. C. Engineer, C. Conversion,  
556 The conversion of biobased feedstocks to liquid fuels through pyrolysis, in:  
557 Energy From Biomass and Wastes Xv, INST GAS TECHNOLOGY, 1991,  
558 pp. 855–876.

559 [7] T. N. Trinh, P. A. Jensen, D. J. Kim, N. O. Knudsen, H. R. Sørensen,  
560 S. Hvilsted, Comparison of lignin, macroalgae, wood, and straw fast pyrol-  
561 ysis, *Energy Fuels* 27 (3) (2013) 1399–1409. doi:10.1021/ef301927y.

562 [8] C. E. Greenhalf, D. J. Nowakowski, A. B. Harms, J. O. Titiloye, A. V.  
563 Bridgwater, A comparative study of straw, perennial grasses and hard-  
564 woods in terms of fast pyrolysis products, *Fuel* 108 (2013) 216–230. doi:  
565 10.1016/j.fuel.2013.01.075.

566 [9] A. V. Bridgwater, G. V. C. Peacocke, Fast pyrolysis processes for biomass,  
567 *Renewable & Sustainable Energy Reviews* 4 (1) (2000) 1–73. doi:10.1016/  
568 S1364-0321(99)00007-6.

569 [10] A. Oasmaa, S. Czernik, Fuel oil quality of biomass pyrolysis oil - State of  
570 the art for the end users, *Energy & Fuels* 13 (4) (1999) 914–921. doi:  
571 10.1021/ef980272b.

- 572 [11] S. Czernik, A. V. Bridgwater, Overview of applications of biomass fast py-  
573 rolysis oil, *Energy & Fuels* 18 (2) (2004) 590–598. doi:10.1021/ef034067u.
- 574 [12] M. S. Talmadge, R. M. Baldwin, M. J. Bidy, R. L. McCormick, G. T.  
575 Beckham, G. A. Ferguson, S. Czernik, K. A. Magrini, T. D. Foust, P. D.  
576 Metelski, C. Hetrick, M. R. Nimlos, A perspective on oxygenated species in  
577 the refinery integration of pyrolysis oil, *Green Chem.* 16 (2) (2014) 407–453.  
578 doi:10.1039/C3GC41951G.
- 579 [13] R. French, S. Czernik, Catalytic pyrolysis of biomass for biofuels produc-  
580 tion, *Fuel Process. Technol.* 91 (1) (2010) 25–32. doi:10.1016/j.fuproc.  
581 2009.08.011.
- 582 [14] K. Maniatis, L. Waldheim, S. Kalligeros, Final Report Building Up the  
583 Future Sub Group on Advanced Biofuels Sustainable Transport Forum,  
584 2017.
- 585 [15] A. d. R. Pinho, M. B. de Almeida, F. L. Mendes, L. C. Casavechia, M. S.  
586 Talmadge, C. M. Kinchin, H. L. Chum, Fast pyrolysis oil from pinewood  
587 chips co-processing with vacuum gas oil in an FCC unit for second gen-  
588 eration fuel production, *Fuel* 188 (2017) 462–473. doi:10.1016/j.fuel.  
589 2016.10.032.
- 590 [16] T. Marker, J. Petri, T. Kalnes, M. McCall, D. Mackowiak, B. Jerosky,  
591 B. Reagan, L. Nemeth, M. Krawczyk, S. Czernik, D. C. Elliott, D. Shon-  
592 nard, Opportunities for Biorenewables in Oil Refineries, Tech. rep., Golden  
593 Field Office, Golden, CO (dec 2005). doi:10.2172/861458.  
594 URL <http://www.osti.gov/servlets/purl/861458-Wv5uum/>
- 595 [17] S. D. Stefanidis, K. G. Kalogiannis, A. A. Lappas, Co-processing bio-oil  
596 in the refinery for drop-in biofuels via fluid catalytic cracking, *Wiley In-  
597 terdisciplinary Reviews: Energy and Environment* (October) (2017) e281.  
598 doi:10.1002/wene.281.

- 599 [18] M. Bertero, U. Sedran, Coprocessing of Bio-oil in Fluid Catalytic Cracking,  
600 Recent Advances in Thermochemical Conversion of Biomass (2015) 355–  
601 381doi:10.1016/B978-0-444-63289-0.00013-2.
- 602 [19] C. Lindfors, V. Paasikallio, E. Kuoppala, M. Reinikainen, A. Oasmaa,  
603 Y. Solantausta, Co-processing of dry bio-oil, catalytic pyrolysis oil, and hy-  
604 drotreated bio-oil in a micro activity test unit, Energy Fuels 29 (6) (2015)  
605 3707–3714. doi:10.1021/acs.energyfuels.5b00339.
- 606 [20] A. de Rezende Pinho, M. B. B. de Almeida, F. L. Mendes, V. L. Ximenes,  
607 Production of lignocellulosic gasoline using fast pyrolysis of biomass and  
608 a conventional refining scheme, Pure Appl. Chem. 86 (5). doi:10.1515/  
609 pac-2013-0914.
- 610 [21] Á. Ibarra, E. Rodríguez, U. Sedran, J. M. Arandes, J. Bilbao, Synergy in  
611 the Cracking of a Blend of Bio-oil and Vacuum Gasoil under Fluid Catalytic  
612 Cracking Conditions, Ind. Eng. Chem. Res. 55 (7) (2016) 1872–1880. doi:  
613 10.1021/acs.iecr.5b04502.
- 614 [22] A. D. R. Pinho, M. B. De Almeida, F. L. Mendes, V. L. Ximenes, L. C.  
615 Casavechia, Co-processing raw bio-oil and gasoil in an FCC Unit, Fuel  
616 Process. Technol. 131 (2015) 159–166. doi:10.1016/j.fuproc.2014.11.  
617 008.
- 618 [23] S. Bezergianni, A. Dimitriadis, O. Kikhtyanin, D. Kubička, Refinery co-  
619 processing of renewable feeds, Prog. Energy Combust. Sci. 68 (2018) 29–64.  
620 doi:10.1016/j.pecs.2018.04.002.
- 621 [24] D. V. Naik, V. Kumar, B. Prasad, Pyrolysis Oil Upgrading to Fuels by  
622 Catalytic Cracking : A Refinery Perspective, in: Prospects of Alternative  
623 Transportation Fuels, 2018, pp. 269 – 295.
- 624 [25] F. A. Agblevor, O. Mante, R. Mcclung, S. T. Oyama, Co-processing of  
625 standard gas oil and biocrude oil to hydrocarbon fuels, Biomass Bioenergy  
626 45 (2012) 130–137. doi:10.1016/j.biombioe.2012.05.024.

- 627 [26] N. Thegarid, G. Fogassy, Y. Schuurman, C. Mirodatos, S. D. Stefanidis,  
628 E. F. Iliopoulou, K. Kalogiannis, A. A. Lappas, Second-generation biofuels  
629 by co-processing catalytic pyrolysis oil in FCC units, *Appl. Catal., B* 145  
630 (2014) 161–166. doi:10.1016/j.apcatb.2013.01.019.
- 631 [27] L. Negahdar, A. Gonzalez-Quiroga, D. Otyuskaya, H. E. Toraman, L. Liu,  
632 J. T. B. H. Jastrzebski, K. M. Van Geem, G. B. Marin, J. W. Thybaut,  
633 B. M. Weckhuysen, K. M. V. Geem, G. B. Marin, J. W. Thybaut, B. M.  
634 Weckhuysen, Characterization and Comparison of Fast Pyrolysis Bio-oils  
635 from Pinewood, Rapeseed Cake, and Wheat Straw Using  $^{13}\text{C}$  NMR and  
636 Comprehensive GC GC, *ACS Sustainable Chemistry and Engineering* 4 (9)  
637 (2016) 4974–4985. doi:10.1021/acssuschemeng.6b01329.
- 638 [28] A. Jensen, K. Dam-Johansen, M. A. Wójtowicz, M. A. Serio, TG-FTIR  
639 study of the influence of potassium chloride on wheat straw pyrolysis, *En-  
640 ergy Fuels* 12 (5) (1998) 929–938. doi:10.1021/ef980008i.
- 641 [29] K. Lazdovica, L. Liepina, V. Kampars, Comparative wheat straw cat-  
642 alytic pyrolysis in the presence of zeolites, Pt/C, and Pd/C by using  
643 TGA-FTIR method, *Fuel Process. Technol.* 138 (2015) 645–653. doi:  
644 10.1016/j.fuproc.2015.07.005.
- 645 [30] N. Bech, M. B. Larsen, P. A. Jensen, K. Dam-Johansen, Modelling solid-  
646 convective flash pyrolysis of straw and wood in the Pyrolysis Centrifuge  
647 Reactor, *Biomass Bioenergy* 33 (6-7) (2009) 999–1011. doi:10.1016/j.  
648 biombioe.2009.03.009.
- 649 [31] A. Eschenbacher, P. A. Jensen, U. B. Henriksen, J. Ahrenfeldt, C. Li, J. Ø.  
650 Duus, U. V. Mentzel, A. D. Jensen, Impact of ZSM-5 deactivation on bio-  
651 oil quality during upgrading of straw derived pyrolysis vapors, *Energy &  
652 Fuels* 33 (1) (2019) 397–412. doi:10.1021/acs.energyfuels.8b03691.
- 653 [32] A. Eschenbacher, P. A. Jensen, U. B. Henriksen, J. Ahrenfeldt, C. Li,  
654 J. Ø. Duus, U. V. Mentzel, A. D. Jensen, Deoxygenation of wheat

- 655 straw fast pyrolysis vapors using HZSM-5, Al<sub>2</sub>O<sub>3</sub>, HZSM-5/Al<sub>2</sub>O<sub>3</sub> extru-  
656 dates, and desilicated HZSM-5/Al<sub>2</sub>O<sub>3</sub> extrudates, *Energy & Fuels* (2019)  
657 [acs.energyfuels.9b00906doi:10.1021/acs.energyfuels.9b00906](https://doi.org/10.1021/acs.energyfuels.9b00906).
- 658 [33] T. Myrstad, H. Engan, Testing of resid FCC catalysts in MAT, *Appl.*  
659 *Catal., A* 171 (1) (1998) 161–165. doi:10.1016/S0926-860X(98)00100-8.
- 660 [34] N. Y. Chen, D. E. Walsh, L. R. Koenig, Fluidized Bed Upgrading of  
661 Wood Pyrolysis Liquids and Related Compounds., ACS Division of Fuel  
662 Chemistry, Preprints 32 (2) (1987) 264–275. doi:10.1021/bk-1988-0376.  
663 ch024.
- 664 [35] S. A. Channiwala, P. P. Parikh, A unified correlation for estimating HHV  
665 of solid, liquid and gaseous fuels, *Fuel* 81 (8) (2002) 1051–1063. doi:  
666 10.1016/S0016-2361(01)00131-4.
- 667 [36] A. V. Bridgwater, Review of fast pyrolysis of biomass and product upgrad-  
668 ing, *Biomass Bioenergy* 38 (2012) 68–94. doi:10.1016/j.biombioe.2011.  
669 01.048.
- 670 [37] R. M. Baldwin, C. J. Feik, Bio-oil stabilization and upgrading by hot gas  
671 filtration, *Energy Fuels* 27 (6) (2013) 3224–3238. doi:10.1021/ef400177t.
- 672 [38] J. Sitzmann, Upgrading of Fast Pyrolysis Oils by Hot Filtration (2009) 135.
- 673 [39] E. F. Iliopoulou, S. D. Stefanidis, K. G. Kalogiannis, A. Delimitis, A. A.  
674 Lappas, K. S. Triantafyllidis, Catalytic upgrading of biomass pyrolysis va-  
675 pors using transition metal-modified ZSM-5 zeolite, *Appl. Catal., B* 127  
676 (2012) 281–290. doi:10.1016/j.apcatb.2012.08.030.
- 677 [40] V. Balasundram, N. Ibrahim, R. M. Kasmani, R. Isha, M. K. A. Hamid,  
678 H. Hasbullah, R. R. Ali, Catalytic upgrading of sugarcane bagasse pyrolysis  
679 vapours over rare earth metal (Ce) loaded HZSM-5: Effect of catalyst to  
680 biomass ratio on the organic compounds in pyrolysis oil, *Appl. Energy*  
681 220 (December 2017) (2018) 787–799. doi:10.1016/j.apenergy.2018.  
682 03.141.



- 683 [41] M. Zhang, F. L. P. Resende, A. Moutsoglou, Catalytic fast pyrolysis of  
684 aspen lignin via Py-GC/MS, *Fuel* 116 (2014) 358–369. doi:10.1016/j.  
685 fuel.2013.07.128.
- 686 [42] K. Wang, K. H. Kim, R. C. Brown, Catalytic pyrolysis of individual  
687 components of lignocellulosic biomass, *Green Chem.* 16 (2) (2014) 727.  
688 doi:10.1039/c3gc41288a.
- 689 [43] C. A. Mullen, A. A. Boateng, Production of Aromatic Hydrocarbons via  
690 Catalytic Pyrolysis of Biomass over Fe-Modified HZSM-5 Zeolites, *ACS*  
691 *Sustainable Chemistry and Engineering* 3 (7) (2015) 1623–1631. doi:10.  
692 1021/acssuschemeng.5b00335.
- 693 [44] M. Brady, J. Keiser, D. Leonard, A. Zacher, K. Bryden, G. Weatherbee,  
694 Corrosion of stainless steels in the riser during co-processing of bio-oils in  
695 a fluid catalytic cracking pilot plant, *Fuel Process. Technol.* 159 (2017)  
696 187–199. doi:10.1016/j.fuproc.2017.01.041.
- 697 [45] P. Bai, U. J. Etim, Z. Yan, S. Mintova, Z. Zhang, Z. Zhong, X. Gao,  
698 Fluid catalytic cracking technology: current status and recent discoveries  
699 on catalyst contamination, *Catalysis Reviews - Science and Engineering*  
700 00 (00) (2018) 1–73. doi:10.1080/01614940.2018.1549011.
- 701 [46] A. R. Stanton, K. Iisa, C. Mukarakate, M. R. Nimlos, Role of Biopolymers  
702 in the Deactivation of ZSM-5 during Catalytic Fast Pyrolysis of Biomass,  
703 *ACS Sustainable Chemistry and Engineering* 6 (8) (2018) 10030–10038.  
704 doi:10.1021/acssuschemeng.8b01333.
- 705 [47] I. Graça, A. M. Carmo, J. M. Lopes, M. F. Ribeiro, Improving HZSM-  
706 5 resistance to phenolic compounds for the bio-oils/FCC feedstocks co-  
707 processing, *Fuel* 140 (2015) 484–494. doi:10.1016/j.fuel.2014.10.002.
- 708 [48] I. Graca, J. M. Lopes, M. F. Ribeiro, F. R. Ribeiro, H. S. Cerqueira, M. B.  
709 B. D. Almeida, Catalytic cracking in the presence of guaiacol 101 (2011)  
710 613–621. doi:10.1016/j.apcatb.2010.11.002.

- 711 [49] G. A. Mills, E. R. Boedeker, A. G. Oblad, Chemical Characterization of  
712 Catalysts. I. Poisoning of Cracking Catalysts by Nitrogen Compounds and  
713 Potassium Ion, *J. Am. Chem. Soc.* 72 (4) (1950) 1554–1560. doi:10.1021/  
714 ja01160a035.
- 715 [50] G. Caeiro, A. F. Costa, H. S. Cerqueira, P. Magnoux, J. M. Lopes, P. Ma-  
716 tias, F. R. Ribeiro, Nitrogen poisoning effect on the catalytic cracking of  
717 gasoil, *Appl. Catal., A* 320 (2007) 8–15. doi:10.1016/j.apcata.2006.  
718 11.031.
- 719 [51] Q. Sheng, G. Wang, Y. Liu, M. M. Husein, C. Gao, J. Gao, Pilot-scale  
720 evaluation of hydrotreating inferior coker gas oil prior to its fluid catalytic  
721 cracking, *Fuel* 226 (November 2017) (2018) 27–34. doi:10.1016/j.fuel.  
722 2018.03.150.
- 723 [52] C. M. Fu, A. M. Schaffer, Effect of Nitrogen Compounds on Cracking Cat-  
724 alysts, *Industrial and Engineering Chemistry Product Research and Devel-*  
725 *opment* 24 (1) (1985) 68–75. doi:10.1021/i300017a013.
- 726 [53] X. Chen, Y. Liu, S. Li, X. Feng, H. Shan, C. Yang, Structure and Com-  
727 position Changes of Nitrogen Compounds during the Catalytic Cracking  
728 Process and Their Deactivating Effect on Catalysts, *Energy Fuels* 31 (4)  
729 (2017) 3659–3668. doi:10.1021/acs.energyfuels.6b03230.
- 730 [54] Z. K. Li, J. S. Gao, G. Wang, Q. Shi, C. M. Xu, Influence of nonbasic  
731 nitrogen compounds and condensed aromatics on coker gas oil catalytic  
732 cracking and their characterization, *Ind. Eng. Chem. Res.* 50 (15) (2011)  
733 9415–9424. doi:10.1021/ie2003973.
- 734 [55] G. Caeiro, P. Magnoux, P. Ayrault, J. M. Lopes, F. R. Ribeiro, Deactivat-  
735 ing effect of coke and basic nitrogen compounds during the methylcyclo-  
736 hexane transformation over H-MFI zeolite, *Chemical Engineering Journal*  
737 120 (1-2) (2006) 43–54. doi:10.1016/j.cej.2006.03.036.

- 738 [56] L. Xu, Q. Yao, Y. Zhang, Y. Fu, Integrated Production of Aromatic Amines  
739 and N-Doped Carbon from Lignin via ex Situ Catalytic Fast Pyrolysis  
740 in the Presence of Ammonia over Zeolites, *ACS Sustainable Chemistry*  
741 *and Engineering* 5 (4) (2017) 2960–2969. doi:10.1021/acssuschemeng.  
742 6b02542.
- 743 [57] L. Xu, Y. Jiang, Q. Yao, Z. Han, Y. Zhang, Y. Fu, Q. Guo, G. W. Huber,  
744 Direct production of indoles via thermo-catalytic conversion of bio-derived  
745 furans with ammonia over zeolites, *Green Chem.* 17 (2) (2015) 1281–1290.  
746 doi:10.1039/c4gc02250e.
- 747 [58] L. Xu, Z. Han, Q. Yao, J. Deng, Y. Zhang, Y. Fu, Q. Guo, Towards the sus-  
748 tainable production of pyridines via thermo-catalytic conversion of glycerol  
749 with ammonia over zeolite catalysts, *Green Chem.* 17 (4) (2015) 2426–2435.  
750 doi:10.1039/c4gc02235a.
- 751 [59] L. Xu, Y. Zhang, Y. Fu, Advances in Upgrading Lignin Pyrolysis Vapors  
752 by ExSitu Catalytic Fast Pyrolysis, *Energy Technology* 5 (1) (2016) 30–51.  
753 doi:10.1002/ente.201600107.
- 754 [60] L. Xu, Q. Yao, J. Deng, Z. Han, Y. Zhang, Y. Fu, G. W. Huber, Q. Guo,  
755 Renewable N-Heterocycles Production by Thermocatalytic Conversion and  
756 Ammonization of Biomass over ZSM-5, *ACS Sustainable Chemistry and*  
757 *Engineering* 3 (11) (2015) 2890–2899. doi:10.1021/acssuschemeng.  
758 5b00841.
- 759 [61] K. Bryden, G. Weatherbee, E. T. Habib, Flexible Pilot Plant Technology  
760 for Evaluation of Unconventional Feedstocks and Processes, in: *Grace Cat-*  
761 *alysts Technologies*, 2013, pp. 32–60.
- 762 [62] H. L. Chum, A. Pinho, U.S. DOE Bioenergy Technologies Office (BETO)  
763 2015 Project Peer Review Excerpt; 2.4.2.303 Brazil Bilateral: Petrobras-  
764 NREL CRADA.

- 765 [63] G. Fogassy, N. Thegarid, Y. Schuurman, C. Mirodatos, From biomass to  
766 bio-gasoline by FCC co-processing: effect of feed composition and cata-  
767 lyst structure on product quality, *Energy & Environmental Science* 4 (12)  
768 (2011) 5068. doi:10.1039/c1ee02012a.
- 769 [64] L. Gueudré, F. Chapon, C. Mirodatos, Y. Schuurman, R. H. Venderbosch,  
770 E. Jordan, S. Wellach, R. M. Gutierrez, Optimizing the bio-gasoline quan-  
771 tity and quality in fluid catalytic cracking co-refining, *Fuel* 192 (2017) 60–  
772 70. doi:10.1016/j.fuel.2016.12.021.
- 773 [65] G. Fogassy, N. Thegarid, G. Toussaint, A. C. van Veen, Y. Schuurman,  
774 C. Mirodatos, Biomass derived feedstock co-processing with vacuum gas  
775 oil for second-generation fuel production in FCC units, *Appl. Catal., B*  
776 96 (3-4) (2010) 476–485. doi:10.1016/j.apcatb.2010.03.008.
- 777 [66] Q. Sheng, G. Wang, Y. Liu, M. M. Husein, C. Gao, Q. Shi, J. Gao,  
778 Combined Hydrotreating and Fluid Catalytic Cracking Processing for the  
779 Conversion of Inferior Coker Gas Oil: Effect on Nitrogen Compounds  
780 and Condensed Aromatics, *Energy Fuels* 32 (4) (2018) 4979–4987. doi:  
781 10.1021/acs.energyfuels.8b00436.
- 782 [67] H. S. Cerqueira, G. Caeiro, L. Costa, F. Ramôa Ribeiro, Deactivation of  
783 FCC catalysts, *J. Mol. Catal. A: Chem.* 292 (1-2) (2008) 1–13. doi:10.  
784 1016/j.molcata.2008.06.014.
- 785 [68] M. Guisnet, F. R. Ribeiro, Deactivation and Regeneration of zeolite cata-  
786 lysts, Imperial College Press: UK, 2011.
- 787 [69] G. W. Young, Fluid catalytic cracker catalyst design for nitrogen tolerance,  
788 *J. Phys. Chem.* 90 (20) (1986) 4894–4900. doi:10.1021/j100411a035.
- 789 [70] A. Imran, E. A. Bramer, K. Seshan, An overview of catalysts in biomass  
790 pyrolysis for production of biofuels, *Biofuel Research Journal* 5 (4) (2018)  
791 872–885. doi:10.18331/BRJ2018.5.4.2.

# Co-processing of Wood and Wheat Straw Derived Pyrolysis Oils with FCC Feed— Product Distribution and Effect of Deoxygenation

## Supporting Information

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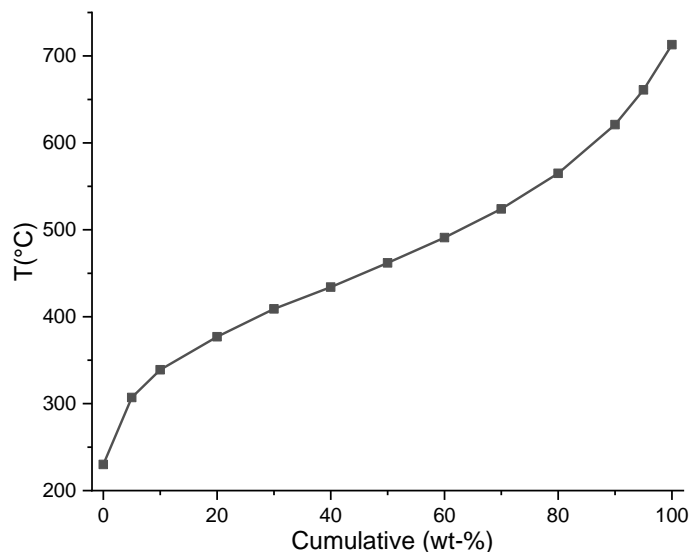
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The supporting information consists of 8 pages, 5 tables and 8 figures.



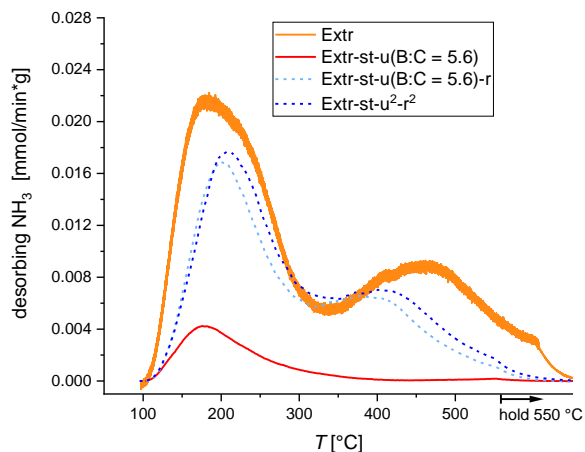
**Fig. 1** Boiling point distribution of the reference feed based on high-temperature simulated distillation.

**Physicochemical characterization of catalyst used for pyrolysis vapor deoxygenation, according to Table S1**

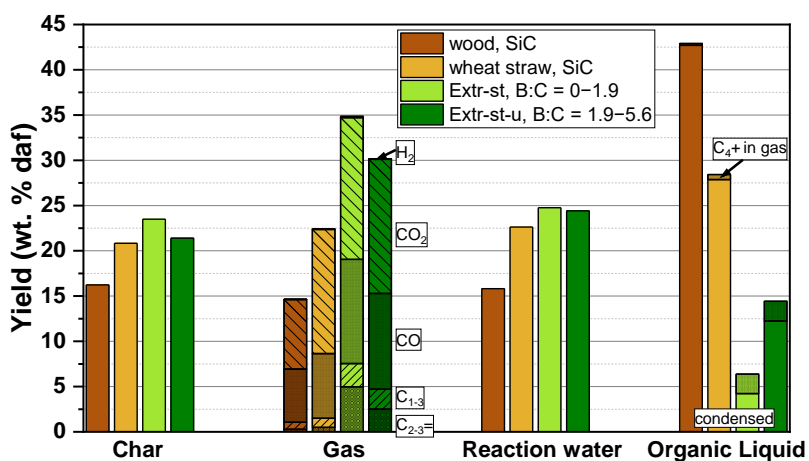
Table S1 summarizes the properties of the freshly calcined HZSM-5/Al<sub>2</sub>O<sub>3</sub> extrudate, after steaming, after coke formation from upgrading to B:C = 5.6, and after combustion of the coke species. The Brønsted acidity quantified by Ethylamine-TPD for the steamed HZSM-5 extrudate amounted to 0.154 mmol NH<sub>3</sub>/g. The steaming and reaction/regeneration cycle decreased the BET surface area from 395 to 353 m<sup>2</sup>/g. The coked catalyst obtained after cumulative feeding of biomass to B:C = 5.6 showed both reduced volume of micro- and mesopores, and a reduced BET surface area of 185 m<sup>2</sup>/g. Furthermore, the catalyst's acidity has been reduced from ~0.39 to ~0.05 mmol NH<sub>3</sub>/g. The NH<sub>3</sub>-TPD profiles are proved in Fig. S1 and show that the strong acidity was completely diminished for the coked catalyst while some weak acidity remained. Combustion of the coke species allowed to regain both weak and strong acidity.

**Table S1** Physicochemical properties of HZSM-5/Al<sub>2</sub>O<sub>3</sub> extrudate.  $V_{\text{micro}}$  and  $S_{\text{micro}}$  were determined by high-resolution low temperature Argon physisorption (87 K), while all other textural parameters were derived from nitrogen adsorption data. Total acidity was determined by NH<sub>3</sub>-TPD. The suffixes 'st', 'u', and 'r' to the catalyst designation indicate steaming, upgrading and regeneration, respectively.

|                         | $V_{\text{micro}}$<br>[cc/g] | $S_{\text{micro}}$<br>[m <sup>2</sup> /g] | $V_{\text{meso}}$<br>[cc/g] | $S_{\text{meso}}$<br>[m <sup>2</sup> /g] | $V_{\text{total}}$ at<br>p/p <sub>0</sub> =0.99 | BET (N <sub>2</sub> )<br>m <sup>2</sup> /g | Total Acidity<br>[mmol NH <sub>3</sub> /g] |
|-------------------------|------------------------------|---|-----------------------------|--|---|--|--|
| Extr                    | 0.12                         | 865                                       | 0.31                        | 178                                      | 0.46  | 395  | 0.486                                      |
| Extr-st                 | n.a.                         | n.a.                                      | 0.32                        | 171                                      | 0.45  | 376  | 0.385                                      |
| Extr-st-u (B:C = 0-5.6) | 0.08                         | 606                                       | 0.11                        | 67                                       | 0.18  | 185  | 0.051                                      |
| Extr-st-u-r             | 0.11                         | 859                                       | 0.33                        | 177                                      | 0.44  | 353  | 0.338                                      |



**Fig. S2** Acidity characterization (by  $\text{NH}_3$ -TPD) of HZSM-5/ $\text{Al}_2\text{O}_3$  extrudates as received, after steaming and use of 260 g catalyst for upgrading of wheat straw derived pyrolysis vapors (500 °C, B:C = 5.6), and after the regeneration of the accumulated coke.



**Fig. S3.** Product distribution obtained for generation of oils: non-catalytic fast pyrolysis oils from wood (pine) and wheat straw were obtained using a SiC bed, while the catalytically upgraded oils were obtained using 260 g steamed HZSM-5 extrudates at 500 °C and wheat straw as feedstock. Coke yield was 5.8 wt-% of the fed (daf) biomass for the catalytic run when operated to a cumulative B:C ratio of 5.6.

**Table S2.** Characterization of moisture (Karl Fischer titration) and elemental analysis of organics content (d.b.) for liquid products obtained for passing wood fast pyrolysis vapors over SiC bed.

| <b>Liquid distribution</b>  | <b>4°C OF</b> | <b>ESP OF</b> | <b>-60°C OF</b> | <b>sum OF<sup>a)</sup></b> | <b>sum WF<sup>b)</sup></b> |
|---|---------------|---------------|-----------------|----------------------------|----------------------------|
| Yield within total collected liquid [wt-% <sub>wb</sub> ] <sup>c)</sup>   | 17.2          | 25.0          | 1.7             | 43.9                       | 56.1                       |
| Moisture [wt-%]   | 11.9          | 4.9           | 9.6             | 7.8                        | 51.5                       |
| Organics distribution within total collected liquid [wt-% <sub>db</sub> ] | 22.4          | 35.1          | 2.2             | 59.8                       | 40.2                       |
| <b>Elements [wt-%<sub>db</sub>]</b>                                       |               |               |                 |                            |                            |
| N   | 0.2           | 0.0           | 1.8             | 0.2                        | n.d.                       |
| C   | 64.9          | 63.0          | 62.9            | 63.7                       | 55.2                       |
| H   | 6.1           | 6.5           | 8.2             | 6.5                        | n.d.                       |
| O   | 28.7          | 30.5          | 27.1            | 29.7                       | n.d.                       |
| <b>HHV [MJ/kg]</b>  | 26.9          | 26.6          | 28.8            | 26.8                       | n.d.                       |
| <b>TAN [mg KOH/g]</b>   | 57.2          | 66.9          | 1.2             | 60.8                       | 66.4                       |

<sup>a)</sup> ‘sum OF’ is the sum of the three oil fractions to the left. <sup>b)</sup> ‘sum WF’ is the sum of aqueous fractions that phase separated from 4°C OF and -60°C OF (results for individual aqueous fractions not shown). <sup>c)</sup> Total collected liquid = sum OF + sum WF

**Table S3.** Characterization of moisture (Karl Fischer titration) and elemental analysis of organics content (d.b.) for liquid products obtained for passing wheat straw fast pyrolysis vapors over SiC bed.

| <b>Liquid distribution</b>  | <b>4°C OF</b> | <b>ESP OF</b> | <b>-60°C OF</b> | <b>sum OF<sup>a)</sup></b> | <b>sum WF<sup>b)</sup></b> |
|---|---------------|---------------|-----------------|----------------------------|----------------------------|
| Yield within total collected liquid [wt-% <sub>wb</sub> ] <sup>c)</sup>   | 18.0          | 17.6          | 2.4             | 37.9                       | 62.1                       |
| Moisture [wt-%]   | 27.6          | 2.4           | 8.6             | 14.7                       | 76.6                       |
| Organics distribution within total collected liquid [wt-% <sub>db</sub> ] | 27.3          | 35.9          | 4.5             | 67.8                       | 30.5                       |
| <b>Elements [wt-%<sub>db</sub>]</b>                                       |               |               |                 |                            |                            |
| N   | 1.8           | 1.3           | 2.2             | 1.6                        | n.d.                       |
| C   | 75.6          | 66.4          | 63.5            | 69.9                       | 54.7                       |
| H   | 6.7           | 7.1           | 8.6             | 7.1                        | n.d.                       |
| O   | 15.9          | 25.1          | 25.6            | 21.4                       | n.d.                       |
| <b>HHV [MJ/kg]</b>  | 32.7          | 29.0          | 29.7            | 30.5                       | n.d.                       |
| <b>TAN [mg KOH/g]</b>   | 50.8          | 54.1          | 50.5            | 52.5                       | 61.4                       |

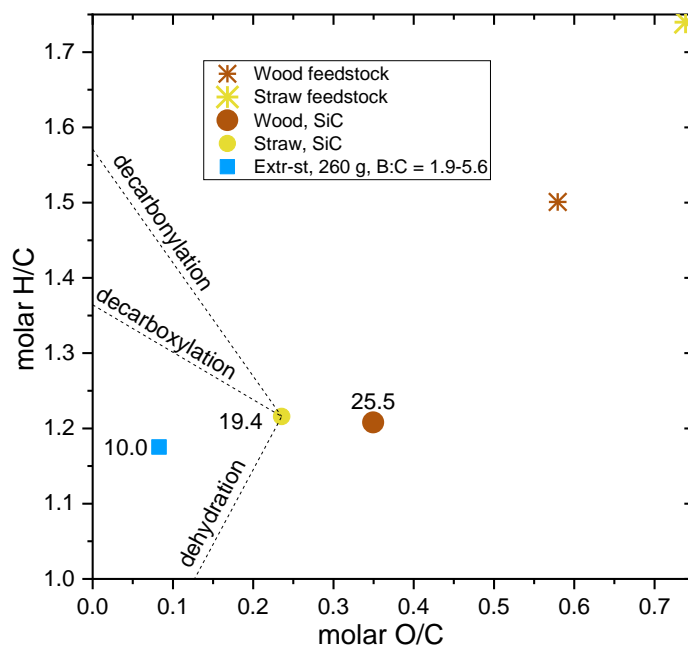
<sup>a)</sup> ‘sum OF’ is the sum of the three oil fractions to the left. <sup>b)</sup> ‘sum WF’ is the sum of aqueous fractions that phase separated from 4°C OF and -60°C OF (results for individual aqueous fractions not shown). <sup>c)</sup> Total collected liquid = sum OF + sum WF



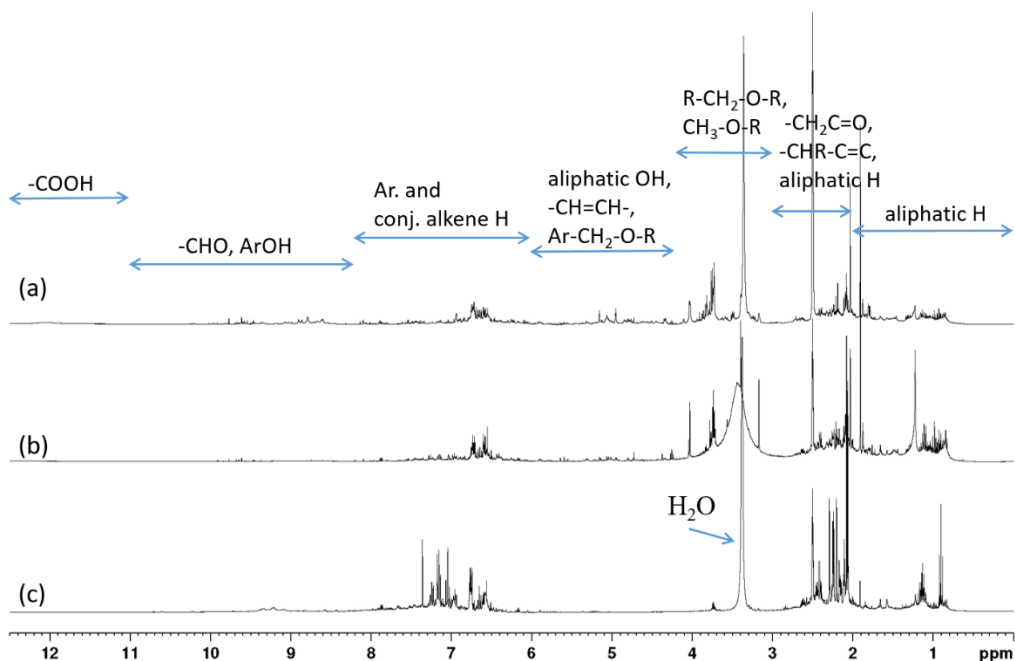
**Table S4.** Characterization of moisture (Karl Fischer titration) and elemental analysis of organics content (d.b.) for liquid products obtained when passing straw pyrolysis vapors over 260 g Extr-st, B:C = 1.9–5.6.

| Liquid distribution   | 4°C OF | ESP OF | -60°C OF | sum OF <sup>a)</sup> | sum WF <sup>b)</sup> |
|---|--------|--------|----------|----------------------|----------------------|
| Yield within total collected liquid [wt-% <sub>wb</sub> ] <sup>c)</sup>   | 7.4    | 8.1    | 7.0      | 22.4                 | 77.6                 |
| Moisture [wt-%]   | 3.8    | 0.6    | 2.7      | 2.3                  | 93.6                 |
| Organics distribution within total collected liquid [wt-% <sub>db</sub> ] | 26.3   | 29.9   | 25.3     | 81.5                 | 18.5                 |
| <b>Elements</b> [wt-% <sub>db</sub> ]                                     |        |        |          |                      |                      |
| N   | 2.6    | 3.2    | 5.0      | 3.6                  | n.d.                 |
| C   | 79.9   | 78.7   | 81.0     | 79.8                 | 41.4                 |
| H   | 7.3    | 7.0    | 9.6      | 7.9                  | n.d.                 |
| O   | 10.2   | 11.1   | 4.5      | 8.8                  | n.d.                 |
| <b>HHV</b> [MJ/kg]  | 35.4   | 34.5   | 39.0     | 36.2                 | n.d.                 |
| <b>TAN</b> [mg KOH/g]   | 35.4   | 34.5   | 39.0     | 36.2                 | n.d.                 |

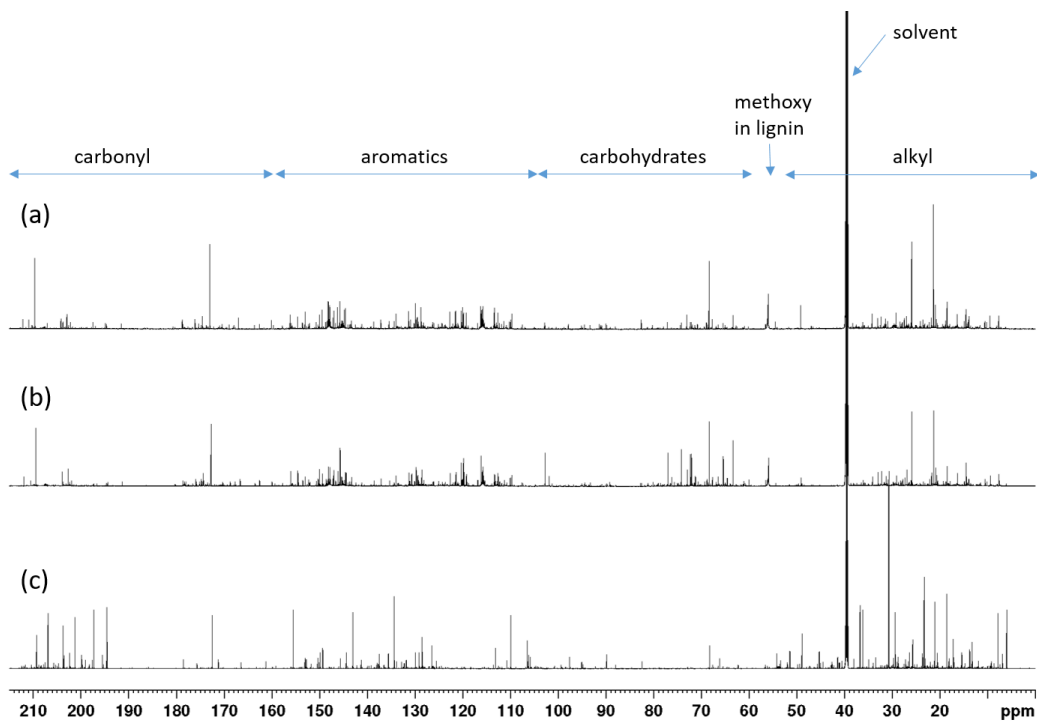
<sup>a)</sup> ‘sum OF’ is the sum of the three oil fractions to the left. <sup>b)</sup> ‘sum WF’ is the sum of aqueous fractions that phase separated from 4°C OF and -60°C OF (results for individual aqueous fractions not shown). <sup>c)</sup> Total collected liquid = sum OF + sum WF



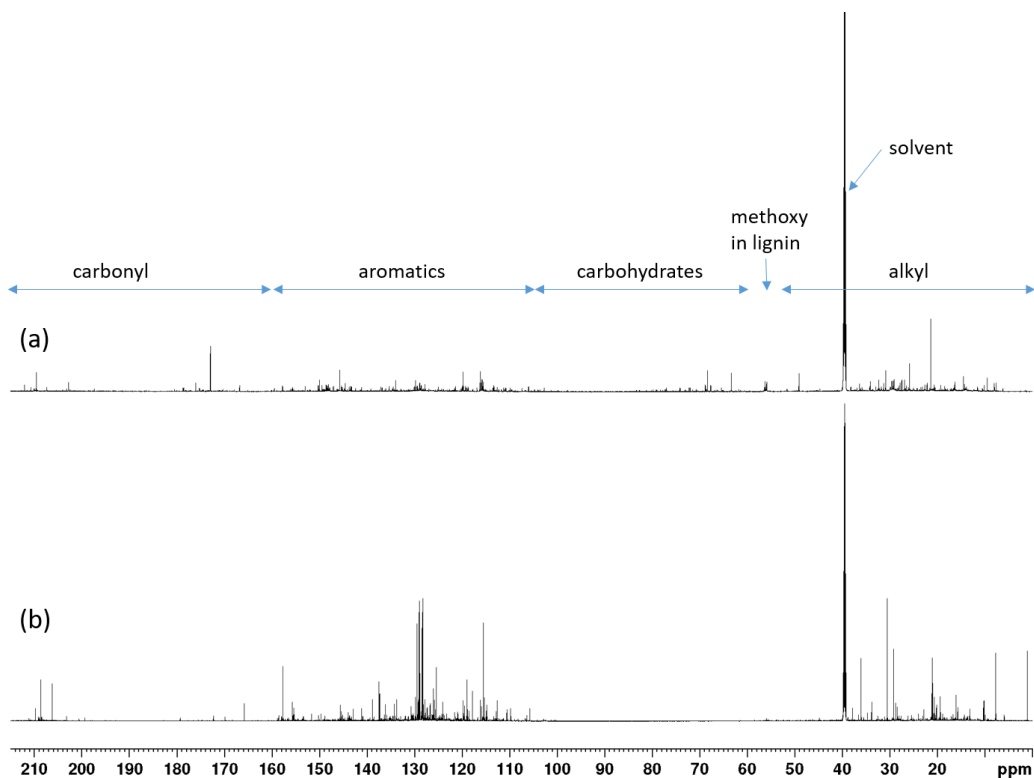
**Fig. S4.** Molar H/C ratio and O/C ratio for the phase separated oil fractions obtained from FP of wood and straw over SiC bed (500 °C), as well as oil obtained from FP of straw and catalytic upgrading using steamed HZSM-5 extrudates as catalyst. H/C and O/C ratio of feedstock are shown for reference. The numbers besides the data points indicate the yield (on daf basis) of the oil fraction.



**Fig. S5**  $^1\text{H}$  NMR spectra of oils from FP of wood (a) and straw (b) over SiC bed (500 °C) as well oil obtained from FP of straw and catalytic upgrading using steamed HZSM-5/ $\text{Al}_2\text{O}_3$  extrudates as catalyst at B:C = 1.9-5.6 (c).



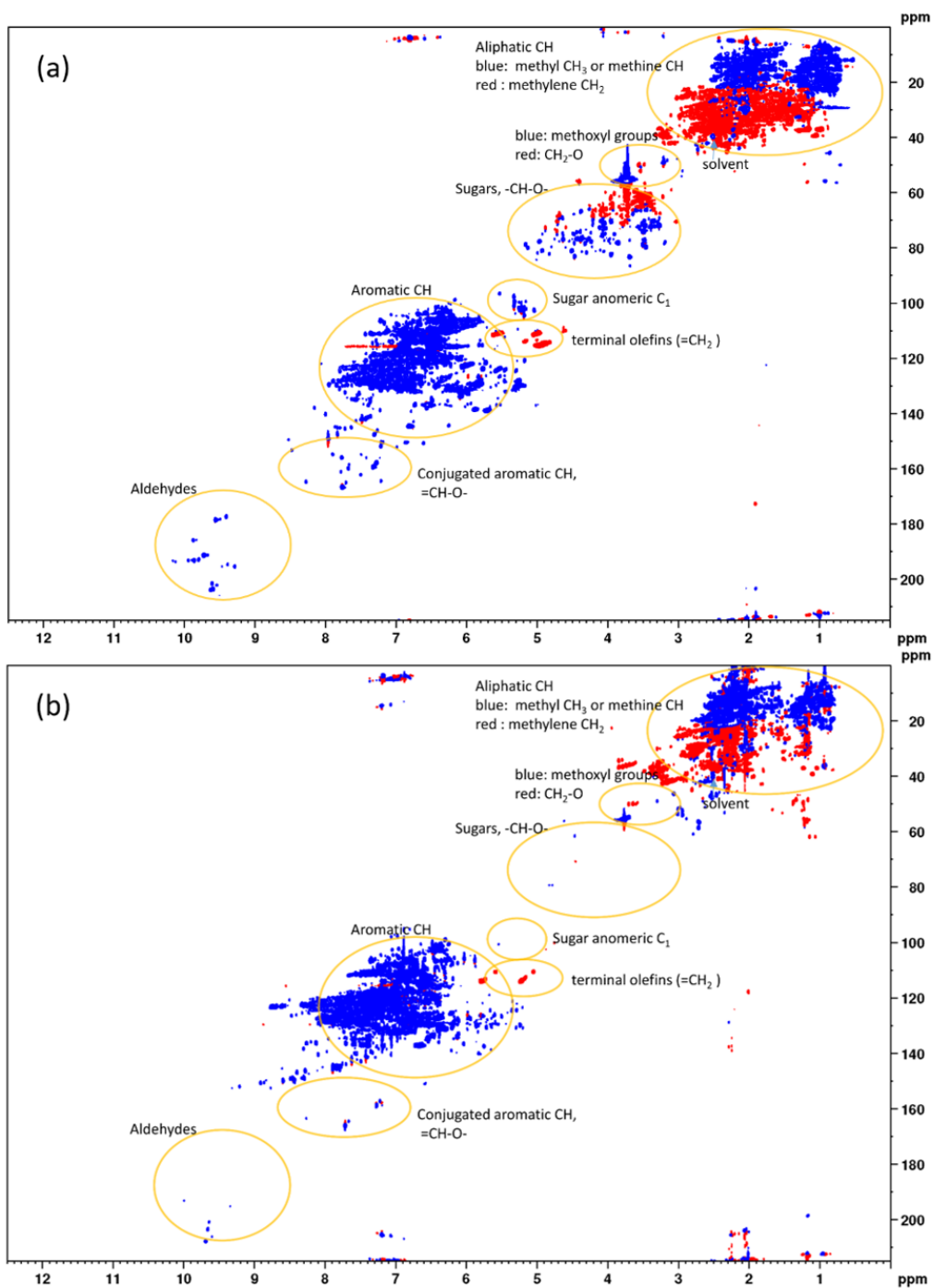
**Fig. S6**  $^{13}\text{C}$  NMR spectra of oil from wood FP and passing the vapors over SiC (500 °C). (a) shows oil collected at 4 °C condensation stage (4 °C OF) (b) shows oil collected at electrostatic precipitator (ESP OF), and (c) shows oil collected at a condensation stage operated at -60 °C (-60 °C OF).



**Fig. S7**  $^{13}\text{C}$  NMR spectra of oil from straw fast pyrolysis over SiC bed (a) and oil obtained from catalytic vapor upgrading using steamed HZSM-5 extrudates as catalyst at B:C = 1.9-5.6 (b).

**Table 5.** Characterization of straw derived oil fractions by GC-MS/FID: Shown is the yield of identified compounds with respect to dry, ash-free wheat straw.

|                             | straw, SiC            | straw, B:C = 1.9-5.6  |
|-----------------------------|-----------------------|-----------------------|
|                             | wt-% of biomass (daf) | wt-% of biomass (daf) |
| Monoaromatics               | 0.23                  | 1.33                  |
| Diaromatics                 | 0.36                  | 0.65                  |
| Polyaromatics (PAH)         | 0.07                  | 0.18                  |
| Aliphatic hydrocarbons      | 0.58                  | 0.64                  |
| Phenols                     | 0.59                  | 1.79                  |
| Methoxy-phenols             | 0.22                  | 0.11                  |
| Furans                      | 0.27                  | 0.14                  |
| Acids                       | 0.68                  | -                     |
| Esters                      | -                     | 0.23                  |
| Alcohols                    | 0.53                  | 0.58                  |
| Aldehydes                   | 0.20                  | 0.11                  |
| Ketones                     | 0.84                  | 0.87                  |
| Nitrogen containing         | 0.16                  | 0.14                  |
| Oxygenates < 0.1 wt-% yield | 0.08                  | 0.04                  |



**Fig. S8** 2D NMR HSQC characterization of oil from straw fast pyrolysis over SiC bed (a) and oil obtained from catalytic vapor upgrading using steamed HZSM-5 extrudates as catalyst at B:C = 1.9-5.6 (b).