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Biofuels and Biomass

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Impact of ZSM-5 deactivation on bio-oil quality during upgrading of straw derived pyrolysis vapors

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KEYWORDS: wheat straw; biomass; fast pyrolysis; H-ZSM-5; deactivation; dealumination; bio-oil; oxygen; NMR characterization; deoxygenation; TAN content

ABSTRACT

In this work, we provide detailed information on the change in product distribution and bio-oil quality during extended feeding of biomass derived fast pyrolysis vapors over ZSM-5. The effect of catalyst deactivation by coking on the resulting oil product characteristics was clarified in order to determine when the vapor upgrading should be stopped and the regeneration initiated. Obtaining a stable catalytic fast pyrolysis (CFP) oil while maintaining good energy recovery is important within the context of potential co-processing these oils with petroleum feedstocks via FCC or hydrotreatment of the whole CFP oil.

Wheat straw derived fast pyrolysis vapors were upgraded in an *ex-situ* fixed bed reactor containing a steamed ZSM-5 catalyst at 500 °C. Oils were collected both for runs starting the upgrading over

1
2
3 21 a fresh (or regenerated) catalyst, and runs which were continued over an increasingly coked zeolite.
4
5 22 The oils were characterized for water content, elemental analysis, total acid number (TAN),
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7 23 chemical composition by GC-MS/FID, size exclusion chromatography (SEC), evaporation
8
9 24 characteristics by TGA, ^1H NMR, ^{13}C NMR and 2D HSQC NMR spectroscopy.
10
11
12 25 With increasing B:C ratio, the yield of deoxygenated hydrocarbons decreased, accompanied by a
13
14 26 breakthrough of primary pyrolysis vapors leading to an increasing organic liquid yield. The oxygen
15
16 27 content of the condensed, phase separated oil fraction increased and the molar O/C ratio of 0.05
17
18 28 and TAN of 6 mg KOH/g for oil collected during B:C = 0 - 1.1 increased to O/C = 0.18 and TAN
19
20 29 = 14 mg KOH/g for oil collected during B:C = 3.6 - 6.2. Oil produced at 90% reduced catalyst
21
22 30 amount and B:C = 0 – 6.5 and B:C = 0 – 12.9 increased the carbon recovery into the oil product
23
24 31 to 23% and 27%, respectively, but led to an increase in O/C ratio from 0.18 to 0.22, thus
25
26 32 approaching the non-catalytic reference case (SiC bed at 500 °C) of O/C = 0.24. Clear differences
27
28 33 in the evaporation behavior of the collected oils were observed, with a shift to more volatile
29
30 34 fractions and less charring for products obtained at low B:C ratio. Characterization of the upgraded
31
32 35 oils with ^{13}C NMR and ^1H NMR indicated a clear enhancement of the aromatics content and a
33
34 36 reduction of sugar and aldehyde compounds. The concentration of carbon within carbonyl,
35
36 37 carbohydrates and methoxy/hydroxyl groups was effectively reduced for oils obtained at low B:C
37
38 38 ratios. Catalyst characterization was performed with XRF, NH_3 -TPD, N_2 and Ar-physisorption,
39
40 39 TEM, and XRD. After steaming and four repeated upgrading/regeneration cycles corresponding
41
42 40 to an accumulated B:C ratio of 40, the zeolite's concentration of strong acid sites measured by
43
44 41 NH_3 -TPD ($T_{\text{des}} > 300\text{ }^\circ\text{C}$) reduced from 0.43 mmol/g for the calcined version to 0.07 mmol/g and
45
46 42 the BET surface area decreased from 468 to 385 m^2/g . The hot gas filter upstream the zeolite bed
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48 43 was found effective in preventing accumulation of potassium on the catalyst.
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INTRODUCTION

Catalytic fast pyrolysis (CFP) of biomass has the potential to produce partially upgraded bio-crudes which could be co-processed in existing petroleum refineries by fluid catalytic cracking or hydrotreating to obtain transportation fuels or chemicals. In an *ex-situ* configuration, the fast pyrolysis (FP) vapors are catalytically upgraded downstream the pyrolysis reactor, which allows to optimize the pyrolysis and upgrading conditions separately. As has been pointed out recently [1], more development and understanding of the catalyst long term stability is necessary. The literature on bench scale *ex-situ* CFP is scattered in terms of reaction conditions and B:C ratio [2–4] hampering a proper evaluation of the process. In order to allow processing of biomass derived FP oils in oil refineries, reduction of the oil's oxygen content and acid number is required [5]. Deoxygenation can be obtained by direct upgrading of the pyrolysis vapors over solid acid catalysts. The upgrading process is operated at atmospheric pressure and temperatures close to those for maximum liquid yields in the pyrolysis unit, which offers potential economic advantages for zeolite deoxygenation over high pressure hydrotreating [6]. To date, the medium pore size ZSM-5 zeolite has shown to provide a high aromatic yield and the lowest amount of coke [7,8] in upgrading of pyrolysis vapors. The overall oil yields are drastically reduced at low B:C ratios, since the fresh catalyst promotes cracking reactions which results in increased yields of reaction water, non-condensable gases and coke [10–13]. For blending of CFP oils with fossil oil at refineries, it may be more desirable to increase the energy recovery in the CFP liquid product and accept that not all of the oxygen has been removed. Recent studies obtained promising results for co-feeding catalytic pyrolysis oils containing ~20 wt-%_{db} O with fossil derived crude at an FCC unit [6,14–16]. As such, the primary goal of this investigation was not to obtain complete deoxygenation of the collected oil product, but rather to obtain a partial reduction in oxygen content in order to upgrade the primary pyrolysis oxygenates sufficiently to be considered for

further upgrading in a refinery setting. Wheat straw was chosen in this work, which is known to be a more challenging feedstock than wood and has led to boiler related problems in heat and power applications due to the high content of alkali rich ash [17–19]. As an agricultural residue, wheat straw is an economically attractive feedstock. The direct contact during catalytic pyrolysis between straw and zeolite would lead to rapid ash accumulation and deactivation of the zeolite by the alkaline ash components [20]. This has led to patent applications involving both the pretreatment of the biomass by washing and the washing out of ash deposits from the catalyst after oxidative regeneration [21,22]. These additional treatment steps add complexity and costs. While hot gas filtration (HGF) of char fines stabilizes the bio-oil [23] and can be seen as non-catalytic *ex-situ* upgrading method, the residence time has to be kept short to limit secondary cracking reactions and losses to gas and char.

The rate and extent of deactivation of the catalyst in catalytic pyrolysis is a major issue. In CFP, deactivation is mainly attributed to coke deposition, which blocks the pores and poisons the active sites of zeolites [24]. Without HGF, some degree of deactivation by deposition of contaminants (ash) originally present in the biomass cannot be excluded either [25]. The rapid decay in site accessibility and number requires frequent regeneration to recover activity. In addition, irreversible dealumination can be caused by steam from i) the pyrolysis process itself, ii) the dehydration reactions during upgrading, and iii) oxidative regeneration. With increasing coke formation on the zeolite, the lumped liquid product is comprised of fully de-oxygenated products obtained at low B:C ratio and products from the breakthrough of primary pyrolysis vapors [26]. Some work has been conducted concerning multiple regeneration/upgrading cycles and investigating the change in oil quality with increasing catalyst deactivation [10,20,27,28] for CFP of woody biomass. These studies concluded that the production of monocyclic aromatics was reduced at increasing B:C ratio

and oxygen containing compounds were converted less efficiently over a partially deactivated catalyst, which was attributed to loss of Brønsted acidity. The coke formation was found to be considerably faster during the initial upgrading [10,11,20] and Horne and coworkers [8] suggested that a partial regeneration of the catalyst may be more effective as it would reduce the initial high losses of the pyrolysis vapors (to coke and non-condensable gases) when passed over the fresh ZSM-5. Noteworthy, these authors worked in a similar scale as this work using 200 g ZSM-5 supported on a clay binder in a fixed bed reactor downstream a fluidized sand bed for pyrolysis (wood shavings feeding rate = 222 g/h). Liquid products were collected at certain intervals corresponding to approximate B:C intervals of 0 - 0.5, 0.5 - 1, 1 - 2 and 2 - 3, respectively. The oxygen content of the oil phase (on wet basis) increased from 15.4 wt-% obtained in the first upgrading interval to 25.7 wt-% during the last interval. It should be stressed that none of these studies considered steaming of the catalyst prior to the multiple upgrading/regeneration cycles. For the freshly calcined zeolite, initially a high rate of dealumination can be expected upon exposure to hydrothermal conditions. Thus, upon start of the vapor upgrading the catalyst activity may decrease both due to coke deposition and simultaneous dealumination. Ong *et al.* [29] varied the steaming duration of ZSM-5 (Si/Al = 87) from 2 to 48 h under 100% steam at 450 °C in order to investigate the extent of dealumination. While the concentration of Lewis acid sites remained almost constant during the steam treatment, the number of Brønsted acid sites decreased steeply reaching half its initial value after 19 h of steaming, but thereafter weakened only slowly reaching ~41% of its initial value after 48 h of steaming. The textural properties were reported to remain unchanged and the crystallinity decreased only by 6% after 48 h of steaming. Corma *et al.* [30] studied the catalytic cracking of naphtha over ZSM-5 with Si/Al ratios of 15, 25 and 40 at 650 °C and a steam vapor fraction between 0% and 35.7%. Their catalyst underwent intense dealumination

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3 114 in the presence of steam as determined by IR pyridine measurements and the initial dealumination
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5 115 rate decreased with increasing Si/Al ratio. Similarly, steaming of a ZSM-5 with Si/Al ~11.5 for 2
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8 116 h at 800 °C with 80 vol-% steam in N₂ carrier gas was found to reduce the amount of strongly
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10 117 adsorbed NH₃ (T_{des} > 300 °C) to about 7% of its initial value [31].
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12 118 The optimal molar Si/Al ratio for CFP of biomass appears to be in the range of 11.5 – 40 [32].
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14 119 Paasikallio and coworkers [20] used 95 kg of spray-dried HZSM-5 catalyst (CBV 5524G) for
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17 120 catalytic upgrading of 2 tons of pine sawdust during a four-day test run in a circulating fluidized-
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19 121 bed reactor. The acidity of the used catalyst was found to decrease as a function of its alkali metal
20
21 122 content (K, Ca, Mg) and P. However, it appears difficult to discern to what extent the loss in
22
23 123 catalyst acidity resulted from the poisoning of acid sites by alkali metals introduced with the
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25 124 biomass or from the dealumination by steam during the vapor upgrading (520 °C) and regeneration
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28 125 procedure (660 °C).
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31 126 Lower Si/Al ratios result in higher acid site density and may result in higher aromatic yields and
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33 127 more severe deoxygenation [33]. However, as was shown by Wan [34], the increased acid site
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35 128 density leads to increased deactivation rates for aromatic products and higher coking rates. The
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38 129 reason for researchers to opt for higher Si/Al ratios of e.g. 40 is likely related to the enhanced
39
40 130 hydrothermal stability of ZSM-5 with lower Al content.
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42 131 In this work, a series of successive upgrading steps of wheat straw derived FP vapors over a
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44 132 steamed ZSM-5 with Si/Al = 29.5 was performed. Liquid product was collected in between the
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47 133 upgrading steps in order to unravel the change in oil-quality and yield towards increasing B:C ratio
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49 134 and catalyst deactivation. Changes in oil properties was followed by analyzing for moisture,
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51 135 elemental composition, GC-MS/FID and acidity. For selected samples, detailed analysis by NMR,
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54 136 SEC and TGA simulated distillation was performed.
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EXPERIMENTAL SECTION

Feedstock and catalyst. Wheat straw pellets were ground and sieved to pass a 1.4 mm sieve. The results of proximate and ultimate straw composition are shown in **Table 1**. The content of moisture, ash, and volatiles was determined according to DS/EN ISO 18134-3 (2015), DS/EN ISO 18122 (2015), and DS/EN ISO 18123 (2015) respectively, and fixed carbon was calculated by difference. The proximate and ultimate ash analysis by ICP and Chlorine extraction was carried out by Force Technology, Denmark. Elemental analysis of the N, C, H and O content (by difference) was performed in-house with a EuroVector EA3000 system. The accurately weighed sample (~2 mg) was loaded into a tin capsule and combusted at 980 °C. The combustion products (N_xO_y, CO₂, H₂O and SO₂/SO₃) passed through a reduction reactor and were converted into N₂, CO₂, H₂O, and SO₂ and subsequently analyzed by GC-TCD. Acetanilide and sulphanilamide were used as calibration standards. The higher heating value of biomass and liquid products was calculated based on the formula developed by Channiwala *et al.* [35], taking the elemental composition and ash content into account. Measurement of the heating value of the feedstock using a Parr 6300 Oxygen bomb calorimeter resulted in 2 – 10 % lower HHV-values compared to the calculated value. This is partly attributed to adsorption of atmospheric moisture prior to analysis. Notably is the high potassium content of the feedstock which is known to have a catalytic effect in promoting char and gas formation during pyrolysis [36].

Table 1. Properties of crushed wheat straw and pine wood pellets

Proximate analysis [wt %]	wheat straw	pine wood
Moisture [a.r.]	6.2%	4.3%
Volatiles [d.b.]	75.5%	82.4%
Ash [d.b.]	5.9%	0.2%

Fixed carbon (by difference)	17.4%	13.1%
HHV _{daf} [MJ/kg]	19.2	19.8
Ultimate analysis [wt% d.b.]		
N	0.9%	0.2%
C	46.5%	51.5%
H	6.7%	6.2%
O	45.8%	41.9%
S	0.08%	0.007%
Cl	0.11%	0.016%
Al	0.02%	0.003%
Ca	0.32%	0.095%
Fe	0.01%	0.003%
K	0.98%	0.048%
Mg	0.07%	0.014%
Na	0.01%	0.010%
P	0.11%	0.005%
Si	1.10%	0.020%

156

157 A ZSM-5 sample with a Si/Al ratio of 29.5 (CBV5524) was obtained from Zeolyst International.

158 It will be abbreviated CBV55 and steaming, biomass pyrolysis vapor upgrading and regeneration

159 is indicated by adding the suffixes “st”, “u^x”, and “r^y”, respectively, with the exponents x and y

160 denoting the number of previous upgrading and regeneration steps the sample underwent. The

161 zeolite powder in ammonium form was calcined under synthetic air flow for 5 h at 550 °C with a

162 heating ramp of 4 °C/min. The calcined zeolite was pelletized, crushed and sieved to obtain the

163 fraction between 250 to 850 μm . In order to collect sufficient liquid product for analysis at low

164 B:C ratios 151 g of dry catalyst with a catalyst volume of 335 ml were packed as a fixed bed into

165 the externally heated reactor (ID = 67mm, length = 250 mm). Tests at higher B:C ratio up to 12.9

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3 166 were performed using 15 g of catalyst (33.5 ml catalyst volume) packed into a smaller externally
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5 167 heated reactor tube (ID = 20mm, length = 190mm). For both reactor sizes, quartz wool and
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7 168 perforated distribution plates were placed between the catalyst bed and gas-inlet/outlet pipes in
8
9 169 order to ensure plug flow behavior and avoid channeling or dead pockets. Steaming was performed
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11 170 in situ prior to the upgrading reaction by injecting water into a preheated nitrogen stream (4
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13 171 NL/min) and passing the steam (~30 vol-%) over the zeolite bed kept at 500 °C for 5 h under
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15 172 atmospheric pressure conditions.
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19 173 **Pyrolysis unit.** A bench scale ablative type fast pyrolysis set-up was modified from previous
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21 174 work [37] according to **Scheme 1**. The centrifugal reactor chamber is a horizontally arranged tube,
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23 175 with rotating arch shaped blades providing mechanical force on the biomass particles pressing
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25 176 them onto the inside of the reactor wall. Previous experience with fast pyrolysis of straw using the
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27 177 centrifugal reactor [1] resulted in uncertainties (± 2 standard deviations) for the product yields of
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29 178 organic oil, reaction water, char, and gas, of 0.7, 0.7, 3.8, and 1.5 wt-% daf, respectively. Compared
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31 179 to previous work, an electrostatic precipitator (ESP) was added to improve the collection of
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33 180 aerosols, and on-line gas analysis of non-condensable gasses was added. The pyrolysis unit can
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35 181 process a feeding rate up to ~8 g/min of biomass. For tests carried out in this work, the feeding
36
37 182 rate was in the range 1 – 1.6 g/min, which allowed stable upgrading of pyrolysis vapors and
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39 183 condensation. The nitrogen carrier gas was preheated to 450 °C and the temperature inside the
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41 184 centrifugal reactor was set to 530 °C. Char particles and fines were captured by a change-in-flow
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43 185 separator, a cyclone, and a ceramic candle filter. Downstream the catalytic reactor the vapors were
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45 186 immediately quenched in a condenser kept at 4 °C. The aerosols generated at the initial
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47 187 condensation stage were captured with the ESP. Downstream the ESP unit the gas stream passed
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49 188 through a series of glass cold fingers immersed in a dry ice/ethanol bath (-60 °C). Any remaining
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traces of condensable compounds were captured by a glass tube filled with rockwool. The flow of non-condensable gases was monitored with a cumulative flow meter. A side stream of non-condensable gases was pumped through a filter to an online gas chromatograph (Thermo Scientific refinery gas analyzer, Trace 1300/1310) with a flame ionization detector (FID) and two thermal conductivity detectors (TCD), which measured the gas composition (H_2 , N_2 , CO , CO_2 , C_1 to C_5 , and C_{6+} hydrocarbons) every 10 minutes. Chromeleon Chromatography Studio software was used for analysis of the chromatograms. A Rosemount NGA 2000 analyzer was used to continuously monitor CO and CO_2 by NDIR, and O_2 by paramagnetism.

Scheme 1. Pyrolysis unit with *ex-situ* fixed bed catalytic reactor for upgrading of vapors.

Experimental procedure. Prior to each experimental run, the system was leak tested. The cooling of the condensation train was started once the reactor system was preheated and flushed sufficiently to avoid condensation of residual moisture. Once stable temperature and gas profiles were established, the experiment was initiated by starting the motor and screw feeder. The rotation speed of the blades in the pyrolysis reactor was set to 1700 rpm and a nitrogen carrier flow of 8

204 Nl/min was used and the biomass feeding rate was in the range 1 – 1.6 g/min. The temperature of
205 the pyrolysis unit, particle separation train and catalyst bed were set to 530 °C, 400 °C, and 500
206 °C respectively. The temperature distribution along the length of the catalyst bed was measured
207 with three thermocouples placed at the beginning, middle and end of the bed, and the difference
208 between bed entry and exit was approximately 10 °C (lower temperature at bed entry). The piping
209 and high temperature valve upstream the reactor was heat traced to approximately 450 °C in order
210 to preheat the gas before entering the catalyst bed. The screw feeder and the operation of the rotary
211 reactor were stopped when the desired experimental time was reached. Any remaining vapors were
212 flushed for about 60 min while maintaining the operating temperatures in the system. The amount
213 of non-condensable gases (NCG) was determined by the GC analysis using nitrogen as internal
214 standard. After flushing of the system, the condensation train was bypassed and the system was
215 cooled to room temperature under nitrogen flow to prevent air diffusion into the system. The
216 amount of collected products was determined gravimetrically by weighing all condensation
217 equipment. For the first cooling stage operating at 4 °C, phase separation into an aqueous phase
218 and an oil/tarry phase could occur. Since the viscous oil stuck to the walls and bottom of the metal
219 condensers, the water phase could be carefully decanted. The remaining oil fraction was
220 determined by weighing of the equipment plus tarry residues. In the following, these fractions will
221 be denoted as “4°C WF” and “4 °C OF” for the aqueous and oil fraction, respectively. For the ESP
222 unit the oil was collected at a bottom receiver, and no phase separation occurred. The ESP oil will
223 be termed “ESP OF”. For the final condensation step at -60 °C, the collected product separates
224 upon melting into an aqueous phase (bottom) and a yellowish oil phase (top). We will refer to
225 these fractions as “-60°C WF” and “-60°C OF”, respectively. The glass condensers were emptied
226 into a measuring flask and the split between oil and water phase was determined by removing the

oil top phase with a pipette. Since the sum of residues remaining in the glass condensers amounts to less than 5% of the total liquid collected at this condensation stage, it was assumed that the traces of oil/water droplets remaining in the condensers consist of the same split between oil and water fraction as determined for the removed liquid. Due to the effectiveness of the condensation train, the gas filters downstream the condensation system did not capture liquid product. Residues sticking to the condensation equipment were not flushed by solvent in order to avoid the introduction and necessity of removal of the solvent. Thus, the operation at bench scale allowed the collection of larger amounts of liquids, which reduced the potential handling and analysis errors related to the collection of small amounts of oil product. After flushing the system at the operating temperature, the catalyst bed was cooled down to ~ 200 °C in a nitrogen flow. Once the high temperature valve (HTV in **Scheme 1**) was closed and the condensation train bypassed, the flow was reversed to enter the reactor bed from the outlet (2 Nl/min). The regeneration was initiated by mixing nitrogen with air (flowrate 2 Nl/min with 2 vol-% O₂) and starting a heating ramp to 580 °C at 1 °C/min. The set-point was held for several hours before the nitrogen was stepwise replaced by increasing amounts of air to achieve a final oxygen concentration of 21 vol-%. The regeneration was assumed complete once no more CO and CO₂ was measured in the effluent gas stream. Initially an empty reactor test and a non-catalytic reference test was performed over a SiC bed material (60 ml, 355 – 500 μ m) maintained at 500 °C, both for wheat straw and pine wood feedstock. Subsequently, five vapor upgrading (wheat straw) experiments were conducted as illustrated in **Scheme 2** using 151 g of CBV55 covering the range of B:C ratios up to 6.2. After the initial run to B:C = 1.7, the coke was burned off. Subsequently, four successive experiments were performed where liquid was collected but no catalyst regeneration was performed. The resulting properties for the mixture of the products obtained within the successive upgrading were calculated

according to their mass yields and elemental composition. As an example, the properties of liquid obtained for $B:C = 0 - 2.5$ were estimated by calculating the properties of liquid obtained for mixing product obtained for $B:C = 0 - 1.1$ and $B:C = 1.1 - 2.5$ according to their mass yields. After the test series using 151 of catalyst, 15 g of regenerated catalyst was transferred to a smaller reactor and two further upgrading experiments were performed in order to obtain oil at $B:C = 0 - 6.5$ and $B:C = 0 - 12.9$ (not shown in scheme). The catalyst at the end of the test series thus underwent four oxidative regenerations and will be termed CBV55-st-u⁷-r⁴.

Scheme 2. Scheme of experimental test series for conversion of straw pyrolysis vapors over 151 g CBV55. Conditions during upgrading: $T_{\text{catalyst}} = 500\text{ }^{\circ}\text{C}$, $\text{WHSV} = 0.64\text{ g}_{\text{biomass}} / (\text{g}_{\text{catalyst}} \cdot \text{h})$, 8 NL/min N_2 flow.

Product characterization. To minimize potential ageing reactions, all liquid products were kept refrigerated at $5\text{ }^{\circ}\text{C}$ after their recovery from the condensation train. The water content of the oil and aqueous phase fractions was determined by Karl Fischer titration (ASTM E203-08). Total acid number determination for selected samples was performed according to ASTM D 664 using an 848 Titrino plus (Metrohm). The TAN analysis method according to ASTM D664 was verified by analyzing a reference sample obtained for 10 mg KOH/g (Paragon Scientific Limited) and proved to correlate within 5 % of the expected value. The elemental composition (nitrogen, carbon, hydrogen) was measured by using an EA3000 CHNS elemental analyzer from Eurovector. For the

sample preparation of aqueous and volatile oil fractions, a special sealing device (Eurovector) and smooth tin capsules were used. Calibration ($R^2 = 0.998$) was performed with acetanilide (>99%) and sulphanilamide (>99%). The analysis of liquids was verified by analyzing volatile model compounds (acetone) and water. In general, the time between liquid sample preparation and injection was kept as short as possible and minimum two replicates were performed per sample. The oxygen content was determined by difference. The higher heating value of the bio-oil was calculated based on the elemental composition using an empirical formula according to Channiwala *et al.* [38]. As the sulfur concentration was below the detection limit of the elemental analyzer, few representative oils were subjected to total sulfur analysis according to ASTM method D5453. All fractions obtained from the different condensation train sections were analyzed separately by using a GC-MS/FID Shimadzu QP 2010 Ultra apparatus equipped with a Supelco Equity 5 column. Identification and quantification of species in the samples was performed by the mass spectrometer and flame ionization detector (FID), respectively. For the analysis, the oil and aqueous fractions were diluted in acetone containing 0.1 mol/L heptane as internal reference. The initial temperature for the GC column was held at 80 °C for 10 min and the column was heated up to 250 °C with an initial heating rate of 2 °C/min up to 100 °C followed by an increased heating rate of 5 °C/min. The final temperature was held for 5 min. A split ratio of 80 was used in the injection section. The MS scanning was set to a range of 20 to 300 m/z. The MS was intentionally turned off between 2.57 to 2.65 minutes in order to avoid saturation by high concentrations of the solvent. The analysis entails the quantitative determination of >200 compounds based on the effective carbon number (ECN) method outlined by Schofield [39]. For the internal standard heptane, a detailed calibration was performed, and the validity of calculated concentrations according to their ECN was periodically verified by calibration of 25 bio-oil model compounds.

292 The relative error between calculated concentrations and concentrations obtained from the
293 calibration can be found in the supporting information, **Table S1**. As can be seen, the calculation
294 by the ECN method underestimates the concentration for most of the components. It should be
295 noted that all oil fractions were analyzed with the same GC method. However, since most
296 polycyclic aromatic hydrocarbons like phenanthrene appeared at the end of the chromatogram,
297 higher MW compounds and oxygenates were not quantified. Up to 64% of the total organic liquid
298 contents could be quantified by GC-MS/FID for oils obtained at low B:C ratio, whereas only 20 -
299 30 % could be quantified for oils obtained over a coked catalyst after reaching a high B:C ratio. A
300 low quantification extent indicates a shift in product distribution towards less volatile species and
301 higher molecular weight range, which was confirmed by TGA simulated distillation and size
302 exclusion chromatography (vide infra).

303 The GPC system comprises Viscotek Data Manager DM 400, Shimadzu SIL-10AD vp auto-
304 sampler, Shimadzu LC-10AD pump/injection, 7.5 x 300 mm PLgel MIXED-E from Agilent and
305 two detectors; namely, a Viscotek RALLS (Right Angle Laser Light Scattering), Model 600, Laser
306 Diode Wavelength of 670nm, and a Viscotek Differential Refractometer/Viscometer, Model 200.
307 THF was used as eluent, and the samples were prepared at the day of analysis. The injection
308 volume was 100 μ l and a flowrate of 0.5 ml/min was utilized. TriSEC GPC software, Version 3.0
309 was used for data export and baseline correction was performed using Origin software. An
310 indication of the approximate molecular weight range was obtained by analysis of a polystyrene
311 standard of 1250 Da, several linear hydrocarbon standards covering the range of 200 – 500 Da,
312 toluene (92 Da), and few exemplary bio-oil model compounds (guaiacol (124 Da), dibenzofuran
313 (168 Da), furfural (96 Da), and phenanthrene (178 Da)). All standards were prepared at a
314 concentration of 1.5 mg/ml. Arrows in the chromatogram indicate where the components eluted.

While dibenzofuran, furfural, and phenanthrene eluted in close proximity to toluene (9.8 ml), guaiacol eluted significantly earlier at 9.5 ml. This indicates that mono and polyaromatics cannot clearly be distinguished with the set-up used. Branched or multi-functional compounds may elute earlier. As such, no absolute molecular weight determination was attempted.

Simulated distillation [40] was used with a heating rate of 50 °C/min to fit the results of the D86 standard using a TGA (Netzsch Jupiter 449F1). 10 – 20 mg of oil was placed into a Pt crucible with perforated lid after weighing of the empty crucible and immediately before the sample weighing and start of the temperature ramp. The temperature program under 150 Nml/min nitrogen was set to heat with 50 °C/min up to 650 °C, hold the temperature for 5 min before cooling to 350 °C. The atmosphere was changed to 10 vol-% oxygen and a heating ramp to 850 °C was initiated in order to combust char residues.

Proton NMR spectra were acquired on Bruker AVANCE 400 MHz spectrometer with a 5 mm CryoProbe Prodigy using approximately 50 mg sample dissolved in 1 mL of deuterated dimethyl sulfoxide (DMSO-d₆). Quantitative ¹³C NMR spectra and ¹H–¹³C HSQC spectra were acquired on a Bruker AVANCE III 800MHz spectrometer with a 5 mm TCI CryoProbe with 100 mg sample solubilized in 200 mL of DMSO-d₆. Both ¹H and ¹³C spectra were recorded at 25 °C using a 30° pulse angle. ¹H experiments were run with 1 s delay, 16 scans. ¹³C NMR were recorded with inverse-gated decoupling, 8 s delay, 512 scans. The edited phase sensitive ¹H–¹³C HSQC experiments were recorded with 2048 × 256 complex data points, 4 scans. The one-bond coupling constant, J_{HC}, was set to 145 Hz. Spectral widths in the proton and carbon dimensions were 16 ppm and 220 ppm, respectively. Transmitter frequency offset of proton and carbon were set at 4.7 ppm and 110 ppm, respectively [41]. All NMR spectra were processed with Topspin 3.5 with zero filling in all dimensions. ¹H and ¹³C chemical shifts were referenced to DMSO-d₆, at 2.50 ppm and

338 39.52 ppm, respectively. Manual baseline-correction and integration of ^{13}C spectra were carried
339 out using Origin software.

340 **Catalyst characterization.** NH_3 -TPD measurements were conducted at a Micromeritics
341 AutoChem II Chemisorption Analyzer. 100 mg of sample were degassed under vacuum conditions
342 while ramping the temperature to 500 °C (heating rate = 10 °C/min). The sample was purged with
343 25 mL/min He for 60 min, followed by cooling to 100 °C under He. 1 vol-% NH_3 in He was dosed
344 over the sample for 120 min, followed by flushing with 25 mL/min He for 60 min. The TPD was
345 conducted at a heating rate of 5 °C/min with 25 mL/min He flowrate and the signal of desorbed
346 NH_3 was measured by a TCD detector.

347 A QuantaChrome AsiQ instrument was used for Ar-physisorption measurements. N_2 -
348 physisorption was conducted at a Quantachrome Novatouch apparatus. Isotherms from Ar-
349 physisorption were analyzed using the NLDFT model applied to the adsorption branch of the
350 isotherm. For N_2 characterization, the BET method and the NLDFT model for the adsorption
351 branch were applied for characterization of the surface area and mesopore distribution,
352 respectively.

353 For XRF characterization, 0.7 g finely ground and dried zeolite powder is weighed accurately
354 and transferred quantitatively to a platinum crucible. 6.3 g 49.75% Lithium metaborate/49.75%
355 Lithium tetraborate/0.5% Lithium bromide was weighed accurately and mixed with the sample in
356 the crucible. The mixture was fused for 7 minutes at 1000 °C followed by 1 minute at 1020 °C,
357 and the resulting fusion melt was poured into a 32 mm diameter Platinum casting dish and cooled,
358 thereby forming a lithium borate glass bead with a 9:1 lithium borate to zeolite ratio. The contents
359 of Al, Si, Na and P in the sample were quantified on a Supermini200 WD-XRF instrument from
360 Rigaku. The calibration of the WD-XRF instrument follows EN ISO 12677 – 2011. The

measurement uncertainty of the analysis of main components is $\pm 3\%$ relative with 95% confidence.

Powder X-ray diffraction (XRD) measurements of zeolite samples was performed using a Huber G670 X-ray diffractometer with a copper tube and a primary quartz monochromator ($\text{CuK}\alpha 1$ radiation, $\lambda = 1.54056 \text{ \AA}$). The diffractometer operated in transmission mode with the sample placed on tape in a thin layer and placed on a rotating disc-holder and data were accumulated in the range of $2\theta = 5 - 100^\circ$ for 1 h.

Results

Catalyst characterization. Physicochemical properties of the parent CBV55 (freshly calcined), the steamed version of it and the regenerated version obtained after multiple upgrading and regeneration steps are summarized in **Table 2**. Results of NH_3 -TPD (**Figure S1**) indicate that the strong acid sites desorbing chemisorbed NH_3 at $T > 275^\circ\text{C}$ amount to 0.43 mmol/g for the parent zeolite. After steaming, the strong acidity decreased to 0.14 mmol/g , about one third of the initial value. After upgrading a total amount of fed biomass corresponding to $\text{B:C} = 7.9$ and two regeneration steps, the strong acidity further decreased to 0.07 mmol/g , corresponding to 49% of the strong acidity remaining after steaming. Interestingly, after additional upgrading of biomass corresponding to an accumulated $\text{B:C} = 20.1$ and two additional coke burn-offs, the acidity did not reduce further. The total acidity measured by NH_3 -TPD after the test series (sum $\text{B:C} = 28$, four regenerations) was reduced to $\sim 80\%$ of the value of the steamed version, which indicates that the acid sites remaining after the steam pretreatment did not change much over the course of the experimental series. The acidity of the zeolite at the end of the test series would correspond to a theoretical molar Si/Al ratio of 65, indicating the extent of dealumination by the combined effect of steaming and use compared to 29.5 for the parent zeolite. Since the stronger acid sites decrease

more compared to the weak acid sites, it seems the stronger acid sites are more prone to hydrolysis of the Si-OH-Al bond, which causes transformation of their tetrahedrally framework positions into octahedrally coordinated, extra-framework positions. This agrees well with Ong *et al.*'s observations [29] that the concentration of Lewis acid sites remained almost constant during steaming of HZSM-5 while the concentration of Brønsted acid sites followed an exponential decay.

The pore structure and surface area of a freshly calcined CBV55, a steamed CBV55 and a sample which has undergone steaming, multiple upgrading experiments (sum B:C = 28) and four oxidative regenerations was characterized by high resolution Ar-physisorption and N₂-physisorption (**Figure S2 and S3**). Reduced N₂ uptake at $p/p_0 < 0.1$ (18% lower) and $p/p_0 > 0.9$ is observed comparing the used CBV55 (st-u⁷-r⁴) with the fresh CBV55. The Ar-physisorption indicates a BET surface area reduction from 485 to 432 m²/g, while N₂-physisorption indicates an even larger reduction in BET surface area from 468 to 385 m²/g. A larger reduction in surface area is observed after steaming (e.g. by partial collapse of instable framework). The reduction in surface area is deemed unlikely to have a pronounced change on the deoxygenation activity of the catalyst, which may rather be attributed to the zeolite's loss of strong acid sites after the steam treatment.

A zeolite sample was analyzed by XRF after the test series to investigate any transfer of alkali metals. No accumulation of potassium was detected, which shows that the hot gas filtration at 350 °C was effective in retaining potassium.

A comparison of the obtained XRD patterns is provided in **Figure S4**, indicating orthorhombic (PNMA) symmetry. The similarity of the XRD patterns between the parent CBV55 and after the steaming and repeated reaction/regeneration cycles indicates that the characteristic MFI framework of ZSM-5 was retained. An estimate of the relative crystallinity of the steamed and

used samples was obtained by measuring the intensity of the diffraction signal of the (051) peak and comparing it to that of the reference un-steamed sample [29]. After baseline subtraction, this method suggests that the relative crystallinity was reduced to 98.7% after steaming and further to 94.3% after the repeated reaction/regeneration cycles. Our characterization results agree well with others who have considered the effect of steaming on ZSM-5 [29] and who studied the deactivation of HZSM-5 zeolite in CFP after repeated reaction-regeneration cycles [42,43]. We note a peak splitting of the XRD peak at $2\theta = 24.4^\circ$ after the steam treatment, which is tentatively attributed a change in unit cell volume. Knöll *et al.* [44] found that the unit cell volume of ZSM-5 decreased with increasing steaming time and therefore correlated well with a decrease in the zeolite's acidity and propylene yield.

Table 2. Physical & chemical characterization for the parent CBV55 (freshly calcined), after steaming (CBV55-st) and after additional upgrading/regeneration steps (CBV55-st-u⁷-r⁴).

	Surface area ^a	Total pore volume ^a at p/p ₀ =0.99	Micropore volume ^b	Mesopore volume ^a	Acidity ^c	Strong acidity ^c desorbing > 275 °C	Molar Si/Al ratio ^d
	[m ² /g]	[cc/g]	[cc/g]	[cc/g]	[mmol/g]	[mmol/g]	-
CBV55	468	0.31	0.22	0.12	0.65	0.43	29.5
CBV55-st	399	0.29	0.17	0.13	0.36	0.14	27.8
CBV55-st-u ⁷ -r ⁴	385	0.28	0.20	0.12	0.25	0.07	29

^a determined by N₂ physisorption; ^b determined by Ar physisorption; ^c determined by NH₃-TPD; ^d determined by XRF

Product distribution. A mass balance closure of 95% was obtained for the SiC case. The mass balance closure obtained for the initial upgrading (B:C = 0 – 1.7) over 151 g CBV55-st was 101%, and the mass balance for the four successive upgrading steps up to B:C = 6.2 including the final coke burn-off over CBV55-st-u-r amounts to 94%. For the investigation of B:C = 6.5 and 12.9

using only 15 g catalyst the mass balance closure was 87 - 90%. Losses are related to residues inside the system and minor volatilization of compounds from the collected liquids with low vapor pressure prior to their gravimetric determination. An empty reactor test at 500°C with straw feedstock yielded 36 wt-% organic liquid, which was reduced to 28% (on daf basis) when the reactor was filled with 60 ml SiC at 500 °C. Using pine wood as feedstock and passing the vapors over SiC under otherwise same conditions resulted in 16.2% char, 15.8% reaction water, 43% organic liquid and 14.7% gas. The differences in yield using wood as feedstock can be attributed to its lower ash content (0.2 wt-%) compared to wheat straw (5.9 wt-%).

A comparison of CO and CO₂ evolution during the regeneration of a coked catalyst (151 g) after B:C = 0 - 1.7 and B:C = 0 - 6.2 and for 15 g coked catalyst after B:C = 0 - 6.5 and B:C = 0 - 12.9 can be found in **Figure S5**. An exemplary temperature profile of the catalyst bed during upgrading to B:C = 12.9 over 15 g catalyst measured at the bed inlet, middle and outlet can be found in **Figure S6**. In **Figure 1**, the product distribution (except coke) obtained from each of the successive upgrading experiments is shown. It should be noted that between each upgrading step the unit is purged with nitrogen, cooled down and reheated for the next upgrading. In [26] it was observed that the signals of olefins and aromatics increase up to a B:C = 0.2 when upgrading pine pyrolysis vapors over HZSM-5. This suggests an induction period to filling up accessible micropores with reactants and establishing the product formation according to the “hydrocarbon pool” mechanism observed for the methanol-to-olefin process [45]. Since the char separation occurred prior to the catalyst bed, the char yield was not influenced by the catalyst operating conditions. The yield of C₂ and C₃ olefins decreased with increased amount of biomass fed to the system. Likewise, a decreasing trend in the amount of reaction water and an increased yield of organic liquid was observed, consistent with a lower degree of protolytic cracking. However, even for B:C = 3.6 - 6.2

the oil yield was 40 % lower relative to the non-catalytic (SiC) reference case. It is noted that after a first regeneration of the catalyst, less gas, water, and oil were formed at B:C = 0 – 1.1 compared to B:C = 0 - 1.7 prior to regeneration, which may be attributed to higher losses to coke since the experiment was stopped at a lower B:C ratio. In order to obtain an overall product distribution including the coke yields, the results obtained for the upgrading experiments over CBV55-st and the four successive B:C conversions over the regenerated catalyst were averaged based on their weight yields (**Figure 2**). The cumulative amount of biomass (daf) converted over these four experiments corresponds to B:C = 6.2. The coke amount determined by coke burn-off at the end of these four experiments was 11.2 wt-% of the coked catalyst bed. This corresponds to 4.2 % of the carbon introduced by the biomass feed during the four successive upgrading steps. **Figure 2** also includes the product distribution obtained from operating at B:C = 0 - 12.9 and B:C = 0 – 6.5 over 15 g catalyst and illustrates the increase in oil yield at higher B:C ratios. A lower degree of conversion can be expected at the reduced amount of catalyst loaded, which explains the lower coke yield of only 1.3 wt-% per daf feed for B:C = 6.5, while the additional vapor contact time when 10 times more catalyst was loaded (B:C = 6.2) resulted in a higher chance of polymerization of aromatic products and thus, elevated coke yields (4.1 wt-% per daf feed). We note that at B:C = 12.9 the yield of reaction water with 15 g catalyst loaded drops below values obtained for the SiC reference bed. Since about twice the volume of SiC was filled compared to 15 g CBV55, additional thermal cracking is possibly the reason for the increased water yield [46]. The C₂ and C₃ olefin yield (C_{2/3} =) decreased with increasing catalyst deactivation, but also the yield of CO, CO₂, and C₁-C₃ hydrocarbons decreased. Little change was observed for the hydrogen yield, accounting to 0.52 wt-% (~2 vol-% in carrier free NCG) for both low and high B:C ratios. Naturally, the coke yields are higher during the initially very active phase of the catalyst and the

rate of coke build-up gradually decreased with time on stream [11]. It is desirable to limit coke formation in order to minimize catalyst deactivation. With higher amounts of biomass fed over the catalyst, the amount of C in coke per biomass fed is reduced since more acid sites become inaccessible or deactivated. Assuming a carbon density of 2 g/cc and taking the total pore volume of microporous CBV55 into account (0.439 cc/g as determined by N₂ physisorption at p/p₀=0.99), it can be estimated that after upgrading to B:C = 6.2, about 14% of the pores were filled with coke. While this may appear low, for a purely microporous ZSM-5 a larger extent of micropore volume may become inaccessible once the pore mouth entries are capped with coke. Coke formation on the external surface (mesopores) was observed by Mukarakate *et al.* [26] and attributed to condensation reactions of unconverted lignin primary products and polymerization of aromatic hydrocarbons.

Figure 1. Product distribution obtained for 151 g CBV55-st for B:C = 0 – 1.7 and successive biomass (straw) feeding over the regenerated catalyst CBV55-st-u-r in comparison to a non-catalytic SiC bed and an empty reactor. Coke is not shown here since it was not determined in the successive upgrading experiments.

Figure 2. Product distribution obtained from upgrading of straw pyrolysis vapors over steamed CBV55 at increasing B:C ratio. Blue and green bars refer to results obtained using 151 g and 15 g catalyst, respectively. Product distribution obtained with SiC bed and empty reactor shown for reference. Conditions: $T_{\text{catalyst}} = 500\text{ }^{\circ}\text{C}$, $\text{WHSV} = 0.64\text{ g}_{\text{biomass}}/(\text{g}_{\text{catalyst}} \cdot \text{h})$, 8 NL/min N_2 flow.

Energy and carbon balance. For each experiment, the resulting heating value (HHV) for the sum of oil fractions ($4^{\circ}\text{C OF} + \text{ESP OF} + -60^{\circ}\text{C OF}$) was estimated based on the HHV and yield of the individual fraction. A detailed listing of the obtained elemental composition and calculated heating values for both oil and aqueous fractions can be found in the supporting information in **Table S2 – S10**. As can be seen in **Table 3**, at low B:C ratio a considerable enhancement of the oil quality is achieved by production of oil with a HHV of 38 MJ/kg compared to the non-catalytic reference case with $\sim 29\text{ MJ/kg}$. Notably, the thermal cracking itself already leads to an energy densification in the liquid product compared to the straw feedstock with $\sim 19\text{ MJ/kg}$. Energy balance closures were in the range of 77 – 93% within this test series. The energy content of the condensed organics is distributed between the condensed oil and aqueous phase (see **Figure S7**). With increasing catalyst deactivation, the energy losses to non-condensable gases decreases. While the HHV for oils obtained at low B:C ratio of 1.7 and 1.1 are higher by about 30% relative to the

SiC case, the energy recovery into the OL, i.e. the sum of condensed OF and WF, is lower compared to the OL obtained from SiC due to the higher losses to coke and CO_x when using a catalyst. Using 151 g of catalyst (B:C = 0 - 6.2) compared to using only 15 g (B:C = 0 - 6.5) improved the liquid properties, but resulted in higher energy losses to gas and coke. The carbon product distribution (**Figure 3**) shows that the carbon yield into the gas phase decreased with increasing B:C ratio, while the carbon recovered into the oil fraction increased and a slight decrease in the C₄₊ products is observed. Less than 2% of biogenic carbon was lost into the phase separated aqueous product stream obtained from the successive vapor upgrading up to B:C = 6.2 using 151 g catalyst. In contrast, using a reduced amount of 15 g catalyst resulted in carbon losses of 4.9 and 5.5% for B:C = 0 – 6.5 and B:C = 0 – 12.9, respectively. The highest amount of 10.3% carbon was lost into the aqueous phase for the SiC reference case. In a recent work by Starace *et al.* [47] it was reviewed that most groups working with CFP report that a significant amount of carbon (3 – 14 wt-% of the original biomass carbon) is retained in the aqueous stream. Different process conditions and biomass types could account for the differences.

Table 3. Comparison of the oil yields and oxygen content, their higher heating values (calculated based on elemental composition) and their energy yields obtained for empty reactor bed, SiC and increasing B:C ratios using 15 g and 151g CBV55-st.

Amount of catalyst		Oil yield of daf biomass [wt-% _{daf}]	wt-% oxygen (dry) in sum OF	Sum OF HHV _{db} [MJ/kg]	Energy yield in sum OF
-	empty reactor	24.6	26.5	27.7	35.1%
95 g	thermal cracking (SiC)	19.4	21.5	29.2	30.4%
151 g	CBV55-st, B:C = 0 - 1.7	9.9	5.6	37.7	19.3%
	CBV55-st-u-r, B:C = 0 - 1.1	7.2	5.7	37.9	14.0%
	CBV55-st-u-r-u, B:C = 1.1 – 2.5	11.6	9.5	35.7	21.4%

Figure 3. Product carbon distributions from empty reactor bed and upgrading straw pyrolysis vapors over SiC and CBV55-st. In (a), the carbon distribution (except coke) obtained from step-wise feeding of biomass up to B:C = 6.2 is shown using 151 g catalyst. In (b), the carbon product distributions including coke obtained for both 151 g and 15 g catalyst is compared for increasing B:C ratios and to the non-catalytic reference case (SiC). Condensed OF and aqueous phase refer to sum OF and sum WF, respectively.

Process optimization. The catalyst performance in terms of recovered oil fraction and reduction in oxygen content with respect to thermal cracking over a SiC bed is suitably compared by plotting the extent of deoxygenation (relative to thermal cracking) against the carbon yield. In a conservative comparison, the (usually oxygenated) organics present in the WF are neglected. Taking the organics dissolved into the WF into account would increase the carbon yield, but may also reduce the overall degree of deoxygenation. The gas phase contribution of olefins and C₄₊ are not taken into account for calculation of the sum OF carbon yield, even though these valuable

deoxygenated compounds may be recovered using appropriate recovery systems. For the test-series of incremental biomass conversion after the first regeneration step, the oxygen content is calculated which would result in the mixture of collected oil fractions up to the B:C ratio at which the experiment was stopped. This way a better understanding of the cumulative oil properties is obtained. **Figure 4** compares the extent of deoxygenation for the sum of OF with the oils carbon yield. It is apparent that a reduced oxygen content can only be achieved at the expense of a reduced carbon yield. According to Venderbosch [48], the properties of the accumulated oils obtained in the lower B:C range up to 6.2 would be classified as region II corresponding to severe deoxygenation at the expense of carbon. The extended B:C range 0 – 12.9 results in mild deoxygenation corresponding to region I in **Figure 4** close to the non-catalytic reference case. However, when comparing the carbon yield and the extent of deoxygenation for the range B:C = 3.6 – 6.2, it appears that only mild deoxygenation takes place over the partly deactivated catalyst. One could consider that the optimal case is to reduce the oxygen content only to an extent necessary to allow stable operation of a hydrodeoxygenation process or successful co-feeding at a refinery's FCC unit. For example, it may be favorable to operate up to a B:C ratio of ~4 in order to obtain oils with ~10 wt-% oxygen at ~56 % relative organics yield (incl. C₄₊) compared to a non-catalytic reference.

Figure 4. Correlation of the relative extent of deoxygenation (to the SiC case, 21.5 wt-% oxygen) with the carbon yield for the sum of oil fractions of each run. Green and blue symbols refer to oil product obtained using 151 g and 15 g catalyst, respectively. Filled symbols correspond to runs starting from B:C = 0 to the indicated B:C value, whereas open symbols indicate runs starting from a partly coked CBV55-st. Half-filled symbols represent calculations of the carbon yield and oxygen content based on the yield and properties of the oils obtained from the consecutive runs without regeneration for 151 g CBV55-st-u-r up to B:C = 6.2 The regions I and II indicate mild and severe deoxygenation, respectively [48].

Oil characterization. Determination of the total acid number was conducted according to ASTM D 664 by potentiometric determination of both oil and aqueous fractions. The acidity of both the oil (sum OF) and aqueous fractions (sum WF) is summarized in **Table 4**. For the oil fractions, a TAN content of 52.3 mg KOH/g resulted for the SiC oil, while at B:C = 0 – 1.1 and B:C = 3.6 – 6.2 over 151 g catalyst the sum of OF had a TAN of 6.4 and 14.3 mg KOH/g, respectively. Since the non-catalytically obtained oil contained more moisture, the acids may dissolve into this fraction to a higher extent compared to the upgraded oils. In accordance with the higher acidity of the oil fractions at increasing B:C ratio, it is found that the TAN for the sum of

WFs also increased towards higher B:C ratios. A clear jump in TAN content of both oil and aqueous fractions was observed when only 15 g of catalyst were used, indicating less efficient vapor upgrading. Interestingly, the TAN content of products obtained from B:C = 0 – 12.9 remained similar as for B:C = 0 – 6.5. This shows that the contact of the reactive vapors with the coked HZSM-5 still reduced the acidity. For the sum OF obtained during B:C = 0 - 12.9, the TAN content was less than 50% of the non-catalytic reference. It should be noted that the acidity for the non-catalytic derived straw oils is lower than for wood derived oils. The TAN content of the wood derived sum of OF and sum of WF of a reference experiment over a SiC bed amounted to 60.8 and 66.5 mg KOH/g, respectively.

Determination of the sulfur content for the sum of OF obtained from SiC, and oils obtained over the freshly regenerated zeolite (B:C = 0 – 1.1) and the coked zeolite (B:C = 3.6 – 6.2) was measured to 0.07, 0.29 and 0.1 wt-%, respectively. The enhanced sulfur content at low B:C ratio (for the most deoxygenated produced) may be attributed to the production of alkylthiophenes from H₂S and olefins or diolefins, which correlates with the enhanced yield of olefins at low B:C ratio [49].

Table 4 - TAN values for the sum of oil fractions and aqueous fractions obtained for the SiC case, and over CBV55-st-u-r (B:C = 0 - 1.1 and B:C = 3.6 - 6.2).

	SiC		B:C = 0 – 1.1 (151 g)		B:C = 3.6 – 6.2 (151 g)		B:C = 0 – 6.5 (15 g)		B:C = 0 – 12.9 (15 g)	
	sum OF	sum WF	sum OF	sum WF	sum OF	sum WF	sum OF	sum WF	sum OF	sum WF
Fraction of collected liquid product	37.9%	62.1%	17.4%	82.6%	29.9%	70.1%	30.7%	69.3%	38.7%	61.3%
TAN [mg KOH/g]	52.3	60.3	6.4	2.7	14.3	4.6	26.0	37.7	22.8	37.6
TAN of total liquid [mg KOH/g]	57.3		3.4		5.6		34.1		31.9	

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3 587 The Van Krevelen plot (**Figure 5**) illustrates the quality of the obtained liquids by plotting the
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5 588 molar H:C against the O:C ratio of the sum of the oil fractions from each upgrading step. The
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7 589 organic liquid lost into the aqueous stream was not included in this comparison due to the
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9 590 uncertainty related to determining the oxygen content of the small amount of organics dissolved
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11 591 in the highly aqueous fractions. A clear reduction in the oxygen content of the oil fractions was
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13 592 observed for the first upgrading step over CBV55-st in comparison to the liquid product obtained
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15 593 for passing the vapors over the SiC bed. However, it is apparent that oxygen was expelled to a
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17 594 high extent in the form of water and therefore hydrogen was lost. After the first upgrading cycle
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19 595 and regeneration of the catalyst, a similar degree of deoxygenation was obtained at a B:C ratio of
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21 596 1.1 compared to 1.7 for the initial upgrading step, however at a slightly reduced H/C ratio. Moving
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23 597 towards H/C of 1 at O/C of zero indicates the formation of aromatics. The incremental feeding of
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25 598 vapors from B:C = 1.1 to 6.2 without regenerating the catalyst decreased the extent of
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27 599 deoxygenation with increasing H/C ratio. When one-tenth of catalyst was used during B:C = 0 –
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29 600 6.5, a higher molar H/C and O/C ratio resulted compared to using 151g catalyst, which can be
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31 601 attributed to a lower extent of conversion of pyrolysis vapors at shorter catalyst contact time. For
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33 602 B:C = 0 – 12.9 the molar O/C ratio further increased along with the H/C ratio, indicating that mild
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35 603 deoxygenation preserved a higher H/C ratio.
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Figure 5. Molar H/C vs. O/C ratio for the sum OFs obtained for increasing amounts of straw pyrolysis vapors fed over CBV55-st (500 °C). SiC bed and empty reactor (500 °C) shown as reference. Square symbols relate to results obtained with 151 g catalyst while triangles refers to oils obtained using only 15 g of CBV55-st. Half-filled symbols constitute calculations properties for the mixture of oils obtained from successive feeding of biomass (see **Scheme 2**). Deoxygenation pathways are indicated by dashed lines.

Based on detailed product analysis of all five condensation fractions by GC-MS/FID, the yields of over 200 quantified components are grouped into monoaromatics, diaromatics, polycyclic aromatics, aliphatic hydrocarbons, phenols, methoxy-phenols, furans/furfural, ester, alcohols, ethers aldehydes and ketones. A detailed list of components of which each group is comprised of can be found in **Table S11 - Table S24**. The grouping was conducted on basis of oxygen functionalities, thus aromatic molecules containing a single oxygen functionality were grouped as oxygenate and not as aromatic. A comparison of detectable groups from quantitative GC-FID analysis for the total organic liquid products is shown in **Figure 6**. Oxygenated components present at yields less than 0.1 wt% were lumped into one category “Lump of Oxygenates < 0.1 wt%”. The results were obtained by analyzing both the aqueous fractions and oil fractions separately, i.e. for

each experiment the five different liquid products were analyzed. The highest yield of aromatics and phenols is obtained at B:C = 0 - 1.7 over steamed CBV55. After regeneration, a lower aromatics yield is obtained at B:C = 0 - 1.1, which may result both from the lower B:C range and thus higher losses to coke and gas, but also the zeolite's acidity may have been slightly reduced by the first upgrading and regeneration cycle. Continued feeding of biomass from B:C = 1.1 - 2.5 and B:C = 2.5 - 3.6 decreases the yield of monoaromatics over the coked catalyst considerably, while additional feeding of biomass beyond B:C = 3.6 reduces the aromatics yields only slightly. It is apparent that the increase in oil yield as a result of catalyst deactivation cannot compensate the loss in aromatics selectivity. Phenols may form from cracking of guaiacol-like molecules, which would indicate that less cracking reactions of these molecules occur with increased coke occluding and poisoning acid sites. When upgrading pine pyrolysis vapors over HZSM-5, it was shown by Mukarakate *et al.* [26] that the intermediate species furans, phenol and cresols reached a maximum at B:C~0.8. These intermediates will desorb at an increased rate out of the pores once the active sites in the catalyst became increasingly poisoned by coke. In this study, the yield of alcohols and ketones increased with higher B:C. The incomplete conversion of these reactive compounds indicates severe catalyst deactivation. It should be kept in mind that these observations are valid only for the detectable GC range. The identified components only account for a certain fraction of the total organic liquid. The oil fraction obtained from the -60 °C condensation stage is well suited for analysis with the column configuration, which allows quantifying up to ~85% of this fraction. More -60 °C OF product is collected at lower B:C ratios, while increasing B:C ratios increase the relative yields of oils collected at the ESP and 4 °C stage. For these fractions, only about 20% can be quantified with the applied chromatographic method. As a result, the range of GC-identifiable organics decreases with increasing catalyst deactivation (**Table S25**). While

644 64.4% could be identified for the sum of OF obtained within B:C = 0 – 1.1, only 27.3% were
645 identified for the sum of OF obtained from B:C = 3.6 - 6.2, and only 11.6% were identified in the
646 SiC case.

647 SEC was conducted for the SiC oil and oils obtained using CBV55-st for operation at B:C = 0 –
648 1.1 and B:C = 3.6 – 6.2 (**Figure S8**). The SEC chromatogram from the SiC oil can be de-
649 convoluted into seven contributions. The majority of the molecular weight distribution appears to
650 be located below 1000 Da, which is quite low compared to reported weight distributions extending
651 up to 10000 Da for non-catalytic wood derived oils [50]. As for non-catalytic bio-oil obtained from
652 straw fast pyrolysis, MW distributions up to 3000 Da have been reported by Trinh *et al.* [51]. The
653 lower molecular weight of our thermal reference oils can be partly attributed to the additional
654 cracking effect upon contact of the vapors with fine char containing high concentration of the
655 biomass indigenous alkaline ashes (especially K) at the hot gas filtration surface and partly to the
656 effect of the SiC bed. A loss of up to 30 wt% of the liquid product yield has been reported in
657 literature by HGF due to cracking reactions occurring upon contact of the vapors with the alkali
658 metals in char, which produces a narrower molecular weight distribution [23,46,52,53]. For oil
659 product obtained at B:C = 0 – 1.1, it can be noted that a very intense refractive index (RI) response
660 results at lower MW, indicating a more narrow distribution in molecular size in the range of
661 toluene. This agrees well with the high aromatic character determined by GC-MS/FID, ¹H NMR
662 and ¹³C NMR, and the improved re-evaporation behavior. For oil obtained over the coked catalyst
663 (B:C = 3.6 – 6.2), the shoulders attributed to the higher MW contributions started to appear in the
664 chromatogram, with exception of the two highest contributions eluting at 7.9 ml and 8.45 ml. For
665 B:C = 3.6 – 6.2, the contribution eluting in proximity to the toluene reference is significantly
666 reduced compared to the severely deoxygenated oil, yet still enhanced compared to the SiC

reference oil. The high intensity of the RI response for oil obtained at B:C = 0 – 1.1 could indicate absorbance effects. A significantly enhanced light scattering (RALLS) response was observed for the oil with the lowest oxygen content (6 wt-% d.b.), while oil obtained over the coked catalyst with an oxygen content of 17 wt-% d.b showed a light scattering intensity close to the SiC oil. The high aromaticity of the more severely deoxygenated oil seems to absorb at the used wavelength of 670 nm, indicating extended conjugations for the higher MW compounds.

Since aromatics such as benzene, toluene, and xylenes (BTX) are of high value, their selectivity within the quantified monoaromatics is of interest (see **Figure 7**). Clearly, the selectivity for BTX compounds decayed at higher B:C ratios. This is in line with results reported for systems utilizing high catalyst to biomass ratio, i.e. B:C << 1, where benzene and toluene are reported as the main liquid products (but at low yields) [54]. For tests conducted with 151 g catalyst up to B:C = 6.2, the benzene selectivity hardly changed, while the selectivity for the toluene and xylene fraction both decreased by about 33% compared to their initial value over a non-coked catalyst. The selectivity of substituted monoaromatic rings including alkyl and alkenyl-benzenes, as well as indanes and indenenes increases at higher B:C ratios to about twice the amount compared to the initial selectivity over a fresh catalyst. This indicates less effective side chain cracking and dealkylation of alkylaromatics with increasing coke formation.

Figure 6. Liquid product characterization by GC-MS/FID: to the left, oil obtained for B:C = 0 – 1.7 (CBV55-st) and four experiments with stepwise increasing B:C in the range 0 – 6.2 (CBV55-st-u-r). To the right, oils obtained at B:C = 0 - 1.7 and 0 - 6.2 over 151 g catalyst are compared with oils obtained at B:C = 0 – 6.5 and 0 - 12.9 using 15 g CBV55 and the SiC oil. Oxygenates in yields < 0.1 wt-% have been lumped to “Lump of Oxygenates < 0.1 wt%”.

Figure 7. Selectivity for monoaromatics as quantified by GC-MS/FID obtained from upgrading successive pyrolysis vapors up to B:C = 6.2 over 151 g CBV55-st. For each experiment, the five

liquid fractions obtained at different condensation stages were analyzed separately and according to their organics content the selectivity is shown for the total organic liquid.

Revaporization efficiency. Conventional petroleum fuels, such as diesel or gas turbine fuels, have a 10 - 90 wt-% distillation between 220–300 °C and 190–240 °C, respectively. Bio-crude reheating will be required for hydroprocessing these hydrocarbon-rich intermediates into gasoline and diesel fuels. Following the recommendation by Venderbosch [48], the charring behavior of the liquid product was investigated by TGA to evaluate the properties of the produced oils. The Research Triangle Institute (RTI) has been developing a methodology to define the thermal stability of bio-crude and determine if the extent of deoxygenation can be correlated with the residual solids remaining after distilling the liquids up to 350 °C [55]. It was found that the revaporization efficiency improves with decreasing oxygen content of the bio-oils with little influence of the catalyst or feedstock type used. In this work, TGA-simulated distillation curves were obtained both for the separate oil fractions obtained at each condensation stage (**Figure S9**), as well as for the mixture of OF according to their yields (**Figure 8a**). The amount of remaining char relative to the oil (d.b.) is reduced from 29.2% for the SiC case to 10.5% for the oil obtained during B:C = 0 - 1.1, and it increases to 22.3% for the oil obtained during B:C = 3.6 – 6.2. Upon heating, the -60°C OFs loose > 80% of their mass below 200 °C. This agrees well with the observed increased range of GC detectable compounds for oils recovered at -60 °C and the low charring tendency is an important aspect to consider for further processing, e.g. hydrotreating, as less than 5% char remained at 300 °C,. While the oil yield over a fresh catalyst is low (14 wt%_{daf}), the extent of possible reheating of the liquids has to be considered when gauging the optimal B:C ratio at which the regeneration should be initiated. For the ESP oil fractions, the mass remaining at 350°C is reduced from 28.4% for the SiC case to 18.8% for B:C = 0 - 1.1 and further increases to 24.7%

for B:C = 3.6 - 6.2. The improved revaporization efficiency of bio-oils with reduced oxygen content agrees with Dayton *et al.*'s findings [55] (**Figure 8b**).

Figure 8. (a) TGA simulated distillation behavior conducted for ~20 mg oil with heating ramp 50°C/min to 650 °C under 150 ml/min N₂. The oils (sum OF) were prepared according to their yields at each condensation stage. OFs were obtained for SiC bed and for B:C = 0 - 1.1 and B:C = 3.6 - 6.2, respectively when straw vapors were passed over 151 g CBV55-st. (b) Correlation of the oils oxygen content with the remaining mass (char) at 350 °C and 550 °C, corrected by the oils moisture content.

¹H NMR results. The processed ¹H NMR spectra of the obtained oil fractions of the SiC case, and from upgrading over CBV55-st-u-r (B:C = 0 – 1.1 and B:C = 3.6 – 6.2) obtained at the different condensation stages are provided as supporting information (**Figure S10 – S12**). For each condensation stage, it was chosen to show the non-catalytic oil at the top, followed by oil from a coked catalyst during B:C = 3.6 – 6.2 (middle) and oil obtained over a fresh catalyst during B:C = 0 – 1.1 (bottom). This way, comparing the spectra from the bottom to top illustrates the changes the oil fraction undergoes with ongoing catalyst deactivation (assuming that the non-catalytic reference case will be approached by an infinitely large B:C ratio). The relative distribution of the different chemical groups could be obtained by assigning the functional groups to their chemical

shift ranges. The water region (3.6 – 3.3 ppm) was excluded for this comparison. The obtained hydrogen percentages for the different oil fractions are summarized in **Table 5**. A higher content of aromatic and conjugated alkene hydrogen (8.2–6.0 ppm) results for the oil obtained at low B:C compared to the non-catalytic reference. Precisely, the aromatic H content for the 4°C OFs and -60°C OFs is about four times higher than for the non-catalytic reference, while for the ESP OFs it is about twice as high. Since the exchangeable proton of phenols might appear at the region of 8.2 – 6.0 ppm as well, the contribution of H bound within hetero-aromatic rings cannot be excluded. While hydrogen contributions from oxygen-containing groups (6.0 – 3.6 ppm) are almost completely absent at low B:C ratio, they start to appear for the oil obtained from a vapor upgrading over a coked catalyst (B:C = 3.6 – 6.2). This is in agreement with the reduced oxygen content of the upgraded oils determined by elemental analysis. It is interesting to note the increase in CHO or ArOH groups towards lower B:C ratio for the 4°C OF and ESP OF, whereas the -60°C OF show the opposite trend. This could be explained by an increased amount of ArOH containing compounds condensed at the 4°C OF and ESP condensation stage at low B:C ratios, whereas the dry ice trap condenses light aldehyde or ketone compounds, which are effectively converted at low B:C ratio with higher catalyst activity.

Table 5. Hydrogen percentage based on the ^1H NMR analysis of bio-oils obtained from passing straw fast pyrolysis vapors over SiC bed (a), over CBV55-st-u-r during B:C = 3.6 – 6.2 (b), and over CBV55-st-u-r during B:C = 0 – 1.1 (c).

Assignment	Chemical shift range (ppm)	H-% for 4 °C OF			H-% for ESP OF			H-% -60 °C OF		
		a	b	c	a	b	c	a	b	c
-COOH	12.5 - 11	0.0%	0.0%	0.1%	0.0%	0.0%	0.1%	0.0%	0.0%	0.0%
CHO, ArOH	11 - 8.2	0.1%	2.8%	3.5%	1.3%	3.0%	3.8%	2.5%	1.7%	1.2%
Aromatics and conjugated alkene H	8.2 - 6	7.8%	21.6%	35.4%	14.8%	21.7%	31.4%	7.8%	25.6%	38.6%

Aliphatic OH, -CH=CH-, Ar-CH ₂ -O-R	6 - 4.2	1.6%	1.2%	0.4%	2.7%	2.3%	0.4%	5.9%	3.0%	0.8%
R-CH ₂ -O-R, CH ₃ -O-R	4.2 - 3.6	17.9%	4.6%	0.6%	10.5%	7.8%	1.5%	9.7%	0.0%	0.1%
-CH ₂ C=O, -CHR-C=C, aliphatic H	3.3 - 2	54.1%	48.0%	54.7%	37.1%	50.7%	56.1%	28.4%	44.9%	52.5%
Aliphatic H	2 - 0	18.4%	21.7%	5.3%	33.6%	14.5%	6.7%	45.6%	24.8%	6.7%

¹³C NMR results. The processed ¹³C NMR spectra of the obtained oil fractions of the SiC case, and from upgrading over CBV55-st-u-r (B:C = 0 – 1.1 and B:C = 3.6 – 6.2) obtained at the different condensation stages are provided as supporting information (**Figure S13 – S15**). The ¹³C NMR spectrum offers the advantage of less overlap of chemical shifts compared to ¹H NMR. The assignment of chemical shift regions was conducted according to Mante *et al.* [56] and Joseph *et al.* [57]. The carbon distributions obtained by integrating the ¹³C NMR spectrum of the oils obtained during the different levels of catalyst activity for each condensation stage are summarized in **Table S26**. The ¹³C NMR analysis confirms a clear influence of the catalyst on the chemical composition of the bio-oil. Oil fractions obtained from the non-catalytic run show a high amount of oxygenated compounds with carbonyl, carbohydrates and methoxy/hydroxyl carbons constituting 37% and 43% of the total C for the 4 °C OF and ESP OF, respectively. For the oil obtained over a coked CBV55 catalyst (B:C = 3.2 – 6.2), the amount of oxygenated compounds in the two stages is reduced to 35% and 34%, respectively. The content of carbohydrates were eliminated significantly at low B:C ratio, and are almost under the limit of detection. Note the overall closely related trends in terms of chemical group composition for the oils collected at different condensation stages, despite their large differences in terms of viscosity and boiling point range. Comparing the oil fractions obtained using SiC with B:C = 0 - 1.1 (CBV55-st-u-r), the carbon related to oxygenated compounds of the 4°C OF was reduced by 31%, while a reduction of carbon bound to oxygen of 57% and 62% is observed for the ESP OF and -60°C OF. Based on

the oil yield distribution at the different condensation stages, the characteristics for the sum of oil fractions can be estimated, as shown in **Table 6**. With increased amount of pyrolysis vapors passed over the zeolite, the carbonyl, carbohydrates, alcohols, ethers, lignin derived methoxy carbon and alkyl fraction increased, whereas the aromatics content rapidly decreased.

Table 6. Carbon distribution for sum of OFs according to ^{13}C NMR characterization of 4 °C OF, ESP OF and -60°C OF, shown for oil obtained from (a) SiC bed, (b) over CBV55-st-u-r during B:C = 3.6 – 6.2 and (c) over CBV55-st-u-r during B:C = 0 – 1.1.

	Yield of sum OF [wt-%daf]	Carbonyl	Aromatics	Carbohydrates, alcohols, ethers	Methoxy in lignin	Alkyl
a	19.4%	17.8%	27.7%	16.9%	2.9%	25.7%
b	13.3%	17.3%	43.6%	11.5%	2.6%	25.0%
c	7.2%	7.1%	62.6%	7.5%	2.2%	20.7%

2D NMR-results. Even though the 1D NMR characterization techniques are essential for quantification, they suffer from spectral overlapping or long relaxation times when applied in the bio-oil analysis [58]. 2D NMR spectra lower the likelihood of overlapping because the signals are spread out into two dimensions. The heteronuclear single-quantum correlation spectroscopy (HSQC) experiment provide single-band connection between protons and carbons. The multiplicity-edited HSQC spectrum correlates chemical shifts of carbons and protons in a phase sensitive way. Methine ($=\text{CH}-$) and methyl ($-\text{CH}_3$) groups will appear as positive signals (blue) whereas methylene groups ($=\text{CH}_2$ or $-\text{CH}_2-$) will present negative intensity (red). A comparison of the 2D NMR spectra of the different oil fractions is found in the supporting information (see **Figure S16 and S18**). For oil collected at B:C = 3.6 – 6.2 (CBV55) the content of sugar derived compounds and alcohols is still partly reduced compared to the SiC oils. The same holds true for aldehydes and to some extent for acid derived compounds. The oil fractions obtained at B:C = 0 –

1.1 stand out by absence of aldehyde compounds, sugar derived compounds/alcohols and methoxy groups.

Non-condensable gases. The formation of dry gas and coke is reduced with increasing catalyst deactivation. **Figure 9** shows the yields of C₂ to C₄ olefins during B:C = 0 – 1.7 over CBV55-st and four successive upgrading steps over the regenerated zeolite. The ethene yield peaked at 3.1% for CBV55-st and at 2.4% after the first regeneration, and it decreased towards higher B:C ratios until leveling out at ~1.4 wt-%. For propene, the yield only slightly decreased at values ~3.7 wt-% for CBV55-st, whereas after the first regeneration cycle the propene yield dropped more rapidly, reaching ~2 wt-% at B:C > 6. n-butenes increased up to B:C~2 after which the yield declined towards higher B:C ratios. For CBV55-st, the yield of iso-butene reached a peak at B:C ~ 0.8 after which the yield slowly dropped. After a first coke-burn off, this peak occurred at B:C ~ 0.5. Further gas composition ratios are discussed in the supporting information (**Figure S19**).

Figure 9. Yield of C₂ to C₄ olefins during increasing B:C ratio over CBV55-st (diamond symbol) and after one oxidative regeneration (squares); The legend in (a) is also valid for plots (b) to (d). The yields obtained from non-catalytic SiC experiment are shown as reference (red dashed line).

Discussion

At low B:C ratio, a high deoxygenation activity results with high yields of CO, CO₂, H₂O, and coke, but at a low oil yield. The obtained oil has desirable properties in terms of reduced acidity and high HHV. With increasing amount of biomass pyrolysis vapors fed over the catalyst, the catalyst deactivates by coke deposition, blocking the access to active sites. Thus, the oil yield increases at the expense of inferior oil quality. The increasing oil yield with higher B:C ratio also increases the energy recovery into the liquid product. The critical point at which the feeding of biomass pyrolysis vapors over the catalyst should be stopped and the regeneration initiated will depend on the process utilizing the oil and its requirements to the oil's quality.

It is of interest to compare our results with other studies, which also varied the exposure of biomass derived pyrolysis vapors over HZSM-5 at similar operating temperature of 450 - 550 °C. To allow better comparison of the obtained oil yields, only results reported for *ex-situ* upgrading are taken into account. Despite the vast amount of research devoted to catalytic fast pyrolysis, often important information as the oils oxygen content or the used biomass to catalyst ratio are missing. Only few references could be found which were devoted to wood and rice husk as feedstock. To the best of our knowledge, no detailed investigation for the change in oil quality for *ex-situ* catalytically upgraded wheat straw derived vapors is available. The reported oil yields on dry-ash-free biomass basis and its oxygen content (d.b.) was related based on increasing dry, ash-free biomass to catalyst ratios, and therefore increasing deactivation of the catalyst (**Figure 10**). With increasing B:C ratio, a steep increase in oxygen content for oils from woody biomass and

acid washed straw [60] is observed compared to the results obtained in this study. It appears that both the oxygen content and oil yield increase asymptotically towards oils obtained from non-catalytic reference cases (~35 wt-% oxygen at 30 wt-% oil yield for woody biomass and acid washed straw). For most of these studies, at $B:C > 3$ the catalyst appears completely deactivated. In comparison, a reduced oxygen content for the straw derived oils from this study is observed extending to higher B:C ratios; however, also the liquid yields are lower which may be attributed partly to the high indigenous ash content of the straw feedstock, which is known to promote the formation of chars and gas [59].

Few studies [6,14,61,62] have investigated the possibility of co-processing CFP oils with vacuum gas oil by blending 10 – 20% of bio-oil. The oil's oxygen content ranged from 20 to 27 wt% in these studies. The oil's maximum oxygen content and functionalities to allow successful processing in a refinery thus determine the B:C ratio at which the vapor upgrading must be stopped, thereby dictating the frequency of catalyst regeneration. When fitting the results found in the literature for woody biomass and acid washed straw by an exponential decay function, it can be estimated that for an oxygen content of ~15% the catalyst regeneration for woody biomass would need to be initiated at a B:C ratio of about 1, whereas for the straw derived oils a six fold amount of biomass could be converted over the same amount of catalyst before regeneration needs to be initiated. A reduced regeneration frequency will extend catalyst lifetime and in general ease the operation. While **Figure 10** was devoted to comparing the results of the obtained liquid from start over the fresh catalyst to a certain B:C ratio, we can also try to compare the oils collected during increasing B:C intervals. The work by Horne and Williams [28] allows this comparison for oils obtained from *ex-situ* vapor upgrading (fast pyrolysis of mixed wood). Suitably, these authors used a similar condensation train comprised of a cooling water and dry ice stage. However, the oxygen

content in the collected oil phase was stated on wet basis without analyzing the water content. We therefore show our results for oxygen content and yields on wet basis for the phase separated oil fractions to facilitate the comparison (**Figure 11**). Similar trends are observed for the oil collected from stepwise upgrading. While lower oil yields result for the straw derived oils, their oxygen content on wet basis at a given B:C ratio is only about 50% compared to that of the wood derived oils.

Figure 10. Comparison of results obtained from this study (open symbols) for upgrading straw pyrolysis vapors with results found in the literature for *ex-situ* upgrading over ZSM-5 type zeolites at different B:C ratios and catalyst temperatures of 500°C. Shown are the “cumulative” oil properties when collected at the indicated daf biomass to catalyst ratios. Square symbols refer to the study of Hernando *et al.* [60] using acid-washed wheat straw (pyrolysis at 550°C) and upgrading the vapors over ZSM-5 at 400°C for various B:C ratios and a single test at 500 °C.

Diamond symbols refer to results from Williams and Nugranad [3] obtained for rice husks, the triangle symbols at the same B:C ratio are obtained for different SiO₂/Al₂O₃ contents of ZSM-5 with beech wood feedstock [2], star symbols refer to results by Iliopoulou *et al.* [4] for beech wood, and the cross symbols refer to results by Williams and Horne [28] reported for mixed wood feedstock and repeated regeneration steps which were found to increase the oil's oxygen content with minor increase in oil yield. Results obtained for the non-catalytic reference case of this study are indicated by horizontal lines for both wood and straw feedstock.

Figure 11. Change in the “differential” oil yields (including moisture) and oxygen content (on wet basis) shown for this study (straw) and results obtained by Horne & Williams [10] for upgrading pyrolysis vapors derived from mixed wood (daf) for the intervals B:C = 0 - 0.5; 0.5 - 1, 1 - 2, and 2 - 3. Shown is the yield of oil fractions, i.e. without taking C₄₊ and aqueous fractions into account.

Conclusion

The change in oil yield during *ex-situ* CFP of wheat straw over an increasingly coked ZSM-5 was correlated with the changes in oil quality. We complemented the assessment of catalyst activity by detailed characterization of both the liquid and gas phase products. With increasing deactivation

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3 881 due to coking, the yields of valuable hydrocarbon product fractions, particularly aromatics and
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5 882 olefins decreased, while a gradual breakthrough of primary pyrolysis vapors increased the oxygen
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7 883 content of the condensed liquid. Bio-crude produced with ZSM-5 at B:C = 1.7 contained higher
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9 884 yields of completely deoxygenated compounds such as monoaromatics (3 wt-% of daf biomass)
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11 885 compared to the non-catalytic oil, but also elevated yields of phenols (0.9 wt-%). While aldehydes,
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13 886 sugars, alcohols and methoxy groups were effectively converted at low B:C ratio, they can be
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15 887 found in increasing amounts in the liquid product slate at a progressed zeolite deactivation. The
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17 888 catalyst maintained activity after steaming and four cycles of vapor upgrading and oxidative
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19 889 regeneration, and the zeolite's acidity decreased by 18% relative to the steamed zeolite. While the
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21 890 results indicate catalyst stability over few reaction-regeneration cycles, investigation of the 'true'
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23 891 long-term stability would require many additional regeneration cycles.
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25 892 The hot gas filtration upstream the zeolite bed was effective in preventing accumulation of
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27 893 potassium on the zeolite. We conclude that the regeneration frequency will depend on the product
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29 894 application. In agreement with CFP of woody biomass reported in literature, the selective
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31 895 production of monoaromatics and olefins can only be achieved at low B:C ratios and requires
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33 896 continuous catalyst regeneration. For fuel production, a high energy yield is paramount which may
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35 897 allow operation toward higher B:C ratio and thereby require reduced regeneration frequency as
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37 898 long as certain fuel requirements are met. The provided characterization of the oil properties in
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39 899 combination with the regeneration and deactivation of the catalyst may assist the development of
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41 900 co-processing of CFP oil from agricultural residues in oil refineries.
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49 901 ASSOCIATED CONTENT

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52 902 **Supporting Information.** NH₃-TPD profiles; Isotherms and pore distribution of fresh and used
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54 903 catalyst obtained from N₂ and Ar physisorption; XRD spectra for fresh and used catalyst; CO
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904 and CO₂ gas profile during regeneration; Catalyst bed temperature profiles during upgrading;
905 Distribution of collected liquids according to condensation stage; Moisture content, HHV and
906 elemental analysis of oil and aqueous fractions; GC-MS/FID identified compounds and product
907 grouping; SEC oil characterization; TGA simulated distillation curves; quantitative ¹H NMR and
908 ¹³C NMR spectra; HSQC NMR spectra for oils collected at different condensation stages.

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920 ABBREVIATIONS

921 CFP, catalytic fast pyrolysis; daf, dry ash-free basis; d.b., dry basis; ECN, effective carbon
922 number; ESP, electrostatic precipitator; FP, fast pyrolysis; HHV, higher heating value; ID, inner
923 diameter; RI, refractive index; SEC, size exclusion chromatography; TGA, thermogravimetric
924 analysis; OF, oil fraction; WF, water fraction;

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