SUPPLEMENTARY INFORMATION

Direct upgrading of fast pyrolysis lignin vapor by HZSM-5 catalyst

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1. Moisture content of HZSM-5

Although the catalysts were pretreated, including size reduction and calcination at 500 °C under air for 5 hours, the pretreated catalysts were simply stored in a bottle for later use. The catalysts probably absorb moisture during the storage. The moisture content of the pretreated HZSM-5 catalyst was then determined by Thermogravimetric analysis (TGA) as weight loss (see Fig.S1 and Table S1.) In Fig. S1 the red dot line is the temperature profile and the blue solid line is the weight loss of the catalyst. Table S1 summarizes the weight losses of the catalyst at corresponding temperatures.

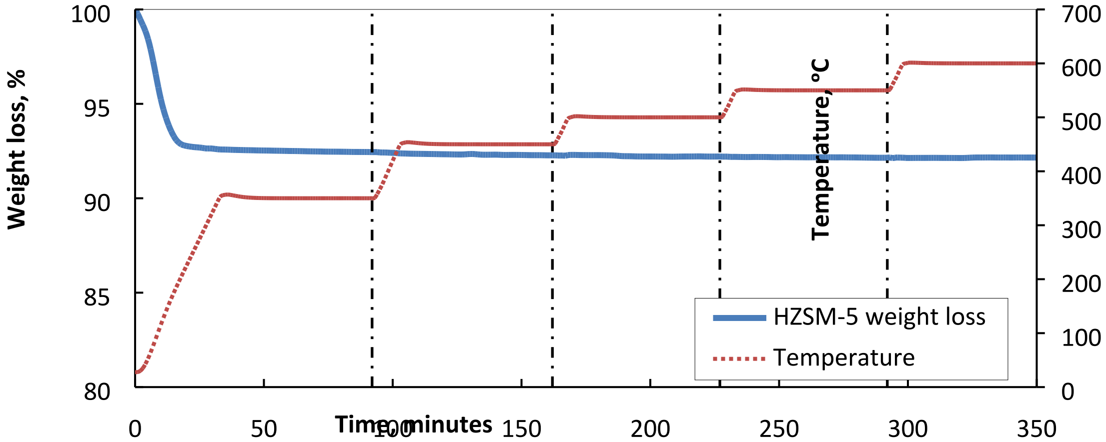

Fig. S1 Thermogravimetric analysis (TGA) of the fresh pretreated HZSM-5 catalyst under nitrogen flow at different temperatures to determine the release of moisture.

Table S1 The weight loss of HZSM-5 at corresponding temperatures during TGA analysis, related to Fig. S1.

Temperature, °C	Weight loss, %
350	7.55
450	7.73
500	7.79
550	7.85
600	7.84

2. Effect of hot gas filter on product yields

Fast pyrolysis of lignin in the Pyrolysis Centrifuge Reactor (PCR) reactor produced a high amount of char with a small particle size. In our case, a cyclone was not efficient enough to separate the char from the gas phase. Hence a hot gas filter was mounted after the cyclone to capture the fine char particles. It has been reported that the hot gas filter had a negative effect on organic yield by cracking the pyrolysis vapor to gases, when the hot gas filter was operated at 400 °C and 500 °C.[1, 2] Similar results were found in this study. The overall product yields from fast pyrolysis of lignin at different temperatures of the hot gas filter are plotted in Fig. S2. The organic liquid yield is reduced from 27.6 wt.%$_{daf}$ to 25 wt.%$_{daf}$, when the temperature of the hot gas filter is increased from 300 °C to 375 °C. The reduction of the organic liquid yield at high filter temperature is mainly because of cracking which produces more gases. A lower temperature of the hot gas filter, 275 °C, gives less yield of organic liquid, due to the partial condensation of the pyrolysis vapor inside the hot gas filter, and consequently slightly higher yield of char. By decreasing the temperature of the hot gas filter to lower than 350 °C, it is possible to minimize the negative effect of the hot gas filter on the organic yield, but a certain reduction of the organic yield cannot be avoided.

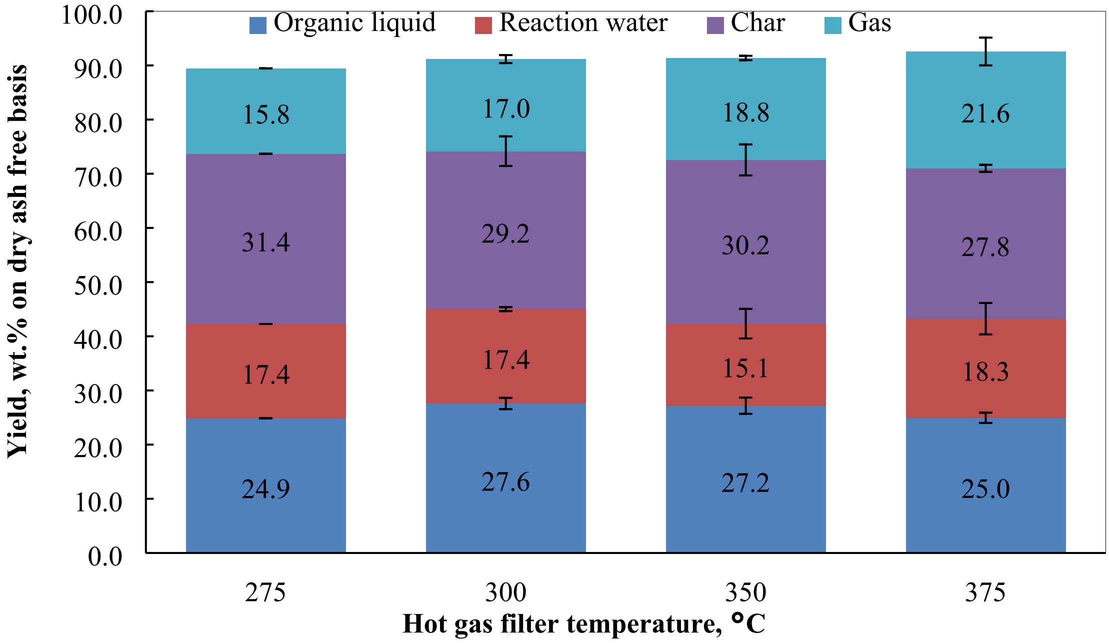

Fig. S2 The product yields from fast pyrolysis of lignin under different filter temperatures. Pyrolysis condition: 1.1-1.8 g/min feeding rate; 1.8 seconds pyrolysis reactor gas residence time; 500 °C pyrolysis temperature.

3. Product yields and standard deviation

Table S2 shows the summary of the average product yields and the standard deviations. The mass balance closure of individual experiment was in the range of 76-96 wt%. The main uncertainties are from the determination of the gas yield, the reaction water yield and the char yield. The amount of gas is somewhat uncertain, because it is calculated by the difference of two relative large numbers, specifically the total volume of gas recorded by a gas meter and the added volume of carrier gas. The uncertainty of the amount of char is fairly high because of the losses during the collection of chars, especially the collection of chars from the hot gas filter. In addition, trace heating is used from the pyrolysis reactor to the cyclone. There might in some cases be cold spots inside the setup, where the chars will stick and then not be collected. From time to time, the setup cleaning was done by sending air to the heated setup to combust any trapped carbonaceous materials inside the setup. After combustion, ash was always collected inside the char bottles and the hot gas filter. The amount of reaction water is determined by total amount of water subtracting the moisture in zeolite and biomass. This might make the determination of the reaction water very sensitive to the accuracy of the moisture in the zeolite and biomass.

Table S2 Summary of the product yields on dry ash free basis and the standard deviations*

Catalyst temperature	no catalyst	350 °C	450 °C	500 °C	550 °C	600 °C
Organic liquid	27.59 (1.04)	3.17 (1.69)	9.13(1.05)	6.97(1.86)	6.95(1.33)	5.65(2.17)
Reaction water	17.41(0.38)	21.22(3.00)	24.20(1.96)	20.89(0.99)	22.61(3.39)	20.47(2.96)
Gas	17.00(0.74)	18.78(2.13)	20.27(1.73)	21.28(2.56)	23.46(2.91)	25.88(4.44)
Char	29.16(2.73)	30.33(2.47)	30.80(1.30)	30.39(2.52)	33.78(2.65)	31.58(1.33)
Coke	-	8.92(0.65)	7.08(0.55)	5.84(0.22)	5.35(0.17)	5.06(0.37)
Mass balance	91.15	82.43	91.48	85.37	92.14	88.64
Aromatic hydrocarbons						
Benzene		0.16(0.03)	0.36(0.04)	0.68	0.89(0.07)	1.61(0.07)
Toulene		0.55(0.03)	0.96(0.12)	1.44	1.76(0.05)	1.62(0.02)
p-Xylene		0.48(<0.01)	0.61(0.05)	0.63	0.53(<0.01)	0.24(0.02)
o-Xylene		0.09(<0.01)	0.14(0.03)	0.14	0.16(0.01)	0.07(0.01)
Ethylbenzene		0.04(<0.01)	0.02(<0.01)	0.02	0.01(<0.01	0.01(<0.01)
Napthalene		-	0.15(0.02)	0.31	0.37(0.03)	0.33(0.07)
Alkyated naphthalenes		-	0.17(0.02)	0.34	0.13(<0.01)	0.08(0.07)
Gas species						
CO_2	11.49(0.38)	10.89(1.27)	10.02(0.59)	9.79(1.28)	10.42(1.29)	10.95(1.83)
CO	4.01(0.27)	4.76(0.61)	5.22(0.33)	5.55(0.71)	6.43(0.82)	7.70(1.41)
CH_4	0.84(0.04)	0.88(0.12)	0.85(0.13)	0.96(0.13)	1.25(0.20)	1.73(0.30)

H_2	0.04(0.01)	0.03(<0.01)	0.04(0.01)	0.06(0.01)	0.08(0.01)	0.16(0.03)
C_2H_4	0.21(0.05)	0.31(0.10)	1.11(0.16)	1.81(0.23)	2.55(0.36)	3.41(0.55)
C_2H_6	0.30(0.05)	0.28(0.03)	0.29(0.06)	0.34(0.05)	0.38(0.06)	0.48(0.07)
C_3H_6	0.12(0.01)	0.22(0.05)	0.80(0.16)	1.21(0.19)	1.11(0.25)	0.93(0.35)
C_3H_8	0(0)	1.44(0.18)	1.96(0.38)	1.57(0.47)	1.24(0.36)	0.50(0.46)

* The numbers in the parentheses are the standard deviations

Initial experiments were conducted by adding isopropanol into the condensers to help the condensation. However some isopropanol was lost during an experiment and the mass balance closure was difficult. Hence in later experiments, the isopropanol was only added after the experiments in order to help collecting the bio-oil in one phase for later analysis. Product yields in Table S2 are reported as the average of initial and later experiment, except the yield of aromatic hydrocarbons. Different results were obtained from the initial experiments and later experiments regarding the yield of aromatic hydrocarbons. We discovered that without the isopropanol to help the condensation, organics with low boiling point such as benzene and toluene were not collected efficiently, which resulted in a yield of aromatic hydrocarbons lower than 1 wt.$\%_{daf}$ regardless of catalyst temperature. For the yield of aromatic hydrocarbons we therefore use only the results with isopropanol to assist the condensation.

4. Raw data of TGA analysis on the spent catalysts

Fig. S3 shows the raw data of the TGA analysis of the spent catalysts. For each analysis, about 6-7 mg of the spent catalysts was chosen from the entrance of the catalyst bed. In Fig. S3, the colored solid lines are the weight losses of the spent catalysts during the TGA analysis and the dotted line is the temperature profile. Firstly, the spent catalysts were heated up to 100 °C and kept there for an hour to release the moisture. However, according to moisture determination of the catalyst (see Fig. S1), the catalyst continuously released a significant amount of moisture until it was heated to 200 °C. Hence, it is assumed that the weight losses, when the spent catalysts were heated up from room temperature to 300 °C, correspond to the release of moisture. The weight losses, when the spent catalysts were heated up from 300 °C to 750 °C under nitrogen flow, correspond to the release of volatiles. The weight losses, when the spent catalysts were heated up from 300 °C to 750 °C under 10 vol.% O_2, corresponds to the combustion of coke.

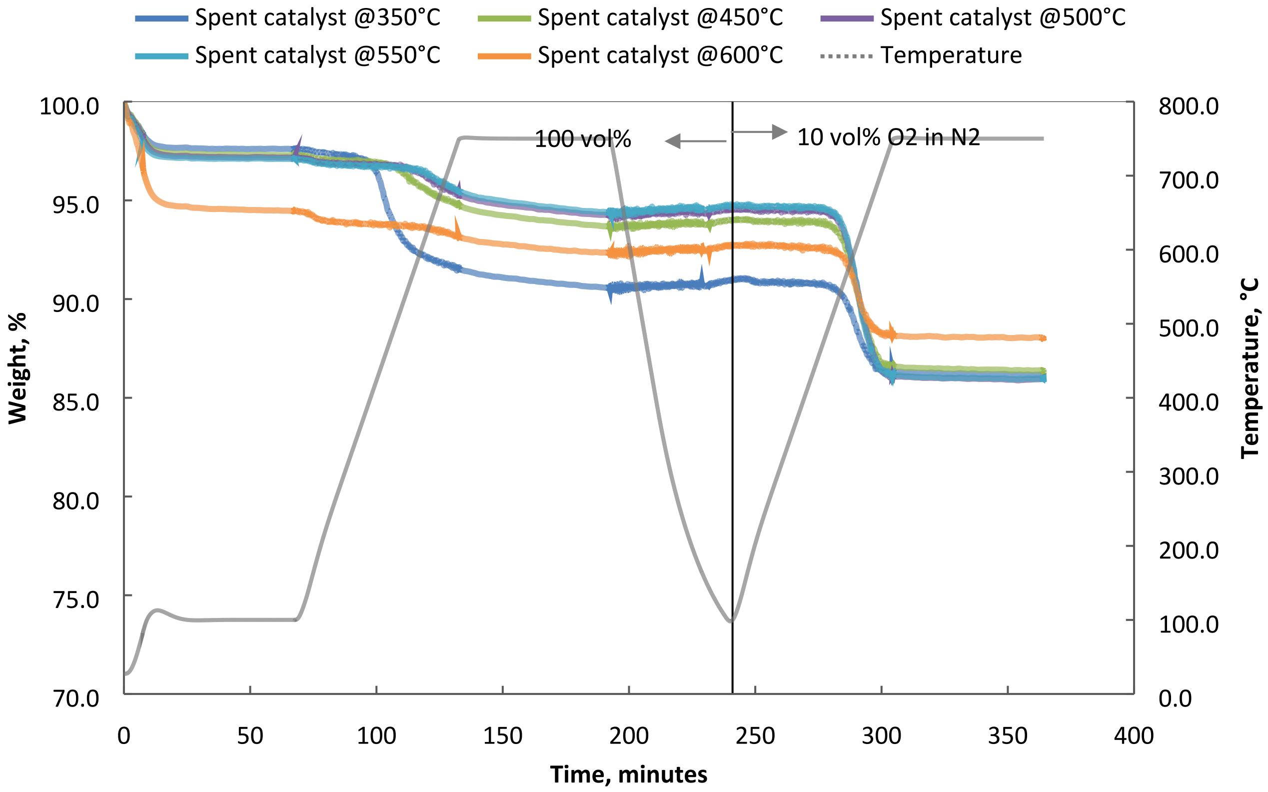

Fig. S3 Thermogravimetric analysis on the spent catalysts by heating up to 750˚C under N_2 flow first and combustion using 10 vol% O_2 later.

REFERENCE

1 P. A. Case, M. C. Wheeler and W. J. Desisto, *Energy Fuels,* 2014, **28**, 3964-3969.

2 W. J. DeSisto, N. Hill, S. H. Beis, S. Mukkamala, J. Joseph, C. Baker, T. Ong, E. A. Stemmler, M. C. Wheeler and B. G. Frederick, *Energy Fuels,* 2010, **24**, 2642-2651.