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Supplementary Information

An improved catalytic pyrolysis concept for renewable aromatics from biomass involving a recycling strategy for co-produced polycyclic aromatic hydrocarbons

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Experimental Section

1. *Ex-situ* catalytic pyrolysis of crude glycerol in a dedicated continuous bench scale unit

Crude glycerol was commercially supplied by Sunoil Biodiesel B.V., The Netherlands. The crude glycerol sample was evaporated, pyrolysed, and aromatized in a dedicated continuous bench-scale unit comprising of a evaporation/pyrolysis unit (520 ^oC), a fixed bed reactor (bed height of 15 cm, 536 ^oC) containing 200 g of shaped H-ZMS-5 zeolite catalyst prepared following a previously established procedure (H-ZMS-5 Si:Al=23/bentonite 60:40, 1-2 mm particles),[36] and a condenser unit. In a typical experiment, the crude glycerol was heated to 70 ^oC and fed (for example using 850 g sample at 3.8 g min^{-1}) to the pyrolysis unit using a N_2 flow of 1.5 L min^{-1}. The products from the fixed bed reactor were cooled using a two-stage condensation sequence (5 ^oC using cooled tap water and -20 ^oC using cooled methanol). Layer separation of the condensed fraction (organics/water) gave an aromatic oil (163.2 g or 19.2 wt.% yield on feed intake (about 70 g of benzene, toluene, and xylenes (BTX) based on GC) and water (215.45 g or 25.3 wt.% yield on feed intake).

2. Distillation of the aromatic oil to separate BTX and the polycyclic aromatic hydrocarbon (PAH) fraction

Typically, the combined crude aromatic bio-oils (3.5 L) from **1** were transferred to a separating funnel and the phases were allowed to settle for 2 d. The phases were separated and the crude bio-oil was dried over Na_2SO_4 and subsequently filtered by suction over a glass filter. The filtered oil (2941 g) was subjected to a coarse distillation under reduced pressure (50 mbar, 40 °C, 110 °C) using a simple distilling set-up, affording a mixture of BTX (1193 g or 40.6 wt.% on feed intake) and a residual oil consisting of high molecular weight aromatics or PAH (1748 g or 59.4 wt.% yield on feed intake).

3. Catalytic hydrogenation of PAH fraction to obtain polycyclic aliphatics (PCA)

Typically, 18.01 g of PAH fraction and $Ru_{5wt.\%}/C$ (0.92 g) were subjected under hydrogen pressure (134.1 bar) in a batch Parr reactor and heated to 305 °C (pressure increased to 157.6 bar). A gradual pressure drop in H_2 pressure was then observed. After stirring for 3.25 h, the reaction was cooled to room temperature and the reaction product was filtered over Whatman syringe filters (0.2 µm), affording an orange oil product (11.6 g or 64.4 wt.% yield of PCA).

In a similar experiment, 15.02 g of PAH fraction and $Ru_{5wt.\%}/C$ (0.76 g) were put under hydrogen pressure (84.4 bar) in a Parr batch reactor and heated to 305 °C (pressure increased to 119.1 bar). A gradual pressure drop in H_2 pressure was then observed. After stirring for 2 h, the reaction was cooled to room temperature and the reaction product was filtered, affording an orange oil product (5 g or 33.3 wt.% yield of PCA (2)).

The PAH fraction and PCA were analyzed by gas chromatography/mass spectrometry (GC/MS-FID) (HP 5890 gas chromatograph equipped with a RTX-1701 capillary column and a quadrupole HP 6890 MSD selective detector attached), nuclear magnetic resonance spectroscopy (^{1}H NMR, Varian Unity Plus, 400 MHz), and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF). For the later, a 15 g L^{-1} solution of DABP (3,4-diaminobenzophenone) in methanol:water mixture (8:2) was used as matrix. The analyses were developed in negative mode.

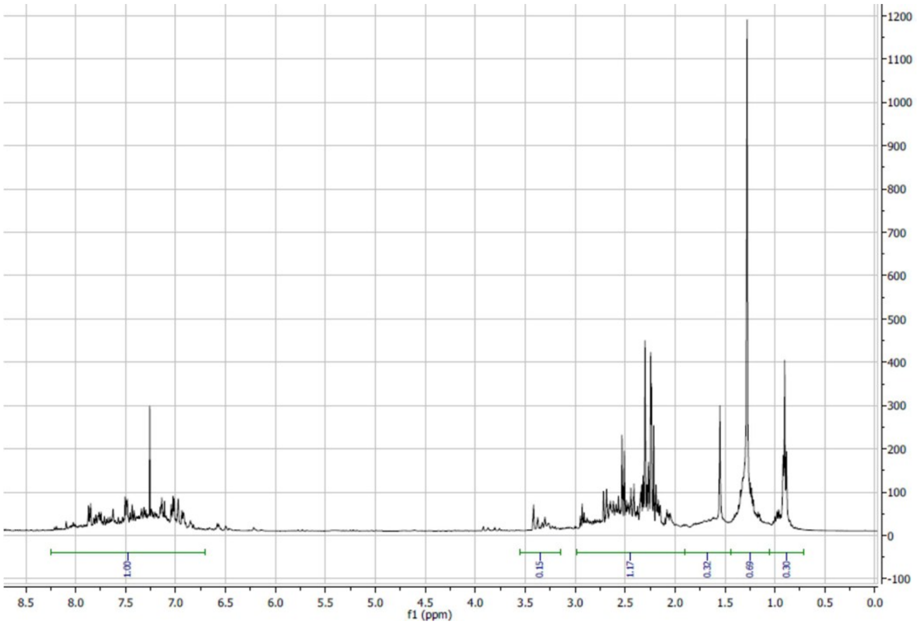
4. *Ex-situ* catalytic pyrolysis of crude glycerol in a small scale reactor at gram-scale

The crude glycerol was pyrolyzed and subsequently upgraded using a small scale reactor set-up comprising of a pyrolysis unit and an upgrading unit connected to each other. A constant stream of N_2 (11 mL min^{-1}) was used to maintain an inert atmosphere. Typically, the pyrolysis unit was filled with crude glycerol (for example using 0.94 g sample) and the upgrading unit was filled with the H-ZSM-5 zeolite catalyst (Si:Al=23) (3.18 g). The reactor was placed in a fluidized sand bath heated at 550 ^{o}C. The pyrolysis took about 15 min to finish with a constant N_2 flow. The pyrolysis vapor was subsequently converted in the upgrading unit via the catalytic treatment. The vapor was subsequently condensed to a temperature of -40 ^{o}C. The amount of condensables was determined by weight. The non-condensable gaseous products were collected in a gas bag and were subsequently analyzed by GC-TCD. The cooling unit was then washed with small amounts of THF, the amount of water was determined using Karl-Fischer titration, and the organic fraction was subsequently calculated by difference. The solid products and spent catalysts were analyzed by thermogravimetric analysis (TGA/SDTA851e analyzer, Mettler-Toledo, USA). Elemental analysis was performed using an EuroEA3000 Elemental Analyzer (Eurovector, Italy). *Ex-situ* catalytic pyrolysis of crude glycerol was performed in duplicate and the average yields of products were reported.

5. *Ex-situ* catalytic (co-)pyrolysis of PAH fraction, PCA fractions, and other biomass feedstocks

Under identical conditions as described in **4**, biomass feedstocks Kraft lignin, cellulose, and Jatropha oil, and the PAH and PCA fractions were catalytically pyrolysed over a H-ZSM-5 catalyst. Catalytic co-pyrolysis of each biomass with PAH or PCA was typically performed at 1:1 wt. ratio (total weight of 1 g) in the presence of H-ZMS-5 catalyst at 1:3 biomass-PCA or PAH mix : catalyst wt. ratio. Catalytic (co-)pyrolysis experiments were performed in duplicate and the average yields of products were likewise reported.

PAH fraction



PCA

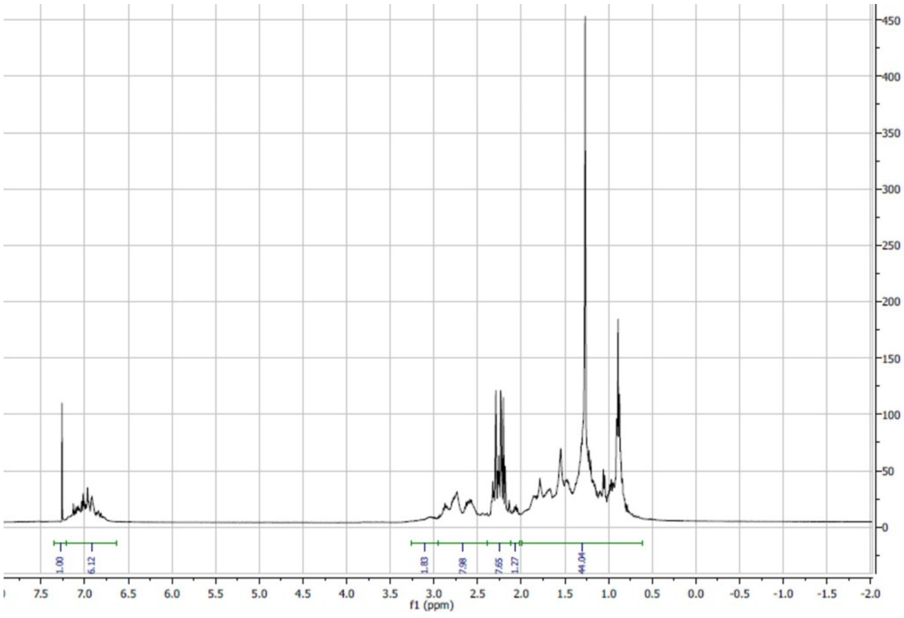


Figure S1. Representative ^{1}H-NMR spectra of the PAH fraction (top) and PCA (bottom).

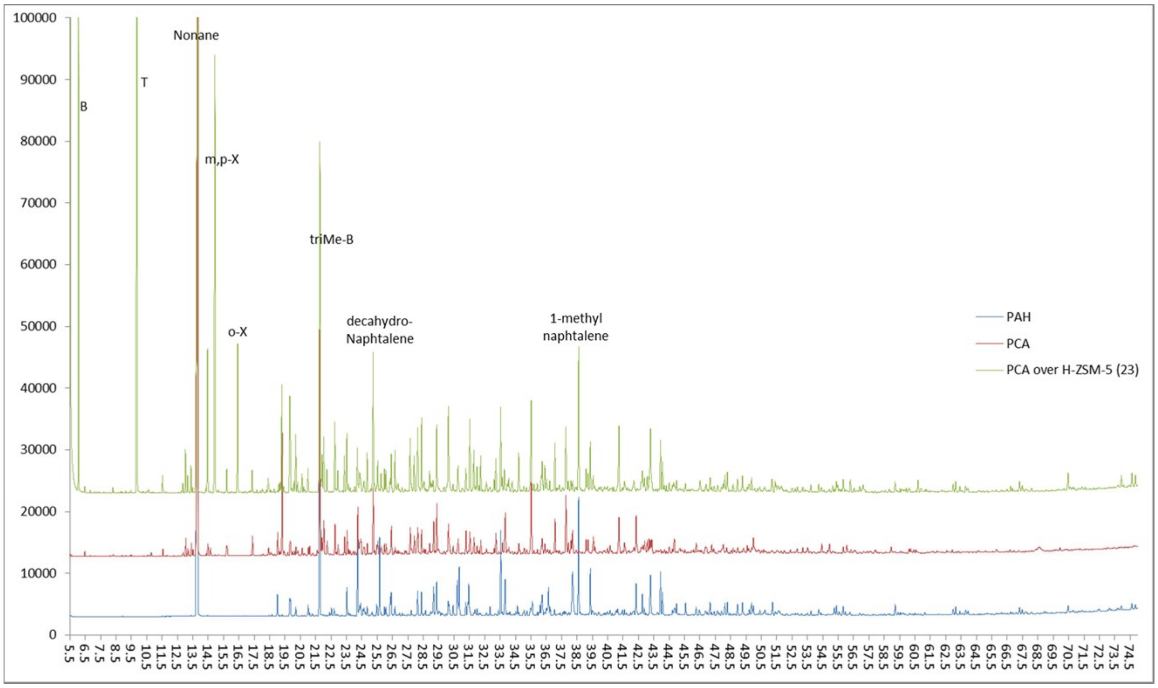
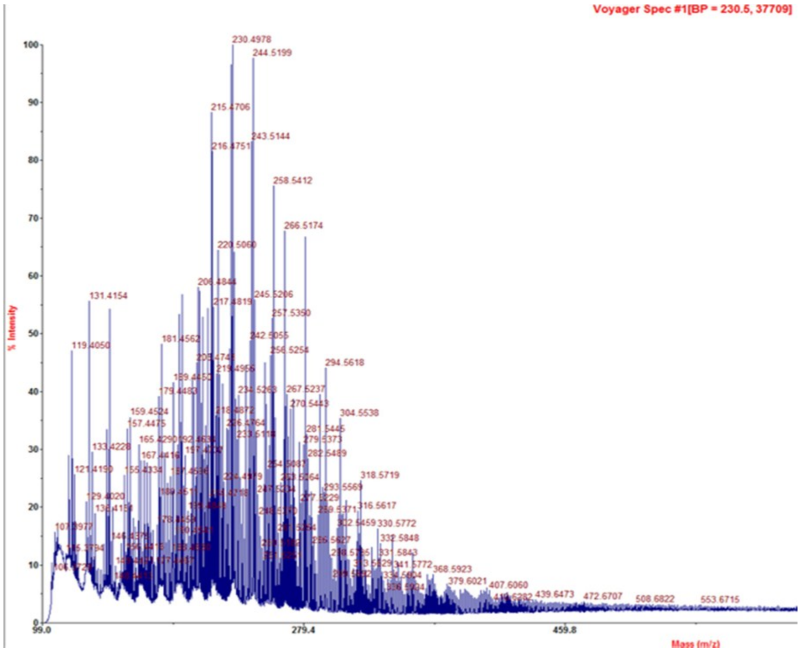


Figure S2. Representative GC chromatograms of the PAH fraction and PCA, and PCA after *ex situ* catalytic pyrolysis in the presence of H-ZSM-5 catalyst.

PAH fraction



PCA

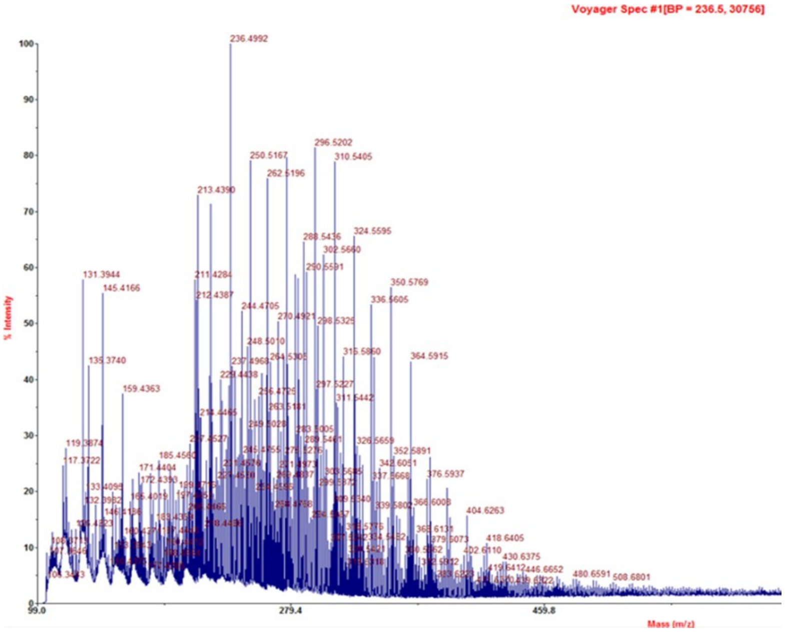


Figure S3. Representative MALDI-TOF spectra of the PAH fraction (top) and PCA (bottom).

Table S1. Composition of the crude glycerol sample used in this study.

	Composition (wt.%)
Water [a]	2.43
CH_3OH [b]	0.05
Glycerol [c]	49
Fatty acid methyl ester (FAME) [c]	4.3
Free fatty acids (FFA) [c]	44.5
Na [d]	0.76
Mg [d]	<0.01
Fe [d]	0.03

[a] determined by Karl Fischer titration

[b] determined by trace gas chromatography analysis

[c] determined by proton nuclear magnetic resonance spectroscopy

[d] determined by atomic absorption spectroscopy

Table S2. Composition of products observed in the GC chromatograms of PAH and PCA, and *ex-situ* catalytic pyrolysis of crude glycerol and PCA in the presence of H-ZSM-5 zeolite catalyst.

RT	**Quality**	***Ex-situ* pyrolysis of crude glycerol over H-ZSM-5 catalyst**	**PAH**	**PCA**	***Ex-situ* pyrolysis of PCA over H-ZSM-5 catalyst**
6.06	94	Benzene			Benzene
8.3	90				Cyclohexane, 1,2-dimethyl-,
9.87	91	Toluene			Toluene
11.54	94				Cyclohexane, 1,3,5-trimethyl-,
12.86	91				Cyclohexane, 1,2,4-trimethyl-
13.03	96			Cyclohexane, 1,2,4-trimethyl-	Cyclohexane, 1,2,4-trimethyl-
13.17	94				Cyclohexane, 1,2,4-trimethyl-
13.39	95				cis-1-Ethyl-3-methyl-cyclohexan
13.49	90				Cyclohexane, 1-ethyl-4-methyl-,
14.47	93	Ethylbenzene			Ethylbenzene
14.94	97	p-Xylene			Benzene, 1,3-dimethyl-
15.72	91				Cyclohexane, 1-ethyl-2-methyl-,
16.43	97	Benzene, 1,2-dimethyl-			Benzene, 1,2-dimethyl-
17.37	96			1H-Indene, octahydro-, trans-	1H-Indene, octahydro-, trans-
18.42	90				Cyclohexane, 1-methyl-2-propyl-
19.02	95		Decane	Decane	
19.11	91				Cyclohexane, diethyl-

19.3	98			1H-Indene, octahydro-, cis-	1H-Indene, octahydro-, cis-
19.8	91	Benzene, 1-ethyl-2-methyl-			
19.82	90		Benzene, 1-ethyl-3-methyl-		Benzene, 1-ethyl-3-methyl-
19.87	90		Benzene, 1-ethyl-2-methyl-		
20.2	90	Benzene, 1-ethyl-3-methyl-			
20.21	96				1,2,4-Trimethylbenzene
20.61	95				Cyclohexane, 1-methyl-2-propyl-
21	91				Benzene, 1,3,5-trimethyl-
21.12	90			Cyclohexane, butyl-	
21.72	94	Benzene, 1,2,3-trimethyl-			
21.77	97		1,2,4-Trimethylbenzene	1,2,4-Trimethylbenzene	1,2,4-Trimethylbenzene
21.92	98			1H-Indene, octahydro-5-methyl-	1H-Indene, octahydro-5-methyl-
22.75	99			Naphthalene, decahydro-, trans-	Naphthalene, decahydro-, trans-
23.37	98			1H-Indene, octahydro-5-methyl-	1H-Indene, octahydro-5-methyl-
23.54	93		1,2,4-Trimethylbenzene	Benzene, 1,2,3-trimethyl-	Benzene, 1,2,3-trimethyl-
24.22	93		Indane		Indane
24.26	95			Undecane	
24.86	95				Benzene, 4-ethyl-1,2-dimethyl-
25.25	99			Naphthalene, decahydro-	Naphthalene, decahydro-
25.55	95				Naphthalene, decahydro-2-methyl

25.67	94		Indene		
25.98	95				Benzene, 4-ethyl-1,2-dimethyl-
26.08	91				Benzene, 1-methyl-4-(1-methylet
26.35	94				Benzene, 2-ethenyl-1,4-dimethyl
26.36	93		Benzene, 1-methyl-2-(2-propenyl)-		
26.43	90		Benzene, 1-ethyl-2,3-dimethyl-		Benzene, 1-ethyl-2,3-dimethyl-
26.44	90			Benzene, 4-ethyl-1,2-dimethyl-	
26.67	90				2,3-Dihydro-1-methylindene
27.65	94				Naphthalene, decahydro-2-methyl
27.92	94				Naphthalene, decahydro-2-methyl
28.15	93		Benzene, 1,2,4,5-tetramethyl-		Benzene, 1,2,4,5-tetramethyl-
28.16	91			Benzene, 4-ethyl-1,2-dimethyl-	
28.4	91		Benzene, 1,2,3,5-tetramethyl-	Benzene, 1,2,3,5-tetramethyl-	Benzene, 1,2,4,5-tetramethyl-
29.18	95		Dodecane	Dodecane	
29.38	93				2,3-Dihydro-1-methylindene
29.39	91			Benzene, 2-ethenyl-1,4-dimethyl	
30.14	96				Benzene, 2-ethenyl-1,4-dimethyl
30.15	93			2,3-Dihydro-1-methylindene	
30.73	96		1H-Indene, 1-methyl-		
30.77	96			Naphthalene, 1,2,3,4-tetrahydro	Naphthalene, 1,2,3,4-tetrahydro

30.85	96		1H-Indene, 1-methyl-		
31.28	92				Benzene, 2-ethenyl-1,3,5-trimet
31.29	95			1H-Indene, 2,3-dihydro-4,7-dime	
31.41	93		Benzene, (1-methyl-2-cyclopropen-1		
31.47	94		Benzene, (1-methyl-2-cyclopropen-1		
31.54	91			Naphthalene, 1,2,3,4-tetrahydro	
31.54	94				Benzene, (2-methyl-1-butenyl)-
31.8	95			1H-Indene, 2,3-dihydro-1,6-dime	1H-Indene, 2,3-dihydro-4,7-dime
32.01	91				1H-Indene, 2,3-dihydro-1,2-dime
32.24	94				Benzene, (2-methyl-1-butenyl)-
32.25	91			1H-Indene, 2,3-dihydro-1,6-dime	
33.24	96			Naphthalene, 1,2,3,4-tetrahydro	Naphthalene, 1,2,3,4-tetrahydro
33.52	94	Naphthalene			
33.55	94		Azulene		Azulene
33.64	94				Naphthalene, 1,2,3,4-tetrahydro
33.79	91				Benzene, 1-(1-methylethenyl)-3-
33.83	95		Tridecane	Tridecane	
34.3	90				1H-Indene, 2,3-dihydro-1,5,7-tr
34.72	96				1H-Indene, 2,3-dihydro-4,7-dime
34.73	90			1H-Indene, 2,3-dihydro-1,3-dime	
35.53	94			Naphthalene, 1,2,3,4-tetrahydro	Naphthalene, 1,2,3,4-tetrahydro

36.18	91				Naphthalene, 1,2,3,4-tetrahydro
36.25	90			Benzene, pentamethyl-	Benzene, pentamethyl-
36.54	90				1H-Indene, 2,3-dihydro-4,5,7-tr
36.66	93		1H-Indene, 1,1-dimethyl-		
37.07	92			Naphthalene, 1,2,3,4-tetrahydro	Naphthalene, 1,2,3,4-tetrahydro
37.79	93			Naphthalene, 1,2,3,4-tetrahydro	Naphthalene, 1,2,3,4-tetrahydro
38.13	90			Naphthalene, 1,2,3,4-tetrahydro	
38.22	95			Tetradecane	
38.57	91	Naphthalene, 1-methyl-			
38.62	94		Naphthalene, 1-methyl-		Naphthalene, 1-methyl-
39.11	94			1,4-Dimethyl-1,2,3,4-tetrahydro	1,4-Dimethyl-1,2,3,4-tetrahydro
39.23	95				1,4-Dimethyl-1,2,3,4-tetrahydro
39.38	94	Naphtalene, 1-methyl	Naphthalene, 1-methyl-		Naphthalene, 1-methyl-
39.56	94			Naphthalene, 6-ethyl-1,2,3,4-te	Naphthalene, 6-ethyl-1,2,3,4-te
39.67	90			Naphthalene, 1,2,3,4-tetrahydro	
40.9	90				3-Ethyl-3-phenyl-1-pentene
41.09	90		Benzene, 1,3,5-trimethyl-2-(1,2-pr		
41.24	96			Naphthalene, 1,2,3,4-tetrahydro	Naphthalene, 1,2,3,4-tetrahydro
42.36	96		Pentadecane	Pentadecane	
42.76	97		Naphthalene, 1-ethyl-		
43.21	95			Naphthalene, 1,2,3,4-tetrahydro	Naphthalene, 1,2,3,4-tetrahydro

43.26	94	Naphthalene, 1,7-dimethyl-			
43.3	98		Naphthalene, 2,6-dimethyl-		
43.3	96				Naphthalene, 1,7-dimethyl-
43.31	91			Naphthalene, 1,2,3,4-tetrahydro	
43.91	93	Naphthalene, 1,7-dimethyl-			
43.95	98		Naphthalene, 1,8-dimethyl-		
43.95	98				Naphthalene, 2,6-dimethyl-
44.04	91	Naphthalene, 2,6-dimethyl-			
44.08	97		Naphthalene, 2,6-dimethyl-		Naphthalene, 2,6-dimethyl-
44.98	96		Naphthalene, 1,3-dimethyl-		Naphthalene, 1,3-dimethyl-
45.58	90		Naphthalene, 1,2-dimethyl-		
47.17	91		Naphthalene, 1,4,6-trimethyl-		Naphthalene, 1,4,6-trimethyl-
48.14	93		Naphthalene, 1,6,7-trimethyl-		Naphthalene, 1,6,7-trimethyl-
48.3	95		Naphthalene, 1,6,7-trimethyl-		Naphthalene, 1,6,7-trimethyl-
48.95	96				Naphthalene, 1,4,5-trimethyl-
48.97	93		Naphthalene, 1,6,7-trimethyl-		
49.28	96		Naphthalene, 1,6,7-trimethyl-		

49.28	97				Naphthalene, 1,4,6-trimethyl-
49.72	93				Naphthalene, 1,4,6-trimethyl-
49.88	96		Naphthalene, 1,6,7-trimethyl-		
49.88	95				Naphthalene, 2,3,6-trimethyl-
50.41	95				Naphthalene, 1,4,6-trimethyl-
53.73	91				Azulene, 7-ethyl-1,4-dimethyl-
54.24	94				Azulene, 7-ethyl-1,4-dimethyl-
54.43	98			Phenanthrene, 1,2,3,4,5,6,7,8-o	
55.15	91				4,4'-Dimethylbiphenyl
55.4	93				4,4'-Dimethylbiphenyl
55.48	91				4,4'-Dimethylbiphenyl
56.54	91				Tricyclo[4.4.1.02,5]undeca-1(10
67.31	91				Phenanthrene, 2,5-dimethyl-

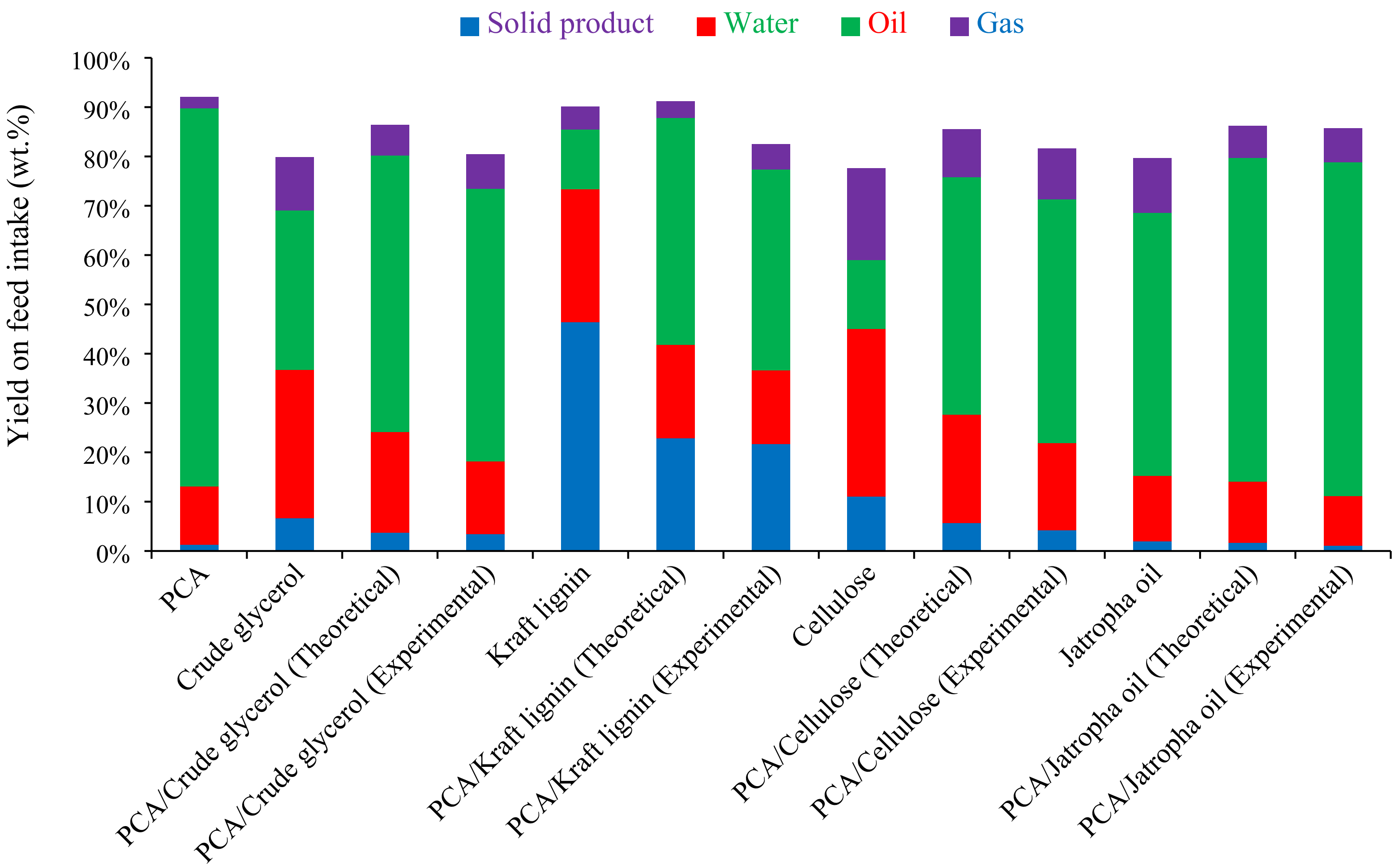


Figure S4. Mass balances for the *ex-situ* catalytic pyrolysis of different biomass feedstocks and co-pyrolysis of each biomass feedstock with PCA at 1:1 wt. ratio (total weight of 1 g) in the presence of H-ZSM-5 zeolite (1:3 feed mix:catalyst wt. ratio, 550 ^{o}C).

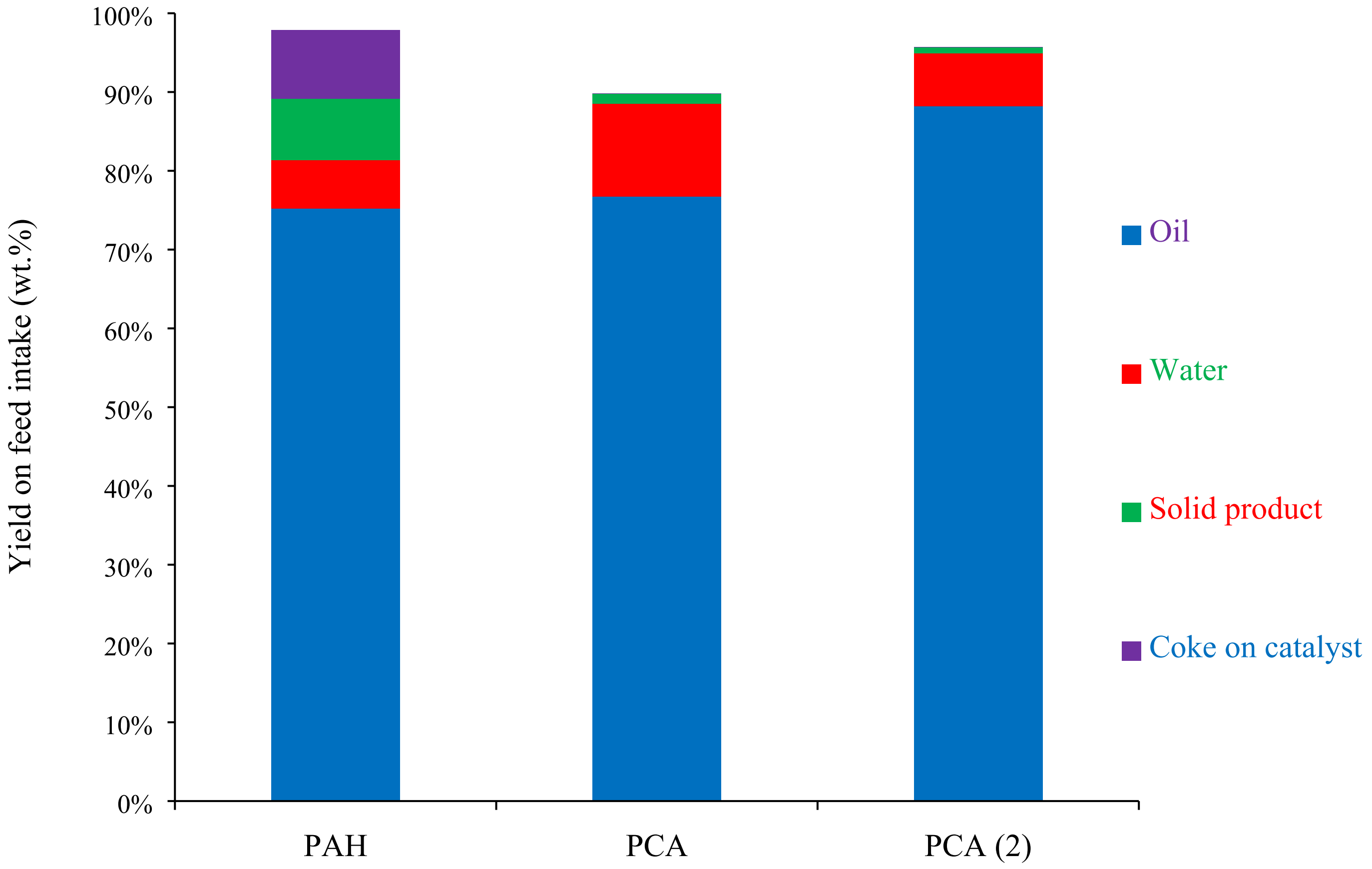


Figure S5. Mass balances for the *ex-situ* catalytic pyrolysis of PAH fraction and PCAs (1 g sample) in the presence of H-ZSM-5 zeolite (1:3 feed mix:catalyst wt. ratio, 550 ^{o}C).

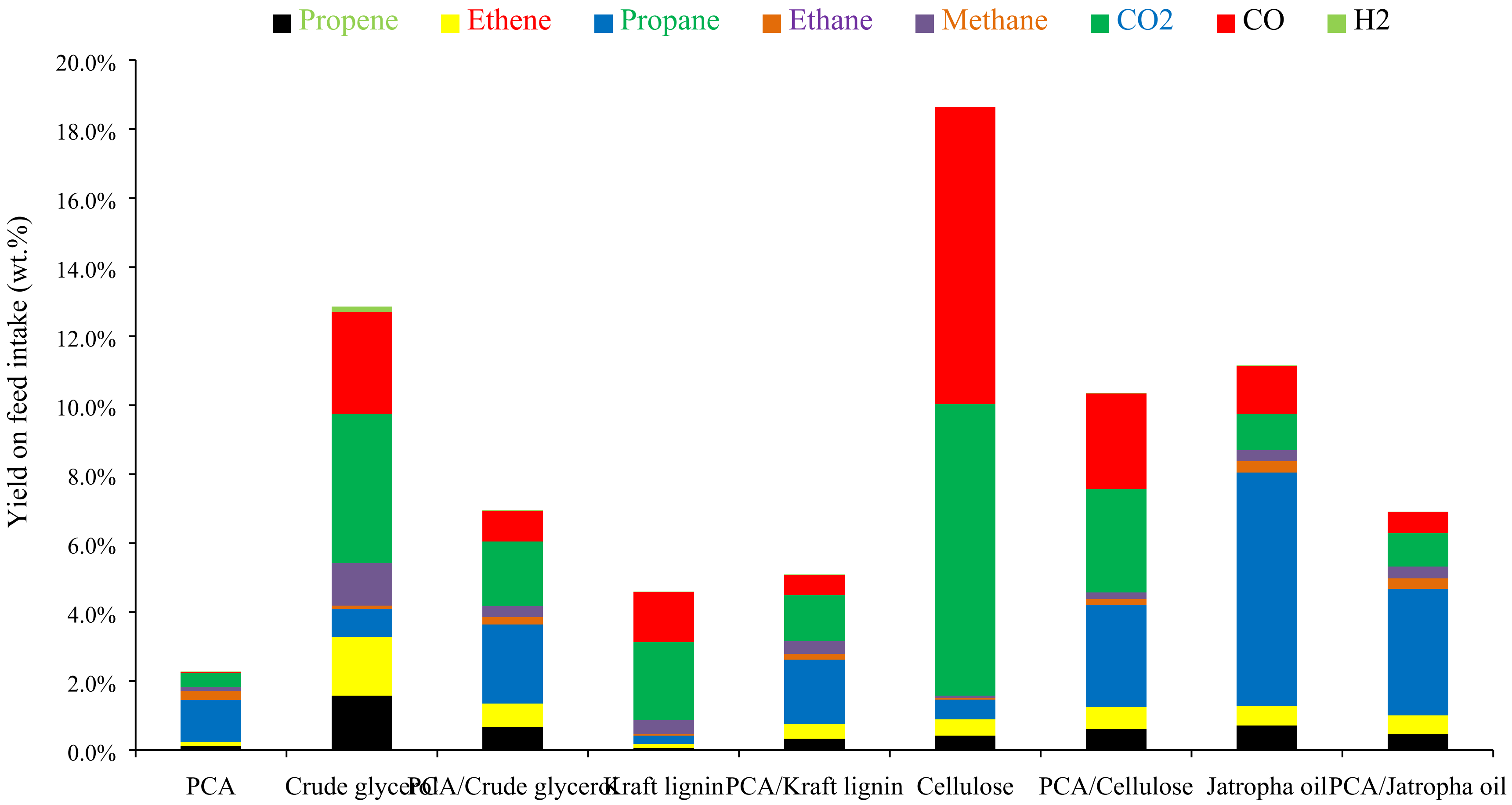


Figure S6. Composition of gaseous products from *ex-situ* catalytic pyrolysis of different biomass feedstocks and co-pyrolysis of each biomass feedstock with PCA at 1:1 wt. ratio (total weight of 1 g) in the presence of H-ZSM-5 zeolite (1:3 feed mix:catalyst wt. ratio, 550 ^{o}C).