catalysts

Article

Supporting Information

Cleanup and Conversion of Biomass Liquefaction Aqueous Phase to C_3 – C_5 Olefins over $Zn_xZr_yO_z$ Catalyst

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S1. Composition of aqueous phase feedstocks at different steps of the clean up protocol

Table S1 LC analysis of USDA-FP feedstock after key steps of clean up protocol. Water is assumed to be the remaining mass balance of the samples.

Compound	Initial	Carbon-Treated	Raffinate[a]	Refined Extract[a]	Pre-distillation[b]	Final Feedstock[b]
% Carbon Retained	100	73.2	15.1	21.7	21.7	15.1
% Carboxylic Acid Retained	100	88.9	24.8	53.5	53.5	45.9
	[wt%]	[wt%]	[wt%]	[wt%]	[wt%]	[wt%]
Sorbital	0.155	0.021	0.023	-	-	
Xylitol	0.086	-	-	-	-	-
Glycoladehyde	0.152	0.019	0.100	0.014	-	-
Glycolic acid	0.475	0.214	0.194	0.349	-	-
Levoglucosan	0.724	0.318	0.288	0.327	-	-
Formic acid	0.351	0.120	0.106	0.963	0.163	0.187
Acetic acid	4.78	3.07	1.45	39.6	8.52	9.24
Ethylene Glycol	0.178	0.132	0.134	0.188	-	-
Levulinic Acid	0.062	0.010	0.013	0.110	-	-
Propionic acid	2.89	1.95	1.47	9.23	1.79	1.68
Methanol	2.11	1.35	1.22	0.319	0.162	0.137
1,2-butandiol	0.033	-	-	0.026	-	-
Ethanol	1.38	0.718	0.538	3.603	0.630	0.674
Acetone	0.162	0.049	0.034	-	-	0.157
Methyl acetate	0.692	-	-	0.424	-	-
1-propanol	0.056	-	-	0.103	-	-

3-methyl-2-cyclopentene-1-one	0.100	-	-	0.002	-	-
Furfual	0.186	-		0.002	-	-
MTBE	-	-	2.69	20.9	3.29	0.161

[a] Aqueous (raffinate) and organic (extract) phases formed by the addition of MTBE in order to perform the LLE.

[b] Water was added to the Organic mixture in order to mitigate process equipment corrosion and achieve desirable steam/carbon ratios.

Table S2 LC analysis of KIT-SP feedstock after key steps of clean up protocol. Water is assumed to be the remaining mass balance of samples.

Compound	Initial	Carbon-Treated	Raffinate[a]	Refined Extract[a]	Pre-distillation[b]	Final Feedstock[b]
% Carbon Retained	100	30.4	11.7	14.9	14.9	11.8
% Carboxylic Acid Retained	100	33.5	6.55	22.2	22.2	22.4
	[wt%]	[wt%]	[wt%]	[wt%]	[w.%]	[wt%]
Sorbital	0.215	0.338	0.360	-	0.050	0.022
Xylitol	0.072	-	0.163	-	-	-
Glycoladehyde	0.274	0.196	1.06	0.279	0.570	0.222
Glycerol	0.910	0.487	0.544	0.159	0.064	0.051
Levoglucosan	3.53	3.41	2.40	1.50	0.328	0.122
Formic acid	0.589	0.466	0.317	1.30	0.655	0.607
Acetic acid	9.68	6.62	1.80	34.3	16.41	20.1
Ethylene Glycol	0.264	0.291	0.238	0.294	-	-
Levulinic Acid	0.130	0.040	0.021	0.127	-	0.010
Propionic acid	2.72	2.07	1.39	5.42	0.441	2.98
Methanol	2.99	2.37	1.88	1.11	0.736	0.688

1,2-butandiol	0.060	0.022	-	0.035	-	-
Ethanol	0.575	0.244	0.089	1.10	0.428	0.666
Acetone	0.216	0.090	0.046	-	-	-
Methyl acetate	0.817	0.059	-	-	-	-
1-propanol	0.032	-	-	-	-	-
3-methyl-2-cyclopentene-1-one	0.269	-	-	-	-	-
1-butanol	1.30	-		-	-	-
MTBE	-	-	2.39	35.2	5.13	0.071

[a] Aqueous (raffinate) and organic (extract) phases formed by the addition of MTBE in order to perform the LLE.

[b] Water was added to the Organic mixture in order to mitigate process equipment corrosion and achieve desirable steam/carbon ratios.

Table S3 ICP analysis of USDA-FP feedstock after key steps of clean up protocol.

Compound	Initial	Carbon-Treated	Raffinate[a]	Refined Extract[a]	Pre-distillation[b]	Final Feedstock[b]
	[ppm]	[ppm]	[ppm]	[ppm]	[ppm]	[ppm]
Al	13.4	2.46	1.73	-	-	-
Ca	115	84.0	77.4	6.77	-	3.20
K	12.3	1560	1450	85.2	24.4	17.2
Mg	17.6	117	94.2	6.85	-	-
Mn	38.4	-	2.12	-	-	-
Na	9.30	202	147	18.3	13.4	12.8
P	11.3	95.1	120	-	-	-
Sr	-	-	-	-	-	-
Si	67.0	43.0	34.3	33.1	-	2.65
S	10.6	65.1	44.9	-	-	-

[a] Aqueous (raffinate) and organic (extract) phases formed by the addition of MTBE in order to perform the LLE.

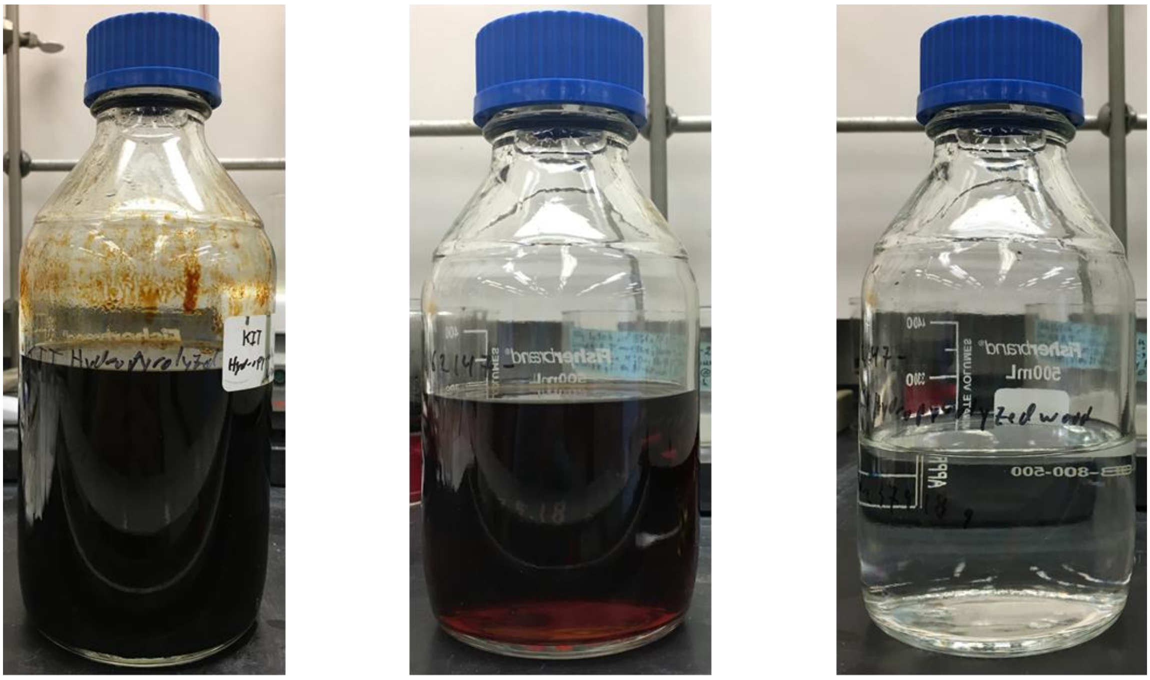
[b] Water was added to the Organic mixture in order to mitigate process equipment corrosion and achieve desirable steam/carbon ratios.

Table S4 ICP analysis of KIT-SP feedstock after key steps of clean up protocol.

Compound	Initial	Carbon-Treated	Raffinate[a]	Refined Extract[a]	Pre-distillation[b]	Final Feedstock[b]
	[ppm]	[ppm]	[ppm]	[ppm]	[ppm]	[ppm]
Al	-	2.85	2.73	7.48	1.55	-
Ca	-	169	181	-	16.3	15.1
K	15.7	4050	1420	20.5	12.8	12.8
Mg	-	288	236	-	-	-
Mn	-	2.75	2.84	-	-	-
Na	28.2	446	365	7.96	10.0	9.64
P	-	252	406	-	-	-
Sr	-	3.15	3.03	-	-	-
Si	-	111	124	38.1	19.1	3.85
S	56.5	68.5	-	-	-	-

[a] Aqueous (raffinate) and organic (extract) phases formed by the addition of MTBE in order to perform the LLE.

[b] Water was added to the Organic mixture in order to mitigate process equipment corrosion and achieve desirable steam/carbon ratios.



A B C

Figure S1 KIT-SP feedstock A) Initial B) During Carbon Treatment, After Third Carbon Treatment ~72 h C) After All Carbon Treatment, Five Carbon Treatments ~120 h

S2. Composition of diluted aqueous phase feedstocks at different steps of the clean up protocol

In addition to the USDA-FP and KIT-SP feedstocks, two additional aqueous phases generated via Catalytic Fast Pyrolysis (CFP) of Pine and Loblolly Pine were also studied for cleanup using continuous LLE, see Table 5. These two samples had lower concentration of organics (5 wt%) than the previously discussed samples, however, the composition profile remained similar with the carboxylic acids being the most abundant compounds. Following continuous LLE, the concentration of acetic acid increased from 0.49 to 13.5 wt% for the Pine sample and from 1.57 to 20.0 wt% for the Loblolly Pine sample. While these values are low compared to the more concentrated feedstocks, they are at levels that are reasonable to process.

Table S5 Summary of dilute feedstock cleanup

	Pine CFP			Loblolly Pine CFT		
	Initial	Raffinate (Aqueous)	Extract (Organic)	Initial	Raffinate (Aqueous)	Extract (Organic)
Acetic Acid [wt.%]	0.492	0.241	13.5	1.569	0.392	20.0
Propionic Acid [wt.%]	0.131	0.047	1.36	1.147	0.416	2.78
Methanol [wt.%]	0.268	0.166	BDL	0.983	0.317	0.791
Ca [ppm]	2.67	22.7	BDL	12.99	49	BDL

Na [ppm]	7.24	130	15.6	6.16	138.0	BDL
K [ppm]	4.23	1327	96.9	4.47	1401	18.5
P [ppm]	15.84	102	BDL	BDL	89.09	BDL
S [ppm]	3.51	BDL	BDL	BDL	BDL	BDL