

Pilot-scale hydrotreating of catalytic fast pyrolysis biocrudes: Process performance and product analysis

Sylvain Verdier¹, Ofei D. Mante², Asger B. Hansen¹, Kristoffer G. Poulsen³, Jan H. Christensen³, Nadia Ammtizboll¹, Jostein Gabrielsen¹, David C. Dayton^{2*}

1: Haldor Topsoe A/S, Haldor Topsøes Allé 1, 2800 Kgs. Lyngby, Denmark.

2: RTI International, 3040 E. Cornwallis Road, Research Triangle Park, NC 27709, USA.

3: Department of Plant and Environmental Sciences, Faculty of Science, University of Copenhagen, Thorvaldsensvej 40, 1871 Frederiksberg, Denmark

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Supplemental Information

Table S1: Relative area counts of groups of pooled compound classes in non-fractionated biocrudes as determined by GC×GC-FID (average of duplicate analyses).

CFP biocrude	Feed F1	Feed F3	Feed F4	Feed F5
Group A (Aliphatics)	11.4	3.5	3.5	2.2
Group B (Aromatics)	29.3	23.6	22.1	24.7
Group C (aliphatic acids, aldehydes, ketones)	23.4	17.0	16.6	13.9
Group D (furan derivatives)	1.2	2.0	2.4	2.9
Group E (non-phenolic oxygenates)	4.5	12.0	12.2	11.3
Group F (phenolics)	26.5	33.0	33.6	37.5
Unknown Oxygenates	3.6	9.0	9.5	7.5

Table S2: Relative area counts of groups of pooled compound classes in the WIS THF fraction of the CFP biocrudes as determined by GC×GC-FID (average of duplicate analyses).

CFP biocrude	Feed F1	Feed F3	Feed F4	Feed F5
Group A (Aliphatics)	4.5	1.6	1.5	1.6
Group B (Aromatics)	30.9	31.1	29.9	30.1
Group C (aliphatic acids, aldehydes, ketones)	9.4	4.7	4.9	4.9
Group D (furan derivatives)	0.6	0.8	1.0	1.3
Group E (non-phenolic oxygenates)	17.1	20.9	21.4	19.3
Group F (phenolics)	19.7	24.3	25.3	28.4
Unknowns Oxygenates	17.7	16.6	16.1	14.3

Table S3: Properties of biocrude F4 and the HDT products obtained during pilot plant Exp. A (WIS-THF fractions)

Run hour	0 (Feed F4)	12	26	42	73	102
S, wt% (D4294)	0.01018	0.01204	0.00171	0.00181	0.00188	0.00195
N, wt ppm (D5762)	966.94	-	-	-	-	-
N, wt ppm (D4629)	-	397.99	1021.28	1373.07	1366.9	1371.01
H, wt% (D7171)	7.02	11.98	11.75	11.02	10.2	9.94
O, wt% (elemental)	28	-	3.08	5.2	8	9.22
C, wt% (elemental)	62.9	-	84.5	85.4	83.2	82.8
SG 60/60°F	-	0.8965	0.9159	0.9469	0.9837	0.9953
Viscosity at 50°C, cSt	-	2.723	4.784	8.568	18.958	24.228
Simulated Distillation						
0.5 wt% (IBP), °C	86	73	80	75	59	58
5 wt%, °C	147	101	102	110	122	125
10 wt%, °C	175	129	131	136	154	155
30 wt%, °C	238	179	199	208	220	222
50 wt%, °C	292	261	293	299	307	310
70 wt%, °C	361	326	352	361	372	380
80 wt%, °C	397	359	402	418	437	450
90 wt%, °C	450	435	488	503	519	530
95 wt%, °C	492	504	544	555	565	573
99.5 wt% (FBP), °C	564	602	607	609	610	611
Group characterization by GC×GC -FID (WIS-THF)(%-area)						
Group A (Aliphatics)	1.5	22.6	-	-	6.7	8.7
Group B (Aromatics)	29.9	64.2	-	-	50.7	51.1
Group C (aliphatic acids, aldehydes, ketones)	4.9	0.3	-	-	0.9	0.9
Group D (furan derivatives)	17.0	N.D.	-	-	N.D.	N.D.
Group E (non-phenolic oxygenates)	21.4	1.8	-	-	9.5	8.9
Group F (phenolics)	25.3	11	-	-	32	29.7
Unknown oxygenates	16.1	0	-	-	0	0

Table S4: Properties of biocrude F3 and the HDT products obtained during pilot plant Exp. B (WIS-THF fractions)

Run hour	0 (Feed F3)	12	28	44	60	76	108	116	145.5
S, wt% (D4294)	0.01081	-	-	-	-	-	-	-	-
N, wt ppm (D5762)	987	-	-	-	-	-	-	-	-
N, wt ppm (D4629)	-	140	505	759	1169	1242	1278	1295	1200
H, wt% (D7171)	7.35	12.8	11.57	10.83	10.48	10.34	10.05	10.01	9.94
O, wt% (elemental)	25.5	1.71	3.18	5.07	6.09	6.77	7.86	7.79	7.85
C, wt% (elemental)	64.5	83.7	84.9	83.0	82.5	82.7	82	81.8	81.7
SG 60/60°F	-	0.8651	0.9126	0.9418	0.9569	0.9659	0.9777	0.9802	0.9838
Moisture content (wt%)	9.35	-	-	-	-	-	-	-	-
Viscosity at 50°C, cSt	-	1.911	3.609	5.593	7.334	9.047	11.035	11.373	12.253
Simulated Distillation									
0.5 wt% (IBP), °C	85	74	73	89	70	72	89	70	90
5 wt%, °C	143	101	93	125	75	81	131	76	141
10 wt%, °C	173	116	123	154	79	131	159	82	168
30 wt%, °C	234	165	191	212	183	207	223	201	224
50 wt%, °C	288	230	269	283	253	276	291	268	297
70 wt%, °C	360	302	338	348	339	350	359	350	359
80 wt%, °C	394	326	370	383	373	387	398	387	396
90 wt%, °C	445	372	446	458	452	464	474	465	470
95 wt%, °C	486	427	503	511	510	517	523	518	521
99.5 wt% (FBP), °C	558	565	576	577	578	578	579	578	579
Group characterization by GC×GC –FID (WIS-THF) (%-area)									
Group A (Aliphatics)	1.6	45.5	20.1	-	-	-	7.8	6.8	8.1
Group B (Aromatics)	31.1	43.4	61.3	-	-	-	47.3	48.4	49.6
Group C (aliphatic acids, aldehydes, ketones)	4.7	0.5	0.3	-	-	-	0.5	0.4	0.3
Group D (Furan derivatives)	0.8	N.D.	N.D.	-	-	-	N.D.	N.D.	N.D.
Group E (non-phenolic oxygenates)	20.9	3.1	3.3	-	-	-	10.3	11.4	9.4
Group F (phenolics)	24.3	7.3	14.6	-	-	-	33.8	32.8	32.3
Unknown O's	16.6	0	0	-	-	-	0	0	0

Table S5: Properties of biocrude F1 and the HDT products obtained during pilot plant Exp. C (WIS-THF fractions)

Run hour	0 (Feed F1)	8	40	64	72	84	116
S, wt% (D4294)	0.027	0.00627	0.000418	0.00065	0.000501	0.000405	0.00075
N, wt ppm (D5762)	708	5	62	217	254	296	350
H, wt% (D7171)	8.3	13.66	12.81	12.32	12.25	12.16	12.07
O, wt% (elemental)	17	0.25	0.54	1.29	1.38	1.59	1.66
C, wt% (elemental)	73.9	83.9	84.1	84.8	83.3	83.5	84.8
SG 60/60°F		0.8304	0.8435	0.8584	0.8608	0.8635	0.8675
Moisture content (wt%)	8						
Viscosity at 60°C, cSt		1.216	1.152	1.233	1.245	1.266	1.298
Simulated Distillation							
0.5 wt% (IBP), °C		67.8	55.6	56.8	56.8	58.6	57.6
5 wt%, °C	123	104	88	91	90	90	92
10 wt%, °C	143	131	101	109	104	105	110
30 wt%, °C	188	166	158	166	165	166	168
50 wt%, °C	220	199	201	208	207	208	210
70 wt%, °C	272	259	271	276	274	274	277
80 wt%, °C	328	292	313	317	316	317	319
90 wt%, °C	394	321	361	370	369	371	372
95 wt%, °C	450	354	416	425	424	428	426
99.5 wt% (FBP), °C	554	431	530	548	542	553	539
Group characterization by GC×GC -FID (WIS-THF) (%-area)							
Group A (Aliphatics)	4.5	88.8	-	-	-	-	29.1
Group B (Aromatics)	30.9	7.8	-	-	-	-	31.4
Group C (aliphatic acids, aldehydes, ketones)	9.4	0.4	-	-	-	-	0.2
Group D (Furan derivatives)	0.6	N.D.	-	-	-	-	N.D.
Group E (non-phenolic oxygenates)	17.1	1.7	-	-	-	-	1.9
Group F (phenolics)	19.7	1.2	-	-	-	-	7.4
Unknown Os	17.7	0	-	-	-	-	0

Table S6: Properties of biocrude F5 and the HDT products obtained during pilot plant Exp. D (WIS-THF fractions)

Run hour	0 (Feed F5)	12	28	36	60
S, wt% (D4294)	0.00582	0.00951		0.003008	0.00353
N, wt ppm (D5762)	-	304	1231	1168	
H, wt% (D7171)	6.49	12.65	10.96	10.41	9.85
O, wt% (elemental)	28.75	1.21	4.84	7.22	8.91
C, wt% (elemental)	62.6	83.8	83.8	80.3	78.2
SG 60/60°F	-	0.8768	0.9518	0.9716	0.9957
Moisture content (wt%)	10.38	-	-	-	-
Viscosity at 60°C, cSt	-	2.143	8.635	11.294	16.183
Simulated Distillation					
0.5 wt% (IBP), °C		58	66	63	69
5 wt%, °C		100	115	81	105
10 wt%, °C		129	146	114	138
30 wt%, °C		193	228	210	223
50 wt%, °C		262	305	297	307
70 wt%, °C		327	382	377	381
80 wt%, °C		365	436	438	443
90 wt%, °C		427	502	512	516
95 wt%, °C		478	544	555	558
99.5 wt% (FBP), °C		584	605	607	607
Group characterization by GC×GC -FID (WIS-THF) (%-area)					
Group A (Aliphatics)	1.6	44.7	22.0	14.1	6.0
Group B (Aromatics)	30.1	47.0	53.6	52.5	49.2
Group C (aliphatic acids, aldehydes, ketones)	4.9	0.4	0.4	0.6	0.6
Group D (Furan derivatives)	1.3	N.D.	N.D.	N.D.	N.D.
Group E (non-phenolic oxygenates)	19.3	1.5	4.7	6.1	10.6
Group F (phenolics)	28.4	6.3	19.1	26.6	33.2
Unknown Os	14.3	0	0	0	0

Figure S1: ^{13}C -NMR spectrum of biocrude F1

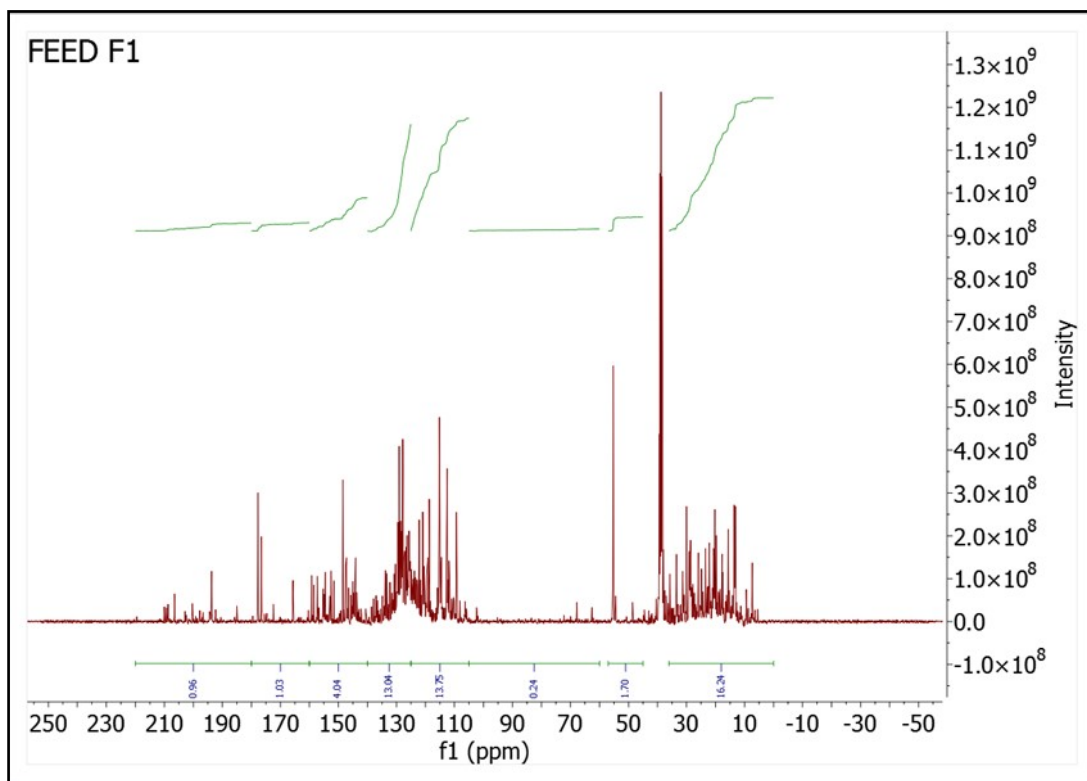


Figure S2: ^{13}C -NMR spectrum of biocrude F3

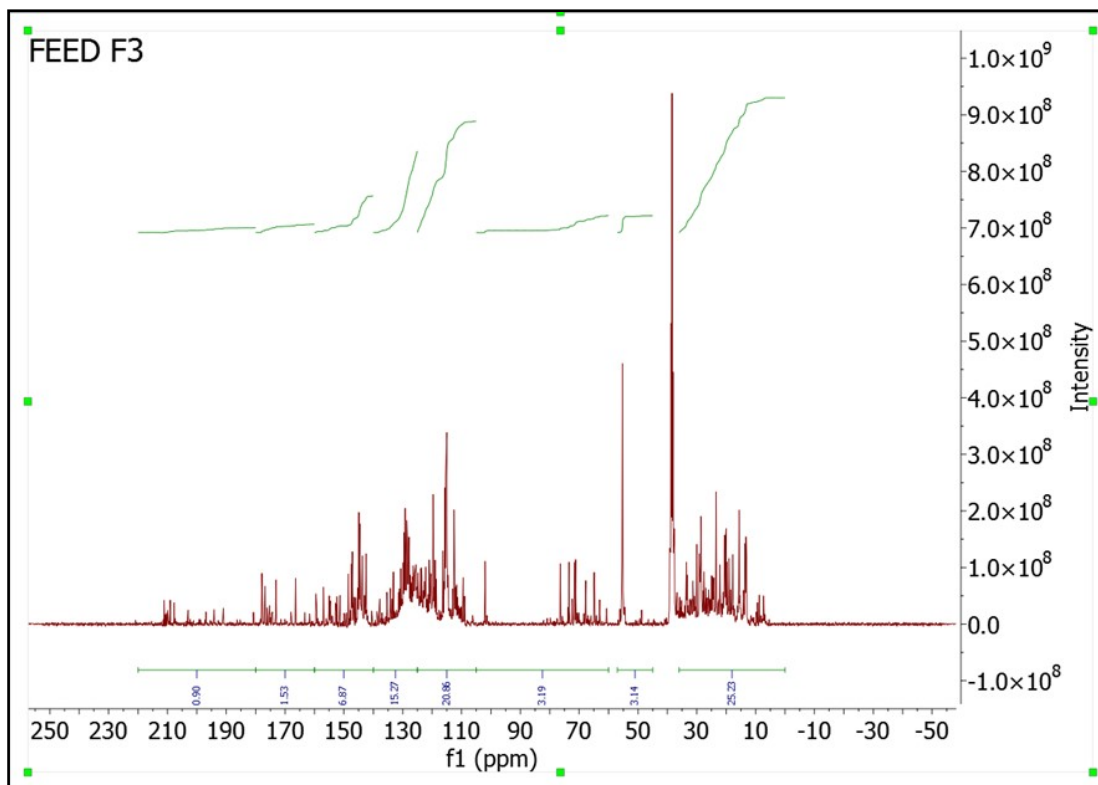


Figure S3: ^{13}C -NMR spectrum of biocrude F4

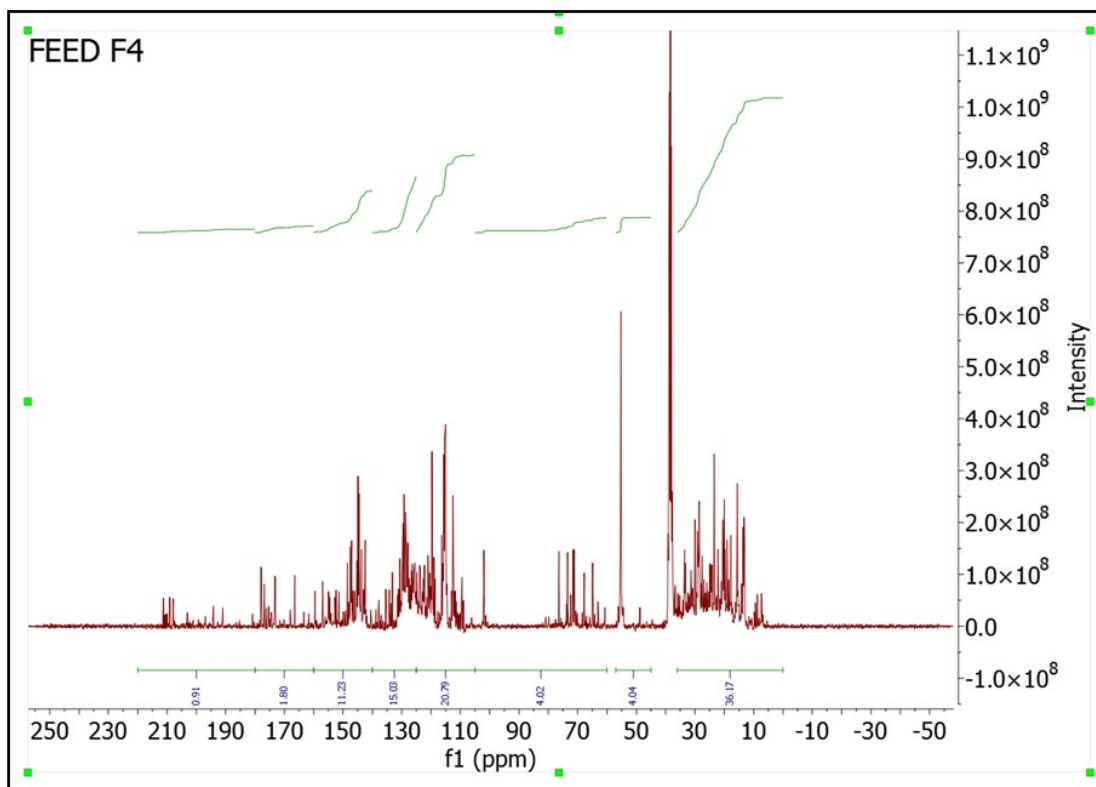


Figure S4: ^{13}C -NMR spectrum of biocrude F5

