

Driving towards cost-competitive biofuels through catalytic fast pyrolysis by rethinking catalyst selection and reactor configuration

Michael B. Griffin,^{a,‡} Kristiina Iisa,^{a,‡} Huamin Wang,^b Abhijit Dutta,^a Kellene A. Orton,^a Richard J. French,^a Daniel M. Santosa,^b Nolan Wilson,^a Earl Christensen,^a Connor Nash,^a Frederick Baddour,^a Kurt Van Allsburg,^a Daniel A. Ruddy,^a Eric C. D. Tan,^a Hao Cai,^c Calvin Mukarakate,^a Joshua A. Schaidle^{a,*}

^a National Renewable Energy Laboratory, 15523 Denver West Pkwy., Golden, CO 80401, USA.

^b Pacific Northwest National Laboratory, 902 Battelle Blvd., Richland, WA 99352 USA

^c Argonne National Laboratory, 9700 Cass Ave., Lemont, IL 60439

[‡]These authors contributed equally to the article.

*Corresponding author: Joshua.Schaidle@nrel.gov

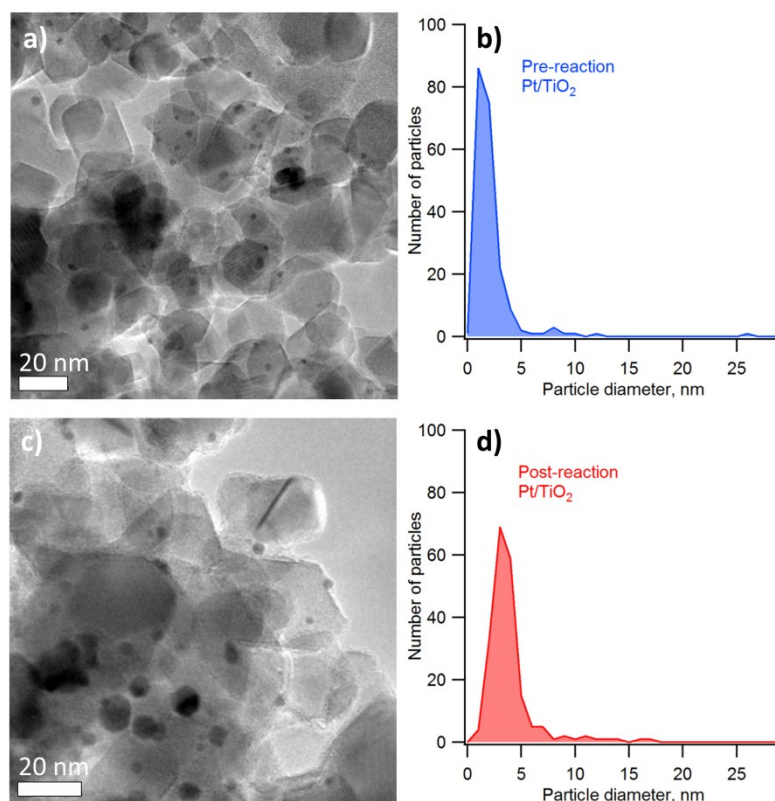


Fig. S1 Representative TEM images and particle size distributions observed from pre-reaction (a-b) and post-reaction (c-d) 2 wt% Pt/TiO₂.

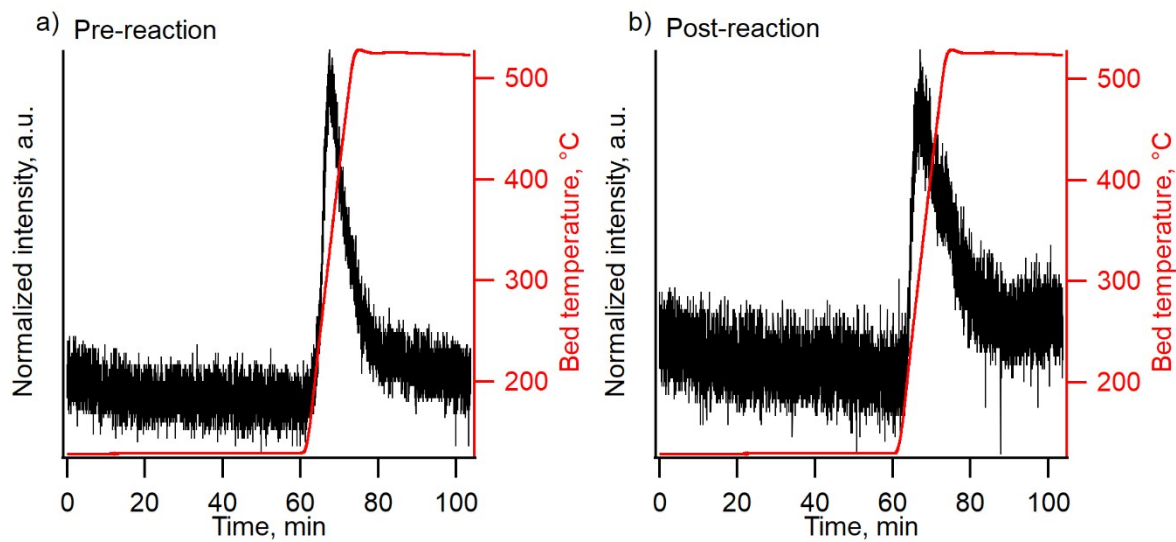


Fig. S2 NH_3 -TPD profiles collected from pre-reaction (a) and post-reaction (b) 2 wt% Pt/ TiO_2 .

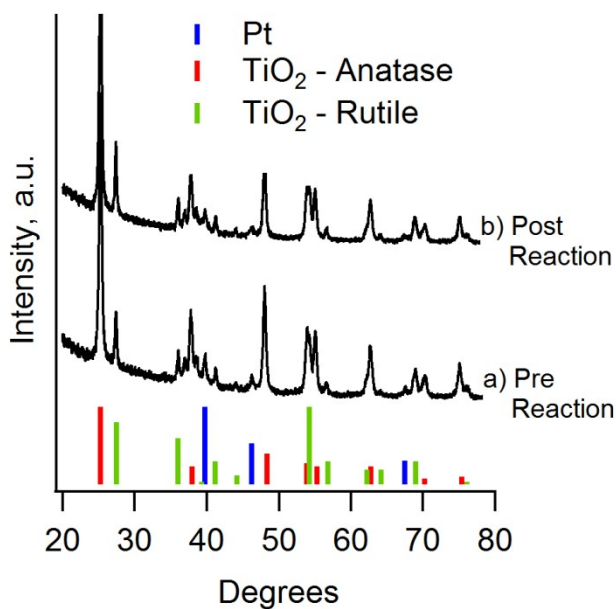


Fig. S3 XRD patterns collected for pre-reaction (a) and post-reaction (b) 2 wt% Pt/ TiO_2 .

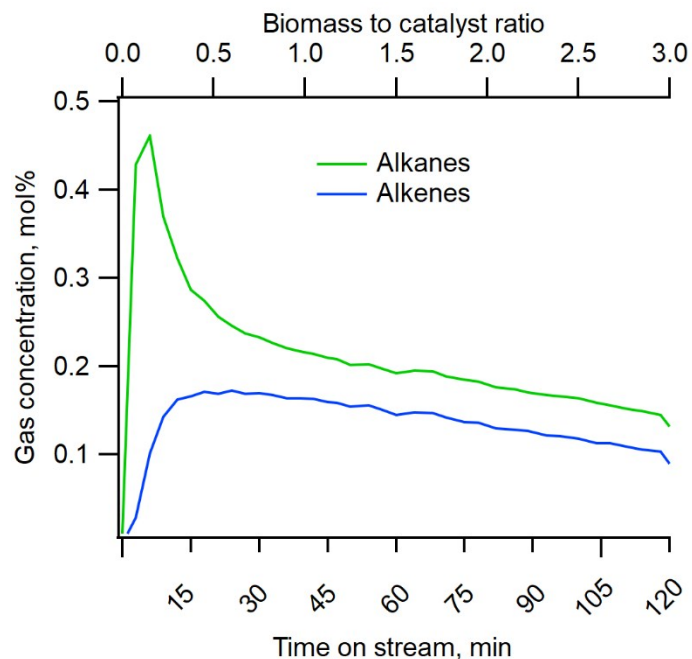


Fig. S4 Intensities of m/z signals from C_2 - C_3 alkanes and alkenes observed during CFP reaction cycles.

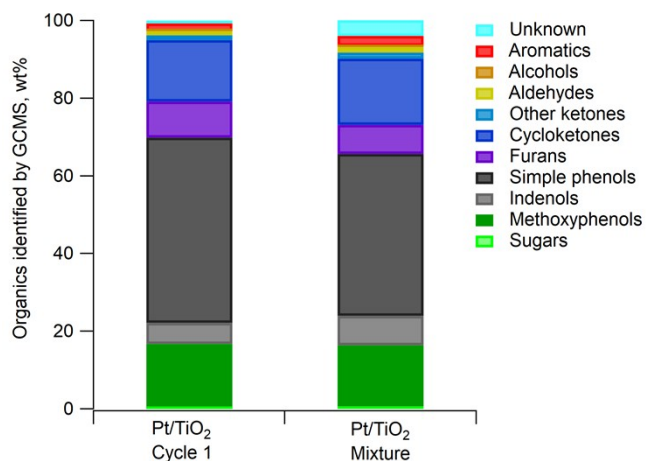


Fig. S5 GC-MS compositional analysis of the CFP-oil from cycle 1 and a mixture of the combined CFP-oil from all 13 cycles. Chromatographable compounds which are identifiable by GC-MS represent 40-50% of the total sample mass.

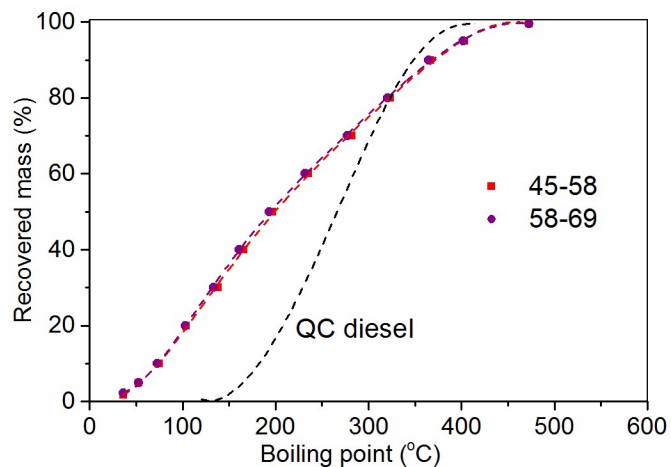


Fig. S6 SIMDIST results for the hydrotreated products collected at different TOS windows compared to that for diesel. The calculated mass fractions for the hydrotreated-CFP oil were 46% gasoline (boiling <184 °C), 28-29% jet A (boiling 153-256 °C), and 38-39% diesel (boiling 184-344 °C).

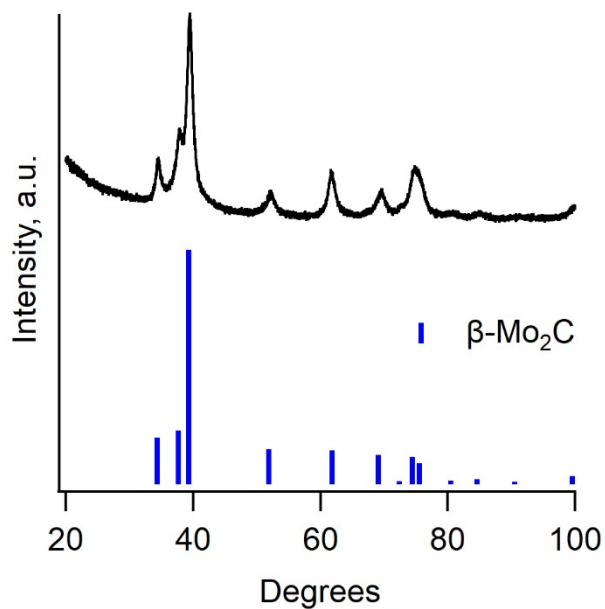


Fig. S7 XRD pattern collected for β -Mo₂C

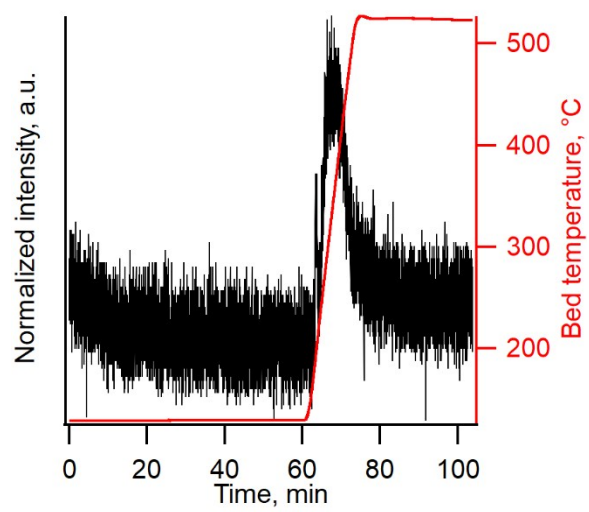


Fig. S8 NH_3 -TPD profile collected from 0.5 wt% Pt/ TiO_2

Table S2. Oxygen distribution during CFP over 2 wt% Pt/TiO₂ and ZSM-5. The values for ZSM-5 are calculated based on data provided in: Iisa, K., *et al.*, *Energy & Fuels*, 2016, **30**, 2144-2157.

Catalyst	Pt/TiO ₂	ZSM-5
Upgrading T, °C	400	500
B:C, g/g	3	1.4
CFP oil O, wt% db	17.3%	19.0%
Organics in oil	10%	5%
Organics in aq.	5%	3%
H ₂ O	49%	55%
O in CO	19%	21%
O in CO ₂	13%	15%
O in char	3%	4%
Total	99%	102%
O removed as		
CO	23%	23%
CO ₂	17%	16%
H ₂ O	60%	61%

Table S3. Major compounds (>0.5 wt% in oil) identified by semi-quantitative GCMS analysis of CFP and hydrotreated oils. Over 200 compounds were quantified and results in Fig. 4 are based on all identified compounds. The compound names are based on matches to NIST database and have not been verified in most cases.

RT, min	Compound	Category	CFP	Hydrotreated	
			Mixture	45-58 h TOS	59-68 TOS
1.50	Pentane	Noncyclic alkane		1.0%	0.9%
3.16	1,4-Dimethylcyclohexane	1-Ring alkane		0.8%	0.8%
3.67	Trans-1,3-dimethylcyclohexane	1-Ring alkane		0.5%	0.5%
4.23	Ethylcyclohexane	1-Ring alkane		2.7%	2.6%
4.31	Toluene	Aromatic hydrocarbon		1.2%	1.2%
5.07	1,2,4-Trimethylcyclohexane	1-Ring alkane		0.9%	0.8%
5.58	1-Ethyl-3-methylcyclohexane (c,t)	1-Ring alkane		0.8%	0.8%
6.12	Propylcyclohexane	1-Ring alkane		3.2%	3.0%
6.23	Cyclopentanone	Cycloketone	1.1%		
6.28	Ethylbenzene	Aromatic hydrocarbon		0.7%	0.7%
6.38	1,4-Xylene, 1,3-Xylene	Aromatic hydrocarbon		0.7%	0.6%
7.04	1-Methyl-2-propylcyclohexane	1-Ring alkane		0.5%	
7.12	1,2-Xylene	Aromatic hydrocarbon			0.5%
7.67	Furan-2-carbaldehyde	Furan	0.6%		
7.94	2-Cyclopenten-1-one	Cycloketone	2.1%		
8.22	Cis-octahydro-1H-Indene	2+Ring hydrogenated		1.2%	1.1%
8.27	Propylbenzene	Aromatic hydrocarbon		1.0%	0.9%
8.50	1-Ethyl-2-methylbenzene	Aromatic hydrocarbon		0.6%	0.6%
9.12	1,2,3-Trimethylbenzene	Aromatic hydrocarbon		0.5%	
9.19	2-Methyl-2-Cyclopenten-1-one	Cycloketone	1.3%		
10.46	Phenol	Simple phenol	3.1%		
10.60	Decahydro-2-methylnaphthalene	2+Ring hydrogenated		0.5%	
10.85	5-Methyl-2-furancarbaldehyde	Furan	0.6%		
10.97	2,3-Dihydro-1H-indene	Aromatic hydrocarbon		1.0%	0.9%
11.16	3-Methyl-2-cyclopenten-1-one	Cycloketone	2.2%		
12.11	2-Methylphenol	Simple phenol	1.4%		
12.28	1-Methyl-3-(1-methylethyl)benzene	Aromatic hydrocarbon		0.5%	
12.63	3/4-Methylphenol	Simple phenol	2.4%		
13.31	2-Methoxyphenol	Methoxyphenol	0.6%		
13.50	2,3-Dihydro-4-methyl-1H-indene	Aromatic hydrocarbon		0.5%	
13.84	2-Ethylphenol	Simple phenol	0.5%		
13.97	1,2,3,4-Tetrahydronaphthalene	2+Ring hydrogenated		0.5%	
14.11	2,4-Dimethylphenol	Simple phenol	0.9%		
14.58	4-Ethylphenol	Simple phenol	0.9%		
14.62	3-Ethylphenol	Simple phenol	1.6%		
15.34	2-Methoxy-4-methylphenol	Methoxyphenol	0.8%		
15.95	2-Ethyl-5-methylphenol	Simple phenol	0.7%		
15.96	1,2,3,4-Tetrahydro-5-methylnaphthalene	2+Ring hydrogenated		0.6%	0.6%
16.34	4/3/2-Propylphenol	Simple phenol	1.5%		
16.39	2-Ethyl-5-methylphenol	Simple phenol	0.7%		
17.52	4-(1-Methylpropyl)phenol	Simple phenol	0.7%		
17.91	4-Ethenyl-2-methoxyphenol	Methoxyphenol	1.1%		
18.16	4-Ethylbenzaldehyde	Other oxygenate (aldehyde)	0.6%		
18.24	2,7-Dimethylnaphthalene	Aromatic hydrocarbon		0.6%	0.5%
18.26	4-(Prop-2-en-1-yl)phenol	Simple phenol	1.1%		
18.35	2-Methoxy-3-(prop-2-en-1-yl)phenol	Methoxyphenol	1.0%		
18.49	Unknown		1.2%		
18.78	1H-Inden-1-ol	Indenol	0.5%		
18.96	2,3-dihydro-1,1,3-trimethyl-1H-Indene	Aromatic hydrocarbon		0.6%	0.5%
19.02	1H-Inden-1-ol	Indenol	0.8%		
19.86	2-Methoxy-4-(prop-2-en-1-yl)phenol	Methoxyphenol	1.6%		
20.11	4-Hydroxy-3-methoxybenzaldehyde	Methoxyphenol	0.5%		
21.03	Unknown			0.6%	
24.59	7-Isopropyl-1,1,4a-trimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene	2+Ring hydrogenated		0.5%	

Table S4. ^{13}C NMR analysis results for CFP-oil and hydrotreated CFP-oil. Assignments are per Happs R., *et al.*, *RSC Adv.*, 2016, 6, 102665.

	Chemical shift, ppm	CFP-Oil Mixture	Hydrotreated CFP-oil
C=O	215.0–166.5	6.1	0.0
Aromatic C-O	166.5–142.0	12.5	5.6
Aromatic C-C	142.0–125.0	5.9	5.6
Aromatic C-H	125.0–95.8	39.3	15.3
Aliphatic C-O	95.8–60.8	3.8	0.0
Methoxyl	60.8–55.2	1.8	0.0
Aliphatic C-C	55.2–0	30.6	73.5

Table S5. Gas and water yields and hydrogen consumption during hydrotreating.

Sample	TOS (h)	45-58	58-69	Average
Produced Water Yield	wt% dry bio-oil basis	17	20	19
Gas Yield	wt% dry bio-oil basis	6.5	6.5	6.5
Gas Carbon yield	%	6.5	6.5	6.5
H ₂ Consumed	wt% dry bio-oil basis	0.034	0.043	0.039
Mass Balance Closure	wt% dry bio-oil basis	95	101	98
Carbon Balance Closure	%	93	98	96
Gas component yields				
CH ₄	wt% dry bio-oil basis	1.7	1.7	1.7
C ₂ H ₆	wt% dry bio-oil basis	1.1	1.1	1.1
C ₃ H ₈	wt% dry bio-oil basis	1.2	1.2	1.2
C ₄ H ₁₀	wt% dry bio-oil basis	1.4	1.4	1.4
C ₅ H ₁₂	wt% dry bio-oil basis	0.5	0.5	0.5
CO	wt% dry bio-oil basis	0.0	0.0	0.0
CO ₂	wt% dry bio-oil basis	0.6	0.6%	0.6%

Table S6. Summary of detailed hydrocarbon analysis (DHA) of the gasoline fraction

PIANO	wt%
Paraffin	7.4
I-Paraffins	3.3
Aromatics	17.0
Mono-Aromatics	15.1
Naphthalenes	0.0
Naphtheno/Olefino-Benzenes	0.2
Indenes	1.6
Naphthenes	65.7
Mono-Naphthenes	65.3
Di/Bicyclo-Naphthenes	0.4
Olefins	0.1
n-Olefins	0.0
Iso-Olefins	0.0
Naphtheno-Olefins	0.1
Di-Olefins	0.0
Oxygenates	0.7
Unidentified	5.8
Plus	0.0
RON and MON	
RON	67.3
MON	61.8
AKI	64.6
Vapor Pressure (psi)	2.6

Table S7. Summary of CFP results for steady-state 0.5% Pt/TiO₂: mass and carbon yields on dry biomass basis, oil composition on dry basis, and gas yields.

Phase	Yield, wt%	Yield, C%	Oil Composition, wt% dry		Gas Yield, wt%	
Oil	31	42	C	74	CH ₄	1.6
Aq.	27	3.2	H	7.4	CO	11
Gas	24	20	N	0.0	CO ₂	7.6
Char	11	17	O	19	CO:CO ₂	1.4
Coke	2.1	4.0	H:C	1.21	C2+ Alkane	1.2
Total	94	86	H ₂ O	4.1	C2+ Alkene	1.4

Table S8. Summary of CFP results for steady-state Mo₂C: mass and carbon yields on dry biomass basis, oil composition on dry basis, and gas yields.

Phase	Yield, wt%	Yield, C%	Oil Composition, wt% dry		Gas Yield, wt%	
Oil	25	37	C	74	CH ₄	2.9
Aq.	28	2.8	H	7.7	CO	12
Gas	32	30	N	0.2	CO ₂	11
Char	9	14	O	18	CO:CO ₂	1.1
Coke	≤1.7%*	≤3%*	H:C	1.24	C2+ Alkane	1.7
Total	95	84	H ₂ O	3.4	C2+ Alkene	4.2

*estimate from a different experiment

Table S9. Compounds used for GCMS calibration

Acetaldehyde
 Benzene
 2,5 Dimethylfuran
 Toluene
 Ethylbenzene
 p-Xylene
 2-Furaldehyde
 2-Cyclopentenone
 Phenol
 1,2,3-Trimethylbenzene
 2,3- Benzofuran
 Indene
 o-Cresol
 o-Methoxyphenol
 1-Naphthol
 Naphthalene
 2-Methylnaphthalene
 Phenanthrene

Procedures For Catalyst Cost Modeling

Materials-only catalyst costs were estimated using the materials consumption from the lab-scale syntheses as described in the main text. Unit prices were obtained assuming a 1000 kg purchase size from chemical suppliers and the Process Economics Program Yearbook, a paid service of IHS Markit Ltd. Where necessary, lab-scale unit prices were extrapolated to this purchase scale by use of a log-log regression.¹ The cost analysis assumes a 100% yield during the wet impregnation step. All prices were corrected to 2014 dollars by use of the US Bureau of Labor Statistics Chemical Producer Price Index.²

1. Qi, W.; Sathre, R.; Morrow, W. R.; Shehabi, A. *Unit price scaling trends for chemical products*; LBNL-189844; LBNL: Berkeley, CA, 2015.
2. Producer Price Index Industry Data for Chemical mfg., Bureau of Labor Statistics, Series ID: "PCU325---325---". <http://data.bls.gov/cgi-bin/srgate>