Electronic Supplementary Material (ESI) for Green Chemistry.

ELECTRONIC SUPPLEMENTARY INFORMATION

Supported molybdenum oxides as effective catalysts for the catalytic fast pyrolysis of lignocellulosic biomass

Karthick Murugappan,[a] Calvin Mukarakate,[b] Sridhar Budhi,[b] Manish Shetty,[a] Mark R. Nimlos*[b] and Yuriy Román-Leshkov*[a]

[a]*Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge MA, 02139*
E-mail: yroman@mit.edu
[b]*National* Renewable Energy Laboratory, 15523 Denver West Parkway, Golden, CO 80401-3393, USA. Email: *Mark.Nimlos@nrel.gov*

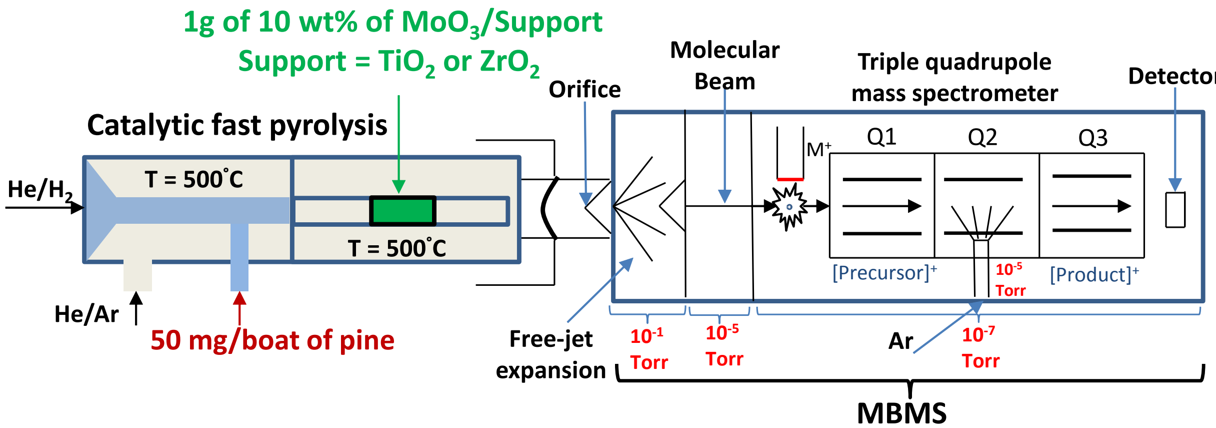


Fig. S1 Schematic of horizontal reactor-MBMS set up.

Typically, pine boats of 50 mg each were pyrolysed sequentially and flown over 1.0 g of catalyst in a 400 $cm^3\ min^{-1}$ of 50 vol% H_2-He mixture. Prior to sampling by the MBMS, the H_2-He gas mixture was further diluted with more He (4000 $cm^3\ min^{-1}$). A dilute stream of Argon (40 $cm^3\ min^{-1}$) was mixed into the He diluent stream to serve as an internal standard.

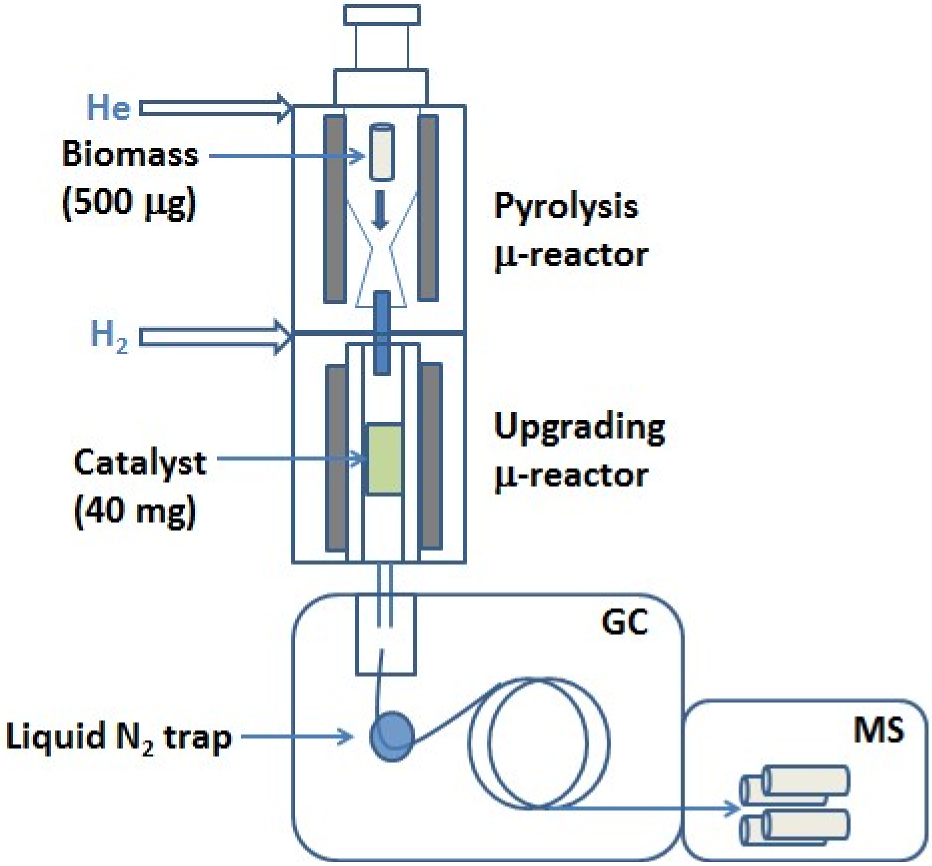
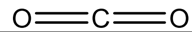
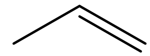
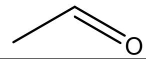
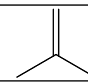
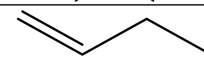
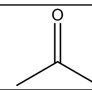
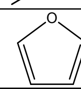
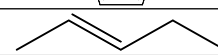
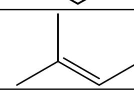
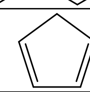
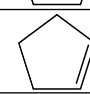
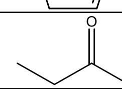
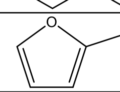
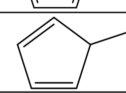
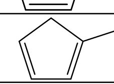
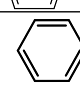
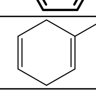
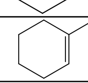
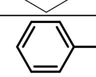
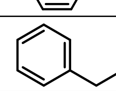
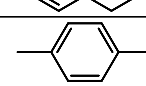
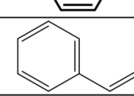
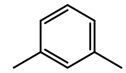
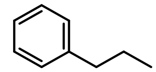
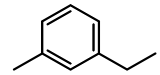
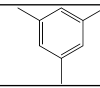
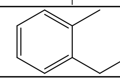
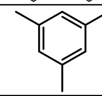
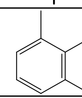
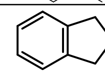
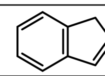
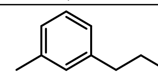
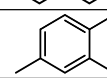
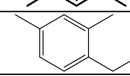
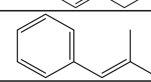
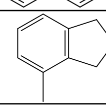
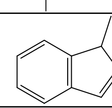
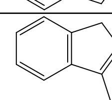
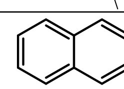
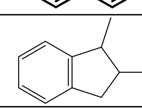
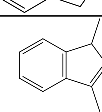
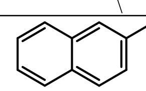
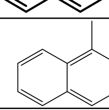


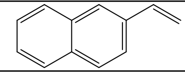
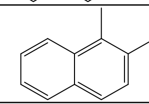
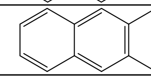
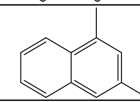
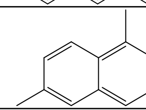
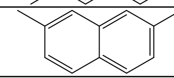
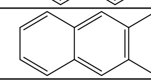
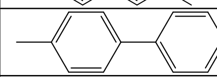
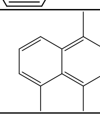
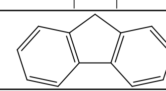
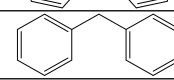
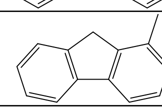
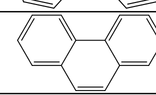
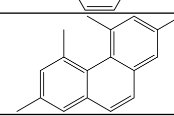
Fig. S2 Schematic of tandem micropyrolyzer-GCMS set up

Typically, pine boats of *ca.* 500 μg each were pyrolysed sequentially and the gases were contacted over 40 mg of catalyst in a 197 cm^3 min^{-1} flow of 71 vol% H_2-He mixture.

Table S1 Products identified by GCMS after the CFP of first pine boat over 10 wt% MoO_3/TiO_2 in the tandem micropyrolyzer.

Retention time/min	m/z	Compound	Structure
1.73	44	carbon dioxide	
1.78	42	propene	
1.87	44	acetaldehyde	
1.90	56	2-methyl-1-propene	
1.94, 1.97	56	1-butene	
2.15	58	Acetone	
2.20	68	Furan	
2.28	70	2-pentene	
2.35	70	2-methyl-2-butene	
2.45	66	1,3-cyclopentadiene	
2.58	68	cyclopentene	
2.81	72	2-Butanone	
2.97	82	2-methylfuran	
3.52	80	5-methyl-1,3-cyclopentadiene	
3.58	80	1-methyl-1,3-cyclopentadiene	
3.81	78	benzene	
5.60	94	1-methyl-1,4-Cyclohexadiene	
5.88	96	1-methylcyclohexene	
5.94	92	toluene	
7.23	106	ethylbenzene	
7.33	106	p-xylene	
7.53	104	styrene	

7.58	106	m-xylene	
8.22	120	propylbenzene	
8.30	120	1-ethyl-3-methyllbenzene	
8.37	120	1,3,5-trimethylbenzene	
8.47	120	1-ethyl-2-methylbenzene	
8.60	120	1,3,5-trimethylbenzene	
8.85	120	1,2,3-trimethylbenzene	
8.96	118	indane	
9.02	116	indene	
9.10	134	1-methyl-3-propylbenzene	
9.15	134	2-ethyl-1,4-dimethylbenzene	
9.34	134	1-ethyl-2,4-dimethylbenzene	
9.39	132	(2-methyl-1-propenyl)benzene	
9.82	132	2,3-dihydro-4-methyl-1H-indene	
9.89	130	1-methyl-1H-indene	
9.93	130	3-methyl-1H-indene	
10.14	128	naphthalene	
10.64	146	2,3-dihydro-1,2-dimethyl-1H-indene	
10.71, 10.75,10.78	144	1,3-dimethyl-1H-indene	
10.95	142	2-methylnaphthalene	
11.06	142	1-methylnaphthalene	

11.48	154	2-ethenylnaphthalene	
11.62	156	1,2-dimethyl-naphthalene	
11.69	156	2,3-dimethylnaphthalene	
11.78	156	1,3-dimethylnaphthalene	
11.80	156	1,6-dimethylnaphthalene	
11.91	156	2,7-dimethylnaphthalene	
12.00	156	2,3-dimethylnaphthalene	
12.15	168	4-methyl-1,1'-Biphenyl	
12.68	170	1,4,5-trimethylnaphthalene	
12.77	166	fluorene	
12.89	168	diphenylmethane	
13.42, 13.46	180	1-methyl-9H-Fluorene	
13.86	178	phenanthrene	
15.95	234	2,4,5,7-tetramethylphenanthrene	

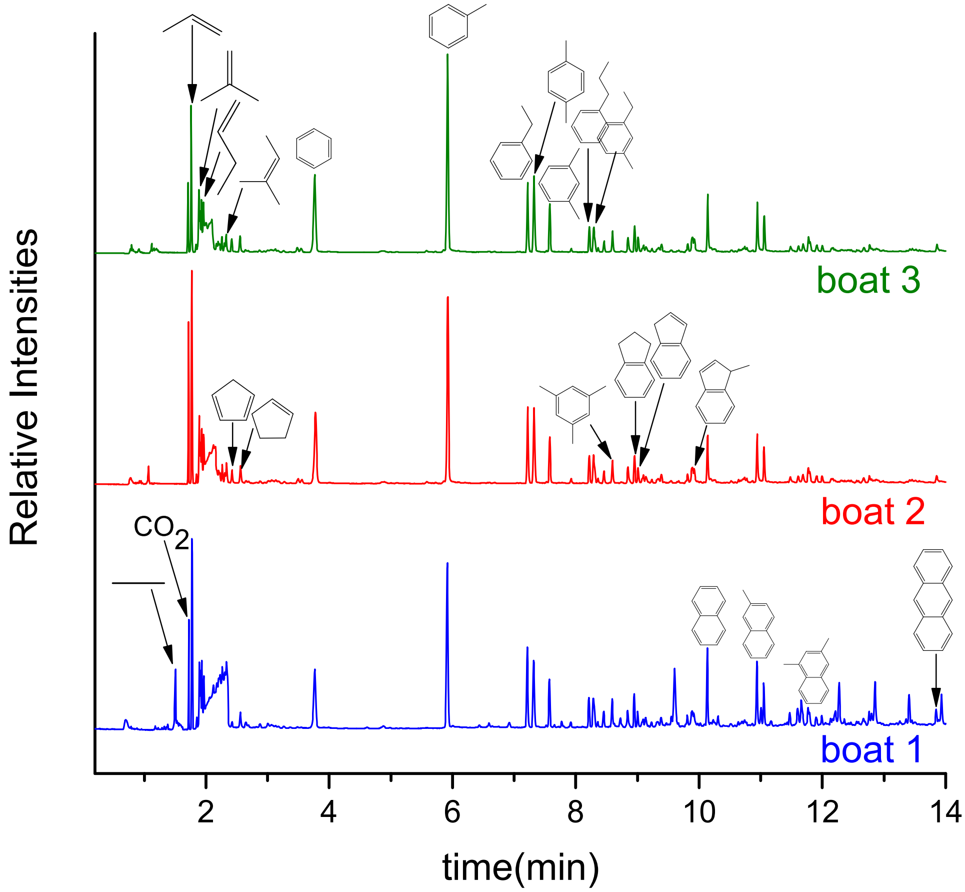
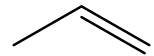
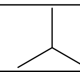
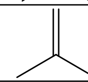
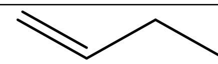
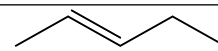
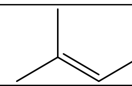
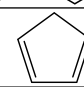
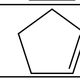
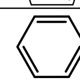
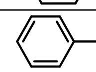
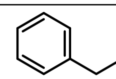
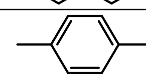
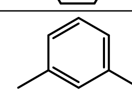
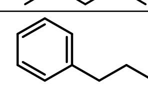
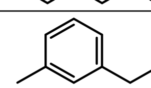
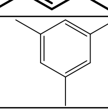
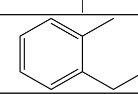
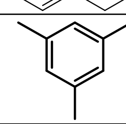
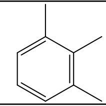
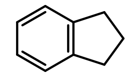
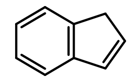
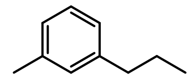
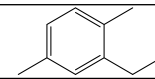
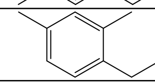
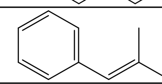
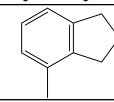
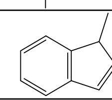
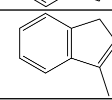
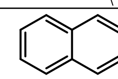
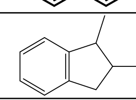
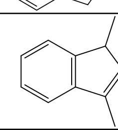
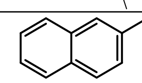
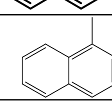
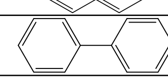
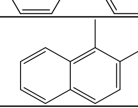
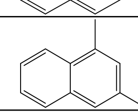
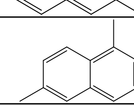
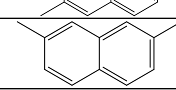
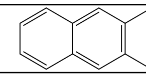
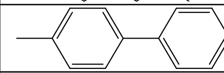
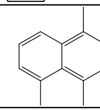
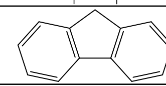
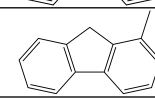
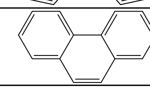
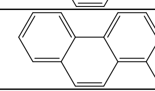
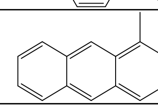


Fig. S3 Product distribution of CFP of pine over 40 mg of 10 wt% MoO_3/ZrO_2 in the micropyrolyzer-GCMS set up. Reaction conditions: catalyst = 40 mg, biomass = 3 boats of 0.5 mg pine, T = 500^{o}C, P_{total} = 1.013 bar (71 vol% H_2-He)

Table S2 Products identified by GCMS after CFP of first pine boat over 10 wt% MoO_3/ZrO_2 in the tandem micropyrolyzer.

Retention time/min	m/z	Compound	Structure
1.51	30	ethane	
1.72	44	carbon dioxide	
1.78	42	Propene	
1.85	58	isobutane	
1.90	56	2-methyl-1-propene	
1.91	58	Butane	
1.94, 1.97	56	1-butene	
2.27	70	2-pentene	
2.33	70	2-methyl-2-butene	
2.42	66	1,3-cyclopentadiene	
2.56	68	cyclopentene	
3.77	78	Benzene	
5.92	92	Toluene	
7.21	106	ethylbenzene	
7.32	106	p-xylene	
7.57	106	m-xylene	
8.21	120	propylbenzene	
8.29	120	1-ethyl-3-methyllbenzene	
8.36	120	1,3,5-trimethylbenzene	
8.45	120	1-ethyl-2-methylbenzene	
8.59	120	1,3,5-trimethylbenzene	

8.84	120	1,2,3-trimethylbenzene	
8.95	118	indane	
9.00	116	indene	
9.09	134	1-methyl-3-propylbenzene	
9.13	134	2-ethyl-1,4-dimethylbenzene	
9.32	134	1-ethyl-2,4-dimethylbenzene	
9.39	132	(2-methyl-1-propenyl)benzene	
9.81	132	2,3-dihydro-4-methyl-1H-indene	
9.89	130	1-methyl-1H-indene	
9.91	130	3-methyl-1H-indene	
10.13	128	naphthalene	
10.64	146	2,3-dihydro-1,2-dimethyl-1H-indene	
10.70, 10.74	144	1,3-dimethyl-1H-indene	
10.94	142	2-methylnaphthalene	
11.05	142	1-methylnaphthalene	
11.47	154	biphenyl	
11.60	156	1,2-dimethyl-naphthalene	
11.77	156	1,3-dimethylnaphthalene	
11.79	156	1,6-dimethylnaphthalene	
11.90	156	2,7-dimethylnaphthalene	

11.99	156	2,3-dimethylnaphthalene	
12.14	168	4-methyl-1,1'-Biphenyl	
12.67	170	1,4,5-trimethylnaphthalene	
12.76	166	fluorene	
13.41	180	1-methyl-9H-Fluorene	
13.85	178	phenanthrene	
14.43	192	1-methylphenanthrene	
14.59	192	1-methylanthracene	

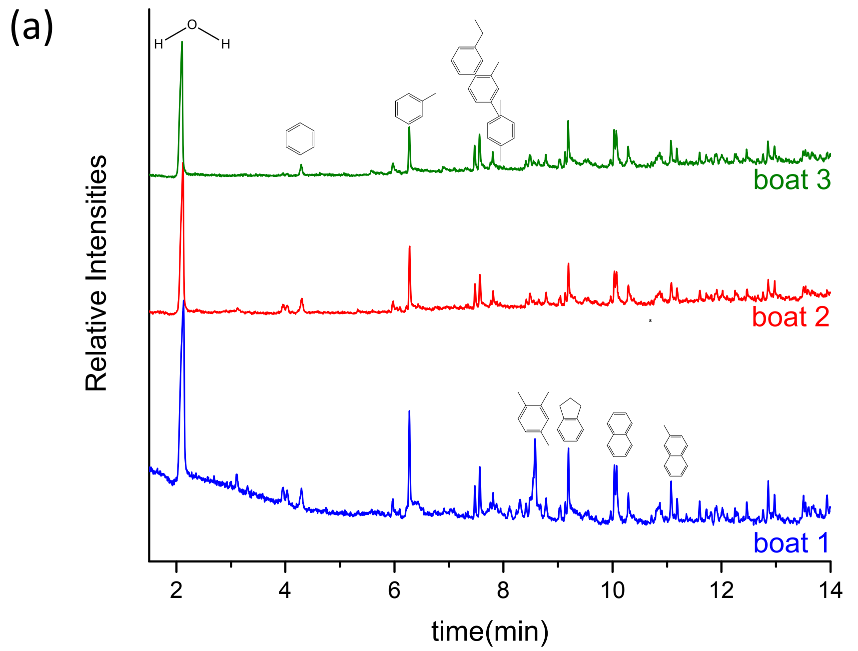


Fig. S4a GCMS chromatograms of the CFP of 3 pine boats over 40 mg of bare TiO_2 support in the micropyrolyzer-GCMS set up. The TiO_2 support shows minimal catalytic activity, and the deoxygenated products decrease in intensity when more pine boats are fed. **Fig. S4b** Overlay of GCMS spectra of CFP of the 3rd pine boat over MoO_3/TiO_2 and support TiO_2 in the micropyrolyzer-GCMS set up. The support TiO_2 shows less intense product peaks than MoO_3/TiO_2.Reaction conditions: catalysts= 40 mg, biomass = 3 boats of 0.5 mg pine, T = 500^{o}C, P_{total} = 1.013 bar (71 vol% H_2-He). The cryo-trap temperature was set to -80°C in both experiments, thereby explaining the absence of alkenes and alkanes.

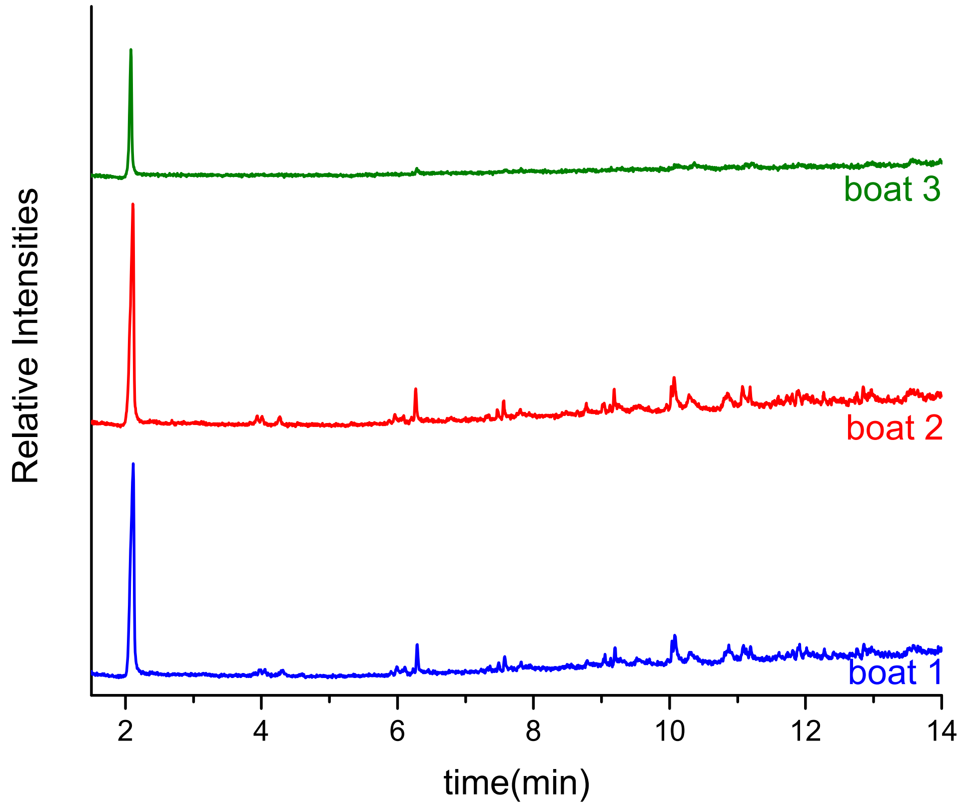


Fig. S5 GCMS chromatograms of the CFP of 3 pine boats over 40 mg of bare ZrO_2 support in the micropyrolyzer-GCMS set up. The ZrO_2 support shows negligible catalytic activity under the reaction conditions investigated. Reaction conditions: catalyst = 40 mg of ZrO_2, biomass = 3 boats of 0.5 mg pine, T = 500^{o}C, P_{total} = 1.013 bar (71 vol% H_2-He)

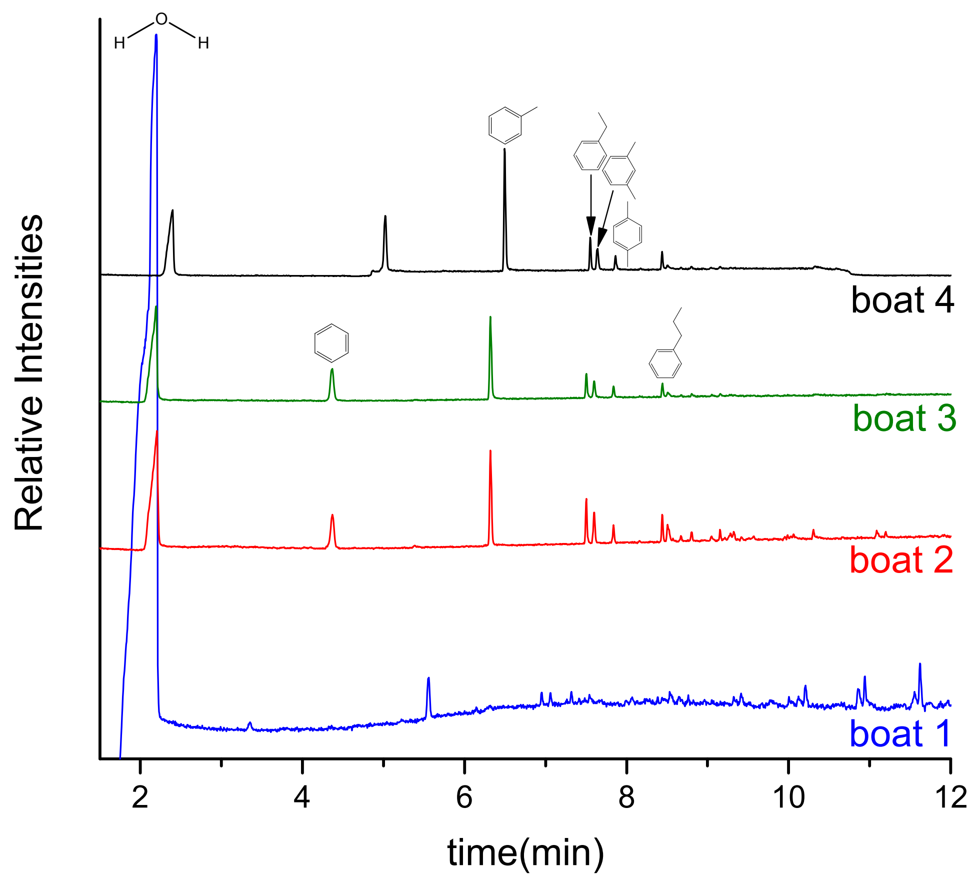


Fig. S6 Product distribution of CFP of pine over 40 mg of MoO_3 in the micropyrolyzer-GCMS set up. Reaction conditions: catalyst = 40 mg, biomass = 4 boats of 0.5 mg pine, T = 500^{o}C, P_{total} = 1.013 bar (71 vol% H_2-He). The cryo-trap temperature was set to -80°C in this experiment, thereby explaining the absence of alkenes and alkanes.

Table S3 Average product yields and selectivity values for the CFP of 3 pine boats over MoO_3/TiO_2, MoO_3/ZrO_2 and HZSM-5 in the micropyrolyzer-GCMS system.

Catalyst	MoO_3/TiO_2	MoO_3/ZrO_2	HZSM-5
Overall Carbon Yield (%)			
Aromatic hydrocarbons	7.4	7.4	17.3
Olefins	19.4	17.2	6.0
Paraffins	2.4	1.8	0.0
Oxygenates	0.4	0.0	0.0
CO_2	2.8	5.0	5.5
Coke	6.8	7.3	11.9
Char	39.4	39.4	39.4
Total	78.6	78.2	80.2
Aromatic hydrocarbons selectivity (%)			
Benzene	28.8	28.0	11.9
Toluene	27.6	31.6	24.2
Xylene	10.1	10.5	14.9
Multi-substituted benzenes	16.5	14.4	3.7
Naphthalenes	8.6	9.6	19.8
Indanes/Indenes	6.6	4.0	12.1
Others	1.8	1.8	13.5
Olefins selectivity (%)			
Ethylene	2.0	2.3	36.0
Propene	62.0	68.6	26.4
Butene	13.5	13.8	0.0
Methylpropene	4.9	4.7	37.6
Pentene	2.8	2.2	0.0
Methylbutene	4.6	4.0	0.0
Cyclopentadiene	4.4	1.6	0.0
Cyclopentene	4.4	2.7	0.0
Cyclohexadiene	1.1	0.0	0.0
Others	0.3	0.2	0.0
Paraffins selectivity (%)			
Ethane	75.7	23.0	0.0
Butane	4.8	44.3	0.0
Dimethylcyclopropane	12.6	20.4	0.0
Cyclopentane	3.5	3.8	0.0
Isobutane	3.5	8.5	0.0

Table S4 Reaction conditions and product distribution from the CFP of biomass over HZSM-5.[1, 2]

Catalyst	HZSM-5	HZSM-5
Biomass	pinewood	Hybrid poplar
Reactor type	micropyrolyzer	micropyrolyzer
Pyrolysis temperature	550°C	500°C
Upgrading temperature	550°C	500°C
Biomass: Catalyst ratio	0.2	0.05
Overall Carbon Yield (%)		
Aromatic hydrocarbons	9.8	15.3
Olefins	N.A.[c]	7.7
Char	N.A.[c]	18.3
Coke	N.A. [c]	26.5
Light gases	N.A. [c]	21.6
Total		89.4
Aromatic hydrocarbons selectivity (%)		
Benzene	9	11.7
Toluene	15	33.7
Xylene	43	19.2
C_9 aromatics[a]	16	9.9
C_{10+} aromatics[b]	17	25.8
Olefins selectivity (%)		
Ethylene	N.A. [c]	50.5
Propene	N.A. [c]	43.7
Butene	N.A. [c]	5.9
Light gases selectivity (%)		
CO	N.A. [c]	69.4
CO_2	N.A. [c]	30.6

[a] C_9 aromatics: indane, indene, alkylbenzenes

[b] C_{10+} aromatics: naphthalenes and higher polyaromatics

[c] N.A. – not quantified in the study

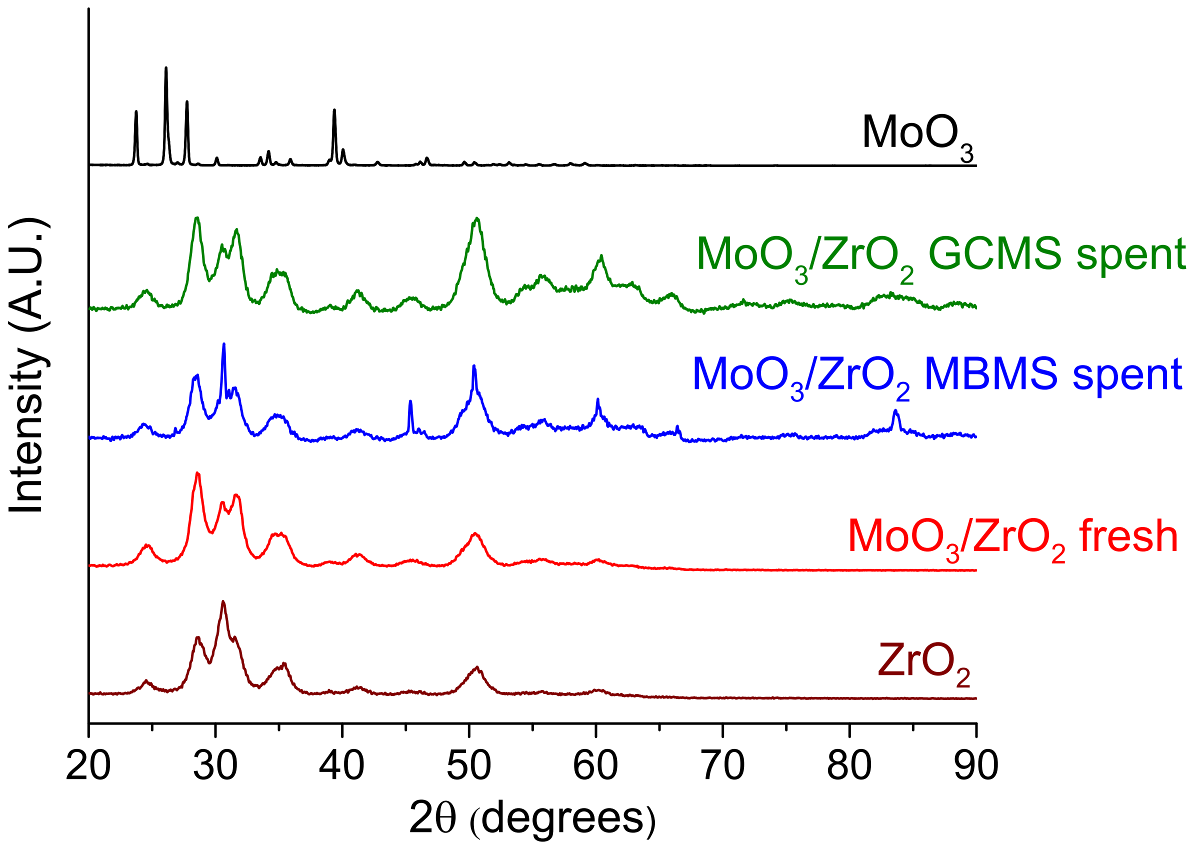


Fig. S7 Normalised PXRD patterns of the fresh and spent MoO_3/ZrO_2 catalysts in comparison with fresh ZrO_2 and MoO_3 samples. The spent MoO_3/ZrO_2 samples from both reactor systems were derived after experiments shown in Fig. 3(b) and S3.

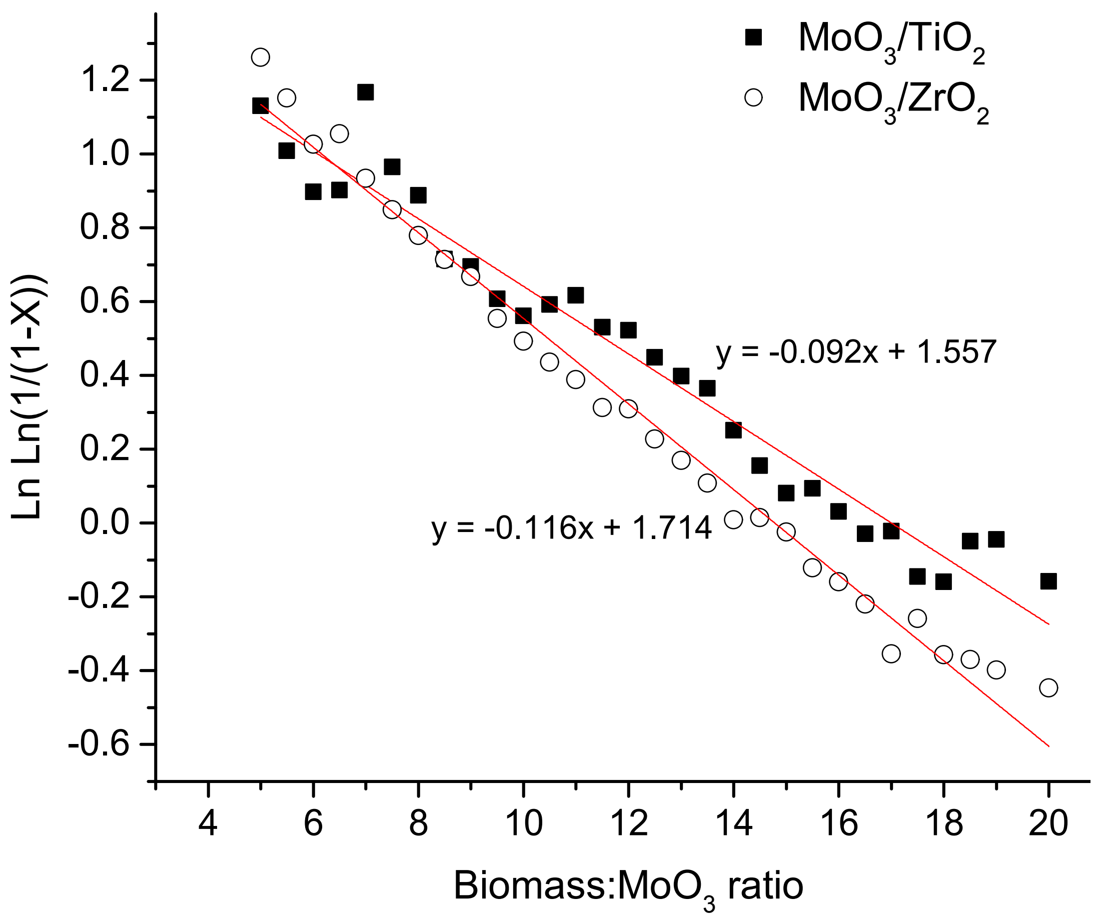


Fig. S8 Deactivation profiles for MoO_3/TiO_2 and MoO_3/ZrO_2 for CFP of pine in the horizontal reactor-MBMS set up fitted to a first-order deactivation model.

References

1. S. Thangalazhy-Gopakumar, S. Adhikari, R. B. Gupta, M. Tu and S. Taylor, *Bioresour. Technol.*, 2011, 102, 6742-6749.
2. K. Wang, P. A. Johnston and R. C. Brown, *Bioresour. Technol.*, 2014, 173, 124-131.