Reactive catalytic fast pyrolysis of biomass to produce high-quality bio-crude

Supplementary Information

S1 Catalyst characterization

Surface area measurements were performed on a surface area analyser (Gemini VII, Micromeritics). The surface area of catalyst was calculated using the Brunauer–Emmett–Teller (BET) equation. Temperature programmed ammonia absorption (NH_3 TPD) was carried out on a chemisorption analyser (Autochem II, Micromeritics) to characterize the strength of acid sites. The procedure was conducted by degassing the catalyst at 120°C, then cooling to lower temperature and exposing the catalyst to a stream of gas phase ammonia. After exposure to ammonia the sample was cooled and the ammonia flow was replaced with inert. The sample was then heated to 700°C. The evolution of ammonia was observed with a thermal conductivity detector. Acid sites on the catalyst bind ammonia. The strength of the acid site was indicated by the temperature at which ammonia was observed to evolve from the catalyst. Temperature programmed reduction (TPR) was performed to measure the temperatures at which the catalyst becomes reduced in the presence of hydrogen. The procedure consists of first degassing the catalyst by heating in flowing inert at 120°C for one hour. After degas, the sample is cooled to 50°C and the gas is switched to a 10% H2 concentration. The sample is then heated to 500°C under flowing hydrogen and reduction is observed by monitoring the hydrogen signal on a thermal conductivity detector.

Table S1. Summary of catalyst characterization result

Catalysts	BET surface area (m^2/g)	NH_3 TPD		H_2 TPR	
		Temp. (°C)	NH_3 uptake (ml /$g_{catalyst}$)	*Temp. (°C)*	H_2 uptake (ml /$g_{catalyst}$)
SA1	114.6	200.2	9.83	None	0
MMO1	79.1	228	12.2	205; 270	51.8
RMO1	106.6	200	6.8	432	2.4
RMO2	171.6	108.6	8.2	421	19.1
HT1	Not analysed	129.5	8.3	376	7.5

S2 Correlation of hydrogen consumption and water formation

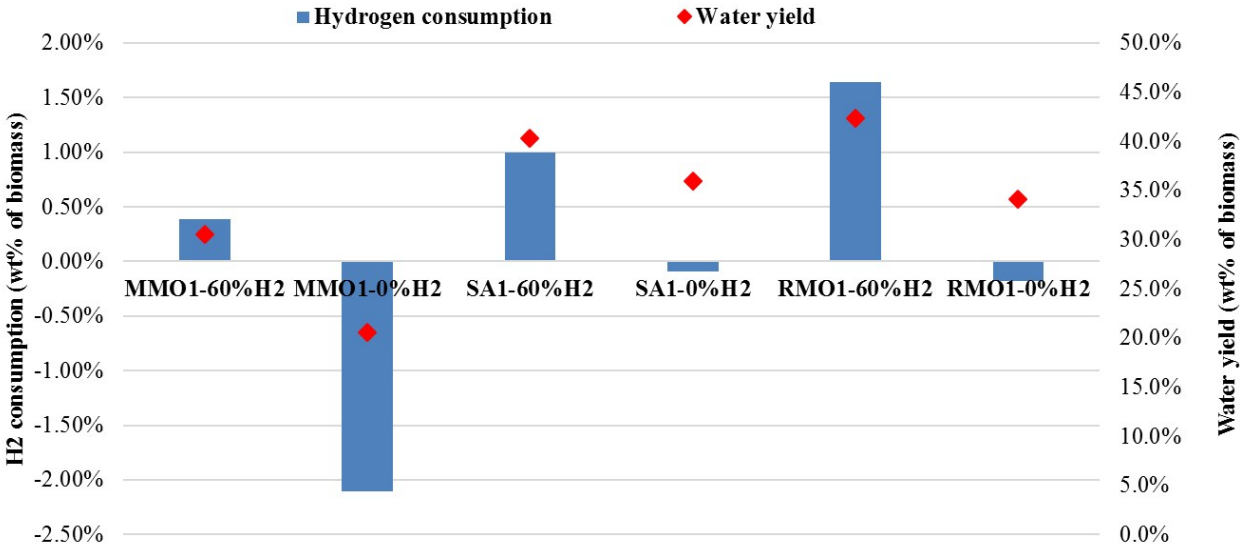

Figure S1. Comparison of hydrogen consumption and yield of water for RCFP and CFP of loblolly pine using different catalysts under temperature of 500 °C

S3. Detailed product distribution

Table S2. Detailed product distribution and characterization for RCFP of loblolly pine using different catalysts (reaction conditions: temperature: 500 °C; hydrogen concentration: 60vol%)

Catalyst	MMO1	SA1	RMO1	HDT1	RMO2
H_2 conc. (vol%)	60	60	60	60	60
Temperature (˚C)	500	500	500	500	500
Overall carbon yield					
Organic liquid	18.2	21.9	23.1	14.6	14.1
Aqueous liquid	1.3	1.7	2.3	1.2	0.5
Gas	40.6	34.8	28.6	38.9	44.3
Solid	27.3	30.4	31.4	26.0	31.5
C_{eff} C_{4+}*	25.0	27.7	36.8	24.4	26.6
H_2 consumption (% $g.g^{-1}$)**	1.0	1.0	1.6	2.6	3.0
Gas breakdown (mole C% of biomass)					
CO	12.6	12.0	9.8	10.0	9.9
CO_2	10.4	5.7	4.1	5.5	6.4
CH_4	5.3	3.5	4.6	7.8	6.6
C_2	1.7	1.6	1.9	3.3	4.7
C_3	3.9	1.8	2.1	3.1	4.9
C_4-C_6	6.8	5.8	13.7	9.8	12.5
*Elemental analysis of organic liquid****					
C (wt%)	74.3	77.5	77.3	84.5	86.4
H (wt%)	7.7	7.5	7.9	7.4	7.4
O (wt%)	17.3	14.4	14.8	7.4	5.4
H/C_{eff}	0.89	0.88	0.93	0.92	0.93
HHV (MJ/Kg)	35.1	36.9	37.5	41.9	43.3
GC-MS/peak area%					
Aliphatics	2.2	1.4	4.1	5.7	7.8
Ketones/furans	14.0	17.6	19.3	5.7	4.4
Acids	2.5	0.3	0.1	0.0	0.0
Monoaromatics	4.6	5.1	12.7	19.7	28.9
PAHs	27.5	37.7	35.1	48.0	48.0
Phenolics	40.8	32.5	22.1	16.4	7.7
Sugars	0.0	0.0	0.0	0.0	0.0
Unidentified	7.1	5.1	6.5	4.4	3.1

*Carbon efficiency of C_{4+} defined as the sum of bio-crude and C_4-C_6 hydrocarbon yield; ** Hydrogen consumption defined as weight percentage of hydrogen consumed to the biomass feed: a negative value corresponds to hydrogen generation, while a positive value corresponds to hydrogen consumption; *** Dry basis.

Table S3. Detailed product distribution and characterization for RCFP of loblolly pine under hydrogen concentration of 0 vol%, 60 vol%, 70 vol%, and 80 vol% (reaction temperature: 450 °C)

Catalyst	**RMO2**	**RMO2**	**RMO2**	**RMO2**
H_2 conc. (vol%)	0	60	70	80
Temperature (°C)	450	450	450	450
Overall carbon yield				
Organic liquid	16.5	17.8	26.1	26.4
Aqueous liquid	8.3	2.6	3.9	2.5
Gas	29.0	35.9	36.2	42.7
Solid	39	33.6	32.3	30.1
C_{eff} C_{4+}*	26.6	31.3	40.6	43.0
H_2 consumption (% $g.g^{-1}$)**	-0.2	2.3	2.4	3.1
Gas breakdown (mole C% of biomass)				
CO	8.3	7.3	8.5	9.0
CO_2	5.0	5.2	5.4	5.9
CH_4	1.7	3.8	3.5	4.3
C_2	0.7	2.7	2.0	3.0
C_3	3.1	3.5	2.9	4.6
C_4-C_6	10.1	13.5	14.5	16.6
*Elemental analysis of organic liquid****				
C (wt%)	71.4	79.9	80.7	84.8
H (wt%)	6.12	8.0	8.0	8.3
O (wt%)	21.4	10.7	10.2	6.2
H/C_{eff}	0.63	1.00	1.01	1.07
HHV (MJ/Kg)	29.3	39.7	40.3	44.0
GC-MS/peak area%				
Aliphatics	2.2	9.2	7.1	7.3
Ketones/furans	19.9	13.6	16.2	10.7
Acids	2.4	0.2	0.0	0.0
Monoaromatics	6.2	20.5	19.1	22.2
PAHs	12.4	46.7	43.1	42.5
Phenolics	50.1	6.8	10.7	13.9
Sugars	0.0	0.0	0.0	0.0
Unidentified	6.8	2.8	3.8	3.3

*Carbon efficiency of C_{4+} defined as the sum of bio-crude and C_4-C_6 hydrocarbon yield; ** Hydrogen consumption defined as weight percentage of hydrogen consumed to the biomass feed; a negative value corresponds to hydrogen generation, while a positive value corresponds to hydrogen consumption; *** Dry basis.

Table S4. Detailed product distribution and characterization for RCFP of loblolly pine at reaction temperature of 400 ˚C, 450 ˚C, and 500 ˚C (hydrogen concentration of 80 vol%)

Catalyst	**RMO2**	**RMO2**	**RMO2**
H_2 conc. (vol%)	80	80	80
Temperature (˚C)	400	450	500
Overall carbon yield			
Organic liquid	24.9	26.4	20.0
Aqueous liquid	6.9	2.5	2.1
Gas	31.4	42.7	51.2
Solid	35.7	30.1	27.2
C_{eff} C_{4+}*	39.1	43.0	35.3
H_2 consumption (% $g.g^{-1}$)**	2.5	3.1	3.2
Gas breakdown (mole C% of biomass)			
CO	6.9	9.0	12.3
CO_2	5.2	5.9	7.4
CH_4	2.0	4.3	7.0
C_2	1.2	3.0	4.6
C_3	2.4	4.6	5.5
C_4-C_6	14.2	16.6	15.3
*Elemental analysis of organic liquid****			
C (wt%)	74.1	84.8	85.0
H (wt%)	7.4	8.3	7.8
O (wt%)	17.7	6.2	5.8
H/C_{eff}	0.84	1.07	1.00
HHV (MJ/Kg)	34.5	44.0	43.1
GC-MS/peak area%			
Aliphatics	5.4	7.3	8.2
Ketones/furans	27.4	10.7	8.8
Acids	1.7	0.0	0.0
Monoaromatics	8.2	22.2	28.1
PAHs	16.0	42.5	41.6
Phenolics	37.5	13.9	10.3
Sugars	0.0	0.0	0.0
Unidentified	3.5	3.3	3.0

*Carbon efficiency of C_{4+} defined as the sum of bio-crude and C_4-C_6 hydrocarbon yield; ** Hydrogen consumption defined as weight percentage of hydrogen consumed to the biomass feed; a negative value corresponds to hydrogen generation, while a positive value corresponds to hydrogen consumption; *** Dry basis.