

In-situ upgrading of whole biomass to biofuel precursors with low average molecular weight and acidity by the use of zeolites mixture

*Haoxi Ben,^{a,b} Fang Huang,^b Liwei Li^c and Arthur J. Ragauskas^{*d,e,f}*

^a School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA 30332, USA.

^b Institute of Paper Science and Technology, Georgia Institute of Technology, Atlanta, GA 30332, USA.

^c School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA
30332, USA.

^d *Department of Chemical and Biomolecular Engineering, University of Tennessee, Knoxville,
Tennessee 37996, USA.*

^e *Department of Forestry, Wildlife, and Fisheries, University of Tennessee, Knoxville, Tennessee 37996,
USA.*

^f *Oak Ridge National Lab, Oak Ridge, Tennessee 37831, USA.*

*Correspondence should be addressed to Professor Arthur J. Ragauskas

Email: aragausk@utk.edu

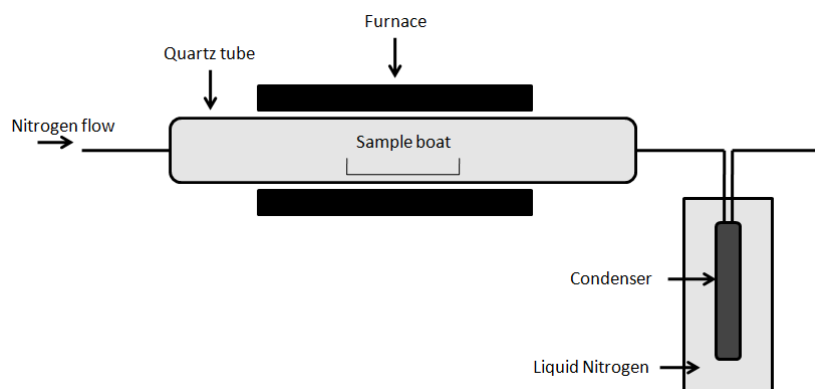


Figure S1. Pyrolysis system used in this work.

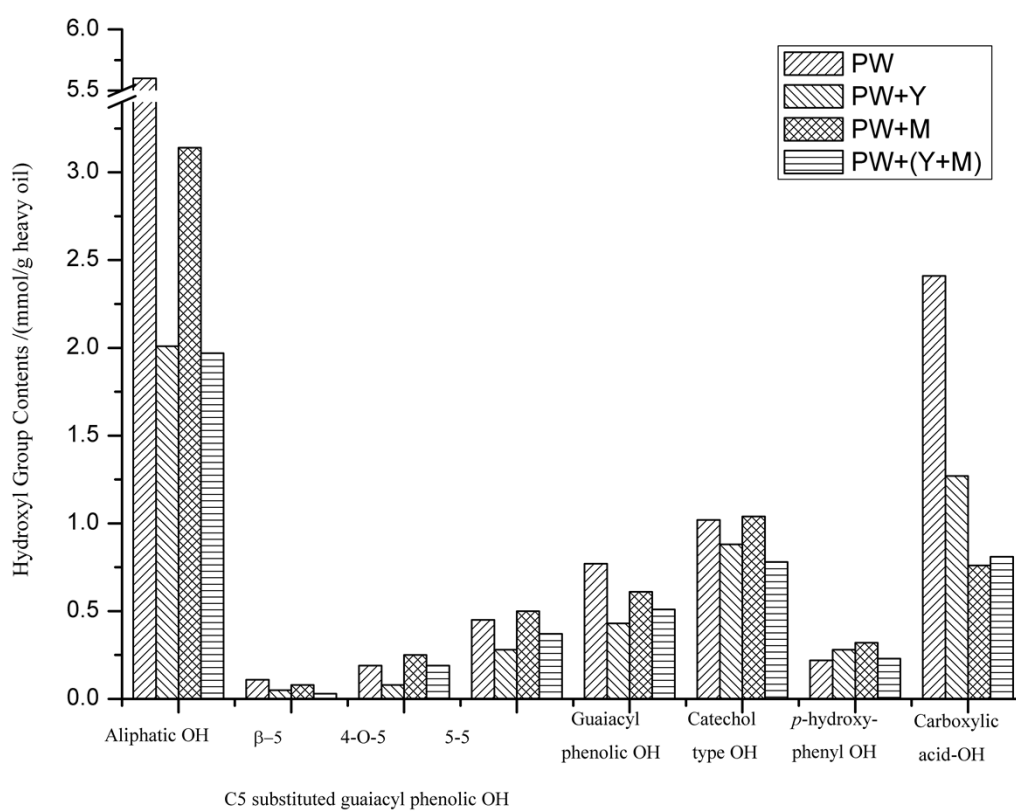


Figure S2. Hydroxyl groups contents of different pyrolysis oils produced from PW, PW+Y, PW+M and PW+(Y+M).

Cold flow properties analysis of pyrolysis oils

All pour points of pyrolysis oils in this study were recorded with a 70XI cloud, pour and freeze point lab analyzer manufactured by Phase Technology. All the tests used manufactory default analysis methods and the data was processed by the analyzer.

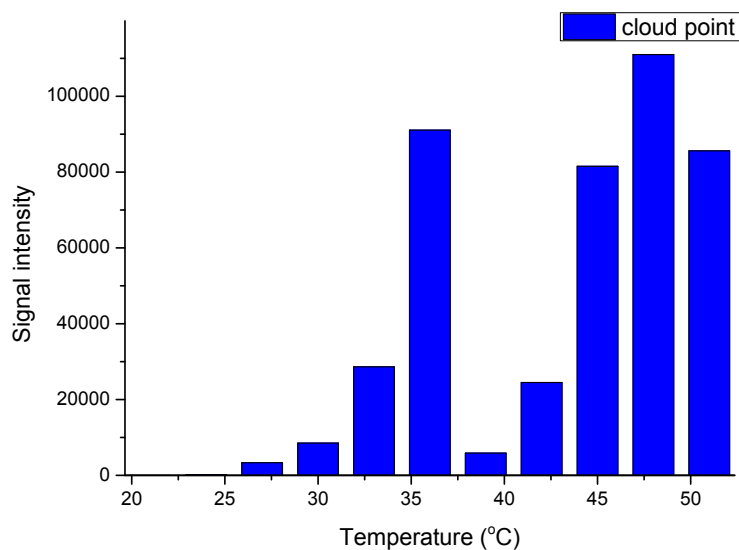


Figure S3. Pour point measurement for the pyrolysis oil produced from pine bark at 600 °C. The Pour point has been detected as 24 °C.

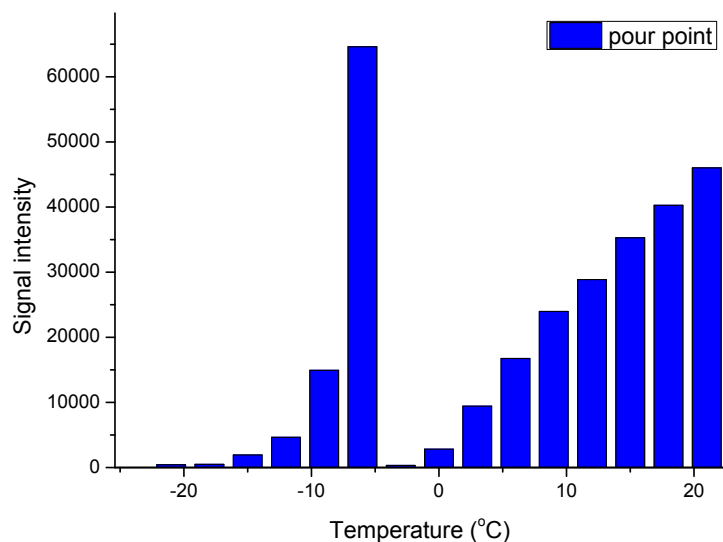


Figure S4. Pour point measurement for the Y zeolite upgraded pyrolysis oil at 600 °C. The Pour point has been detected as -21 °C.

The pour point of a liquid is the lowest temperature at which it becomes semi solid and loses its flow characteristics. The cloud point of a fluid is the temperature at which dissolved solids are no longer completely soluble, precipitating as a second phase giving the fluid a cloudy appearance. For example, when the diesel fuel is cooled to reach the "cloud point", this is the temperature at which paraffin wax falls out of solution and starts to form wax crystals in the fuel. As the diesel is further cooled, it will eventually reach the "pour point". This is the temperature at which diesel will no longer flow or the point at which fuel gels or turns solid. Normally, the cloud point for diesel is ~ -12 to -30 °C and the pour point is ~ -23 to -40 °C.

The cloud points for all types of heavy oils were undetectable by this cold flow properties analyzer. Pour point for pyrolysis oils produced from pine bark and Y zeolite upgraded pyrolysis oils were examined and the results are shown in Figures S3 and S4. For pine bark pyrolysis oils, the pour point is 24 °C, which is much higher than the normal fuels. The results also show that the flow capability dramatically decreased around $35-40$ °C. Very interestingly, for the Y zeolite upgraded pyrolysis oil, the molecular weight decreased to the gasoline range (~ 150 g/mol) and the pour point also drop to -21 °C, which is closed to the pour point of diesel. The control pyrolysis oil has a pour point of 24 °C, which means by using zeolite during the thermal conversion process this important cold flow properties decreased by ~ 45 °C. In addition, the flow capability dramatically decreased around -5 °C, which is also decreased by ~ 45 °C compare to the control pyrolysis oil.

Recovery of zeolites

After the pyrolysis process, the mixture of zeolites and char was soaked and stirred in 2 % H₂SO₄ solution for one hour. After that, the solid residue (zeolite and char) was collected by filtration. The recovered residue was then washed with DI water until to neutral pH. This neutral residue was burned in the muffle furnace at 550 °C overnight to remove the char. The recovered zeolites were then re-activated in the pyrolysis tube at 500 °C under nitrogen for 6 h prior to the mixing with fresh biomass samples.

In this study, the zeolites were used 3 times. In the first time pyrolysis, the zeolite was fresh product. During the second and third pyrolysis, the zeolites were obtained from the recycling process.

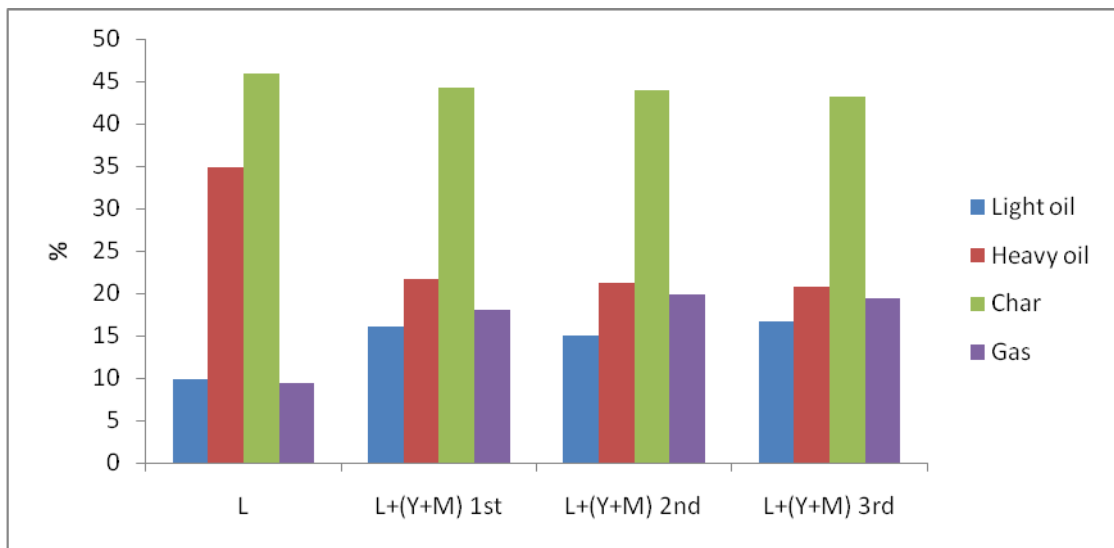


Figure S5. Yields (wt%) of light oil, heavy oil, char (excludes the weight of zeolite) and gas for the pyrolysis of biomass (lignin, L) and pyrolysis with 1.0/1.0 ($W_{\text{additive}}/W_{\text{lignin}}$) of ‘Y+M’ zeolites (both fresh and recovered) as additives at 600 °C for 10 min.

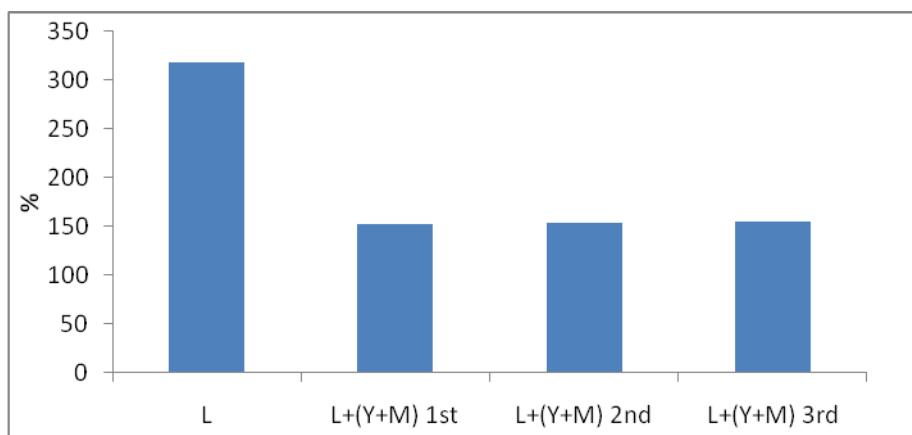


Figure S6. Molecular weight distributions (M_w) of heavy oils produced by pyrolysis of biomass (lignin, L) and pyrolysis with 1.0/1.0 ($W_{\text{additive}}/W_{\text{lignin}}$) of ‘Y+M’ zeolites (both fresh and recovered) as additives at 600 °C for 10 min.

GC-MS analysis of pyrolysis products

The GC-MS analysis of pyrolysis products was conducted by Agilent 5975C MSD and 7890A GC with a 7693 auto sampler. The Agilent HP-5MS, 19091S-433 column was used. The GC oven was programmed with the following temperature regime: hold at 50 °C for 5 min, ramp to 80 °C at 5 °C/min and hold at 80 °C for 5 min, then ramp to 200 °C at 2 °C/min and hold at 200 °C for 5 min.

Table S1. Major chemical composition of heavy oil produced by pyrolysis of lignin and lignin with 1.0/1.0 ($W_{\text{additive}}/W_{\text{lignin}}$) of Y, B and M zeolite as additive at 600 °C for 10 min, detected by GC-MS.

softwood kraft lignin		Lignin + Y		Lignin + B		Lignin + M	
Area (%)	Chemical name	Area (%)	Chemical name	Area (%)	Chemical name	Area (%)	Chemical name
3.53	Phenol	1.65	3-Penten-2-one, 4-methyl-	2.34	3-Penten-2-one, 4-methyl-	2.75	2-Pentanone, 4-hydroxy-4-methyl-
4.66	Phenol, 2-methyl-	9.25	Phenol	9.15	Phenol	3.98	Phenol
3.13	Phenol, 4-methyl-	9.13	Phenol, 2-methyl-	9.96	Phenol, 2-methyl-	5.39	Phenol, 2-methyl-

26.65	Phenol, 2-methoxy-	14.31	Phenol, 3-methyl-	14.95	Phenol, 4-methyl-	5.48	Phenol, 4-methyl-
3.48	Phenol, 2,4-dimethyl-	11.49	Phenol, 2-ethoxy-	9.96	Phenol, 2-methoxy-	16.83	Phenol, 2-methoxy-
7.75	Phenol, 2-methoxy-4-methyl-	2.09	Phenol, 2,6-dimethyl-	5.41	Phenol, 2,4-dimethyl-	6.73	Phenol, 2,4-dimethyl-
14.03	1,2-Benzenediol	5.18	Phenol, 2,4-dimethyl-	5.92	Phenol, 2,5-dimethyl-	12.45	Phenol, 2-methoxy-4-methyl-
0.69	Phenol, 2-ethyl-5-methyl-	4.51	Phenol, 2,4-dimethyl-	2.12	Phenol, 3,5-dimethyl-	12.47	1,2-Benzenediol
3.13	1,2-Benzenediol, 3-methyl-	1.82	Phenol, 3,5-dimethyl-	7.53	Azulene	1.90	Benzene, 1-ethyl-4-methoxy-
8.61	Phenol, 4-ethyl-2-methoxy-	6.22	Naphthalene	11.82	1,2-Benzenediol	4.43	1,2-Benzenediol, 3-methyl-
7.23	1,2-Benzenediol, 4-methyl-	1.57	Phenol, 2-methoxy-4-methyl-	3.78	1,2-Benzenediol, 3-methyl-	10.62	Phenol, 4-ethyl-2-methoxy-
6.25	2-Methoxy-4-vinylphenol	2.21	Phenol, 3,4-dimethyl-	7.14	Naphthalene, 2-methyl-	9.85	1,2-Benzenediol, 4-methyl-
3.53	1,3-Benzenediol, 4-ethyl-	12.62	1,2-Benzenediol	4.68	1,2-Benzenediol, 4-methyl-	4.42	4-Ethylcatechol
4.48	Phenol, 2-methoxy-4-(1-propenyl)-, (E)-	3.53	1,2-Benzenediol, 3-methyl-	3.19	Naphthalene, 2-methyl-	2.63	Phenol, 2-methoxy-4-(1-propenyl)-, (E)-
2.79	Benzeneacetic acid, 4-hydroxy-3-methoxy-	4.78	Naphthalene, 1-methyl-	2.08	Naphthalene, 1,3-dimethyl-		
		5.60	1,2-Benzenediol, 4-methyl-				
		2.09	Naphthalene, 1-methyl-				
		1.93	Naphthalene, 1,4-dimethyl-				
