



Pyrolysis of Kraft Lignin

Haoxi Ben, Arthur J. Ragauskas.

School of Chemistry and Biochemistry, Institute of Paper Science and Technology
Georgia Institute of Technology, Atlanta, Georgia 30332, USA.



Background

Known petroleum reserves are predicted to be consumed in less than fifty years at present rates of consumption. Cellulose from wood and other biomass is now generally recognized as a major renewable resource for fuels and chemicals. As the second most abundant biomass component and the primary renewable aromatic resource in nature, lignin, however, has received much less attention than plant polysaccharides as a resource for biofuels. For example, the US paper industry produces over 50 million tons of extracted lignin per year and yet only 2% of this material is used commercially in products. The remainder is burned as a low value fuel to recover energy. Pyrolysis of lignin is a promising approach that is being investigated to upgrade this biopolymer into higher value products including biofuels and aromatic chemicals.

Experimental

Pyrolysis experiments were conducted in a quartz pyrolysis tube heated with a split-tube furnace in an inert atmosphere at atmospheric pressure. The influence of different temperature and different additives on the pyrolysis of kraft lignin was studied. Gel permeation chromatography (GPC), quantitative ^{13}C Nuclear Magnetic Resonance (NMR) and ^{31}P NMR were used to characterize the pyrolysis oils.



Figure 1. Pyrolysis system



Figure 2. Pyrolysis products, char (left), heavy oil (middle) and light oil (right).

Results and Discussions

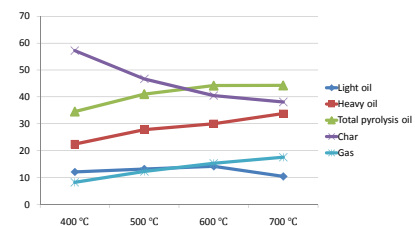


Figure 3. The yields of pyrolysis products for the pyrolysis of kraft lignin at different temperatures.

- ❖ The liquid products from pyrolysis contained two immiscible phases--the heavy oil and light oil.
- ❖ The yields of char decreased linearly from 57%-38% with increased reactor temperature.
- ❖ The yields of pyrolysis oil increased from 34%-44% with increased pyrolysis temperature.
- ❖ 700 °C was found as the point of primary decomposition of lignin and the secondary decomposition of pyrolysis oil.
- ❖ The additives have very limited effects on the primary decomposition of lignin.
- ❖ NiCl_2 and H-ZSM-5 could enhance the secondary decomposition of pyrolysis heavy oil to the light oil or gas.

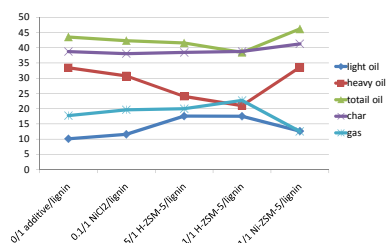


Figure 4. The yields of pyrolysis products for the pyrolysis of kraft lignin with different additives.

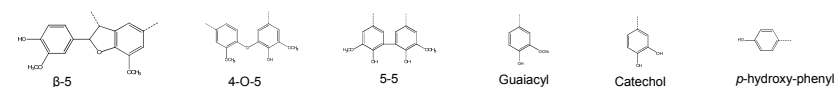
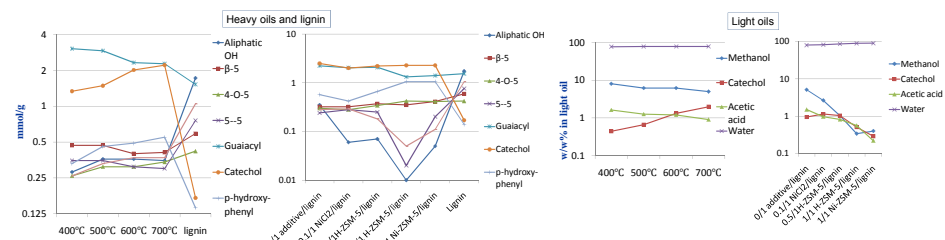


Figure 5. ^{31}P NMR results for heavy oils and lignin (left) and light oils (right).

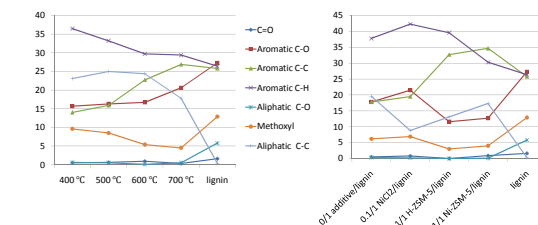
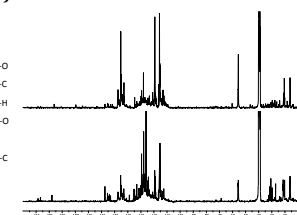


Figure 6. ^{13}C NMR spectra and results for heavy oils and lignin.



Quantitative ^{13}C NMR spectra for the heavy oil produced by pyrolysis of SW kraft lignin (top) and pyrolysis of SW kraft lignin with Ni-ZSM-5 as the additive (bottom) at 700 °C for 10 min

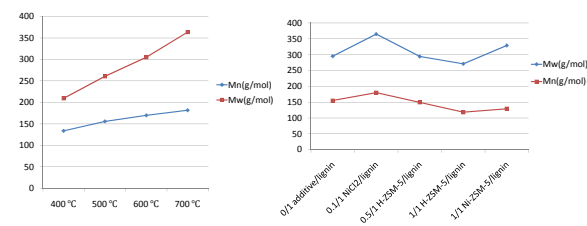
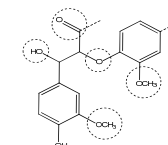


Figure 7. Molecular weight distribution of heavy oils



Aliphatic hydroxyl groups, carboxyl groups, Ar-methoxyl groups and the ether bonds in the lignin are the primary functional groups to decompose during the pyrolysis.

Conclusions

- ❖ The light oil contained nearly 80 w/w% water and another 10 w/w% was methanol, catechol and acetic acid.
- ❖ At higher temperature, there would be more aromatic C-O and C-C bond in the heavy oil, and the heavy oil would have a larger molecular weight and polydispersity value.
- ❖ After the use of zeolite, the concentration of water in light oil increased, In contrast, the yields of methanol and acetic acid in the light oil decreased.
- ❖ The carbonyl groups and the aliphatic C-O bonds are almost completely decomposed, and compare to the lignin, about 80% of methoxyl groups are eliminated after pyrolysis with H-ZSM-5 zeolite as the additive.
- ❖ H-ZSM-5 zeolite could improve the decomposition of all the primary decomposed functional groups during the pyrolysis.
- ❖ H-ZSM-5 zeolite could also improve the deoxygenation during the pyrolysis of lignin.
- ❖ After the use of H-ZSM-5 zeolite the bio-oil would have a lower molecular weight.