



Pyrolysis of Kraft Lignin

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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

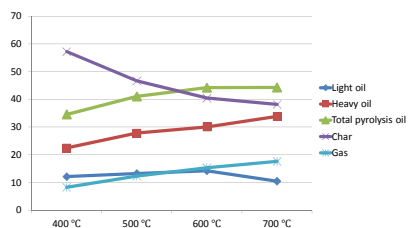


Figure 3. The yields of pyrolysis products for the pyrolysis of kraft lignin at different temperatures.

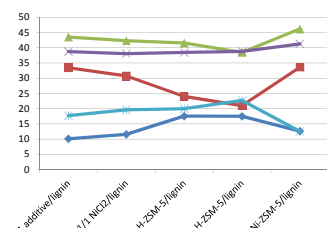


Figure 4. The yields of pyrolysis products for the pyrolysis of kraft lignin with different additives.

In general, the liquid products from pyrolysis contained two immiscible phases, which are referred to as the heavy oil and light oil. The yields of char decreased linearly from 57%-38% with increased reactor temperature. In contrast, the yields of pyrolysis oil increased from 34%-44% with increased pyrolysis temperature. A treatment temperature of 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. In contrast, NiCl₂ and H-ZSM-5 could enhance the secondary decomposition of pyrolysis heavy oil to the light oil or gas.

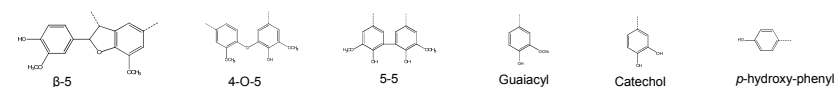
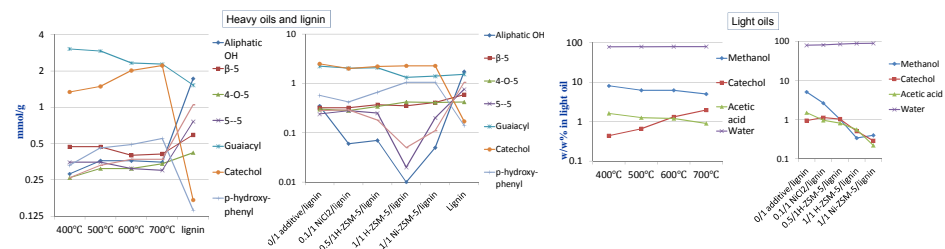


Figure 5. ^{31}P NMR results for heavy oils and lignin (left) and light oils (right).

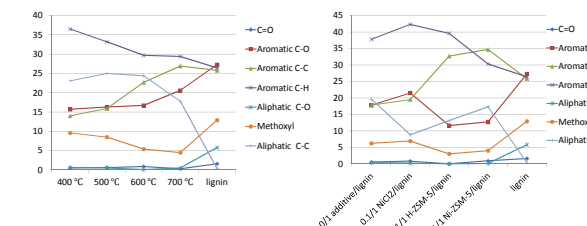


Figure 6. ^{13}C NMR spectra and results for heavy oils and lignin.

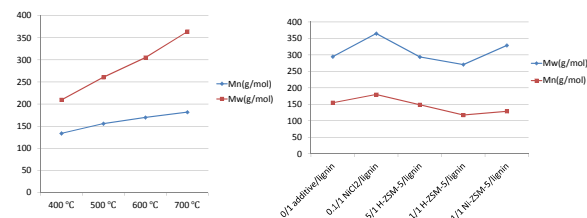
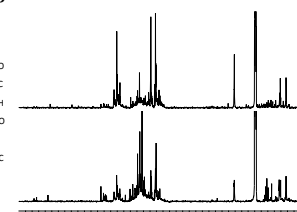


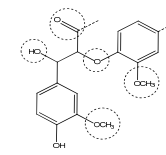
Figure 7. Molecular weight distribution of heavy oils

Conclusions

The ^{31}P NMR results for the light oil showed that it contained nearly 80 w/w% water and another 10 w/w% was methanol, catechol and acetic acid. The large amount of water was attributed to dehydration reactions of lignin during pyrolysis. Further, the results of ^{13}C NMR and GPC indicated that 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. The ^{31}P NMR results for the light oil showed that after the use of zeolite, the concentration of water in light oil increased, which is the evidence for the improved dehydration by the zeolite during the pyrolysis. In contrast, the yields of methanol and acetic acid in the light oil decreased, which indicate that zeolite could improve the decomposition of the aliphatic OH and carboxyl group in the lignin during the pyrolysis. The results of ^{13}C and ^{31}P NMR for the heavy oils indicated that 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. Therefore, it could be concluded that zeolite could improve the decomposition of all the primary decomposed functional groups during the pyrolysis. Further, the results of ^{13}C NMR indicated that after the use of H-ZSM-5 zeolite, there would be less aromatic C-O, less methoxyl, less aliphatic C-O and less carbonyl bond in the heavy oil, which indicate that H-ZSM-5 could also improve the deoxygenation during the pyrolysis of lignin. The results of GPC show that after the use of H-ZSM-5 zeolite the bio-oil would have a lower molecular weight.



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



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.