



Pyrolysis of Kraft Lignin at Different Temperature



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Background

Known petroleum reserves will be consumed in less than 50 years at the present rate of consumption. Wood and other biomass has been recognized as a major world resource for renewable energy and chemicals. As the second most abundant biomass component and the only renewable aromatic resource in nature, lignin, however, has received much less attention than cellulose. Pyrolysis of lignin is one approach that has been investigated to upgrade this material into higher value products—biofuel and aromatic chemical.

Experimental

The pyrolysis of kraft lignin was accomplished in a quartz pyrolysis tube heated with a split-tube furnace in an inert atmosphere at atmospheric pressure. 400 °, 500 °, 600 ° and 700 °C were chosen as reaction temperatures for a series of pyrolysis studies. Gel permeation chromatography (GPC), quantitative ¹³C Nuclear Magnetic Resonance (NMR) and ³¹P NMR were used to characterize the pyrolysis oils.



Figure 1. Pyrolysis system



Figure 2. Products of pyrolysis, char (left), heavy oil (middle) and light oil (right).

Results and Discussions

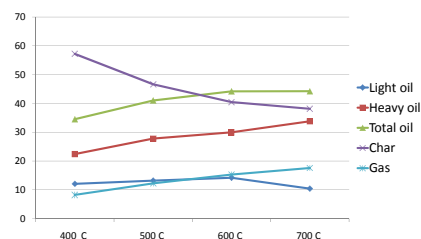


Figure 3. The yields of pyrolysis products

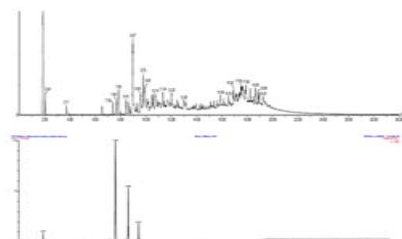


Figure 4. GC-MS results for heavy(top) and light oil(bottom)

In general, the liquid products from pyrolysis contained two immiscible phases, which are referred to as a 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.

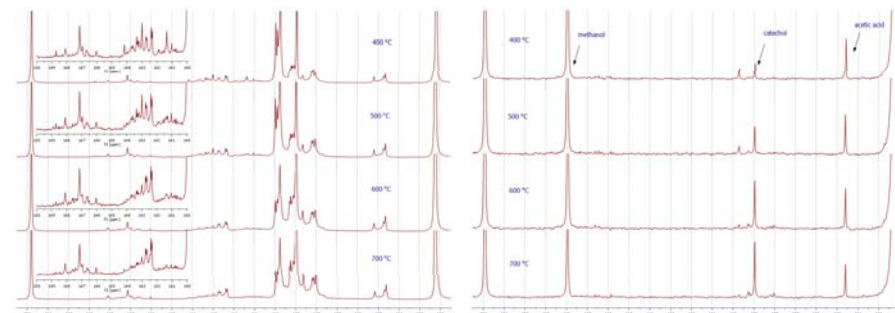


Figure 5. ³¹P NMR spectra for heavy oil (left) and light oil (right).

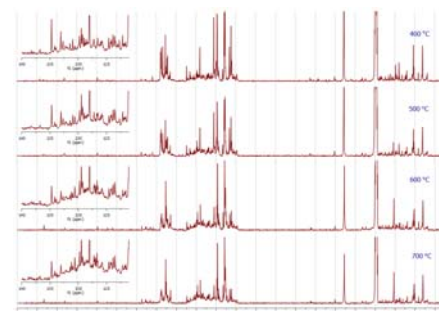


Figure 6. ¹³C NMR spectra for heavy oil .

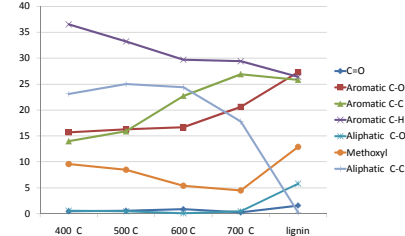


Figure 7. Integration results for SW kraft lignin and different heavy oils, detected by quantitative ¹³C NMR

Conclusions

The large amount of water in the light oil was attributed to lignin dehydration reactions occurring during pyrolysis. Based on the results of ¹³C and ³¹P NMR for the heavy oil, the aliphatic OH, carboxyl and methoxy group in the lignin are the primary functional groups to decompose during the pyrolysis, the cleavage of ether bonds in the lignin is another primary decomposition reaction occurring during the thermal treatment. Furthermore, the results of GPC analysis indicated that lower pyrolysis temperatures yielded a heavy oil with lower weight average molecular weight and lower polydispersity values.

Table 1. Hydroxyl group contents of SW kraft lignin and heavy oils, determined by quantitative ³¹P NMR.

Functional group	Hydroxyl Group Contents (mmol/g)			
	400 °C	500 °C	600 °C	700 °C
Aliphatic OH	0.28	0.36	0.36	0.35
C ₅ substituted	β-5	0.47	0.47	0.40
	4-O-5	0.26	0.31	0.31
Phenolic OH	5-5	0.35	0.35	0.31
	Guaiacyl	3.05	2.93	2.33
Guaiacyl phenolic OH	Catechol	1.34	1.49	2.02
	p-hydroxy-phenyl	0.33	0.46	0.49
Acid-OH	0.26	0.33	0.37	

Table 2. Hydroxyl group contents of light oils, determined by quantitative ³¹P NMR.

Functional group	Hydroxyl Group Contents (mmol/g)			
	400 °C	500 °C	600 °C	700 °C
Aliphatic-OH (methanol)	2.53	1.95	1.95	1.57
C ₅ substituted	β-5	0.00	0.00	0.00
	4-O-5	0.00	0.00	0.00
Phenolic OH	5-5	0.00	0.00	0.00
	Guaiacyl	0.08	0.06	0.09
Guaiacyl phenolic OH	Catechol	0.08	0.12	0.24
	p-hydroxy-phenyl	0.00	0.01	0.04
Acid-OH (acetic acid)	0.27	0.21	0.20	
Water	43.61	44.10	44.36	

Table 3. Molecular weight distribution and polydispersity of heavy oils

	Mn(g/mol)	Mw (g/mol)	D(Mw/Mn)
400 °C	133.75	209.54	1.57
500 °C	155.80	260.64	1.67
600 °C	169.72	304.95	1.80
700 °C	181.65	363.78	2.00

Compared to the starting lignin, the heavy oils contained less aliphatic hydroxyl groups, C₂ substituted condensed phenolics and carboxylic acid groups. In contrast, the content of guaiacyl, p-hydroxy phenolic groups and catechols were increased after pyrolysis. The ¹³C NMR of the heavy oil showed that the carbonyl group and methoxy group content was significantly reduced after pyrolysis, especially at higher reactor temperatures. The number of aromatic C=O and C-C bonds increased in the pyrolysis oil as the operating temperature of the pyrolysis reactor was increased