Pyrolysis of Lignin in a Laboratory Fluidized Bed Reactor

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ABSTRACT

In this paper lignin pyrolysis was performed at temperatures between 400 and 550 °C with analysis of the bio-oil and determination of yields of oil, char and gases. For comparison, woody biomass was also pyrolysed at 450°C. A tubular fluidized bed reactor purged with N₂-gas was used for pyrolysis, while the pyrolysis gases were cooled in several steps to -20º, and the remaining aerosols were removed with a particulate filter. Compared to pyrolysis of biomass, lignin gave a high char yield, around 50%, while the oil yield was much lower, around 25%. The pyrolysis behavior of lignin posed special problems, as lignin is prone to agglomeration which can cause loss of fluidization. The decomposition of lignin was also studied with a thermogravimetric analyser. At 500 °C about 50 % of the lignin remained as char, while 37% remained at 988 °C.

Keywords: Pyrolysis, lignin

1. INTRODUCTION

Lignin is a major constituent of biomass. It is a cross-linked, highly branched three-dimensional polymer with no exact structure. Lignin is synthesized in plants from three
monomeric units, p-coumaryl, coniferyl, and sinapyl alcohol [1]. Fast pyrolysis of biomass for the production bio-oil has attracted ever more interest in recent years, and is covered for example by Mohan et al. in a review article [2]. Several literature review articles on pyrolysis of lignin have also been published during the recent years [3-5].

Fast pyrolysis of lignin has recently been studied in an international collaboration between 14 laboratories in eight different countries. The results showed that pyrolysis of lignin produces a heavy tarry bio-oil in lower quantities than in pyrolysis of lignocellulosic biomass, while the char yield is much higher, around 50%. Lignin was also prone to cause plugging and agglomeration problems [6]. Sharma et al. reported in a study on pyrolysis of lignin that the char yield was 62% at 400°C, and decreased to 40% at 750°C [7]. Lignin has also been found to decompose much slower than other biomass components, over a broader temperature range, mainly around 200-500°C [8]. The degradation products of lignin pyrolysis have been studied by Alén et al. [9].

In this paper we characterize lignin fast pyrolysis at temperatures of 400-550°C. We present a way of successfully pretreating the lignin so that it can be fed with a screw feeder into a reactor, and determine the yields of char, bio-oil and light gas (CO and CO₂). We also analyse the composition of the bio-oil. For comparison, we have also pyrolysed woody biomass with the same laboratory setup.

2. EXPERIMENTAL

2.1 Materials

Lignin and woody biomass was used as raw materials for the pyrolysis experiments. The lignin for the experiments was supplied by SEKAB, Sweden. It had been produced by enzymatic hydrolysis of softwood. The woody biomass used was pine, pinus silvestris, which had been ground into sawdust in a laboratory mill.

2.2 Fluidized bed reactor setup

The reactor setup used in the pyrolysis experiments can be seen in Figures 1 and 2, respectively. It consisted of a lignin feeder, a fluidized bed reactor, a set of coolers and particle filters. The setup has previously been used for catalytic pyrolysis of woody biomass [10].

The lignin feeder was a Schenk AccuRate MOD102M screw feeder. The feeder, along with its connection to the reactor, was hermetically sealed so that no air would leak into the reactor. The fluidized bed reactor was made of Sandvik Sanicro 31 HT alloy. It consisted of a lower part, where the fluidization gas was heated, and an upper fluidization part where the lignin was pyrolysed. The length of the pre-heating and pyrolysis parts where 267 and 102 mm, respectively. The reactor had an inner diameter of 34 mm with a wall thickness of 4 mm. The reactor was inside a Carbolite split tube furnace model VST.
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Figure 1: A schematic of the fluidized bed setup. The pyrolysis reactor consists of a preheating zone (1) and a fluidized bed reactor (2)

2 l/min $N_2$

Feeder

1.3 l/min $N_2$

Gas analysis

Vent

-78°C

Filters

-20°C

12/400, which was controlled by a 3216P1 model controller. The reactor was thus heated from the outside.

The pyrolysis vapours were transported from the reactor through a steel pipe which was heated to 400°C. The steel pipe led the vapours into a series of five coolers made of Pyrex glass. The first cooler was a jacketed one, while the second and fifth coolers were cooled with an internal spiral. In the third and fourth coolers, the pyrolysis vapours travelled through a spiral inside the coolers. All five coolers were filled with ethylene glycol cooled with a Lauda Ecoline RE106 to -20°C. After this set of coolers, the remaining aerosols in the gas stream were captured by two particulate filters, which consisted of layers of cotton wool in glass tubes. Finally, the pyrolysis vapours were led into two coolers made of Pyrex glass and cooled by a mixture of -78°C dry ice and acetone. After this step a side stream of the remaining pyrolysis gases were fed to the CO and CO$_2$ analysers.

The gas flows of nitrogen were controlled by Brooks® 5850S mass flow controllers. The temperature in the pyrolysis reactor was measured by a K-type thermocouple, whose signal was logged on a computer.

Figure 2: A photograph of the reactor setup

2.3 Gas analysis

A side stream of the gases which remained uncondensed after the cooling were analysed by a Ten-3-Gas analyser for CO and CO$_2$. The concentrations in volumetric percentage
(X_i) were recorded by a computer. The molar flows \( \dot{n}_i \) of CO and CO_2 were calculated by solving the equations:

\[
\begin{align*}
X_{CO} & = \frac{\dot{n}_{CO}}{\dot{n}_{CO} + \dot{n}_{CO_2} + \dot{n}_{N_2}} \\
X_{CO_2} & = \frac{\dot{n}_{CO_2}}{\dot{n}_{CO} + \dot{n}_{CO_2} + \dot{n}_{N_2}}
\end{align*}
\]

The total masses of CO and CO_2 were calculated by integrating the area below the mass flow curves, which had been calculated by multiplying the molar flows with the molar weights of CO and CO_2. The yield was calculated by dividing the mass of the gases with the amount of original dry mass of the lignin or biomass used in the experiment.

2.4 Bio-oil analysis

The water content of the bio-oil was analysed by means of Karl Fischer titration. 10 mg of the bio-oil was titrated in methanol. It was assumed that all water condensed in the first cooler.

The bio-oil was also analysed by gas chromatography and the compounds were determined by mass spectra (GC-MS). The analysis procedure has been described before by Aho et al. [11]. Prior to analysis, the bio-oil was diluted in methanol. The column used in the GC-MS was an Agilent DB-Petro 50 m column, with an inner diameter of 0.2 mm and a film thickness of 0.5 \( \mu \)m. The heating of the column began with an isothermal period at 40°C for 10 minutes. The temperature was then raised to 200°C with four different successive heating rates, 0.90°C/min between 40°C and 75°C, 1.10°C/min between 75°C and 120°C, and finally 10°C/min between 120°C and 200°C. At the final temperature, 200°C, there was an isothermal period for 20 minutes. The inlet pressure of the column was 135 kPa and the scanning range was 10-300 amu. The applied solvent delay time was 6 min.

2.5 Experimental procedure

Thermogravimetric analysis was performed on the lignin sample. The lignin, and the woody biomass sample, was also pyrolysed in the fluidized bed. In the case of thermogravimetric analysis, the untreated lignin was heated from 30°C to 988°C, with a 20°C/min heating rate in a flow of 100 ml/min nitrogen. At 100°C, the sample was dried for 15 minutes.

In the case of pyrolysis in the fluidized bed, the untreated lignin in the form of a powder was not suited for feeding into the reactor. Initial experimental runs indicated that untreated lignin, which was in the form a fine powder, tended to plug the feeding screw and cause damage to the feeder, especially since the lignin might partially pyrolyse in the screw. The lignin was therefore pretreated by suspending it in water and then drying it at 105°C for 24 hours. This caused the dust particles to agglomerate and form larger
particles. The lignin was then screened, and a size fraction of 355-500 µm was used for the experiments. The same fraction, 355-500 µm, was also used for the biomass sample, which was in the form of sawdust.

The pyrolysis was carried out in the fluidized bed reactor. The fluidized bed consisted of 40 g of quartz sand, screened to a fraction of 100-150 µm. About 15 g of lignin or biomass was fed. Fluidization was obtained by feeding 1.3 l/min of nitrogen through the bottom of the reactor. A nitrogen flow of 2 l/min was also fed through the feeder to ensure easier feeding. The pyrolysis gases were condensed and captured in the first set of coolers, in the particulate filters and in the last set of coolers. A side stream of noncondensable gases was fed to the CO and CO₂ analysers. Pyrolysis experiments were conducted at 400, 450, 500 and 550°C.

When all biomass had been fed to the reactor and the concentrations of CO and CO₂ diminished to zero the heating was turned off. After the experiment the amounts of char and bio-oil were gravimetrically determined. All the char remained in the bed, while the bio-oil remained on the surfaces of the coolers and in the filters.

3. RESULTS & DISCUSSION

Thermogravimetric analysis illustrated that decomposition starts at about 200°C. At 500°C, about 50% of the lignin remained as char and at 988°C 37% of it remained as char. The thermogravimetric curve from 150-980°C can be seen in Figure 3. The mass release rate is highest around 360°C.

![Figure 3: Thermogravimetric weight percentage and mass release rate curves (dX/dT) for the untreated lignin, at a heating rate of 20°C/min.](image)

The yields of char, oil and gas from the experiments in the fluidized bed reactor are shown in Figure 5. At 400 and 450°C the char yield was high, about 50%, and the oil yield low – about 25% – compared to pyrolysis of woody biomass at the same
temperature. The CO and CO$_2$ yields were comparable for both materials. Similar results were observed for lignin at 500°C. At 550°C, the char yield was lower while gas yield was very high. The large gas yield was could be expected since the lignin had agglomerated and formed larger structures which blocked the flow of the fluidization gas. This caused the CO and CO$_2$ flows to seem larger than they actually were, as the flow of nitrogen was actually lower than the value used in the calculations. The agglomeration of char at 550°C is visualized in Figure 4. The CO and CO$_2$ yields as well as the CO/CO$_2$ ratio can be seen in Figure 6. The CO/CO$_2$ ratio rose as the temperature rose.

The mass balance closure was 88-95% for the experiments at 450°C and 500°C. Only insignificant amounts of condensed vapours were captured in the last coolers, which were cooled by -78°C dry ice in acetone. The combination of cooling to -20°C and particulate filters was sufficient to achieve a high mass balance closure. At 550°C, the mass balance closure exceeded 100% due to the incorrect values for CO and CO$_2$.

Figure 4. Agglomeration of char after pyrolysis at 550°C.

Figure 5: The yields of different phases as weight percentage of original dry mass for pyrolysis of woody biomass and hydrolysis lignin.
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SEM-images of the untreated lignin and char from pyrolysis at 450°C can be seen in Figure 8. In Figure 9, the untreated and pyrolysed samples can be seen in magnification. The pyrolysed char sample is significantly sintered compared to the original, untreated lignin.

Figure 6: Yields of CO and CO₂ as weight percentage of original dry mass, and CO/CO₂ ratios for pyrolysis of woody biomass and hydrolysis lignin.

SEM-images of the untreated lignin and char from pyrolysis at 450°C can be seen in Figure 8. In Figure 9, the untreated and pyrolysed samples can be seen in magnification. The pyrolysed char sample is significantly sintered compared to the original, untreated lignin.

Figure 8: A) untreated lignin, B) char from pyrolysis at 450°C. The smaller pieces in the image are sand while the larger are lignin char.
The compounds identified by GC-MS can be seen in Figure 10. All identified compounds are aromatic and most are phenolic, having methoxy side chains.

![Diagram of compounds](image)

**Figure 9:** SEM-images at 5000x magnification. A) untreated lignin, B) char from pyrolysis at 450°C.
Pyrolysis of lignin produced a high amount of char compared to pyrolysis of woody biomass, around 50% of the original fuel, and lower quantities of bio-oil, about 25%. The yield of gas was comparable to that of woody biomass. The char yield was slightly lower at higher temperatures. A number of aromatic compounds which were mostly phenolic could be identified with GC-MS in the bio-oil.

The mass balance coverage of the laboratory setup was around 90-95%. The combination of five spiral coolers cooled by -20°C glycol and two particulate filters could capture most condensable material in the pyrolysis vapours. Further cooling by a -78°C mixture of dry ice and acetone only condensed insignificant amounts of pyrolysis vapours and did not improve the mass balance closure.
Lignin tended to agglomerate and form larger structures during pyrolysis, especially at higher temperatures (550°C). This caused problems in fluidization and resulted in plugging in the reactor. Plugging in the feeding unit was avoided by pretreating the lignin and feeding a size fraction of 355-500 µm instead of the untreated lignin which was in the form of a fine dust.

5. REFERENCES


6. ACKNOWLEDGEMENTS

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