CONVENTIONAL PYROLYSIS OF SPRUCE WOOD AND HAZELNUT SHELL DELIVERING OILY PRODUCTS

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Abstract: The effects of initial moisture composition used in conventional pyrolysis of spruce wood, hazelnut shell and wheat straw on the yields of total oily products were studied. The yields of total oily products of spruce wood (moisture content: 6.5%), hazelnut shell (moisture content: 6.0%) and wheat straw (moisture content: 6.2%) increase from 8.4, 6.7 and 27.4%, respectively, while increasing pyrolysis temperature from 575 to 700 K. The yields of total oily products from hazelnut shell (moisture content: 30.7%) increase from 14.6 to 35.9% with increasing pyrolysis temperature from 600 to 693K while the yields of total oily products from hazelnut shell (moisture content: 0%) increase from 10.8 to 23.8% with increasing pyrolysis temperature from 600 to 703K in nitrogen medium. The results indicated that the presence of moisture influenced significantly the thermal degradation degrees of the biomass samples during pyrolysis.

Keywords: pyrolysis, oily, shell.

1. INTRODUCTION

The thermo-chemical conversion of biomass (pyrolysis, gasification, combustion) is one of the most promising non-nuclear forms of future energy. It is a renewable source of energy and has many advantages from an ecological point of view. The pyrolysis is degradation of biomass by heat in the absence of oxygen which results in the production of charcoal, liquid and gaseous products. Pyrolysis can be used as an independent process for the production of useful fuels and/or chemicals.

Depending on the operating conditions, the pyrolysis process can be divided into three subclasses: conventional pyrolysis (carbonization), fast pyrolysis and flash pyrolysis.

Table 1-The range of main operating parameters for pyrolysis processes [1]

<table>
<thead>
<tr>
<th></th>
<th>Conventional pyrolysis</th>
<th>Fast pyrolysis</th>
<th>Flash pyrolysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrolysis temperature (K)</td>
<td>550-950</td>
<td>850-1250</td>
<td>1050-1300</td>
</tr>
<tr>
<td>Heating rate (K/s)</td>
<td>0.1-1</td>
<td>10-200</td>
<td>&gt;1000</td>
</tr>
<tr>
<td>Particle size (mm)</td>
<td>5-50</td>
<td>&lt;1</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>Heating time (s)</td>
<td>450-550</td>
<td>0.5-10</td>
<td>&lt;0.5</td>
</tr>
</tbody>
</table>

High yields of liquefied products can be obtained under optimized conditions: very high sample heating and heat transfer rate that requires a finely ground wood type biomass feed, carefully controlled pyrolysis temperature of around 750K and rapid cooling of pyrolysis vapours to give the oily product.

At present, the preferred technology for production of oily products is fast or flash pyrolysis at high temperatures with very short residence times. The aim of this work was the effects of initial moisture contents on the yields of oily products from conventional pyrolysis (slow heating rates, low to intermediate temperatures and long residence times) of spruce wood, hazelnut shell and wheat straw.

Table 2-Chemical compositions of wet biomass samples[2]

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>O</th>
<th>Ash</th>
<th>Cl</th>
<th>Moisture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spruce wood</td>
<td>20.3</td>
<td>2.4</td>
<td>0.1</td>
<td>16.5</td>
<td>0.04</td>
<td>0.11</td>
<td>60.5</td>
</tr>
<tr>
<td>Hazelnut shell</td>
<td>34.8</td>
<td>3.9</td>
<td>0.7</td>
<td>28.3</td>
<td>1.42</td>
<td>0.12</td>
<td>30.7</td>
</tr>
<tr>
<td>Wheat straw</td>
<td>27.5</td>
<td>3.5</td>
<td>0.4</td>
<td>22.8</td>
<td>9.96</td>
<td>0.98</td>
<td>34.7</td>
</tr>
</tbody>
</table>

2. EXPERIMENTAL

The biomass samples (spruce wood, hazelnut shell and wheat straw) were ground and then sieved a size range of 0.180 and 0.250mm sieve. The heating was carried out from 298 to 825 K. The experimental runs were carried out with dried samples (0% moisture), air dried samples, wet samples and in nitrogen medium.

In order to assess the thermal behaviour of the samples, moisture losses and reaction water yields were determined in pyrolysis runs. The oil yields from pyrolysis processes were determined for each sample with different moisture content.

The pyrolysis experiments were carried out in a stainless steel tube with height 95.1 mm, i.d. 17.0mm and o.d. 19.0 mm. Its total volume was about 21.6 ml. The ground sample was weight for a run 1.00 g and pyrolyzed in the tube. Heat to tube was supplied from external electrical heater and the power was adjusted to give an appropriate heat up time. The simple thermocouple (NiCr—constantan) was placed directly in the pyrolysis medium. For each run, the heater was started at 298K and terminated when the desired temperature. The pyrolysis products were collected within three different groups as condensables as oily products with two phases (aqueous
phase and tarry materials phase), non-condensable gaseous products and solid residue (charcoal)[4-7]. The oily products were separated into two fractions using benzene by simple liquid–liquid extraction in a separator funnel. The benzene soluble from oily products were called as total water-insoluble or tarry materials.

3. RESULTS AND DISCUSSION

Pyrolysis of biomass is complex functions of the experimental conditions, under which the pyrolysis process proceeds. The most important factors, which affect the yield and composition of the volatile fraction liberated, are: biomass species, chemical and structural composition of biomass, particle size, temperature (i.e. temperature-time history), heating conventional pyrolysis rate, atmosphere, pressure and reactor configuration.[1-3]

Total water produced from pyrolysis (TWPP) was calculated as follow:

\[
\text{TWPP} = \text{moisture content} - \text{water from dehydration and pyrolysis reactions (1)}
\]

Figs. 2-3 show the curves for the TWPPs versus temperature for the biomass samples with the runs of 0.2, 0.5, 1.0 and 5.0 K/s heating rate. The rate of TWPP was the lowest in a 0.2 K/s heating run.

The correlation equations for the TWPP versus the temperature of pyrolysis \((T)\) and related correlation coefficients \((r)\) from Figs. 2–3 are:

For spruce wood:
\[
\text{TWPP} = 0.1481T - 59171, \ r = 0.9112 \quad (2)
\]

For hazelnut shell:
\[
\text{TWPP} = 0.0650T - 27.063, \ r = 0.9582 \quad (3)
\]
As can be seen from Eq. (2)–(3) [4-7], there is highly correlation between the TWPP and the temperature of pyrolysis (7) for all runs. Figs. 4–7 show the curves for total water produced from pyrolysis (TWPP) versus pyrolysis temperature for the biomass samples with different moisture contents. The presence of moisture in biomass influences its behaviour during pyrolysis and affects the physical properties and quality of the pyrolysis liquid: qualitative observations show that dry feed material led to the production of very viscous oil, particularly at higher reaction temperatures. The range of temperatures covered 575–825K and the range of feed moisture contents from bone dry to 11.5, 10.5 and 12.0% wet basis for the samples of spruce, hazelnut shell and wheat straw, respectively. The heating rate was 5 K/s. The results obtained show that for higher feed moisture contents the maximum liquid yield on a dry feed basis occurs at the range of 690–700K temperatures. The water yield decreases with increasing pyrolysis temperature and that higher feed moisture content slightly increases reaction water. Figs. 8–10 show the plots for total oil (aqueous phase + tarry materials phase) yields of pyrolyses versus pyrolysis temperature for the biomass samples with different moisture contents. The yields of gaseous products increase with increasing pyrolysis temperature for all runs. In general, the yields of oily products increase with increasing pyrolysis temperature.
4. CONCLUSION

In this work, the effects of initial moisture contents on the yields of oily products from conventional pyrolysis (slow heating rates, low to intermediate temperatures and long residence times) of spruce wood, hazelnut shell and wheat straw have been investigated. The liquid fraction of the pyrolysis products consists of two phases: an aqueous phase containing a wide variety of organo-oxygen compounds of low molecular weight and a non-aqueous phase containing water-insoluble organics (mainly aromatics) of high molecular weight. This phase is called as tarry materials or tar and is the product of greatest interest. The ratios of acetic acid, methanol, and acetone of aqueous phase were higher than those of non-aqueous phase.

If the purpose is to maximize the yield of liquid products resulting from biomass pyrolysis, a low temperature, high heating rate, short gas residence time process would be required. For a high char production, a low temperature, low heating rate process would be chosen. If the purpose were to maximize the yield of fuel gas resulting from pyrolysis, a high temperature, low heating rate, long gas residence time process would be preferred. In general, the yields of oily products increase with increasing pyrolysis temperature from 575 to 700K then it decreases with increasing the temperature. The yield of total oil increases with increasing the initial moisture content of the sample.

Qualitative observations show that dry feed material led to the production of very viscous oil, particularly at higher reaction temperatures. The highest liquid yield from spruce wood pyrolysis, 39.7% dry feed basis, was found for initial moisture content 60.5% and reactor temperature 689 K, condition that also gave the lowest viscosity.

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