Effect of Operation Conditions on Pyrolysis of Larch Sawdust in a Bubbling Fluidized Bed

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Abstract
In this study, a bubbling fluidized bed pyrolyzer (0.076 m I.D. and 0.8 m high) was employed to investigate the fast pyrolysis characteristics of larch sawdust which is abundant in Korea. The effects of operation conditions, such as bed temperature (350-550 °C), fluidization velocity ratio (Uo/Umf : 2.0-6.0), and feeding rate (2.2-7.0 g/min) on product yields and their chemical components were studied. The number of chemical compounds in the bio-oil decreased with the increasing bed temperature because of secondary pyrolysis. The effects of the Uo/Umf ratio and feeding rate on bio-oil compositions were relatively lower than those of the bed temperature.

Keywords: pyrolysis, bubbling fluidized bed, larch sawdust, bio oil

1. Introduction
Globally, the demand for renewable and sustainable energy sources has increased due to energy and environmental issues. Biomass is considered to be a promising resource to convert into sustainable energy. Thermochemical conversion methods, such as combustion and gasification, have been widely developed as ways to produce power, heat and other types of energy. Irrespective of the route, the inherent first step toward the thermochemical treatment of biomass is pyrolysis. Therefore, the pyrolysis step should be investigated, to obtain a solid understanding of combustion and gasification[1-3].

Also, many researchers have been focusing on pyrolysis, due to its higher yield of liquid phase, to generate energy and valuable chemicals from various biomass resources. Fast pyrolysis is a high temperature process in which the feedstock is rapidly heated, in the absence of air, and be carefully controlled to get high yields of liquid. There are three essential features of the fast pyrolysis process, which include a higher heat transfer rate, precise temperature control, and the rapid cooling of the pyrolysis product. In particular, a fluidized bed process can promote heat transfer from a heat source to raw materials through vivid mixing. Therefore, previous researches have been focused on fast pyrolysis using fluidized bed processes[4-7].

Biomass is a mixture of cellulose, hemicellulose, lignin and minor amounts of other organics which may decompose at different rates, and by different mechanisms or pathways. Various natural and derived materials, such as woody and herbaceous plant species (including grass), wood wastes, bagasse, agricultural and industrial residues, waste paper, municipal solid waste, sawdust, biosolid, and so forth, are typically included in biomass resources. Biomass is easily converted into gases, vapors, tar components and a carbon rich solid residue by pyrolysis.
In fluidized bed pyrolyzers, bed temperature and gas velocity might be the most important operation factor in determining yields and compositions, and so most studies have dealt with the effect of bed temperature and gas velocity on pyrolysis yields. Though operation conditions (including bed temperature, gas velocity, feeding rate, bed height, \( \frac{U_o}{U_{mf}} \) (\( U_o \) : operation gas velocity, \( U_{mf} \) : minimum fluidized bed velocity) should affect the yields and compositions, the available studies on the effects of feeding rate, \( \frac{U_o}{U_{mf}} \) and other conditions on compositions in bio oil are not enough. Therefore the effect of temperature, feed rate, bed height, and the \( \frac{U_o}{U_{mf}} \) ratio on the compositions in bio-oil from pyrolysis was investigated using a gas chromatography-mass selective detector (GC-MSD) in a bubbling fluidized bed reactor in this study.

2. Experimental

2.1. Larch sawdust

The sawdust used in this work was larch, which is an abundant tree species in Korea and is used often in reforestation. Proximate and elemental analyses (LECO Corp) were carried out, the details of which were shown in the previous study[7]. In general, compared to other raw materials, the oxygen content of larch sawdust is high, while the carbon content is relatively low. Sawdust samples were dried at 110~120 °C for about 48 h, and then divided into 0.25~1 mm size samples for pyrolysis. The final moisture content of sawdust sample was below 1 wt%.

2.2. Bubbling fluidized bed reactor

All pyrolysis tests were done in a lab-scale bubbling fluidized bed process, and nitrogen was used as the fluidizing gas. A detailed scheme of the bubbling fluidized bed pyrolyzer (I.D. 0.076 m and 0.8 m high) was shown in previous researches[5,7]. The fluidized bed apparatus consisted of MFC (MGF-Series, Rich Field), a gas pre-heater, a fluidized bed reactor, a screw feeder, a quencher and an electrostatic precipitator. The fluidizing gas was preheated in the heater before entering the bottom of the reactor; the distributor (for uniform gas distribution) was a sintered metal plate. The sawdust entered the top of the fluidized bed by way of the screw feeder; the feeding rate of the sawdust was regulated by a DC motor controller. A thermocouple was located beside reactor to measure the bed temperature. The fluid bed material was silicon carbide, of the Geldart B type. The connecting pipe between the reactor and the quencher was heated to 400 °C to avoid the condensation of tar vapor. To capture the bio-oil mist, an electrostatic precipitator and quencher was equipped at the exit of the fluidized reactor. The refrigerants used in the cooling process in the quencher were ice-water and ethylene glycol, which were circulated by a master flux pump and chiller. After the quenchers, the gases (which were metered by a flow meter) passed through the electrostatic precipitator, which effectively trapped any remaining oil mist. 2 KW Electric heaters were installed at the bubbling fluidized bed to raise the reactor temperature.

All system components were weighed separately, before and after each run. After weighing and collecting the product, the collection system was washed out with acetone. The experiments were carried out to determine the effects of product yield and composition in the variable processes, and can be expected to gain valuable chemical stocks (for instance, pyrolyngene acid)[8].

In the past, sawdust has been recycled into low value products, as the bulking agent of organic material composting and the raw material of a veneer board. Because the particle size of sawdust is generally fine, sawdust is well suited for fast pyrolysis, with very high heat transfer condition. Korea’s geography and climactic conditions support agriculture and forestry, which means there is a rich source of biomass available. Of the tree species in Korea, the larch- which is a conifer-accounts for approximately 79%, which means that the raw material for sawdust comes predominantly from conifer tree[9].

Table 1. Operation Conditions in the Bubbling Fluidized Bed Pyrolyzer

| Operation conditions | Range         |
|----------------------|---------------|
| Temperature (°C)     | 350~550       |
| Bed particle size (μm) | 40~128       |
| feeding rate (g/min) | 2.2~7.0       |
| L/D ratio            | 1.0~3.0       |
| \( \frac{U_o}{U_{mf}} \) | 2.0~6.0      |

Table 2. Qualitatively Determined Bio Oil Products[5]

| No. | RT (min) | compounds                                      |
|-----|----------|-----------------------------------------------|
| 1   | 2.63     | acetyl                                        |
| 2   | 2.79     | propionic acid                                 |
| 3   | 6.19     | furfural                                       |
| 4   | 7.62     | 2,5-Dimethoxytetrahydrofuran                   |
| 5   | 8.50     | 2,5H-furanone                                  |
| 6   | 9.60     | 5-methylfurfural                               |
| 7   | 9.94     | phenol                                         |
| 8   | 10.87    | corylone                                       |
| 9   | 11.34    | o-cresol                                       |
| 10  | 11.71    | m- or p-cresol                                 |
| 11  | 11.97    | guaiacol                                       |
| 12  | 12.94    | 3,5-dimethylphenol                             |
| 13  | 13.56    | naphtalene                                     |
| 14  | 13.70    | pyrocatechol                                   |
| 15  | 13.94    | 1,4,3,6-Dianhydro-d-glucopyranose              |
| 16  | 14.17    | 5-(hydroxymethyl)-furfural                     |
| 17  | 14.70    | 3-methoxyacetal                                |
| 18  | 14.80    | hydroquinone                                   |
| 19  | 14.95    | 4-ethyl-2-methoxyphenol                        |
| 20  | 15.04    | 4-methylfurfural                               |
| 21  | 15.70    | 2-methylfurydroquinone                         |
| 22  | 15.95    | syringol                                       |
| 23  | 16.32    | 4-ethylresorcin                                |
| 24  | 17.20    | vanillic acid                                  |
| 25  | 17.24    | isoeugenol                                     |
| 26  | 17.82    | levoglucosan                                   |
| 27  | 18.20    | 2,3,5-trimethoxytoluene                        |
| 28  | 19.10    | methoxyeugenol                                 |
| 29  | 19.77    | syringe aldehyde                               |
| 30  | 20.58    | acetylone                                       |
process parameters. The process parameters in this study are: temperature, feeding rate, and Uo/Umf. The process parameter is shown in Table 1. The minimum fluidized bed velocity of bed material was 1.65 cm/s and residence time of this study was between 0.7 and 2.3 sec.

The analysis procedure and methods were written in previous studies and components of the bio-oil could be determined by GC-MS analysis [5,7]. The pyrolysis oils were dissolved in methanol, since they are soluble in methanol, and the solutions obtained were analyzed by mass-selective detection. The system (HP 5973) was controlled by a ChemStation computer (HP KAYAK XA). The interpretation of the mass spectra obtained by gas chromatography-mass spectrometry (GC-MS) was based on automatic library search (Wiley 275) and on literature data and was shown in Table 2 [5].

3. Results and Discussion

3.1. Influence of pyrolysis temperature

Bed temperature in fluidized bed pyrolyzers has been known to be an important parameter in the conversion of biomass into bio-oil, char and gas. Generally the yield of bio-oil and char had a maximum value and decreased as bed temperature increased, but the gas yield increased with bed temperature because the excess supply of heat from the increasing bed temperature might convert liquid fraction from biomass pyrolysis into gas components of a low molecular weight [5,10-13]. In Figure 1, the chemical compounds in bio-oil, with bed temperature, are shown. As can be seen, the number of chemical compounds decreased with the increasing bed temperature. Phenol compounds increased with the increasing bed temperature, but guaiacol and syringol compounds decreased due to thermal degradation. In previous study, the detectable compounds of the bio oil were acetic acid, ketones, derivatives of furan, phenolics, esters, fatty acids and compounds with high molecular weights including syringol and guaiacol, which were generated by 1st degradation and were converted into compounds with low molecular weights by 2nd degradation [3,5,7].

3.2. Influence of fluidized bed velocity

Fluidizing gas velocity can affect residence time and mixing efficiency in various fluidized bed reactors. To investigate the effects of the Uo/Umf ratios on the products’ yield, as well as the compositions of the bio oil, experiments were performed at various Uo/Umf ratios from 2.0 to 6.0 and these results are shown in Figure 2. It was observed that bio-oil yields increased from 55 to 58 wt% as the Uo/Umf ratios were raised from 2.0 to 4.0 and decreased a little at the much higher Uo/Umf ratios, similar to previous results [5]. In this study, the optimum Uo/Umf ratio was 4.0 and the maximum yield of oil products was 58 wt%. As the efficiency of the physical mixing of sawdust and bed material increased with an increasing gas velocity, the heat transfer between the hot bed material and the sawdust might be promoted in bubbling fluidized bed reactors. Lee et al. said the thermal cracking
and the yield of gas had increased due to an increasing heat transfer between the biomass and the fluidized bed materials; the yield of organic compounds decreased over an optimum $U_o/U_{mf}$ condition, due to the excess fluidizing gas and poor mixing effect[5].

Also, the residence time of the gas-phase products and their chance of radical forming reactions reduced as the volumetric rate of fluidizing gas increased. When the $U_o/U_{mf}$ ratio was larger than 4.0, the excess gas for fluidization was not good for pyrolysis because of the rapid heat loss. Therefore, the yield of char increased and the yields of bio-oil and gas phase decreased with the increasing gas velocities. Even if the changes in the product yield were very small, since the properties of the product oil were so different. At the $U_o/U_{mf}$ ratio of 2.0, the yield of high viscosity oil (like tar) decreased and the yield of low viscosity oil (like water) increased respectively.

The total ion chromatograms of bio-oil from the rapid pyrolysis with gas velocities were shown in Figure 3. As can be seen in Figure 2, it was observed that the chemicals in bio-oil increased as the $U_o/U_{mf}$ ratio was raised from 2.0 to 6.0. The increase of gas velocity promoted a vigorous mixing, improvement of heat transfer and a decrease in retention time in fluidized bed[5,7]. The efficiency of the heat transfer decreased, and the retention time was getting longer under the optimum range of gas velocity, so it was decided that some compounds (like quaiacol and syringol) were converted into low molecular weight compounds. However, high molecular weight compounds were collected beyond the optimum gas velocity. Heo et al. said higher fluidizing gas flow minimizes the possibility of the secondary reactions, such as thermal cracking, re-polymerization, and re-condensation[1].

### 3.3. Influence of feeding rate

In the pyrolysis process, the external heat capacity must be supplied in order to maintain a regular temperature that equals the heat absorption capacity of the raw materials. Therefore, decision of the optimum feeding rate is very important to obtain the maximum bio-oil yield in a bubbling fluidized bed pyrolyzer. The effect of the feeding rate on bio-oil production was shown in Figure 4 and total ion chromatograms of sawdust pyrolysis with feeding rates from 2.2 g/min to 7.0 g/min were shown in Figure 5; the mean bed particle size was 40 m, the L/D (L: Bed height of fluidized bed, D: Bed diameter) ratio was 2.0, the reaction temperature was 400 °C and the $U_o/U_{mf}$ ratio was 4.0. As can be seen, bio-oil yield decreased and gas yield increased with increasing feeding rate at these conditions.

Heo et al.[1] said that a higher feeding rate can efficiently prevent pyrolysis vapors from being converted into gas via secondary cracking in the dense bed, resulting in an increased bio-oil yield when the temperature of the dense bed is higher than that of freeboard. However, pyrolysis temperature in the bubbling fluidized bed pyrolyzer was lower than that of Heo et al.[1], secondary cracking in the dense bed might increase with increasing feeding rates and resulted in an increase of gas yield. Also, the feeding type of this study was top feeding and the supply quantity of raw material was larger than the solid-solid mixing, the heat transfer between the raw materials and the fluidizing bed materials reduced, resulting in slow pyrolysis by degrees which accelerated secondary degradation and the increasing of gas product.
4. Conclusions

The fast pyrolysis of sawdust was conducted in a lab-scale bubbling fluidized bed pyrolyzer, and the influence of the reaction conditions on the chemical characteristics of the obtained bio-oils was investigated over a range of variables as follows: a bed temperature of 350-550 °C, a $U_o/U_{mf}$ ratio of 2.0-6.0, and a feeding rate of 2.2-7.0 g/min. The bio-oil yield increased up to a $U_o/U_{mf}$ ratio of 4.0 and decreased over the optimum point. The maximum yield of bio-oil was obtained at the condition ($U_o/U_{mf}$ ratio : 4.0 and feeding rate: 2.2 g/min). The number of chemical compounds in bio-oils decreased with increasing bed temperature. Syringol, guaiacol, and various phenol compounds were detected in bio-oil, and the chemical compounds in bio-oil were affected by operation conditions such as bed temperature, gas velocity, and feeding rates.

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