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Original article

유동층 반응기를 이용한 Medium-Density Fiberboard의 급속 열분해

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Fast pyrolysis of Medium-Density Fiberboard Using a Fluidized Bed Reactor

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Medium-density fiberboard의 최적 열분해 조건을 찾기 위해 유동층 반응기를 이용하여 다양한 실험조건에서 급속열분해 실험을 수행하였다. 열분해 온도를 425 ℃와 575 ℃ 사이에서 변화시켰을 때, 525 ℃에서 최대 바이오오일 수율 52 wt%를 얻을 수 있었다. 열분해 온도가 높을수록 생성되는 바이오오일의 품질이 좋은 것으로 나타났다. 높은 온도에서 열분해 반응을 수행할 경우, 상당한 양의 oxygenates 및 acids 물질들이 분해되고, 대신 aromatics와 phenolics 같은 고부가가치 물질들이 생성되었다. 기체상 생성물의 대부분은 CO와 CO_2였다. 열분해 온도가 높을수록 CO와 C_1-C_4 탄화수소 생성량이 많았다.

Fast pyrolysis of medium-density fiberboard was carried out using a fluidized-bed reactor under various conditions to find an optimum pyrolysis condition. When the pyrolysis temperature was varied between 425 ℃ and 575 ℃, the maximum bio-oil yield of 52 wt% was obtained at 525 ℃. The quality of the bio-oil product increased with increasing pyrolysis temperature. Pyrolysis at a high temperature removed significant amounts of oxygenates and acids, producing more valuable species such as aromatics and phenolics. The main gaseous products were CO and CO_2. The yields of CO and C_1-C_4 hydrocarbons increased with increasing the pyrolysis temperature.

Keywords: *fast pyrolysis, medium-density fiberboard, fluidized-bed reactor, pyrolysis temperature, bio-oil*

1. Introduction

Fossil fuels are the energy source used most widely in modernized countries. Its limited reserves and uneven distribution are expected to bring about another energy crisis in the near future. In this regard, efforts are being made over the world to find alternative energy resources that can replace fossil fuels. Air pollution and global warming caused by the combustion of fossil fuels are another problems that stimulate the development of cleaner and renewable energy production technologies.

Biomass is a generic term referring to materials derived from living organisms, such as plant, plant-derived materials, dead animals, organic waste, etc. Biomass is regarded as a renewable energy resource because it is carbon-neutral; the carbon that it contains stems from the photosynthesis of plants (assimilation of carbon dioxide in air). Among other renewable energy resources, biomass has received particularly significant attention because it can be used not only for producing energy but also for producing solid, liquid and gaseous fuels[1-13]. In addition, biomass can be used even for producing chemical feedstock materials for the petrochemical industry, which cannot be achieved from any other renewable energy sources. One of the most widely used methods for converting biomass to fuels or chemical feedstock materials is pyrolysis[8-13].

Municipal waste often contains various woody biomass materials. Recycling of woody biomass is difficult in terms of sorting, collection, transport and storage in South Korea. Most recycling practice of woody biomass in Korea is using physical processing, which can be applied only to limited situations. Pyrolysis of woody biomass can be a way for promoting the recycling of woody biomass.

Fast pyrolysis using a fluidized-bed reactor is known to be the best way for obtaining high bio-oil yield from biomass [14]. The fluidized-bed reactor is easy to build, operate, separate char after reaction, and scale

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Table 1. Results of Proximate and Ultimate Analyses

Proximate analysis (wt%)		Ultimate analysis (wt%)	
Moisture	2.1	C	53.9
Volatile matter	77.9	H	4.4
Fixed carbon	17.2	O	39.8
Ash	2.8	N	1.9
		S	-

up. Uniform temperature in the reactor is another important merit of the fluidized-bed reactor.

Various woody biomass materials have been used for pyrolysis. Medium-density fiberboard (MDF), one of the most frequently found woody waste materials in Korea, has also been applied to the pyrolysis experiments[15,16]. However, batch reactors or pyrolyzers were used for those experiments; the fluidized-bed reactor has never been employed for the pyrolysis of MDF.

In this study, the fast pyrolysis of MDF was carried out using a fluidized-bed reactor. Experiments were conducted under various conditions to find an optimum pyrolysis condition. The effects of the pyrolysis conditions on the composition of product bio-oil were also investigated.

2. Experimental

2.1. Preparation of Biomass Samples

MDF was pulverized and sieved into uniform size of 0.6～1 mm before being used for the experiments. The composition of all MDF particles was assumed to be identical. The particle samples were dried for 24 h in an oven maintained at 110 ℃ before experiment to minimize the moisture content in the product oil.

Proximate and ultimate analyses were performed for MDF in our previous study[15]. The results are briefly summarized in Table 1. The ash content was shown to be higher than that of typical woody biomass.

2.2. Pyrolysis Experiment

The experimental system, including a lab-scale fluidized-bed reactor, used in the study of Kim[14] was used in the present study. One can refer to Kim[14] for the detailed description of the system. 1.5 kg of white alumina particles (NANKO ABEASIVES, Japan) with an average size of 250 mm was used as the fluid sand. The MDF sample is fed from a silo into the reactor. High-temperature nitrogen gas flow was used to fluidize the fluid sand.

The product vapor is condensed into oil when it passes through two condensers connected in series. The liquid droplets that are not collected in the condensers are deposited in an electrostatic precipitator. Most solid product, char, remains in the bottom of the reactor, while suspended char particles are removed by a cyclone. The gaseous products that were not condensed in the condensers were collected in a Teflon bag. The Teflon bag was replaced with a new one every 20 min.

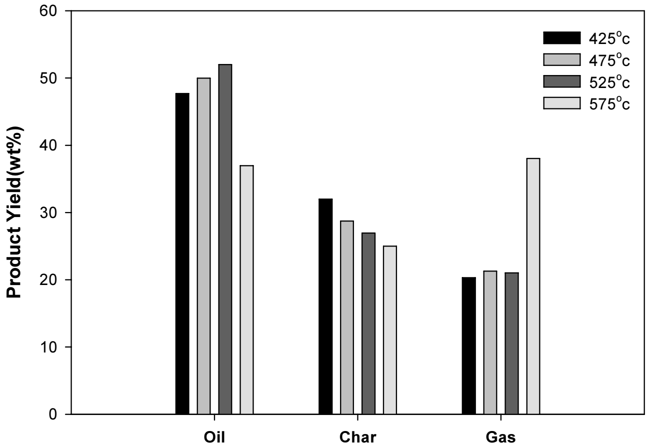

Figure 1. Comparison of bio-oil, char and gas yields obtained at different pyrolysis temperatures.

2.3. Product Analysis

The bio-oil yield was obtained by weighing the mass of bio-oil collected in the condensers. The char yield was calculated from the difference between the fluid sand mass values measured before and after the reaction. The gas yield was determined by subtracting the yields of bio-oil and char from unity.

Composition analysis was performed for the product bio-oil using gas chromatography (GC; HP 6890N)/mass spectrometry (MS; HP 5973 inert Mass Spectral Detector). An HP-5MS (30 m × 0.25 mm × 0.25 μm) column was used for the analysis. The mass spectra were interpreted based on an automatic library (NIST05a). Prior to the composition analysis, the bio-oil was stirred sufficiently using a stirrer to obtain a homogeneous sample for the analysis. The sample was extracted using a syringe after the stirring process. One can refer to Kim et al.[14] for the detailed procedure of the GC/MS analysis.

The gaseous products collected in the Teflon bags were analyzed quantitatively using GC (ACME 6000, Young Lin Instrument Co., Ltd). CO, CO_2, H_2 and CH_4 were analyzed using a thermal conductivity detector equipped with a Carboxen 1000 column, whereas hydrocarbons were analyzed using a flame ionization detector equipped with an HP-plot Al_2O_3/KCl column. The response factor required for the analysis program was calculated using the Kaiser formula.

3. Results and Discussion

Figure 1 shows the yields of gas, oil and char obtained at different pyrolysis temperatures. The gas yield increased, while the char yield decreased, with increasing pyrolysis temperature as was expected. This trend is almost universally observed in the pyrolysis of biomass because a supply of more thermal energy can promote the breakage of carbon bonds.

The oil yield increased with increasing temperature until the pyrolysis temperature reached 525 ℃. According to Lin et al.[17], high heat transfer rate is desirable to suppress the formation of coke, which implies that high temperature is advantageous for the production of oil species. This is believed to be the reason why the oil yield increased

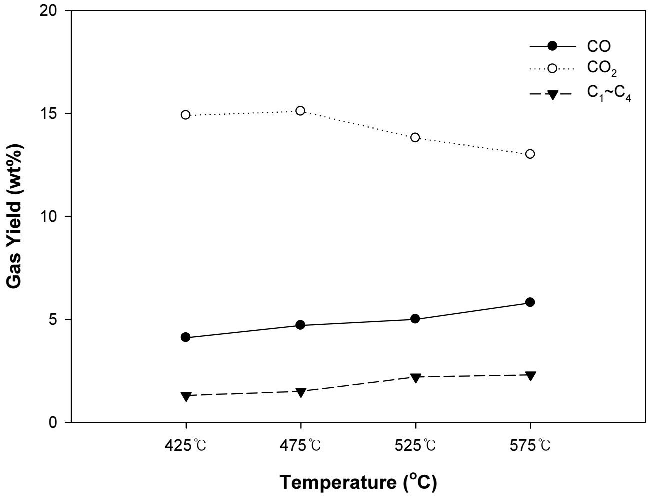

Figure 2. Comparison of product gas yields obtained at different pyrolysis temperatures.

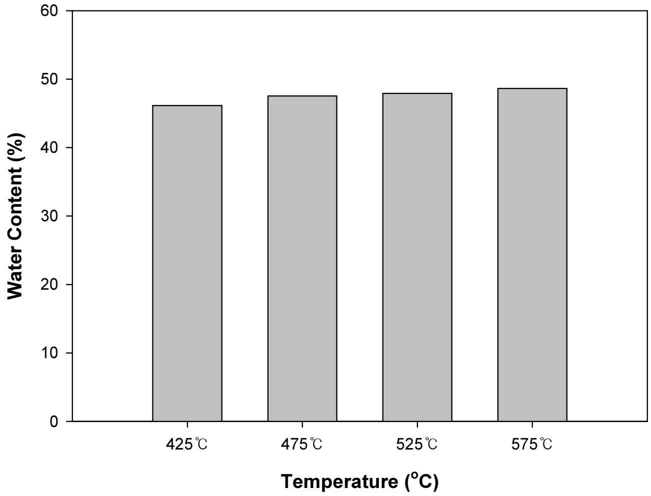

Figure 3. Comparison of water contents in bio-oil obtained at different pyrolysis temperatures.

with increasing pyrolysis temperature in this study. When the temperature was raised further to 575 ℃, however, the oil yield decreased dramatically, accompanied by an abrupt increase in the gas yield. This phenomenon can be attributed to secondary cracking of oil compounds to lighter species that have lower boiling points than the condenser temperature. Therefore, the optimum temperature to obtain high oil yield was determined to be 525 ℃.

Figure 2 compares the yields of the gas species produced at different pyrolysis temperatures. CO and CO_2 accounted for almost 90% of total gaseous products, indicating that decarboxylation and decarbonylation were the main reactions during the pyrolysis of MDF. The yield of CO_2 decreased, whereas those of CO and C_1-C_4 hydrocarbons increased, with increasing temperature. This result suggests that decarbonylation and demethylation were enhanced at high temperature.

Moisture contained in bio-oil affects the properties of the oil, such as viscosity, heating value, density, stability, pH, and homogeneity[18]. Although high moisture content in bio-oil can suppress the formation of nitrogen oxide during the combustion of the oil and decreases viscosity enhancing liquidity, it can cause several adverse effects; it decreases heating value, causes the phase separation occasionally, and increases the time and energy required for ignition[19]. The water content in the bio-oil produced in this study increased slowly with increasing pyrolysis temperature, probably due to the enhanced dehydration reaction at high temperature (Figure 3). The water content was 45~50% throughout the temperature range tested in this study, which is higher than that of typical pyrolysis product oil (~30%). This may be attributed to the decomposition of adhesives contained in MDF. However, further investigation is needed for better understanding.

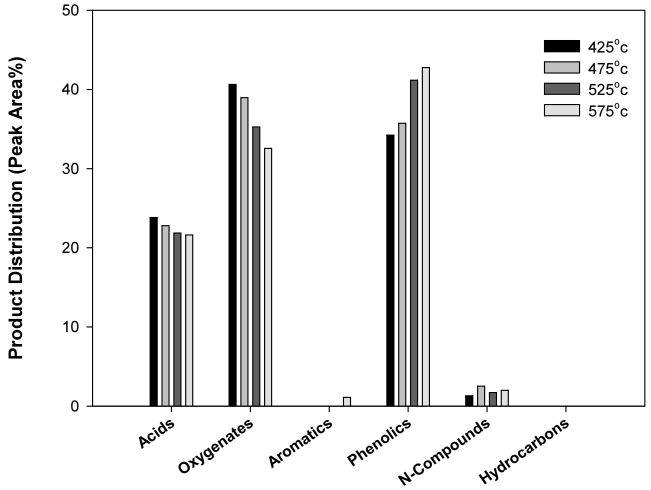

Figure 4. Comparison of bio-oil compositions obtained at different pyrolysis temperatures.

Figure 4 compares the species distributions obtained at different pyrolysis temperatures. All the chemical species contained in bio-oil were categorized into six groups : acids, oxygenates, aromatics, phenolics, N-compounds, and hydrocarbons. The fractions of oxygenates and acids, which reduce the heating value and stability of bio-oil, decreased with increasing pyrolysis temperature. This can be attributed to enhanced cracking and deoxygenation of oxygenates and acids at high temperature. Aromatics were not detected below 575 ℃, indicating that high temperature is essential for the production of aromatics. The fraction of phenolics increased rapidly with increasing temperature. This can be ascribed to the promotion of the decomposition of lignin contained in MDF into phenolics at high temperature[20,21]. A little amount of N-compounds were also produced, stemming from the nitrogen contained in MDF. The effect of temperature on the fraction of N-compound was not profound.

4. Conclusions

The pyrolysis of MDF was carried out using a fluidized-bed reactor at different temperatures : 425, 475, 525, and 575 ℃. The maximum bio-oil yield of 52 wt% was obtained at 525 ℃.

The moisture content of the bio-oil produced slowly increased with increasing temperature, indicating that dehydration was enhanced at high temperature. Increasing the pyrolysis temperature resulted in the improvement of the bio-oil quality; the yields of oxygenates and acids were reduced, while those of aromatics and phenolics were increased. CO and CO_2 accounted for the most part of gas product. The yield of CO_2 decreased, while those of CO and C_1-C_4 hydrocarbons increased, with increasing pyrolysis temperature.

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