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Production of biofuels from pine needle via catalytic fast pyrolysis over HBeta

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Abstract–The thermal and catalytic pyrolysis of pine needles over HBeta catalysts with different SiO_2/Al_2O_3 ratios (25 and 300) were investigated by thermogravimetric analysis (TGA) and pyrolyzer-gas chromatography/mass spectrometry. TGA showed that the main decomposition of pine needles occurred between 150 and 550 °C. The catalytic DTG curves revealed the same decomposition temperature region as the non-catalytic TG curve of pine needles. Pyrolyzer-gas chromatography/mass spectrometry suggested that the effective catalytic conversion of pyrolyzate intermediates and other hydrocarbons to aromatic hydrocarbons can be achieved using HBeta catalysts at 600 °C. HBeta(25) produced a larger amount of aromatic hydrocarbons than HBeta(300) because of its higher acid amounts. By increasing the reaction temperature from 500 to 700 °C, the formation of benzene, toluene, ethylbenzene, xylenes (BTEXs) and other polycyclic aromatic hydrocarbons was increased with a concomitant decrease in phenolics and other oxygenates. The formation efficiency of BTEXs was increased further by increasing the catalyst loading.

Keywords: Pine Needle, Catalytic Pyrolysis, BTEX, HBeta

INTRODUCTION

Research on biofuels has attracted considerable attention as a possible replacement for petrochemical fuels from biomass [1]. Biofuels, such as bio-ethanol and biodiesel, are obtained through reactions, such as fermentation and trans-esterification, respectively [2]. Especially, the production process of bio-ethanol and biodiesel was already commercialized, and they are blended with fossil fuels for their use [2]. However, the bio-ethanol and biodiesel are mostly produced from edible feedstock, and many researchers are considering the effective conversion of non-edible feedstock. The thermochemical conversion of biomass can produce gas, liquid, and solid fuels, such as syngas, bio-oil, and bio-char, respectively [3]. In particular, this thermochemical conversion method has an advantage because large amounts and various kinds of biomass can be converted easily in a shorter time than other biological conversion methods of biomass [4]. Among thermochemical conversion methods, pyrolysis can produce a large amount of bio-oil via the thermal decomposition of biomass at medium high temperature under inert atmosphere. The bio-oil obtained from biomass pyrolysis can be used as fuel or chemical feedstock easily.

Many types of biomass have been applied to bio-oil production in recent decades [5]. In addition, many researchers have focused on the conversion of agricultural and forest biomass waste to bio-oil using pyrolysis technology. Among the many kinds of wood biomass, pine trees are harvested widely all over the world and are distributed widely in South Korea. A pine tree produces large amounts of pine needles during its growth that accumulate on the ground. These pine needles need to be eliminated because of their high potential as a forest fire-causing material [6]. The regular collection of pine needles from forests and their conversion to renewable energy can be the candidate not only for the stable maintenance of forests, but also for renewable energy production. On the other hand, there has been little research interest on the pyrolysis of pine needles compared to other biomass [7-10]. Although bio-oil can be produced from the pyrolysis of pine needles, its high oxygen content, low pH, and low heating value, as observed with the pyrolysis of other biomass, limit its actual application as a biofuel or biochemical feedstock.

Meanwhile, the catalytic pyrolysis of biomass or catalytic upgrading of biomass pyrolysis oil can be applied to produce more stable and higher quality bio-oil from biomass. Although the production of high quality oil from the catalytic pyrolysis of biomass can be a candidate method for the production of high quality oil using an appropriate catalyst, such as microporous zeolites [11], mesoporous zeolites [12], and hierarchical zeolites [13], their actual application to the pyrolysis of pine needles has not been reported.

Therefore, the catalytic pyrolysis of pine needles was investigated using a HBeta catalyst because of its high commercial availability, high acidity, and suitable pore size on the conversion of pyrolyzate intermediates. To determine the optimal conditions for the catalytic pyrolysis of pine needle over HBeta, a range of parameters, such as the SiO_2/Al_2O_3 ratio, catalyst to sample ratio, and reaction temperature, were evaluated by pyrolyzer-gas chromatography/mass spectrometry (Py-GC/MS).

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EXPERIMENTAL

1. Pine Needle

Pine needles scatted under the trees in Baebong mountain of Seoul city were collected, milled, dried, and sieved as powder form. Proximate and ultimate analyses were performed using the procedure reported elsewhere [14]. The content of water, volatiles, fixed carbon and ash was 2.8, 85.8, 8.5, and 2.9 wt%, respectively. In addition, the content of C, H, N and O was 1.26, 50.26, 6.4, and 42.08 wt%, respectively.

2. Thermogravimetric Analysis (TGA)

Thermal decomposition properties of pine needle was carried out using a TGA (Pyris 1, Perkin Elmer). For this, a 1.0 mg pine needle sample was heated from ambient temperature to 800 °C at 30 °C/min under flowing nitrogen at 50 mL/min.

3. Catalyst

Two types of HBeta, HBeta(25) and HBeta(300), having different SiO_2/Al_2O_3 ratios (25 and 300), respectively, were used. The acidity of HBeta can influence the catalytic pyrolysis activity, and the ammonia temperature programmed desorption (NH_3-TPD) of HBeta catalysts was performed according to the procedure reported elsewhere [15].

4. Catalytic Pyrolysis

Thermal and catalytic pyrolysis and an analysis of its product were performed using a Py-GC/MS (Py-3030D, Frontier Laboratories; 7890A/5975 inert MSD, Agilent Technologies) as shown in Fig. 1. For non-catalytic pyrolysis, a 1.0 mg sample of pine needle was pyrolyzed under isothermal conditions at 500, 600, and 700 °C. In the case of catalytic pyrolysis, different amounts of catalyst (1.0, 3.0, and 5.0 mg) were also added to the sample cup and mixed together with 1.0 mg of pine needle to assess the effects of the catalyst to sample ratio. The products emitted from the thermal and catalytic pyrolysis of pine needles were analyzed by GC connected directly to the pyrolyzer.

RESULTS AND DISCUSSION

1. Catalysts

The BET surface area of HBeta(25) and HBeta(300) was 680 and 620 m^2/g, respectively. The NH_3-TPD curves of HBeta(25) and HBeta(300) are shown in Fig. 2. Compared to HBeta(300), HBeta(25)

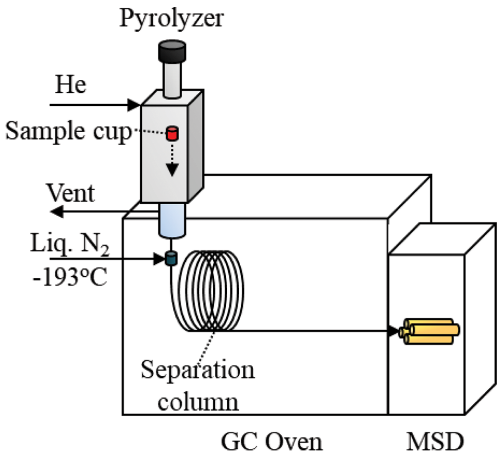


Fig. 1. Schematic diagram of Py-GC/MS.

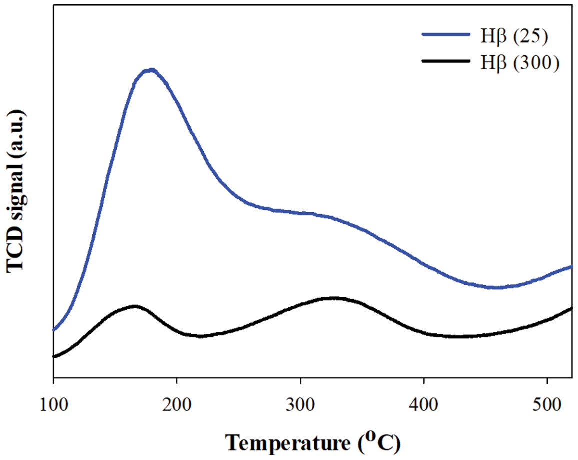
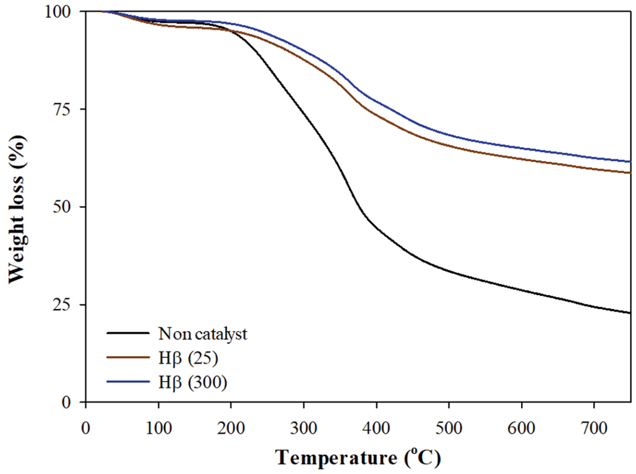
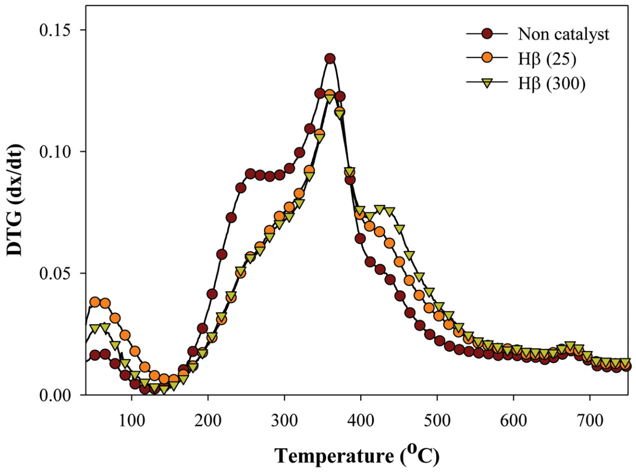


Fig. 2. NH_3-TPD curves of HBeta catalysts.



(a) TG curves



(b) DTG curves

Fig. 3. TG and DTG curves obtained from the TG analysis of pine needles at 20 °C/min.

has the higher ammonia desorption peak intensity. This implies that HBeta(25) has higher amount of acid sites than HBeta(300). The ammonia desorption peak temperatures of HBeta(25), 180 °C and 330 °C, were also higher than those of HBeta(300), 165 °C and 328 °C. This indicates that HBeta(25) has the stronger acidity than HBeta(300).

2. TGA

As shown in Fig. 3, the pyrolysis of pine needles was initiated from 150 °C and continued to 600 °C during non-isothermal TGA at 20 °C/min. The main decomposition of pine needle occurred at between 150 and 550 °C and showed the merged derivative thermogravimetry (DTG) curve pattern of hemicellulose, cellulose, and lignin. Hemicellulose decomposed first at the initial stages of biomass (temperatures lower than 300 °C) [16]. Cellulose decomposed between 300 and 400 °C and lignin had a wide decomposition temperature range between 200 and 600 °C, mainly [14]. The catalytic DTG curve of pine needles had the same decomposition temperature region with that of the non-catalytic thermogravimetry (TG) curve. This suggests that the pine needles decomposed first by the thermal decomposition because the direct diffusion of the lignocellulosic components of pine needles, i.e., hemicellulose, cellulose and lignin, to the pores of the HBeta catalysts are limited owing to the pore size of HBeta (ca. 0.67 nm) and the pyrolyzates are upgraded over the HBeta catalysts.

3. Pyrolysis of Pine Needles

Fig. 4 shows the product distribution of the bio-oil produced from the thermal and catalytic pyrolysis of pine needles at 600 °C. In the case of non-catalytic pyrolysis, most of the products in oil were oxygenates, such as acids (e.g., acetic acid), ketones (e.g., acetone), and furans. Significant quantities of hydrocarbons (1,2-butadiene, 3-methyl-, etc.) were also produced from the pyrolysis of other biomass but not in large quantities. This can be explained by the presence of rosin in pine needles [17]. The phenolics and aromatic hydrocarbons were also produced from lignin decomposition.

Compared to non-catalytic pyrolysis, the catalytic pyrolysis of pine needles produced a much smaller amount of hydrocarbons and oxygenates, and most of the products consisted of aromatic hydrocarbons. Among these aromatic hydrocarbons, benzene, toluene, ethylbenzene, and xylenes (BTEXs) are useful products as an additive for petrochemical fuels and gasoline. The formation of BTEXs highlights the high economic value of the catalytic pyrolysis process of pine needle. Hydrocarbons can be converted to aromatic hydrocarbons by oligomerization, cyclization, or dehydrogenation reactions after primary decomposition over an acidic zeolite catalyst [13]. Therefore, the production of aromatic hydrocarbons with the elimination of other hydrocarbons during the catalytic pyrolysis of pine needles indicates that the large amount of hydrocarbons produced by the non-catalytic pyrolysis can be transformed efficiently to aromatic hydrocarbons over HBeta catalysts. Large amounts of oxygen-containing pyrolyzates of pine needles were also converted to aromatic hydrocarbons. Schultz et al. [18] reported that oxygen-containing pyrolyzates, such as acetic acid and acetone, can be transformed to aromatic hydrocarbons on the acid sites of HBeta. Compared to the catalytic pyrolysis of pine needle over HBeta(300), pyrolysis over HBeta(25) produced a larger amount of BETXs and other mono aromatic hydrocarbons (MAHs). This implies that the catalyst performance on the formation of aromatic hydrocarbons via the catalytic pyrolysis of pine needle increases according to the acid strength of HBeta.

Fig. 5 shows the effects of temperature on the pyrolysis of waste pine needles. As the temperature increased, the BTEX yield increased sharply and the yield of MAHs decreased. This suggests that the dealkylation of alkylated aromatic hydrocarbons on the catalyst accelerates with increasing temperature. In addition, the production of phenolics and oxygenates is also decreased. This suggests that the conversion of phenolics and oxygenates can be achieved more efficiently by applying a higher reaction temperature.

Fig. 6 shows the product change with increasing catalyst amount on the catalytic pyrolysis of pine needles at 600 °C. By increasing the sample to catalyst ratio, the amount of BTEXs, MAHs, and PAHs increased with decreasing content of phenolics, oxygenates, and other hydrocarbons, suggesting that deoxygenation and aromati-

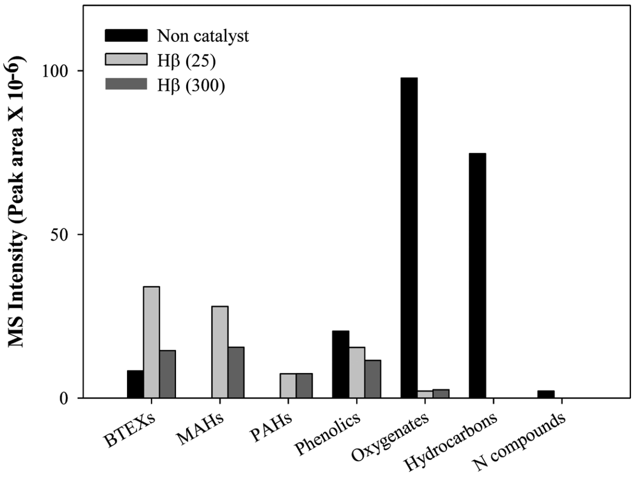


Fig. 4. Product distribution of each chemical group in the product oil obtained from the thermal and catalytic pyrolysis of pine needles at 600 °C.

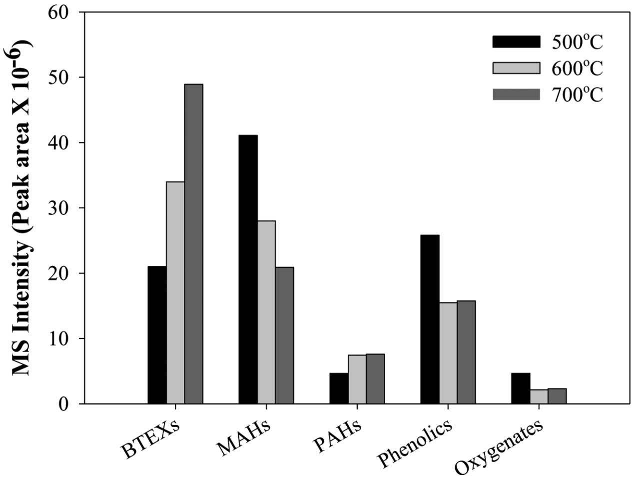


Fig. 5. The effect of reaction temperature on the product distribution obtained from the catalytic pyrolysis of pine needles over of pyrolysis of waste pine needles over HBeta(25).

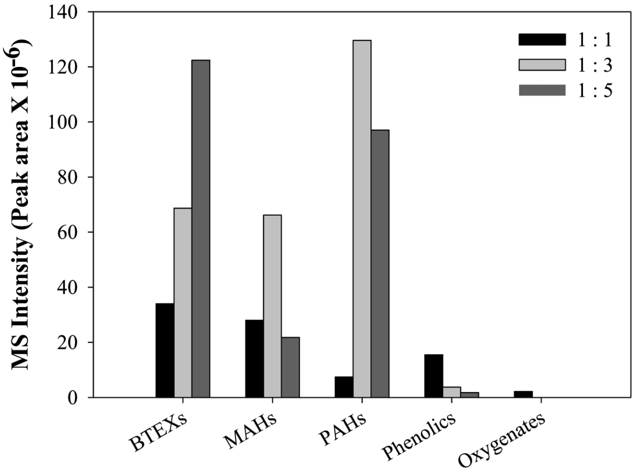


Fig. 6. The effect of sample to catalyst ratio on the product distribution of pyrolysis of pine needles at 600 °C.

zation can be enhanced by increasing the catalyst amount. The amounts of BTEXs were increased by increasing the sample to catalyst ratio from 1/3 to 1/5. In addition, the amounts of MAHs and PAHs produced decreased, suggesting an active dealkylation reaction, leading a decrease in the alkylated aromatic hydrocarbons and a decrease in the formation of PAHs, which can be formed by a Diels-Alder reaction between alkylated aromatic hydrocarbons and other hydrocarbons.

CONCLUSION

Although the use of HBeta on the pyrolysis of pine needles could not decrease its decomposition temperature, it increased the yield of aromatic hydrocarbons because of the effective conversion of oxygenated and linear hydrocarbons over the HBeta catalysts. HBeta(25) provided higher efficiency on the formation of aromatic hydrocarbons than HBeta(300) owing to its higher acidity. The yields of benzene, toluene, ethylbenzene, and xylenes were increased by increasing the catalytic reaction temperature from 500 to 700 °C and increasing the catalyst loading.

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