

Article

In-Situ Catalytic Fast Pyrolysis of Pinecone over HY Catalysts

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Abstract: The in-situ catalytic fast pyrolysis of pinecone over HY catalysts, HY(30; SiO₂/Al₂O₃), HY(60), and 1% Ni/HY(30), was studied by TGA and Py-GC/MS. Thermal and catalytic TGA indicated that the main decomposition temperature region of pinecone, from 200 to 400 °C, was not changed using HY catalysts. On the other hand, the DTG peak heights were differentiated by the additional use of HY catalysts. Py-GC/MS analysis showed that the efficient conversion of phenols and other oxygenates formed from the pyrolysis of pinecone to aromatic hydrocarbons could be achieved using HY catalysts. Of the HY catalysts assessed, HY(30), showed higher efficiency in the production of aromatic hydrocarbons than HY(60) because of its higher acidity. The aromatic hydrocarbon production was increased further by increasing the pyrolysis temperature from 500 to 600 °C and increasing the amount of catalyst due to the enhanced cracking ability and overall acidity. The use of 1% Ni/HY(30) also increased the amount of monoaromatic hydrocarbons compared to the use of HY(30) due to the additional role of Ni in enhancing the deoxygenation and aromatization of reaction intermediates.

Keywords: pinecone; HY; aromatic hydrocarbons; Py-GC/MS

1. Introduction

Recently, the frequency of abnormal weather due to global warming has been increasing, and its intensity has also become stronger than before. For example, the temperature in France in June 2019 approached 45 °C. In this regard, the use of renewable energy is essential to reduce global warming, the main cause of climate change, and biofuels are a significant source of renewable energy [1–5]. Among the biofuels, the importance of bio-oil is increasing because it can be used both as a biofuel and as chemical feedstock. Bio-oil is produced from the pyrolysis of biomass, and the characteristics of bio-oil obtained from biomass pyrolysis are differentiated according to the biomass species [6]. In particular, many studies have been conducted to produce bio-oils by applying non-edible biomass as the pyrolysis

source instead of edible biomass [7–9]. Among various types of non-edible biomass, lignocellulosic biomass pyrolysis, including pine trees, has been studied intensively [10].

Of the range of woody biomass in Korea, pinewood is the one of the most widely distributed wood species in Korea from ancient times. Pinewood has been used widely to construct Korean traditional houses, and a large amount of pinewood waste is emitted as a byproduct. Therefore, pyrolysis research related to pine waste such as pinecones and needles has been carried out worldwide, including Korea. On the other hand, as more pine trees are cultivated, a larger amount of cones will be generated annually. Recently, pinecones have been regarded as a biomass resource that can be used as biofuel, and the pyrolysis of pinecones has been reported [11]. However, most studies on pinecone pyrolysis have focused on the production and application of biochar, and very few studies have reported on the production and quality analysis of bio-oil from pinecones via thermo-chemical conversion technologies [12,13]. Therefore, the pyrolysis processes that produce bio-oil from pinecones require more research. In addition, the bio-oil obtained from the non-catalytic fast pyrolysis (NCFP) of pinecones can be used as a low-grade fuel only owing to its high oxygen content. Therefore, it is necessary to convert it to high-grade fuels with low oxygen contents or valuable biochemicals with high economic value by applying the appropriate catalytic upgrading [14–16]. On the other hand, there are no reports on the production of bio-oils with a low oxygen content or valuable chemical feedstock via the catalytic fast pyrolysis (CFP) of pinecones.

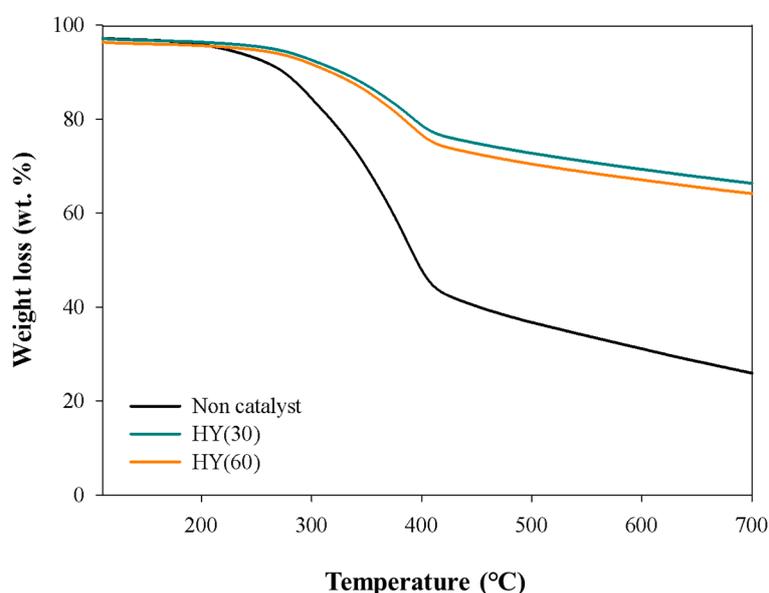
This study examined the CFP of pinecones to produce high-quality biofuel with low oxygen contents by thermogravimetric (TG) analysis and pyrolyzer-gas chromatography/mass spectrometry (Py-GC/MS). For this purpose, HY—a typical microporous catalyst used widely in petrochemical cracking reactions—was selected as a reaction catalyst. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios of the catalysts were varied to investigate the effects of the acid characteristics of HY on the CFP. To investigate the effects of the process conditions, the reaction temperature and catalyst amount were also differentiated. The effects of Ni impregnation into HY(30) on the CFP of pinecones were also assessed.

2. Results and Discussion

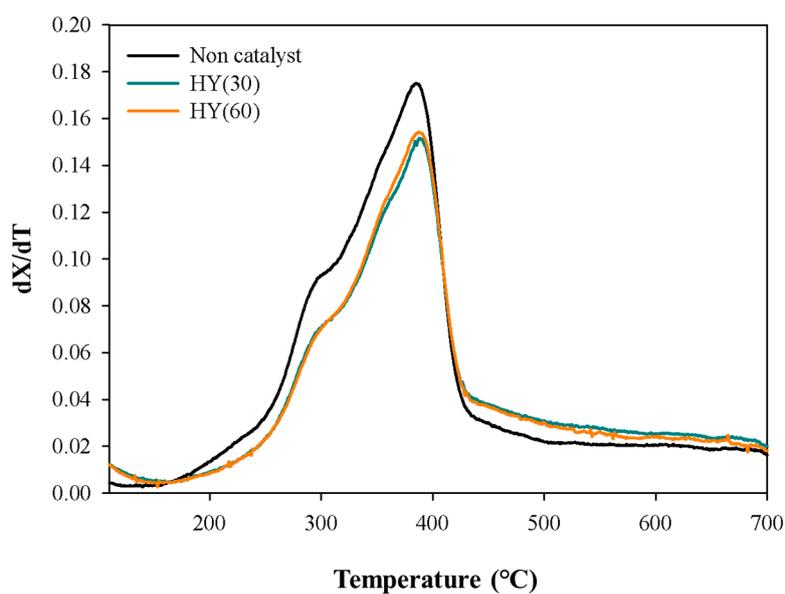
2.1. TG Analysis

Figure 1 shows the thermal and catalytic TG and DTG curves of pinecone over HY catalysts. The non-catalytic TG curve of pinecone suggests that it decomposed rapidly at between 200 and 400 °C because of the main decomposition of the lignocellulosic components of biomass (lignin, hemicellulose, and cellulose) [17] and that this continued up to a higher temperature than 600 °C due to char stabilization [18,19]. The catalytic TG and DTG curves of pinecone also revealed the same decomposition temperature region as those obtained from the non-catalytic TGA. On the other hand, the catalytic DTG peak heights of pinecone over both HY(30) and HY(60) were lower at temperatures less than 400 °C and higher at the temperature greater than 400 °C compared to the non-catalytic DTG curve. This can be explained by the CFP behavior of biomass. The lignocellulosic components of biomass converted to pyrolyzates consisted mainly of oxygen-containing pyrolyzates such as acids, aldehydes, furans, levoglucosan, and phenols during the CFP of biomass. These pyrolyzates are converted to light olefins and aromatic hydrocarbons over the catalysts [20]. Although their formation amounts can be differentiated according to the CFP condition and the catalyst species, coke can form at the surface of the catalyst and inside of the catalyst pores, thereby poisoning the catalyst. Therefore, some CFP intermediates cannot be vaporized and fixed to the catalyst as thermal coke and catalyst coke, as shown in the DTG peak height of pinecones at temperatures lower than 400 °C. If a considerable amount of coke is deposited on the catalyst, the coke is also stabilized at higher temperatures with the elimination of oxygen and the formation of more thermally stable polyaromatic coke [21]. The CFP of pinecone over HY catalysts can increase the amount of volatile emission at temperatures higher than 400 °C. Compared to the catalytic DTG curve of pinecones over HY(60), that over HY(30) showed a lower DTG peak height at temperatures less than 400 °C and higher at temperatures greater than 400 °C.

This suggests that HY(30) produces a larger amount of coke at temperatures lower than 400 °C and emits a larger amount of volatiles during the coke stabilization at temperatures higher than 400 °C [22].



(a) TG curve



(b) DTG curve

Figure 1. TG and DTG curves obtained from the thermal and catalytic TG analysis of pinecone at 20 °C/min over HY catalysts.

2.2. Py-GC/MS Analysis

Table 1 lists the absolute MS peak areas for the products obtained from the NCFP of pinecone at 600 °C. The NCFP of pinecones mainly produced large amounts of oxygen-containing pyrolyzates, classified into furans, acids, phenols, aldehydes, ketones, and levoglucosan, along with minor amounts of hydrocarbons and N-containing compounds. Acetic acid and furans are the typical pyrolyzates of woody biomass [23]. Levoglucosan, the primary decomposition product of cellulose [24], comprised

the largest portion of oxygen-containing pyrolyzates of pinecone. Many phenolic products, such as phenol, methyl phenol, methoxy phenol, methyl methoxy phenol, ethyl methoxy phenol, vinyl methoxy phenol, eugenol, and propenyl methoxy phenol, are also produced by the decomposition of lignin in pinecones [25,26].

Table 1. Absolute MS peak area of the products obtained from the non-catalytic fast pyrolysis (NCFP) of pinecone at 600 °C. BTEX: benzene, toluene, ethyl benzene, and xylene.

| | Compound | Group | Peak Area ($\times 10^{-6}$) |
|----|-----------------------------------|--------------|-----------------------------------|
| 1 | Methyl furan | Furans | 2.41 |
| 2 | Acetic acid | Acids | 30.05 |
| 3 | Hydroxy propanone | Ketones | 6.22 |
| 4 | Toluene | BTEXs | 3.81 |
| 5 | Methyl pyruvate | Esters | 5.02 |
| 6 | Furfural | Furans | 6.39 |
| 7 | Hydroxy cyclopentenone | Ketones | 10 |
| 8 | Furanone | Ketones | 5.22 |
| 9 | Methyl pyrimidinone | N compounds | 8.22 |
| 10 | Phenol | Phenolics | 4.23 |
| 11 | Methylimino perhydro oxazine | N compounds | 8.82 |
| 12 | Hydroxy methyl cyclopentenone | Ketones | 3.26 |
| 13 | Methyl phenol | Phenolics | 3.68 |
| 14 | Dimethyl hydroxyl furanone | Ketones | 3.16 |
| 15 | Methoxy phenol | Phenolics | 7.47 |
| 16 | 1,2-Benzenediol | Phenolics | 25.74 |
| 17 | Methyl methoxy phenol | Phenolics | 23.5 |
| 18 | Hydroxymethyl furancarboxaldehyde | Aldehydes | 8.85 |
| 19 | Ethyl methoxy phenol | Phenolics | 3.07 |
| 20 | Methyl benzenediol | Phenolics | 10.87 |
| 21 | Vinyl methoxy phenol | Phenolics | 17.46 |
| 22 | Eugenol | Phenolics | 3.16 |
| 23 | Hexanoic acid | Acids | 26.71 |
| 24 | Vanillin | Phenolics | 5.36 |
| 25 | Propenyl methoxy phenol | Phenolics | 17.43 |
| 26 | Levoglucofan | Levoglucofan | 195.10 |
| 27 | Hydroxy methoxy cinnamaldehyde | Aldehydes | 4.57 |

By applying the CFP of pinecone over HY catalysts, the amounts of oxygen-containing pyrolyzates decreased significantly with the formation of aromatic hydrocarbons, as shown in Figure 2. The contents of phenolics and other oxygenates also decreased after applying both HY catalysts to the pyrolysis of pinecone. This suggests that both HYs are efficient catalysts for the conversion of oxygen-containing pyrolyzates of pinecone to aromatic hydrocarbons. Compared to the CFP of pinecone over HY(60), that over HY(30) produced a larger amount of aromatic hydrocarbons because of its higher acidity. During the CFP of biomass, the lignocellulosic components of biomass (e.g., hemicellulose and cellulose) are converted to oxygen-containing pyrolyzates and light hydrocarbons via catalytic cracking, dehydration, decarboxylation, decarbonylation, dealkylation, and dealkoxylation [27]. These hydrocarbons form a hydrocarbon pool inside the pores of the acid catalysts and produce aromatic hydrocarbons [28]. In the case of the CFP of lignin, its main pyrolyzates (e.g., alkyl phenols and alkoxy phenols) are converted to aromatic hydrocarbons via additional dealkylation and dealkoxylation reactions of phenolic pyrolyzates over acid catalysts [29].

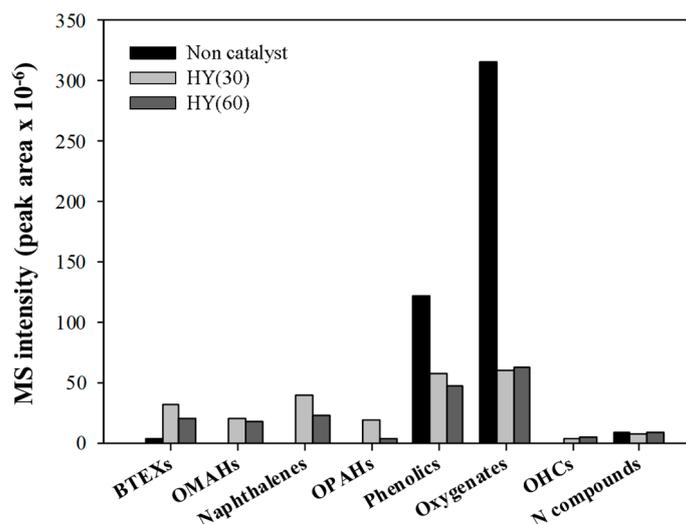


Figure 2. The absolute MS peak areas for each chemical group obtained from the thermal and catalytic fast pyrolysis of pine cone at 600 °C over HY(30) and HY(60). OMAHs: other monoaromatic hydrocarbons; OPAHs: other polyaromatic hydrocarbons.

Figure 3 shows the effects of the CFP reaction temperature on the formation of aromatic hydrocarbons via the CFP of pinecone over HY(30). Larger amounts of benzene, toluene, ethyl benzene, and xylenes (BTEXs), other monoaromatic hydrocarbons (OMAHs), naphthalenes, and other polyaromatic hydrocarbons (OPAHs) were formed by increasing the reaction temperature from 500 to 600 °C. The amounts of phenolics and other oxygenates decreased with increasing reaction temperature. This also confirms that the formation of aromatic hydrocarbons during the CFP of pinecone is related to the effective conversion of phenolics and other oxygenates to aromatic hydrocarbons via the aromatization of deoxygenated light olefins and the dealkylation and dealkoxylation of large molecular weight phenols. The higher production efficiency of aromatic hydrocarbons by increasing the reaction temperature on the CFP of pinecone can be explained by the increased catalytic cracking efficiency at higher temperatures [22] and the increased diffusion efficiency of large molecular weight reaction intermediates to the expanded catalysts' pores [22,30]. When the reaction temperature was increased to 600 °C, the yield of naphthalenes (one class of PAHs) was increased. Naphthalene is an important material in the organic chemical industry and is used widely as a resin [31], solvent [32], or dye [33].

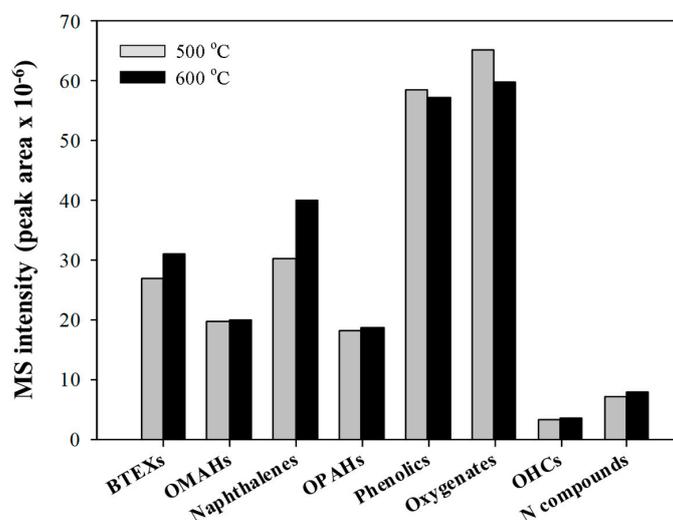


Figure 3. The absolute MS peak areas for each chemical group obtained from the thermal and catalytic pyrolysis of pine cone at different temperatures over HY(30).

Figure 4 shows the effect of the catalyst amount on the CFP of pinecone over HY catalysts. The level of aromatic hydrocarbon production was also increased by decreasing the sample-to-catalyst ratio from 4:1 to 1:4 on the CFP of the same amount of pinecone (1 mg). This means that an increase in the overall number of acid sites by increasing the catalyst amount can increase the formation efficiency of aromatic hydrocarbons during the CFP of pinecone. In addition, the nitrogen compounds were converted completely when the amount of the catalyst was increased. In particular, most of the product formed from the CFP of pinecone consisted of aromatic hydrocarbons together with a small amount of phenolics when a sample-to-catalyst ratio of 1:4 was applied to the reaction.

Figure 5 shows the effects of 1% Ni/HY(30) on the production of aromatics during the CFP of pinecone at 600 °C. Compared to HY(30), 1% Ni/HY(30) produced larger amounts of BTEXs. On the other hand, the amounts of naphthalenes and OPAHs were decreased using Ni/HY(30) instead of HY(30). This indicates that the selectivity toward to MAHs can be increased using a Ni-impregnated HY catalyst, although the overall acidity of HY(30) was decreased slightly by the Ni impregnation (Figure 6). In addition, the amount of oxygenates were decreased for Ni/HY(30). This may imply that the catalytic pyrolysis intermediates could be more efficiently converted to MAHs over Ni by enhancing deoxygenation. The effective role of Ni in the formation of MAHs has also been reported by other researchers. Ben and Ragauskas [34] commented that the deoxygenation reaction of biomass pyrolysis intermediates can be increased by the additional use of NiCl₂ with HZSM-5. Dai et al. [35] suggested that Ni strongly promoted direct deoxygenation reactions such as the decarboxylation, decarbonylation, and dehydration of oxygenates.

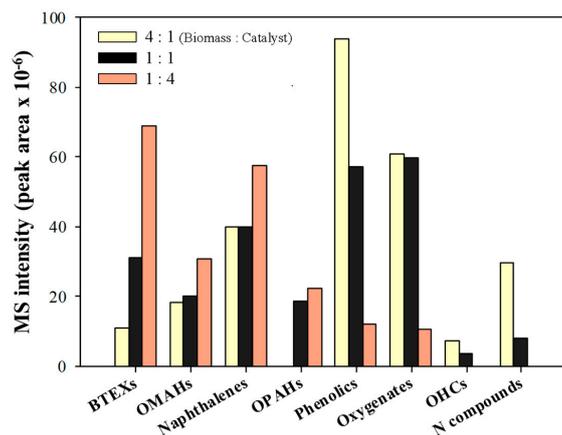


Figure 4. The absolute MS peak areas for each chemical group obtained from the catalytic fast pyrolysis of pinecone at different sample-to-catalyst ratios at 600 °C over HY(30).

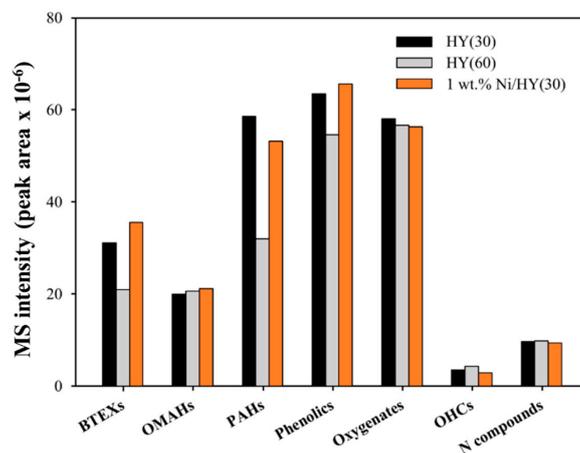


Figure 5. The absolute MS peak areas for each chemical group obtained from the catalytic fast pyrolysis of pinecone over Ni/HY at 600 °C.

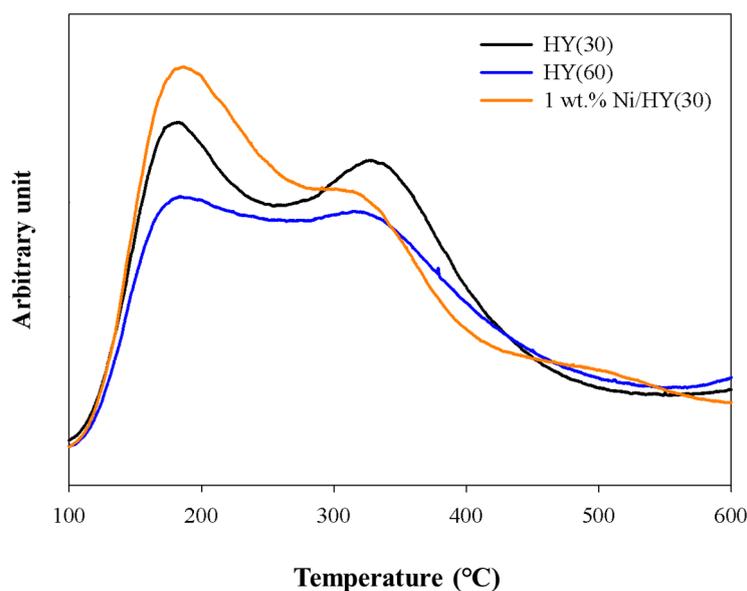


Figure 6. NH_3 TPD of catalysts.

3. Materials and Methods

3.1. Pinecone

Pinecones, which were emitted as waste biomass separated from pinewood by natural free falling, were pulverized to the same size. Ultimate and proximate analyses of pinecone (Table 2) were performed to determine its physico-chemical properties according to the procedure reported elsewhere [36]. Proximate analysis indicated that the pinecone had a high content of volatiles (83.0%). The moisture, fixed carbon, and ash contents of the pinecone were 2.1%, 13.4%, and 1.5%, respectively. Ultimate analysis of pinecone showed that carbon and oxygen accounted for more than 93.0% of the total organic elements together with low hydrogen (5.9%) and nitrogen (0.3%) contents. This suggests that a high-efficiency deoxygenation reaction is required to obtain high-quality oil with high carbon and hydrogen contents.

Table 2. The ultimate and proximate analysis results of pinecone used in this study.

| | | |
|---------------------------------------|----------------|-------|
| Proximate Analysis (wt.%) | Water | 2.1 |
| | Volatiles | 83.0 |
| | Fixed carbon | 13.4 |
| | Ash | 1.5 |
| Sum | | 100.0 |
| Ultimate Analysis ^a (wt.%) | C | 43.9 |
| | H | 5.9 |
| | O ^b | 49.9 |
| | N | 0.3 |
| Sum | | 100.0 |

^a On a dry basis, ^b By difference.

3.2. Catalysts

Two types of HY—HY(30) and HY(60), having $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios of 30 and 60—respectively, were obtained from Zeolyst (Conshohocken, PA, USA). The BET surface areas of HY(30) and HY(60) were given as 780 and 720 m^2/g from Zeolyst, respectively. Ni (1 wt.%) was impregnated on HY(30) using nickel nitrate. NH_3 -temperature programmed desorption (NH_3 -TPD) was performed to study the

acidity of HY zeolites. Additionally, pyridine FT-IR measurements were performed to study different kinds of acid sites (Brönsted and Lewis acid sites). The detailed procedures are described in the Supplementary Information.

As shown in the NH_3 -TPD curve of the HYs (Figure 6), both HY catalysts had two ammonia desorption temperature regions at approximately 180 °C and 330 °C, which were assigned to weak Brönsted acid sites or Lewis acid sites and medium Brönsted acid sites, respectively [37]. Between the two catalysts, HY(30) showed a larger amount of acid sites than HY(60) (Table 3). The substitution of proton with Ni^{2+} by the addition of Ni to HY(30) can lead to a reduction in the number of medium Brönsted acid sites and an increase in the number of Lewis acid sites. As shown in Figure 7, Ni addition increased Lewis acid sites density (peak at 1455 cm^{-1}) [38] and decreased Brönsted acid sites (peak at 1545 cm^{-1}) [38].

Table 3. Amount of acid sites determined by NH_3 -TPD.

| | Amount of Weak Acid Sites (mmol/g) | Amount of Medium Brönsted Acid Sites (mmol/g) | Amount of Total Acid Sites (mmol/g) |
|------------------|------------------------------------|---|-------------------------------------|
| HY(60) | 5.649 | 5.885 | 11.534 |
| HY(30) | 6.402 | 7.184 | 13.586 |
| 1 wt.% Ni/HY(30) | 7.710 | 4.657 | 12.367 |

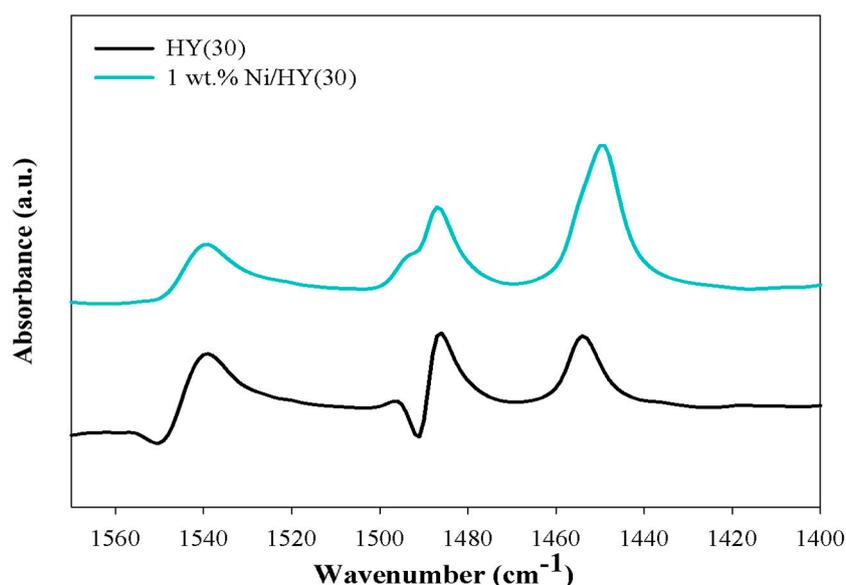


Figure 7. Pyridine FT-IR of HY(30) and Ni/HY(30) catalysts.

3.3. TGA

TGA (Pyris Diamond, Perkin Elmer) of pinecone was performed. For this, 1 mg of pinecone was heated from ambient temperature to 800 °C under a nitrogen atmosphere with a flow rate of 50 mL/min. In the case of catalytic TGA, an additional amount of catalyst (1 mg) was added to the TGA sample containing 1 mg of pinecone.

3.4. Py-GC/MS Analysis

NCFP and CFP of pinecone over HY catalysts and their product analysis were performed at the same time using a micro-furnace-type pyrolyzer (Py-3030D, Frontier Laboratories, Fukushima, Japan)-GC/MS(7890A/5975C, Agilent Technology, Santa Clara, CA, USA). For the NCFP of pinecone, 1 mg of pinecone in the pyrolyzer sample cup was decomposed at 500 or 600 °C and the product vapor was analyzed by GC/MS. In case of the CFP of pinecone, different amounts of catalyst (0.25, 1.00,

or 4.00 mg) were added to the same amount of pinecone sample (1 mg) and mixed in the pyrolysis sample cup. The prepared catalyst/sample mixture was free-fallen into the pyrolyzer heater for the CFP reaction, and the sample pyrolysis temperature and GC analysis conditions used in NCFP were also applied to the CFP. The detailed procedure is shown in the Supplementary Information.

4. Conclusions

The effectiveness of the CFP of biomass over HY catalysts for the production of aromatic hydrocarbons was examined by TGA and Py-GC/MS analysis. Although the main decomposition temperature of pinecone was not changed using the HY catalysts, the amount of aromatic hydrocarbons from the pyrolysis of pinecone was increased significantly using the HY catalysts. Between the two catalysts, HY(30) produced a larger amount of aromatic hydrocarbons than HY(60) because of its high acidity. By increasing the reaction temperature from 500 to 600 °C and decreasing sample-to-catalyst ratio from 4:1 to 1:4, the production of monoaromatic hydrocarbons during the catalytic pyrolysis of pinecone was also increased. The use of 1% Ni/HY(30) on the catalytic pyrolysis of pinecone further increased production efficiency of monoaromatic hydrocarbons, with a decrease in the formation of polyaromatics compared to HY(30) owing to enhancement of deoxygenation and aromatization.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4344/9/12/1034/s1>.

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