

Research Article

Catalytic Rapid Pyrolysis of *Quercus variabilis* over Nanoporous Catalysts

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Catalytic rapid pyrolysis of *Quercus variabilis*, a Korean native tree species, was carried out using Py-GC/MS. Mesoporous MFI, which has both nanopores and micropores, and three nanoporous materials, Al-MCM-41, Al-SBA-15, and γ -Al₂O₃, were used as the catalyst. The acid sites of mesoporous MFI were strong Brønsted acid sites, whereas those of nanoporous materials were mostly weak acid sites. The composition of the product bio-oil varied greatly depending on the acid characteristics of the catalyst used. Phenolics were the most abundant species in the bio-oil, followed by acids and furanics, obtained over Al-MCM-41 or Al-SBA-15 with weak acid sites, whereas aromatics were the most abundant species produced over mesoporous MFI with strong acid sites, followed by phenolics. Aromatics, phenolics, and furanics are all important chemicals contributing to the improvement of bio-oil quality.

1. Introduction

Due to global warming, CO₂ reduction has become a major issue over the world [1–3]. In this regard, biomass has been regarded as one of the possible solutions to reduce atmospheric CO₂. Although biomass is distributed much more evenly throughout the world than fossil fuels, the biomass resources are less abundant in Korea than in other parts of Asia, for example, Southeast Asia. The most common biomass found in Korea is forest biomass, amounting to approximately 6,369,000 ha in 2010. Cork oak (*Quercus variabilis*) accounts for the largest fraction of Korean forest biomass reserves, 24.17%; therefore, active use of *Quercus variabilis* is needed for the effective energy production from Korean forest biomass. However, most researches on biomass-to-energy conversion conducted in Korea have used wood biomass imported from foreign countries, while the application of

representative Korean native trees to the production of bio-fuels or biochemicals has been rarer. Therefore, the research on the biofuel production using representative Korean native trees is crucial for national bioenergy independence and the diversification of bioenergy resources. Among the processes that produce biofuels from biomass, rapid pyrolysis aims at producing liquid-phase biofuel, called bio-oil [4–10].

In particular, catalytic rapid pyrolysis, in which a catalyst is additionally employed in a rapid pyrolysis process, can remarkably reduce the oxygen content in bio-oil, enabling the production of high-quality bio-oil (with high heating rate, low acidity, low O/C ratio, etc.). There are two types of catalysis processes used for rapid pyrolysis: high-pressure catalysis and atmospheric-pressure catalysis. Compared to the high-pressure catalysis that requires expensive hydrogen gas, the atmospheric-pressure catalysis can be conducted more economically using zeolite-derived catalysts.

A number of papers on catalytic rapid pyrolysis of wood over porous materials have recently been published over the world [11–20]. Various characteristics of porous materials, for example, quantity and strength of acid sites, surface area, pore size, and crystallinity, have been shown to influence the reforming of bio-oil. As was mentioned above, however, researches on the rapid pyrolysis or catalytic pyrolysis of Korean native *Quercus variabilis* have never been reported.

In this study, the rapid pyrolysis of *Quercus variabilis* was carried out for the first time. The catalytic pyrolysis of *Quercus variabilis* was also performed over various mesoporous materials. The effects of the properties of mesoporous materials on the bio-oil reforming were investigated.

2. Experimental

2.1. *Quercus variabilis*. *Quercus variabilis* cultivated in Korea Forest Research Institute was used for this study. Proximate analysis performed following a procedure described in a previous study [12] showed that *Quercus variabilis* consisted of 1.1 wt% of moisture, 83.2 wt% of volatile matter, 12.3 wt% of fixed carbon, and 3.5 wt% of ash. *Quercus variabilis* contains 71.8% of holocellulose and 28.2% of lignin.

2.2. Thermogravimetric Analysis (TGA). TGA was performed to examine the decomposition behavior of *Quercus variabilis*. About 2 mg of sample was pyrolyzed for analysis. Nitrogen gas with a flow rate of 40 mL/min was used as the purge gas, while nitrogen gas at a flow rate of 20 mL/min was used as the sample gas. During the analysis, the temperature was increased from room temperature to 800°C at a heating rate of 30°C/min.

2.3. Synthesis and Characterization of Catalysts. Al-SBA-15 and Al-MCM-41, which are representative regular mesoporous materials, were synthesized using the methods suggested previously [21, 22]. Mesoporous MFI, which has both mesopores and micropores, was also synthesized using a method reported in a previous study [23]. γ -Al₂O₃ was purchased from Sigma-Aldrich. BET surface area analysis and NH₃ TPD were performed to investigate the pore structure and acid characteristics of the catalysts [21–23].

2.4. Rapid Pyrolysis Experiments. The noncatalytic pyrolysis of *Quercus variabilis* was carried out using a fixed-bed reactor. One can refer to a previous study [12] for detailed procedure. On the other hand, the noncatalytic and catalytic pyrolyses of *Quercus variabilis* were conducted using Py-GC/MS to examine the effects of catalytic reforming on the product distribution quickly. The reaction temperature and ratio of biomass/catalyst were 530°C and 1/1, respectively. One can refer to a previous report [12] for detailed procedure.

3. Results and Discussion

3.1. Thermal Analysis of *Quercus variabilis*. Figure 1 shows the thermal decomposition behavior of *Quercus variabilis*.

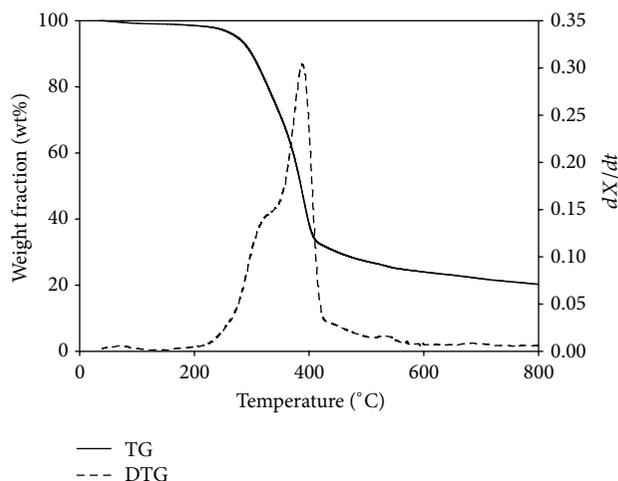


FIGURE 1: TG/DTG curves of *Quercus variabilis*.

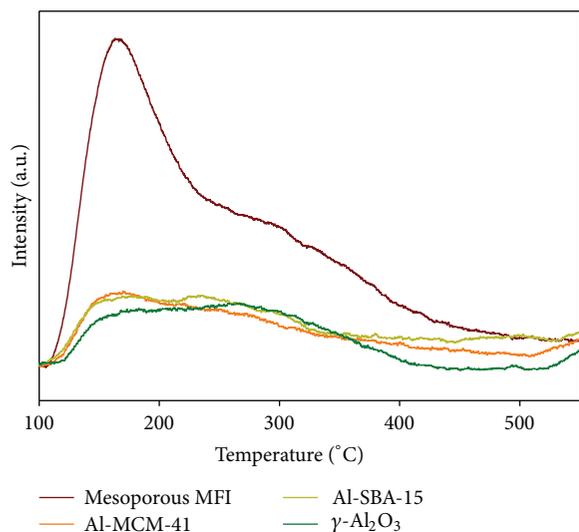
TABLE 1: Physical properties of catalysts.

| Material | S_{BET} (m ² /g) | V_{Total} (cm ³ /g) | Pore size (nm) |
|-------------------|--------------------------------------|---|----------------|
| Mesoporous MFI | 460 | 3.8 | 4.9 |
| Al-MCM-41 | 848 | 0.64 | 2.8 |
| Al-SBA-15 | 531 | 0.63 | 6.1 |
| γ -Alumina | 70 | 0.12 | 8.3 |

A shoulder peak indicating the decomposition of hemicellulose appeared around 300°C, whereas a peak representing the decomposition of cellulose appeared around 390°C. A wide peak for the decomposition of lignin is shown above 400°C. Generally, hemicellulose, which is amorphous with low crystallinity, is decomposed earlier than more crystalline cellulose [24]. Lignin is decomposed at higher temperature than hemicellulose and cellulose because of its characteristic aromatic network. The shoulder peak shown in Figure 1 indicates a considerable amount of hemicellulose contained in the biomass sample, suggesting significant production of acetic acid from its pyrolysis via the detachment of acetal functional groups [25].

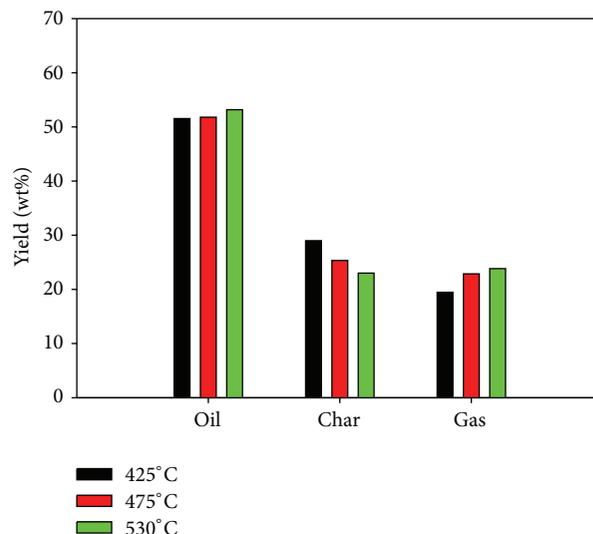
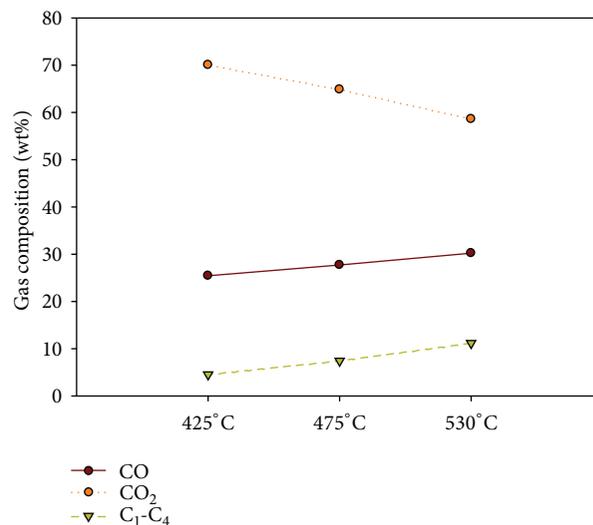
3.2. Characterization of Catalysts. The physical properties of the catalysts used in this study were summarized in Table 1. The specific surface areas of mesoporous MFI, Al-MCM-41, Al-SBA-15, and γ -Al₂O₃ were 460, 848, 531, and 70, respectively, whereas their pore sizes were 4.9, 2.8, 6.1, and 8.3, respectively. NH₃-TPD analysis showed that the order of acid site quantity was mesoporous MFI > Al-SBA-15 \approx Al-MCM-41 \approx γ -Al₂O₃ (Figure 2). Mesoporous MFI showed a peak representing strong acid sites at a high temperature of 400°C, whereas the other catalysts were shown to have only weak acid sites (represented by low-temperature peaks). This result indicates that mesoporous MFI is superior to the others in terms of the acid characteristics.

3.3. Rapid Pyrolysis of Cork Oak. Figure 3 shows the results of noncatalytic rapid pyrolysis of *Quercus variabilis*. Among the

FIGURE 2: NH_3 TPD of catalysts.

results obtained within the temperature range of 425–530 °C, the results obtained at 530 °C showed the largest bio-oil yield with the gas yield of about 20%. The char yield decreased with increasing temperature. This result implies that the decomposition of biomass to small-molecular-mass species is dominant over the biomass-to-char conversion at high temperature because of enhanced heat transfer to biomass sample particles. Figure 4 compares the gas compositions obtained at different pyrolysis temperatures. CO_2 was the most abundant gas species at all temperatures tested, whereas the fraction of hydrocarbon was the lowest. The fraction of CO_2 decreased with increasing temperature, whereas those of CO and $\text{C}_1\text{--C}_4$ hydrocarbons increased, indicating that decarbonylation, demethoxylation, and dealkylation are promoted at high temperature but decarboxylation is suppressed.

3.4. Catalytic Rapid Pyrolysis of *Quercus variabilis* Using Py-GC/MS. The results of catalytic rapid pyrolysis obtained using Py-GC/MS are shown in Figure 5. Hundreds of species contained in the product bio-oil were divided into 6 groups: acids (including acetic acid), oxygenates (including levoglucosan and ketones), furanics (including furfural and furans), (monocyclic) aromatics (including toluene and xylene), PAHs (including naphthalene and branched naphthalenes), and phenolics (including phenol, methoxy-phenol, and benzenediol). As shown in Figure 5, catalytic pyrolysis led to significantly different product distribution from that obtained from noncatalytic pyrolysis. In particular, mesoporous MFI, which has strong acid sites, led to a huge increase of the fraction of aromatics, which were hardly produced from noncatalytic pyrolysis. The fractions of PAHs and furans were also increased by catalysis, whereas those of oxygenates and phenolics, which were the main products of noncatalytic pyrolysis, were decreased by catalysis. Another product group whose fraction was reduced by catalysis was acids. The product compositions obtained over Al-MCM-41

FIGURE 3: Yield of pyrolysis of *Quercus variabilis*.FIGURE 4: Gas components during pyrolysis of *Quercus variabilis*.

and Al-SBA-15, which have only weak acid sites, were quite different from that obtained over mesoporous MFI. They also reduced the fractions of oxygenates and phenolics and increased the fraction of furanics but they did not promote the production of aromatics and PAHs. The fraction of acids was rather increased by catalysis over Al-MCM-41 or Al-SBA-15. Meanwhile $\gamma\text{-Al}_2\text{O}_3$ showed decrease of oxygenates. The difference between mesoporous MFI and the two nanoporous materials (Al-MCM-41 and Al-SBA-15) is attributed to the difference in their acid characteristics because their pore structure is not different a lot in that all of them have mesopores. However, the different activity of $\gamma\text{-Al}_2\text{O}_3$ may be due to its irregular pore geometry, low surface area, and acid characteristics. More detailed examination of the effects of acid characteristics of catalysts on the product composition follows.

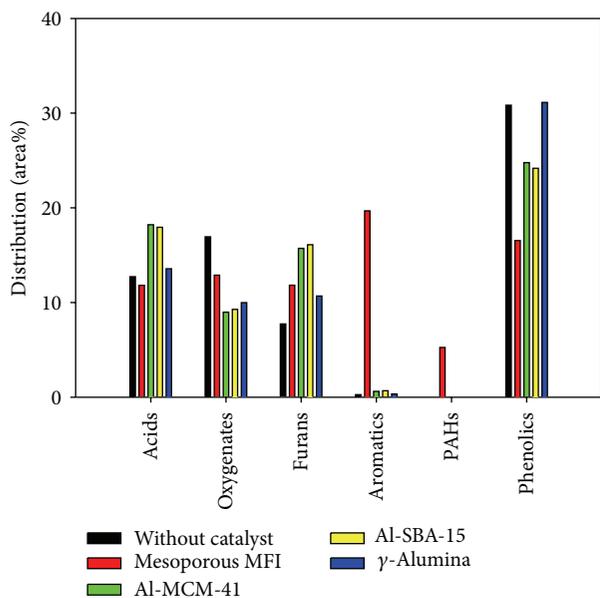


FIGURE 5: Product distribution of catalytic pyrolysis of *Quercus variabilis* over nanoporous catalysts.

Figure 6 shows the detailed species distribution of oxygenates. The main oxygenate species obtained from non-catalytic rapid pyrolysis was levoglucosan. Upon catalytic pyrolysis over any of the catalysts used in this study, however, levoglucosan was removed completely. All the catalysts used in this study had mesopores larger than 2 nm, into which levoglucosan (kinetic diameter: 0.67 nm [26]) can diffuse easily and undergo dehydration reaction on the acid sites. Apparently, this conversion of levoglucosan does not need strong acid sites because Al-MCM-41, Al-SBA-15, and γ -Al₂O₃, which have only weak acid sites, also removed levoglucosan completely. Conversely, HZSM-5, whose pores are smaller (ca. 0.56 nm) than levoglucosan molecule, did not remove levoglucosan in spite of its strong acid sites (private result). This demonstrates that the pore size is a more important factor than the strength of acid sites, determining the conversion of levoglucosan.

Figure 7 shows the detailed species distribution of furanic compounds. Compared to noncatalytic pyrolysis, catalytic pyrolysis resulted in higher fractions of alkyl furans and furfural. In particular, Al-SBA-15 and Al-MCM-41, which have only weak acid sites, led to a larger increase of the fraction of furanic compounds than mesoporous MFI with strong acid sites and γ -Al₂O₃ with irregular mesopores and lowest surface area. Increased production of furanic compounds is beneficial because they are important chemical intermediates. Therefore, in order to maximize the yield of furanic compounds, the pyrolysis process needs to be optimized using weak acid sites catalysts. Further researches are needed for this issue.

Figure 8 shows the detailed species distribution of aromatics. Aromatics are known to be produced from the reaction intermediates, such as furanics, phenolics, aldehydes, and esters, via dehydration, cracking, decarboxylation,

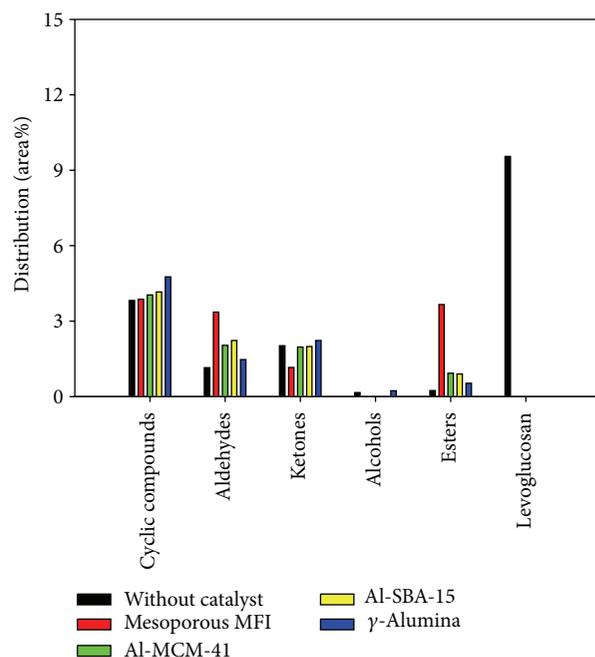


FIGURE 6: Product distribution of oxygenates via catalytic pyrolysis of *Quercus variabilis* over nanoporous catalysts.

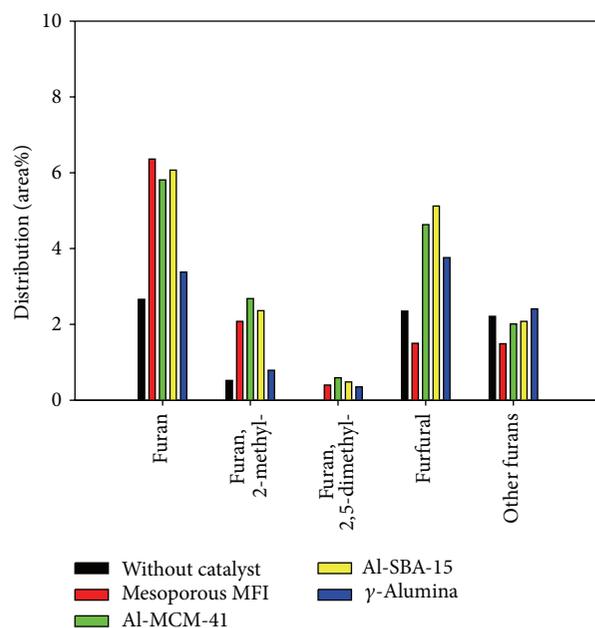


FIGURE 7: Product distribution of furans via catalytic pyrolysis of *Quercus variabilis* over nanoporous catalysts.

decarboxylation, oligomerization, and aromatization [27]. Because these reactions tend to take place more easily on strong Brønsted acid sites [27], mesoporous MFI led to the largest fraction of aromatics. Because of their weak acid sites, Al-SBA-15, Al-MCM-41, and γ -Al₂O₃ could not promote sufficiently the conversion of reaction intermediates (e.g.,

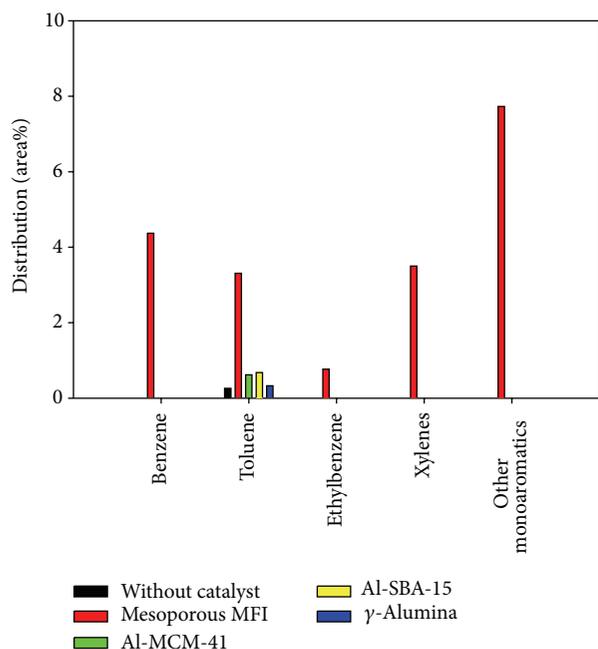


FIGURE 8: Product distribution of monoaromatics via catalytic pyrolysis of *Quercus variabilis* over nanoporous catalysts.

furans) to aromatics, resulting in high fraction of furanics and low fraction of aromatics.

The reduction of phenolics was also more profound in the case of mesoporous MFI because cracking, deoxygenation, and demethylation reactions required for the conversion of phenolics were promoted on strong acid sites.

4. Conclusions

Rapid pyrolysis and catalytic pyrolysis of *Quercus variabilis* were carried out for the first time. In the case of noncatalytic pyrolysis, the bio-oil yield increased with increasing temperature, which was attributed to enhanced heat transfer to biomass particle surface at high temperature. In the case of catalytic pyrolysis, the pore size and acid characteristics imposed large effects on the bio-oil composition. Mesoporous MFI, which has the highest strength and quantity of acid sites among the catalysts tested, showed the highest selectivity toward aromatics because dehydration, cracking, dealkylation, deoxygenation, oligomerization, and aromatization reactions were promoted on its strong acid sites. On the other hand, Al-SBA-15, Al-MCM-41, and γ -Al₂O₃, which have only weak acid sites, showed high selectivity toward furanic compounds.

Disclosure

Hyeon Koo Kang and In-Gu Lee are co-first authors.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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