Ex-situ Catalytic Pyrolysis of Korean Native Oak Tree over Microporous Zeolites

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Abstract
Ex-situ catalytic pyrolysis of a Korean native oak tree over microporous zeolites (HZSM-5, HBeta, and HY) was performed by using a fixed bed reactor. The effect of sample to catalyst ratio and reaction temperature was also investigated to optimize production conditions of high quality bio-oil. Among three catalysts, HZSM-5 showed the highest aromatic formation due to its proper pore size and strong acidity. Although HY and HBeta also showed the catalytic activity, they produced larger amounts of coke due to their larger pore size. The smaller ratio of the sample to the catalyst and higher reaction temperature were also required to maximize the yields of aromatic hydrocarbons via the catalytic pyrolysis of oak tree over HZSM-5.

Keywords: bio-oil, catalytic pyrolysis, oak tree, zeolite, aromatic hydrocarbons

1. Introduction

Worldwide energy security is being threatened by the fossil fuel shortage and unstable crude oil price[1-4]. Therefore, many countries are focusing on the development of alternative energy. Climate change and increased air contamination due to the intensive use of fossil fuel are also promoting the research for the renewable energy development. Among various kinds of renewable energy, biomass is being considered as the candidate energy source which can replace the fossil fuels[6-8].

Biomass pyrolysis is one of the thermal conversion techniques which can produce valuable byproducts in forms of gas, oil, and char under non-oxygen atmosphere at medium temperature (mainly from 400 to 600 °C). Many researchers have investigated the fast pyrolysis of biomass to obtain large amounts of high quality bio-oil because bio-oil can be transported and stored easily[5,9] and used as a fuel and/or chemical feedstock[3]. However, the actual use of bio-oil produced by the thermal pyrolysis of biomass is limited due to its low quality containing high oxygen content[3,10,11]. Therefore, additional process for the deoxygenation is required to upgrade the quality of biomass pyrolysis oil. Various kinds of reaction such as catalytic pyrolysis of biomass, hydrodeoxygenation of bio-oil, catalytic co-pyrolysis of biomass with plastics or alcohols have been suggested and investigated for improvement of the bio-oil quality[1-3,10-14]. In case of catalytic pyrolysis of biomass, various kinds of catalyst such as microporous zeolites (HZSM-5, HBeta, and HY) and mesoporous catalysts (Al-SBA-15, Al-MCM-41, and mesoporous MFI) were used to upgrade the bio-oil quality.
Although many researchers already reported the catalytic pyrolysis of various kinds of biomass, the catalytic pyrolysis research for Korean native wood species were rarely investigated. Recently, Kang et al.[15] reported the catalytic pyrolysis of the Korean native oak tree over mesoporous MFI and nanoporous materials (Al-MCM-41, Al-SBA-15, and Al(OH)₃). They obtained the highest yields for aromatic hydrocarbons from the catalytic pyrolysis reaction over mesoporous MFI catalysts. Although microporous zeolites are known to be effective catalysts for the catalytic pyrolysis of lignocellulosic biomass[13,16], the catalytic pyrolysis of a Korean native oak tree over microporous catalysts has never been reported, yet.

Therefore, the catalytic pyrolysis of the Korean native oak tree was investigated by applying HZSM-5, HBeta, and HY as the catalysts in this study. The effects of reaction conditions such as sample to catalyst ratio and reaction temperature on the catalytic reaction of oak tree were also investigated by reaction using a fixed-bed reactor and product analysis using gas chromatography/mass spectrometry (GC/MS), GC/flame ionization detector (FID) and thermal conductivity detector (TCD).

## 2. Materials and Methods

### 2.1. Oak tree

Oriental oak tree (*Quercus variabilis*), obtained from Korea Forest Research Institute, was used as the biomass sample in this study. The oak tree was ground by a knife milling device, sieved to make its particle size smaller than 1 mm and dried at 80 °C for 6 hours. Table 1 shows the results of proximate and ultimate analyses of oak tree after air dry.

### 2.2. Catalysts

Three kinds of commercially available zeolite catalyst, HZSM-5 (SiO₂/Al₂O₃ = 30), HBeta (SiO₂/Al₂O₃ = 38), and HY (SiO₂/Al₂O₃ = 30), were purchased from Zeolyst International. All of these catalysts were calcined at 500 °C under air for 5 hours. To compare the acidity of each catalyst, NH₃-TPD (temperature-programmed desorption of ammonia) analysis was carried out according to the method reported in the literature[16].

### 2.3. Thermogravimetric (TG) analysis

To know the thermal property of oak tree, TG analysis was performed using a TG analyzer (Pyris Diamond, Perkin Elmer Co.). About 2 mg of sample was heated from ambient temperature to 800 °C at a heating rate of 20 °C/min under 120 mL/min of nitrogen atmosphere.

## 3. Results and Discussion

### 3.1. Characterization of catalysts

The textural properties of HZSM-5, HBeta, and HY, supplied by the manufacturer of the catalysts, are shown in Table 3. HBeta and HY have large surface areas (710 m²/g for HBeta, 780 m²/g for HY) and pore sizes (ca. 0.67 nm for HBeta, ca. 0.74 nm for HY), compared to those of HZSM-5 (405 m²/g, ca. 0.55 nm).

The acidity of each catalyst obtained by NH₃-TPD analysis is shown in Figure 2. All catalysts had both weak and strong acid sites which can be monitored at around 200 and 400 °C. Among three catalysts, HZSM-5 had the largest NH₃-TPD curve area, followed in order by HBeta and HY. This indicates that HZSM-5 is the strongest catalyst among them in the aspect of the acid characteristics, followed in order by HBeta and HY.

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Table 1. Physico-chemical Characteristics of Korean Native Oak Tree (*Quercus variabilis*)

| Proximate analysis (wt%)[15] | Ultimate analysis (wt%) |
|-----------------------------|-------------------------|
| Moisture                    | C                       |
| Volatiles                   | H                       |
| Fixed carbon                | Oa                      |
| Ash                         | N                       |
|                             |                         |

* By difference

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Figure 1. Schematic diagram of a fixed bed reactor system[17].
Table 2. Detailed Analysis Conditions of GC/TCD, GC/FID, and GC/MS

| Instrument       | GC/MS                  | GC/TCD                          | GC/FID                          |
|------------------|------------------------|---------------------------------|---------------------------------|
| Column description | 7890A GC, Agilent technologies/5975C inert MSD, Agilent technologies | Carboxen 1000 (15 ft × 1/8 in) | HP-plot Al2O3/KCl (50 m × 0.32 mm × 8.00 µm) |
| Target compounds | Organic compounds in oil product | CO, CO2, CH4 in gas product | C1-C4 hydrocarbons in gas product |

Table 3. Physical Properties of Catalysts

| Catalyst | SiO2/Al2O3 (mole ratio) | BET Surface area (m²/g) | Pore size (nm) |
|----------|------------------------|-------------------------|---------------|
| HZSM-5   | 30                     | 405                     | 0.51 × 0.55   |
| HBeta    | 38                     | 710                     | 0.66 × 0.67   |
| HY       | 30                     | 780                     | 0.74 × 0.74   |

3.2. TG analysis of oak tree

Wood pyrolysis consists of the decomposition of hemicellulose, cellulose and lignin which are the lignocellulosic components of woody biomass. Hemicellulose is decomposed at the lowest temperature region (200-350 °C) due to its thermally unstable structure[1,15]. Subsequently, cellulose is decomposed rapidly in the narrow temperature range (350-400 °C). Meanwhile, lignin decomposition has the widest temperature region and is continued up to high temperature around 600 °C[18]. Figure 3 shows the TG and DTG curves of an oak tree. DTG curve of oak tree had the overlapped peak, which consists of a left shoulder peak (#1) and right tailing peak (#3) on both sides of main decomposition peak (#2). Each peak can be assigned as the decomposition of hemicellulose (#1), cellulose (#2) and lignin (#3). The overlapped peak shape of the oak tree DTG curve indicates that hemicellulose and cellulose have the overlapped decomposition temperature range. After the TG analysis, about 20% of solid residue remained in the sample cup.

3.3. Catalytic pyrolysis of oak tree

Figure 4(a) show the gas, oil, char, and coke yields obtained from the thermal and catalytic pyrolysis of oak tree at 530 °C. The yields of char were not changed by the use of catalysts because the amount of char in the ex-situ catalytic pyrolysis reaction is concluded by the thermal pyrolysis in the first reactor. Meanwhile, the yield of oil was decreased with the increase of gas and coke yield by the catalytic upgrading of vapor-phase pyrolysis products in the second reactor. This indicates that the main catalytic reactions of pyrolysis products are related to the catalytic cracking of condensable oil which produces small molecules oils, gas, and coke. Figure 4(b) shows the yields of CO, CO2, and light hydrocarbons obtained from the ex-situ catalytic pyrolysis of an oak tree at 530 °C. Compared to the thermal pyrolysis, the amount of CO and light hydrocarbons were greatly increased by the catalytic upgrading over all three catalysts. This indicates that decarbonylation and dealkylation of pyrolysis products of the oak tree are major catalytic reactions during catalytic upgrading. Catalytic pyrolysis of biomass involves various kinds of catalytic reaction such as dehydration, decarbonylation, decarboxylation, dealkylation and oligomerization of the primary pyrolysis products of lignocellulosic biomass components[19]. The overall catalytic activity is also differentiated by the properties of catalyst. For example, the pore size can be the important

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factor to enhance the selectivity for the target compounds. The amount of coke deposited in the pore of catalysts can also be different depending on the pore size of catalyst. Control of coke amount is the important factor on the catalytic pyrolysis because coke deposition is the main reason for the decrease of catalytic activity due to the poisoning of acid sites. As shown in Figure 4(a), their amounts deposited in each catalyst were highest on HY (30), followed by HBeta (38) and HZSM-5 (30) suggesting HBeta and HY can be deactivated faster than HZSM-5. Fast deactivation of HBeta than HZSM-5 was also found on the ex-situ catalytic pyrolysis of other biomass reported in our previous study[20].

Table 4 shows the detailed chemical distribution of the oil obtained from the thermal and catalytic pyrolysis of oak tree at 530 °C. In case of thermal pyrolysis, the specific pyrolyzates of lignocellulosic biomass components, such as acetic acid from hemicellulose, levoglucosan from cellulose, and phenols from lignin, were produced[6]. Most of them are the oxygen containing compounds. The amounts of oxygen containing compounds were decreased with the formation of aromatic hydrocarbons over all three catalysts. In case of HY, large amount of large molecular phenols such as 2,6-dimethoxy-4-(2-propenyl)-phenol were decreased from 3.54% to 0.47% and levoglucosan from 6.34% to

| No. | Compounds                                      | Without catalyst | HZSM-5 | HBeta | HY   |
|-----|------------------------------------------------|------------------|--------|-------|------|
| 1   | Acetic acid                                    | 10.81            | 3.02   | 9.93  | 12.79|
| 2   | 2-Propanone, 1-hydroxy-                        | 2.47             | 0.75   | 2.59  | 3.56 |
| 3   | Furfural                                       | 4.04             | 1.77   | 4.85  | 6.53 |
| 4   | 2-Furannethanol                                 | 1.86             | N/D^a  | N/D^a | N/D^a|
| 5   | 1,2-Cyclopentanone                              | 2.09             | 0.72   | 1.93  | 1.76 |
| 6   | Phenol                                         | 0.56             | 2.29   | 2.02  | 2.12 |
| 7   | Phenol, 2-methoxy-                             | 1.89             | 1.26   | 2.07  | 2.54 |
| 8   | Phenol, 2-methoxy-4-methyl-                    | 1.90             | 1.34   | 2.42  | 3.09 |
| 9   | 1,2-Benzenediol, 3-methoxy-                    | 1.85             | 1.56   | 2.56  | 2.34 |
| 10  | Phenol, 4-ethyl-2-methoxy-                     | 1.58             | 1.36   | 2.09  | 2.90 |
| 11  | 2-Methoxy-4-vinylphenol                        | 2.06             | 1.05   | 1.41  | 1.15 |
| 12  | Phenol, 2,6-dimethoxy-                         | 4.38             | 2.95   | 3.77  | 4.09 |
| 13  | Benzoic acid, 4-hydroxy-3-methoxy-             | 3.36             | 2.56   | 2.68  | 2.35 |
| 14  | 1,6-Anhydro-beta-D-glucopyranose (levoglucosan)| 6.34             | 1.10   | 2.56  | N/D^a|
| 15  | Benzene, 1,2,3-trimethoxy-5-methyl              | 1.51             | 1.07   | 1.72  | 1.13 |
| 16  | Phenol, 2,6-dimethoxy-4-(2-propenyl)-          | 3.54             | 1.34   | 0.64  | 0.47 |
| 17  | Toluene                                        | N/D^a            | 3.00   | 0.13  | 0.57 |
| 18  | Xylene                                         | N/D^a            | 12.86  | 2.24  | 2.21 |
| 19  | Naphthalene                                    | N/D^a            | 3.25   | 2.03  | 0.72 |
| 20  | Naphthalene, (di)methyl                        | N/D^a            | 12.43  | 11.97 | 8.67 |

* Not Detected as a GC/MS peak.

Figure 4. The yields of gas, oil, and char (a) and detailed gas yields (b) obtained from the thermal and catalytic pyrolysis of oak tree at 530 °C.
Table 5. GC/MS Peak area% of Bio-oil Produced from the Thermal and Catalytic Pyrolysis of Oak Tree over Different Amounts of HZSM-5 at 530 °C

| No. | Compounds                              | Without catalyst | HZSM-5 5/1 | HZSM-5 10/1 |
|-----|----------------------------------------|------------------|------------|-------------|
| 1   | Acetic acid                            | 10.81            | 3.02       | 11.42       |
| 2   | 2-Propanone, 1-hydroxy-               | 2.47             | 0.75       | 2.87        |
| 3   | Furfural                               | 4.04             | 1.77       | 3.74        |
| 4   | 2-Furannmethanol                       | 1.86             | N/Da       | N/Da        |
| 5   | 1,2-Cyclopentanedione                  | 2.09             | 0.72       | 2.05        |
| 6   | Phenol                                 | 0.56             | 2.29       | 1.13        |
| 7   | Phenol, 2-methoxy-                    | 1.89             | 1.26       | 1.65        |
| 8   | Phenol, 2-methoxy-4-methyl-            | 1.90             | 1.34       | 2.31        |
| 9   | 1,2-Benzenediol, 3-methoxy-           | 1.85             | 1.56       | 4.23        |
| 10  | Phenol, 4-ethyl-2-methoxy-             | 1.58             | 1.36       | 1.55        |
| 11  | 2-Methoxy-4-vinylphenol                | 2.06             | 1.05       | 1.45        |
| 12  | Phenol, 2,6-dimethoxy-                | 4.38             | 2.95       | 4.07        |
| 13  | Benzoic acid, 4-hydroxy-3-methoxy-     | 3.36             | 2.56       | 4.69        |
| 14  | 1,6-Anhydro-β-D-glucopyranose (levoglucosan) | 6.34        | 1.10       | 5.08        |
| 15  | Benzene, 1,2,3-trimethoxy-5-methyl      | 1.51             | 1.07       | 1.40        |
| 16  | Phenol, 2,6-dimethoxy-4-(2-propenyl)- | 3.54             | 1.34       | 0.52        |
| 17  | Toluene                                | N/Da             | 3.00       | 0.66        |
| 18  | Xylene                                 | N/Da             | 12.86      | 3.01        |
| 19  | Naphthalene                            | N/Da             | 3.25       | 0.85        |
| 20  | Naphthalene, (di)methyl                | N/Da             | 12.43      | 4.89        |

* Not Detected as a GC/MS peak.

Figure 5. The yields of gas, oil, and char (a) and detailed gas yields (b) obtained from the thermal and catalytic pyrolysis of oak tree over different amount of HZSM-5 at 530 °C.

0%. The high elimination of large molecular pyrolyzates over HY can be explained by the easier diffusion of reactant molecules into the large pore of HY. The catalytic reaction over HBeta produced larger amounts of aromatic hydrocarbons than HY. Stronger activity in the formation of aromatic hydrocarbons over HBeta than that over HY can be explained by the stronger acidity of HBeta than that of HY as shown in Figure 2. As expected, HZSM-5 which has the strongest acidity among three catalysts showed the highest aromatic formation.

Especially, the selectivity of xylene over HZSM-5 was quite higher than those over HY and HBeta. Higher selectivity of BTEXs over HZSM-5 can be explained by the proper pore size of HZSM-5 for the production of mono-aromatic[13,21]. To know the effect of the amount of catalyst, sample to catalyst (S/C) ratio was increased from 5/1 to 10/1 by decreasing the amount of catalyst from 0.6 g to 0.3 g for the catalytic pyrolysis of oak tree (3 g). The catalytic pyrolysis over 0.3 g of HZSM-5 showed higher...
Table 6. GC/MS Peak area% of Bio-oil Produced from the Thermal and Catalytic Pyrolysis of Oak Tree over HZSM-5 at Different Reaction Temperatures

| No. | Compounds                        | Area%     |
|-----|----------------------------------|-----------|
|     |                                  | ZSM-5 5/1| ZSM-5 5/1| ZSM-5 5/1|
| 1   | Acetic acid                      | 3.02      | 5.49     | 9.89     |
| 2   | 2-Propanone, 1-hydroxy-          | 0.75      | 4.05     | 4.16     |
| 3   | Furfural                         | 1.77      | 3.66     | 3.95     |
| 4   | 2-Furannmethanol                 | N/Da      | N/Da     | N/Da     |
| 5   | 1,2-Cyclopentanedinone           | 0.72      | 1.71     | 3.95     |
| 6   | Phenol                           | 2.29      | 1.71     | 0.92     |
| 7   | Phenol, 2-methoxy-               | 1.26      | 2.47     | 3.32     |
| 8   | Phenol, 2-methoxy-4-methyl-      | 1.34      | 2.07     | 2.90     |
| 9   | 1,2-Benzenediol, 3-methoxy-      | 1.56      | 1.83     | 1.80     |
| 10  | Phenol, 4-ethyl-2-methoxy-       | 1.36      | 2.25     | 2.07     |
| 11  | 2-Methoxy-4-vinylphenol          | 1.05      | 1.71     | 1.68     |
| 12  | Phenol, 2,6-dimethoxy-           | 2.95      | 5.09     | 6.4      |
| 13  | Benzoic acid, 4-hydroxy-3-methoxy-| 2.56      | 4.26     | 5.07     |
| 14  | 1,6-Anhydro-beta-D-glucopyranose (levoglucosan) | 1.10 | 1.62 | 1.34 |
| 15  | Benzene, 1,2,3-trimethoxy-5-methyl | 1.07 | 2.54 | 3.18 |
| 16  | Phenol, 2,6-dimethoxy-4(2-propeny)- | 1.54 | 0.64 | 0.75 |
| 17  | Toluene                          | 3.00      | 1.29     | 0.38     |
| 18  | Xylene                           | 12.86     | 6.36     | 3.06     |
| 19  | Naphthalene                      | 3.25      | 2.05     | 1.12     |
| 20  | Naphthalene, (di)methyl          | 12.43     | 8.39     | 4.06     |

* Not Detected as a GC/MS peak.

Figure 6. The yields of gas, oil, and char (a) and detailed gas yields (b) obtained from the catalytic pyrolysis of oak tree over HZSM-5 at different reaction temperatures.

yield of oil and lower yields of gas and coke than those over 0.6 g of HZSM-5 (Figure 5(a)). The yields of CO and light hydrocarbons were also smaller over 0.3 g of HZSM-5 (Figure 5(b)). The amounts of aromatic produced over 0.3 g of HZSM-5 were also quite lower than those over 0.6 mg of HZSM-5 (Table 5). These indicate that catalytic activity for aromatics formation is declined by decreasing the amount of HZSM-5 applied for the catalytic pyrolysis of an oak tree. Small amount of HZSM-5 also influenced the composition of phenolic compounds. The selectivity for mono-phenol was also decreased by applying smaller amounts of HZSM-5 together with the higher selectivity for high molecular methoxy-alkyl phenols. This indicates that the demethoxylation and dealkylation of methoxy-alkyl phenols, the important catalytic pyrolysis reactions of lignin over HZSM-5, are also highly influenced by the amount of catalyst.

Reaction temperature also influenced the catalytic pyrolysis of an oak tree over HZSM-5 (Figure 6). The catalytic pyrolysis at the higher
temperature (530 °C) produced the lower char and higher gas yields than those obtained at the lower temperature. Meanwhile, the yields of oil and coke obtained at the different reaction temperature were not so different. Interestingly, the yields for CO and light hydrocarbons were dramatically increased by increasing the reaction temperature. These phenomena explain that the reaction efficiency for catalytic upgrading of pyrolysis products over HZSM-5 is increased at the higher reaction temperature by the increase of catalytic reactions such as cracking and decarboxylation.[20]

Table 6 shows the GC/MS area% of bio-oils obtained from the catalytic pyrolysis of an oak tree at different reaction temperatures. As expected with the results shown in Figure 6, the selectivity for aromatic hydrocarbons was increased by applying the higher reaction temperature. At the higher reaction temperature, the selectivity for methoxy-alkyl phenols was decreased together with the increased selectivity of monophenol. These results indicate that the aromatization, dealkylation, and demethylation reactions are promoted by increasing the reaction temperature.[20,22]

4. Conclusions

Ex-situ catalytic pyrolysis of a Korean native oak tree over HZSM-5 was performed using a two stage fixed bed reactor. HZSM-5 showed the strongest activity for aromatic formation due to its higher acidity and proper pore size than HY and HBeta. HY having the largest pore size among the catalysts applied in this study showed the greatest cracking efficiency for large molecular pyrolysis products such as levoglucosan and methoxy-alkyl phenols due to its large pore size; however, larger amount of coke was produced. HY and HBeta produced smaller amounts of aromatics than HZSM-5 due to their lower acidity. The aromatic formation efficiency over HZSM-5 was also highly influenced by the sample to catalyst ratio and reaction temperature. It was concluded that sufficiently high temperature (530 °C) and proper sample to catalyst ratio (5/1) have to be supplied to the catalytic pyrolysis system to increase the yields of aromatic hydrocarbons.

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