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Catalytic Pyrolysis of *Pinus densiflora* Over Mesoporous Al₂O₃ Catalysts

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The thermal and catalytic pyrolysis of *Pinus densiflora* (*P. densiflora*) were performed to test the catalytic cracking efficiency of two mesoporous Al_2O_3 catalysts with different surface areas. Thermogravimetric analysis (TGA) of *P. densiflora* showed that the differential TG (DTG) peak heights obtained from catalytic pyrolysis were smaller than those of non-catalytic pyrolysis due to the conversion of the reaction intermediates to coke. Pyrolyzer-gas chromatography/mass spectrometry analysis/flame ionization detection (Py-GC/MS/FID) suggested that using the Al_2O_3 catalysts, the yields of phenols and levoglucosan decreased with a concomitant increase in the yields of aldehydes, alcohol, ketones, and furans. Between the two catalysts, Al_2O_3 -B prepared by spray pyrolysis showed higher cracking efficiency than Al_2O_3 -A prepared by hydrothermal method because of its larger surface area.

Keywords: *Pinus densiflora*, Mesoporous Al₂O₃, Catalytic Pyrolysis.

1. INTRODUCTION

Owing to the decreased energy source and climate change due to global warming, the development of renewable energy has become an important worldwide research area. Biomass is a candidate renewable energy source that can produce gas, liquid, and solid products via proper thermal conversion technologies.^{1–17} Pyrolysis is an appropriate method for producing large quantities of bio-oil from many kinds of biomass. On the other hand, the use of bio-oil obtained from the pyrolysis of biomass is limited by its low quality with high acidity, corrosiveness, water content, and oxygen content.^{2, 5, 6} To overcome the limitations of bio-oil, catalytic pyrolysis has been studied extensively and many kinds of catalysts, such as zeolites and metal catalysts, have been applied.¹⁸⁻²¹ Al₂O₃ is a low-cost catalyst with potential use for the catalytic pyrolysis of biomass. Nevertheless, its low catalytic efficiency is considered a problem.

One of the possible ways to increase the catalytic activity is to increase the pore size, which can be very

effective on catalytic pyrolysis because the pyrolysis products of biomass contain considerable amounts of large molecular compounds.^{21, 22}

In this study, the catalytic pyrolysis of *Pinus densiflora* (*P. densiflora*) over two types of mesoporous catalyst with different properties was investigated by thermogravimetric analysis (TGA) and pyrolyzer-gas chromatography/mass spectrometry/flame ionization detector (Py-GC/MS/FID).

2. EXPERIMENTAL DETAILS

2.1. Samples

P. densiflora, obtained from the National Institute of Forest Science in Korea, was cryo-milled using a ball milling device with liquid nitrogen, dried at 80 °C for 4 hours, and sieved to make a size between 75 and 200 μ m.

2.2. Catalysts

Two types of mesoporous alumina were synthesized using the procedures reported elsewhere.^{23,24} Mesoporous alumina-A (Al₂O₃-A) was synthesized by stirring a mixture solution of cetyltrimethylammoniumbromide

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(CTAB), distilled water, and ethanol at 60 °C for 20 min. Subsequently, an ammonia solution (30 wt.% NH₃) and aluminum tri-sec-butoxide were added and stirred at 60 °C for 3 hours. The precipitates after stirring were collected using a vacuum filter and dried at 100 °C for 24 h. Al₂O₃-A was finally obtained by calcination of the precipitates at 600 °C for 6 h. Mesoporous alumina-B (Al₂O₃-B) was synthesized using a spray pyrolysis process. For this, aluminum nitrate and CTAB (CTAB to aluminum molar ratio: 0.3) were used. Spray pyrolysis process was carried out at 700 °C under an air flow of 20 L/min and calcined at 550 °C for 3 h.

The Brunauer, Emmett, and Teller (BET) surface areas of the synthesized catalysts were characterized using a Belsorp mini II (MicrotracBel, Japan) for nitrogen sorption and the crystal structures were examined by wide angle X-ray diffraction (XRD, Rigaku D-MAX 3) using Cu-K α radiation at 40 kV and 40 mA.

2.3. TG Analysis

TGA (Pyris Diamond, Perkin Elmer) was used to determine the thermal properties of the thermal and catalytic pyrolysis of *P. densiflora*. For this, 6 mg of *P. densiflora* was heated from ambient temperature to 600 °C at a heating rate of 20 °C/min under flowing nitrogen at 140 mL/min. For catalytic pyrolysis, 6 mg of Al_2O_3 catalyst was mixed together with *P. densiflora*.

2.4. In-Situ Catalytic Pyrolysis

A multi-shot Py (EGA/PY-3030D, Frontier Laboratories Ltd.)-GC/MS/FID (7890A/5975C inert, Agilent Technologies) was used to identify the products from the thermal and catalytic pyrolysis of P. densiflora. P. densiflora (1 mg) or a mixture of *P. densiflora* and catalyst (2 mg) in a SUS sample cup was free-fallen into a pre-heated pyrolyzer heater (400 °C and 600 °C). The chemicals emitted from the pyrolyzer were transferred to a capillary column (UA-5, 30 m \times 0.25 mm \times 0.25 μ m; Frontier Laboratories Ltd.) via a GC split/splitless inlet and cyro-focused (2 min) at the front part of the column using a MicroJet cryo trap (MJT-1030E, Frontier Laboratories Ltd.). After cyro-focusing, the chemicals were separated in a column according to the GC oven program, from 40 °C (5 min) to 320 °C (10 min) at a heating rate 20 °C/min. Each MS peak on the chromatograms was identified by the NIST 8th (National Institute of Standards and Technology, USA) and/or F-search (F-search all in one, Frontier Laboratories Ltd.) libraries. Py-GC/FID analysis was also conducted to compare the amounts of the products by a comparison of the peak area of each chemical.

3. RESULTS AND DISCUSSION

3.1. Characterization of Mesoporous Al₂O₃ Catalysts

The results of N_2 -sorption indicated that the surface area of Al_2O_3 -B (260 m²/g) was much larger than that of Al_2O_3 -A

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(177 m²/g). Both catalysts showed a type IV hysteresis loop indicating the presence of mesopores. The wide-angle XRD pattern of mesoporous Al₂O₃-A synthesized in this study showed the three typical peaks of cubic γ -Al₂O₃ (Fig. 1(a)). Al₂O₃-B (Fig. 1(b)) showed a broad diffraction peak, indicating that the alumina particles might have disordered warm- or sponge-like mesostructures.^{23, 24}

3.2. TG Analysis

Figure 2 presents the differential TG (DTG) curves showing the thermal and catalytic pyrolysis of *P. densiflora* over Al_2O_3 catalysts at a heating rate of 20 °C/min. The decomposition of *P. densiflora* started at approximately 200 °C, and then decomposed rapidly to 400 °C. Although the maximum decomposition temperatures (T_{max})s of the thermal and catalytic pyrolysis of *P. densiflora* were similar, their peak heights were quite different. Compared to noncatalytic pyrolysis, catalytic pyrolysis showed lower peak heights due to the formation of solid coke on the external surface or in the pores of the catalysts.



Figure 1. XRD patterns of mesoporous alumina (a)Al $_2O_3$ -A, (b) Al $_2O_3$ -B.

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Figure 2. DTG curves obtained from thermal and catalytic TG analysis of *P. densiflora* over different mesoporous Al_2O_3 catalysts.

3.3. Pyrolysis of P. densiflora

Figure 3 shows the absolute peak areas for each chemical group obtained from the non-catalytic pyrolysis of *P. densi-flora* at 400 °C and 600 °C. As expected, the amounts of oxygen-containing compounds were higher in the products obtained from pyrolysis at 400 and 600 °C.^{25–27} Compared to 400 °C, large amounts of aldehydes, alcohols, and phenols were obtained due to the increased cracking efficiency and the additional decomposition of lignin at the higher temperatures.²⁸ The content of aromatics were also Sun increased by non-catalytic pyrolysis at 600, °C.⁴⁵

3.4. In-Situ Catalytic Pyrolysis

Figure 4 shows the product distributions obtained from the thermal and catalytic pyrolysis of *P. densiflora* over the Al_2O_3 catalysts at 400 °C and 600 °C, respectively. Compared to non-catalytic pyrolysis, catalytic pyrolysis resulted in increased amounts of aldehydes, alcohol, ketones, furans together with decreased quantities of phenols and anhydrosugars due to the catalytic effect. Lee et al.²⁹ reported increased yields of furan and decreased



Figure 3. FID peak area distribution for the chemical groups obtained from the pyrolysis of *P. densiflora* at 400 and 600 °C.





Figure 4. FID peak area distribution for the chemical groups obtained from catalytic pyrolysis of *P. densiflora* over Al_2O_3 catalysts at (a) 400 and (b) 600 °C.

yields of anhydrosugars, such as levoglucosan. Between the two Al_2O_3 catalysts, Al_2O_3 -B showed higher catalytic activity with a further decrease in the quantities of phenols and anhydrosugars produced. The aromatics were also increased further using Al_2O_3 -B. The higher catalytic activity of Al_2O_3 -B can be explained by its larger BET surface area than Al_2O_3 -A.

Table I lists the detail peak areas of the major products, which can be classified into aromatics, phenols and anhydrosugars, obtained from the catalytic pyrolysis of *P. densiflora* over both Al_2O_3 catalysts at 600 °C. Compared to non-catalytic pyrolysis, catalytic pyrolysis over Al_2O_3 -A produced smaller amounts of branched phenols (cresols, guaiacols, eugenols, and vanillin) and levoglucosan. The amounts of these branched phenols and levoglucosan were decreased further using Al_2O_3 -B together with an increase in the mono-phenol yield, which also

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Table I. The detailed peak areas for phenolics and levoglusosan obtained from the thermal and catalytic pyrolsysis of *P. densiflora* at 600 °C. (Units: FID peak area $\times 10^{-6}$).

Catalyst	No catalyst	Al ₂ O ₃ -A	Al ₂ O ₃ -B
Phenol	16.3	20.9	25.2
Cresols	18.8	16.6	17.9
Guaiacols	93.0	82.6	73.5
Eugenols	62.0	56.5	34.6
Vanillin	34.0	33.8	12.6
Levoglucosan	157.7	123.3	19.8

indicates a much higher catalytic cracking efficiency of Al_2O_3 -B than Al_2O_3 -A.

4. CONCLUSION

The non-catalytic pyrolysis of *P. densiflora* revealed a higher cracking efficiency at a higher temperature. Compared to non-catalytic pyrolysis, catalytic pyrolysis produced smaller amounts of aldehydes, alcohol, ketones, and furans as well as lower levels of phenols and anhydrosugars. Between two catalysts, Al_2O_3 -B showed higher catalytic cracking efficiency than Al_2O_3 -A due to its larger BET surface area.

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