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Stabilization of bio-oil over a low cost dolomite catalyst

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Abstract−A low cost alkaline catalyst of dolomite ($CaMg(CO_3)_2$) was used to stabilize acacia sawdust bio-oil mixed with methanol. The upgrading efficiency was evaluated in terms of the total acid number (TAN) and viscosity. A change in the dolomite calcination temperature from 700 to 900 °C led to a significant change in the TAN and viscosity of the methanol-added bio-oil. Dolomite activated at higher temperatures had larger amounts of active CaO and MgO species due to the enhanced decarboxylation of calcium and magnesium carbonates. An increase in the dolomite content (1-5 wt%) decreased the TAN value of bio-oil remarkably. A thermal aging test of the methanol-added bio-oil upgraded using dolomite (calcined at 900 °C) at 50 °C for 24 h was carried out by storing the bio-oil at 80 °C for one week. Although the TAN value increased after the aging process, it was still lower than the TAN of raw bio-oil. In addition, increasing the methanol content (10-30 wt%) decreased the TAN and viscosity of the bio-oil significantly.

Keywords: Dolomite, CaO/MgO, Bio-oil Stabilization, Bio-oil Aging, TAN, Viscosity

INTRODUCTION

Pyrolysis oil (bio-oil) contains a wide variety of reactive oxygenated compounds, including phenols, acids, aldehydes, ketones, alcohols, and sugars, that can react during bio-oil storage and make it an unstable oil that cannot be used directly as an engine fuel [1-4]. Blending bio-oil with alcohols, such as ethanol and methanol, leads to bio-oil stabilization during the storage period [5]. The immediate effect of alcohol addition to bio-oil is a decrease in viscosity due to bio-oil dilution, decreased reactivity of the components present in bio-oil, and a reduction of chain growth through chemical reactions between the bio-oil components and alcohol [6]. In addition, esterification and acetalization reactions that occur between alcohols and the acid and aldehyde compounds of bio-oil, respectively, can reduce the acidity of bio-oil and improve its stability [7]. The catalytic upgrading of alcohol-added bio-oil facilitates these reactions, leading to the enhanced stability of bio-oil. Although acid catalysts, such as ion exchange resins, have been used in the stabilization of alcohol-added bio-oil [7-9], alkaline catalysts, such as dolomite, have been rarely used in the upgrading of bio-oil. Valle et al. [10] examined the upgrading of ethanol-added bio-oil using dolomite in a continuous process; a bio-oil with a high selectivity of phenol (86.4%) and alkylphenols (5.3%) was obtained. They reported that reactive components, such as carboxylic acids, sugars, esters, aldehydes, and guaiacols, were converted to less reactive compounds of acetones and alkylphenols through a series of ketonization, esterification, demethylation, demethoxylation, and dehydration reactions. The thermal treatment of dolomite (natural mineral) elevates its activity due to the formation of CaO and MgO species through the decarboxylation of calcium and magnesium carbonates. Calcium and magnesium oxides can act as active sites for reactions, such as cracking/decomposition, esterification and reforming, leading to improved stability of bio-oil. For example, supported and unsupported CaO catalysts were used for biodiesel production through the transesterification of vegetable oils and methanol [11-16]. MacLeod et al. [17] used the CaO- and MgO-supported metal oxide catalysts for the transesterification of rapeseed oil and methanol to biodiesel.

In this study, acacia sawdust bio-oil was upgraded using methanol and dolomite catalysts calcined at different temperatures. The catalyst efficiency in bio-oil upgrading was evaluated in terms of the viscosity and total acid number (TAN) of the bio-oil. The effects of the catalyst and methanol loading on the TAN and viscosity of bio-oil were examined. The upgraded bio-oil was also stored at 80 °C for one week, and the changes in TAN and viscosity were monitored to determine its stability.

EXPERIMENTAL

Acacia sawdust pyrolysis oil (bio-oil) was prepared using a bubble fluidized bed (BFB) reactor operating at 500 °C under a nitrogen atmosphere. The biphasic bio-oil consisted of aqueous and organic parts at a ratio of 1 : 1 w/w. Methanol (MeOH, >99.9%, Sigma

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Aldrich) was added to the biphasic bio-oil (10-30 wt% methanol) and the mixture was treated at 50 °C and 350 rpm for 24 h in a three-neck flask coupled with a reflux condenser, stirrer, and thermocouple. Before the experiments, the dolomite (Sungshin Co., Ltd.) catalyst (1-5 wt%) was calcined at different temperatures (700, 800, and 900 °C) for 2 h under air. The Brunauer, Emmett, and Teller (BET) surface area, and pore volume were determined by nitrogen isothermal adsorption-desorption. The crystalline phase and elemental analysis of the dolomite catalyst was performed by X-ray diffraction (XRD) and inductively coupled plasma atomic emission spectroscopy (ICP-AES), respectively. After the upgrading reaction, the reactor was cooled to room temperature and the solid catalyst was separated from the liquid bio-oil by vacuum filtration. The bio-oil (before and after the upgrading process) was analyzed for its viscosity and TAN according to the national standard methods of KS M ISO 3104:2008 and KS M ISO 6618:2003, respectively. An aging test of the upgraded methanol-added bio-oil was carried out at 80 °C for one week, and the aged bio-oil was then analyzed as described above.

RESULTS AND DISCUSSION

The TAN, viscosity, and water content of the acacia sawdust bio-oil were 96.74 gKOH/g, 47.26 mm^2/s, and 30.60 wt%, respectively (Fig. 1). The treatment of methanol-added bio-oil (10 wt% methanol) at 50 °C and 350 rpm for 24 h led to a decrease in TAN, viscosity, and water content of the bio-oil to 80.34 gKOH/g, 14.04 mm^2/s, and 25.44 wt%, respectively. The dilution effect of methanol may cause a decrease in TAN, viscosity, and water content. Methanol addition can also suppress the aging reactions, such as polymerization, which leads to the formation of heavy molecules and an increase in viscosity [8,18]. The esterification and acetalization of methanol with acids and aldehydes in bio-oil, respectively, can be another reason for the decrease in TAN and viscosity of methanol-added bio-oil. The catalytic upgrading of methanol-added bio-oil was conducted using dolomite as a catalyst. The effects of the calcination temperature of dolomite on the TAN, viscosity, and water content of methanol-added bio-oil were examined. The content of methanol and dolomite in bio-oil was fixed to 10 and 5 wt%, respectively. As shown in Fig. 1, a decrease in the TAN and water content of the bio-oil was negligible when dolomite was calcined at 700 °C, whereas the bio-oil viscosity was increased by 26%. In contrast, bio-oil upgrading using the dolomite catalysts calcined at 800 and 900 °C resulted in a significant decrease in TAN and an increase in viscosity. In addition, the water content of the bio-oil increased slightly after being upgraded over the dolomite activated at 800 and 900 °C. XRD of the dolomite calcined at different temperatures revealed no structural changes in the dolomite after calcination at 700 °C, whereas the calcination at 800 and 900 °C led to the formation of CaO and MgO species due to the decomposition of $CaCO_3$ and $MgCO_3$, respectively. In addition, the pore volume and surface area of the dolomite catalyst were increased by calcination at higher temperatures. Table 1 lists the physicochemical characteristics of the dolomite catalysts. The enhanced catalytic activity of dolomite can be linked to the appearance of CaO

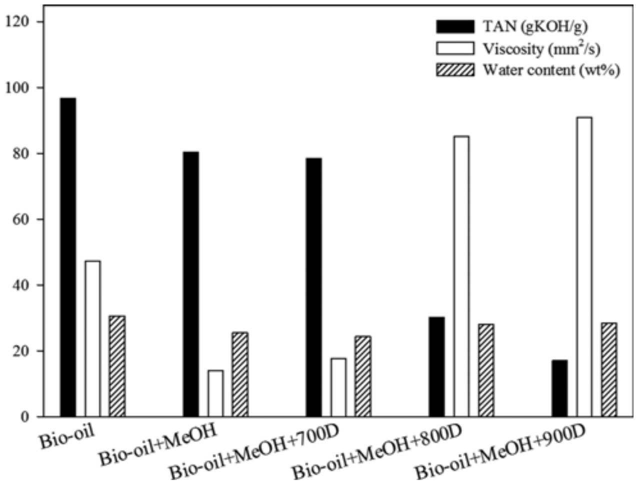

Fig. 1. Effect of dolomite calcination temperature on TAN, viscosity and water content of methanol-added bio-oil (10 wt% methanol) upgraded at 50 °C for 24 h. 700D, 800D and 900D: dolomite calcined at 700, 800 and 900 °C.

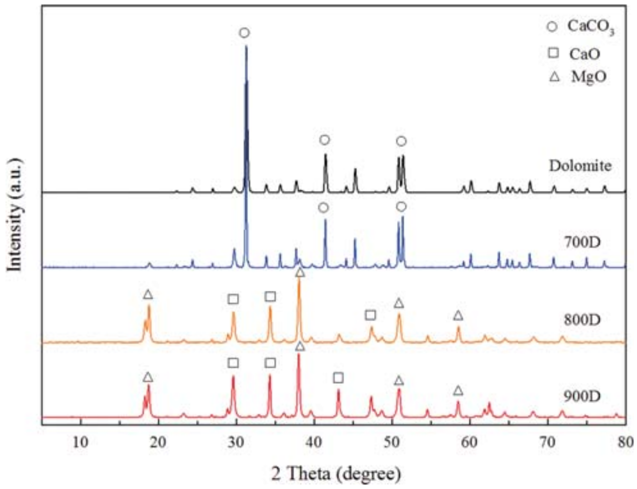

Fig. 2. XRD patterns of dolomite calcined at different temperatures. 700D, 800D and 900D: dolomite calcined at 700, 800 and 900 °C.

Table 1. Physicochemical properties of dolomite activated at different temperatures

Catalyst	Ca (wt%)	Mg (wt%)	BET surface area (m^2/g)	Pore volume (cm^3/g)
Uncalcined dolomite	22.74	11.1	0.68	0.004
Dolomite calcined at 700 °C	24.33	14.45	2.58	0.022
Dolomite calcined at 800 °C	35.8	21.08	14.2	0.069
Dolomite calcined at 900 °C	36.69	21.21	6.9	0.021

Table 2. Content of Ca and Mg in the methanol-added bio-oil upgraded using dolomite calcined at different temperatures

Feed condition	Ca (wt%)	Mg (wt%)
Bio-oil+MeOH[a]	0.014	0.001
Bio-oil+MeOH[a]+700D[b]	0.377	0.183
Bio-oil+MeOH[a]+800D[c]	2.257	1.068
Bio-oil+MeOH[a]+900D[d]	2.369	1.110

[a] 10 wt% methanol
[b] Dolomite calcined at 700 °C
[c] Dolomite calcined at 800 °C
[d] Dolomite calcined at 900 °C

and MgO species, which react with the bio-oil components and produce calcium and magnesium hydroxides. The vigorous reaction of CaO with water produces $Ca(OH)_2$, which can be ionized to Ca^{2+} and OH^-. The hydroxide ions can react with the acid compounds of the bio-oil, leading to a decrease in TAN. Similarly, MgO can react with water to produce $Mg(OH)_2$. In addition, MgO may react with the carboxylic acids of bio-oil, such as acetic acid to form magnesium acetate, which can be reacted further with MgO and water to form magnesium hydroxide [19]. Elemental analysis of the upgraded bio-oil by ICP-AES revealed an increase in the calcium and magnesium contents, indicating a reaction of CaO and MgO with the compounds present in bio-oil (Table 2). The ICP results of the dolomite calcined at different temperatures also showed that the Ca and Mg content in dolomite increased with increasing calcination temperature, leading to an increase in the calcium and magnesium content of bio-oil. The esterification of methanol with the acid compounds in bio-oil, which were catalyzed by CaO and MgO species, could be another cause of the decrease in the TAN of methanol-added bio-oil [11-17]. The lowest TAN value was obtained using dolomite calcined at 900 °C, which has the highest concentrations of CaO and MgO species. The increase in the viscosity of bio-oil might be due to the production of high molecular weight species through reactions between the organic components of bio-oil catalyzed by CaO and MgO. Furthermore, the increased water content could be due to esterification/acetalization reactions between methanol and the acid/aldehyde compounds of bio-oil giving water and esters/acetals.

The methanol content in the bio-oil influences the catalytic activity of the dolomite catalyst calcined at 900 °C, as shown in Fig. 3. The catalytic upgrading of methanol-added bio-oil (with a methanol content of 10-30 wt%) at 50 °C for 24 h using the dolomite generally decreased the TAN, and a maximum reduction of 94% was achieved using 30 wt% methanol. In contrast, the addition of 10 wt% methanol to the bio-oil increased the viscosity of bio-oil considerably. A further increase in methanol content to 20 and 30 wt%, however, decreased the viscosity of bio-oil due to both a dilution effect and suppression of the aging reactions, such as polymerization, which results in high molecular weight species and high viscosity. A thermal aging test of the raw bio-oil was also carried out by storing the bio-oil at 80 °C for one week. The TAN of the raw bio-oil was increased after the aging process, whereas its viscosity decreased. The aging test of the methanol-added bio-oil upgraded using dolomite showed that the increase in TAN and viscosity was far less significant in the bio-oil mixed with 20 and 30 wt% of methanol. Although an increase in the methanol content increases the stability of bio-oil, an increase in the amount of solvent may not be desirable from an economic point of view.

To examine the effects of the catalyst content on TAN and viscosity of the bio-oil, the bio-oil was upgraded at 50 °C for 24 h using different loadings of dolomite calcined at 900 °C (1, 2, 3, and 5 wt%). The stability of the bio-oils upgraded using different catalyst contents was also tested through a thermal aging process. No considerable change in the TAN and viscosity of the bio-oil upgraded over 1 wt% dolomite was observed after the aging process (Fig. 4). In contrast, the TAN of the bio-oil decreased progressively with increasing catalyst loading from 2 wt% to 5 wt%, and the TAN of the upgraded bio-oil increased after the thermal aging process. On the other hand, with 3 and 5 wt% dolomite, the increased TAN value of the upgraded bio-oil after the aging process was still lower than that of the raw bio-oil. In contrast to the TAN, increasing the catalyst loading from 1 to 5 wt% led to a progressive increase in

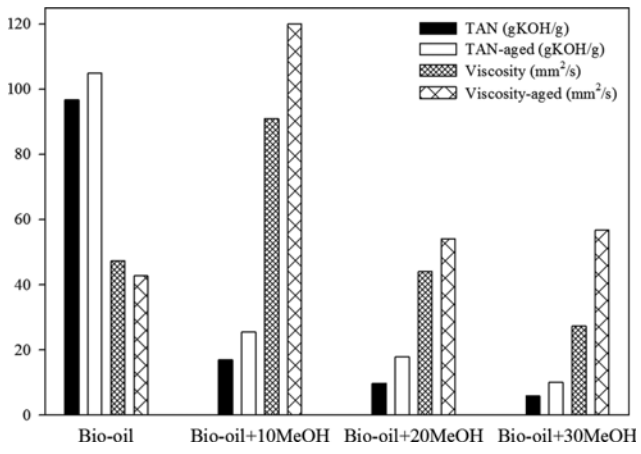

Fig. 3. Effect of methanol content (10-30 wt%) on TAN and viscosity of bio-oil upgraded at 50 °C for 24 h using dolomite calcined at 900 °C.

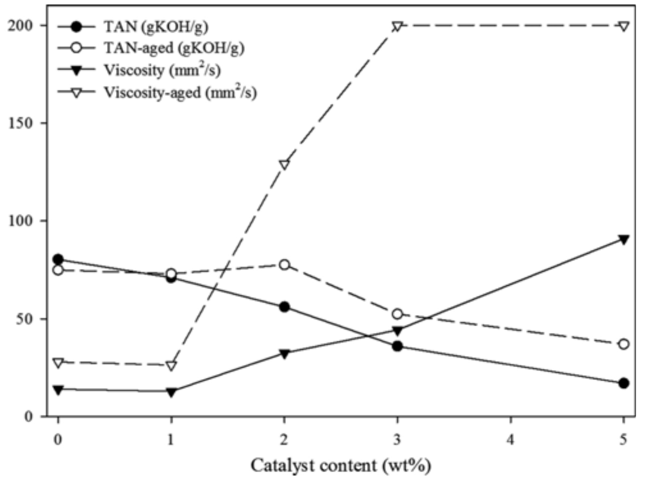

Fig. 4. Effect of dolomite content on TAN and viscosity of methanol-added bio-oil upgraded at 50 °C for 24 h.

the viscosity of bio-oil; larger amounts of catalyst can accelerate the chemical reactions, leading to the production of high molecular weight species and a corresponding increase in bio-oil viscosity. The use of 2 and 3 wt% dolomite led to a remarkable increase in the viscosity of aged bio-oil, whereas the viscosity of aged bio-oil was relatively constant at catalyst loadings from 3 to 5 wt%.

CONCLUSIONS

In the catalytic upgrading of methanol-added bio-oil using dolomite, increasing the calcination temperature of the catalyst to 900 °C led to the largest decrease in the TAN value of bio-oil due to the increased amounts of catalytic active species of CaO and MgO. The large reduction of bio-oil TAN was attributed to the reactions of CaO and MgO with bio-oil components, such as water and carboxylic acids, as well as enhanced esterification between methanol and the acid compounds of bio-oil. A remarkable decrease in the TAN of bio-oil was also achieved by increasing the dolomite content from 1 to 5 wt%, and the increased TAN values of the upgraded bio-oils after the aging process (storage at 80 °C for one week) were still lower than those of the raw bio-oil. On the other hand, the catalytic upgrading of the methanol-added bio-oil using 1-5 wt% of dolomite increased the bio-oil viscosity due to the enhanced catalytic reactions, leading to the formation of high molecular weight species. Although the bio-oil upgraded using 2 and 3 wt% dolomite led to a remarkable increase in viscosity after the aging process, the viscosity of the aged bio-oil was relatively constant at catalyst contents ranging from 3 to 5 wt%.

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