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Upgrading of pyrolysis bio-oil using WO_3/ZrO_2 and Amberlyst catalysts: Evaluation of acid number and viscosity

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Abstract−Tungstated zirconia (WO_3/ZrO_2 with WO_3 loadings of 9.9 (WZ9.9), 15.5 (WZ15.5), and 15.7 wt% (WZ15.7)) and Amberlyst (15, 35, 36, 39 and 45) catalysts were employed to upgrade pyrolysis bio-oil of acacia sawdust through an esterification reaction using methanol at atmospheric pressure and room temperature or 80 °C. The upgrading efficiency was evaluated by measuring the total acid number (TAN) and viscosity. The viscosity and TAN of the resulting upgraded bio-oil were found to be dependent on the calcination temperature of the WO_3/ZrO_2 catalysts. At room temperature, the largest decrease in viscosity and TAN of the bio-oil and methanol mixture was obtained using WZ9.9 tungstated zirconia calcined at 900 °C. An increase in reaction temperature to 80 °C improved the flowability and TAN of the methanol-added bio-oil using WZ9.9 activated at 900 °C. The product distribution of the bio-oil upgraded using methanol revealed esterification to be the dominant reaction pathway under the reaction conditions of this study. When the ether extracted bio-oil was upgraded at 80 °C using methanol over catalysts, the Amberlyst catalysts were found more effective than tungstated zirconia catalysts in enhancing the esterification reaction and reducing TAN.

Keywords: Bio-oil, Upgrading, Esterification, Viscosity, Total Acid Number (TAN)

INTRODUCTION

Many efforts have been made to find appropriate renewable energy processes to replace fossil fuels and relieve global warming [1-4]. Bio-oil obtained from the pyrolysis of biomass is an interesting substitution for depleted fossil fuels and can be used as a raw material for the production of valuable chemicals [5-7]. Bio-oil, however, has a complicated composition consisting of more than 400 different organic compounds, such as acids, phenols, aldehydes, ketones, alcohols, ethers, and furans [8,9]. The presence of a variety of reactive compounds in bio-oil makes it chemically an unstable liquid with high viscosity, high corrosiveness, and low heating value [10,11]. In addition to its complicated composition, the high content of water (15-30 wt%) and oxygen (30-40 wt%) in bio-oil limits its direct application as a fuel [5,8,12,13]. Therefore, bio-oil upgrading is essential to make it stable before being used as liquid fuel or chemical product [14-16]. Thus far, bio-oil upgrading has been carried out using a range of technologies, such as hydrotreating, catalytic cracking, steam reforming, esterification, and emulsification [17-19].

One of the important ways for upgrading bio-oil is to stabilize it by diluting with solvents, such as alcohols. Thus far, methanol and ethanol have mainly been used for bio-oil stabilization. The immediate effects of solvent addition to bio-oil are a reduction of its viscosity and an increase in its heating value. The decrease in bio-oil viscosity by solvent addition is caused by the physical dilution of bio-oil, reduced reactivity of the compounds present in bio-oil and the suppressed chain growth due to the chemical reactions between the solvent and bio-oil components [16,20]. Enhanced heating value of the mixture of bio-oil and solvent could be due to the higher heating value of the solvent compared to bio-oil [16]. The addition of solvents, such as alcohols, into bio-oil can improve its acidity and stability through esterification (Eq. (1)) and acetalization (Eq. (2)) between an alcohol with acids and aldehydes, respectively [6,19,21,22]. Use of acid catalysts with Brønsted acidity can improve the esterification and acetalization of bio-oil. Both homogeneous and heterogeneous acidic catalysts can be used for bio-oil upgrading. The use of solid acid catalysts, such as ion exchange resins, could be more interesting than the use of homogeneous acid catalysts because of the easy separation of the catalyst, the final upgraded bio-oil product, and catalyst reusability [23]. Ion exchange resins of Amberlysts with a low usage temperature of ≤120 °C are considered efficient catalysts for bio-oil stabilization through esterification and acetalization. The strong Brønsted acidity and reusability of Amberlyst catalysts as well as being environmentally benign and commercially available make them quite useful for bio-oil upgrading. Weerachanchai et al. [24] used Amberlyst 15 to upgrade

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Table 1. Physical properties of Amberlyst solid acid resin catalysts

Product name	Surface area (m^2/g)	Pore size (Å)	Concentration of acid sites (eq/kg)	Maximum operating temperature (°C)
Amberlyst 15	53	300	4.70	120
Amberlyst 35	50	300	5.20	150
Amberlyst 36	33	240	5.40	150
Amberlyst 39	32	230	5.00	130
Amberlyst 45	49	190	≥2.95	170

palm shell bio-oil with methanol through esterification at 60 °C; 13.3% esterification without a catalyst was enhanced fivefold using 5 wt% Amberlyst 15. Palm fatty acid distillate was esterified to biodiesel (97% yield) using methanol and Amberlyst 15 at 60 °C [25]. Li et al. [6] used Amberlyst 70 at 70-170 °C for the esterification and acetalization of bio-oil produced from the pyrolysis of mallee woody biomass.

$$R_1COOH+R\text{-}OH \leftrightarrow R_1COOR+H_2O \quad (1)$$

$$R_1CHO+2R\text{-}OH \leftrightarrow R_1CH(OR)_2+H_2O \quad (2)$$

In this study, bio-oil obtained from the pyrolysis of acacia sawdust was upgraded using methanol and commercial catalysts of WO_3/ZrO_2 and Amberlyst under low operating conditions of atmospheric pressure and room temperature or 80 °C. To the best of the authors' knowledge, there are no reports of the upgrading of pyrolysis bio-oil through esterification using tungstated zirconia catalysts. The viscosity and TAN were determined to evaluate the efficiency of the catalysts in bio-oil upgrading. The effects of the calcination temperature for the preparation of WO_3/ZrO_2 catalysts on bio-oil upgrading at room temperature were investigated. The most efficient WO_3/ZrO_2 catalyst for bio-oil upgrading at room temperature was used in bio-oil treatment at 80 °C. Liquid-liquid extraction of bio-oil using ether as a solvent was carried out to separate the compounds in the bio-oil with similar functional groups for further upgrading using methanol and the WO_3/ZrO_2 and Amberlyst catalysts at 80 °C. Qualitative analysis of the crude and upgraded bio-oil was performed by gas chromatography/mass spectrometry (GC/MS) to estimate the reaction mechanisms of bio-oil upgrading.

MATERIALS AND METHODS

1. Materials

Bio-oil obtained from Daekyung ESCO Co., Ltd. in the Republic of Korea was produced from the pyrolysis of acacia sawdust at 500 °C using a bubble fluidized bed (BFB) reactor. The bio-oil was composed of two phases of EP (electrostatic precipitator; oil-like phase) and a quencher (water like phase) at a ratio of 3 : 7 w/w. The water content of the quencher and EP phases was >60% and <10%, respectively. The EP phase of the pyrolysis bio-oil was categorized as EP oil (A), EP oil (B) and EP oil (C) based on the date of production. Methanol (MeOH, >99.9%) and ether (99.5%) were purchased from Sigma Aldrich and SAMCHUN, respectively. WO_3/ZrO_2 (WZ9.9 (WO_3 9.9%), WZ15.5 (WO_3 15.5%), and WZ15.7 (WO_3 15.7%)) catalysts were purchased from MEL chemicals. Before the experiments, the WO_3/ZrO_2 catalysts were calcined for 2 h and pelletized to a 1.0-1.5 mm diameter. The calcination temperature of the WZ9.9 and WZ15.5 samples was optimized in the range, 600-900 °C, because the calcination temperature affects the crystal shape of the WO_3/ZrO_2 catalyst. Calcination temperatures of 600 and 700 °C were not tested for the WZ15.7 sample because it had been calcined at 800 °C before purchase. Therefore, WZ15.7 was only calcined at 800 and 900 °C. The Amberlyst solid acid resin catalysts (Amberlyst 15 (wet), Amberlyst 35 (wet), Amberlyst 36 (wet), Amberlyst 39 (wet), and Amberlyst 45 (dry)) were purchased from Dow Chemical. Table 1 lists the physical properties of the Amberlyst catalysts. All the Amberlyst catalysts were dried overnight at 110 °C and before application.

2. Catalyst Characterization

An automated gas sorption system (TriStar, Micromeritics) was used for the isothermal (−196 °C) adsorption/desorption of nitrogen to determine the surface area and pore size distribution of the zirconia-supported tungsten (WO_3/ZrO_2) catalyst samples using the Brunauer-Emmett-Teller (BET) equation and the Barrett-Joyner-Halenda (BJH) method, respectively. Prior to analysis, all catalyst samples were degassed in a vacuum at 200 °C for 2 h. X-ray dif-

Fig. 1. Raw bio-oil and EE bio-oil.

fraction (XRD) of the WO_3/ZrO_2 catalysts were recorded using a D/Max 2000 V/PC X-ray diffractometer equipped with a Cu Kα radiation source at 40 kW and 20 mA.

3. Ether Extraction

To mix the chemicals with similar functional groups present in the two phases of the bio-oil (EP and quencher) and to remove the solid phase and mass transfer limitation between the two phases of bio-oil, ether extraction of bio-oil (EE bio-oil) was carried out using a bio-oil to ether ratio of 1 : 3 w/w (Fig. 1). The ether soluble compounds of bio-oil were extracted using a rotary evaporator at 70 °C.

4. Bio-oil Upgrading

A 500 ml three-neck flask equipped with a thermocouple, stirrer, and reflux condenser was used as the bio-oil upgrading reactor. The bio-oil, methanol, and catalyst were loaded inside the reactor, which then was heated with a heating mantle. The reaction was at room temperature or 80 °C and a stirring speed of 350 rpm for 3 h or 24 h. After the reaction, the reactor was cooled to ambient temperature and the solid catalysts were separated from the liquid bio-oil by passing the product through a sieve with the openings of ≤100 μm.

5. Product Analysis

The viscosity and the total acid number (TAN) of the upgraded bio-oil were measured. The viscosity was measured at 40 °C according to the KS M ISO 3104:2008 (national standard). The TAN values for the bio-oil samples were determined based on KS M ISO 6618:2003 (national standard). The product distribution of the raw and upgraded bio-oil was evaluated using gas chromatography/mass spectrometry (GC/MS 7890A Agilent Technologies). An ultra-alloy-5 column (30 m×250 μm×0.25 μm) was employed and the GC was equipped with a split injector at 300 °C and a split ratio of 10 : 1. Pure helium was used as the carrier gas at a flow rate of 1 ml/min. The GC oven temperature program was as follows: 40 °C for 4 min, 40-200 °C at 5 °C/min, 200-300 °C at 20 °C/min, and 300 °C for 10 min. Compound identification was carried out using the NIST (National Institute of Standards and Technology) library.

Table 2. Viscosity and TAN of EP oils produced from pyrolysis of acacia sawdust at different dates

	EP oil (A)	EP oil (B)	EP oil (C)
Viscosity (mm^2/s)	71.68	310.40	>500
TAN (mgKOH/g)	71.73	78.90	89.92

Table 3. Viscosity, TAN and water content of EP oil, quencher oil and EE bio-oil

	EP oil (C)	Quencher oil	EE bio-oil
Viscosity (mm^2/s)	>500	1.33	61.58
TAN (mgKOH/g)	89.92	40.31	156.54
Water content (wt%)	7	62	10

RESULTS AND DISCUSSION

1. Bio-oil Properties

Table 2 lists the viscosity and TAN of the EP oils of the acacia sawdust bio-oil used in this study. The liquid-liquid extraction of bio-oil using ether was used to remove the undesirable compounds of pyrolytic lignin oligomers considered as the main cause for catalyst deactivation in the bio-oil upgrading process. According to the GC/MS chromatograms (Fig. 2) of EP oil (C), quencher oil, ether soluble and insoluble phases, efficient extraction of acetic acids, phenols, and guaiacols was achieved from raw bio-oil using the ether solvent. The pyrolytic sugars were removed effectively from the ether extracted bio-oil (EE bio-oil). Table 3 lists the viscosity, TAN and water content of the two phases of raw bio-oil (EP and quencher) and ether-extracted bio-oil. The removal of heavy compounds of pyrolytic sugars and lignin oligomers resulted in a remarkable decrease in bio-oil viscosity. Moreover, an increased TAN of the EE bio-oil could be due to the high separation of acids from the bio-oil by an ether solvent.

2. Characteristics of Catalysts

Table 4 summarizes the physicochemical properties of the zir-

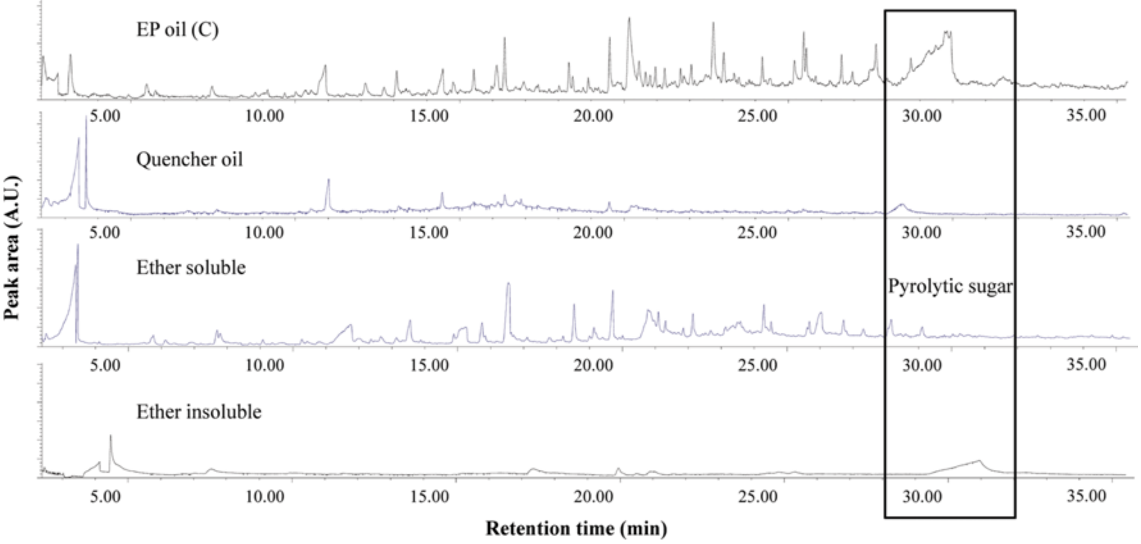

Fig. 2. GC/MS chromatograms of EP oil (C), quencher oil, ether soluble, and ether insoluble phases.

Table 4. Physicochemical properties of WO_3/ZrO_2 catalysts

Catalyst	WO_3 content (wt%)	Calcination temperature (°C)	Surface area (m^2/g)	Total pore volume (cm^3/g)	Pore size (Å)
WZ9.9	9.9	600	101.85	0.20	77.88
		700	76.65	0.19	97.08
		800	61.35	0.18	117.68
		900	34.16	0.14	160.45
WZ15.5	15.5	600	86.10	0.29	133.22
		700	86.10	0.29	165.86
		800	52.41	0.25	192.75
		900	38.79	0.21	212.31
WZ15.7	15.7	800	53.45	0.24	181.11
		900	37.96	0.17	179.95

conia-supported tungsten (WO_3/ZrO_2) catalysts calcined at different temperatures. An evaluation of the surface area, total pore volume, and pore size showed that the surface area and total pore volume decreased with increasing calcination temperature, while the pore size exhibited an increasing trend with increasing calcination temperature (in the case of WZ15.7, pore size was almost constant at the two calcination temperatures of 800 and 900 °C). The increasing pore sizes of the WO_3/ZrO_2 catalysts with increasing calcination temperature could be due to collapse of the initial porous structure of the catalysts at high temperatures. Pore sizes larger than 2 nm confirmed the mesoporous structure of all the WO_3/ZrO_2 catalysts.

Fig. 3 shows XRD patterns of the WO_3/ZrO_2 catalysts calcined at different temperatures in the range, 600-900 °C. The narrow XRD

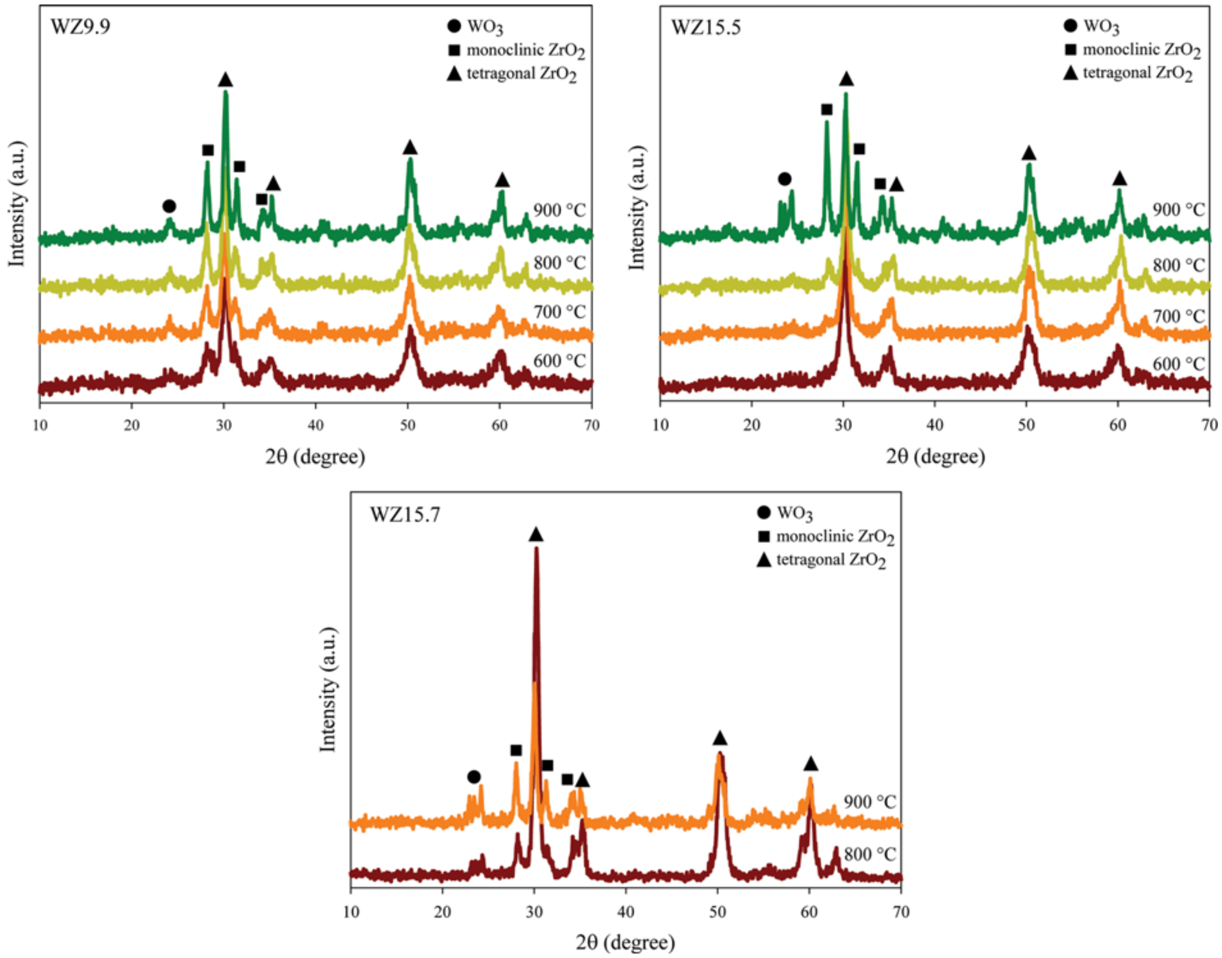

Fig. 3. XRD patterns of WO_3/ZrO_2 catalysts calcined at different temperatures.

peaks indicate the crystallinity of the WO_3/ZrO_2 catalysts. All the samples exhibited XRD peaks for both monoclinic and tetragonal zirconia at high calcination temperatures. No monoclinic phase of zirconia was observed in the WZ15.5 sample calcined at low temperatures of 600 and 700 °C. An increase in the calcination temperature led to the formation of the monoclinic form of ZrO_2 from the tetragonal form of ZrO_2. At calcination temperatures lower than 800 °C, there were no XRD peaks for tungsten crystallites, showing that tungsten species were highly dispersed on zirconia. The increase in calcination temperature resulted in the formation of detectable WO_3 phases at 2θ value of 23°. The increase in WO_3 loading from 9.9 to 15.7 wt% stabilized the tetragonal phase of zirconia. XRD of WZ9.9 and WZ15.5 showed that the crystallinity of the tetragonal phase of zirconia was stabilized by increasing the calcination temperature. In contrast, in WZ15.7, the sharpness of the tetragonal ZrO_2 peaks decreased with increasing calcination temperature.

3. Catalytic Activity

3-1. Effect of Calcination Temperature of WO_3/ZrO_2 Catalysts on Bio-oil Upgrading at Room Temperature

To improve the properties of raw bio-oil, methanol was added to the EP oil (A) at 10 wt% of EP oil, and the mixture was treated at room temperature for 3 h. An evaluation of the viscosity and TAN of the methanol-added EP oil showed that both viscosity and TAN were reduced by the addition of methanol (Table 5). Methanol addition could suppress the aging reactions, such as polymerization, which results in heavy molecular weight compounds and high viscosity. In addition, the dilution effect of methanol could be another cause of the remarkable decrease in viscosity. The catalytic performance of the WO_3/ZrO_2 catalysts (WZ9.9, WZ15.5, and WZ15.7) activated at different calcination temperatures (600-900 °C) was studied in the upgrading of blended bio-oil (mixture of EP oil (A) and methanol) at room temperature for 3 h. As shown in Table 5, the optimal calcination temperatures for the WZ9.9 and WZ15.5 catalysts for the minimum viscosity and TAN of blended bio-oil were 900 and 600 °C, respectively. In contrast, there was no optimal value for a calcination temperature of WZ15.7 catalyst due to the increase in both the viscosity and TAN of the methanol-added bio-oil using this catalyst calcined at 800 and 900 °C. Considering the efficiency of the three types of tungstated zirconia catalysts (WZ9.9, WZ15.5 and WZ15.7) for the decrease in viscosity and TAN of the blended bio-oil, WZ9.9 calcined at 900 °C, which resulted in the lowest viscosity and TAN values, was employed for further study on bio-oil upgrading. The improved catalytic activity of WZ9.9 at a high calcination temperature of 900 °C could be due to the presence of acidic WO_3 species as well as the tetragonal and monoclinic forms of zirconia (refer to the XRD analysis results in Fig. 3).

Table 5. Effect of calcination temperature of WO_3/ZrO_2 catalysts on bio-oil upgrading at room temperature for 3 h

		Viscosity (mm^2/s)	TAN (mgKOH/g)
EP oil (A)		71.68	71.73
Without catalyst[a]		21.97	65.08
Catalyst	Calcination temperature (°C)	Viscosity (mm^2/s)	TAN (mgKOH/g)
WZ9.9[b]	600	21.04	68.46
	700	20.37	64.46
	800	20.01	64.58
	900	18.96	61.70
WZ15.5[b]	600	19.45	62.65
	700	19.62	67.77
	800	19.94	65.87
	900	21.83	66.04
WZ15.7[b]	800	30.66	68.31
	900	27.76	68.93

[a] EP oil (A)+10 wt% MeOH

[b] EP oil (A)+10 wt% MeOH+3 wt% catalyst

3-2. Bio-oil Upgrading Using WO_3/ZrO_2 (WZ9.9) at 80 °C

The catalytic activity of the tungstated zirconia catalyst (WZ9.9, calcined at 900 °C) on the decrease in viscosity and TAN of bio-oil (EP oil (B)) was investigated at 80 °C and 24 h reaction time. The addition of 10 wt% methanol to the EP oil decreased the viscosity by 41.71% (Fig. 4). Methanol addition to crude bio-oil decreases the both initial viscosity of bio-oil and its increasing rate [16,20]. The reduced increasing rate of viscosity using methanol could be due to physical dilution, change in the microstructure of the bio-oil, and the suppression of chain growth by the methanol reaction with bio-oil components [16,20]. The application of 5 wt% of WO_3/ZrO_2 catalyst for the upgrading of the methanol-added bio-oil decreased the viscosity significantly. The viscosity was decreased by 56.58% at 80 °C and a reaction time of 24 h, whereas this reduction was only 13.70% at room temperature and 3 h. Further increase in catalyst content (10 wt%) did not reduce the viscosity significantly. The TAN of methanol-added bio-oil (73.00 mgKOH/g) was decreased to 70.13 and 64.86 mgKOH/g using the 5 and 10 wt% catalyst, respectively. The TAN of the blended bio-oil was reduced from 65.08 to 61.70 mgKOH/g by upgrading at room temperature for 3 h. Qualitative analysis of the product distribution of the upgraded bio-oil shows that the selectivity of acids, which

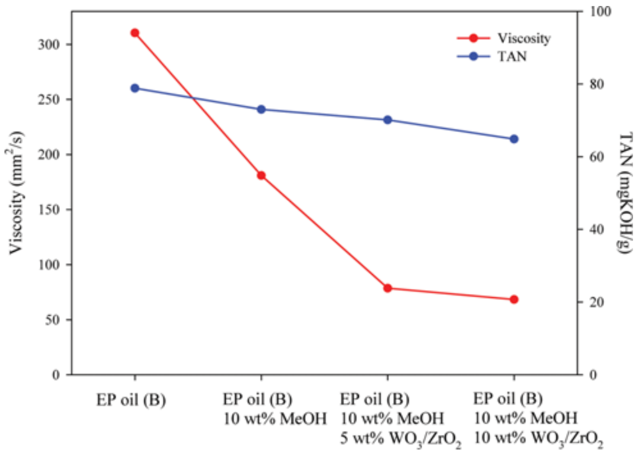

Fig. 4. Viscosity and TAN of EP oil (B) upgraded using WO_3/ZrO_2 catalyst at 80 °C for 24 h.

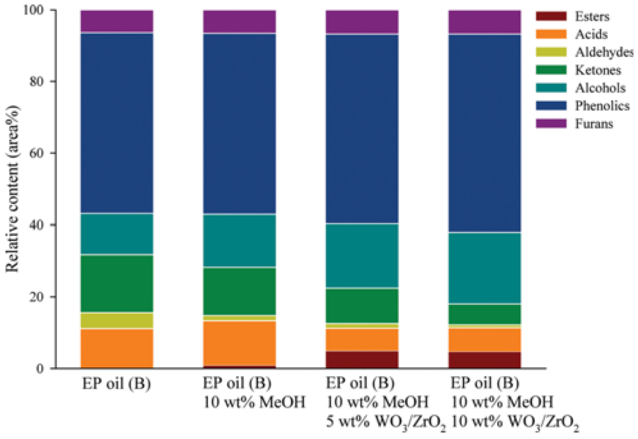

Fig. 5. Product distribution of the EP oil (B) upgraded using WO_3/ZrO_2 catalyst at 80 °C for 24 h.

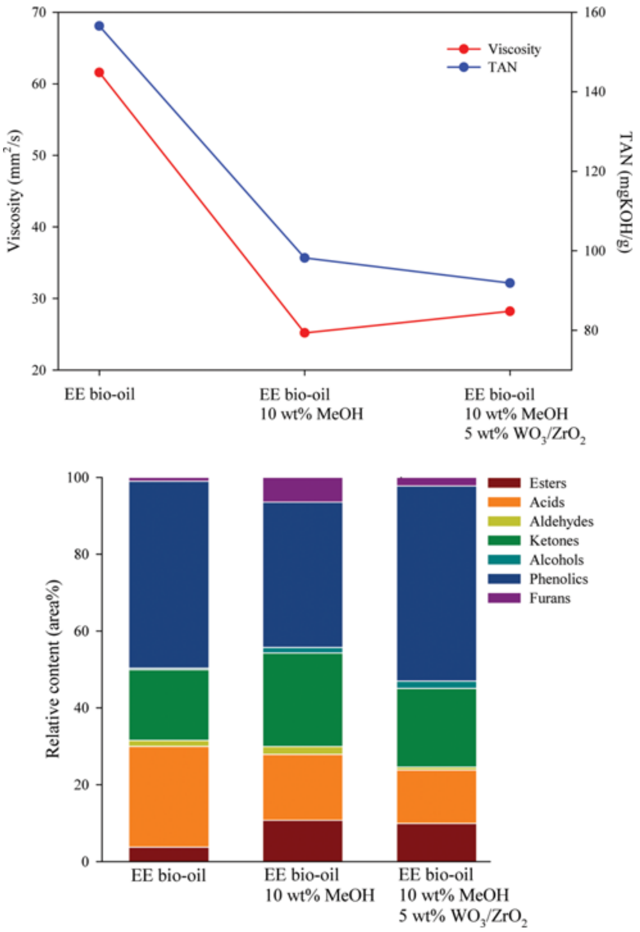

Fig. 6. Viscosity, TAN and product distribution of the EE bio-oil upgraded using 5 wt% of WO_3/ZrO_2 catalyst at 80 °C for 24 h.

are supposed to be products of the aging process, was decreased favorably by the addition of methanol to bio-oil (Fig. 5). In contrast, methanol addition preferably increased the selectivity of the esters because the acid compounds of bio-oil, such as carboxylic acids, could be involved in an esterification reaction with methanol. Bio-oil upgrading through esterification could reduce its corrosiveness by decreasing the content of carboxylic acids, and also prevent other reactions, such as the homopolymerization of aldehydes and polymerization of phenol/aldehyde catalyzed by carboxylic acids [24]. Compared to the non-upgraded bio-oil, the selectivity of the aldehydes and ketones (carbonyl groups) in the upgraded bio-oil was reduced using methanol, indicating that methanol reacts with aldehydes and ketones. The use of 5 wt% tungstated zirconia improved esterification remarkably in the upgrading process of methanol-added bio-oil. Further increases in catalyst content to 10 wt% did not alter the distribution of esters. On the other hand, the selectivity of carbonyl groups was reduced preferably by increasing the catalyst content.

3-3. Upgrading of EE Bio-oil Using WO_3/ZrO_2 (WZ9.9) at 80 °C

The liquid-liquid extraction of bio-oil using ether as a solvent was carried out to separate the organic acids, esters, aldehydes, ketones, alcohols, furans, and phenolics for further upgrading at 80 °C for 24 h. The addition of 10 wt% methanol to the EE bio-oil led to a decrease in viscosity and TAN (Fig. 6). Catalytic upgrading of the mixture of methanol and EE bio-oil using the WO_3/ZrO_2 (WZ9.9, calcined at 900 °C) catalyst resulted in an increase in viscosity and decrease in TAN. The increase in bio-oil viscosity could be due to the formation of large molecular compounds from the reactions of organic compounds present in the methanol-added EE bio-oil catalyzed by the tungstated zirconia catalyst. In fact, the separation of bio-oil components using ether facilitated the chemical reactions of those compounds over the acid catalyst of WO_3/ZrO_2. Fig. 6 presents the results of the qualitative analysis of the upgraded EE bio-oil. As illustrated, the upgrading of the EE bio-oil using methanol in the absence of a catalyst resulted in a decrease in the selectivity of acidic compounds and an increase in the selectivity of carbonyl compounds (aldehydes and ketones). The use of an acid catalyst of WO_3/ZrO_2 decreased the selectivity of both acidic and carbonyl groups of methanol-added EE bio-oil. The decrease in the selectivity of phenolics in the methanol-added EE bio-oil upgraded in the absence of a catalyst shows that methanol was involved in the reactions with the phenolic compounds of bio-oil. In contrast, upgrading the methanol-added EE bio-oil using the tungstated zirconia catalyst increased the selectivity of the phenolic compounds. Therefore, the possibility of a reaction between methanol and phenolics was reduced in the presence of an acid catalyst of WO_3/ZrO_2 because methanol was involved favorably in the reaction with acids/carbonyls on the acid sites of the catalyst rather than the reaction with phenolic compounds.

3-4. Upgrading of EE Bio-oil Using Amberlyst Catalysts at 80 °C

Solid acid catalysts of Amberlyst (15, 35, 36, 39 and 45) at 5 wt% were used to upgrade the methanol-added EE bio-oil at 80 °C for 24 h. The use of these catalysts resulted in an increase in viscosity; the highest viscosity of 429.23 mm^2/s was observed using Amberlyst 39 (Fig. 7). On the other hand, the solid acid catalysts of Amberlysts reduced the TAN of the upgraded bio-oil; Amberlyst 45 gave the lowest TAN of 75.83 mgKOH/g. Fig. 8 shows the qualitative results of product distribution in the upgraded EE bio-oil. The maximum decrease in the selectivity of acids (23.32%) and the increase in the selectivity of esters (85.41%) were achieved over Amberlyst 35, indicating that it was an efficient catalyst for the esterification of bio-

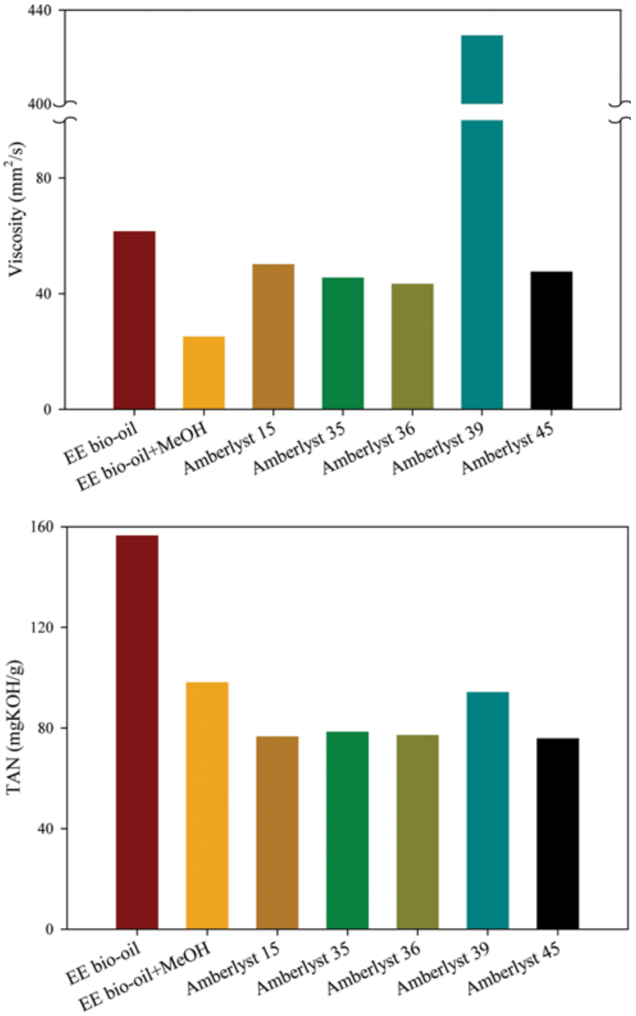

Fig. 7. Effect of Amberlyst catalysts (5 wt%) on viscosity and TAN of the mixture of methanol (10 wt%) and EE bio-oil upgraded at 80 °C for 24 h.

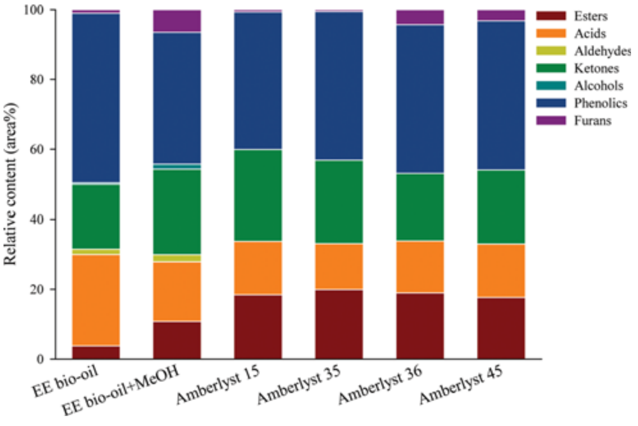

Fig. 8. Effect of Amberlyst catalysts (5 wt%) on product selectivity of the mixture of methanol (10 wt%) and EE bio-oil upgraded at 80 °C for 24 h.

oil. Generally, the porous structure and high acidity of sulfonic solid acids of Amberlyst make them efficient catalysts for an esterification reaction. In addition, the aldehydes had been removed completely using all Amberlyst catalysts. Based on the data obtained in this study, the Amberlyst catalysts (except Amberlyst 39) resulted in a larger reduction of TAN compared to WO_3/ZrO_2 (WZ9.9); TAN was reduced by 6.42 and 22.77% over tungstated zirconia and Amberlyst 45 catalysts, respectively. On the other hand, use of the WO_3/ZrO_2 catalyst led to a smaller increase in viscosity compared to the Amberlyst catalysts; the lowest viscosity value obtained using the Amberlysts (43.41 mm^2/s) was still higher than the viscosity achieved using the WO_3/ZrO_2 catalyst (28.21 mm^2/s). The larger decrease in TAN and increase in viscosity of the methanol-added EE bio-oil upgraded over the Amberlyst catalysts could be due to the enhanced catalytic activity of Amberlyst compared to that of the tungstated zirconia.

CONCLUSIONS

The performance of WO_3/ZrO_2 (with WO_3 loadings of 9.9, 15.5 and 15.7 wt%) and Amberlyst (15, 35, 36, 39, and 45) catalysts was evaluated for the upgrading of crude bio-oil and EE bio-oil by esterification with methanol at atmospheric pressure and room temperature/80 °C. The ether extraction of bio-oil was carried out to remove the undesirable compounds of pyrolytic sugars and lignin oligomers that cause the low activity of catalysts in bio-oil upgrading. The viscosity and TAN values of bio-oil were decreased by the addition of methanol to crude bio-oil due to physical dilution, change in bio-oil microstructure, and chain growth prevention caused by the reaction of methanol with bio-oil compounds. The use of tungstated zirconia catalysts resulted in a decrease in viscosity and TAN of crude bio-oil. The catalytic behavior of the tungstated zirconia calcined at different temperatures showed that the calcination temperature affects the bio-oil upgrading efficiency by influencing the catalyst structure. The largest decrease in viscosity (13.70%) and TAN (5.20%) of methanol-added bio-oil at room temperature was achieved using WO_3/ZrO_2 (WZ9.9) calcined at 900 °C. On the other hand, the viscosity of the methanol-added EE bio-oil was increased using WO_3/ZrO_2. This could be due to the formation of heavy molecules through the chemical reactions of bio-oil compounds over the acid sites of the catalyst, indicating that the separation of bio-oil compounds by ether extraction facilitated these reactions. The qualitative analysis of the upgraded product samples by GC/MS showed that the selectivity of the acids was reduced on tungstated zirconia through esterification. Replacing tungstated zirconia with Amberlyst catalysts in the upgrading of methanol-added EE bio-oil resulted in a significant decrease in TAN: a 6.43% and 22.68% decrease in TAN over tungstated zirconia and Amberlyst 45, respectively. Compared to WO_3/ZrO_2, the Amberlyst catalysts resulted in a larger increase in the viscosity of methanol-added EE bio-oil. The higher bio-oil viscosity and lower bio-oil TAN over the Amberlyst catalysts could be due to their stronger acid sites compared to WO_3/ZrO_2.

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