

## **Effect of support on activity of Mg-Ni-Mo catalyst for hydrodeoxygenation of bio-tar in supercritical ethanol**

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### **ABSTRACT**

The effect of supports (activated charcoal, H-type zeolites, TiO<sub>2</sub>, γ-Al<sub>2</sub>O<sub>3</sub>) on the activity of Mg-Ni-Mo catalyst for hydrodeoxygenation (HDO) reaction of bio-tar in supercritical ethanol was investigated using a batch reactor at 300°C, 30bar<sub>N<sub>2</sub></sub>. The water content and TAN (total acid value) of upgraded bio-tar were significantly decreased from 14.80% to 0.34% and 40.3mgKOHg<sup>-1</sup> to 20.9mgKOHg<sup>-1</sup>, respectively, and the HHV (higher heating value) was remarkably increased from 26.4 to 34.2 MJ/kg over Mg-Ni-Mo/activated charcoal catalyst. GC-MS analysis indicated that a variety of reactions including decarbonylation, decarboxylation, hydrodeoxygenation, esterification, and ring alkylation reaction occurred over the catalysts.

### **1. INTRODUCTION**

Nowadays, lignocellulosic biomass as a sustainable carbon source has received a significant attention for the production of bio-fuels and commodity chemicals (Zhang 2015). Liquid product obtained by fast pyrolysis of lignocellulosic biomass has much higher energy density than biomass itself but still contains high amounts of oxygen in the form of water and oxygenates (Oasmaa 2010). This oxygen determines unique properties of the pyrolysis oil such as high acidity, low heating value and high viscosity (Alsbou 2014). Different upgrading methods including hydrodeoxygenation (HDO) and catalytic cracking are under development to improve the quality of the pyrolysis oil by removing the organic oxygen (Furimsky 2010, Robinson 2016). Especially, the catalytic hydrodeoxygenation of bio-oil is regarded as a promising process that converts bio-oils to valuable hydrocarbons via hydrodeoxygenation (Robinson 2016). However, it generally requires the hydrogen-rich environment in the reaction, leading to the high cost of upgrading processes (Gu 2011). Therefore, efficient upgrading process of crude bio-oil in the absence of hydrogen feed to increase the properties of bio-oil is needed. Recently, supercritical fluids have unique properties as excellent reaction media of its

complete miscibility with gas and liquid products, providing one-phase reaction process (Hengst 2015, Ruddy 2014). Also, faster mass and heat transfer rates, gas-like low viscosity and high diffusivity and liquid-like density, would reduce the reaction time and promote the hydrodeoxygenation reactions. Especially, ethanol served as a hydrogen donor solvent in supercritical condition to improve the properties of upgraded oil through the depolymerization of high molecular components (Ruddy 2014). In this work, a catalytic upgrading of bio-tar was studied with the purpose of reducing the oxygen content and increasing the heating value, in-situ hydrogen supply. The various supports (activated charcoal, H-type zeolites,  $\text{TiO}_2$ ,  $\gamma\text{-Al}_2\text{O}_3$ ) on the activity of Mg-Ni-Mo catalysts and supercritical ethanol were used as catalysts and as a hydrogen donor, respectively.

## 2. Experimental

The Mg-Ni-Mo catalysts were synthesized by incipient wetness impregnation method and reduced in  $\text{H}_2$  (400°C, 5h) after drying (105°C, 12h) and calcination (500°C, 3h,  $\text{N}_2$ ). Metal precursors including 25wt% Ni, 10wt% Mo and 2wt% Mg of support loading on various supports in sequence. The catalytic tests were conducted in a 100ml batch reactor at 300°C, 30bar initial pressure and 0min without external hydrogen supply under supercritical ethanol condition. After reaction, qualitative analysis of liquid and gas products by a GC-MS and GC-TCD-FID, respectively. Moreover, TAN, water content, HHV and elemental analysis of liquid products determine the properties of upgraded oil were performed.

## 3. Results and discussion

Table. 1 shows the textural properties of Mg-Ni-Mo supported catalysts. As seen from Table. 1 the BET surface area ( $S_{\text{BET}}$ ) of Mg-Ni-Mo/AC, Mg-Ni-Mo/HY and Mg-Ni-Mo/HM is 518.4, 530.4, and 221.3 $\text{m}^2\text{g}^{-1}$ , respectively, indicating the mesopores mainly dominate the total pore volume. Among the 5 catalysts, Mg-Ni-Mo/AC has the highest mesopore volume and moderate micropores. This means that facile diffusion through mesopores can improve access of reactant and prevent coke generation. The large pore size ( $d_p$ ) with Mg-No-Mo/ $\text{TiO}_2$  and Mg-Ni-Mo/ $\gamma\text{-Al}_2\text{O}_3$  have large mesoporous structures, but the surface areas (40.8, 54.63 $\text{m}^2\text{g}^{-1}$ , respectively) are too small compare to activated charcoal and zeolite-based catalysts.

Table. 1 Textural properties of catalysts

Sample	$S_{\text{BET}}$ ( $\text{m}^2\text{g}^{-1}$ )	$V_p$ ( $\text{cm}^3\text{g}^{-1}$ )	Mesopore $V_p$ ( $\text{cm}^3\text{g}^{-1}$ )	$d_p$ (nm)
Mg-Ni-Mo/AC	518.4	0.45	0.29	3.51
Mg-Ni-Mo/HY	530.8	0.35	0.17	2.61
Mg-Ni-Mo/HM	221.3	0.20	0.12	3.66
Mg-Ni-Mo/ $\text{TiO}_2$	40.8	0.17	0.16	16.98
Mg-Ni-Mo/ $\gamma\text{-Al}_2\text{O}_3$	54.6	0.19	0.18	14.65

Table. 2 shows the yields of liquid, gas and solid products obtained from upgrading of bio-tar over various catalysts. The higher yields of desirable liquid products were obtained with Mg-Ni-Mo/AC and Mg-No-Mo/TiO<sub>2</sub>. However, the relatively lower yields of liquid products were obtained in Mg-Ni-Mo/HY and Mg-Ni-Mo/HM. It can be seen that the zeolite-based catalysts generated the large amount of cokes due to its strong acid sites. On the other hand, solid product yields in less than 13wt% were obtained over all Mg-Ni-Mo supported catalysts, suggesting that the alkaline property may play a key role to increase the metal dispersion in preventing coke formation (Tang 2009). As clearly shows in Table 2, the product yields are strongly dependent on the types of supports with Mg-Ni-Mo catalysts.

Table. 2 Product yields of upgraded bio-tar

Wt.%	MgNiMo/AC	MgNiMo/HY	MgNiMo/HM	MgNiMo/TiO <sub>2</sub>	MgNiMo/r-Al <sub>2</sub> O <sub>3</sub>
Liquid	76.6	64.5	59.5	80.6	70.1
Gas	13.9	22.8	28.7	18.4	20.1
Solid	9.5	12.7	11.8	1.0	9.8

For more investigation of the upgraded bio-tar, the major components of bio-tar such as acids, aldehydes, alcohols, esters, ketones, phenols, aromatics, hydrocarbons and nitrogen-containing compounds, presented in Fig.1a. It could find that the content of acids, aldehydes, alcohols were decreased in the upgrading process over all tested catalysts. Meanwhile, the content of esters, ketones, ethers, phenolics were increased in the upgraded bio-tar. These results means that the acids efficiently converted into esters via esterification, and the alkylation of phenolics were occurred during upgrading process. Moreover, aldehydes were dramatically decreased from 13.26% to less than 1% because the aldehydes could be converted to phenolics via hydrodeoxygenation and decarbonylation reaction.

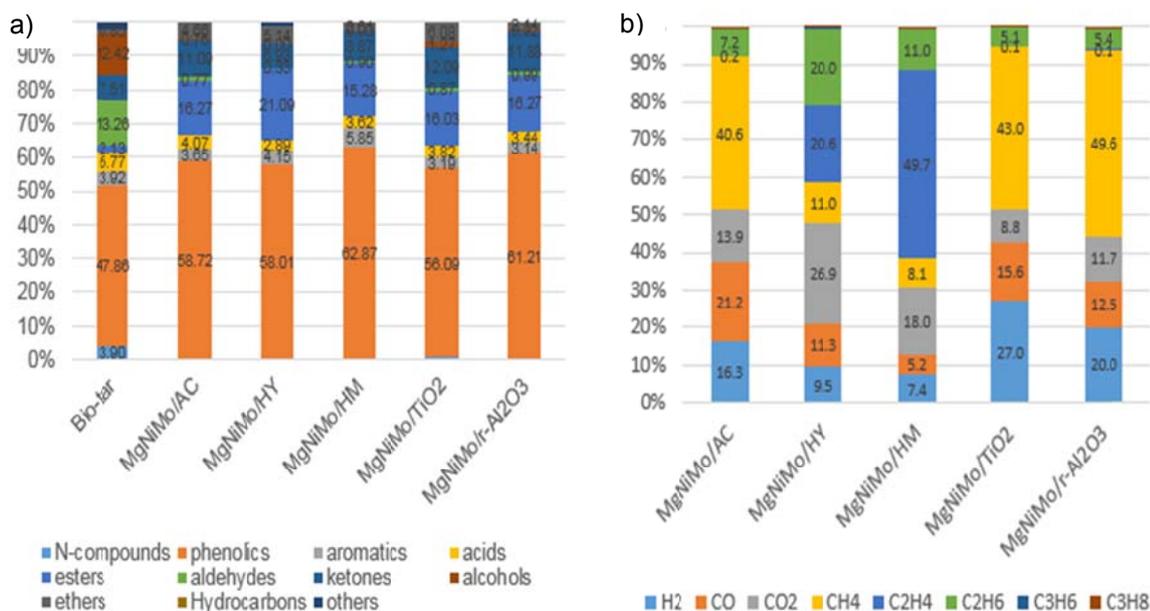


Fig.1 Distribution of a) liquid and b) gas products (300°C, 30bar<sub>N<sub>2</sub></sub>, 0min)

The gas product composition showed in Fig.1b. The main components were CO, CO<sub>2</sub>, H<sub>2</sub> and CH<sub>4</sub>, which may come via decarbonylation, decarboxylation, ethanol steam reforming, water gas shift reaction and methanation with Mg-Ni-Mo/AC, Mg-Ni-Mo/TiO<sub>2</sub>, and Mg-Ni-Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. On the other hand, CO, CO<sub>2</sub>, H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> produced by decarbonylation, decarboxylation, dehydration and methanation with Mg-Ni-Mo/HY and Mg-Ni-Mo/HM due to its acidic properties of catalysts.

A comparison of water content, TAN, oxygen content, and HHV listed in Table.3. Among the all catalysts, Mg-Ni-Mo/AC showed reduced water content by more than 98% compared to the crude bio-tar. The upgraded bio-tar showed lower TAN (20.9mgKOHg<sup>-1</sup>) than that of the crude bio-tar (40.3mgKOHg<sup>-1</sup>). These results clearly indicates an effective conversion of the acids in the crude bio-tar to esters in supercritical condition. The main reaction attributed to the esterification reaction with acid and ethanol. Moreover, the upgrade bio-tar exhibited the increasing HHV by up to 23% from 26.4MJ/kg to 34.2MJ/kg. The lowest oxygen content of 15.89wt% and the highest carbon and hydrogen contents of 75.67 and 8.03wt%, respectively.

Table. 3 Properties of the bio-tar and upgraded oils with various catalysts

Case	Raw material /Catalyst	H <sub>2</sub> O content (%)	TAN (mgKOHg <sup>-1</sup> )	Elemental Analysis (%)				HHV (MJ/kg)
				C	H	O	N	
1	Bio-tar	14.80	40.3	61.90	6.80	31.30	0.10	26.3
2	MgNiMo/AC	0.34	20.9	75.67	8.03	15.89	0.41	34.2
3	MgNiMo/HY	0.73	17.2	74.33	7.59	17.95	0.13	32.9
4	MgNiMo/HM	0.57	18.5	75.13	7.44	17.14	0.29	33.1
5	MgNiMo/TiO <sub>2</sub>	0.63	18.1	73.30	7.83	18.74	0.13	32.8
6	MgNiMo/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	0.53	21.2	74.25	7.90	17.59	0.26	33.4

### 3. CONCLUSIONS

Catalytic upgrading of bio-tar have investigated with the purpose of reducing the oxygen content, acid value and increasing the heating value, in the absence of external supply of hydrogen. The effect of supports (activated charcoal, H-type zeolites, TiO<sub>2</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) on the activity of Mg-Ni-Mo catalyst for HDO reaction of bio-tar in supercritical ethanol was investigated using a batch reactor at 300°C, 30bar<sub>N2</sub>. The water content and TAN of upgraded bio-tar were significantly decreased from 14.80% to 0.34% and 40.3mgKOHg<sup>-1</sup> to 20.9mgKOHg<sup>-1</sup>, respectively, and the HHV (higher heating value) was remarkably increased from 26.4 to 34.2 MJ/kg over Mg-Ni-Mo/activated charcoal catalyst. The efficient upgrading reactions such as decarbonylation, decarboxylation, hydrodeoxygenation, esterification, and ring alkylation reaction occurred over the catalysts.

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