Catalytic upgrading of bio-tar over Mg-Ni-Mo/activated charcoal catalyst in supercritical ethanol

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Bio-tar derived from fast pyrolysis of biomass, which is a unique carbon-based renewable resource, has a great potential as a transportation fuel [1]. However, bio-tar can not be directly applied as high quality fuels directly due to its poor physical and chemical properties, such as high oxygen content, strong acidity and lower heating value [2]. Thus, efficient thermochemical processes have to be developed to upgrade the poor quality of biotar. Recently, the catalytic hydrotreatment of bio-oil is regarded as a promising process that converts bio-oils to valuable hydrocarbons via hydrodeoxygenation [3]. However, it generally requires the hydrogen-rich environment in the reaction, leading to the high cost of upgrading processes [4].

In this work, a catalytic upgrading of biotar was studied with the purpose of reducing the oxygen content and increasing the heating value, in the absence of external supply of hydrogen. The Mg-Ni-Mo/activated charcoal catalyst and supercritical ethanol were used as a catalyst and as a hydrogen donor, respectively [5].

Table 1 shows that the water content and the total acid number (TAN) of upgraded biotar were significantly decreased from 14.80% to 0.67% and 40.0 mgKOH/g to 18.7 mgKOH/g at 350 °C, respectively. In addition, the high heating value (HHV) was remarkably increased from 26.39 to 36.26 MJ/kg. This result suggests that the catalytic upgrading of bio-tar is effectively achieved over the Mg-Ni-Mo/activated charcoal catalyst under supercritical ethanol conditions. Figure 1 displays the liquid product distribution of upgraded bio-tar. The upgraded bio-tar with the lowest content of acids and aldehydes was obtained at 350°C and 1/9 bio-tar to ethanol ratio, respectively, accompanied by the increasing of ester content via esterification reaction.

	H ₂ O content (%)	TAN (mgKOH/ g)	Elemental Analysis (%)				HHV (MJ/kg)
			С	Н	0	Ν	
Biotar	14.80	40.0	61.9	6.8	31.3	0.1	26.39
275°C	0.55	25.3	75.4	8.0	16.2	0.4	34.04
300°C	0.52	22.1	78.2	8.3	12.9	0.5	35.73
325°C	0.58	20.4	77.9	8.6	13.1	0.4	35.88
350°C	0.67	18.7	78.3	8.7	12.5	0.4	36.26
1/9 ^a	0.10	17.3	76.2	9.4	13.8	0.6	36.29
$2/8^{a}$	0.67	18.7	78.3	8.7	12.5	0.4	36.26
3/7 ^a	1.11	20.1	78.6	8.5	12.5	0.4	36.06
4/6 ^a	0.48	19.5	79.6	8.3	11.8	0.3	36.24

Table 1. Properties of the bio-tar and upgraded oils with different reaction conditions.

^a Weight ratio of bio-tar to ethanol.



Fig. 1. Liquid product distribution of raw biotar and upgraded bio-tar.

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