Upgrading of Bio-oil through TAN Reduction by Esterification using a Solid Acid Catalyst

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With the rapid increase in global energy demand and increasing environmental and sustainability challenges, biomass fuels as renewable energy sources have increasingly been considered as a key option to substitute conventional fossil fuels. Currently, biomass and waste contribute to around 10% of the global energy supply [1]. Waste biomass, sourced from non-food lignocellulose, sugars, and triglycerides is the only sustainable source of carbon that can provide low cost solutions for transportation fuels [2]. The presence of acidic compounds results in thermally unstable and highly corrosive oil. Total acid number (TAN), defined as the number of milligrams of KOH required to neutralize the acidity of 1 g of oil, is a commonly accepted criterion for oil acidity [3].

A number of methods have been proposed in literature to deacidify acidic oil. Esterification of carboxylic acids is a widely studied and industrially important reaction. Esterification has been previously used for diesel fuel and vacuum distillate. This process has shown the ability to reduce the acidity of high acidic crude oils. Esterification of the corrosive acidic components in bio-oil is proposed as a simple pre-treatment to improve the stability of oils during storage and transportation prior to subsequent upgrading.

The addition of small concentrations of ethanol or methanol (<10%) has been observed to improve bio-oil stabilization, 15–17 drastically reducing the ageing rate of the bio-oil via homogeneous reactions initiated by the organic acid itself.

In this study, bio-oil derived from the pyrolysis of saw-dust at 460˚C was used as the reaction feedstock, which consists of light oil with high moisture content and heavy oil with low moisture content. After the moisture content of bio-oil was reduced by evaporation, pretreated bio-oil was used for the upgrading by esterification. Bio-oil 1 g was reacted with methanol (1 g) under Amberlyst® 15 (10%, 20%) at 100°C for 1h. Amberlyst® 15 is a commercial solid acid esterification catalyst.

After reaction, TAN of heavy oil was decreased to 25.6 from 59.7 mg KOH/g and light oil was decreased to 14.0 from 63.5 mg KOH/g. Through esterification using a solid acid catalyst, TAN decreased efficiently. Additionally, through supercritical ethanol reaction, TAN is expected to decrease to lower level and aldehyde, ketone, and acid are also expected to decrease.

The esterified bio-oil could possibly be used in the more robust combustion engines, such as slow and medium-speed diesel engines, that require lower acidity and water content than that found in the conventional pyrolysis bio-oil.

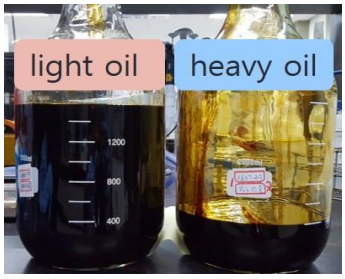

Fig.1 Bio-oil prepared from saw-dust

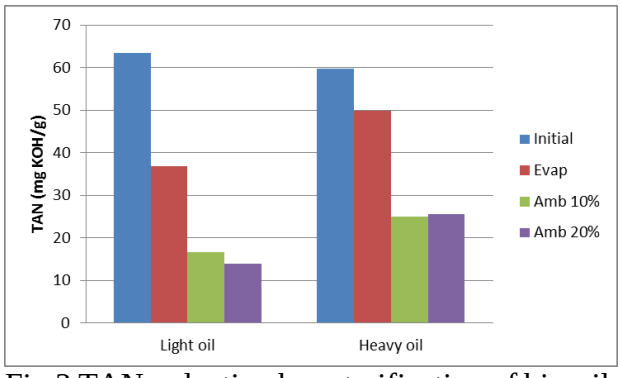

Fig.2 TAN reduction by esterification of bio-oil

REFERENCES

[1] A.A. Khan, W. de Jong, P.J. Jansens, H. Spliethoff, Fuel Processing Technology, 90 (2009) 21–50.
[2] Armaroli N and Balzani V, Angew Chem - Int Edit, 46 (2007) 52–66.
[3] Wang YAN-ZHEN, Li Jin-Yun, Sun Xue-Ying, Fuel, 116 (2008) 723-728.