Deoxygenation of Pyrolysis Oil through Pretreatment and Supercritical Ethanol Reaction

Ji-Yeon Park, Bora Nam, Sun-A Choi, Won-Jin Jeon, Jin-Hyuk Lee, In-Gu Lee*
Biomass and Waste Energy Laboratory, Korea Institute of Energy Research, Daejeon, South Korea

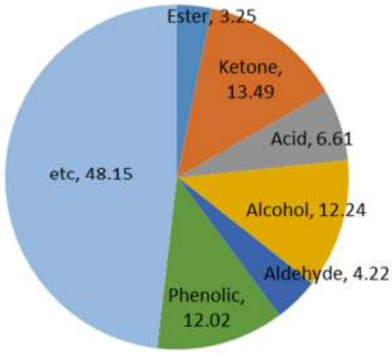
*E-mail: samwe04@kier.re.kr

Bio-oil is produced from the fast pyrolysis of lignocellulosic biomass. Although bio-oil is one of the most promising clean and renewable energy resources to replace the fossil fuel, it has undesirable properties such as high moisture content, high oxygen content, high acid value, low heating value, and high reactivity caused by the presence of oxygenated and unsaturated compounds.

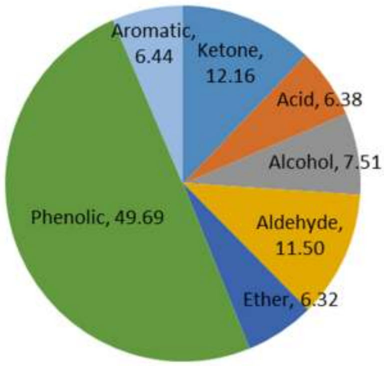
Aldehydes and phenolic species tend to polymerize easily and increase the oil viscosity. The high moisture content and oxygenated compounds result in low heating values and immiscibility with conventional fossil fuels. The high acidic compounds result in thermally unstable and highly corrosive oil.

Therefore, the upgrading of bio-oil with lower oxygen and acidic species is required to replace fossil fuels. A lot of upgrading techniques such as catalytic cracking, hydrodeoxygenation, and steam reforming have been reported for bio-oil upgrading. Another route for bio-oil upgrading is to remove organic acids by esterification with alcohol and an acid catalyst. The quality of bio-oil can be enhanced by decreasing acidity, viscosity and other characteristics. Recently, esterification under supercritical fluids such as water, methanol or ethanol has been attracted on the removal of organic acids in bio-oil with or without catalysts due to the unique properties of the supercritical fluid system with faster rates of mass and heat transfer, liquid-like density and dissolving power, gas-like diffusivity and viscosity. Ethanol reacts with carboxylic acids in bio-oil to produce the corresponding esters and acts as a reactant medium in the supercritical system.

In the present 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 under supercritical ethanol w/wo a catalyst. The oxygen content of heavy oil decreased to 28% from 34%, while the oxygen content of light oil decreased to 42% from 62%. Through supercritical ethanol reaction, the oxygen content is expected to decrease to lower level. The major components of light oil were ketone, alcohol, phenolic, and levoglucosan, while the major components of heavy oil were phenolic, ketone, and aldehyde. Through supercritical ethanol reaction, the aldehyde, ketone, and acid are expected to decrease.



(a) Light oil



(b) Heavy oil
Fig.1 Compositions of Bio-oil

REFERENCES

[1] X. Zhang, Q. Zhang, T. Wang, B. Li, Y. Xu, L. Ma, Fuel, 179 (2016) 312.
[2] Q. Zhang, Y. Xu, Y. Li, T. Wang, Q. Zhang, L. Ma, M. He, K. Li, Applied Energy, 160 (2015) 633.
[3] H. Prajitno, R. Insyani, J. Park, C. Ryu, J. Kim, Applied Energy, 172 (2016) 12.
[4] A.R.K. Gollakota, M. Reddy, M.D. Subramanyam, N. Kishore, Renewable and Sustainable Energy Reviews, 58 (2016) 1543.