

Blending effects of supercritical fluids as solvents for upgrading of pyrolysis oil

Bora Nam, Ji-Yeon Park, Sun-A Choi and In-Gu Lee*

Biomass and Waste Energy Laboratory, Korea Institute of Energy Research, Daejeon, South Korea
samwe04@kier.re.kr

ABSTRACT

Bio-oil derived from the pyrolysis of saw-dust was upgraded through supercritical reaction. Bio-oil consisted 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, bio-oil was used for the upgrading under supercritical fluids. Ethanol was blended with other solvents such as acetone, acetaldehyde, acetic acid, and ethyl acetate to enhance the efficiency of deoxygenation. The oxygen content of bio-oil decreased to 21% from 34%. A catalyst, MgNiMO/AC, was used to decrease the oxygen content less than 20%. After application of the catalyst, the oxygen content decreased to 16%.

1. INTRODUCTION

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 (Zhang *et al.*, 2016).

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 (Zhang *et al.*, 2016).

Therefore, the upgrading of bio-oil with lower oxygen and acidic species is required to replace the fossil fuel. A lot of upgrading techniques such as catalytic cracking, hydrodeoxygenation, and steam reforming have been reported for bio-oil upgrading. Nickel catalysts were usually adopted to upgrade bio-oil but can be eroded with the decrease in the catalytic activity in the presence of high acetic compounds. Some noble metal catalysts with good acid resistance have been screened for the upgrading of bio-oil (Zhang *et al.*, 2015).

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 (Zhang *et al.*, 2015).

As well as alcohols such as ethanol and methanol, other solvents such as ketones, aldehydes, and acids can be used as supercritical fluids for bio-oil upgrading. In the present study, ethanol was blended with other solvents including acetone, acetaldehyde, acetic acid, and ethyl acetate under supercritical fluid conditions. The changes in properties of compositions, oxygen content, acid number, etc. according to solvents used were investigated.

2. EXPERIMENTAL METHODS

Bio-oil derived from the pyrolysis of saw-dust at ~460°C was used as the reaction feedstock, which consisted of light oil with high moisture content and heavy oil with low moisture content. The moisture content of bio-oil was reduced by vacuum evaporation (EYELA N-2100, Japan). Bio-oil after evaporation was used for the upgrading under supercritical fluids.

Autoclave reactor with a capacity of 200 mL was used for the reaction. The autoclave reactor was heated with an electric heating system and the temperature was measured with a thermocouple. A total amount of 100g (90g solvent and 10g bio-oil) was mixed and fed into autoclave. The reaction was performed at 340°C and initial pressure under nitrogen gas of 30 bar by stirring the mixture at a rate of 500 rpm for 60 minutes and then cooled down with water circulation to room temperature (Kim *et al.*, 2011). The mass ratio of ethanol to other solvents was 7:3.

To enhance the efficiency of deoxygenation, a catalyst, MgNiMo/AC (the BET surface area was 518 m²/g.) of 1 and 2wt% of total supercritical fluids, was used. All gas, liquid, and solid products were collected from the reactor for analyses.

The analyses of bio-oils and all liquid products after supercritical reaction were performed on an Agilent GC 7890A gas chromatograph (HP-5 column) equipped with a mass spectrometer (5975C). The compounds were identified using the National Institute of Standards and Technology (NIST) Mass Spectral Library. The analyses of gas products were performed by GC with a TCD, TDX-01 column, and GC with a FID, Porapak-Q column. The acid numbers and moisture contents of bio-oils were determined with TitroLine 7750 KF (Germany). Elemental compositions of the bio-oils were analyzed by an elemental analyzer (FLASH 2000 series).

3. RESULTS AND DISCUSSION

3.1 Properties of pyrolysis oil derived from saw-dust

The moisture contents and acid numbers of bio-oils were 63% and 63 mg KOH/g in light oil and 14% and 58 mg KOH/g in heavy oil. The oxygen contents of bio-oils were 63% in light oil and 34% in heavy oil (Table 1).

Table 1. Compositions of pyrolysis oil

	Light oil	Heavy oil
Moisture content (%)	63.3	14.3
Acid number (mg KOH/ g)	62.8	57.7
C (%)	29.0	59.3
H (%)	8.6	6.7
N (%)	0.0	0.1
O (%)	62.5	33.9

3.2 Upgrading of bio-oil through supercritical reaction

When the mixture of ethanol and acetaldehyde was used as a supercritical fluid, the amount of phenolic compounds decreased and the amount of alcohols increased (Fig. 1).

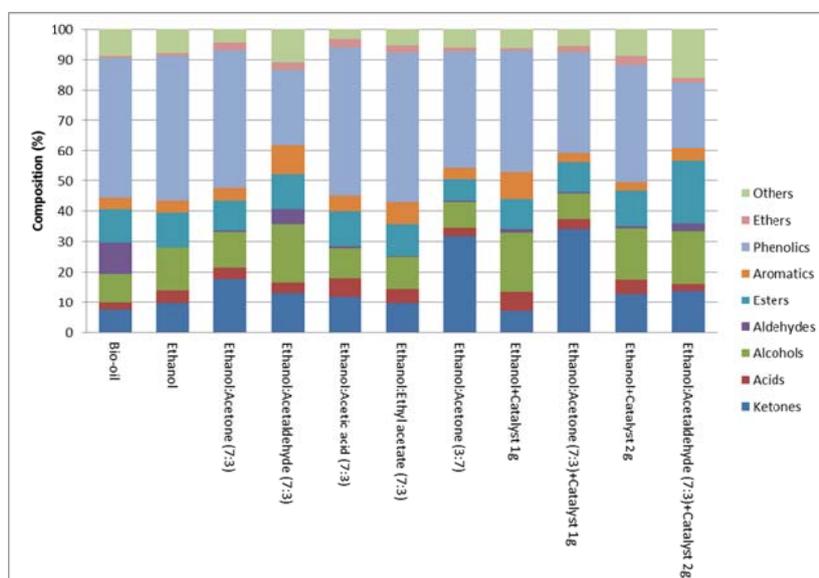


Fig. 1 GC-MS analyses of pyrolysis oil and upgraded pyrolysis oil

When the mixtures of ethanol and other solvents were used as supercritical fluids, the oxygen content decreased (Fig. 2). When a catalyst was used during supercritical reaction, the deoxygenation enhanced and the oxygen content decreased additionally.

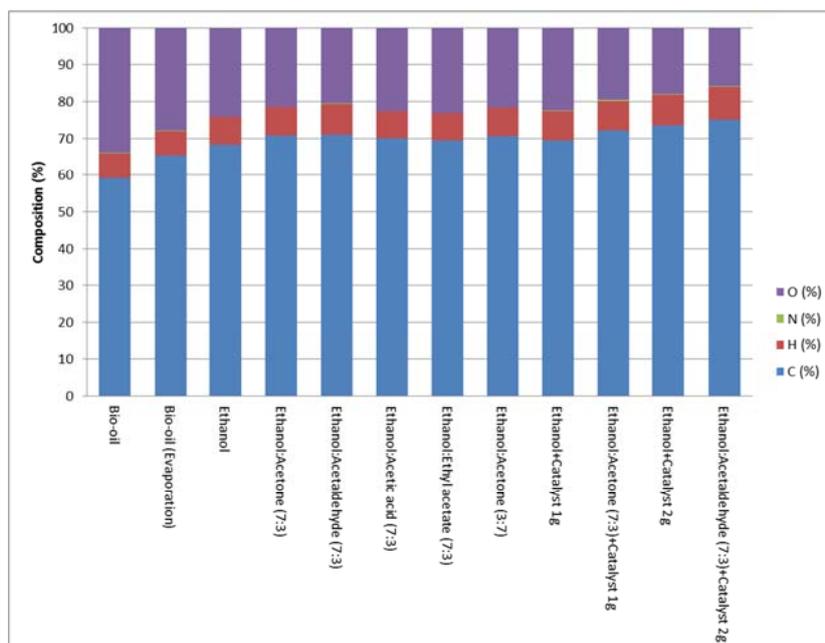


Fig. 2 Compositions of pyrolysis oil and upgraded pyrolysis oil

4. SUMMARY

Bio-oil was prepared from the pyrolysis of saw-dust. Bio-oil had two separate layers: light oil containing sugar and heavy oil containing phenolic compounds. Bio-oil showed high moisture content, high oxygen content, and high acid number. Ethanol and other solvents produced hydrogen gas during supercritical reaction. The oxygen contents and acid numbers of bio-oils decreased after supercritical reaction of bio-oil and solvents. The efficiency of deoxygenation increased when a catalyst was used.

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