Effects of supercritical fluids in catalytic upgrading of pyrolysis oil

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Highlights

- Hydrogen gas was produced from solvents during supercritical-fluid reaction.
- Hydrogen gas from solvents was used to upgrade pyrolysis oil.
- Oxygen content of pyrolysis oil decreased after supercritical-fluid reaction with a catalyst.

1. Introduction

Pyrolysis oil is produced from the fast pyrolysis of lignocellulosic biomass. Although pyrolysis 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 pyrolysis 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 pyrolysis-oil upgrading. Nickel catalysts were usually adopted to upgrade pyrolysis 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 pyrolysis oil. Recently, esterification under supercritical fluids such as water, methanol or ethanol has been attracted on the removal of organic acids in pyrolysis 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 pyrolysis oil to produce the corresponding esters and acts as a reactant medium in the supercritical system.

As well as alcohols such as ethanol and methanol, other solvents such as ketones, aldehydes, and acids can be used as supercritical fluids for pyrolysis-oil upgrading. In the present study, various kinds of solvents were examined for supercritical-fluid reactions. The changes in properties of compositions, oxygen content, acid number, etc. according to solvents used were investigated.

2. Methods

Alcohols (methanol, ethanol, butanol, and hexanol) and acids (formic acid and acetic acid), acetone, and acetaldehyde were used as supercritical solvents. Pyrolysis oil derived from the pyrolysis of saw-dust was used as the reaction feedstock. 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 of solvents and/or pyrolysis oil was fed into autoclave. The reaction was performed at 340C 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. Ethanol was blended with other solvents for supercritical-fluid reaction. To enhance the efficiency of deoxygenation, a catalyst, MgNiMo/AC (the BET surface area was 518 m^2/g.) of 1, 2, and 4wt% of total supercritical fluids, was used. All gas, liquid, and solid products were collected from the reactor for analyses.

The analyses of pyrolysis oil 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 (NITS) 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.

3. Results and discussion

When ethanol was used as a supercritical fluid with/without a catalyst, the gas products were analyzed. A major gas product was hydrogen gas. The amount of hydrogen gas increased with the increase in a catalyst (Fig.1a). In an ethanol condition, methane production was relatively high. In conditions of various alcohols, methanol showed the highest hydrogen production while butanol showed the lowest hydrogen production (Fig.1b). In alcohols except for ethanol, the amount of carbon monoxide was relatively high.

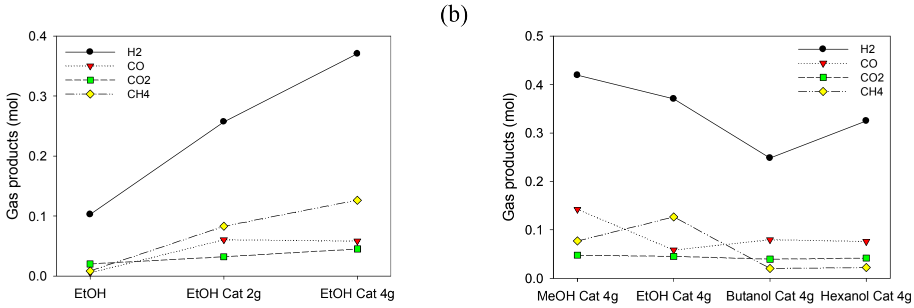

Figure 1. Gas production after supercritical-fluid reaction of solvents

When supercritical-fluid reaction was performed for the catalytic upgrading of pyrolysis oil, the amount of hydrogen decreased because it was used to upgrade pyrolysis oil (Fig.2). After the reaction, oxygen contents of pyrolysis oil decreased (Fig.3).

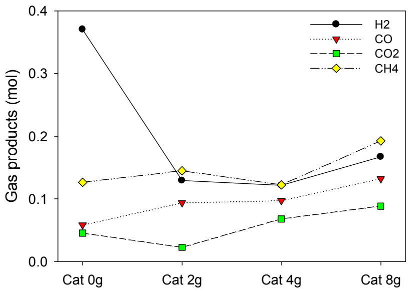

Figure 2. Gas production after supercritical-fluid reaction of pyrolysis oil

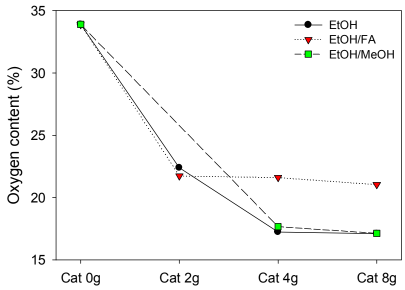

Figure 3. Oxygen contents after supercritical-fluid reaction of pyrolysis oil

4. Conclusions

When pyrolysis oil reacted with supercritical solvents under catalytic conditions, hydrogen produced during supercritical-fluid reaction was used to upgrade pyrolysis oil. Oxygen content, moisture content, and acid number decreased after the reaction. We optimized the reaction conditions to enhance the deoxygenation of pyrolysis oil through the generation of hydrogen gas from solvents under supercritical conditions.

References

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Keywords

Pyrolysis oil; Supercritical fluid; Catalytic hydrodeoxygenation; oil upgrading