Lignin conversion to low molecular weight bio-oil over HZSM-5 in subcritical water

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INTRODUCTION

With the continuous depletion of fossil fuels sources, lignocellulosic biomass that is riches in organic carbon has recently drawn immense interest for the production of fuels and value-added chemicals (Rana M., Islam M. N. et al., 2018). Lignin, a major component of lignocellulosic biomass, is commercially isolated from the pulp and paper industry waste black liquor. However, due to improper utilization, most of it is burned to generate heat energy in the recovery boiler. Recently, several techniques have been applied for the depolymerization of lignin to aromatic chemicals. Among them, hydrothermal liquefaction has attracted a great attention, due to the use of sub- (< 370 °C) and super-critical (> 370 °C) water that is considered as a green solvent. In near critical conditions (sub- or super), water act as a catalyst and a reactant. On the other hand, protonated zeolite (HZSM-5) has been proven to be an effective catalyst for reducing serious char formation simultaneously upgrading the bio-oil quality. Thus, by considering these intriguing properties, in the present study, lignin (extracted from the industrial waste black liquor) depolymerization was carried out using subcritical water and HZSM-5 catalyst in order to understand their effect on the lignin depolymerized products yield.

MATERIALS AND METHODS

Lignin isolation

The lignin used in this study was isolated from the black liquor by following acid hydrolysis (50 % H_2SO4) precipitation method.

Preparation of HZSM-5

HZSM-5 catalyst was prepared via following a hydrothermal method found in the literature (Hosseini S., Taghizadeh M. et al., 2012). After synthesis, the catalyst was characterized by XRD and SEM-EDS analyses.

Lignin depolymerization

3.0 g of lignin and 90 mL of de-ionized water with or without HZSM-5 catalyst were inserted into a 150 mL of hydrothermal reactor. Reaction temperature, time and catalyst weight were varied from (250 to 350) °C, (0.5 to 3) h, and (0.5 to 2) wt.%, respectively.

RESULTS AND DISCUSSION

Catalyst (HZSM-5) characterization

Figures 1 shows the SEM images and elemental mapping, while Figure 2 shows the XRD spectrum of HZSM-5. These figures (Figs. 1 and 2) gave evidence of the presence of Si, Al and O elements in the HZSM-5, and thereby confirming the successful synthesis of HZSM-5.

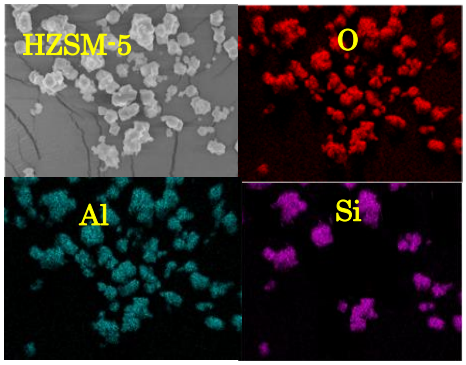

Figure 1 SEM image and elemental mapping of HZSM-5.

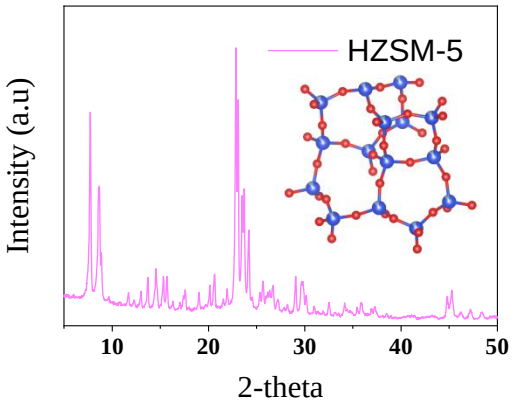

Figure 2 XRD spectrum of HZSM-5.

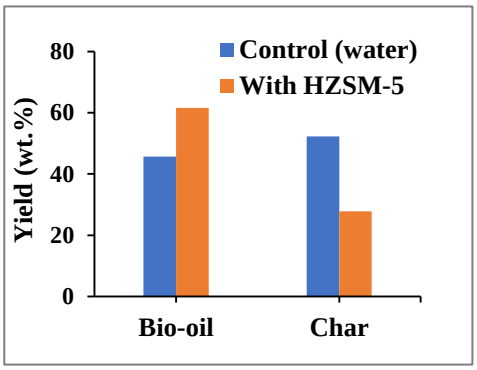

Figure 3 Experimental results (bio-oil and char yields)

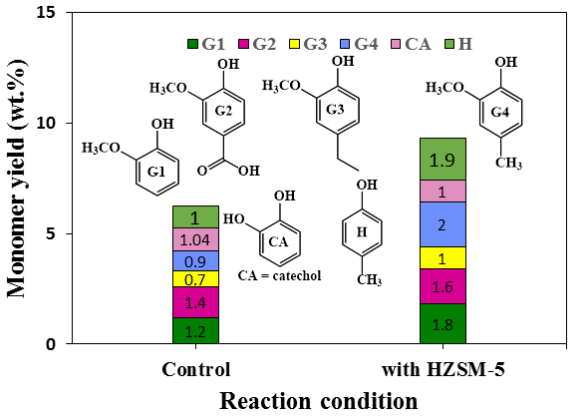

Figure 4 Major monomers in bio-oil.

Yields of lignin depolymerized products and characterization of bio-oil:

The highest yield of bio-oil (61.2 wt.%) with low yield of char (27.8 wt.%) were achieved at the optimized reaction conditions of 300 °C, 2 h and 1.0 g of HZSM-5 catalyst in subcritical water (Figure 3). The GC-MS results showed that the bio-oil contained mainly low molecular weight monomeric compounds as shown in Figure 4.

CONCLUSION

The objective of this study was to manage and to convert pulp and paper industry waste black liquor into value-added chemicals. A maximum bio-oil yield of 61.2 wt.% containing 9.4 wt.% low molecular weight monomers was obtained at 300 °C, 2 h, and 1.0 g of HZSM-5 catalyst. These results indicate that in subcritical water, HZSM-5 acted as an effective catalyst for enhancing the bio-oil yield and reducing the char formation, suggesting that the process applied in the present study could be an alternative to the other existed processes wherein huge amount of organic solvent are used to depolymerize lignin.

ACKNOWLEDGEMENT

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