

Two-Step Hydrodeoxygenation of Furan Derivatives to Diesel Fuels

Jang-Woo Seo^{1,2}, Jae-Wook Choi¹, Dong-Jin Suh¹, Jeong-Myeong Ha^{1*}

1 Clean Energy Research Center, Korea Institute of Science and Technology, Seoul 02792, Republic of Korea; 2 Division of Energy and Environment, KIST School, Korea University of Science and Technology, Seoul 02792, Republic of Korea

**Corresponding author: jmha@kist.re.kr*

Highlights

- Two-step hydrodeoxygenation increased the yields of deoxygenates.
- The first stage process hydrogenates the reactants with the ring opening.
- The 80% of oil phase product represented the diesel fuels.

1. Introduction

Lignocellulose is one of the popular feedstocks to obtain renewable energy because wood and grass, which are examples of lignocellulose, is abundant, cheap, and inedible. Lignocellulose is composed of cellulose, hemicellulose, and lignin, while cellulose and hemicellulose can be depolymerized to hexose and pentose sugars both of which can be converted to platform chemicals for a lot of chemical products. Pentose, including xylose, is not easily fermented, and can remain as a residue during the fermentation of lignocellulose-derived sugars. Oligomerization and deoxygenation of pentose molecules have been suggested to produce diesel-like hydrocarbon fuels [1]. In this study, we condensed 2-methylfuran(2MF), which can be obtained by the modification of xylose, to produce C15 hydrocarbons as trimers of 2MF. The hydrodeoxygenation (HDO) was further performed to obtain diesel fuels. The two-step HDO process was attempted to remove the oxygen atoms in the trimers, which improved the yield of diesel fuels by reducing the formation of cokes [2].

2. Methods

A mixture of 2-methylfuran (2MF) and furfural (2.05:1 (mol/mol)) was mixed with Amberlyst-15 at 85 °C for 5 hours. Sticky red liquid was prepared and filtered to remove solid particles, which is used as a feeds of HDO process. The two-step HDO process was performed using H₂ gas (600 mL/min) at 100 bar. The first-step hydrotreating (HYT) and the second-step HDO catalysts were placed in the reactor. The HYT catalyst bed was heated to 150 - 250 °C and the HDO catalyst bed was heated to 250 - 300 °C. The liquid phase reactant was supplied to the reactor at 0.1 mL/min. The product was collected and analyzed using GC-MS/FID, FT-IR, Karl Fischer titration, elemental analysis, and SimDist-GC.

3. Results and discussion

Biphasic mixture of liquid products was obtained by the two-step HDO. The lower phase liquid was confirmed as water. Transparent colorless upper phase liquid was a mixture of hydrocarbons, which was further analyzed in this study. FT-IR analysis observed the disappearance of characteristic peaks of trimers and the increase of peaks of C-H bonds indicating the conversion of trimers to deoxygenated saturated hydrocarbons (Figure 1). The FT-IR results of hydrotreated products at the exit of the first-step hydrotreating exhibited the characteristic peaks of hydroxyls, carbonyls, and tetrahydrofuran ring although the characteristic peaks of trimers disappeared. Based on these results, the roles of the first-step hydrotreating is the hydrogenation of unsaturated rings and the ring opening ether cleavage. The elemental analysis indicated that both one-step and two-step HDO processes produced the oil-phase products containing oxygen content less than 1 wt%. The liquid yield of two-step process was greater than 90%, which is larger than the corresponding one-step process exhibiting the liquid yield lower than 70%. SimDist-GC confirmed that approximately 80% of oil represented the diesel fuels.

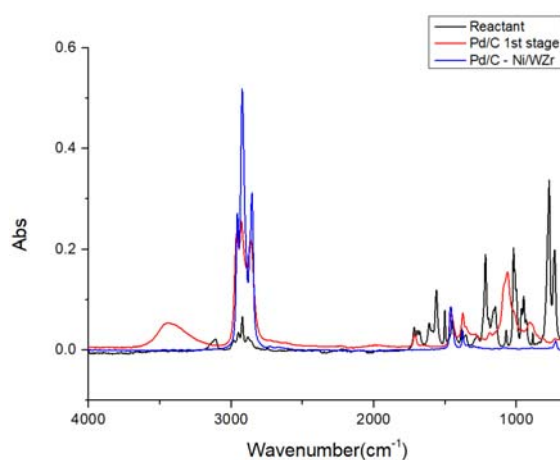


Figure 1. FT-IR analysis of one-step and two-step processes.

4. Conclusions

Two-step HDO process was performed to obtain diesel fuels from the trimers of furan derivatives. The yield of hydrocarbon fuels increased when the two-step HDO process substituted the one-step HDO process. From the FT-IR analysis, the first-step reaction hydrogenated the reactant and opened the ring structure. The oxygen content of hydrocarbon product was lower than 1 wt% and the 80% of oil product represented the diesel fuels.

References

- [1] I. Yati, M. Yeom, J.-W. Choi, H. Choo, D.J. Suh, J.-M. Ha, Appl. Catal. A 495 (2015) 200-205.
- [2] I. Kim, A.A. Dwiatmoko, J.-W. Choi, D.J. Suh, J. Jae, J.-M. Ha, J. Ind. Chem. Eng. 56 (2017) 74-81.

Keywords

Lignocellulose; Hydrodeoxygenation; Catalyst; Furans