Maximizing Biojet Fuel Production from Triglyceride: Effects of the Hydrocracking Catalyst and Deoxygenation/Hydrocracking Steps

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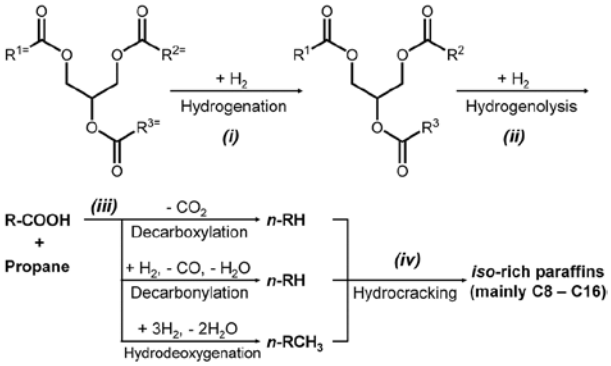
Abstract: Various parameters in the catalytic hydroconversion of triglycerides were investigated for maximizing the biojet fuel production. The results demonstrated that the two-step process composed of separate hydrotreating/hydrocracking steps is more advantageous than the single-step process in terms of high biojet fuel yield, suppressed production of aromatic compounds, and long catalyst lifetime. In the two-step process, the diffusion characteristics of the multibranched hydrocarbon in the hydrocracking catalysts could be correlated with the biojet fuel yields and the *iso*/*n*-paraffin ratios. Consequently, Pt supported on nanocrystalline BEA zeolite produced the largest biojet fuel yield with high *iso*-paraffin content as a result of suppressed overcracking.

Keywords: Biojet fuel, Hydrocracking, Zeolite

1. Introduction

Catalytic processes to produce transportation fuels from biomass have been extensively investigated by the requirement to replace petroleum-based fuels with sustainable carbon sources and thus to decrease CO_2 emissions. In the case of jet fuel, in this regard, the oil-to-jet process (Scheme 1) is most widely adapted in industry, and the produced fuels have been tested by commercial airlines. In the present work, we investigated the effects of different reaction process (two-step vs single-step reaction processes), reaction conditions, and types of hydrocracking catalysts on the production of biojet fuel from triglycerides (palm oil). The investigation demonstrated that the two-step process composed of separate hydrotreating and hydrocracking steps is markedly more advantageous than the single-step process in terms of high biojet fuel yield, suppressed production of aromatic compounds, and long catalyst lifetime. Therefore, the effects of the structural properties of hydrocracking catalysts (i.e., zeolite-supported Pt catalysts) and reaction conditions on biojet fuel yields and hydrocarbon distributions were carefully investigated in the two-step process [1].



Scheme 1. Reaction pathways for the hydroconversion of triglycerides into biojet fuel (Oil-to-jet process)

2. Experimental

As a hydrotreating catalyst, 1 wt% Pt was supported on γ-Al_2O_3 via incipient wetness impregnation using an aqueous solution of $Pt(NH_3)_4(NO_3)_2$. As a hydrocracking catalyst, 1 wt% Pt was supported on the prepared H^+-form zeolite samples (Bulk-ZSM-5, Nano-ZSM-5, Bulk-Beta, Nano-Beta). All catalytic reactions were carried out in a stainless steel down-flow fixed-bed reactor. In the two-step reaction, palm oil was first hydrotreated with 1 wt% Pt/γ-Al_2O_3 as the catalyst. The liquid hydrocarbons were separated and used as the reactant for the second hydrocracking step. Hydrocracking reaction was carried out at 488-523 K, 2.0 MPa total pressure, and WHSV = 2.0 h^{-1}. For single-step hydroconversion, palm oil was directly hydroconverted at 568 K, 2.0 MPa total pressure, and WHSV = 2.0 h^{-1} using 1 wt% Pt/Nano-Beta as a catalyst. The liquid products collected in a liquid trap were analyzed with GC equipped with FID, and the gaseous products were analyzed using an online GC equipped with FID detector.

3. Results and discussion

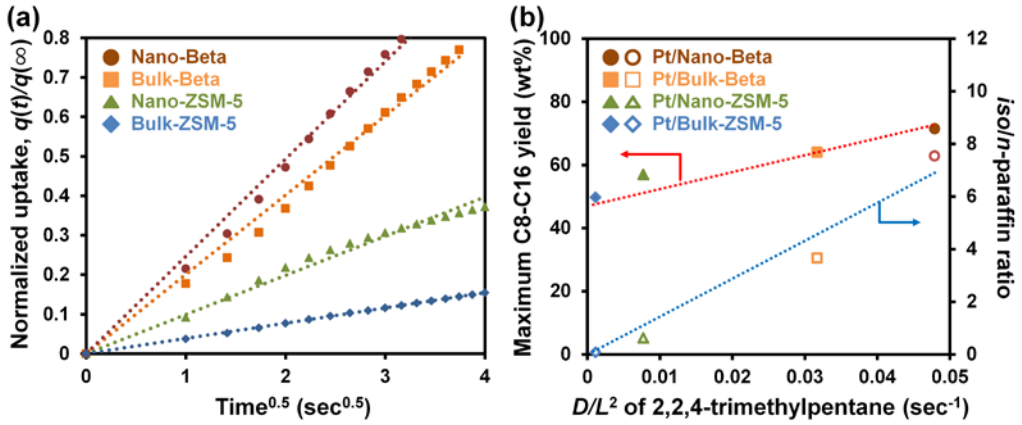


Figure 1. (a) Adsorption rates of 2,2,4-trimethylpentane in zeolite samples. (b) Correlation between the maximum achievable C8-C16 yields, *iso*/*n*-paraffin ratios in the hydrocracking products and D/L^2 of 2,2,4-trimethylpentane in hydrocracking catalysts.

The effects of the zeolite microporous structures and crystallite sizes on hydrocarbon diffusion were investigated using 2,2,4-trimethylpentane as a model adsorbate. As shown in Fig. 1a, the D/L^2 values increased in the order of Bulk-ZSM-5 < Nano-ZSM-5 << Bulk-Beta < Nano-Beta. These results suggest that diffusion of the tribranched model hydrocarbon is drastically slower in ZSM-5 (MFI) containing 10-MR microporous channels than in zeolite Beta (BEA) with 12-MR channels. As shown in Fig. 1b, the maximum achievable C8-C16 yields increased in the order of Pt/Bulk-ZSM-5 < Pt/Nano-ZSM-5 < Pt/Bulk-Beta < Pt/Nano-Beta. Under the conditions allowing the maximum C8-C16 yields, the *iso*/*n*-paraffin ratio of products also increased in the same order. The maximum achievable C8-C16 yield and *iso*/*n*-paraffin ratio of hydrocracking products were linearly correlated with the diffusivity of 2,2,4-trimethylpentane in the hydrocracking catalysts. These results strongly suggest that fast diffusion of highly isomerized products out of zeolite micropores before overcracking is essential for obtaining high yield of C8-C16 with *iso*/*n*-paraffin ratio. Consequently, the large-pore zeolite Beta in a nanocrystalline form with the fastest molecular diffusion characteristics appears to be the best acid support for hydrocracking catalysts.

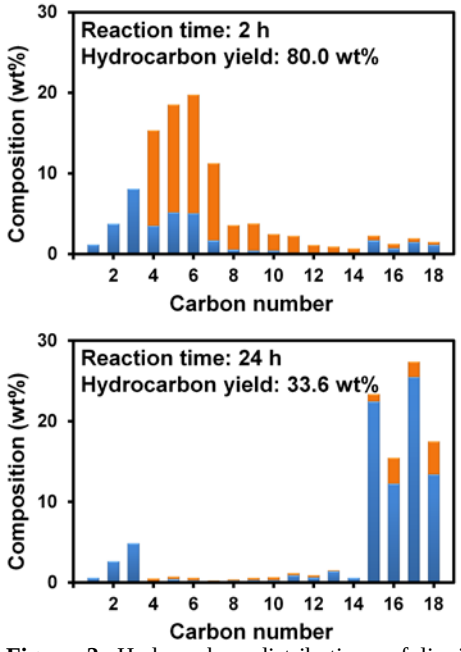


Figure 2. Hydrocarbon distributions of liquid and gas products obtained after single-step hydroconversion of palm oil over Pt/Nano-Beta.

We additionally studied the feasibility of a single-step hydroconversion of palm oil using Pt/Nano-Beta catalyst. The most notable difference between the single-step hydroconversion and the two-step reaction process was in the fast deactivation of the catalyst. In contrast to the separate hydrotreating and hydrocracking reactions that exhibited negligible catalyst deactivation up to 4 d, the single-step hydroconversion (Fig. 2) showed very fast deactivation within 24 h. This phenomenon can be attributed to the generation of CO during the decarbonylation of fatty acids, which can poison Pt catalyst.

4. Conclusions

In summary, we investigated the effects of various reaction parameters on the conversion of triglycerides into biojet fuel. The results demonstrated that the two-step process composed of separate hydrotreating/hydrocracking reaction steps is more advantageous than the single-step hydroconversion process in terms of high biojet fuel yield, suppression of the formation of aromatic species, and long catalyst lifetime. In the two-step reaction procedure, a nanocrystalline large-pore BEA zeolite with facile molecular diffusion characteristics produced the highest jet fuel yield as a result of suppressed overcracking.

References

1. M. Y. Kim, J.-K. Kim, M.-E. Lee, S. Lee, M. Choi, ACS Catal., 7 (2017) 6256.