Jet fuel synthesis from Fischer–Tropsch product under mild hydrocracking conditions using Pt-loaded catalysts

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HIGHLIGHTS

- Screening studies of Pt catalyst support were performed for high jet fuel yield.
- Pt-loaded β-type zeolite catalyst exhibited high corresponding jet fuel yield.
- High corresponding jet fuel yield was obtained under mild conditions.

ARTICLE INFO

ABSTRACT

The development of effective Pt-loaded catalysts for high jet fuel yield was investigated in hydrocracking step in the proposed conversion process from biomass to jet fuel. Screening studies of Pt-loaded catalyst supports were performed using an autoclave in hydrocracking of n-$C_{28}H_{58}$ and n-$C_{36}H_{74}$ as model compounds over ten different supports loaded with Pt (Pt content: 0.5 wt%). The Pt-loaded β-type zeolite catalyst exhibited a high corresponding jet fuel yield using both feedstocks. The effect of the reaction temperature, reaction pressure, and Pt content on the hydrocracking behavior was studied in hydrocracking of n-$C_{36}H_{74}$ over Pt-loaded β-type zeolite catalyst. The corresponding jet fuel yield was maximized at 250–350 °C, and 0.9–1.4 MPa, and 0.1–1.0 wt% Pt content. The liquid product with carbon numbers 5–68 was obtained as Fischer–Tropsch (FT) product through the operation of a bench-scale biomass-to-liquid (BTL) plant. The effect of the reaction temperature and reaction pressure on the hydrocracking behavior was investigated in hydrocracking of the FT product over Pt-loaded β-type zeolite catalyst (Pt content: 0.1 wt%). The corresponding jet fuel yield was the maximum value (21.5%) at 250 °C and 1.5 MPa.

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1. Introduction

The annual consumption of transportable liquid fuel in Japan is approximately 90 billion liter. Airline companies account for approximately 8 billion liter. The consumption of liquid fuel derived from fossil fuels can be reduced by using fuel cell vehicles, electric vehicles, and hybrid vehicles for land transportation, whereas hydrocarbon liquid fuels have prospective application for light-weight airplanes in which the fuel consumption is more efficient. Jet fuel is standardized by the American Society for Testing Materials (ASTM) D1655 and contains hydrocarbons with carbon numbers 9–15. Currently, jet fuel is produced by distillation of the crude oil, followed by hydrotreating and hydrocracking [1]. Taking the amount of fossil fuel consumed and the resultant emission of CO_2 into the atmosphere into account, it is necessary

to develop conversion technologies from biomass to jet fuel because biomass is the only renewable energy resource that can be converted to jet fuel.

Among the bioenergy conversion technologies from biomass to hydrocarbons, the biomass-to-liquid (BTL) process comprising biomass gasification, gas cleaning, gas compression, Fischer–Tropsch (FT) synthesis, hydrocracking, and distillation is particularly promising. The process can utilize a greater variety of feedstock than other conversion technologies because the feedstock is gasified to syngas ($CO + H_2$). Life-cycle assessment indicates that the process emits less greenhouse gases than liquid fuel production processes using fossil fuels [2,3]. Consequently, there has been a significant focus on the development of the BTL process which produces hydrocarbon liquid fuels such as gasoline and light oil [4–6]. However, no commercial BTL plants are currently operating because of the lack of feasible economics. In a study by Fujimoto et al., simulation of a process comprising steam gasification, gas compression, FT synthesis, hydrocracking, and distillation indicates that the

input energy for the production of steam as a gasifying agent, for gas compression and distillation was the dominant input energy for the process [7]. The authors have successfully accomplished the production of 16 L of hydrocarbon liquid fuel per day by operating a bench-scale BTL plant utilizing woody biomass gasification with oxygen-enriched air/CO_2 and FT synthesis using the Ru/Mn/Al_2O_3 catalyst [8]. To decrease the input energy for distillation, it is necessary to develop a hydrocracking catalyst which exhibits a high jet fuel yield under mild conditions.

Bifunctional catalysts for hydrocracking of the FT product require an appropriate combination of metal sites active for hydrogenation/dehydrogenation and solid acid sites active for isomerization/cracking for high jet fuel yield. As metal sites, precious metals such as Pt [9–13] and Pd [14], as well as Ni [15], Ni–Mo [16,17], Ni–W [18,19], Co–Mo [20,21], and WS_2 [22] have been reported. As solid acid catalysts, zeolite [23,24], SiO_2–Al_2O_3 [9,11], montmorillonite [12], Al_2O_3 [14,16], $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ [10], TiO_2–SiO_2 [17], WO_3/ZrO_2 [13], and sulfated zirconia [13] have been reported. Pt catalysts are particularly applicable to BTL process because they exhibit high activity and selectivity to the middle distillate under mild conditions [9,11]. However, it is necessary to make the platinum usage as low as possible because it is extremely expensive. Hydrocracking catalysts with low Pt content have not been fully investigated under mild reaction conditions. In the present study, as the first step in the development of hydrocracking catalysts for achieving high jet fuel yield, screening studies were performed for catalyst supports using 10 types of supports. The jet fuel production under mild conditions was investigated using Pt-loaded catalysts with low Pt content.

2. Experimental

2.1. Preparation of FT product by BTL plant operation

Fig. 1 shows a flow diagram of the proposed process from biomass to jet fuel. The process comprises biomass gasification, FT synthesis, hydrocracking, and distillation. A slurry bed reactor is utilized in the FT synthesis to facilitate temperature control. The FT product is mixed with hydrocarbons recycled from the distillation unit is supplied to the hydrocracking unit without distillation, followed by distillation to obtain jet fuel. Fractions with carbon numbers greater than 16 and residual hydrogen are recycled to the hydrocracking unit. Therefore, the feedstock of the hydrocracking reaction in the process would contain hydrocarbons with carbon numbers 9–15, that is, corresponding jet fuel.

In the present study, the feedstock of the hydrocracking reaction was synthesized as the FT product throughout an operation of a bench-scale BTL plant constructed at AIST Chugoku (Hiroshima, Japan). The details of operating conditions were reported in the previous paper [8]. Eucalyptus tips (20–30 mm) were employed as a feedstock. The feed gas for FT synthesis was prepared by the gasification of the feedstock with oxygen-enriched air/CO_2, followed by gas cleaning with activated carbons and a scrubber, H_2/CO adjustment, and CO_2 removal. The resultant gas comprised 29.4% CO, 60.6% H_2, 5.3% N_2, 4.5% CH_4, and 0.2% CO_2. A slurry bed reactor (inner volume: 12.5 L) was employed as an

FT synthesis reactor [25]. *n*-Hexadecane (Nacalai Tesque, 4 L) as an organic solvent was charged into the reactor to form a slurry phase at an initial stage. The Co–Mn–Zr/SiO_2 catalyst (Co content: 20 wt%, Mn content: 2 wt%, Zr content: 8 wt%) was prepared by the impregnation method [26]. The catalyst weight was 500 g. The feed gas flow rate, reaction pressure, and reaction temperature were 4.8 m^3 (STP) h^{-1}, 3 MPa, and 260–280 °C, respectively. The final product comprised the product gas, FT product, and condensate. The FT product was obtained as a liquid that remained in the reactor after the reaction. The organic phase was collected as condensate in a condenser installed downstream of the reactor.

The product gas and FT product were analyzed using gas chromatographs equipped with a thermal conductivity detector (Micro GC 3000A, Agilent, column: Molecular Sieve and Plot U) and a flame ionization detector (GC353B, GL Sciences, column: Ultra ALLOY-DX30). The CHNS contents of the FT product were analyzed using an elemental analyzer (FLASH 2000, Thermo Scientific).

The CO conversion is defined as follows:

$$\text{CO conversion } (\%) = (F_{CO,inlet} - F_{CO,outlet})/F_{CO,inlet} \times 100 \quad (1)$$

where $F_{CO,inlet}$ (mol h^{-1}) and $F_{CO,outlet}$ (mol h^{-1}) are the average inlet and outlet CO flow rates during the reaction, respectively.

The FT product and condensate were a mixture of hydrocarbons synthesized in FT synthesis and *n*-hexadecane the for temperature control. Therefore, the distribution to the product gas, FT product, and condensate on a carbon basis (i.e., Y_g, Y_{FT}, Y_c) and loss are defined as follows:

$$Y_g \ (\%) = (F_{C,outlet} \times \text{reaction time})$$
$$/(F_{C,inlet} \times \text{reaction time} + M_{C,solvent}) \times 100 \quad (2)$$

$$Y_{FT} \ (\%) = M_{C,\text{FT product}}/(F_{C,inlet} \times \text{reaction time} + M_{C,solvent}) \times 100 \quad (3)$$

$$Y_c \ (\%) = M_{C,condensate}/(F_{C,inlet} \times \text{reaction time} + M_{C,solvent}) \times 100 \quad (4)$$

$$\text{Loss } (\%) = 100 - Y_g - Y_{FT} - Y_c \quad (5)$$

where $F_{C,inlet}$ (mol h^{-1}) and $F_{C,outlet}$ (mol h^{-1}) are the average flow rates of the inlet and outlet gases on a carbon basis, respectively. $M_{C,\text{FT product}}$ (mol), $M_{C,condensate}$ (mol), and $M_{C,solvent}$ (mol) are the carbon numbers in the FT product, condensate, and *n*-hexadecane charged as the organic solvent at the initial stage.

2.2. Preparation of hydrocracking catalysts

Pt catalysts for hydrocracking were prepared by the impregnation method. The following 10 types of supports were employed: four types of silica–alumina: SiO_2–Al_2O_3 308 (Si/Al = 8.7, Fuji Silysia, denoted as SiO_2–Al_2O_3), JRC-SAH-1 (Catalyst Society of Japan, denoted as SAH-1), JRC-SAL-3 (13% Al_2O_3, Catalyst Society of Japan, denoted as SAL-3), JRC-SAL-4 (Si/Al = 5.5, Catalyst Society of Japan, denoted as SAL-4); three types of zeolites: HSZ-385HUA (Si/Al = 93, Y-type zeolite, Tosoh, denoted as 385HUA), HSZ-640HOA (Si/Al = 15, mordenite-type zeolite, Tosoh, denoted as
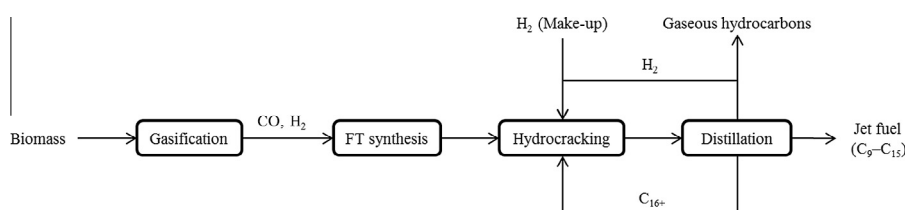

Fig. 1. Proposed process flow diagram.