Optimization of Process Conditions for Hydrotreating Biodiesel from Gutter Oil

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Abstract. In this paper, the catalyst Ni-Pt/γ-Al₂O₃ was prepared by method of fractional steps and impregnation with gutter oil as raw material. Ni and Pt were selected as active components and γ-Al₂O₃ as carrier under 400℃ setting conditions. The results showed that the reaction space velocity was 0.5 h⁻¹, reaction pressure was 8.0 Mpa, hydrogen oil ratio was 1200:1, under the condition of above-mentioned facts, the pour point of biodiesel obtained from gutter oil hydrogenation was reduced by 9℃, cetane number was 57, yield was 74.03%. The yield of light component was significantly promoted, below 160℃ fraction yield above 3.5%, the yield of diesel fractions could be reached 55.2%, the yield increased by 15%. This process greatly increased the additional value for the gutter oil and provided experimental basis for producing diesel fraction from gutter oil.

1. Introduction

Biodiesel refers to the process of converting animal and vegetable oils into hydrocarbon fuels with similar quality to fossil fuels under certain conditions through hydrodeoxidation and other technologies. Compared with petrochemical diesel, biodiesel is one of the most potential alternative fuels because of its richer source of raw materials, lower sulfur content and less environmental pollution after combustion[1]. At present, biodiesel has gradually begun to be industrialized and promoted. For example, UOP company in the United States and Petrobras company in Brazil have developed mature catalytic hydrogenation processes of animal and vegetable oils[2]. The main constraint to the industrialization of biodiesel is the high cost of crude oil. According to statistics, 80% of the preparation cost of biodiesel is raw materials[3], and a large number of oil crops will occupy land resources with food crops, so the adoption of cheap raw materials is the key to large-scale industrialization of biodiesel.

The annual consumption of vegetable oil and animal fat by Chinese residents is about 22.5 million tons, and 3 million to 5 million tons of cooking oil will be produced every year, and 2 million to 3 million tons of cooking oil will be returned to the table[4]. Gutter oil contains a large number of harmful substances to the human body, once eaten, it will seriously endanger human health. The best solution is to recycle, and turn waste into treasure. Therefore, the production of biodiesel with gutter oil as the raw material has a wide range of raw materials, which can not only avoid the gutter oil entering the food chain, but also realize the resource utilization of gutter oil, which can alleviate the fuel shortage to a certain extent.
This paper took gutter oil as raw material, $\gamma$-Al$_2$O$_3$ as carrier, selected Ni and Pt as active components, prepared catalyst Ni-Pt/$\gamma$-Al$_2$O$_3$ by step impregnation method, investigated the yield and cetane value of hydrofining biodiesel of gutter oil under different process conditions, and provided technical reference for the resource utilization of gutter oil.

2. Materials and methods

2.1 Materials
Main reagents: nickel nitrate, chloroplatinic acid, $\gamma$-Al$_2$O$_3$ are analytical pure, sinopharmaceutical group chemical reagents co., LTD.

Main instruments: muffle furnace, jiangsu nantong county agricultural scientific instrument factory; Wm-2a oil-free gas compressor, tianjin second medical equipment factory; Hydrogenation reaction device, self-made hydrogenation reaction device; Tablet press, changchun instrument general factory; Double plunger type micro pump, Beijing Oriental instrument factory.

Gutter oil from liaoning petrochemical university longyuan group food and beverage department.

2.2 Preparation of Ni-Pt/$\gamma$-Al$_2$O$_3$ catalyst
50g $\gamma$-Al$_2$O$_3$, 7.5mL 8% nickel nitrate solution and 7.5mL 0.2% chloroplatinic acid solution were respectively taken and mixed in three flasks with a blender. Put good solution at 110 ℃ for 24 h, electric vacuum drying oven and then transferred to a certain temperature in the muffle furnace roasting time, made of Ni-Pt/$\gamma$-Al$_2$O$_3$ catalyst.

2.3 Hydrofining test unit
The Ni-Pt/$\gamma$-Al$_2$O$_3$ hydrofining unit was a small fixed bed reactor with an internal diameter of 20mm and a length of 500mm. It was made of stainless steel tubes and the catalyst filling capacity is about 80mL. The outer of the reactor was heated by heating jacket, the temperature was measured by thermocouple, and the temperature was controlled by automatic instrument, so that the central temperature of the catalyst bed was controlled at the specified reaction temperature. Reaction pressure was indicated by pressure gauge. The feed oil was pumped into the reactor by metering pump and mixed with hydrogen at certain pressure into the reactor. The raw oil was reacted with the catalyst in liquid-solid polyphase and was discharged into the product tank through the condenser. The product after the reactor entered the product tank and was removed by the sampler.

2.4 Performance and yield of diesel fuel
The performance of diesel oil was characterized by cetane number, which was determined by the “National Standard of the People's Republic of China: Determination of Cetane Number of Diesel Oil” (GB/ t386-2010).

Diesel yield = consumption of gutter oil/refined diesel×100%

3. Results and discussions

3.1 Effect of hydrogenation pressure on the yield of biodiesel
The reaction temperature was 400℃, airspeed was 0.5 h$^{-1}$, hydrogen to oil ratio was 1200: 1, examines the different effect of hydrogenation reaction under pressure. The variation of product oil yield was shown in Figure 1.
From Figure 1, it was concluded that the product yield increases with the increasing of reaction pressure. The hydrogenation of oil was a reaction of decreasing volume, and increasing pressure was conducive to the reaction in a positive direction. However, increasing the reaction pressure could also impose more stringent requirements on the material of the equipment, which would lead to the reduction of the safety factor and bring certain difficulties to industrial production, which was not conducive to future production. With the experimental exploration and analysis, we finally selected the optimal hydrogenation pressure of 8.0 MPa.

3.2 Effect of hydrogenation reaction airspeed on biodiesel yield
The pressure 8.0 MPa, reaction temperature 400 ℃, hydrogen oil than in 1200, examines the different reaction synthesis effect of airspeed, the yield of the final product was shown in Figure 2.

According to Figure 2, when the airspeed was 0.5h⁻¹, the product yield was relatively high, which was the result of sufficient reaction due to the increased contact between oil and catalyst. However, although reducing airspeed could improve the oil production rate, it could also reduce the production capacity, which was not conducive to large-scale industrial production. Therefore, in industrial production, economic benefit should be estimated according to its specific situation, so as to determine the optimal volume airspeed.

3.3 Effect of hydrogenation reaction time on the yield of biodiesel
The pressure 8.0 MPa, space velocity, hydrogen oil than 0.5 h⁻¹, 1200:1 under the constant temperature
400 °C, as the reaction time, the influence on the effect of the reaction. The change of product oil yield was shown in Figure 3.

![Figure 3. Effect of reaction time on the yield of biodiesel](image)

According to Figure 3, it could be concluded that the reaction time showed an upward trend from 4 h to 12 h, and the product yield also reached the maximum when the reaction time reached 12 h. However, as the time gone, the product yield also declines due to the decrease of the active components in the catalyst.

3.4 Effect of different hydrogen oil ratio on biodiesel yield
The pressure was 8.0 MPa, space velocity was 0.5 h⁻¹, reaction temperature was 400°C, under the condition of invariable, examined the effects of the reaction under the different hydrogen to oil ratio. The variation of product oil yield was shown in Figure 4.

![Figure 4. Effect of different hydrogen oil ratio on biodiesel yield](image)

It could be seen from Figure 4, when the hydrogen-oil ratio reached 1200:1, the catalyst performance reached the best effect, the yield reached the maximum, so the hydrogen-oil ratio was 1200:1 for the experiment.

4. Conclusion
Through the Ni-Pt/γ-Al₂O₃ preparation conditions, it was concluded that the optimum process conditions of cooking oil hydrotreating of biodiesel, when the hydrogenation temperature is 400 °C, pressure is 8.0 MPa, airspeed 0.5h⁻¹ volume, hydrogen oil ratio of 1200:1, cooking oil yield could reach 74.03%.
Acknowledgements
This work was financially supported by the National Natural Science Foundation of China (41701364), Liaoning Province PhD Startup Fund (20170520109) and Liaoning Province PhD Startup Fund (201601333).

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