Study on Synthesis Process of Ni-Pt /γ-Al₂O₃ Catalyst for Biodiesel Production from Waste Oil

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Abstract. Ni-Pt /γ-Al₂O₃ catalyst was prepared by step impregnation method with waste oil as raw material and Ni-Pt /γ-Al₂O₃ as carrier. Results showed that the waste oil used by catalytic hydrogenation of Ni-Pt the best preparation technology of Al₂O₃ catalyst for calcination temperature was 450 ℃, the roasting time was 4 h, Ni/Pt ratio of 1:1, and the corresponding biological diesel oil production rate was 81.5%. A biodiesel yield of the regenerated catalyst was low and decreased with the increase of regeneration times. This process can improve the added value of gutter oil and provide experimental basis for the production of diesel distillate from waste oil.

1.Introduction
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 waste oil will be produced every year, among which 2 million to 3 million tons of cooking oil will return to the table [1-3]. Gutter oil contains a large number of harmful substances to the human body, once eaten, will seriously harm human’s health, the best solution is to recycle, turn waste into treasure.

Biodiesel refers to the process of converting animal and vegetable oils into hydrocarbon fuels with similar quality to fossil fuels under certain conditions through hydro deoxygenation and other technologies. Compared with petrochemical diesel, biodiesel is one of the most promising alternative fuels because of its richer source of raw materials, lower sulfur content in raw materials and less environmental pollution after combustion [4-5]. According to statistics, 80% of the preparation cost of biodiesel is the cost of raw materials [6-8], 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.

This paper took waste oil as raw material, γ-Al₂O₃ as the carrier, Ni and Pt as the active components, and used the stepped-impregnation method to prepare the catalyst Ni-Pt /γ-Al₂O₃. The effects of the catalysts corresponding to different preparation processes and the regenerated catalysts on the yield of biodiesel were investigated, providing a technical reference for the resource utilization of waste oil.

2.Materials and methods

2.1.Experimental materials
The main reagent: Nickel nitrate; Ni-Pt /γ-Al₂O₃; All chloroplatinic acids were analytically pure, Sinopharm group chemical reagent co. LTD; Activated carbon, Liyang Zijin activated carbon co., LTD. The main instrument: Hydrogenation refining unit, self-restraint; The horse boiling furnace, Jiangsu...
Nantong county agricultural scientific instrument factory; Tablet press, Changchun instrument general factory; WM-2A oil-free gas compressor, Tianjin second medical device factory; Double plunger type micro pump, Beijing Oriental instrument factory. Waste Oil (Shenyang Qianqian Chemical Plant, Industrial products)

2.2. Waste oil pretreatment
Put a certain amount of waste oil at three in the flask, at 90 °C constant temperature water bath heating 2 h. The supernatant was added to the activated carbon with the mass fraction of 5% of the waste oil. The activated carbon was continuously stirred for 1 h and then left for 12 h to be filtered to remove the activated carbon.

2.3. Preparation of Ni/SiO$_2$-$\gamma$-Al$_2$O$_3$ Catalyst
Adding 6.0% Ni(NO$_3$) of 10mL to 10mL Deionized Water. The Ni(NO$_3$) was fully mixed with the carrier SiO$_2$-$\gamma$-Al$_2$O$_3$ (80-100 mesh) by co-impregnation method. At 70 °C, the mixing time was 48 h. The samples were then filtered in vacuum to obtain semi-dry catalysts. The agent was packed in a beaker and placed in a drying box for dehydration. The Ni/SiO$_2$-$\gamma$-Al$_2$O$_3$ catalyst was obtained after the concentration of the drying box was set at 110 °C, and then roasted in a muffle furnace at 550 °C for 8 h, after cooling, the Ni/SiO$_2$-$\gamma$-Al$_2$O$_3$ catalyst was obtained.

2.4. Homemade hydrogenation refinement experiment
Catalytic hydrofining of biodiesel from waste oil is mainly carried out in a fixed bed reactor. The inner diameter of the fixed bed reactor is 20mm and the length is 500mm, which is made of stainless steel tube. The catalyst filling capacity is 80g. The external of the fixed bed reactor is heated by a heating jacket, the temperature is measured by a thermocouple, and the temperature is controlled by an automatic instrument, so that the temperature in the center of the catalyst bed is controlled within a certain range. Reaction pressure was indicated by pressure gauge. After pretreatment, the gutter oil was pumped into the reaction device by metering pump and mixed with hydrogen at a certain pressure to enter the fixed bed reactor. The raw oil and the catalyst were gas-liquid-solid multiphase reactions, and the product biodiesel after the reaction was put into the product tank and taken out by the sampler. The process of hydrofining reaction unit was shown in Figure 1.

![Figure 1. Hydrofining reaction unit](image)

2.5. Performance and yield of biodiesel
The performance of biodiesel was characterized by cetane number, which was determined by "national standard of the People's Republic of China: determination of cetane number in diesel oil" (GB/t386-2010).

Biodiesel yield = consumption of waste oil /biodiesel 100%
3. Results and discussions

3.1. Roasting temperature of catalyst
Ni-Pt/γ-Al₂O₃ catalysts were prepared by mixing 50 g γ-Al₂O₃, 7.5 mL of 8% nickel nitrate solution and 7.5 mL of 0.2% chloroplatinic acid solution in three flasks, drying at 110°C for 24 hours and calcining in muffle ovens at 440, 460, 480, 500 and 520 °C for 3 hours, respectively. The influence of the catalysts obtained under different roasting temperatures on the yield of biodiesel was investigated, and the results were shown in Figure 2.

Figure 2. Effects of catalysts on the yield of biodiesel at different roasting temperatures

As can be seen from Figure 2, with the increase of temperature, the production of biodiesel increased first and then decreased. When the catalyst calcination temperature was 480°C, the biodiesel production rate was at its maximum, at 78.0%. This was due to the degradation of the catalyst skeleton structure at ultra-high temperature, resulting in the decreased activity of the catalyst. Thus, 480 °C was the best roasting temperature.

3.2. Roasting time of catalyst
Ni-Pt/γ-Al₂O₃ catalysts were prepared by mixing 50 g of γ-Al₂O₃, 7.5 mL of nickel nitrate solution and 7.5 mL of chloroplatinic acid solution in three flasks, drying at 110°C for 24 hours and calcining in a muffle furnace at 480°C for 2, 3, 4, 5 and 6 hours respectively. The influence of the catalysts obtained under different roasting time conditions on the yield of biodiesel was investigated, and the results are shown in Figure 3.

Figure 3. The effect of different roasting time on the yield of biodiesel

As can be seen from Figure 3, with the increase of roasting time, the production of biodiesel
increased first and then decreased. When the roasting time was 4 h, the yield of biodiesel reached the maximum value of 81.2%. When the continuous roasting of the catalyst continued, the activity of the catalyst decreased for a long time, so the yield of biodiesel decreased. Therefore, the optimal roasting time of the catalyst Ni-Pt/γ-Al₂O₃ was 4 h.

### 3.3. Different Ni/Pt ratios in the catalyst

Ni-Pt/γ-Al₂O₃ catalyst was prepared by mixing 3.75, 7.5, 15, 22.5 and 30 mL chloroplatinic acid solution with 50 g γ-Al₂O₃ and 7.5 mL of 8% nickel nitrate solution in three flasks, mixing fully, drying at 110°C for 24 h and calcining in a muffle furnace at 480 °C for 4 h. The results were shown in Figure 4.

![Figure 4. Effects of catalysts with different Ni/Pt ratios on the yield of biodiesel](image)

As can be seen from Figure 4, with the increase of Ni/Pt ratio, the production of biodiesel first increased and then decreased. When the Ni/Pt ratio was 1.0, the production rate of biodiesel was 81.5%. Therefore, the optimal Ni/Pt ratio of catalyst Ni-Pt/γ-Al₂O₃ was 1:1.

### 3.4. Catalyst Ni-Pt/γ-Al₂O₃ regeneration

After a period of use, the catalyst will gradually lose its activity due to changes in composition and structure. At this time, the catalyst needs to be regenerated.

The inactivation of Ni-Pt/γ-Al₂O₃ catalysts at 650 °C in the muffle furnace roasting 8 h, after cooling, the catalyst was regenerated. The influence of regenerated catalyst and fresh catalyst on the yield of biodiesel was investigated, and the results were shown in Table 1.

| Ni-Pt/γ-Al₂O₃ catalysts | Biodiesel yield % |
|-------------------------|------------------|
| Fresh catalyst          | 81.5             |
| Regeneration of the first catalyst | 72.5           |
| Regeneration of a second catalyst | 59.2           |

As can be seen from Table 1, compared with the fresh catalyst, the yield of biodiesel corresponding to the regenerated catalyst was low, and with the increase of regeneration times, the yield of biodiesel gradually decreased. This may be due to the loss of the active component of the catalyst in the reaction process, and the generated side reactants cover the surface of the catalyst, resulting in the decrease of the specific surface area of the catalyst and thus the decreased activity of the catalyst.

### 4. Conclusion

In waste oil as raw material, through catalytic hydrogenation of biodiesel, the catalyst used for the Ni-Pt/γ-Al₂O₃, its preparing process: calcination temperature was 450°C, roasting time was 4 h, Ni/Pt ratio of 1:1, corresponding to the biodiesel production rate reached 81.5%.

The regeneration performance of the catalyst Ni-Pt/γ-Al₂O₃ was investigated. The results showed that the biodiesel yield of the regenerated catalyst was low, and the biodiesel yield decreased with the
increase of regeneration times.

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