Optimization of Process Conditions for Hydrogenation of Waste Oil

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Abstract. Ni/SiO₂-γ-Al₂O₃ catalyst was prepared by co-impregnation method, study on the performance change of hydrotreating product oil, get the optimum process conditions for hydrotreating waste oil. The results showed that the hydrogenation effect of waste oil hydrotreating was better under the conditions of reaction temperature 250℃, hydrogen pressure 7.9 MPa, space velocity 0.5h⁻¹ and hydrogen oil volume ratio 1000-1200:1. The bromine value of the oil was 0.18gBr/(100g oil), the residual carbon was 0.012, the sulfur content was 0.37 ug/g, the colorimetric value was less than 0.5, and the freezing point was -37℃, kinematic viscosity had almost no loss, the performance of waste oil after hydrogenation had been greatly improved.

1.Introduction
Since 1990's, catalytic hydrogenation technology has been developed rapidly in major refining countries in the world[1-2]. The growth rate is much higher than that of catalytic cracking, heat treatment and catalytic reforming[3-4]. The global capacity of hydrogenation units has reached 23.78 billion t/a[5]. Hydrocracking technology has been basically mature. But with the continuous improvement of catalyst level and process level, it has gradually formed its own characteristics[6-7]. Because of the influence of the source of raw materials and the improvement of product quality of lube base oil, the influence of developed countries on the production of lube base oils has been developed from the traditional solvent process to the hydrogenation process, nearly 80% of the base oil is produced by hydrogenation.

However, the domestic production of lube base oil by hydrogenation process lags behind that of foreign countries, and most of them still use the traditional solvent refining process to produce lubricating oil typeⅡ base oil.

2.Materials and methods

2.1 Experimental materials
Main reagents: Waste Oil (Shenyang Qianqian Chemical Plant, Industrial products); SiO₂ (Shenyang Jiao Black Factory, Industrial products); Nickel nitrate (Analytical Pure, Chinese Medicine Group Chemical Reagent 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.

2.2 Hydrofining test unit
The experiment was carried out with a small hydrogenation reactor. After removing the impurity water, the waste oil was pushed into the hydrogenation unit with reciprocating pump, and the waste oil and hydrogen were put into the hydrogenation unit at the same time. Hydrogenation, hydrogen to oil ratio, oil and gas flow suitable for entering, to obtain high-quality lubricating oil products. Before the hydrogenation of waste oil, nitrogen gas was tested, pressured and operated, and then the hydrogenation experiment of waste oil was carried out under the premise of complete process safety.

2.3 Preparation of Ni/SiO₂-γ-Al₂O₃ Catalyst
Adding 6.0% Ni(NO₃) of 10mL to 10mL Deionized Water. The Ni(NO₃) was fully mixed with the carrier SiO₂-γ-Al₂O₃ (80-100 mesh) by co-impregnation method. At 70 ℃, 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/SiO₂-γ-Al₂O₃ catalyst was obtained after the concentration of the drying box was set at 110 ℃, and then roasted in a muffle furnace at 550 ℃ for 8 h, after cooling, the Ni/SiO₂-γ-Al₂O₃ catalyst was obtained.

3. Results and discussions

3.1 Effect of hydrogenation of waste oil on airspeed
Under the conditions of hydrogen oil volume ratio of 1200:1, guaranteed temperature of 250 ℃ and hydrogen pressure of 8.0 MPa, the effect of space velocity on the refined fruit was studied. The oil performance of the product varies with space velocity was shown in Figure 1 and Figure 2.

![Figure 1. Effect of airspeed on bromine value of product oil](image)

As can be seen from Figure 2, when the space velocity is increased from 0.5 h⁻¹ to 0.9 h⁻¹, the bromine value increases from 0.18 gBr (100g oil)⁻¹ to 0.67 gBr (100g oil)⁻¹. Because of the increase of space velocity, the time of feedstock flow through the reactor was shortened, and the hydrogenation effect became worse, so the bromine value increased.
As can be seen from Figure 2, the space velocity increased from 0.5 h\(^{-1}\) to 0.9 h\(^{-1}\) and the viscosity decreased from 15.5 mm\(^2\)s\(^{-1}\) to 11.13 mm\(^2\)s\(^{-1}\). This is due to the increase of airspeed and the deterioration of hydrogenation efficiency. However, if the airspeed is reduced, though the hydrogenation effect becomes better, the production efficiency of the product oil will be reduced. Therefore, the optimum airspeed value should be selected according to the actual situation in actual production.

3.2 Effect of Hydrogenation pressure on waste Oil

Keeping temperature 250 °C and space velocity 0.5 h\(^{-1}\), the volume ratio of hydrogen to oil 1:200:1 was kept constant. The oil properties of the product were investigated when the hydrogen pressure increased from 5.0 MPa to 8.0 MPa. Hydrofining pressure and oil properties are shown in Figure 3, Figure 4.

As can be seen from Figure 3, during the whole process of pressure raising, the performance indexes of each oil product have been improved. When the pressure increased from 5.0 MPa to 7.0 MPa, the change was significant. If the bromine value is reduced from 0.78 g Br (100g bromine)\(^{-1}\) to 0.53 g Br (100g bromine)\(^{-1}\). However, when the pressure increased from 7.0 MPa to 8.0 MPa, the change was not significant, the bromine value only decreased from 0.53 g Br (100g bromine)\(^{-1}\) to 0.47 g Br (100g bromine)\(^{-1}\).
Figure 4. Effect of hydrogenation pressure on viscosity of product oil

Figure 4 showed that the viscosity of oil increased from 11.0 to 13.4 in the process of increasing the pressure from 5.0 MPa to 8.0 MPa, which is not obvious. After 8.0 MPa, the viscosity does not change. From the point of view of thermodynamics, increasing the pressure is beneficial to the hydrogenation, that is, the high temperature is favorable to the hydrogenation. However, when the pressure increases to a certain extent, the effect of supercharging on hydrogenation efficiency is no longer significant. Suitable hydrogen pressure can be adopted in actual production according to actual conditions such as product demand, economy and so on.

3.3 Influence of waste Oil temperature

Under the pressure of 8.0 MPa, space velocity 0.5 h⁻¹ hydrogen oil volume ratio of 1200:1, the hydrogenation efficiency, hydrofining temperature and oil performance of the product were investigated at different reaction temperatures as shown in Figure 5 and Figure 6.

Figure 5. Effect of temperature on bromine value of product oil

From Figure 5, it can be seen that when the temperature rises from 200 °C to 250 °C, the bromine value decreases from 0.47 g Br (100g bromine)⁻¹ to 0.30 g Br (100g bromine)⁻¹. The change of bromine value is very weak, because when the reaction rate reaches a certain value, the growth of bromine value is slow, resulting in the decrease of bromine value is also slow.
Figure 6 showed that the viscosity of oil increases with the increase of temperature. But it's slow enough to stay the same. There are two reasons for this. It is mainly determined by the reaction rate constant $k$, which is limited by thermodynamics. The $k$ value increases with the increase of temperature. Because hydrofining is an exothermic reaction, increasing temperature leads to the increase of reaction rate constant $K$, but the $K_p$ value of chemical equilibrium constant decreases. However, when the temperature increases to a certain extent, the reaction rate reaches the maximum, and the reaction rate decreases with the increase of the temperature, so the viscosity of the product oil does not increase very quickly. The hydrofining reaction is exothermic and the chemical equilibrium constant $K_p$ decreases with the increase of temperature.

4. Conclusion

Using Ni/SiO$_2$$-\gamma$-Al$_2$O$_3$ as hydrogenation catalyst, the optimum operation conditions of waste oil hydrofining were as follows: temperature 250 $^\circ$C, hydrogen pressure 7.9 MPa, space velocity 0.5 h$^{-1}$. Under this condition, the performance of refined lube oil is improved.

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