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Hydrofining and Pour Point Depressing Tandem Technology for Catalyzing Diesel

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This paper aims at studying the hydrofining and pour point depressing tandem technology for catalyzing diesel. Through hydrofining oil mixture of MIP diesel and DCC diesel and catalyst, it is found from the experimental data that the catalyst can fully exert its catalytic effect on the hydrofining and pour point depressing tandem process, effectively reducing the sulfur content of diesel.

1. Introduction

The demand of gasoline is far higher than that of diesel in China. The manufacturing technique of improving the diesel is attracting more and more attention from experts and scholars. When the demand for pour point depressing diesel in northern winter is relatively high, it is of great practical significance to study the hydrofining and pour point depressing tandem technology for catalyzing diesel.

2. Literature review

With the ever-increasing environmental protection requirements, the quality of diesel oil has become increasingly stringent. The Qianguo Petrochemical heavy oil catalyzed the diesel oil quality is poor, the sulfur content is greater than 0.13w%, and the oxidation stability total insoluble matter is greater than 10mg/100mL. It has become the difficult problem which confuses the enterprise production. Hydrotreating is a fundamental means of improving the properties of catalyzed diesel. At present, the domestic mature diesel hydrogenation technology can be roughly divided into three categories: hydrorefining, hydrogenation and hydrogenation. The FC-20 catalyst developed by the Fushun Research Institute has the function of hydrogenation and isomerization cracking. It adopts a novel process in which a series of FH-98 refining catalyst and FC-20 catalyst are connected in series, and can not only achieve the refining function but also produce low condensation point diesel oil. In the implementation of the decondensation production scheme, the fuel freezing point is reduced from -3°C to -20°C under the conditions of pressure 7.2MPa, pour condensation volume velocity of 1.45h-1 and average condensation reaction temperature of 387.7°C (Wang et al., 2011).
The winter weather in the northern regions is cold, and motor vehicles have a great demand for low-condensation diesel. When China National Petroleum Corporation Qianguo Petrochemical Co., Ltd. overhauled in 2007, the catalytic cracking unit used the new MIP technology, and the hydrogenation-decreasing device refined catalyst (FH-98 hydrofining catalyst) was regenerated to replace the declining-condensation catalyst. The hydrogen declining condensation catalyst developed and produced by Changchun Huigong Purification Industry Co., Ltd. was used. Among them, HPDW-1 type hydrogen-promoting dehydration catalyst is a ZSM-5 molecular sieve catalyst that has been treated by a special method, which has the characteristics of strong selectivity and strong ammonia resistance. The low-quality diesel oil or straight-run wax-containing distillate oil is first hydrorefined in the hydrotreating catalyst bed, and the refined oil is directly sent into the hydrogen-decreasing condensation catalyst bed for shape-selective catalytic cracking, and the cracked material is subjected to hydrogenation and supplementary refining. The experimental and industrial application data show that the activity of FH-98 and HPDW-1 catalyst is suitable for a series application. The process has good hydrotreating and pour point depressing effect, and can produce low condensation point, ultra-low sulfur, low density, low T95 and high cetane number diesel. The successful

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application of this technology has opened up a new way for the production of low-temperature clean diesel fuel, which is suitable for the production of northern refineries (Shu et al., 2015).

In order to improve the low-temperature flow performance of diesel oil and increase the cetane number, Sinopec Research Institute of Petroleum and Chemical Engineering developed the hydro-refining and dewaxing technology and its RHC-130 hydro-degradation and depressurization catalyst. The research results show that RHC-130 has good adaptability to straight run diesel oil, catalytic cracked diesel oil, coker gas oil and diesel oil and their mixed oils, and it can produce different brands of low-condensate diesel oil meeting the national V emission standard under mild reaction conditions, with a large reduction in condensation point, high cetane number, good performance and high diesel yield (Meng et al., 2017).

Using programming support environment FreePascal and FreeBasic, the program providing to calculate values of efficient rate constants for hydrogenation reactions of benz- and dibenzothiophenes in the process of diesel fuel hydrofining, is developed. The basis of the developed algorithm of solving reverse kinetic problem is the method of optimization by scanning the permissible scan area, which let it possible to make calculations with inaccuracy not exceeding 0.007%. By using the developed program, is conducted the calculation of velocity constants and activation energy of transforming individual sulphur compounds on the basis of laboratory stand experimental data, obtained under different conditions. The program can be implemented in oil and gas industry (Krivtcova et al., 2015). FHUDS-6 catalyst for diesel ultra-deep hydrodesulfurization developed by Fushun Research Institute of Petroleum and Petrochemical was applied to the 30×104t/a hydrorefining unit of Xi’an Petrochemical Company. The commercial application results showed that the clear diesel, which contained no more than 20 μg/g of sulfur and the quality of which could meet national diesel standard Ⅳ,was produced with straight-run diesel, vacuum tower diesel and catalytic cracking diesel (the mass fractions were 56%, 13%, 31%, respectively, sulfur content 5280 μg/g) as material under the condition of average reaction temperature 357.6°C, inlet pressure of reactor no less than 7.2 MPa, main catalyst volumetric space velocity 2.37 h-1, hydrogen to oil volume ratio 370 (Xue et al., 2013). Because of the peculiarities of the structure of the active components formed at high temperatures, these catalysts can be used both without supports and in a blend with conventionally formed catalysts on supports. The synthesized catalysts are several times more effective than conventional catalysts and maintain the residual sulfur content at the 30-35 ppm level (Kolesnikov et al., 2014).

Production of low setting point diesel from pure coking diesel by the hydrofining process and pour point depression process was investigated in a 100 mL fixed-bed continuous hydrogenation reactor. It shows that when reaction temperature is 390°C, the first reactor’s space velocity is 1.5 h-1; and the second reactor space’s velocity is 1.8 h-1, freezing point is-29°C, the naphtha can be used as ethylene cracking raw material (Chen et al., 2013).

3. Experimental principle and experimental method

Hydrofining technology of diesel is suitable for small-scale diesel refining enterprises that use the direct distillation of diesel with a higher proportion of hexadecane organic compounds and a lower proportion of catalytic diesel. In the specific application of this technology, it is common to directly process the diesel products obtained through catalytic processing and the diesel products obtained through other production methods by hydrofining technology so that the actual sulfur content can effectively meet the requirement of sulfur content of diesel products in technical standards. Besides, the content of hexadecane organic compounds in the diesel can increase by 2-6 units and recovery of refined diesel finished products increases to over 98.00%, and the consumption rate mass fraction level of hydrogen is strictly controlled within 1.00%.

The catalyst used in this experiment is hydrofining catalyst and pour point depressing catalyst. The former is prepared by impregnating the active metal component with a carrier, mainly composed of binary active component of VIB metal and VIII metal. Through comparative analysis, FH-98 is chosen as the refined catalyst. The latter is a bifunctional catalyst composed of a metal hydrofining component and an acid carrier, mainly abiding by the principle of hydrocracking reaction. By comparative analysis, FC-20 is chosen as the hydrocracking catalyst.

4. Experimental results and analysis

4.1 Raw materials and processes

Raw oil. Hydrofining-modification-heterogeneous pour point depressing raw material is oil mixture of MIP diesel and DCC diesel and the main properties are in Table 1. Diesel hydrofining/pour point depressing catalyst is 200mL small-scale hydrofining experiment device for performance evaluation and the process is shown in Figure 1.

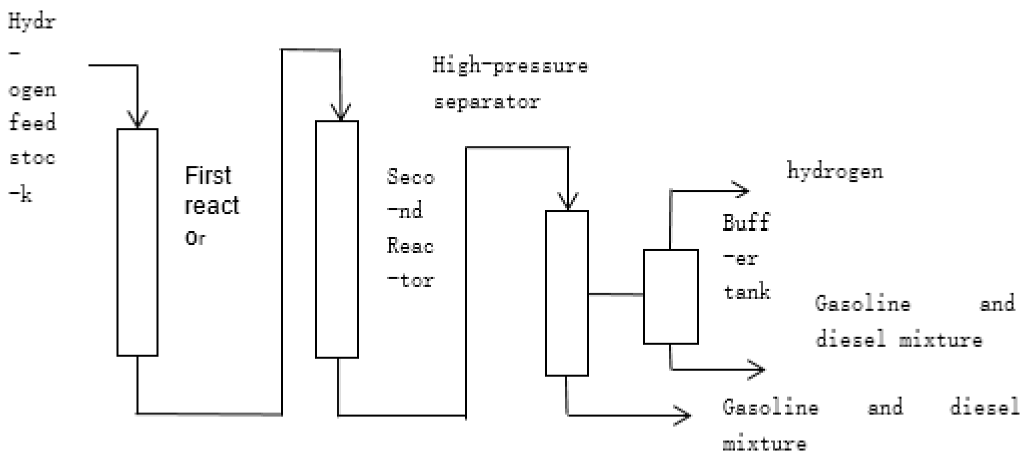

Figure 1: 200mL small hydrofining experiment flow

Catalyst. Composition and properties of hydrofining catalyst, modification catalyst, heterogeneous pour point depressing catalyst are in Table 2. Raw oil is mixed with mixed hydrogen after heat exchange and heated to the required temperature, then sequentially enters hydrofining-modification and heterogeneous pour point depressing reactors. Under the pour point depressing state and catalysts of FF-36, 3963, and FC-20, the raw oil carries out hydrodesulfurization, denitrification, olefin saturation and other chemical reactions. The reaction products are cooled to 50 °C, and then enter into cold high separator to separate oil, gas, and water. Most of the gas goes into the circulating hydrogen system and sulfur-containing sewage is sent to the outside of the device and the generating oil goes into the cold low separator. A small amount of flashed gas is discharged into the gas pipe to generate oil which is heated to 270 °C and enters the stripper. Diesel is obtained by stripping steam, cooled to 50 °C and sent out as a diesel product.

Table 1: The main properties of feedstock

project	Hydrofining of raw materials	Heterogeneous coagulation material
density	0.930	0.875
Initial boiling point	186	180
50°C	275	271
90°C	330	325
Dry point	370	365
Solidifying point	-5	-7
Sulfur content	8000	<5
Cetane number	28	37

Table 2: Catalyst composition and properties

project	FF-36	3963	FC-20
Active metal	Mo-Ni	W-Ni	W-Ni
Hole capacity	>0.32	>0.28	>0.30
Specific surface	>160	>200	>180
Shape	Clover strip	Clover strip	Cylindrical bar
Outer diameter	1.1-1.3	1.1-1.5	1.5-1.7
length	3-8	3-8	3-8
Packing density	0.80	0.76	0.92
Packing density	≧180	0.76	≧180

After being placed into the reactor, the catalyst is wet-vulcanized with kerosene containing CS2. And after the vulcanization is completed, the raw oil is switched to hydrofining evaluation. The raw oil is mixed with hydrogen and then enters the reactor to contact with the catalyst to undergo hydrofining/ heterogeneous pour point depressing reaction. The reaction products are respectively conducted gas-liquid separation in a high-pressure separator and a buffer tank, and the produced oil is cut into gasoline and diesel by TBP fractional device. Condensation point of diesel is determined and reaction temperature is adjusted according to the condensation point of diesel so as to achieve certain refined depth and corresponding pour point depressing effect.
Main hydrofining-modification and heterogeneous pour point depressing process parameters are in Table 3.

Table 3: Hydrofining-modification and heterogeneous pour point depressing process conditions

project	content
Total inlet pressure	10
Fresh feed volume	41.667
Inlet hydrogen oil volume ratio	700:1
A layer of inlet temperature	332
A layer of temperature difference	40
Second floor inlet temperature	370
Second floor temperature difference	21
Second floor temperature difference	381

The hydrofining-modification reactor is divided into three beds. The first bed contains 0.187 tons of FZC-100 catalyst, 0.335 tons of FZC-102B catalyst, 0.831 tons of FZC-103 catalyst, and 5.734 tons of FF-36 catalyst. The second bed contains 12.186 tons of FF-36 catalyst and the third bed contains 17.07 tons of 3963 catalyst. The heterogeneous depressing reactor is divided into two beds. The first bed contains 15.116 tons of FC-20 catalyst and the second bed contains 12.365 tons of FC-20 catalyst and 2.392 tons of FF-36 catalyst. The packing density of FZC-100 catalyst, FZC-102B catalyst, FZC-103 catalyst, FF-36 catalyst and FC-20 catalyst is respectively 0.85 t/m^3, 0.50 t/m^3, 0.62 t/m^3, 0.80 t/m^3, 3963 catalyst packing density 0.76 t/m^3, and 0.92 t/m^3. The initial condition of catalyst sulfidation is the total circulation of hydrogen in the heating furnace. The inlet temperature of hydrofining-modification reactor is 190°C and the inlet temperature of heterogeneous pour point depressing reactor is 185-190°C. The volume fraction of circulating hydrogen is not less than 85% and the dew point temperature is lower than -19°C.
Determination of sulfidation ending point. Under the condition that the bed temperature of the hydrofining-modification reactor is close to 370°C and concentration of H2S in circulating hydrogen is 10~20 m L/L, it shall meet the following conditions: (1) the dew-point spread of inlet gas of hydrofining-modification reactor and outlet gas of pour point depressing reactor is not more than 3°C, and lower than -19°C. (2) concentration of H2S inlet gas of hydrofining-modification reactor and outlet gas of pour point depressing reactor is basically the same. (3) high separator has no water to continue to generate. When the above conditions are met, it is thought that the sulfidation ending point is reached. Then continue to keep the temperature for one hour.

4.2 Hydrofining-modification calibration results

The inlet amount of hydrofining-modification-heterogeneous pour point depressing device runs by 42 t/h. Under the condition, the yield of hydrofining products is: 1.05% of acid gas, 7.04% of crude gasoline, 91.5% of refined diesel and the total liquid yield is 99.59%. The properties of products are in Table 4.
As can be seen from Table 4, when the device runs at full capacity, the average temperature of the hydrofining-modification reactor is 341 ° C and the sulfur content of the hydrofining diesel is below 50 μg/g, which reaches the national IV diesel standard; meanwhile, the relative density of diesel decreases from 0.930 g/cm3 to 0.864 g/cm3, and the hexadecane number increases by 8-9. It is shown that the FZC-100, FZC-102B, FZC-103, FF-36 and 3963 catalysts can achieve ideal results at lower reaction temperatures. The hydrofining-modification catalysts have excellent activity and desulfurization performance.

Table 4: The main properties of the product

project	Hydrofining products	Heterogeneous coagulation products
gasoline		
density	0.701	0.690
Distillation process	28-177	24-175
Sulfur content	120	118
Diesel		
density	0.864	0.851
Distillation process		
Sulfur content	48	41

4.3 Heterogeneous pour point depressing calibration results

Hydrofining evaluation of the oil mixture [w (coker diesel): w (catalytic diesel) = 55:45] is carried out.
It can be seen from the results in Table 5 that under the conditions that the catalyst developed by the oil mixture as raw material is used, the total space velocity is 1.5h-1, the reaction pressure is 9.5MPa, the volume ratio of hydrogen and oil is 800: 1, the reaction temperature in the refining section is 350 °C, the yield of diesel was 98.19%, the sulfur and nitrogen contents are both less than 50μg/g, and the ratio of hexadecane number and raw oil mixture increases by 1.1 units. When the reaction temperature increases to the refining section of 366°C and pour point depressing section of 381 °C and other conditions are the same, the total liquid yield of the catalyst is 99.13%, 0.62% higher than the reference catalyst, and the diesel yield is 0.52% lower than the reference catalyst, and the pour point depressing rate is 1.8°C higher than the reference catalyst. As a whole, the performance of developed catalyst has reached or even surpassed the performance of reference catalyst.

Table 5: Mixed oil feedstock hydrofining evaluation results

catalyst		Process conditions				Liquid yield
		Reaction stress/ρ: Volume space velocity/temperature				
Refined program	Development agent	9.5	800:1	1.5	350/360	100.62%
	Reference agent					100.50%
Pour solution	Development agent	9.5	800:1	1.5	366/381	99.13%
	Reference agent					98.51%

4.4 Efficiency analysis

In the specific application of diesel hydrofining, the introduction of a special kind of catalyst medium, use of disposable or partial recycle production technology process can effectively control the temperature, pressure and other technical parameters in the specific chemical reactions so as to achieve conversion rate of technical level within a certain range of technical applications of diesel mixture. On this basis, the yield differences, as well as different gasoline products and diesel products and byproducts represented mainly by hydrogen sulfide, dry gas and liquefied petroleum gas can be achieved.
At this stage, the configuration quantity of catalytic cracking technology of chemical engineering industry which has been formed and put into operation in mainland China, accounts for about 30.00% of the average data of the production and processing crude oil products. The average recovery rate of catalytic diesel products is examined by 23.00% of amplitude control level. Ten million tons of crude oil smelting manufacturers usually need to configure the catalytic diesel hydrocracking production technology devices with production efficiency of 700.00kt/a as a technical benchmark. Usually, the material balance parameter index data of improved process condition and the material balance parameter index data before the process improvement can be compared and analyzed to obtain the analysis results of basic production efficiency.
In the concrete process of catalyzing diesel hydrocracking, the final determination of the material components of gasoline products ranges from 38.50% to 53.30%, which is significantly higher than the gasoline output capacity under the background of diesel products modified technology. On the basis, the actual recovery rate of the effective finished products such as gasoline, dry gas and liquefied petroleum gas will increase as the catalytic diesel conversion rate improves. The hydrogen elemental components in the specific chemical reaction will increase as the actual level of conversion of diesel products increases.

5. Conclusion

At present, the demand of gasoline is far higher than that of diesel in China. The study on the hydrofining and pour point depressing tandem technology for catalyzing diesel is helpful to improve the production technology of diesel, save the production cost of enterprises and create good social benefits for enterprises.
The experiment shows that the catalyst can fully exert its catalytic effect on the hydrofining and pour point depressing tandem process, effectively reducing the sulfur content of diesel, which is environmentally friendly. At the same time, heterogeneous pour point depressing scheme and hydrofining can be flexibly converted to produce clean diesel with low demand for low pour point diesel and to improve the economic and social benefits of the enterprises.

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