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HYDROTREATING OF LIGHT ATMOSPHERIC GAS OIL AND ITS MIXTURE WITH GASOLINE

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Abstract

It is known that when hydrotreating heavy crude oil, the addition of lighter fractions provides a higher degree of sulfur removal. The aim of this work is to study the quality of the hydrogenate mixed with the gasoline fraction when hydrotreating light atmospheric gas oil. Hydrotreating was carried out using a flow-through laboratory unit on an aluminum-cobalt-molybdenum catalyst. The total sulfur content was analyzed according to ASTM D4294 method, saturated and aromatic hydrocarbons were determined by the liquid adsorption chromatography on the silica gel. The paper describes the influence of the technological parameters such as temperature and feed space velocity (FSV) on the degree of sulfur removal from the light atmospheric gas oil. As a result, the optimal parameters of the process are T=340°C and FSV = 2 h^{-1}. The paper shows the influence of the feedstock composition, the degree of the gasoline fraction involvement, on the chemical composition and quality parameters of the products. It is found that the hydrotreating depth of the light atmospheric gas oil increases with the addition of 5 % gasoline fraction. When hydrotreating atmospheric gas oil mixed with the gasoline fraction, compared with the initial atmospheric gas oil hydrotreating, the degree of sulfur removal grows by 2 %. The content of aromatic hydrocarbons in the hydrogenate decreases, and saturated hydrocarbons – increases.

***Keywords**: Hydrotreating; Atmospheric gas oil; Gasoline; Sulfur content.*

1. Introduction

Currently, the global trend of oil refining is an increase in the consumption of transport fuels while reducing the consumption of petroleum products in the energy and industrial sectors. Moreover, the quality of crude oil is constantly deteriorating, i.e. the oil is sour and has an increased density [1-5]. Thus, there is a global task to improve the secondary processes of oil refining, one of which is the process of hydrotreating [6-12].

The most important part of the hydrotreating process is to increase the degree of desulfurization of the feedstock. This becomes possible, on the one hand, with the improvement of the catalyst properties, on the other hand – with the appropriate preparation of the feedstock, the dispersion of which would be as high as possible for contacting with the active centers of the catalyst.

Recently, more and more researchers began to pay attention to the processes of hydrotreating of the target feedstock with various hydrocarbon additives. Vegetable oils, oil fractions, products of thermal and thermocatalytic processes can be used as additives [13-17].

So, the work [18] investigates the quality of the hydrogenates while co-hydrotreating the diesel fractions mixed with the coking gasoline (up to 40 %) and the coking light gas oil (up to 40 %). The influence of the feedstock and conditions of the processes on the chemical composition and quality parameters of the products is presented. The authors show that the residual sulfur content in the hydrotreated diesel fraction in all cases exceeds the sulfur content in the stable hydrotreated diesel fractions obtained from the mixed feedstock. Similar results were obtained by hydrotreating the mixtures of straight-run fractions and thermal contact cracking gas oils.

One of the options for processing the low-quality secondary gasolines is also their hydrotreating in a mixture with the straight-run diesel fractions. According to the industrial mileage [19], the addition of up to 7 wt. %. of the gasoline increases the degree of desulfurization of the diesel fraction, a larger amount (up to 10 wt. %) decreases it.

Consequently, various hydrocarbon additives to the feedstock contribute to an increase in the degree of their hydrodesulfurization. However, there is no systematic research on this subject and it is of scientific interest. In this regard, the purpose of this work is to study the quality of the hydrogenate while hydrotreating the light atmospheric gas oil and co-hydrotreating the light atmospheric gas oil mixed with the gasoline.

2. Experimental

2.1. The description of the laboratory experimental unit

The experimental unit used in the work is designed to study the processes under high pressure conditions in the flow mode, at a maximum pressure of 90 bar and a maximum temperature of 700°C. The technological scheme of the laboratory hydrotreating unit is shown in Figure 1. The unit includes three blocks: for the distribution of hydrogen and the feedstock, the reaction and the product separation.

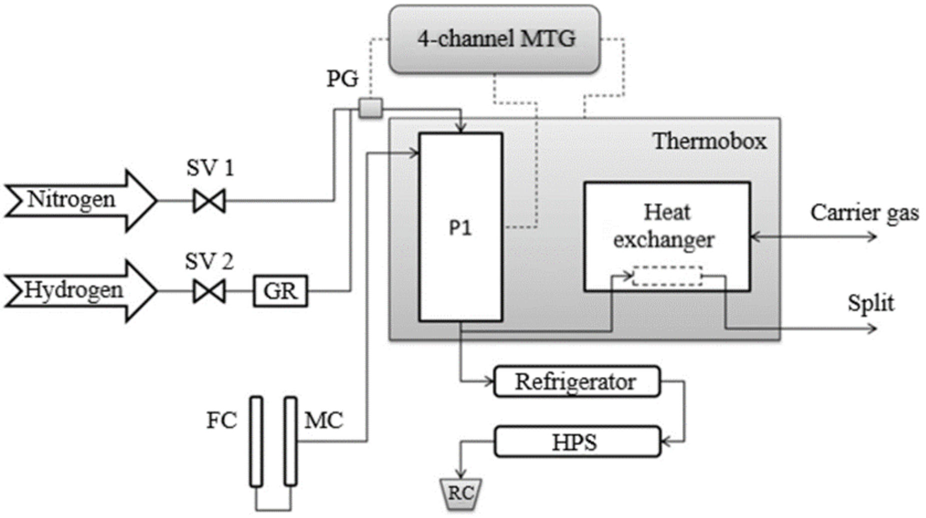

Figure 1. Technological scheme of laboratory catalytic unit: SV – stop valve; GR – gas regulator; PR – pressure reactor; HPS – high-pressure separator; PG – pressure gauge; RC – receiving container; MTG – microprocessing temperature gauge; MC – measuring container; FC – feedstock container.

For the experiments, a flow-type reactor made of stainless steel was used; it allows carrying out the process under high pressures. The reactor design is shown in Figure 2. The internal diameter of the reactor is 12 mm and the maximum volume of the loaded catalyst is 10 cm^3.

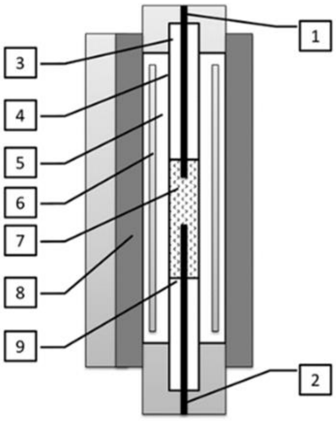

Figure 2. Tube wall reactor: 1, 2 – thermocouples, 3 – evaporator, 4 – vessel hull, 5 – copper bandage, 6 – furnace, 7 – catalyst bed, 8 – thermoinsulation, 9 – grid

2.2. Conducting the hydrotreating process

The fraction of the light atmospheric gas oil with a total sulfur content of 0.699 wt. %. and a mixture of the atmospheric gas oil (95, 85 and 75 volume %) with the light gasoline fraction (5, 15 and 25 volume %) respectively were chosen as the feedstock for the laboratory studies. The physical and chemical characteristics of the light atmospheric gas oil and the gasoline fraction are presented in Table 1.

Table. 1. Physical and chemical characteristics of light atmospheric gas oil and gasoline fraction

Parameters	Light atmospheric gas oil	Gasoline fraction
	0.875	0.730
Fractional composition, evaporate % vol.		
IBP, °C	230	40
50% vol., °C	350	115
FBP, °C	380	146
Viscosity, mm^2/s	20.08	0.63
Sulfur content, wt. %.	0.699	0.003
Saturated hydrocarbon content, wt. %.	63.89	73.4
Aromatic hydrocarbon content, wt. %.	36.11	26.59

In the hydrotreating process an aluminum-nickel-molybdenum catalyst intended for deep hydrotreating of petroleum fractions was used. The characteristics of the catalyst are presented in Table 2. The size of the catalyst pellets loaded into the reactor is 1-2 mm, the catalyst charge capacity - 7 cm^3.

Table. 2. Characteristics of hydrotreating catalyst

Characteristic	Parameter
Bulk weight, g/cm^3	0.55 – 0.75
Content, wt. %:	
CoO	12.0
NiO	2.2
MoO_3	> 13.0
Na_2O	> 0.4
Carrier	Active aluminum oxide
Durability, kg/mm	> 2.0

Before using, the catalyst was sulfided with the feedstock containing dimethyldisulfide (DMDS) in the presence of hydrogen under high pressure. Sulfiding was carried out directly in the reactor using a light straight-run diesel fraction with a sulfide sulfur content of 0.654 %, according to the following procedure:

1) Catalyst drying in a hydrogen stream at a temperature of 140°C;
2) Catalyst wetting with the feedstock and pressure increasing in the reactor up to 3.5 MPa;
3) Temperature increasing in the reactor up to 240°C at a velocity of 50°C/hour;
4) Low-temperature sulfiding at 240°C for 8 hours;
5) Temperature increasing up to 340°C at a velocity of 50°C/hour;
6) High-temperature sulfiding at 340°C for 8 hours.

The sulfiding mixture was fed to the reactor at a space velocity of 2 h^{-1}, at a pressure of 3.5 MPa and a ratio of H_2/feedstock = 300/1. Hydrotreating was carried out on a flow-through laboratory unit at the temperatures of 340°C, 360°C and 380°C, a hydrogen pressure of 3.5 MPa, a feedstock space velocity of 2 h^{-1}, 3 h^{-1} and 5 h^{-1}, the ratio of hydrogen to the feedstock 350/1. The temperature in the reactor was maintained with an accuracy of ±0.5°C; pressure ±0.1 MPa; feedstock consumption ±0.2 mL/h; hydrogen consumption ±0.2 L/h.

Feedstock and hydrogen were fed into the reactor from top to bottom: the diesel fraction was pumped by a high-pressure dosing pump; the hydrogen supply was automatically regulated by a dispenser. The temperature in the reactor located in the air thermostat was set and maintained by a thermoregulator. A thermocouple was used to measure the tempe-rature in the catalyst bed. The pressure in the system was set by means of a high-pressure reactor and was controlled by a standard pressure gauge.

The reaction products were fed into a water refrigerator-condenser. The liquid reaction products were collected for analysis by draining into the receiver. The gaseous products through the valve-throttle went to the six-pass valve, through which the gas was split into the atmosphere.

2.3. Analysis of feedstock and products after hydrotreating process

The feedstock and the obtained hydrogenate were analyzed after the unit had been switched to stationary mode.

The total sulfur content was determined using an energy dispersive X-ray fluorescence analyzer according to ASTM D4294 "Standard Test Method for Sulfur in Petroleum and Petroleum Products by Energy Dispersive X-ray Fluorescence Spectrometry".

The saturated and aromatic hydrocarbons were determined by the liquid adsorption chromatography on the silica gel, pre-calcined at 180°C for 4 hours. The chromatographic column was filled with the sorbent in the ratio sample:sorbent equal to 1:40 by weight. The silica gel was moistened with petroleum ether (PE). The sample was mixed with PE and evenly distributed over the entire surface of the sorbent. Further, the paraffin-naphthenic hydrocarbons were separated by PE, aromatic hydrocarbons were eluted by a mixture of PE:toluene in the ratio of 6:1. After separating the diesel fuel into fractions, the solvent was distilled (up to 3-5 ml) on a rotary evaporator at a bath temperature of 40-45°C. The samples were placed in a suction drier and brought to a constant mass, weighed.

3. Results and discussion

3.1. Influence of technological conditions on the process of light atmospheric gas oil hydrotreating

The results of the light atmospheric gas oil hydrotreating by varying the process temperature and feed space velocity (FSV) are shown in Tables 3 and 4.

Table. 3. Results of light atmospheric gas oil hydrotreating by varying process temperature (FSV=3 h^{-1}, H_2/feedstock=500/1, P=3.5 MPa)

Parameter	Initial AGO	Temperature, °C 340	 360	 380	 400
Sulfur content, wt. %.	0.6990	0.0608	0.0590	0.0587	0.0476
Sulfur removal degree, %	-	91.3	91.5	91.6	93.2
Aromatic hydrocarbon content, wt. %.	36.11	34.30	30.92	29.50	36.36
Saturated hydrocarbon content, wt. %	63.89	65.70	69.18	70.50	63.64

Table. 4. Results of light atmospheric gas oil hydrotreating by varying feed space velocity (T=340 °C, H_2/feedstock=350/1, P=3.5 MPa)

Parameter	Initial AGO	FSV, h^{-1} 2	 3	 5
Sulfur content, wt. %.	0.699	0.0543	0.0547	0.0578
Sulfur removal degree, %	-	92.2	92.2	91.7
Aromatic hydrocarbon content, wt. %.	36.11	35.19	37.81	39.25
Saturated hydrocarbon content, wt. %	63.89	64.81	62.19	60.75

The analysis of the results (Table 3) shows that with an increase in the temperature of the hydrotreating process, the degree of sulfur removal from the feedstock – light atmospheric gas oil, varies slightly from 91.3 to 93.2 % and reaches its maximum value of 93.2 % at 400°C.

In the temperature range from 340 to 360°C, there is a decrease in the proportion of aromatic hydrocarbons and an increase in the proportion of saturated hydrocarbons. With a further increase in the temperature up to 400 °C, the equilibrium of the hydrogenation reactions of the aromatic compounds is shifted towards the initial components, which leads to a decrease in the amount of the saturated hydrocarbons. The optimum in this case is the temperature T=340°C, since its further increase does not have a significant effect on the composition of the hydrogenate and the degree of sulfur removal.

The analysis of the results of the hydrotreating process (Table 4) shows that at a high feed space velocity within 5 h^{-1}, the degree of light atmospheric gas oil hydrotreating is 91.7 %. With a decrease in FSV up to 3 h^{-1}, the degree of hydrotreating increases up to 92.2 % and remains constant at FSV equal to 2 h^{-1}. The degree of the atmospheric gas oil hydrotreating rises with a decrease in FSV as a consequence of increasing the contact time of feedstock with the catalyst and deeper hydrogenation reactions. As a result, the optimal parameters of the process were T = 340°C and FSV = 2 h^{-1}.

3.2. Hydrotreating of light atmospheric gas oil with gasoline fraction

The results of hydrotreating of the light atmospheric gas oil mixed with the gasoline fraction are shown in Table 5.

Table. 5. Results of hydrotreating of light atmospheric gas oil (AGO) mixed with gasoline fraction (GF) (T=340 °C, H_2/feedstock=350/1, P=3.5 MPa, FSV=2 h^{-1})

Fraction mixture	Content in fraction mixture, wt. %			Content in hydrotreated atmospheric gas oil, wt. %			Hydrotreating degree, %
	sulfur	saturated hydrocarbons	aromatic hydrocarbons	sulfur	saturated hydrocarbons	aromatic hydrocarbons	
100% AGO	0.699	63.88	36.11	0.061	64.81	35.19	91.3
95% AGO + 5% GF	0.674	65.67	34.33	0.049	67.26	32.73	92.5
85% AGO + 15% GF	0.668	68.13	31.87	0.045	70.94	29.06	93.3
75% AGO + 25% GF	0.621	70.67	29.33	0.042	71.54	28.46	93.3

In the mixture of the light atmospheric gas oil with the gasoline fraction, the total sulfur content in the feedstock is reduced by dilution. Dilution also has a positive effect on the hydrodesulfurization reactions. In the case of the addition of the gasoline fraction (5 %), the sulfur content in the hydrogenate is significantly reduced from 0.0608 up to 0.0499 wt. %. The degree of sulfur removal from the initial mixture varies from 91.3, when hydrotreating the atmospheric gas oil, up to 93.3 % in the mixture with 15 % of the gasoline fraction. At the same time, the increase in the content of the gasoline fraction up to 25 % does not increase the degree of hydrotreating.

In the case of adding the gasoline fraction to the atmospheric gas oil, the viscosity of the feedstock decreases, which can improve the diffusion of hydrogen to the catalyst surface through the liquid phase film and lead to an increase in the degree of hydrodesulfurization [20].

When hydrotreating the atmospheric gas oil mixed with the gasoline fraction, compared with the atmospheric gas oil hydrotreating, the degree of sulfur removal grows by 2 %. The content of aromatic hydrocarbons in the hydrogenate decreases, and saturated hydrocarbons – increases.

Therefore, the additives to the feedstock can act as a regulator of the thickness of the liquid phase film on the surface of the catalyst, increasing the access of the hydrocarbons to the active centers. Thus, the use of the gasoline fraction in the hydrotreating process of the light atmospheric gas oil leads to the decrease in the content of sulfur and unsaturated hydrocarbons.

4. Conclusions

1. The use of other oil fractions in the hydrotreating of the target feedstock leads to an increase in the depth of hydrodesulfurization. In this paper, the hydrotreating process of light atmospheric gas oil mixed the gasoline fraction is considered. Hydrotreating was carried out using a flow-through laboratory unit on a catalyst. It was found that when hydrotreating light atmospheric gas oil, the optimal parameters of the process are T = 340°C, H_2/feedstock=350/1, P=3.5 MPa, and FSV = 2 h^{-1}. The temperature increase of more than 340°C does not significantly affect the composition of the hydrogenate and the degree of sulfur removal. At FSV = 2 h^{-1}, the greatest degree of hydrotreating is observed as a consequence of a longer stay of the feedstock in the reactor.
2. It was found that when the gasoline fraction is added to the light atmospheric gas oil, the sulfur and aromatic hydrocarbon content in the hydrogenate is significantly reduced, and the proportion of the saturated hydrocarbons increases. The greatest effect is achieved by adding the gasoline fraction (5 %) to the light atmospheric gas oil. The total sulfur content is reduced from 0.061 to 0.049 wt. %. The increase in the content of the gasoline fraction up to 25 % does not increase the degree of hydrotreating.
3. When hydrotreating the atmospheric gas oil mixed with the gasoline fraction, compared with the atmospheric gas oil hydrotreating, the degree of sulfur removal grows by 2 %. The content of the aromatic hydrocarbons in the hydrogenate decreases, and the content of the saturated ones increases.
4. The additives to the feedstock can regulate the thickness of the liquid phase film on the surface of the catalyst enhancing the diffusion of hydrogen to the catalyst surface through the liquid phase film and leading to an increase in the degree of hydrodesulfurization. Thus, the use of the gasoline fraction in the hydrotreating process of the light atmospheric gas oil leads to the decrease in the content of sulfur and unsaturated hydrocarbons in the hydrogenate compared to the hydrotreating of the initial atmospheric gas oil.

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