

Changing the composition of the group hydrocarbons of diesel fractions in the process of hydrotreating

N Krivtcova^{1,a}, K Baklashkina^{1,b}, Sh Sabiev^{1,c}, E Krivtsov^{2,d} and A Syskina^{1,e}

¹ 634050, Russia, Tomsk, Lenin Avenue 30, National Research Tomsk Polytechnic University

² 634021, Russia, Tomsk, Akademichesky avenue 4, Institute of petroleum chemistry SB RAS

E-mail: ^akrivtcova@mail.ru, ^bksenija.baklashkina@gmail.com,

^csabiyev.shyngys@gmail.com, ^djohn@ipc.tsc.ru, ^eannesyskina@yahoo.com

Abstract. Change in group composition of sulfur compounds and structural group composition of the diesel fractions in the course of hydrotreating is presented in the paper. The removal degree of sulfur compounds is shown to comprise 95.8 % rel. The homologs of benzothiophenes are removed for 93.9 % rel., ones of the dibenzothiophenes are for 90.7 % rel. A considerable change in group composition of diesel fraction is established in the course of hydrotreating. Hydrogenation degree of aromatic hydrocarbons is 24.4 % wt., the amount of saturated hydrocarbons has increased by 20.4 % wt.

1. Introduction

The main industrial process for sulfur removal is catalytic hydrodesulphurization in which sulfur compounds (SC) break down forming hydrogen sulfide, and the hydrocarbonic part of raw material molecules is restored and remains as a part of the target liquid products [1]. However, tougher ecological requirements to gasolines and diesel fuels [2-5] dictate the need of increase in capital and operational expenditures for production of fuels with low sulfur content. Generally, an increase in production costs is caused by an increase in hydrogen partial pressure in the system and decline in reactor capacity [6-8]. [1] It is believed that it is possible to obtain the motor fuel that meets the strictest standards via improving catalysts and reactors, optimizing technological processes. So, temperature increase of the process causes increase in hydrogenolysis depth of SC, and leads to deeper hydrogenation of aromatic and olefin hydrocarbons. However, the undesirable reactions of hydrocracking leading to formation of gasoline and merkaptan increasing the total sulfur content in the products are also possible.

The paper is aimed at studying influences of temperature and time on the content of sulfur compounds and structural group composition of the diesel fraction in the course of hydrotreating.

2. Experiment

2.1. Diesel hydrotreating

Hydrotreating of diesel fuel with the total sulfur content of 1.430 % wt. was carried out on the laboratory catalytic reactor, the flow-through system with the evaporator, the reactor on the special metal gauze of which the catalyst is placed, the condenser, and the hydrogenate receiver.



Hydrotreating was performed with the aluminum-cobalt-molybdenum catalyst GKD-202, the granule size is 1-2 mm, the catalyst volume in the reactor is 10 ml.

The raw materials and hydrogen came to the reactor from top downward: the diesel fraction was supplied with the high pressure dosing pump; hydrogen supply was regulated with the automatic batcher. The reactor temperature in the air heating oven was set and maintained by the temperature regulator providing the heat accuracy of ± 0.5 °C. The thermocouple placed in the pocket in the center of the reactor is used for temperature measurement in the catalyst layer. System pressure was measured by means of the high pressure reducer and controlled according to the indications of the standard pressure gauge.

The products of reaction came to the water cooler-condenser. The liquid products of reaction were gathered for the analysis by discharge in the receiver. The gaseous products via the throttle gate came to the six-port valve by means of which gas is dumped into the atmosphere.

Diesel fuel was hydrotreated under the following experimental conditions: the volume rate for liquid raw materials was 2 h^{-1} , pressure was 3,5 MPas, hydrogen/raw materials ratio was 300/1, temperature was 340, 360 and 380 °C.

2.2. Methods of analysis for initial diesel fuel and hydrotreating products

The method of gas-liquid chromatography (GLC) was used to identify the sulfur compounds. GLC was conducted with use of the chromatograph "Kristall 2000M" which includes $25 \text{ m} \times 0.22 \text{ mm}$ quartz capillary column with SE-54 stationary phase, gas carrier is helium. The sulfur-selective flame photometric detector (FPD) was used for analysis of sulfur compounds. There was a linear increase in column heating oven temperature from 50 to 290°C, the heating rate was 4 degrees per minute. The qualitative composition of sulfur compounds was determined by comparing the retention times of the individual compounds (Di-n-hexyl sulfide, benzothiophene, dibenzothiophene) and the analyzed components. Also the literature data was used. The quantitative composition of sulfur compound groups and individual isomers was determined by analyzing the space of chromatographic peak areas, obtained by calculating the space of peak areas (% rel.) in relation to the total sulfur content in the sample (% wt.).

To determine the total sulfur concentration in the initial diesel fuel and the hydrogenate the spectral photometer SPECTROSKAN-S was used.

The group hydrocarbonic composition of the initial distillate was determined by means of the liquid adsorption chromatography on the activated aluminum oxide of the II activity degree according to the method of Brockman (the certified method № 1216-2006 of Institute of petroleum chemistry SB RAS). The chromatographic column, which is $75 \times 1.8 \text{ cm}$ in size, was filled with the sorbent in the "wet" method for removal of sorbent wetting heat and reduction of channel forming in the sample-to-sorbent ratio of 1:80 by weight. The quantity of the sample was mixed with hexane and evenly distributed on all the surface of the sorbent. Then the fractions of saturated, mono- and bi-aromatic hydrocarbons were separated by n-hexane, the tri-aromatic hydrocarbons were eluted by the mixture of hexane and benzene (3:1 by volume).

The structural group analysis of the diesel fraction was carried out by the n-d-M method which is widely used for research of medium and heavy fractions of oil so far. Hydrocarbons mixture of the studied fraction is presented in the form of one "average molecule" the properties of which are defined in the ratio of arene and cycloalkane fragments and alkane chains.

For calculation of structural group composition of the fractions by the n-d-M method, it is necessary to experimentally define the following physical constants:

1. The index of refraction within the accuracy of ± 0.0001 was defined with the IRF-22 refractometer at 20 °C.

2. Density within the accuracy of $\pm 0.0002 \text{ g/ml}$ was determined by the picnometer method at 20 °C according to GOST 17310-2002.

3. Molecular weight within the accuracy of $\pm 3\%$ rel. was found according to the tables, for this reason viscosity was defined at 20 °C, 50 °C, 100 °C in accordance with GOST 33-2000.

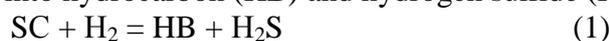
3. Results and discussion

In the course of hydrotreating of the diesel fraction with the total sulfur content of 1.430 % wt., the maximum degree of SC removal was 94.5, 95.0, 95.8% at the process temperature of 340, 360 and 380 °C, respectively. Change in the total sulfur content in the course of hydrotreating of diesel fuel depending on time of the process at a temperature of 380 °C is presented in table 1.

Table 1. Change in the total sulfur content in the course of hydrotreating at a temperature of 380 °C

Process duration, h	S _{tot.} , % wt.	Removal degree S _{tot.} , %
0	1.430	–
2	0.094	93.92
4	0.079	94.47
6	0.070	95.10
8	0.060	95.80

Using the formalized reaction of sulfur compounds (SC) transformation in the environment of hydrogen (H₂) into hydrocarbon (HB) and hydrogen sulfide (H₂S):



it is possible to determine transformation rate and to compose the kinetic model considering concentration change in sulfur compounds in the course of hydrotreating:

$$W = k \cdot C_{\text{SC}} \cdot C_{\text{H}_2},$$

$$\frac{dC_{\text{SC}}}{dt} = -k C_{\text{SC}} C_{\text{H}_2},$$

where W is chemical reaction rate (1); k – reaction rate constant; C – substance concentration.

After calculation of the inverse kinetic equation, the rate constant of sulfur compounds (SC) transformation on the GDK-202 catalyst was 3.02 s⁻¹.

It is established that the initial fraction contains a wide set of SC – sulfides, homologs of benzo- and dibenzothiophenes (table 2). There are 41% of BT homologs, about 14 % rel. of DBT homologs in the initial fraction. The hydrotreating products contain a limited set of compounds in the composition; they generally are homologs of benzo- and dibenzothiophenes. In the hydrotreating products C the percent of dibenzothiophene sulfur increases up to 48, 47, and 27% of the total sulfur at 340, 360, and 380 °, respectively. According to the data of the chromatographic analysis, the strongest compounds are 4-methyl-DBT and 4,6-dimethyl-DBT the content of which falls no more, than 20% rel.

Table 2. Sulfur content in the sulfur compound groups in the initial fraction and hydrotreating product (8 h)

Fraction	Composition, % wt.					
	C ₁ BT	C ₂ BT	C ₃ BT	DBT	C ₁ DBT	C ₂ BT
Initial	0.0340	0.2020	0.3510	0.0360	0.0880	0.0800
After hydrotreating (340 °C)	0.0017	0.0128	0.0222	0.0236	0.0036	0.0095
After hydrotreating (360 °C)	0.0019	0.0125	0.0219	0.0220	0.0030	0.0071
After hydrotreating (380 °C)	0.0020	0.0152	0.0228	0.0028	0.0065	0.0073

The kinetic researches [9, 10] have shown that these molecules are rather slowly hydrogenated to the dihydrothiophene derivatives. These unstable intermediate products will easily be transformed by two stage hydrogenation into tetrahydro- and hexahydrothiophene compounds or desulphurized with obtaining biphenyl derivatives.

Change in the group hydrocarbonic composition and structural group composition of the initial diesel fraction and hydrotreating products is presented in tables 3 and 4. The general tendency is decrease in the total number of aromatic compounds and, as a result, increase in a percent of saturated compounds.

Table 3. Change in the group composition of the initial fraction and hydrotreating product

Fraction	Composition, % wt.			
	SHB	mono-arenes	bi-arenes	tri-arenes
Initial	53.8	28.2	13.8	2.2
After hydrotreating	64.8	21.1	10.4	1.9

Table 4. Structural group composition of the initial fraction and hydrotreating products

Process duration, h	C _A	C _C	K _A	K _T	C _N	C _P	K _N
0	19.68	60.08	0.50	1.46	45.40	40.90	0.96
2	18.00	59.10	0.50	1.54	41.00	40.90	1.14
4	23.00	54.00	0.50	1.50	31.00	46.00	1.00
6	24.90	52.70	0.60	1.45	26.30	47.30	0.85
8	24.91	30.00	0.60	2.00	14.91	70.00	1.40

Ca - the carbon content in the aromatic compounds; Cc - the carbon content in the cyclic compound (aromatic + naphthenic); K_A – the average number of aromatic rings in a molecule; K_T – the total number of rings (aromatic + naphthenic); C_N - the carbon percent in the naphthenic compounds, %; C_P - the carbon percent in the paraffin compounds, %; K_N - the average number of naphthenic rings in a molecule.

Hydrotreating leads to decrease in quantity of bi- and tri-aromatic hydrocarbons more than twice, the content of monoaromatic hydrocarbons decreases from 28.2 to 21.1 % wt. in the products. There is a significant increase in a percent of saturated hydrocarbons from 53.8 to 64.8 % wt. These changes favorably affect commodity properties of the obtained product. It is known that tendency to hydrogenation of aromatic compounds changes in the following row: tri-aromatic > bi-aromatic > monoaromatic. It is established that the use of the GKD-202 catalyst in the course of hydrotreating leads to approximately equal removal (in (% rel. from the initial quantity) of all groups of aromatic compounds.

According to the structural group analysis of the diesel fraction before and after the process of hydrotreating, there is an increase in paraffin compounds and decrease in the number of aromatic compounds. The average number of aromatic rings also reduces.

4. Conclusion

It is established that the use of the GKD-202 catalyst in the course of hydrotreating of the diesel fraction allows removing more than 95.8 % rel. from the initial quantity of sulfur in the raw materials. It is shown that the removal degree of sulfuraromatic compounds falls with increase in quantity and size of alkyl substitutes. Dibenzothiophenes derivatives are removed much worse than the homologs of benzothiophenes.

The analysis of the initial fraction SC and hydrotreating products has shown that the compounds 4-methyl-DBT and 4,6-dimethyl-DBT are stable and are practically not exposed to hydrogenolysis with the GKD-202 catalyst.

It is established that there is a change in group and structural group composition of the fraction in the course of hydrotreating. The degree of aromatic hydrocarbons removal is 24.4% while the quantity of saturated hydrocarbons increases 20.4%.

5. References

- [1] Chertkov Ya, Spirkin V 1971 *Moscow chemistry*. Sulfur and oxygen compounds of oil distillates. pp. 307.
- [2] Babich I and Moulijn J 2003 *Science and technology of novel processes for deep desulfurization of oil refinery streams*. a review Vol. **82** (6) pp. 607-631.
- [3] Mitusova T, Polina E and Kalinina M 2002 *Moscow Equipment*. Modern diesel fuels and its additives. pp. 63.
- [4] Kaminsky E and Havkin V 2001 *Moscow Equipment*. Deep oil refining: technological and ecological aspects. pp. 384
- [5] Danilov A 2003 *Moscow Equipment*. Introduction to chemmotology. pp. 464.
- [6] Elshin A, Grishanov G and Mikishev V 2003 Oil processing and petrochemistry. Vol. **8** pp. 26.
- [7] Kaminsky E, Melik-Akhazarov T and Havkin V 1998 *Science and technology of hydrocarbons*. Vol. **1** pp. 68.
- [8] Kaminsky E, Havkin V, Kurganov V 2000 *World of oil products*. Vol. **2** pp. 9.
- [9] Meille V, Schulz E, Lemire M and Vrinat K 1997 *J.Catal.* Hydrodesulfurization of Alkyldibenzothiophenes over a NiMo/Al₂O₃ Catalyst: Kinetics and Mechanism. Vol. **170** pp. 29-36.
- [10] Krivtsova N, Krivtsov E, Ivanchina E and Golovko A 2013 *Basic Researches*. Kinetics of hydrodesulfurization of diesel fraction. Vol. **8-3** pp. 640-644.