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Mathematical modelling of diesel fuel hydrodesulfurization kinetics

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Abstract

The experimental data for hydrogenation of sulfur compounds including benzothiophenes (BT) and dibenzothiophenes (DBT) in the diesel fuel with 1.4 mass% of sulfur content is obtained using the laboratory setup with the aluminum-cobalt-molybdenum catalyst GKD-202 at the pressure of 3.5 MPa and different temperatures. The sulfur compound removal factor reaches 98 mass%. Dynamics of DBT and BT concentrations allowed designing a kinetic model represented by the system of differential equations of individual sulfur compound rates. The kinetic model was included in the developed software. The basis of the algorithm for reverse kinetic problem solution is the method of scanning through predefined range of constants. This enables performing the calculation with an error not exceeding 0.007%. The obtained data confirmed that chemical activity increases in the order: DBT, BT, sulfides. The rate of desulfurization decreases with increase in alkyl substituents concentrations. DBT desulfurization is much worse than the one of BT. The calculated data allowed building the graphs representing BT and DBT concentration dynamics.

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Keywords: Mathematical modeling; programming; hydrotreating process; diesel fraction; benzothiophene; dibenzothiophene; reaction rate constant; activation energy.

1. Introduction

In the process of catalytic hydrotreating petroleum products undergo the series of chemical reactions with a goal of removing heteroatomic compounds, such as sulfur-containing hydrocarbons. Subsequently the amount of sulfur compounds in the petroleum products, such as diesel fuel, greatly decreases. This provides higher quality of fuel and

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accordance to modern fuel standards and ecological restrictions. Also, sulfur compounds may be poisonous for expensive catalysts used in subsequent production processes. All these points make the hydrotreating process very demanded nowadays and applied to any petroleum refinery^{1,2}.

Given these conditions the topicality of hydrotreating processes forces new researches to appear in this branch of science including development of computer modeling systems, which implement various mathematical models of this process³.

2. Experiment

The hydrotreating process of diesel fuel with 1.4 mass% of sulfur content was carried out with use of the laboratory catalytic equipment. This laboratory setup is represented by the vaporizer, condenser, products storage and reactor with a special metallic grid with the catalyst. The volume of the catalyst is 20 ml.

The diesel fuel fraction and hydrogen are fed to the reactor from top to bottom. The feed is supplied with the high pressure dosing pump. The hydrogen feed is regulated by the automatic dispenser. The temperature in the reactor in the air thermostat is supported by the thermal regulator that ensures the accuracy of the heat with error not greater than 0.5 degrees. To measure the temperature in the catalyst bed the thermocouple is used, placed in the pocket located at the center of the reactor. The system pressure is set using the high-pressure reducer and controlled by the data of the exemplary gauge.

The reaction products flow into the water condenser. The liquid products are collected for analysis of the reaction by pouring into the receiver. The gaseous products enter the six-way valve through the valve choke. Thus, the gas discharges into the atmosphere.

The aluminum-cobalt-molybdenum catalyst GKD-202 (Novokuibyshevsk catalyst plant Ltd.) for petroleum hydrotreating was used. GKD-202 is the catalyst produced in Russia which has a shape of cylinder granules. Al₂O₃ is used as a carrier, and nickel and molybdenum are used as active metals. The reactor was charged with 10 ml of the sample catalyst with the granule size of 1-2 mm.

The catalyst was preliminarily sulfided directly in the reactor before use. The straight diesel fraction with 0.4 mass% content of sulfur was used for this. Sulfidation included the next steps:

- drying of the catalyst in the stream of nitrogen at the temperature of 120°C;
- supplying the reactor with hydrogen and increasing pressure to 3.5 MPa;
- wetting the catalyst with feed;
- increasing temperature in the reactor to 240°C;
- sulfiding at 240°C for 2 hours (low-temperature stage);
- increasing temperature to 340°C;
- sulfiding at 340°C for 2 hours (high-temperature stage).

The sulfiding mixture was fed to the reactor with the volume rate of 2 h⁻¹ at the H₂:feed =300:1 ratio.

Hydrotreating process was carried out under the next conditions: volume rate of the feed – 2 h⁻¹; hydrogen pressure – 3.5 MPa; ratio of hydrogen to feed – 300:1; temperatures – 340°C, 360°C and 380°C.

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

The method of gas-liquid chromatography (GLC) was used to identify the group of sulfur compounds. GLC was conducted with use of the chromatograph "Kristall 2000M" which includes 25 m × 0.22 mm quartz capillary column with SE-54 stationary phase. Helium was used as a carrier gas. When using the flame photometric detector (FPD) for analysis of sulfur compounds there was a linear increase in temperature from 50 to 290°C. The heating rate of the column was 4 degrees per minute.

The qualitative composition of sulfur compounds was determined by comparing the retention times of the individual compounds (hexyl sulfide, benzothiophene, dibenzothiophene) and 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 peak areas obtained by calculation of the space below the graph (relative percent) in relation to the total sulfur content in the sample (weight percent).

The general aim of this research work is to determine the kinetic parameters of the chemical reactions during the process of hydrodesulfurization, i.e. the purpose is to solve the reverse kinetic problem. In addition, the activation energy is calculated for each route of chemical reactions. The dynamics of such sulfur-containing hydrocarbons as dibenzothiophenes (DBT), sulfides (S) and benzothiophenes (BT) were chosen for study because of high diversity and prevalence of these components in petroleum products, especially in diesel fuel. Along with reverse problem solution the chemical mechanism formalization and computer software development, which implements this mathematical model, were carried out.

In any case the number of individual sulfur-containing hydrocarbons in diesel fuel from the feedstock can reach 400. So, it is impossible to calculate the concentrations and study the dynamics of each particular sulfur compound even with the use of powerful computers. This leads to the requirement of kinetic scheme formalization to reduce the amount of calculation with such methods as aggregation of active components considering their thermodynamic potentials. On the other side, the mathematical model developed with such methods should be adequately sensitive to various compositions of diesel fuel feedstock. This enables the modeling system to calculate properties of desulfurized products with acceptable accuracy^{4,5}.

In the frame of current research various models of hydrotreating process have been developed in recent years^{6,7}. The thermodynamic calculations for the reactions in the process of diesel fuel hydrotreating were used to develop the formalized kinetic scheme (Fig. 1). All homologous series of sulfur-containing hydrocarbons were merged into virtual “pseudocomponents” based on the calculations of their isobaric-isothermal potential observed in the process of their hydrogenation.

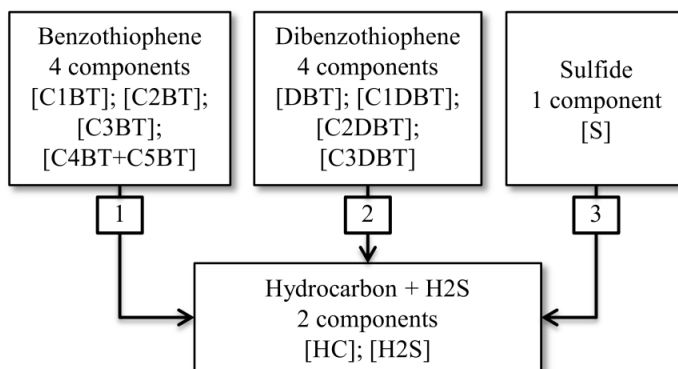


Fig. 1. The formalized kinetic scheme of diesel fuel hydrotreating process

On the basis of the kinetic scheme shown above the mathematical model was designed. This system of differential equations (Table 1) representing the law of mass action is used in the computer program. The next assumptions were used before the mathematical model development :

- all reactions of hydrogenolysis are considered to be first-order quasi-homogenous reactions;
- there is no considerable effect of diffusion, so equations are based on the law of mass action;

Table 1. The mathematical model of sulfur compound hydrogenolysis

Group of sulphur compounds	Differential equation
Benzothiophenes	$\frac{dC_{benzothiophene}}{d\tau} = -k_1 C_{benzothiophene} C_{H_2}$
Dibenzothiophenes	$\frac{dC_{dibenzothiophene}}{d\tau} = -k_2 C_{dibenzothiophene} C_{H_2}$
Sulfides	$\frac{dC_{sulf}}{d\tau} = -k_3 C_{sulf} C_{H_2}$

The reaction speeds of hydrogenolysis on all three routes can differ significantly depending on various reaction activity of sulfur-containing hydrocarbons⁸. For example, the sulfides tend to hydrogenate at higher speeds than benzothiophenes and dibenzothiophenes. Hence, the residues of sulfur-containing hydrocarbons may have different composition depending on their initial concentrations in the feed. This fact explains the necessity of developing computer modeling system to calculate hydrotreating product composition. At the first stage it is required to obtain the kinetic parameters⁹. According to various examples in the literature this can be achieved by solving the reverse kinetic problem using numeric methods of differential equation solving and search methods¹⁰.

3. Results

In the frame of current research the software was developed to implement the solution of reverse kinetic problem which is based on the model of diesel fuel desulfurization. This software is developed using programming environments FreePascal and FreeBasic. Its main function is to calculate the kinetic parameters, i.e. to find the effective rate constants for all routes specified in the desulfurization process model^{11,12}. The initial and final concentrations of the components involved in the model are used as the input data.

The quasi-homogenous model in the form of differential equations is included in the source code. The method of optimization by scanning is used to solve these equations. This method developed in this research represents modified realization of full factorial experiment. All possible combinations of rate constants k_i are enumerated in the cycle with the limited amount of repeats $N = S^K$ (where S – a number of scan points, K – a number of kinetic parameters to find using the scan step h). The test calculation of product concentrations using Runge-Kutta method for each combination is carried out. The product concentrations are calculated for each chemical rate constant by using three scan points: central point and two side points $k_i^* - h$; $k_i^* + h$.

The optimal combination of kinetic parameters is selected in the cycle. The sum of concentration differences is used to select the optimal combination (1).

$$R = \sum_{i=0}^p (C_{exp,i} - C_{calc,i})^2 \quad (1)$$

p – a number of concentrations which should be compared with experimental data; $C_{exp,i}$ – experimental concentration; $C_{calc,i}$ – calculated concentration.

The cycle is being repeated until the scan step h is not greater than the specified limit of precision $h \leq \varepsilon$.

The developed software was used in the processing of the experimental data obtained with the laboratory setup. The experimental data is presented in Table 2.

Table 2. Molar concentrations (mole/l) of components in the feed and products of the experiment

Identified component	Feed	Temperature, °C		
		340	360	380
S	0.006813	0.000546	0.000548	0.000460
C1BT	0.001063	0.000058	0.000054	0.000065
C2BT	0.006313	0.000390	0.000400	0.000474
C3BT	0.010969	0.000686	0.000695	0.000713
(C4+C5)BT	0.011688	0.000688	0.000738	0.000585
DBT	0.001125	0.000094	0.000111	0.000087
C1DBT	0.002750	0.000220	0.000298	0.000203
C2DBT	0.002500	0.000243	0.000326	0.000228
C3DBT	0.000531	0.000148	0.000148	0.000121

The experiment was aimed at studying kinetics of benzothiophenes, sulfides, and dibenzothiophenes. Thus, the initial data includes the molar concentrations of these substances homologues in the feed and products at different

temperatures. This allows calculating not only the rate constants but also the activation energies for each of the components.

The graph was designed to represent the dynamics of the molar concentrations of sulfur compounds depending on the reaction time (Fig. 2). The concentration of hydrocarbons increases due to hydrogenation process, i.e. these are hydrogenated sulfur compounds without sulfur heteroatoms.

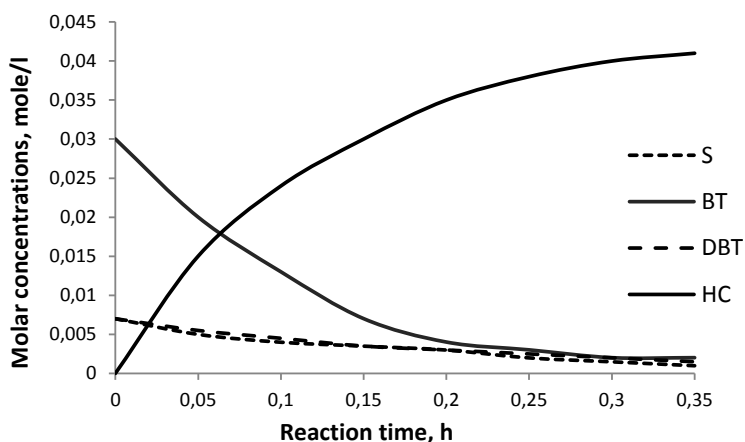


Fig. 2. The concentration dynamics of some sulfur compounds (S, BT, DBT) and hydrocarbons (HC)

As a result, the values of the effective rate constants are calculated using the designed algorithm for different temperatures (Fig. 3).

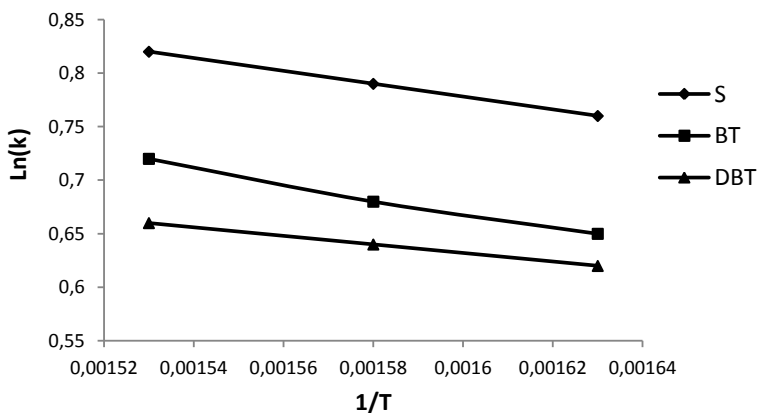


Fig. 3. The dynamics of effective chemical rate constants depending on process temperature

The numeric values of these kinetic parameters along with calculated activation energies are shown in Table 3. There are one sulfide pseudocomponent and four homologues for benzothiophenes and dibenzothiophenes. The results of the final concentration calculation using the developed software show a relatively high accuracy according to the data obtained experimentally.

$$\delta = \frac{|c_{exp} - c_{catc}|}{c_{exp}} * 100\% \quad (2)$$

The relative error δ calculated by the software according to the formula (2) is not higher than 0.007% for all components, it indicates a high level of adequacy of the mathematical model to the real process and the accuracy of the effective constant search algorithm.

Where C_{exp} is the concentration of the component obtained experimentally, C_{calc} is the calculated concentration.

Table 3. The effective reaction rate constants and activation energies, h⁻¹

Identified component	340°C	360°C	380°C	Relative error, %	Activation energy, J/mole
S	1.907	1.971	2.036	0.002	17.6
C1BT	2.191	2.153	2.114	0.006	95.9
C2BT	2.104	2.030	1.956	0.006	54.8
C3BT	2.094	2.080	2.065	0.006	79.8
(C4+C5)BT	2.140	2.201	2.262	0.007	225.9
DBT	1.877	1.907	1.937	0.007	126.7
C1DBT	1.907	1.938	1.969	0.006	147.1
C2DBT	1.761	1.786	1.810	0.006	271.5
C3DBT	0.968	1.043	1.118	0.007	387.4

The catalyst performs well in the hydrotreating process removing about 98 mass% of sulfur from the diesel fraction. The obtained data confirmed that chemical activity increases in the order: DBT, BT, sulfides. The rate of desulfurization decreases with increase in alkyl substituents. This is confirmed by the literature^{13,14}. DBT desulfurization is much worse than the one of BT. According to the data of the activation energy a group of sulfur compounds such as C2-dibenzothiophenes, C3-benzothiophenes, and C4-benzothiophenes¹⁵ was the most difficult to be hydrogenated.

4. Conclusion

The hydrotreating process of diesel fuel with 1.4 mass% of sulfur content is carried out with use of the laboratory catalytic setup. The aluminum-cobalt-molybdenum catalyst GKD-202 for petroleum hydrotreating is applied. The gas-liquid chromatography method is used to identify the group of sulfur compounds. The chromatograph "Kristall 2000M" was used.

The general aim of this research work is to find the kinetic parameters of the chemical reactions in the process of hydrodesulfurization, and it was achieved. The activation energy is calculated for each route of chemical reactions with accent on the dynamics of such sulfur-containing hydrocarbons as dibenzothiophenes, sulfides, and benzothiophenes.

In this research both the mathematical model and the computer software were designed to solve the reverse kinetic problem for the model of diesel fuel desulfurization. Thus, the effective reaction rate constants and activation energy were obtained.

The results of the final concentration calculation using the developed software show a relatively high accuracy according to the data obtained experimentally. The relative error calculated by the software is not higher than 0.007% for all components. This fact indicates a high level of adequacy of the mathematical model to the real process and the accuracy of the effective constants search algorithm.

The catalyst performs well in the hydrotreating process removing about 98 mass% of sulfur from the diesel fraction. The obtained data confirmed that chemical activity increases in the order: DBT, BT, sulfides. The rate of desulfurization decreases with increase in alkyl substituents. DBT exposed desulfurization is much worse than the one of BT. A group of sulfur compounds such as C₂-dibenzothiophenes, C₃-benzothiophenes, and C₄-benzothiophenes was the most difficult to be desulfurized. The calculated data allowed building the graphs representing BT and DBT concentration dynamics.

References

1. Anne Belinda Bjerre, Emil Sorensen. Hydrodesulfurization of Sulfur-Containing Polyaromatic Compound in Light Oil. *Ind. Eng. Chem. Res* 1992;. **31**: 1577–1580.
2. Prasenjeet Ghosh, Arthur T. Andrews, Richard J. Quann, and Thomas R. Halbert. Detailed Kinetic Model for the Hydro-desulfurization of FCC Naphtha. *Energy Fuels* 2009; **23**: 5743–5759.
3. Ed Palmer, Stan Polcar and Anne Wong. Clean diesel hydrotreating. Design considerations for clean diesel hydrotreating. *PTQ*; 2009. p. 91-100.
4. Belinskaya N.S., Ivanchina E.D., Ivashkina E.N., Silko G.Yu., Frantsyna E.V. Optimization of the process setting mode of diesel fuels hydrodeparaffinization by mathematical modeling. *Izvestiya vuzov: Chemistry and Chemical Technology* 2014; **11**: 90-92
5. Dolganova I.O., Ivashkina E.N., Ivanchina E.D. Mathematical modeling in problems of increasing the efficiency of the plant production of linear alkyl benzenes. *Bulletin of the Tomsk Polytechnic University* 2011; **3**: 109-112.
6. Krivtsova N.I., Ivanchina E.D., Tataurshchikov A.A., Zanin I.K. Study of activity of industrial catalysts of hydropurification of diesel fuel on mathematical model. *Izvestiya Vuzov. Chemistry and Chemical Technology. Ivanovo* 2014; **11**: 81 – 83.
7. Krivtsova N.I., Ivanchina E.D., Zanin I.V., Landl Yu.I., Tataurshchikov A.A. Kinetic laws of turning sulfur-containing compounds at hydrotreating of oil diesel fraction. *Izvestia Tomskogo politekhnicheskogo universiteta* 2013; **3**: 83 – 86.
8. Schuit C. A. and B. C. Gates. Chemistry and Engineering of Catalytic Hydrodesulfurization. Department of Chemical Engineering University of Delaware, Newark, Delaware. *AIChE Journal* 1973; **3**: 417-438.
9. Usheva N.V., Kravtsov A.V. *Macrokinecs of chemical processes and reactors design: Laboratory practices*. Tomsk: Tomsk Polytechnic University; 2006.
10. Ivanchina E.D., Ivashkina E.N., Frantsyna E.V., Dolganov I.M. *Optimization of the higher paraffins dehydrogenation reactor unit using the method of mathematical modeling*. Tomsk: Publishing house of TPU; 2014 .
11. Boyarinov A.I. *Optimization methods in chemical technology*. Moscow: Chemistry; 1975.
12. Krivtsova N.I., Krivtsov E.B., Ivanchina E.D., Golovko A.K. Kinetics of hydrodesulfurization of diesel fraction . *Basic Researches* 2013; **8**-**3**: 640-644.
13. Michael T. Klein. *Molecular modeling in heavy hydrocarbon conversions*. Boca Raton, Florida: CRC Press; 2005.
14. Al-Zeghayer Y.S., Sunderland P., Al-Masry W., Al-Mubaddel F., Ibrahim A.A., Bhartiya B.K., Jibril B.Y. Activity of CoMo/g-Al₂O₃ as a catalyst in hydrodesulfurization: effects of Co/Mo ratio and drying condition . *Applied Catalysis A: General* 2005. p. 163–171.
15. Satterfield C.N., Modell M. and Wilkens J.A. Simultaneous Catalytic Hydrodenitrogenation of Pyridine and Hydrodesulfurization of Thiophene. *Ind. Eng. Chem. Process Des. Dev.* 1980; **19**: 154-160.