Mathematical modeling of diesel fuel hydrotreating

A Tataurshikov[1,3], E Ivanchina[1,4], N Krivtcova[1,5], E Krivtsov[2,6] and A Syskina[1,7]

[1] National Research Tomsk Polytechnic University, Lenin Avenue 30, Tomsk, 634050, Russia
[2] Institute of petroleum chemistry SB RAS, Akademichesky Avenue 4, Tomsk, 634021, Russia

E-mail: [3] tataurshikov@yandex.ru, [4] ied@tpu.ru, [5] krivtcova@mail.ru, [6] john@ipc.tsc.ru, [7] annesyskina@yahoo.com

Abstract. Hydrotreating of the diesel fraction with the high initial sulfur content of 1,4 mass% is carried out in the flow-through laboratory setup with the industrial GKD-202 catalyst at various process temperature. On the basis of the experimental data the regularities of the hydrogenation reactions are revealed, and the formalized scheme of sulfur-containing components (sulfides, benzothiophenes, and dibenzothiophenes) transformations is made. The mathematical model of hydrotreating process is developed, the constant values for the reaction rate of hydrodesulfurization of the specified components are calculated.

1.Introduction

Hydrotreating is one of the main processes of secondary processing of oil raw materials; it is directed on considerable reduction of the content of heteroatomic compounds in oil products. Hydrotreating process is applied for production and upgrading of various oil products: gasoline, kerosene, diesel fuel, vacuum gasoil, and oil fractions. The wide use of hydrotreating process is caused, first of all, by introduction of increasing volume of sulphur and high-sulphur oil to the production cycle. The important aspect making introduction of hydrotreating process relevant is sensitivity of expensive catalysts to heteroatomic components, which are catalytic poisons. Toughening of ecological requirements to sulfur content in fuel, need of increase in oil refining depth necessitate improvement of hydrotreating process [1,2]. Application of mathematical modeling methods allow predicting conditions of hydrotreating process and quality of products that will considerably increase the depth of oil refining and will provide observance of all existing environmental standards [3].

The purpose of this work is to develop the mathematical model of diesel fuel hydrotreating and to calculate the constant values for the reaction rate of hydrodesulfurization of sulfides, benzo- and dibenzothiophenes.

2. Mathematical modeling of diesel fuel hydrotreating

2.1. Thermodynamic analysis and formalized scheme of transformations
Sulphur compounds of diesel fractions are mainly presented by sulfides, homologs and benzologs of thiophenes and, to a lesser extent, mercaptans, and disulfides. Thermodynamic calculation is always an initial stage of mathematical modeling based on physical and chemical laws and pretending to be highly adequate to the real process.

In this work the thermodynamic parameters of hydrotreating process including enthalpy, entropy, Gibbs energy were obtained with the computer program GaussianView and Gaussian 03; the method of calculation is DFT (Density Functional Study). As theoretical basis the B3LYP model, density functional theory of Becke (B3) and electronic correlation of Lee, Yang, and Parr are chosen. The basis is a 6-311G set. The conditions of hydrotreating process for calculation are the temperature of 340 °C and pressure of 3 MPa. The results of thermodynamic calculations of hydrogenation and hydrocracking reactions of the main sulfur compounds are presented in table 1.

Table 1. Values of enthalpy and Gibbs energy for hydrogenation reactions of sulfur compounds.

Sulphur compounds	Reaction	ΔH, kJ / mole	ΔG, kJ / mole
Sulphides	$C_5H_{11}SC_5H_{11} + H_2 \rightarrow C_5H_{11}SH + C_5H_{12}$	−65.60	−81.32
	$C_5H_{11}SH + H_2 \rightarrow C_5H_{15} + H_2S$	−67.66	−77.45
	$C_5H_{12}SC_5H_{12} + 2H_2 \rightarrow 2C_5H_{12} + H_2S$	−133.26	−158.77
Benzothiophenes	$C_8H_6S + H_2 \rightarrow C_8H_8S$	−78.97	−17.96
	$C_8H_8S + H_2 \rightarrow C_8H_{10}S$	−50.61	−13.21
	$C_8H_{10}S + H_2 \rightarrow C_8H_{10} + H_2S$	−72.00	−84.16
	$C_8H_6S + 3H_2 \rightarrow C_8H_{10} + H_2S$	−201.58	−115.33
Dibenzothiophenes	$C_{12}H_8S + H_2 \rightarrow C_{12}H_8 + H_2S$	−94.79	−64.99

On the basis of the data presented in table 1 the hydrogenation rate of sulfur compounds decreases: sulfides > benzothiophenes > dibenzothiophenes that is also confirmed by the literature data [3,4].

As any secondary process of oil processing diesel fuel hydrotreating includes a large number of parallel chemical reactions. Their aggregation in groups, or so-called pseudo-components, is made to reduce the number of individual component reactions. The mathematical model constructed on the basis of the reduced kinetic scheme is to keep the predicting ability, and also remain sensitive to the changes of raw material structure [5]. All groups of sulfur-containing organic compounds (mercaptans, sulfides, disulfides, thiophenes, benzothiophenes, and dibenzothiophenes) were formalized in separate groups of pseudo-components according to the value of isobaric and isothermal potential of their hydrogenation by hydrogen to the corresponding hydrocarbons and hydrogen sulfide. On the basis of the calculations of thermodynamic parameters for the desulphurization reactions of diesel fuel the formalized kinetic scheme of substance transformations (figure 1) is created.
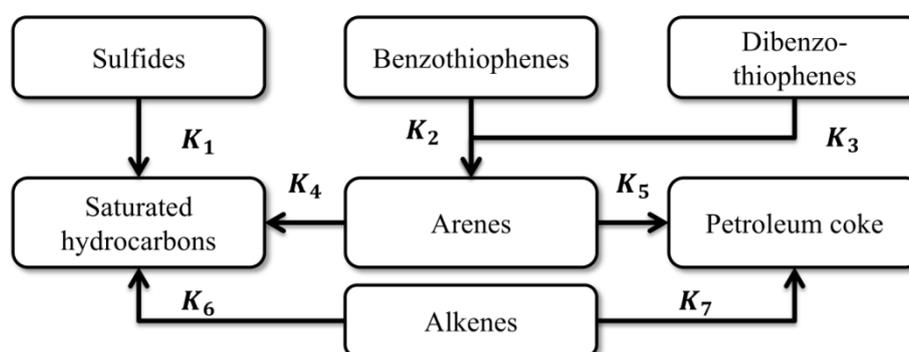

Figure 1. Formalized scheme of diesel fuel hydrotreating transformations.

According to the early results [6,7] it is established that grouping of sulfides, benzothiophenes, and dibenzothiophenes is caused by considerable distinction of chemical reaction rates for different groups of sulfur compounds. Depending on the structure of heteroatomic compounds in the raw materials of

hydrotreating, conditions of process and catalyst the total sulfur content can be different at the exit from the reactor.

Except transformation of sulfur compounds such reactions as hydrogenation of aromatic and olefin hydrocarbons to saturated hydrocarbons and formation of coke structures are reflected in the formalized scheme of transformations.

Development of mathematical model based on the created kinetic scheme will allow predicting the quantitative sulfur content in the hydrogenate and selecting the optimum temperature of the process [8,9].

The mathematical model is realized in the form of the computer modeling system (CMS) [10], which is based on the experimental data obtained on the laboratory catalytic setup. When developing the mathematical model (table 2) the following assumptions are made: all reactions of hydrogenolysis are the reactions of the first order in quasihomogeneous conditions; reactions occur in the kinetic area; the order of reactions is the first [11,12]. The mathematical model according to the formalized scheme of compound transformations (figure 1) is presented in the form of a number of the differential equations of substance concentration change depending on time.

Table 2. Mathematic model (C_i – molar concentration; τ – contact time; k_i – reaction rate constant).

Component	Equation
Sulfides	$\dfrac{dC_S}{d\tau} = -k_1 C_S C_{H_2}$
Benzothiophenes	$\dfrac{dC_{BT}}{d\tau} = -k_2 C_{BT} C_{H_2}$
Dibenzothiophenes	$\dfrac{dC_{DBT}}{d\tau} = -k_3 C_{DBT} C_{H_2}$
Alkenes	$\dfrac{dC_{Alk}}{d\tau} = -k_6 C_{Alk} C_{H_2} - k_7 C_{Alk}$
Saturated hydrocarbons	$\dfrac{dC_{Sat.h.}}{d\tau} = k_1 C_S C_{H_2} + k_4 C_{Ar} C_{H_2} + k_6 C_{ol} C_{H_2}$
Aromatic hydrocarbons	$\dfrac{dC_{Ar}}{d\tau} = k_2 C_{BT} C_{H_2} - k_4 C_{Ar} C_{H_2} - k_S C_{Ar}$
Petroleum coke	$\dfrac{dC_{coke}}{d\tau} = k_7 C_{ol} + k_S C_{Ar}$

2.2. Hydrotreating of diesel fuel on the laboratory setup
Hydrotreating of diesel fuel with the total sulfur content of 1,4 mass% was carried out on the laboratory catalytic setup which is the flow-through system with the evaporator, the reactor on the special metal grid with the catalyst, the condenser, and the receiver of the hydrogenate. In the work the alumino-nickel-molybdenum catalyst GKD-202 was used, the volume of the catalyst loaded into the reactor was 10 ml, the size of the granules was 1-2 mm.

Sulphidation of the catalyst was carried out directly in the reactor with the straight-run diesel fraction containing 0,4 mass% of sulphidic sulfur. The catalyst was preliminarily dried up in the nitrogen stream at the temperature of 120 ºC. Then hydrogen was supplied to the reactor with increase in pressure to 3.5 MPa. The diesel sulfiding chemical was fed with simultaneous temperature increase to 240 ºC. The low-temperature stage of sulphidation was carried out at 240 ºC during 2 h. The high-temperature stage was at 340 ºC during 2 h. The sulfiding mixture was fed at the volume rate of 2 h-1 with the H2/raw materials = 300/1 ratio.

Hydrotreating of diesel fuel was carried out under the following conditions: the volume rate of raw material supply is 2 h-1, the pressure is 3,5 MPa, the ratio hydrogen/raw materials is 300/1, the temperature is 340, 360, and 380 °C.

The spectrophotometer SPECTROSKAN-S was used for quantitative determination of sulphur content in the initial fraction and hydrogenates.

The method of gas-liquid chromatography (GLC) was applied for identification of sulphur compound groups. GLC was carried out on the chromatograph Crystal-2000M with the quartz capillary column of 25 м×0.22 mm, the stationary phase is SE-54; the carrier gas is helium. When using the flame photometric detector (FPD) for analysis of sulphur compounds the temperature increased linearly from 50 to 290 °C, the rate of column heating was 4 deg/min. The temperature of the detector was 180 °C. The qualitative structure of sulphur compounds was determined by comparison of the retention times of the individual compounds and the analyzed components, and the literature data was also used [5]. The quantitative content of the sulphur compound groups and unattached isomers was determined by the areas of the chromatographic peaks; and the obtained peak areas (in rel. %) were recalculated for the total sulfur content in the sample (in mass%). The change of the sulphur compound structure is presented in table 3.

Table 3. Sulfur content in sulphur compounds of the initial fraction and hydrogenates.

Component	Content, % wt.			
	Feed	340 ℃	360 ℃	380 ℃
S_o	1.4040	0.0980	1.0061	0.0939
S_{sul}	0.2180	0.0175	0.0175	0.0147
C_1BT	0.0341	0.0019	0.0017	0.0021
C_2BT	0.2020	0.0125	0.0128	0.0152
C_3BT	0.3510	0.0220	0.0222	0.0228
$(C_4+C_5)BT$	0.3742	0.0220	0.0236	0.0187
DBT	0.0360	0.0030	0.0036	0.0028
C_1DBT	0.0879	0.0071	0.0095	0.0065
C_2DBT	0.0801	0.0078	0.0104	0.0073
C_3DBT	0.0171	0.0047	0.0047	0.0039

*2.3. Calculation results of reaction rate constants of hydrodesulfurization*

The reaction rate constants for hydrodesulfurization of the identified groups of sulphur compounds are calculated on the basis of the data on their content change in the initial diesel fuel and hydrogenates (table 3). The basis of the program was formed by the kinetic model developed according to the law of mass action [13,14]. The calculation results of the final concentration of sulphur compounds by means of the developed program showed high adequacy of the obtained data to the experimental one. The relative error doesn't exceed 0,007 mass% for all components. The values of effective reaction rate constants of sulphur compound transformation obtained by the reverse kinetic task solution are presented in table 4.

It is established that with the increase in temperature of hydrotreating the reaction rate constants of all sulphur compound groups hydrogenolysis rise. The reaction rate constants of benzothiophene hydrogenolysis have the greatest values. It is possibly caused by their initially high content in the initial diesel fuel and also easy hydrogenation of C2-C3 bonds. The smallest values of reaction rate constants are noted at the most substituted C3- dibenzothiophene homologs. The obtained results correspond to the literature data [15–17].

The removal of the identified sulphur compound groups depending on the hydrotreating process temperature is shown in figure 4.

Table 4. Effective reaction rate constants of sulphur compound hydrodesulfurization, h^{-1}.

Component	Temperature, °C		
	340	360	380
S_{sul}	1.907	1.971	2.036
C_1BT	2.191	2.153	2.114
C_2BT	2.104	2.030	1.956
C3BT	2.094	2.080	2.065
$(C_4+C_5)BT$	2.140	2.201	2.262
DBT	1.877	1.907	1.937
C_1DBT	1.907	1.938	1.969
C_2DBT	1.761	1.786	1.810
C_3DBT	0.968	1.043	1.118
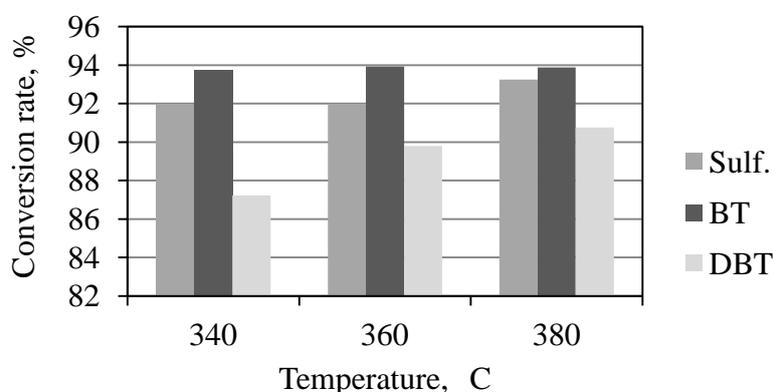
Figure 4. The removal degree of the sulphur compounds depending
on the hydrotreating process temperature.

The greatest extent of removal from the raw materials is noted at the benzothiophene homologs (in all experiments). Sulfides are the second in terms of conversion (93,2 mass% is removed at 380 °C). The difference in number of remote sulfides is insignificant at temperatures of 340 °C and 360 °C. The hydrogenolysis depth of the dibenzothiophene homologs very strongly depends on the temperature of the process and reaches 90,8 mass% at 380 °C.

3. Conclusion

In this work the mathematical model of diesel fuel hydrotreating is developed on the basis of the physical and chemical regularities of the process. The thermodynamic and kinetic parameters of the desulphurization reactions of sulfur compounds are estimated in the hydrotreating process. On the basis of the presented data the rate of sulfur compound hydrogenation decreases: sulfides > benzothiophenes > dibenzothiophenes that is also confirmed by the literature data. The developed formalized scheme of transformations and kinetic model consider transformations of sulfur compounds, hydrogenation of aromatic and olefin hydrocarbons, and formation of coke structures. The model was based on the experimental data obtained on the laboratory setup with the GKD-202 catalyst.

The results of calculation of the final concentration by means of the developed program showed high adequacy to the experimental data. The relative error doesn't exceed 0.007 mass% for all components. This fact speaks for high adequacy of the mathematical model to the real process and accuracy of algorithm for effective constant search.

The obtained results can be applied for forecasting the total sulfur content in the hydrogenate depending on the changing structure of raw materials and technological conditions on the hydrotreating setup for process optimization.

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