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DIESEL FUEL HYDROTREATING MODELLING AND CALCULATION OF MATERIAL AND THERMAL BALANCES USING DATA OF INDUSTRIAL UNIT LG-24/7

A. A. Tataurschikov *, E. D. Ivanchina, N. I. Krivtcova and A. A. Syskina

1 Institute of Natural Resources, Tomsk Polytechnic University, Russia

Abstract

Mathematical modeling of the diesel hydrodesulphurization was performed. Material and thermal balances are calculated, taking into account the kinetics and thermal effects of reaction with the presence of sulfur-containing compounds, including homologues of benzothiophene and dibenzothiophene. Experimental data were obtained from the industrial hydrodesulphurization set LG-24/7. The values of activation energy and Thiele modulus were calculated. An analysis of the process laws was performed.

Keywords: hydrotreating; mathematical modelling; industrial unit; diesel; fuel; material balance; thermal balance.

1. Introduction

Hydrotreating is the process of chemical conversion of substances under the influence of hydrogen, high pressure and high temperature with use of a catalyst. This process relates to hydrogenation processes in the petrochemical technology. Petroleum fractions are hydrotreated to reduce the sulfur compounds in petroleum products. Accompanying effect of this process is the saturation of unsaturated hydrocarbons, reduction of resin and oxygenates content, and hydrocracking of hydrocarbon molecules. Hydrotreating is one of the most common refining process and is used in almost any refinery. Major oil fraction subjected to a hydrotreating process include: gasoline fractions (fractions and straight-run fraction of catalytic cracking); kerosene fractions; vacuum gas oil; diesel oil.

Currently hydrogenation processes occupy a leading place among the secondary processes of refining crude oil, which is dictated by several factors: a continuous increase of sulfur-containing oils in the overall balance of the global refining; improvement and tightening of regulatory standards and international standards, contributing to the protection of nature and ensure a better quality of commodity petroleum products [1].

The main objective of this study is to model the reactor of hydrotreating process taking into account the dynamics of sulfur-containing compounds (SCC) concentrations, such as sulfides, benzothiophene (BT) and dibenzothiophene (DBT), and, the last stage of modelling is the choice of the reactor model.

2. Experimental part

2.1. Thermodynamics and kinetics

A list of possible reactions is compiled on the basis of experimental data. The change of Gibbs free energy provided by the reactions calculated using software packages HyperChem and Gaussian 09 [5-7]. In previous work, studies were conducted to determine the kinetic parameters of the hydrodesulfurization reactions [8]. These rate constants and the activation energy are incorporated in the mathematical model. These parameters are calculated for each of the sulfur compounds in the model and are shown in Table 1.

Table 1 Gibbs free energy change and chemical rate constants

No.	$\Delta G, \dfrac{kJ}{mole}$	Chemical rate constant k, h^{-1}	Reaction
1	-95,3	2,114	$(C_1BT)\ C_9H_8S + 6H_2 \rightarrow C_9H_{18} + H_2S$
2	-83,5	2,065	$(C_2BT)\ C_{10}H_{10}S + 6H_2 \rightarrow C_{10}H_{20} + H_2S$
3	-71,1	1,956	$(C_3BT)\ C_{11}H_{12}S + 6H_2 \rightarrow C_{11}H_{22} + H_2S$
4	-65,1	1,907	$(DBT)\ C_{12}H_8S + 6H_2 \rightarrow C_{12}H_{22} + H_2S$
5	-54,3	1,877	$(C_1DBT)\ C_{13}H_{10}S + 6H_2 \rightarrow C_{13}H_{24} + H_2S$
6	-53,7	1,761	$(C_2DBT)\ C_{14}H_{12}S + 6H_2 \rightarrow C_{14}H_{26} + H_2S$
7	-49,4	0,968	$(C_3DBT)\ C_{15}H_{14}S + 6H_2 \rightarrow C_{15}H_{28} + H_2S$

The basis of the developed mathematical model is built on the hydrodesulfurization reaction of individual groups of organic sulfur compounds such as sulfides, benzothiophene, dibenzo-thiophene. Also, the model takes into account hydrogenolysis reaction products: saturated and aromatic hydrocarbons.

The developed mathematical model based on the law of mass action and is a system of diffe-rential equations, which reflect changes in the concentrations of the reactants (Table 2). Thus, the mathematical model performs a material balance calculation of sulfur compounds during hydro-treating.

Table 2. Mathematical equations of the hydrodesulfurization model

Benzothiophenes	Dibenzothiophenes
$\begin{cases} W_1 = k_{C_1BT} C_{C_1BT} C_{H_2}^v \\ W_2 = k_{C_2BT} C_{C_2BT} C_{H_2}^v \\ W_3 = k_{C_3BT} C_{C_3BT} C_{H_2}^v \end{cases}$	$\begin{cases} W_4 = k_{DBT} C_{DBT} C_{H_2}^v \\ W_5 = k_{C_1DBT} C_{C_1DBT} C_{H_2}^v \\ W_6 = k_{C_2DBT} C_{C_2DBT} C_{H_2}^v \\ W_7 = k_{C_3DBT} C_{C_3DBT} C_{H_2}^v \end{cases}$
$\begin{cases} \dfrac{dC_{C_1BT}}{dt} = -W_1 \\ \dfrac{dC_{C_2BT}}{dt} = -W_2 \\ \dfrac{dC_{C_3BT}}{dt} = -W_3 \end{cases}$	$\begin{cases} \dfrac{dC_{DBT}}{dt} = -W_4 \\ \dfrac{dC_{C_1DBT}}{dt} = -W_5 \\ \dfrac{dC_{C_2DBT}}{dt} = -W_6 \\ \dfrac{dC_{C_3DBT}}{dt} = -W_7 \end{cases}$

Initial conditions: $dC_i = C_{i,0}$; $t = 0$

In this system of equations allows calculating sulfides, benzothiophenes and dibenzo-thiophenes concentrations respectively, as well as saturated and aromatic hydrocarbons, hydro-gen, hydrogen sulfide, according to the given reactions in Table 1.

The chemical reaction rate constants on all routes are calculated according to the Arrhenius equation. Thus, the effect of temperature on the reaction rate and, accordingly, the depth of the hydrodesulfurization, are taken into account.

These calculations provide information about the possible limits of the reactants' conversion, output of products and limits of the thermal conditions of the reactor. At the same time, they do not provide opportunities to judge reactor design parameters (volume of the catalyst load, size and structural features of the reactor).

2.2. Hydrodynamics in the hydrotreating reactor

In order to be able to say that the kinetic model can be applied to simulate the hydrotreating process used types of catalysts, it is necessary to prove that all of us are interested in the chemical

processes taking place in the kinetic region. Thus, the rate-limiting step should be the kinetic when the overall rate of conversion of sulfur compounds in practice depends on the rate of chemical reaction, excluding the influence of the external transport and diffusion in the catalyst pores.

Modelling of reactions kinetics on the surface of the catalyst allows to estimate chemical reactions rates depending on conditions (feed composition, temperature, pressure, type of the catalyst).

For the first-order reactions (which are described by equation $W(C) = kC$) the rate depending on inner-diffusion limits may be described by the expression:

$$W_{observed} = \eta W\left(C_{surface}\right) \tag{3.1}$$

where η – coefficient of catalyst's grain utilization:

$$\eta = \frac{1}{\varphi}\left(cth(\varphi) - \frac{1}{\varphi}\right) \tag{3.2}$$

φ – Thiele module calculated by the formula [3]:

$$\phi = \ell \cdot \sqrt{\frac{W_0}{CD_{effective}}} \tag{3.3}$$

where ℓ - the length of the pores of the catalyst grains, m; k - rate constant of a chemical reaction, sec^{-1}; $D_{effective}$ - effective diffusion coefficient, $\frac{m^2}{s}$.

The formula for the calculation of the effective diffusion coefficient is as follows [3]:

$$D_{eff} = D\left[1 - \exp\left(-\frac{D_K}{D}\right)\right] \tag{3.4}$$

where D_k – Knudsen's diffusion coefficient, $\frac{m^2}{s}$; D – molecular diffusion coefficient, $\frac{m^2}{s}$;

The linear size of the catalyst granules HR-538 is up to 2.6 mm. So, the maximum free path length of the molecule can be taken as half that size: $l = 2,6 / 2 = 1.3\ mm$.

In previous work [4] conversion rate constants for the respective groups of sulfur compounds were obtained by solving the reverse kinetic problem. The average activation energy of hydrodesulfurization for modern hydrotreating catalysts is about 130 $\frac{kJ}{mol}$.

Taking into account that the average pore radius in the hydrotreating catalysts varies from 30 to 50 Å, it is possible to calculate the molecular diffusion coefficients and Thiele factor. Obtained Thiele factor values are given in the table 3.

Table 3. Thiele factor and efficiency factor for the hydrotreating catalyst with an average pore radius of 40 Å

Temperature, °K	Thiele factor (ϕ)	Efficiency factor
623	0,302876	0,970504
633	0,367813	0,957218
643	0,443955	0,939098
653	0,532748	0,915027
663	0,635757	0,883991
673	0,754665	0,845307

Obviously, all the necessary reactions in the hydrotreating of diesel fuel occur in the kinetic area ($\varphi << 10$), therefore, the removal of sulfur from petroleum is limited only by catalytic quality – its physico-chemical properties and activity. Consequently, the most important step is to develop a kinetic model of hydrotreating, which doesn't take into account the factors of diffusive transport of reactants inside the reactor to the catalyst surface and removal of the products.

2.3. Object of research

Technological scheme of the typical hydrotreating unit is shown in Figure 1. In the most general case, the raw material, having pre-heating, falls in the hydrotreating reactor R major part of the whole process, where the catalytic hydrotreating of diesel fraction is performed. Here a reaction of sulfur compounds to form hydrogen sulfide is performed on the surface of the hydrogenation catalyst. The hydrogen-containing gas (HCG) is separated from the vapor-liquid mixture in the separators S-1 and S-2 and enters to the column C-2 for recovery of pure hydrogen. Column C-1 is used for separation of vapor-liquid mixture into a gas fraction and the basic product - hydrotreated diesel fuel [2].
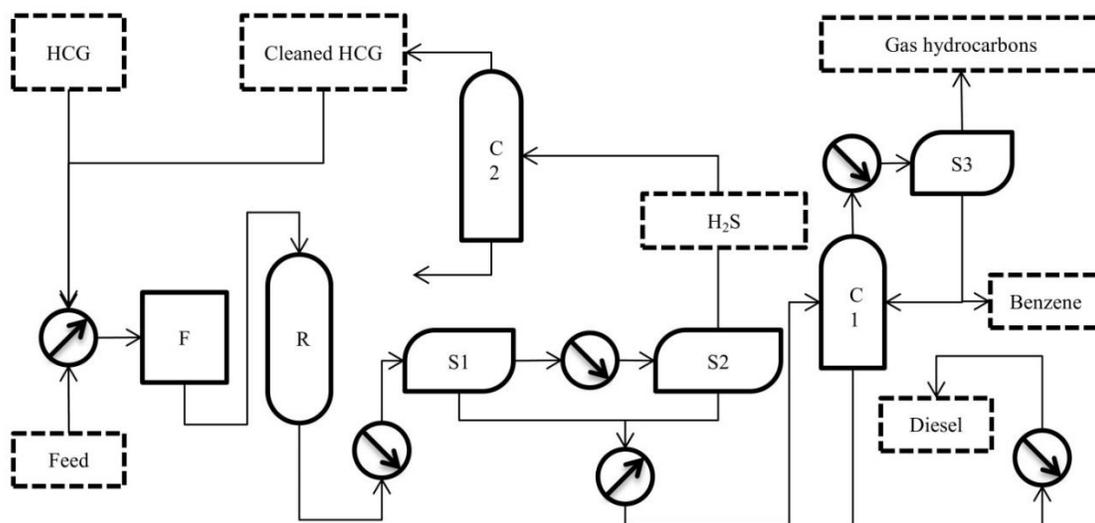
Fig. 1. Technological scheme of typical hydrodesulfurization unit

Formal requirements to the quality of motor fuels introduced in the Resolution of the Russian Federation from February 27, 2008 №118 "On approval of the technical regulation „On requirements to automobile and aviation gasoline, diesel and marine fuel, jet fuel and heating oil".

The requirements of GOST R 52368-2005 brought into line with the legal requirements of Euro-3 standard and higher. Prior to that, the production of fuels used GOST 305-82. The main difference from the EN 590 standard in the GOST R 52368-2005 is that diesel is divided into three categories depending on the amount of sulfur contained. Diesel Type 3 can also be called a completely purified.

The plant used Axens catalyst HR-538, which properties are given in the table 4. The catalyst activity in respect of certain SCC counted as part of the effective rate constants was calculated previously.

Table 4 HR-538 catalyst properties

Diameter of catalyst particles, mm	1.2; 1.6; 2.5
Composition:	
Nickel (NiO), % mass.	3.5
Molybdenum (MoO$_3$), % mass.	17.0
Surface, m^2/g	210

3. Results and discussion

An experimental data was taken from the monitoring file of hydrodesulfurization unit "LG-24/7" which uses HR-538 catalyst. Monitoring file reflects the state of technological parameters and differing sulfur content of feed. Excerpt from the monitoring data is shown in table 5.

Table 5. Experimental and calculated data

Date	28.Dec.2014	01.Jan.2015	03.Jan.2015
Initial sulfur content, % mass.	0,9100	0,8000	0,8300
Experimental product sulfur content, % mass.	0,0040	0,0040	0,0030
Calculated product sulphur content, % mass.	0,0040	0,0039	0,0029
Relative sulphur calculation error, %	0	2,5	3,3
Effective reaction rate constant, h^{-1}	5,400	2,892	3,081
Volume rate of feed/catalyst, h^{-1}	1,00	1,83	1,83
Overall ΔH, kJ	81,00	43,38	46,22
Experimental product temperature, $°C$	327,111	338,105	338,048
Calculated product temperature, $°C$	331,111	342,105	341,048
Relative temperature calculation error, %	1,208054	1,169232	0,879642

The results of the sulphur-containing compounds material balance calculation with use of developed mathematical model demonstrate high accuracy according to the data which was obtained experimentally from hydrodesulfurization unit "LG-24/7". The relative difference between experimental and calculated data does not exceed 4–7% for all calculated components.

Calculation of overall process ΔH is accurate. Relative error of ending temperature calculation is not higher than 1,5%. ΔH of the hydrodesulfurization process varies from 40 to 80 kJ.

4. Conclusion

Catalyst shows high activity performing hydrodesulfurization with sulfur-containing compounds removal up to 98 mass% from fraction of diesel fuel. Chemical activity of SCC is increasing in the row: dibenzothiophenes, benzothiophenes, sulfides. Rate of hydrodesulfurization decreases when the number of alkyl substituents in BT and DBT homologues is increasing, consequently, hydrogenation rate of DBT is much worse than that of BT.

List of symbols

k_i	chemical rate constant	v	the stoichiometric ratio
C_i	the current concentration of the substance i		

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*Corresponding author, address: Chemical Engineering Department, Tomsk Polytechnic University, 30, Lenin Avenue, Tomsk, 634050, Russia; tel.: (+7-9234) 265254; e-mail: tataurshikov@yandex.ru