

NON-STATIONARY MATHEMATICAL MODEL OF INDUSTRIAL DIESEL FUEL HYDROTREATING PROCESS

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Abstract

Catalytic hydrotreating is widely used in secondary petroleum refining industry. The main purpose of this process is to significantly lower sulfur content in the petroleum products. Currently, there is a lack of industrially applicable mathematical models of diesel hydrotreating, especially the models which take into account the reaction kinetics and catalyst deactivation.

In this paper, research is focused at processing of experimental data from laboratory equipment and industrial hydrotreating unit and developing mathematical model, which adequately describe industrial data of hydrotreating industrial unit with the use of current view of chemical mechanism and catalyst deactivation.

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

1. Introduction

Hydrotreating of diesel fraction is used to remove heteroatoms (including atoms of sulfur, nitrogen and oxygen), polycyclic aromatic hydrocarbons and metals [1-4]. Concentration of these compounds is rising accordingly with a boiling temperature of the fraction [5-7]. The industrial process of hydrotreating is performed in relatively mild conditions but yet should be effective – conversion rate of the diesel fraction should not be lower than 98-99% [8-10]. The most general purpose of this process is to significantly reduce a sulfur amount in a wide range of petroleum products including naphtha, diesel, gas-oil, kerosene and heavy oil fractions which consequently are used as a raw material for catalytic processes [11-12]. This prevalence of catalytic hydrotreating have such origins as, firstly, introduction of more high-sulfur crude oils extraction into petroleum refining industry all over the world in the last years [13-15], and, secondly, economically disadvantageous catalyst poisoning in consequent of refining processes, such as gasoline reforming and catalytic hydrocracking [16]. The third main reason is the introduction of strict environmental requirements to the content of heteroatom substances in fuel, as well as aromatic hydrocarbons amount [17]. All these reasons dictate the necessity not only for a wider use of hydrotreating process, but also more complex research of deep heterocatalytic mechanisms, including mathematical modeling, which could help in optimization of the process, development of new catalysts and proposal of new reactor construction concepts [18]. Use of mathematical modeling method allows researchers to predict new conditions and product quality, develop new proposals for industrial process optimization [19-21].

The aim of this research is to develop a dynamic mathematical model of diesel hydrotreating reactor with non-stationary material balance and thermal balance including calculation of coke formation.

2. Object of research

Technological scheme of the typical hydrotreating unit is shown in Figure 1. In the most general case the raw material arrives to the hydrotreating reactor "R" after being pre-heated

in the furnace "F". Reactor is the major part of the whole process, where the catalytic hydrotreating of diesel fraction is performed. A group of reactions of hydrogen sulfide formation from sulfur compounds are occurring 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 the column "C-2" for recovery of pure hydrogen. Column "C-1" is used for separation of vapor-liquid mixture to a gas fraction and the main product – hydrotreated diesel fuel [22].

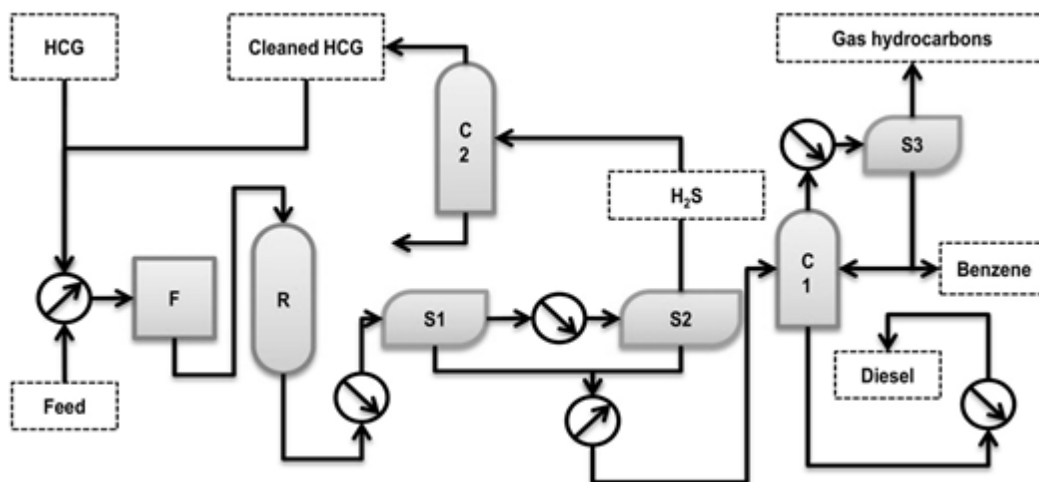


Fig. 1. Scheme of the typical hydrodesulfurization unit. Note: circles with arrow faced upwards are heaters; downwards – coolers

The plant uses catalyst HR-538 manufactured by Axens (France). Properties of the catalyst are given in Table 1. The catalyst activity towards certain sulfur-containing compounds is counted as part of the effective rate constants, which was calculated previously [23-24].

Table 1. 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

The data which was used to calculate kinetic parameters for developed model was obtained both from laboratory equipment and from industrial hydrotreating and deparafinization unit. The laboratory experiment was performed with use of such equipment as gas-liquid chromatograph unit "Kristal-2000M" to measure sulfur-containing substances concentrations in diesel product.

The fixed-bed mini-reactor was used to simulate industrial hydrotreating process in the laboratory. Fraction of diesel fuel (boiling range is 180–320 C) with a total sulfur content of 1.4%wt. was used as the feed for the reactor. Al-Ni-Mo catalyst was used in the laboratory setup which consists of a flow system with an evaporator, reactor with a special metal grid where the catalyst was placed onto. The products of reaction were received into a condenser. The hydrotreating process was carried out with 10 mL of the Al-Ni-Mo HR-538 catalyst loaded onto a metal grid of mini-reactor in the form of granules with a diameter of 1-2 mm.

The feed and hydrogen ran through a reactor from the top to the bottom. Diesel fraction was fed to the reactor with a high pressure dosing pump. Pure hydrogen supply was controlled with automatic dispenser. The temperature in the reactor was supported on desired level by an air thermostat. Temperature controller provides heating accuracy not worse than $\pm 0.5^{\circ}\text{C}$. Thermocouple was used to measure the temperature in the catalyst bed. Catalyst was placed

in a pocket at the center of the reactor. The system pressure was set with a high-pressure reducer at the end of product flow.

In current laboratory setup the water-cooled condenser is used to gather products of hydrotreating from the reactor. Then, liquid products were gathered to the receiver for further analysis. Unlike liquid products, gases were released to the atmosphere through six-way valve.

Before an experiment the process of catalyst sulphidation was performed in the reactor. This process involved a straight-run diesel fraction as a sulphiding feed. Sulphur concentration in the feed was approximately 0.4% mass. Sulphidation was performed with the next steps and conditions:

1. Catalyst drying using nitrogen gas stream with the temperature of 120°C;
2. Increase of the pressure in the reactor to 3.5 MPa and start of hydrogen feed;
3. The catalyst wetting by raw diesel fraction;
4. Increase of the temperature to 240°C;
5. 2-hour sulphidation process under 240°C (phase of low temperature);
6. Increase of the temperature to 340°C;
7. 2-hour sulphidation process under 340°C (the phase of high temperature);

Feed ran through the reactor with 2 h⁻¹ volume velocity. Volume ratio of hydrogen to the diesel was: H₂/feed=300/1. After being sulphided the catalyst is ready to operate in hydrodesulphurization process under the next conditions:

Table 2. In-laboratory hydrodesulphurization conditions

Volumetric flow rate of feed	2 h ⁻¹ (relatively to catalyst's volume)
Pressure	3.5 MPa
Hydrogen/Diesel volume ratio	300/1
Temperatures	340°C, 360°C, 380°C

Spectral photometer "Spectroscan-S" was used to determine and measure the initial containment of sulfur in diesel fuel.

The method of gas-liquid chromatography was used to measure concentrations of sulfur in the products according to their homologue groups. Method of GLC was performed using a "Crystal-2000M" chromatograph. It has a quartz column with 25 m × 0,22 mm dimensions. Helium is used as a carrier gas. Under a temperature increase in the column of "Crystal-2000M" with a 4 degree/minute rate the flame photometric detector was used for analysis of sulfur compounds in products of desulfurization.

3. Experimental

3.1. Thermodynamics and chemical mechanism

Sulfur compounds are present in diesel fractions mainly in the form sulfides, homologues of thiophenes and, in lesser amounts, by mercaptanes and disulfides. In general, the initial stage of mathematical model development is the thermodynamic calculation. This stage is based on the physical and chemical laws and ensures a high degree of model's accordance to the real hydrotreating process.

In the frame of current research the thermodynamic parameters were calculated including Gibbs energy and enthalpy for each individual reaction of hydrodesulfurization of sulfur-containing-compounds [25]. In this work, the thermodynamic parameters of the hydrotreating process, including enthalpy, entropy, Gibbs energy were calculated using a computer program packages "GaussianView" and "Gaussian 09". The calculation method of DFT (Density Functional Study) was used. B3LYP model was chosen as a theoretical approach, as well as density functional theory (B3) and the electronic correlation (LYP). Basis is the set 6-311G. There were also the hydrotreating process conditions under which the calculation was performed, including a temperature of 340°C and a pressure of 3 MPa. Results of thermodynamic calculations of hydrogenation and hydrocracking reactions of several sulfur-containing compounds representatives are presented in Table 3.

Table 3. Values of enthalpy and Gibbs energy of sulfur compounds' hydrogenation reactions

Sulfur compounds group	Reaction	ΔH , kJ/mole	ΔG , kJ/mole
Sulfides	$C_5H_{11}SC_5H_{11} + H_2 \rightarrow C_5H_{11}SH + C_5H_{12}$	-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
Mercaptan	$C_2H_5SH + H_2 \rightarrow C_2H_6 + H_2S$	-67.29	-78.35
Disulphides	$CH_3SSC_4H_9 + H_2 \rightarrow CH_3SH + C_4H_9S$	-38.39	-57.74
	$CH_3SH + H_2 \rightarrow CH_4 + H_2S$	-78.46	-76.61
	$C_4H_9SH + H_2 \rightarrow C_4H_{10} + H_2S$	-55.41	-70.00
	$CH_3SSC_4H_9 + 3H_2 \rightarrow CH_4 + C_4H_{10} + 2H_2S$	-172.25	-204.35
Thiophenes	$C_4H_4S + 2H_2 \rightarrow C_4H_6 + H_2S$	-78.56	-52.47
	$C_4H_6 + H_2 \rightarrow C_4H_8$	-121.06	-62.89
	$C_4H_8 + H_2 \rightarrow C_4H_{10}$	-111.04	-46.92
	$C_4H_4S + 4H_2 \rightarrow C_4H_{10} + H_2S$	-310.66	-162.29
Benzothiophenes (BT)	$C_8H_6S + H_2 \rightarrow C_8H_8S$	-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 (DBT)	$C_{12}H_8S + H_2 \rightarrow C_{12}H_8 + H_2S$	-94.79	-64.99

On the basis of the data presented in Table 3 the next law is predicted: the rate of hydrogenation of sulfur compounds decreased in the series: sulfides > benzothiophenes > dibenzothiophenes, which is also confirmed by related data in the literature [26-28].

Like any process of secondary refining, hydrotreating of diesel fuel involves a large amount of chemical reactions which occur simultaneously. The so-called aggregation of different sulfur-containing components to the homologue groups is made to reduce the number of individual reaction components and, thus, reduce the amount of calculations. Any mathematical model must keep predictive power [29]. In addition, it must to remain being sensitive to the feed composition changes through hydrotreating unit's operational cycle.

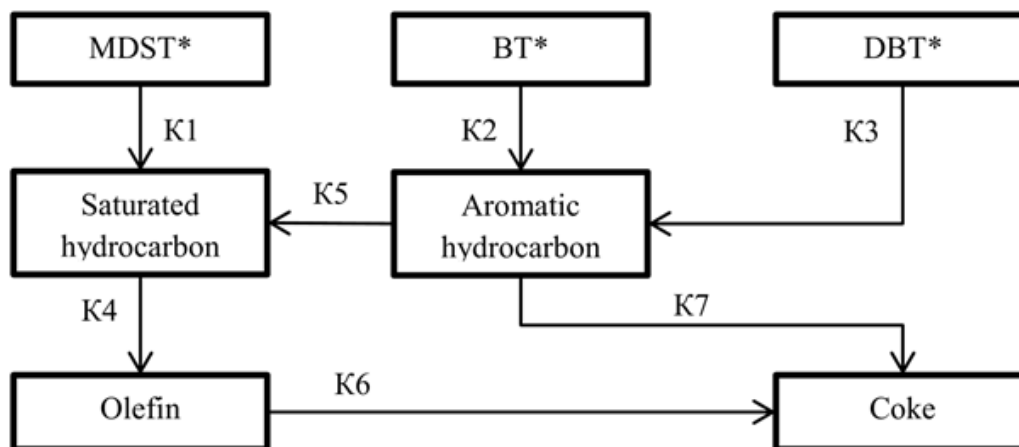


Fig. 2. Formalized kinetic scheme of hydrodesulfurization reactions* MDST – mercaptan, sulfide, disulfide, thiophene; BT – benzothiophene; DBT – dibenzothiophene

On the basis of thermodynamic parameters calculations a formalized kinetic scheme of substances transformations had been created (Fig. 2.).

All sulfur-containing substances (including mercaptanes, sulfides, disulfides, thiophenes, benzothiophene and dibenzothiophene) were joined together into separate groups (or "pseudo-components"). The rule of isobaric-isothermal potential of hydrogenation was used. Additional data on the role and kinetic parameters of saturated hydrocarbons, arenes and olefins in the process of hydrogenation was gathered from literature [30-34].

3.2. Mathematical model

The basis of the developed mathematical model is built on the hydrotreating reaction of individual groups of organic sulfur compounds such as sulfides, benzothiophene, dibenzothiophene. 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 differential equations, which reflect changes in the concentrations of the reactants. Thus, the mathematical model performs a material balance calculation of sulfur compounds during hydrotreating.

Table 4. Material and thermal balance

Reaction rate equations	Differential equations
	$G * \frac{\partial C_{MDST}}{\partial Z} + G * \frac{\partial C_{MDST}}{\partial V} = -A_1 * W_1$
	$G * \frac{\partial C_{BT}}{\partial Z} + G * \frac{\partial C_{BT}}{\partial V} = -A_2 * W_2$
	$G * \frac{\partial C_{DBT}}{\partial Z} + G * \frac{\partial C_{DBT}}{\partial V} = -A_3 * W_3$
	$G * \frac{\partial C_{SHC}}{\partial Z} + G * \frac{\partial C_{SHC}}{\partial V} = A_1 * W_1 + A_5 * W_5 - A_4 * W_4$
	$G * \frac{\partial C_{Arom}}{\partial Z} + G * \frac{\partial C_{Arom}}{\partial V} = A_2 * W_2 + A_3 * W_3 - A_5 * W_5 - A_7 * W_7$
	$G * \frac{\partial C_{Olefins}}{\partial Z} + G * \frac{\partial C_{Olefins}}{\partial V} = A_4 * W_4 - A_6 * W_6$
	$G * \frac{\partial C_{Coke}}{\partial Z} + G * \frac{\partial C_{Coke}}{\partial V} = A_6 * W_6 + A_7 * W_7$
	(there: <i>Arom</i> – aromatic hydrocarbons)
	Thermal balance
	Initial conditions
	$Z = 0; t = 0$ $V = 0; C_i = C_{i,0}$ $T = T_0$

there: Z – the volume of total refined feed, m^3 ; V – volume of catalyst, m^3 ; k_i – chemical rate constant, h^{-1} ; C_i – the current concentration of the substance i , mole/ m^3 ; v – the stoichiometric ratio; A_i – relative catalyst activity towards certain route i ; t – reaction time, h ; p – amount of pseudo-components; W_i – chemical reaction rate on the route i ; Q_i – thermal effect of chemical reaction on the route i , $kJ/mole$; G – feed flow rate, m^3/h .

3.3. Experimental data

Experimental data was obtained both from laboratory equipment and industrial hydrotreating unit monitoring database. The excerpt of laboratory data is shown in the Table 5

Table 5. Laboratory experiment results: initial and final concentrations of sulfur-containing compounds in diesel fraction

Component	Initial	Temperature, °C		
		340	360	380
Mass concentration, % mass. · 10 ⁻³				
MDST	218.00	17.46	17.52	14.74
C1-BT	35.00	1.87	1.72	2.07
C2-BT	200.00	12.47	12.70	15.16
C3-BT	351.00	21.95	22.34	22.90
(C4+C5)-BT	372.00	22.01	23.50	18.72
DBT	40.00	3.00	3.56	2.77
C1-DBT	87.00	7.05	9.52	6.49
C2-DBT	82.00	7.77	10.32	7.29
C3-DBT	19.00	4.72	4.72	3.87
Total sulphur	1404.00	98.30	105.93	94.01

The industrial data includes operational conditions for each day of unit operation. These conditions include diesel fraction feed flow rate, initial sulfur content, pressure, temperature of the feed and products, as shown in the Table 6.

Table 6. Excerpt from "LG-24/7" hydrodesulphurization unit's monitoring data

Date	Day	Feed flow rate m ³ /h	Density of diesel fraction t/m ³	Sulphur in diesel fraction, %m	Initial temperature, °C	Product temperature, °C	Sulfur in product, ppm
26.01.2014	153	110.138	0.796	0.40	330.146	338.216	4.0
24.04.2014	241	115.339	0.798	0.38	325.107	332.149	11.0
12.05.2014	259	109.835	0.797	0.42	328.085	335.097	9.0
20.08.2014	359	100.073	0.798	0.50	341.712	349.556	2.0
02.02.2015	525	84.810	0.790	0.35	320.069	327.103	1.9
24.04.2015	606	90.853	0.791	0.30	313.942	319.845	12.0

Experimental data was used in the calculation of the rate constants (Table 6) for the conversion of individual sulphur components in the industrial unit. The process of finding the kinetic parameters was performed by comparing the calculated sulfur content with the experimental total yield of sulfur using the method of least squares.

 Table 7. Effective reaction rate constants and relative error based on laboratory experiment data, h⁻¹

Identified component	340°C	360°C	380°C	Relative error, %
S	1.907	1.971	2.036	0.002
C1BT	2.191	2.153	2.114	0.006
C2BT	2.104	2.030	1.956	0.006
C3BT	2.094	2.080	2.065	0.006
(C4+C5)BT	2.140	2.201	2.262	0.007
DBT	1.877	1.907	1.937	0.007
C1DBT	1.907	1.938	1.969	0.006
C2DBT	1.761	1.786	1.810	0.006
C3DBT	0.968	1.043	1.118	0.007

4. Results discussion

Table 8 shows the results of calculations used the developed model.

Table 8. Product temperatures and sulfur concentrations

Day	Calculated sulfur in product, ppm	Calculated temperature of product, °C
153	4.0	341.4
241	11.9	336.2
259	9.4	339.8
359	2.1	354.8
525	2.0	327.5
606	11.1	320.6

Activity of the catalyst in the beginning and the end of examined period (3 years) of unit functionality, linear functional relation between total productivity and the activity of the catalyst are calculated and introduced in the mathematical model. Thus, the model takes the catalyst's activity loss into account. The regression functional equation (1) was formed to adequately predict the catalyst activity due to coke formation after specified time period of hydrotreating unit functioning:

$$A = 0.1 \cdot 10^{-7} \cdot Z + 0.8948 \quad (1)$$

where: A – relative catalyst activity; Z – tons of refined feed.

5. Conclusion

General calculation of the main process parameters is satisfyingly accurate. Relative error of ending temperature calculation does not exceed 1.5%. Thermal effect of the hydrotreating process varies between 60–80 kJ/mole. The results of the sulphur-containing compounds material balance calculation with use of developed mathematical model are demonstrating high accuracy in accordance to the data which was obtained from industrial hydrotreating unit. The relative difference between monitored and calculated total sulfur concentrations in hydrotreated products does not exceed 4–8%.

HR-538 Al-Ni-Mo catalyst shows high activity with removal of sulfur up to 98–99% mass. from diesel fraction when performing diesel hydrotreating. Chemical activity of sulfur-containing compounds increases in the row from dibenzothiophenes, benzothiophenes to sulfides. Rate of hydrotreating decreases when the number of alkyl substituents in BT and DBT homologues is increasing, consequently, hydrogenation rate of DBT is much lower than that of BT.

The conclusions made based on calculated data. Thus, the catalyst's activity loss by nearly 1/3 of its beginning activity is observed. This could be caused by imperfections in diesel fuel fraction composition and in technological parameters at hydrotreating reactors of industrial unit.

Developed mathematical model allows making conclusions on initial reasons which influence the overall process quality and helps in making a decisions in the questions of process optimization.

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