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REVERSE KINETIC PROBLEM FOR DIESEL FRACTION HYDROTREATING PROCESS

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Hydrotreating is a catalytic process of chemical substances conversion in the presence of hydrogen under high pressure and temperature. Petroleum fractions are hydrotreated to reduce sulfur compounds in petroleum products including commercial gasoline and diesel fuel. A side effect of this process is the saturation of unsaturated hydrocarbons, heavy oils and oxygenated compounds reduction, and hydrocracking of hydrocarbon molecules. Hydrotreating is one of the most common refining processes applied virtually to any refinery.

The increasing role of hydrotreating processes in the refining industry makes it necessary to develop software systems that implement the mathematical model of hydrotreating.

The main purpose of this research is to solve the reverse kinetic problem for process of diesel fuel hydrotreating with the focus on dynamics of sulfur-containing substances, such as sulfides, benzothiophenes and dibenzothiophenes and other non-sulfuric hydrocarbons. Also, the mechanism formalization and development of computer program implementing mathematical model was performed.

The number of components for hydrotreating reaching 300-400, it is impossible to consider each particular component of the process while developing the mathematical model. Thus, the formalization of the kinetic scheme is required to calculate the shorter list of components. However, a mathematical model developed on the basis of such formalized kinetic scheme should be sensitive to the varying composition of feed. Only in this case, the modeling system can be able to predict the properties of hydrotreatment products.

Previous different models had been developed in the frame of current research of hydrotreatment kynetics, performed on the basis of the Department of Chemical Technology of Fuel and Chemical Cybernetics [1,2].

A kinetic scheme has been developed basing on thermodynamic calculations of reactions present in diesel fuel hydrotreatment process (Fig. 1). All groups of sulfur containing substations were merged into “pseudocomponents” according to their isobaric-isothermal potential of hydrogenation process of these components.

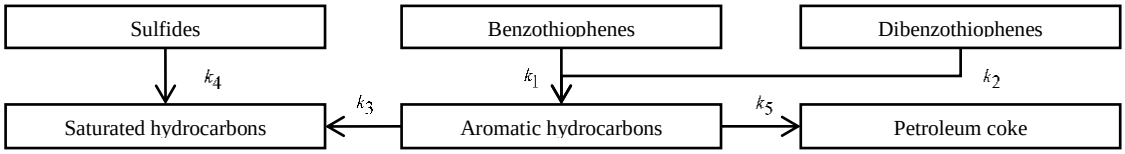

Fig. 1. Formalized kinetic scheme of diesel fuel hydrotreatment process

At the same time, the hydrogenolysis reaction speeds of different sulfur compounds vary significantly. Thus, the sulfur residues in the hydrotreated product can fluctuate greatly depending on initial composition of sulfur compounds in feed. Hence, there arises a need to develop a computer modeling system to calculate product composition of hydrotreatment. First of all, it is necessary to obtain kinetic parameters of the reactions. These parameters can be used to predict ratio of sulfur compounds in products. This is the main goal of solving the reverse kinetic problem.

The part of mathematic model based on the formalized kinetic scheme represents the equations of main sulfur-containing pseudocomponents, and is shown in Table 1.

Table 1

Part of mathematic model representing sulfur-containing pseudocomponents (C_i – molar concentration; τ – contact time; k_i – reaction rate constant)

Pseudocomponent	Equation
Sulfides	$\frac{dC_{sulf}}{d\tau} = -k_4 C_{sulf} C_{H_2}^2$
Benzothiophenes	$\frac{dC_{BT}}{d\tau} = -k_1 C_{BT} C_{H_2}^2$
Dibenzothiophenes	$\frac{dC_{DBT}}{d\tau} = -k_2 C_{DBT} C_{H_2}$
Saturated hydrocarbons	$\frac{dC_{hydrocarb}}{d\tau} = k_4 C_{sulf} C_{H_2} + k_3 C_{aromatic} C_{H_2}$
Aromatic hydrocarbons	$\frac{dC_{aromatic}}{d\tau} = k_1 C_{BT} C_{H_2} + k_2 C_{DBT} C_{H_2} - k_3 C_{aromatic} C_{H_2} - k_5 C_{aromatic}$
Petroleum coke	$\frac{dC_{p.coke}}{d\tau} = k_5 C_{aromatic}$

This mathematical model is formalized and quasi-homogenous, consequently all kinetic constants $k_1 \ldots k_5$ are effective, i.e. they represent combinations of intermediate stage reactions constants [3].

In the frame of the research, the computer program (Fig. 2) has been developed in the Department of Chemical Technology of Fuel and Chemical Cybernetics to solve the reverse kinetic problem.

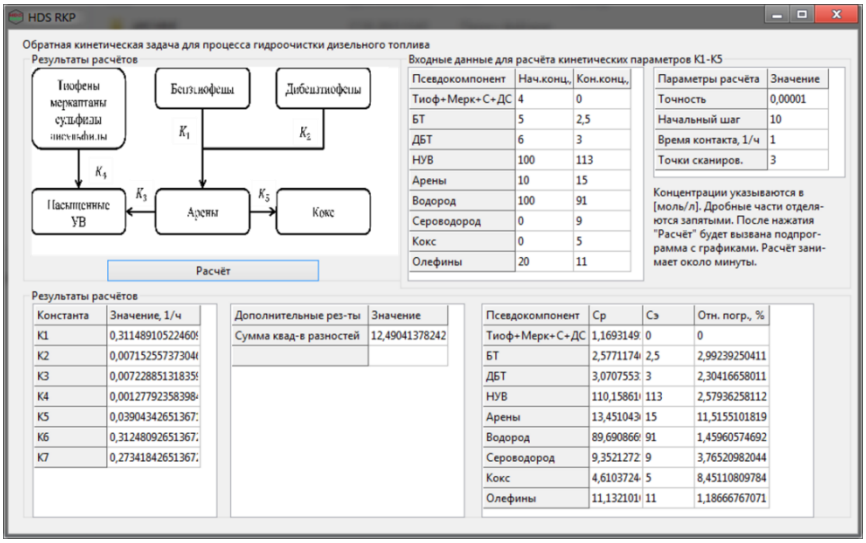

Fig. 2. Interface of program for solving reverse kinetic problem

Experimental data were obtained by using the following laboratory equipment: vaporizer and reactor with special metallic grid to place the catalyst on it. It provided the following conditions: hydrogen pressure – 4 MPa; hydrogen/feed volume ratio – 400/1; feed volume rate – 1.5 ml/sec; presence time of feed – 1/3 hours; catalyst mass – 4 g; temperature – 390°C; catalyst – RK-442.

The straight fraction of diesel fuel (initial boiling point 200°C, end 360°C) was chosen as a feed. Both experimental and calculated molar flow rates with calculation error analysis are presented in Table 2.

Table 2

Experimental molar flow rates, results calculated by model and calculation error analysis

Pseudocomponent	Experimental		Model	Error analysis	
	Begin	End	End	Absolute	Relative
	Mole per hour	Mole per hour	Mole per hour	Mole per hour	%
Saturated hydrocarbons	0.051214	0.065277	0.064653	0.0006238	1.057
Aromatic hydrocarbons	0.043015	0.034277	0.033113	0.0011637	3.514
Benzothiophenes	0.001637	0.000024	0.000024	0.0000001	0.256
Dibenzothiophenes	0.001023	0.000300	0.000300	0.0000000	0.007
Sulfides	0.000897	0.000014	0.000014	0.0000000	1.362
Petroleum coke	0.000000	0.005452	0.005296	0.0001563	2.952

Calculated mole per hour flow rates are almost the same as experimental. Inadequate results on sulfides and saturated hydrocarbons may be caused by the fact that these pseudocomponents should be calculated in a more detailed model. The chemical reaction rate constants for routes 1…5 (Fig. 1) calculated by program are presented in Table 3.

Table 3

Calculated effective constants of reaction speed for routes 1…5

Route	Effective constant	Route	Effective constant	Route	Effective constant
	h^{-1}		h^{-1}		h^{-1}
1	0.827	3	0.036	5	0.415
2	0.940	4	0.846		

As the results show, the sulfides, benzothiophenes and dibenzothiophenes are the most reactive in the hydrotreatment process. Aromatic hydrocarbons in case of use an RK-442 catalyst tend to hydrogenate to the saturated hydrocarbons at lower speed. The catalyst demonstrates very good desulfurization activity, although there are still big residues of aromatics. Intensive petroleum coke formation is caused by high process temperature (390°C) during the experiment.

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KARST DEVELOPMENT IN CAMBRIAN LIMESTONES

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Russian gas pipeline system is one of the largest in the world. In 2012, the length of the main pipelines is more than 175 thousand kilometers. According to official statistics of «Gazprom» 42 % of all accidents of gas pipelines are connected with direct or indirect influence of natural factors.One of the biggest problem occurs with pipeline, which is called «The Power of Siberia». The length of the dangerous part is 160 kilometers. This section starts from Chayandinskoye deposit. The route of this pipeline is located on the territory of Lensky Ulus of the Sakha Republic (Yakutia). There are difficult climate conditions, for example, the temperature in winter can change from −25 °C to −62 °C, shift from winter to spring is usually sharp with big difference between night and day temperatures. Moreover, this place has territory, which is rich in karst. From year to year, there are developing new sinkholes. Development of karst is connected with fractured rocks. Ground water circulates through it; consequently, there occurs dissolution and removal of soluble minerals. Therefore, this place is located in the most difficult conditions, which are seriously complicated by karst [3].

To start solving this problem, firstly, it is necessary to predict the deformations of the pipelines using a forecasting of the area. However, often it is not possible to know when sinkhole will open, so secondly, monitoring of bending pipeline is necessary to operatively fix an accident. Efficient solution can be found if we can use the modern methods of monitoring and protection of pipelines.

The first method is represented by pipeline's protection with bored piles. The invention relates to the construction and operation of pipelines and can be used to prevent accidents in pipelines caused by karst failures. The problem is solved due to the fact that in the known method of protection of pipelines from emergency situations caused by karst dolines, which reveal the pipeline (Figure 1). On both sides, bored piles 1 are performed, placed under the pipeline 2 metal lodgement 3. Metal lodgement is connected with bored piles, covered pipeline the ground, bored piles are performed so that the pile heads were above the earth's surface, as met-al lodgement use the half pipe of larger diameter than the diameter of the pipeline. Metal lodgement is connected with bored piles with a steel rope 5, which is bypass pipe, and the ends of the rope are fixed on the tip piles 4 using a tension clutch regulating the tension of the rope. In addition, at the ends of the cord before compression couplings there are sensors - 8. This prototype is shown in Figure 1 [1].

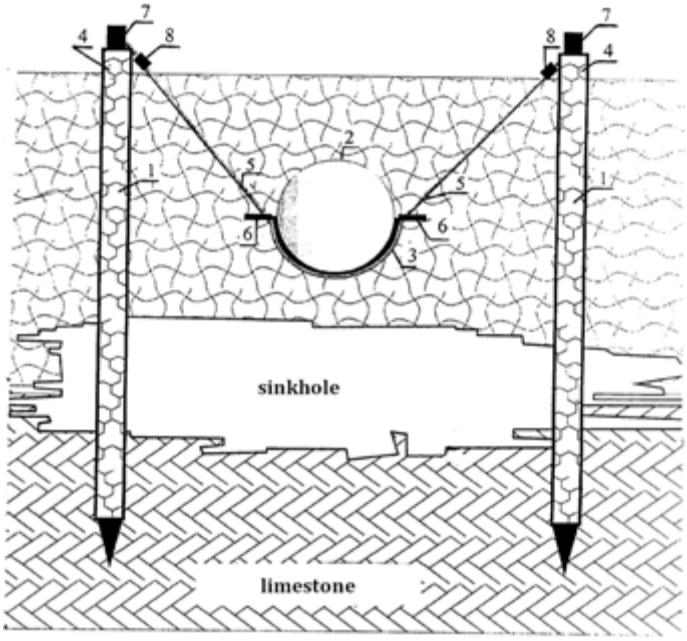

Fig. 1. Protection with bored piles:1 – device comprises bored piles, 2 – pipeline, 3 –metal lodgment,4 –top of piles, 5 – steel cable, 6 – loop,7 – clamping sleeves, 8 – sensors