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Article

Mathematical modeling of the process of hydrotreating diesel fuel from organosulfur impurities

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Abstract: Hydrotreating of diesel fuel is a major catalytic process for motor fuel production. This process aims to reduce the organosulfur content in the fuel to 10 parts per million (ppm) in order to meet environmental standards. However, this deep purification of diesel fuel requires the use of an expensive catalyst at hydrotreating plants, which have giant reactors with a capacity of 200–600 cubic meters. Such a volume of reactors is associated with the use of methods of classical kinetics of chemical reactions, when all the raw materials of the process are in the reactor until the required conversion depth is reached, while hydrotreating has its own specific features. All known mathematical models for diesel fuel hydrotreating take into account different nuances of the process, but they all have one common disadvantage: they use approximate, often crude, ideas about the composition of multicomponent raw materials, such as diesel oil fractions, which contain several dozen different organosulfur compounds with varying activity in hydrogenation reactions. Most often, these raw materials are represented in a mathematical model as a combination of two to six pseudo-components, or lumps, that combine sulfo-organic impurities from one or more homologous groups. Such a theoretical framework allows us to model the current state of hydrotreating technology, but it does not advance it. We propose a new approach to mathematical modeling of diesel fuel hydrotreatment, which better takes into account the actual features of the process. The structure of the mathematical model considers the composition of the raw material as a set of 10–20 narrow fractions. In each fraction, the set of hydrogenated organosulfur impurities is treated as a single pseudo-component. Another feature of the model is the use of different rate constants for different organosulfur impurities in the raw material, represented as a continuous kinetic characteristic that changes over time. This allows us to integrate the system of differential equations in the model and adapt the rate constant to the concentration of the hydrogenated organosulfur impurity at any given time during the process. The developed model has also made it possible to propose a new technology, hydrotreatment: separating the feedstock into two or three wide fractions, combining the corresponding narrow fractions, and then subjecting them to separate hydrogenation processes. This differential hydrotreatment technique will allow for a reduction of the catalyst load in the hydrotreatment unit by almost 50% while maintaining its efficiency or for doubling the efficiency while maintaining the same catalyst load with traditional technology.

Keywords: diesel fuel; hydrodesulfurization process; mathematical modeling; diesel feedstock; reaction rate constant; industrial reactor block

1. Introduction

Hydrotreating of diesel fuel is one of the most large-scale catalytic processes in oil refining. Mathematical modeling of this process is complicated by its implementation in a three-phase system: liquid feedstock, hydrogen-containing gas, and double-functional solid catalysts that provide homolytic and heterolytic hydrogenation reactions of numerous organosulfur compounds, which significantly complicates the formation of mathematical models of the process [1–5]. In industry, hydrotreater process flow sheets are conservative in terms of the hardware of the reactor plant and usually represent a complex of two to four reactors operating in series. The required loading of the catalyst into the reactors is proportional to the productivity of the installation and increases extensively (several times) with an increase in the purification depth. For Euro 5 vehicles, the sulfur content in diesel fuel is limited to 10 ppm (1 ppm = one part per million = 1 mg/kg), which is achieved by increasing the contact time of the feedstock with the catalyst in the hydrotreating reactors [6]. For this reason, the loading of expensive catalyst into the reactor block of the plant reaches 200–600 m^3.

The degree of activity of sulfur compounds in hydrogenolysis reactions is different and decreases in the following order: Mercaptanes > sulfides > thiophenes > benzothiophenes > dibenzothiophenes. At the same time, the most difficultly hydrogenated compounds of the thiophene series are concentrated mainly in heavy fractions boiling above 330 °C [7–10]. It is characteristic that the quality and depth of diesel fuel hydrotreatment, the cleaning process as a whole, are determined by the interaction with hydrogen of a relatively small amount of hardly hydrogenated organic sulfur impurities, while easily hydrogenated components have already undergone hydrogenolysis.

In most chemical processes, all or a significant portion of the raw materials are involved in the reaction. The kinetics, hydrodynamics, energy of the process, and degree of transformation of the feedstock determine the required reaction time and, accordingly, the size of the reactor. However, three factors lead to a significant increase in the hydrotreating reactor compared to reactors for other reactor processes. Firstly, the content of initial organosulfur compounds in the raw materials is very low—only a few hundred or even tens of parts per million. Even the content of total sulfur, converted to hydrogen sulfide, in the raw materials is between 1.5% and 0.5%. Thirdly, the reaction rate constant makes the main error in the calculations. This parameter is determined experimentally by the change in conversion over reaction time. However, if for simple reactions the time of sampling for the analysis of the residual concentration of the raw material component does not matter, then for multicomponent hydrotreating reactions, the value of the reaction rate constant for the pseudo-component is very important for sampling time. At the beginning of the process, rapidly hydrogenated components produce high calculating values of the rate constant, which decrease by the end of hydrotreating, when difficult-to-hydrogenate impurities, such as dibenzothiophenes, remain in the reaction mixture.

In this situation, the assessment of the composition of the initial diesel fuel by hydrogenated components is of particular importance, which is necessary for mathematical modeling of the process [7,8,11–14]. The purpose of this work is to develop a new variant of the model of hydrotreating raw materials and the related search for new technological solutions for the process of hydrotreating diesel fuel.

In response to these challenges, this paper introduces a novel model for characterizing the composition of the initial diesel fuel by hydrogenated organosulfur impurities. In the proposed model, the feedstock is considering as a set of 10–20 narrow fractions sequentially separated from the raw materials as their boiling point increases, in each of which all organosulfur impurities are combining into a single pseudo-component. The new model has several advantages over the well-known models of hydrotreating raw materials. Firstly, a large number of pseudo-components compared to 2–6 pseudo-components of known models significantly increases the level of accuracy of the model. Secondly, the analytical determination of the concentration of pseudo-components is significantly simplified in our model: the concentration of a pseudo-component in a narrow fraction can be determined by a simple analysis of the total sulfur content. Existing methods require the identification of organosulfur impurities and their quantification using precise analytical instruments. Thirdly, and this is perhaps the most important and fundamental difference, in the new model, the pseudo-component content refers only to the amount of a narrow fraction in the raw material, whereas in the known models, the concentration of pseudo-components is in the entire flow of hydrotreating raw materials.

The primary objective of this work is to adapt a classical mathematical model of a chemical process, which is represented by a system of differential equations, to include the effects of kinetics, hydrodynamics, and energy, as well as an additional factor: the dependence of reaction rate constant values on the composition of a multicomponent reaction mixture, which varies over time. The adaptation was provided by replacing a number of discrete values of reaction rate constants with a continuous kinetic characteristic. In addition, the task of finding optimal temperature limits for dividing the initial diesel fuel into two or three wide fractions was solved, minimizing the subsequent loading of the catalyst into the corresponding reactors.

The key contribution of this work is the introduction of a new model of raw materials into the theoretical basis for modeling the hydrotreating process, which made it possible to substantiate the possibility of differential hydrotreating of diesel fuel.

The novelty of this research lies in two main innovations: The development of a new model of raw materials describing the content of a multicomponent admixture of organosulfur substances in it in the form of a number of narrow fractions, each of which contains one pseudo-component, which includes sulfur, and the creation of a new technology for its differential hydrotreating. That technology consists in the preliminary fractionation of raw materials into theoretically valid two or three fractions, which are then individually hydrogenated in various hydrotreating reactors. Together, these improvements make it possible to increase the productivity of hydrotreating plants or reduce the loading of catalyst into the plant’s reactors.

The remainder of this paper is structured as follows: Section 2 presents computer procedures and features of the developed programs. Section 3, consisting of 5 subsections, presents theoretical aspects, numerical calculation results, and their discussion. In subsection 3.1, methods of characterizing hydrotreating raw materials by the content of organosulfuric impurity are discussed, and a new model is substantiated. In subsection 3.2, the replacement of discrete reaction rate constants with a continuous kinetic characteristic is justified. Subsection 3.3 provides an analysis of the efficiency of the industrial reactor unit of diesel fuel hydrotreating and proves that any variants of modern reactor units, including several reactors, are equivalent to a single reactor with an equal catalyst load. Section 3.4 of the development of perspective schemes of the reactor blocks for the hydrotreating unit provides numerous examples of calculations confirming the effectiveness of differential hydrotreating of diesel fuel. In subsection 3.5, the main regularities of the new differential process are given. In subsection 3.6, some of the controversies of hydrotreating modeling are discussed. Section 4 provides brief conclusions on the work as a whole.

2. Computational procedures and programs

Since in this work we solved the problem of comparing different variants of hydrotreatment reactor blocks from the point of view of removing organosulfur impurities *under identical technological conditions*, the need for a complex hierarchical model of catalytic hydrotreating was no longer needed. Due to this, the reactor was calculated on the basis of the following assumptions:

- Quasi-homogeneous reaction stream within the reactor;
- Constant velocities of local flow jets and hydrodynamic model of ideal displacement in the reactor;
- Isothermicity of the process;
- Stationary nature of the process;
- Constant activity of the catalyst in time τ;
- The content of total organosulfur in the feedstock or in its narrow fractions is considered as an organosulfur pseudo-component, and its concentration in the stream is determined by analysis for total sulfur;
- Constant rates of the hydrodesulfurization reactions of the pseudo-components are effective.

Under these assumptions, the mathematical model of a hydrotreating reactor, when analyzing the process by N organosulfur pseudo-components, takes the following form of a system of equations:

$$\begin{cases} \frac{dC_{S1}}{d\tau} = -k_1 C_{S1} \\ \frac{dC_{S1}}{d\tau} == -k_1 C_{S1} \\ \frac{dC_{S2}}{d\tau} = -k_2 C_{S2} \\ \frac{dC_{Si}}{d\tau} - k_i C_{Si} \end{cases} \tag{1}$$

where C_{Si} and k_i are the concentration of the organosulfur component and the effective reaction rate constant of the *i*-th pseudo-component, respectively.

The numerical values of the concentration of organosulfur components in the hydrotreating feedstock and the effective rate constants of the hydrodesulfurization reactions were taken from independent literature sources.

The mathematical model (1) is solved by the Runge-Kutta method, and the calculation program made it possible to determine the change in the concentration of pseudo-components during the process, the residence time of the reaction mixture in the reactor at which will be until a given degree of purification of feedstock. The volume of the catalyst in the reactor was further calculated by the reaction time.

Model (1) with the above assumptions was used when comparing different configurations of industrial reaction blocks of hydrotreating plants.

3. Results and discussion

3.1. Methods of characterizing hydrotreating raw materials by the content of organosulfur impurities

The identification of an extremely complete set of dozens of organosulfur components in diesel fuel (**Figure 1a**) and the development of a database of numerous reaction paths are practically impossible due to the scale of the task. To this problem are added the high cost of the necessary reagents, the complexity of analysis methods, and the need to use expensive precision equipmen*t to* determine the concentration of individual organosulfur impurities in fractions in ppm [15,16]. Instead, the total sulfur content of the feedstock (as the first model of diesel fuel composition in terms of organosulfur content) is often used in calculations to characterize the raw material. In many cases, in the experimental study of the hydrotreatment process, a feedstock-first model was used, in which dibenzothiophene was presented as the only generalizing hydrogenated component instead of a set of organosulfur impurities [17–20] (**Figure 1b**). However, in this case, using the first model will lead to an excessively long reaction time, since the reaction rate constant of dibenzothiophene will then be applied to all sulfur-containing components.

Most often, researchers consider the second model—the grouping of organosulfur impurities of the same homologous series as a kind of conditional pseudo-component (**Figure 1c**) or two-lump, three-lump, or four-lump kinetic model, which includes corresponding groups of higher-, high-, low-, and lower-reactivity portions of feedstock [21–24]. But that model does not take into account the fact that homologues, or groups with significantly different boiling points, also have different reactivity. In addition, in this situation, the selection of fractions of various homologues from the hydrotreating feedstock is also very laborious. In addition, calculations based on the second model take into account the concentrations of pseudo-components based on the volume of the entire feedstock; this also applies to the calculation of the volume of the catalyst in the reactor. Therefore, the required volume of the catalyst is determined by the pseudo-component that reacts the slowest, which inevitably increases the volume of the catalyst. In this regard, we propose, *as a third model*, to consider the feedstock of the hydrotreating process as a set of several narrow fractions, in each of which a set of organosulfur impurities is considered as a conditional pseudo-component (**Figure 1d**). Their content in a narrow fraction is determined using the simplest and most accessible total sulfur content analysis [25]. This makes it possible to simplify the constructed mathematical models for comparative analysis of various hydrotreating schemes. In fact, the third model allows us to calculate the hydrotreating process in conditional local jets (narrow fractions) of processed raw materials, that is, to differentiate the hydrotreating process and calculate various configurations of reaction blocks (**Figure 2**).

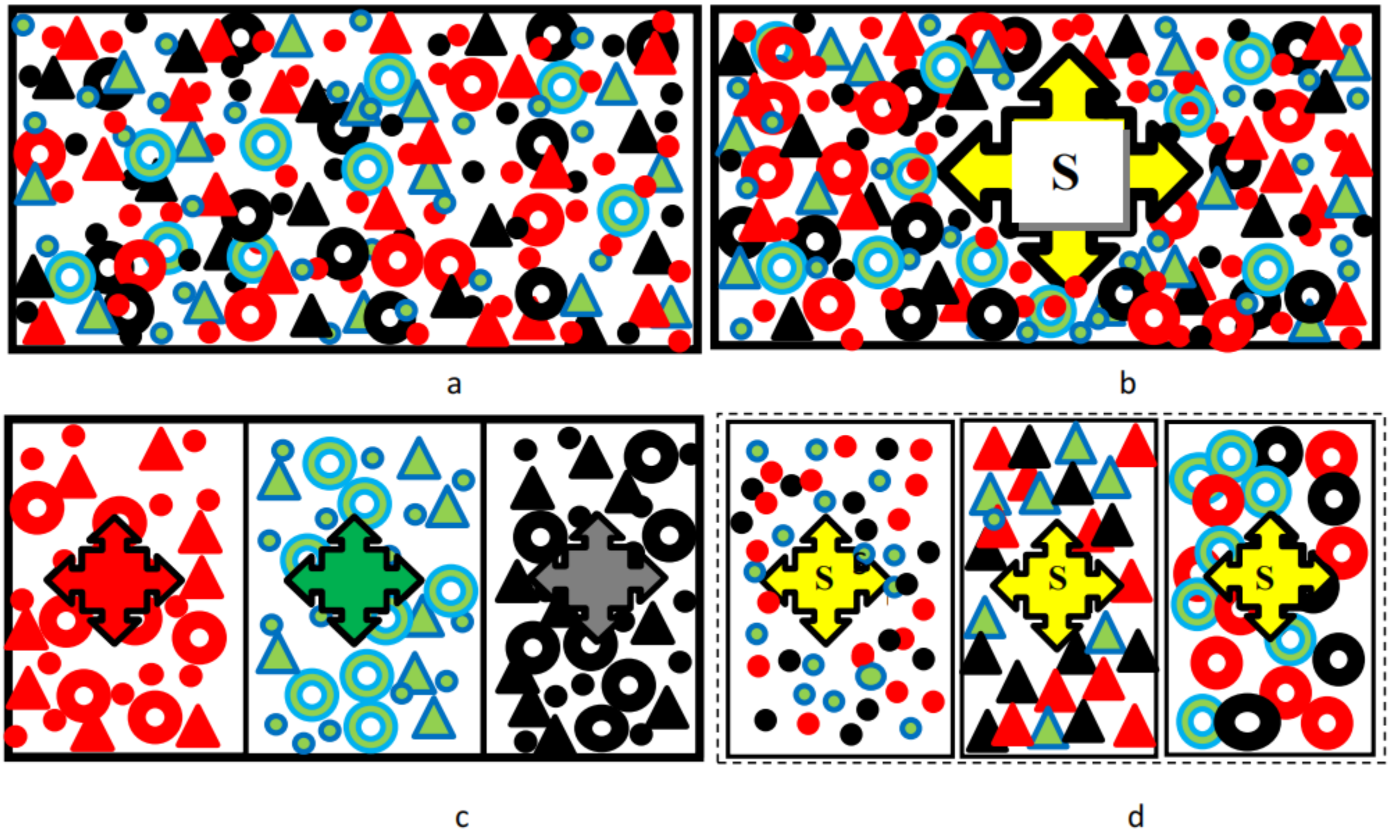

Figure 1. Models characterizing hydrotreating raw materials by the content of organosulfur impurities: **(a)** The totality of many different components with specific concentrations in a single raw material; **(b)** characterization of this set by a single analysis for total sulfur; **(c)** combining homologues into one pseudo-component, for example, three; **(d)** separation of raw materials into several narrow fractions with analysis of each of them for the content of total sulfur, for example, three.

●, ▲, and ○-homologues, e.g. disulfides, with successively increasing boiling points and decreasing reactivity.

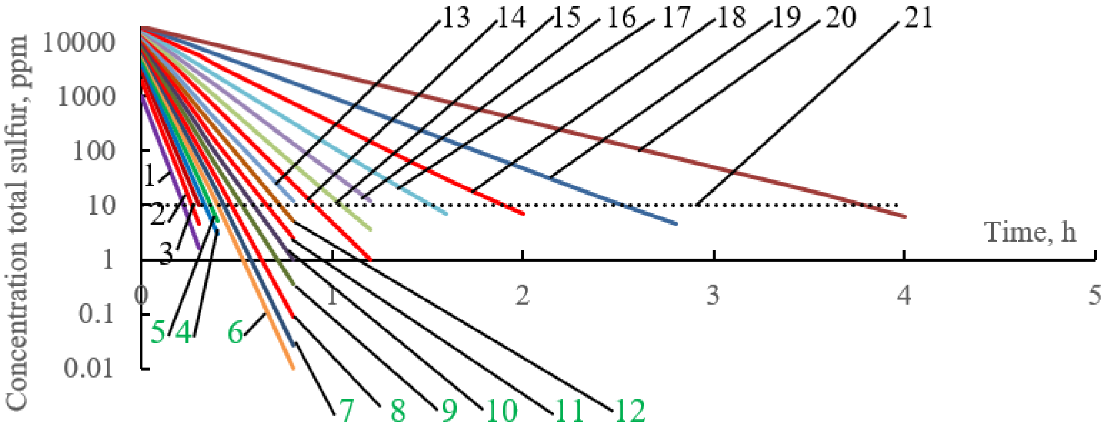

Figure 2. The change of the concentration of pseudo-components during the separate hydrotreating of 20 narrow fractions of raw materials (diesel fuel) by the numbers of narrow fractions from 1 to 20, starting with the lightest; line 21—the permissible total sulfur content in narrow fractions after hydrotreating (10 ppm).

Subsequent studies have shown that it is most expedient to divide the raw material into 16 or 8 equal narrow fractions.

3.2. Reaction rate constant or kinetic characteristic?

The development of an experiment to determine the rate constants of hydrodesulfurization reactions for diesel fuel is very different from classical experiments on mono reactions [26,27]. Usually, the calculation of the effective reaction rate constant $k_{(i,ef)}$ for a specific i-th component of the raw material of the reaction system is determined by the change in its composition over time from the start of the experiment $C_{i,o} - C_{i,\tau}$; then

$$k_{i,ef} = \frac{1}{\tau} ln\left(\frac{C_{i,0}}{C_{i,\tau}}\right) \tag{2}$$

The various components differ significantly from each other. In this regard, at the beginning of the process, with a short contact time, the highly active components of the raw material with a high value of the reaction rate constants react intensively. At the end of the process, low components react slowly, with a low value of the reaction rate constant. The processing of a number of materials for the calculated hydrotreating of model raw materials and experiments on desulfurization of real diesel fuel showed that the effective reaction rate constants decrease as the reaction depth increases, that is, the duration of the hydrodesulfurization process. For example, mathematical processing of experimental data on the hydrotreating of three fractions of diesel fuel at a pilot plant (Lebedev et al. experiment [28]) showed that the value of the effective rate constant could increase by 3–4 times as the depth of diesel fuel purification increases, as the depth of desulfurization increases (**Table 1**).

Table 1. Change in the values of sulfur concentrations at the exit from the reactor C and the effective reaction time constants k_{ef} in the process of hydrotreating fractions 160–300 °C, 160–360 °C, and 300–360 °C.

τ, h.	**Temperature, °C**	**Fraction 160 °C–300 °C**		**Fraction 160 °C–360 °C**		**Fraction 300 °C–360 °C**	
		C, % [28]	k_{ef}, h^{-1}	C, % [28]	k_{ef}, h^{-1}	C, % [28]	k_{ef}, h^{-1}
1.00	340	0.020	3.8	0.15	2.1	0.19	2.0
	350	0.017	4.0	0.13	2.2	0.16	2.2
	360	0.015	4.1	0.11	2.4	0.14	2.4
0.50	340	0.035	6.5	0.18	3.7	0.35	2.9
	350	0.030	6.8	0.16	4.0	0.29	3.2
	360	0.025	7.2	0.13	4.4	0.25	3.5
0.33	340	0.050	8.7	0.22	5.0	0.46	3.5
	350	0.044	9.1	0.19	5.5	0.41	3.8
	360	0.040	9.4	0.16	6.0	0.37	4.1
0.25	340	0.068	10.4	0.25	6.2	0.62	3.5
	350	0.060	10.9	0.22	6.7	0.55	3.9
	360	0.050	11.6	0.18	7.5	0.5	4.3
0.20	340	0.080	12.2	0.28	7.2	–	–
	350	0.071	12.8	0.25	7.7	–	–
	360	0.060	13.7	0.22	8.4	–	–

Table 1. (*Continued*).

***τ*, h.**	**Temperature, °C**	**Fraction 160 °C–300 °C**		**Fraction 160 °C–360 °C**		**Fraction 300 °C–360 °C**	
		C, % [28]	k_{ef}, h^{-1}	C, % [28]	k_{ef}, h^{-1}	C, % [28]	k_{ef}, h^{-1}
0.16	340	0.095	13.6	0,30	8.2	–	–
	350	0.080	14.7	0.27	8.8	–	–
	360	0.070	15.5	0.25	9.3	–	–
0.14	340	0.110	14.9	–	–	–	–
	350	0.097	15.7	–	–	–	–
	360	0.090	16.3	–	–	–	–

Thus, the analysis of the chemistry of hydrotreatment indicates that the hydrotreatment process as a whole with the integral method for determining total sulfur can and should be characterizing not by essentially degenerate effective reaction rate constants but by variable ***kinetic characteristics K***, which naturally change during the process. It can be assumed that the kinetic characteristic can also serve to describe other multi-reaction systems, the patterns of which are determined as the result of the analysis of the group composition.

Regularly, the kinetic characteristic $K = f(\tau)$ reflects the observed change in the effective rate constant of the reaction of a complex multicomponent system as a whole. Both for model systems and for real diesel fuel, $K = f(\tau)$ are qualitatively similar. The form of the dependence of the reaction kinetic characteristic K on the contact time of the reaction mixture with the catalyst τ is characteristic of a hyperbolic-type function of the form

$$K = f(\tau) = M/(1 + A\tau) \tag{3}$$

where A and M are empirical approximation coefficients of the kinetic characteristic of the experimental data set by values of the effective rate constants.

Let us consider mathematical modelling of the diesel hydrotreating process using the concept of ‘kinetic characteristic’ and expressing the composition of feedstock by sulfo-organic impurities as the total sulfur content C_S. For a steady-state process, the simplest mathematical model of a hydrotreating reactor, assuming quasi-homogeneous reaction and ideal displacement mode for the flow, is expressed as

$$\frac{dC_S}{d\tau_{cond}} = -\left(\frac{M}{1 + A\tau_{cond}}\right)\frac{dC_S}{d\tau_{cond}} - W\frac{dC_S}{dl} = 0 \tag{4}$$

where W is flow rate and l is catalyst bed height in the reactor.

A high-quality validation of the applicability of the mathematical model of hydrotreatment (4), based on the use of the concept of kinetic characteristics, was performed in [29] using the database on hydrotreatment of model systems and diesel fuel at the pilot plant [28].

The advantages of using kinetic characteristics over the application of the only natural values of reaction rate constants in mathematical modeling of hydrotreating kinetics of fractions 160 °C–360 °C are clearly illustrated in **Figure 3**.

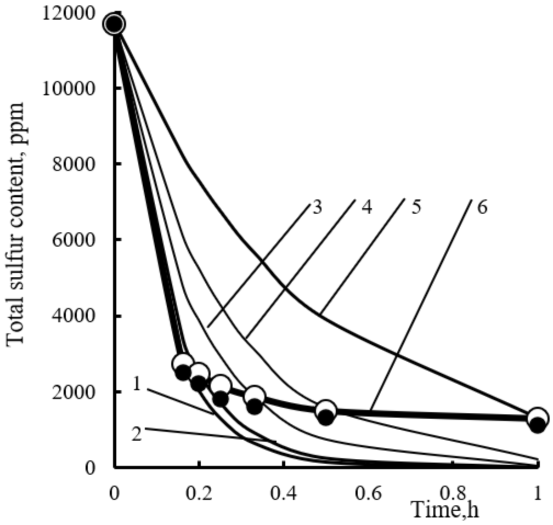

Figure 3. The change in the total sulfur content in the hydrogenate over time for hydrotreating diesel fuel fractions 180–360 °C, calculated from the unit reaction rate constants determined from experimental data [22] for reaction times of 0.2 h (1), 0.25 h (2), 0.33 h (3), 0.5 h (4), and 1.0 h (5), and with kinetic characteristics (curve (6) and ○). ●—is experimental data on [22].

When we calculate kinetic curves for complex multicomponent reaction systems, such as diesel fuel, based on effective rate constants, the results obtained are predictably inadequate for the actual process. Each of the calculated kinetic curves of the total sulfur change in purified diesel fuel (curves 1–5 in **Figure 3**) coincide with the real kinetic curve 6 in **Figure 3** at only one point (the black points). Each of these points corresponds to a specific time of the diesel fuel hydrotreating experiment (**Table 1**), at which the corresponding effective reaction rate constant was calculated. The description of the series of values of the reaction rate constants from **Table 1** by the kinetic characteristic (Equation (3)) made it possible to calculate the kinetic curve of the diesel fuel hydrotreating process fairly accurately according to Equation (4).

Since the mathematical modeling of the hydrotreating process using only the one reaction rate constant leads to an incorrect value of hydrotreating duration, this puts additional requirements on the method of conducting experiments. In order to increase the accuracy of the kinetic dependence formation, it is recommended to carry out at least three experimental determinations of the k_{eff}, respectively, for three positions of the τ. At the same time, it is recommending working in the area of sufficiently large values of τ, although this significantly complicates the experiment. So, if only 5–10 cm^3 of catalyst is loaded into the reactor in the experiment, it is difficult to ensure a uniform supply of reagents (raw materials and hydrogen-containing gas) in micro quantities.

So, for example, if into the microreactor is loaded only 5–10 cm^3 of the catalyst, then it is difficult to ensure the supply of reagents (raw material and hydrogen-containing gas) in micro quantities. If a volume ratio of raw materials/catalyst is equal to 0.5 h^{-1} and a reaction time is 2 h, it is necessary to ensure the consumption of diesel fuel of 2.5–5 cm^3 per hour in the reactor to ensure the stability of the process.

Mathematical modeling of the hydrodesulfurization process based on kinetic characteristics has been successfully applied to analyze this process on model systems and real diesel fuels.

3.3. Analysis of efficiency of industrial reactor units of diesel fuel hydrotreating

The variety of types of layout for the reactor unit of hydrotreating plants (**Figure 4**) requires their comparison from the standpoint of minimizing the loading of the catalyst to obtain high-quality diesel fuel. Since the reactors are structurally the same in all schemes, when solving the problem, it was assumed that in the reactors, with the assumptions made, the temperature and concentration profiles in the height of the catalyst layer should be practically the same.

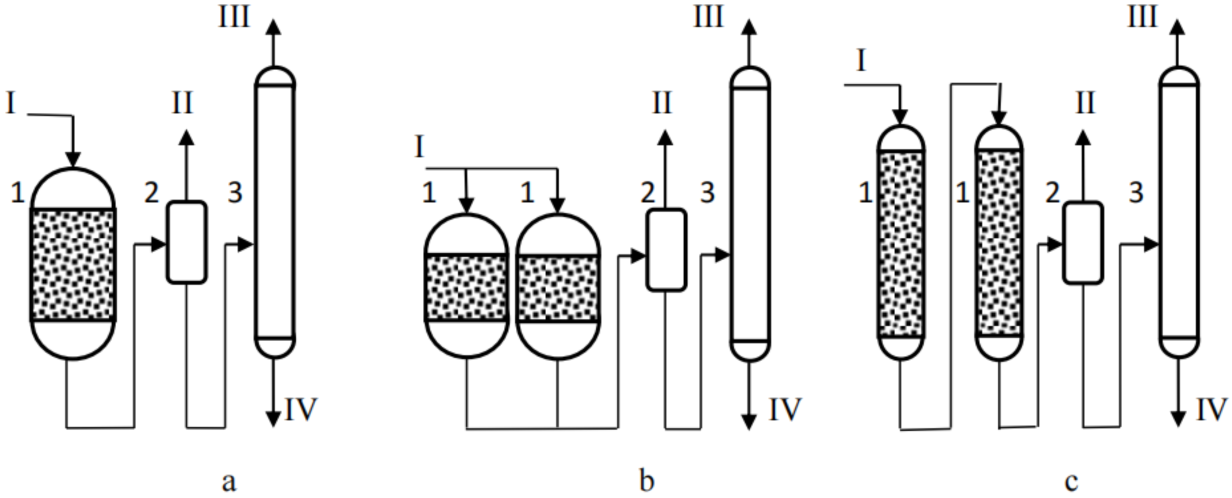

Figure 4. Concepts for reactor units of the process of hydrotreating diesel fuel. **(a)** Single-reactor system; **(b)** block double-reactor with parallel supply of raw materials; **(c)** double-reactor unit with a consistent supply of raw material.

1—reactor, 2—separator, 3—stabilization column. I—a mixture of raw materials with hydrogen-containing gas, II—blowing off of hydrogen-containing gas, III—light hydrocarbons and hydrogen sulfide, IV—purified diesel fuel.

To compare different hydrotreating reactor systems (**Figure 4**), mathematical modeling of the hydrodesulfurization process of 250 m^3/h of diesel fuel with a sulfur content of 6000 ppm, the volumetric feed rate of feedstock of 2 h^{-1} and the accepted effective rate constant of the hydrodesulfurization reaction of 2 h^{-1} was performed [30]. The efficiency of the reaction system, which provides the final sulfur concentration in purified diesel fuel from 500 to 10 ppm, was estimated from the total volume of the catalyst in the reactors of the hydrotreating plant. Calculations have shown (**Table 2**) that the volume of the catalyst in a single reactor and in a parallel and sequential reactor system required to achieve a given residual sulfur concentration in diesel fuel is the same, and the configuration of the installation scheme is determined by technical limitations. This conclusion is valid also for a four-reactor [23], as well as for a combined parallel-serial circuit, allowing us to assume that all actual industrial reactor units, regardless of their configuration and number of reactors, are equivalent to the operation of a single big reactor.

Table 2. Results of mathematical modeling of various reaction units of diesel fuel hydrotreating plants for different systems (**Figure 4a**–**c**).

Concentration of sulfur in feed stock, ppm	**Final concentration of sulfur in purified fuel, ppm**	**Duration of reaction, h**			**The volume of the catalyst in the system, m^3**		
		a	**b**	**c**	**a**	**b**	**c**
6000	2000	0.550	0.550	0.550	68.8	68.8	68.8
6000	500	1.245	1.245	1.245	155.6	155.6	155.6
6000	350	1.420	1.420	1.420	177.5	177.5	177.5
6000	50	2.395	2.395	2.395	299.4	299.4	299.4
6000	10	3.199	3.199	3.199	400.0	400.0	400.0

The performed calculations allowed us to draw the following conclusions.

1) Mathematical model (1), under accepted assumptions, allows comparing the efficiency of various reaction blocks for a hydrotreating plant according to the required catalyst loading;

2) Calculating catalyst loading into the reaction unit is sensitive to the depth of purification of diesel fuel from organosulfur impurities;

3) The concentration of organosulfur purities in calculations could be expressed by analyzing total sulfur (the first model of the composition of raw materials according to impurities of organometallic compounds);

4) Calculated loading of the catalyst into the reactor unit is close in magnitude to its loading at industrial hydrotreating plants.

3.4. Development of perspective schemes of the reactor blocs for the hydrotreating unit

The representation of the model of hydrotreating raw materials as a third model in the form of several narrow fractions (**Figure 1d**) with different boiling points and, accordingly, different reactivity of the organosulfur components included in these fractions made it possible to consider differential hydrotreating, that is, to purify not all raw materials, but some of their parts separately. The proposed solution is the opposite of the one discussed in [31].

The advantages of this approach to carrying out a diesel hydrotreating process can be easily demonstrated by the following example [32].

Assume that diesel fuel in the amount G = 100 t/h goes to the hydrotreatment unit for deep desulfurization. Let us consider two options for treatment of this fuel to remove organosulfur impurities from this fuel. First, this feedstock can be desulfurized in the traditional way in one reactor. Second, the raw materials can be preliminarily divided into two fractions (distillate and residue) if there is a reserve distillation column in the hydrotreating unit, and then these fractions can be hydrogenated and purified from sulfur individually in two reactors. The first light (low boiling) fraction in quantity G = 80 t/h contains sulfur-organic components easily fully hydrogenated within 1 h. Second heavy (high-boiling) fraction of G = 20 t/h containing organosulfur components, which are difficult and slow to react with hydrogen within 3 h.

For deep hydrotreating of diesel fuel, the required loading of the catalyst into the reactors G_{kat} can be calculated as

$$G_{kat} = G_F \cdot \tau_R \tag{5}$$

where G_F—the feed of raw materials, t/h, and τ_R—the duration of the reaction, h.

If all the feedstock was in contact with the catalyst for 3 h for complete removal of both easily and slowly hydrated sulfur-organic components, the required loading of catalyst in the reactor G_{kat} will be equal to 300 t (100 t/h, 3 h) (**Figure 5a**). If we carry out the hydrogenation of two fractions of feedstock separately in two reactors, then we could achieve the necessary loading of the catalyst in the first reactor, 80 t (as 80 t/h·1 h), and in the second reactor, 60 t (as 20 t/h·3 h) (**Figure 5b**). In that case, the total loading of the catalyst in two reactors of the reactor block will make only 140 t instead of 300 t in one reactor.

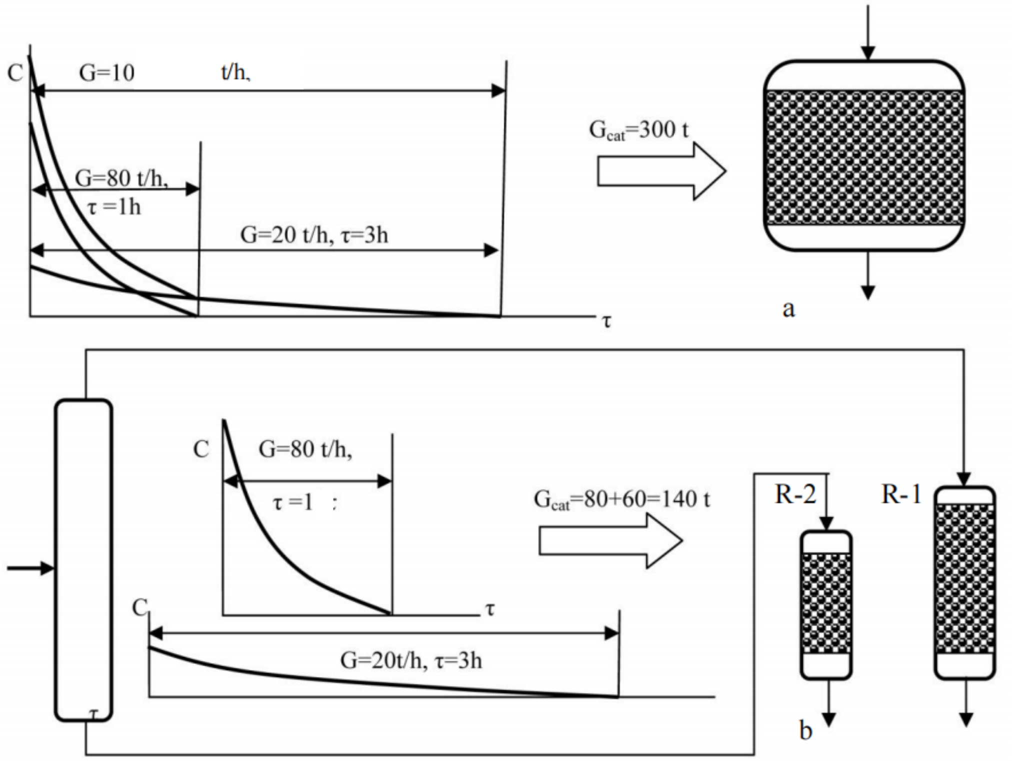

Figure 5. Illustration of the principle of differential hydrogenation of diesel fractions. **(a)** Usual hydrotreating; **(b)** differential hydrotreating.

In mathematical modeling of the hydrotreating process of diesel fuel pre-fractionated into light and heavy broad fractions in separate reactors, calculations of hydrodesulphurization of several variants of model fuel as feedstock were performed. In each variant of calculation, the distribution of sulfur-organic components in each broad fraction at the time of the chemical process, with the achievement of a concentration of total sulfur at the outlet of the corresponding reactor being 10 ppm, and the necessary volume of catalyst in each reactor and as a whole in both reactors were determined. The feedstock (fraction 180 °C–360 °C) was divided into 16, 8, or 4 narrow fractions, from which wide fractions were formed. 8 variants of various (linear, nonlinear, and extreme) non-distribution functions of sulfur over narrow fractions were considered (**Figure 6**).

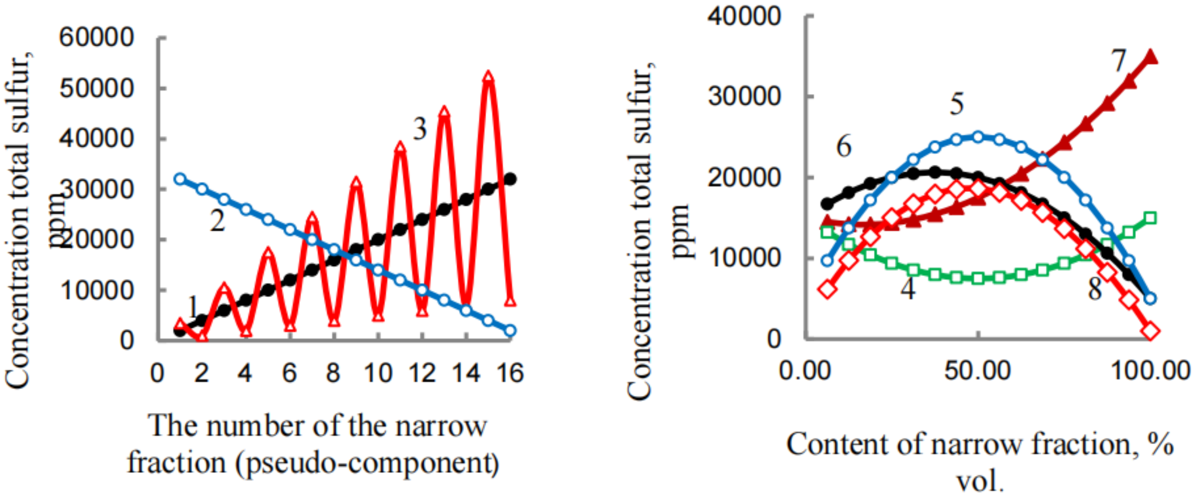

Figure 6. Options for distribution of total sulfur by hydrotreating raw materials (1–8 is the number of the raw material variant according to **Table 3**).

Calculations showed that in all cases of mathematical modeling of the process, the loading of the catalyst into two reactors during differential hydrotreating of diesel fuel is much lower than during conventional hydrotreating (**Figure 7**). An increase in the number of narrow fractions increases the level of calculation accuracy (**Table 3**). Thus, there is such a boundary of division of two fractions at which the hydrotreating process can be realized at minimum catalyst loading in two reactors.

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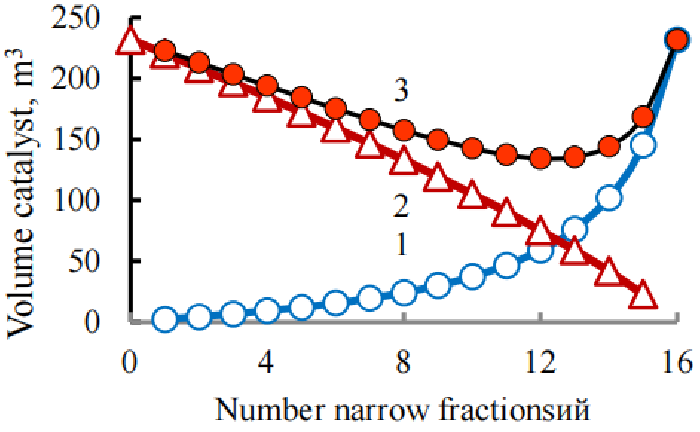


Figure 7. The influence of the number of narrow fractions introduced into the composition of light and wide fractions on the loading of the catalyst into the first reactor (1), the second reactor (2) and in total into both reactors of the hydrotreating unit (3) when dividing the raw materials into 16 narrow fractions and taking into account, respectively, 16 pseudo-components.

Table 3. Summary data on the dependence of the total volume of the loaded catalyst in two reactors for different variants of the distribution of total sulfur in the feedstock*. If possible, move the title of the table 3 to the next page.

Number of narrow fractions (pseudo-components) in feed	**Distribution of narrow fractions by reactor *R*-1 and *R*-2**	**The total volume of the loaded catalyst in two reactors, m^3, with options for the distribution of total sulfur in the feedstock according to Figure 6**							
		1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
16	1/2…16	252.4	247.0	375.8	184.6	331.8	332.0	514.0	434.6
	1, 2/3…16	239.9	239.8	358.6	181.4	318.8	319.0	488.8	414.6
	1…3/4…16	227.3	232.4	343.2	177.8	305.6	305.8	463.0	394.0
	1…4/5+…16	214.7	224.6	324.4	174.2	292.2	292.2	437.2	373.0
	1…5/6…16	202.0	216.6	310.6	170.4	278.8	278.6	411.2	351.8
	1…6/7…16	189.4	208.4	289.4	166.6	265.4	265.0	385.2	330.2
	1…7/8…16	176/9	200.2	278.6	162.8	252.2	251.4	359.6	308.8
	1+…8/9…16	164.6	192.0	254.6	159.2	239.2	238.0	334.2	287.4
	1…9/10…16	152.8	184.0	249.0	156.0	226.8	225.0	309.8	266.4
	1…10/11…16	141.5	176.4	221.4	153.6	215.2	212.8	286.6	246.6
	1…11/12…16	131.5	170.0	226.0	**152.4**	205.2	202.0	265.8	228.6
	1…12/13…16	123.5	165.0	194.6	153.2	198.0	193.8	249.4	214.0
	1…13/14…16	**119.4**	**163.2**	224.0	157.8	**195.8**	**190.0**	**240.8**	**206.0**
	1…14/15, 16	123.5	168.0	**192.4**	16.0	203.4	196.0	249.4	212.2
	1…15/16	149.5	188.0	316.4	192.6	234.8	225.6	302.4	256.0
8	1/2…8	268.9	335.6	535.6	332.2	413.0	402.4	545.8	470.2
	1, 2/3…8	239.9	307.6	477.8	304.2	373.8	364.8	487.2	421.8
	1…3/4…8	211.1	279.0	420.4	276.2	334.8	326.6	428.2	372.4
	1…4/5+…8	182.9	250.6	364.4	249.0	296.6	289.4	370.4	323.0
	1…5/6…8	156.7	224.0	312.2	224.4	261.8	254.8	316.6	276.2
	1…6/7…8	**136.5**	**203.8**	**272.0**	**207.4**	**235.8**	**228.4**	**275.2**	**239.4**
	1…7/8	137.1	205.8	273.0	215.0	240.0	230.6	276.0	238.4
4	1/2…4	263.7	399.0	525.2	414.8	459.6	443.4	533.8	466.4
	1, 2/3…4	199.9	314.8	398.4	325.6	356.8	344.8	404.0	355.8
	1…3/4	**148.8**	**247.0**	**375.8**	**184.6**	**331.8**	**332.0**	**514.0**	**434.6**

***** Calculations of the hydrotreating process and loading of the catalyst into the reactors were performed by V.A. Zhilina.

Verification and validation of the mathematical model of hydrotreating (1) taking into account the third model of feedstock in the form of a set of 16 narrow fractions [32] (**Table 4**) was carried out by checking the equality of loading of the catalyst into the industrial reactor block (**Figure 8a**) and the single reactor (**Figure 8b**). The technological conditions were the same for all blocks. The initial data were taken from S.A. Loginov et al. [33] as the results of the survey of the industrial unit L-24-6 for diesel fuel hydrotreating in three reactors (**Figure 8a**). This unit reduced the total sulfur content in the 136 t/h fuel from 10000 ppm to 300 ppm. In addition, the problem of estimating the need for a catalyst for this plant was solved while ensuring a reduction in the sulfur concentration to 10 ppm in a single reactor (**Figure 8c**) and in two reactors with optimal separate hydrogenation (**Figure 8d**).

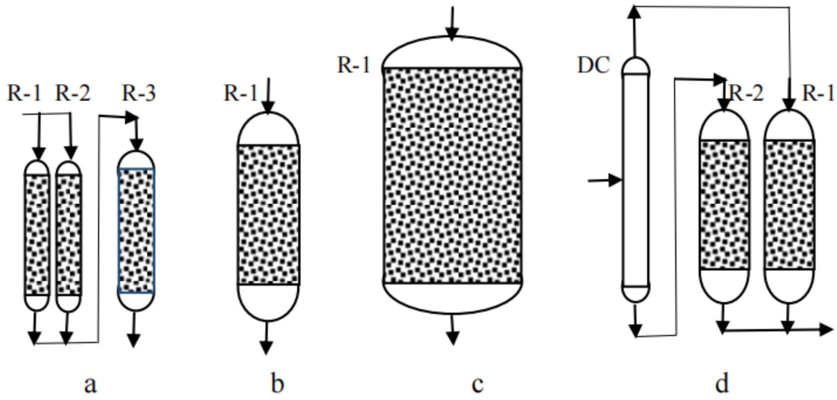


Figure 8. Configurations of reaction blocks with a decrease in the sulfur concentration in diesel fuel **(a**,**b)** at 300 ppm and **(c,d)** at 10 ppm: **(a)** industrial unit, **(b**,**c)** single reactor, and **(d)** new differential hydrogenation.

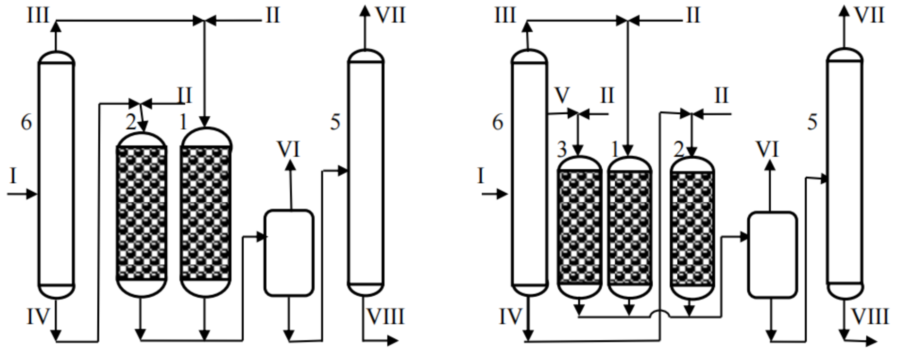
R-1, *R*-2, *R*-3–reactor; DC–distillation column.

Table 4. Results of verification and simulation of the reactor block of an industrial hydrotreating unit.

Parameters	**Industrial unit [33]**			**Calculated unit**			
	Figure 8a			**Figure 8b**	**Figure 8c**	**Figure 8d**	
	***R*-1**	***R*-2**	***R*-3**	***R*-1**	***R*-1**	***R*-1**	***R*-2**
Consumption of raw materials, m^3/h	68	68	136	136	136	109.5	26.5
Sulfur concentration at the inlet, ppm	10,500–12,000		655	10,000	10,000	9257	13,320
Sulfur concentration at the outlet, ppm	810	500	300	300	10	10	10
Reaction time, h	–	–	–	1.1	4.5	1.1	6.2
Catalyst mass in reactor, t	11.9	12.6	31.4	56.1	227.5	44.7	58.3

Validation of the model (1) indicates its high quality in solving the problems of analyzing various hydrotreating schemes under the same technological conditions. The estimated catalyst load in a unit reactor was 56.1 tons, while the actual load in three reactors of the industrial unit is 55.9 tons. The relative error of the calculation of hydrotreating according to the model is 0.4%. An increase in the depth of purification of diesel fuel from organosulfur impurities from 97% to 99.9% (concentration of impurities = 10 ppm) requires a 4-fold increase in the loading of the catalyst unit in classical hydrotreating, while in the case of differential hydrotreating, the need for a catalyst will increase only by 1.84 times.

Calculations have shown that the efficiency of hydrotreating is largely affected by the overloading of the reactor *R*-1 with heavy wide fractions and the reactor *R*-2 with light wide fractions (**Figure 9a**). There is no doubt that it is expedient to combine a part of these fractions into the third flow of the medium-wide fraction subjected to hydrotreating in a separate third reactor, *R*-3. This fraction can be obtained in the rectification column of the hydrotreater plant as a side stream. The reactor *R*-3 becomes additional equipment of the unit (**Figure 9b**). The kinetics of one of the variants of hydrodesulfurization of 16 pseudo-components of the feedstock of the process divided into three wide fractions are shown in **Figure 10**.

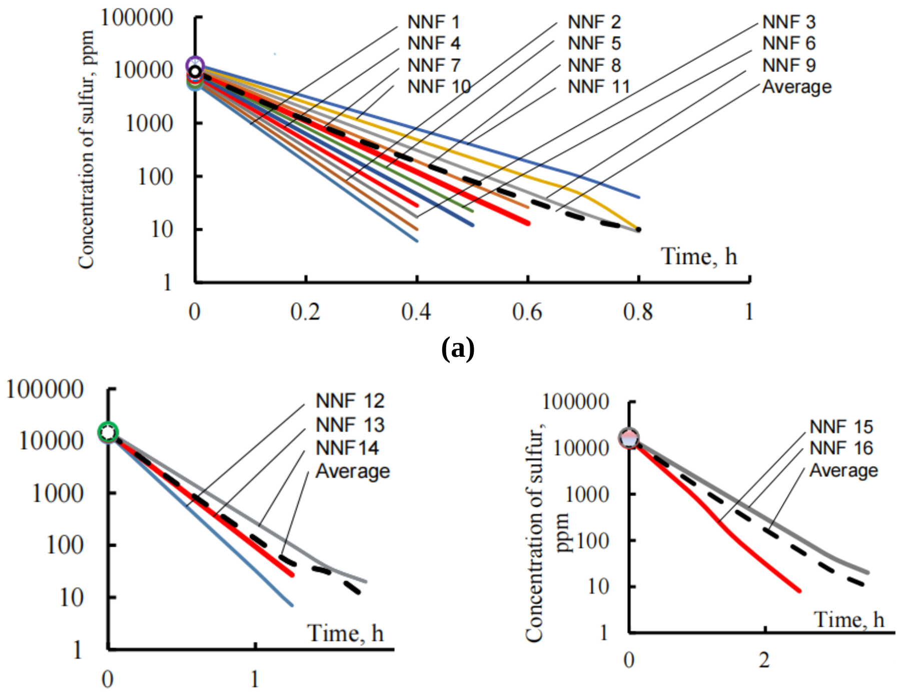


a

b

Figure 9. Basic technological schemes of reactor units for differential hydrotreating diesel fuel: **(a)** two-reactor and **(b)** three-reactor [34,35].

Apparatuses: 1—reactor *R*-1, 2—reactor *R*-2, 3—reactor *R*-3, 4—separator, 5—stabilizer, 6—distillation column. Streams: I—raw materials, II—hydrogen-containing gas (HCG), III—light fraction of raw materials, IV—heavy fraction of raw materials, V—medium fraction of raw materials, VI—recirculate HCG, VII—hydrocarbon gas, VIII—purified diesel fuel.



(a)

(b) **(c)**

Figure 10. Kinetics of hydrodesulfurization of pseudo-components contained in narrow fractions forming reactor feedstock: **(a)** *R*-1; **(b)** *R*-3; and **(c)** *R*-2 (NNF—umber of narrow fractions, average sulfur content in a wide fraction).

Mathematical modeling of a three-reactor scheme of a hydrotreating unit, all other things being equal, showed that when a set of narrow fractions forming a medium-wide fraction sent to the reactor *R*-3 is formed, a rather diverse variability of solutions appears on the selection of temperature boundaries for the beginning and end of boiling of the middle fraction. It is characteristic that the transition from a two-reactor to a three-reactor hydrotreating scheme is accompanied by an additional decrease in the total volume of catalyst loading into the reactor unit due to the elimination of the previously discussed factors that negatively affect the operation of the reactors *R*-1 and *R*-2 of the two-reactor scheme.

When selecting the temperature limits of the medium-wide fraction, the adopted set of narrow fractions provides a monotonic change in the volume of the catalyst loaded into the reactor *R*-3 **(Figure 11)**, while the calculated volume of the total load in all three reactors also has a minimum **(Figure 12)**, like for a two-reactor scheme. However, if a two-reactor unit has a single minimum of catalyst loading, many local extremums of the minimum type are forming when calculating a three-reactor unit. When searching for a global extremum, it is necessary to use a scanning method with a sequential change in the range of narrow fractions that form a wide medium fraction for the new reactor *R*-3.

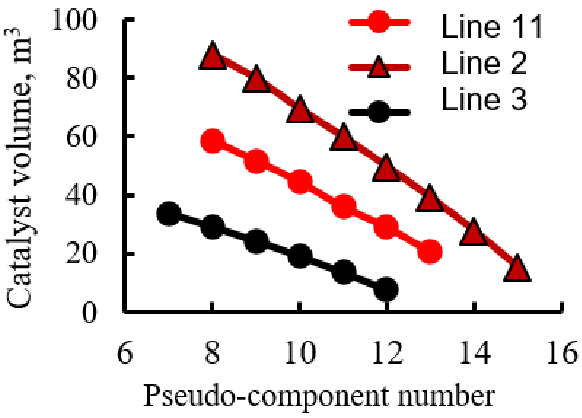


Figure 11. Dependence of the volume of catalyst loaded into the *R*-3 reactor on the numbers of narrow fractions that form its raw material: Line 1—narrow fractions 11–14, line 2—narrow fractions 12–15, line 3—narrow fractions 9–12.

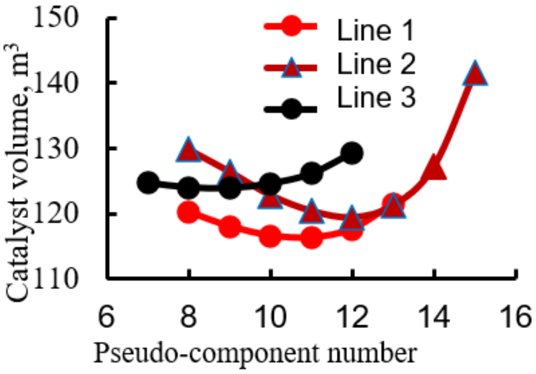


Figure 12. Dependence of the volume of catalyst loaded into the block on the numbers of narrow fractions, feedstock of the R-3: Line 1—narrow fractions 11–14, line 2—narrow fractions 12 ... 15, line 3—narrow fractions 9–12.

An additional feature of the tasks solved in optimizing the three-reactor hydrotreating scheme is their variability. It is possible not only to minimize the catalyst loading with optimal distribution of narrow fractions of diesel fuel into three wide fractions but also to choose such a distribution option in order to calculate the catalyst volumes approximately the same in all three reactors. At the same time, the total volume of the catalyst is close enough to the global minimum of the catalyst, which allows the reactors to be designed as identical equipment.

Considering the required volume of loading an expensive catalyst into the reactor unit as an optimality criterion *R*, we can assume that each calculation option allows us to determine the local optimum, and their comparison allows us to identify the global optimum for solving the problem (**Table 5**).

Table 5. Comparison of characteristics of one-, two- and three-reactor units of plants for differentiated hydrotreatment of diesel fuel.

Characteristics of reactor unit	**Reactors**		
	***R*-1**	***R*-3**	***R*-2**
One-reactor unit (R = 231.7 m^3)			
Distribution of pseudo-components	1–16		
Feedstock consumption, m^3/h	100		
Duration of contact of feedstock with catalyst, h	2.31		
Catalyst volume in reactor, m^3	231.7		
Optimal two-reactor unit (R = 134.2 m^3)			
Temperature limits of boiling of wide fractions, ℃	180-315		315-360
Distribution of pseudo-components	1–12		13…16
Feedstock consumption, m^3/h	75		25
Duration of contact of feedstock with catalyst, h	0.78		3.00
Catalyst volume in reactor, m^3	59.0		75.2
Three-reactor unit (option 1-local optimum; R = 123.9m^3)			
Temperature limits of boiling of wide fractions, ℃	180-270	270-315	315-360
Distribution of pseudo-components	1–8	9…12	13…16
Feedstock consumption, m^3/h	50	25	25
Duration of contact of feedstock with catalyst, h	0.49	0.97	3.00
Catalyst volume in reactor, m^3	24.4	24.3	75.2
Three-reactor unit (option. 2-local optimum; R = 119.4m^3)			
Temperature limits of boiling of wide fractions, ℃	180-303.7	303.7-348.7	348.7-360
Distribution of pseudo-components	1–11	12…15	16
Feedstock consumption, m^3/h	68.75	25	6.25
Duration of contact of feedstock with catalyst, h	0.68	2.00	3.70
Catalyst volume in reactor, m^3	46.6	23.1	49.7
Optimal three-reactor unit (option 3-global optimum; R = 111.3 m^3)			
Temperature limits of boiling of wide fractions, ℃	180-292.5	292.5-337.5	337.5-360
Distribution of pseudo-components	1…10	11…14	15…16
Feedstock consumption, m^3/h	62.5	25	12.5
Duration of contact of feedstock with catalyst, h	0.60	1.48	3.35
Catalyst volume in reactor, m^3	37.4	41.9	32.0

The temperature boundaries of the beginning and end of boiling of the broad fractions in **Table 5** were determined by searching for the minimum *R* of the total loading of the catalyst into the reactor block unit, which is considered as a criterion of optimality *R* of the diesel fuel hydrotreating process by the equations for two-reactor blocks:

$$R = \sum_{i=1}^{i=Z} \frac{G_{Fi} \ln \frac{C_{S0i}}{C_{Siend}}}{R1_{F/C} k_i} + \sum_{i=Z+1}^{i=N} \frac{G_{Fi} \ln \frac{C_{S0i}}{C_{Siend}}}{R2_{F/C} k_i} = \min, \tag{6}$$

for three-reactor block:

$$R = \sum_{i=1}^{i=X} \frac{G_{Fi} \ln \frac{C_{S0i}}{C_{Siend}}}{R1_{F/C} k_i} + \sum_{i=X+1}^{i=Y} \frac{G_{Fi} \ln \frac{C_{S0i}}{C_{Siend}}}{R3_{F/C} k_i} + \sum_{i=Y+1}^{i=N} \frac{G_{Fi} \ln \frac{C_{S0i}}{C_{Siend}}}{R2_{F/C} k_i} = \min, \tag{7}$$

where in Equation (6), Z and $Z + 1$ are the numbers of the last and first narrow fractions between the light and heavy wide fractions, and in Equation (7), X and $X + 1$, Y and Y+1 are accordingly the numbers of the last and first narrow fractions between the light and middle and between the middle and heavy wide fractions. In both equations, N is the total number of narrow fractions in the raw material, and for the i-th narrow fraction, G_{Fi}, C_{S0i}, C_{Siend}, and k_i are accordingly consumption of the narrow fraction, concentration of total sulfur before hydrotreating, final concentration of total sulfur, and effective rate constant; $R1_{F/C}$, $R2_{F/C}$, and $R3_{F/C}$ are the specific volume capacity of the catalyst (LHSV) in the first, second, and third reactors (m^3 of raw materials/m^3 of catalyst per hour).

It can be assumed that a further increase in the number of hydrotreating reactors to the limit of the number of narrow fractions will lead to a further decrease in the required catalyst load in the reactor unit, but this will most likely be inefficient from an economic standpoint due to an increase in the cost of numerous non-standard equipment. For example, with 16 narrow fractions and their differential hydrogenation in 16 reactors, the reactor loading will vary from 2.3 m^3 in the first reactor to 23.1 m^3 in the sixteenth reactor, totaling 108.5 m^3, which is only 2.8 m^3 less than for three reactors

The three-reactor scheme, compared with the two-reactor scheme, makes it possible to reduce the catalyst loading, depending on the option of forming the medium-wide fraction, from 7 to 13% and bring the reduction in catalyst loading to 50% from the currently used “one-reactor” variant of diesel fuel hydrotreatment (**Figure 13**).

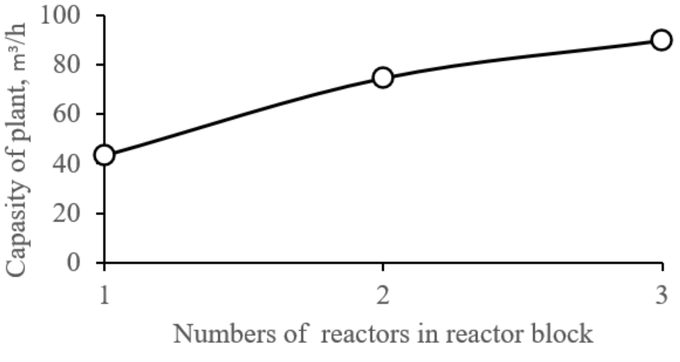


Figure 13. Change in the capacity of the hydrotreating unit when replacing a single-reactor unit with a two- and three-reactor differential hydrotreating scheme for diesel fuel with the same catalyst load of 100 m^3.

It can be assumed that a further increase in the number of hydrotreating reactors to the limit of the number of narrow fractions will lead to a further decrease in the required catalyst load in the reactor unit, but this will most likely be inefficient from an economic standpoint due to an increase in the cost of numerous non-standard equipment. For example, with 16 narrow fractions and their differential hydrogenation in 16 reactors, the reactor loading will vary from 2.3 m^3 in the first reactor to 23.1 m^3 in the sixteenth reactor, totaling 108.5 m^3, which is only 2.8 m^3 less than the global optimum of 111.3 m^3.

A feature of the process scheme of differentiated hydrotreatment is the need for computer control of the process of distribution of wide fractions in reactors with a change in the flow rate and composition of the feedstock.

The principle of differential hydrotreating can also be useful in other multi-reaction chemical processes, where targeted reactions occur simultaneously with a large number of substances that differ significantly in physicochemical properties and reactivity.

3.5. The main regularities of the differential chemical multicomponent process

- The process localizes the flows of raw materials with a significant difference in the reactivity of the reacting components.
- The localized flow has been forming on the basis of a set of narrow fractions with known physicochemical properties.
- A set of reacting components of a narrow fraction has been considered as a pseudo-component (lump) using the third model of a multicomponent reaction system.
- Number of narrow fractions is from 8 to 20.
- Increasing the number of narrow fractions increases the technical efficiency of the process.
- The differential process, all other things being equal, makes it possible to reduce the consumption of the catalyst in comparison with single direct-flow processes.
- The differential process, all other things being equal, makes it possible to increase the amount of processed raw materials in comparison with direct-flow processes.
- The differential process, all other things being equal, makes it possible to increase the depth of transformation of raw materials in comparison with direct-flow processes.
- The differential process, with other things being equal, allows, in a non-optimal operating mode, to increase the amount of processed raw materials and the depth of its purification and reduce the consumption of the catalyst compared to direct-flow processes.
- When the feedstock is split into two wide fractions, the optimality function of the *differential process has a single minimum.
- When dividing the feedstock into three wide fractions, the optimality function of the differential process has many local minima and one global minimum.

3.6. Discussion of contradictions

When analyzing the results of mathematical modeling of the hydrotreating process, the question arises about the acceptability of using the values of the rate constants of hydrogenation reactions of organosulfur impurities k_i according to literature data for modeling the process implemented on other initial data (composition of raw materials, catalyst, etc.). The classical kinetics of simple chemical (especially homogeneous) reactions in modeling allows the calculation of the necessary real reaction duration to achieve the necessary conversion of the starting material or to achieve a maximum or quasi-equilibrium concentration of the final product. Further, the volume of the reactor is calculated from the productivity of the industrial process and the required calculated reaction time. However, when modeling hydrotreating, this transparent methodology is complicated by the introduction of additional conditions and assumptions into the solution.

The modern method of mathematical modeling of the hydrotreating process does not take into account a number of significant factors, due to which the solution of the problems of its modeling of the process as the possibility of an analytical study independent of the experiment encounters a large number of gaps. These gaps, in my opinion, lead to the fact that mathematical modeling is reduced to formalizing a specific experiment, not allowing it to go beyond its boundaries. Such gaps include:

1) The models do not take into account the real flow rate of the hydrogen-containing gas, which is why in the reaction rate equation the transition from the true reaction rate constant k_i to the effective constant $K_{ef,i}$:

$$\frac{dC_{Si}}{d\tau} = k_i C_{Si} C_{H_2} = k_{ef,i} C_{Si} \tag{8}$$

which does not take into account the possible change in the flow rate of hydrogen-containing gas and catalyst activity;

2) Integration of Equation (8) does not calculate the necessary real duration of contact of the reaction mixture with the catalyst, but a certain conditional reaction time;
3) The content of organosulfur impurities is arbitrarily generalized by several pseudo-components.

The listed experimental errors lead to a decrease in the quality of mathematical modeling of hydrotreating; therefore, the process of hydrodesulfurization of organosulfur impurities is most often studied on model solutions for a comparative assessment of the effectiveness of [7,11,17–21,36] or comparison of the catalytic activity of hydrogenated impurities [15,28,37–40]. **Table 6** shows the values of the rate constants for hydrogenation of dibenzothiophene as one of the hardly hydrogenated components of diesel fuel, obtained by a number of researchers, recalculated to a common single dimension of h^{-1}.

Table 6. Comparison of rate constants for hydrogenation of dibenzothiophene at different temperatures and catalysts.

Sample	Catalyst	Reference	Temperature, T, °C	Rate constant, k, h^{-1}	Relating the growth rate of the reaction rate constant to increasing temperature
1	$CoMoS/Al_2O_3$	[38]	300	0.42	$k_{320}/k_{300} = 2.85$ $k_{340}/k_{320} = 2.05$
			320	1.20	
			340	2.46	
2	$CoMo/Al_2O_3$	[15]	340	1.887	$k_{360}/k_{340} = 1.01$ $k_{380}/k_{360} = 1.02$
			360	1.907	
			380	1.936	
3	SupCat	[40]	240	0.03	$k_{250}/k_{240} = 1.63$ $k_{360}/k_{250} = 1.53$
			250	0.049	
			260	0.075	
4	BulkCat	[40]	240	0.059	$k_{250}/k_{240} = 1.10$ $k_{260}/k_{250} = 1.35$
			250	0.065	
			260	0.088	

The materials from four series of laboratory experiments on the hydrogenation of dibenzothiophene (**Table 6**) show that at least one series probably had some violations in the experimental methodology, since there is practically no dependence of the reaction rate constant on temperature. For the rest of the series, this dependence in coordinates Ln(k) = f(1/T) is close to linear (**Figure 14**).

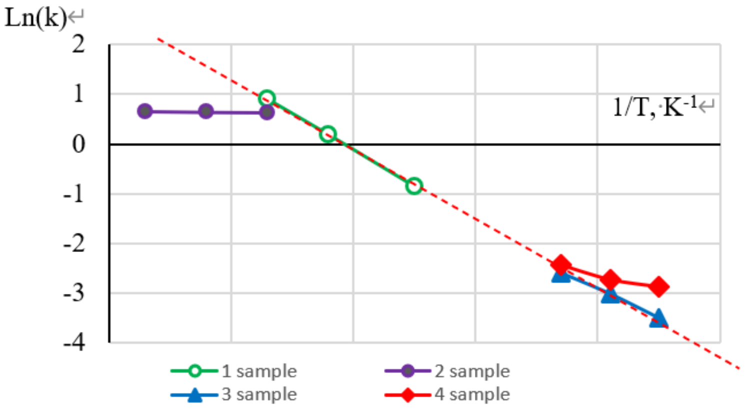


Figure 14. Dependence of the reaction rate constant k on temperature T as Ln(k) = f(1/T). Number of samples in **Table 6**.

It can be confidently assumed that the use of diesel fuel hydrotreating in mathematical modeling based on independent external experimental data on the kinetics of hydrogenation of impurities for process design does not guarantee the reliability of the calculated data. However, in our series of studies [4,29,30, 32,34,35] on the analysis and development of reactor block circuits, provided that the parameters of their operation are identical, the errors of the constants used in the calculations are not significant. If the approximate values of the reaction rate constants in the calculations were replaced with more accurate ones, the numerical values of the catalyst volumes in the reactor units would naturally change slightly, but the ratios between the catalyst loads in different reactor blocks would remain virtually unchanged.

Therefore, the planned detailed study and analysis of hydrotreating fractionation of diesel fuel in two or three reactors would make it possible to recommend these new technologies for industrial use.

It can be argued that the use of diesel fuel hydrotreating in mathematical modeling based on independent external experimental data on the kinetics of hydrogenation of impurities for process design does not guarantee the reliability of the calculated data.

4. Conclusion

In this paper, a comprehensive study of the hydrodesulfurization process of diesel fuel was carried out, during which its specific features were characterized, leading to low technical efficiency of hydrotreating compared with other similar chemical processes. It has been shown mathematically and by simulations that reactor blocks of industrial plants with a sequential or parallel reactor layout scheme are equivalent to a single reactor with the same total catalyst load, and the configuration of the reactor unit is determined only by technical situations.

An analysis of the disadvantages of existing models of diesel fuel composition for hydrogenation of organosulfur impurities led to the development of a new model of such a multicomponent raw material in the form of a series of 10–20 narrow fractions, each of which includes a combination of several organosulfur impurities, considered as a single pseudo-component. This model has a number of advantages over currently used diesel fuel models, which use only two to six pseudo-components. The main advantages of the new model are the ability to characterize the sulfur content in pseudo-components by simple analysis for total sulfur and that the new model finally made it possible to see the distribution of pseudo-components in the structure of the converted stream localized in narrow fractions for any composition of raw materials by organosulfur impurities.

It is substantiated that the possibility of replacing discrete reaction rate constants with a continuous kinetic characteristic is what made it possible to adapt the mathematical model of hydrotreating to real process conditions.

The fundamentally new technology for hydrotreating diesel fuel has been proposed. This technology consists of the preliminary fractionation of raw materials into theoretically valid wide fractions consisting of a set of N narrow fractions with specific N pseudo-components reflecting the actual distribution of sulfur in the feedstock. The resulting wide fractions of diesel fuel are individually hydrogenating in various hydrotreating reactors. After passing through the reactors, the wide fractions combine and stabilize with the formation of commercial diesel fuel. An optimization method has been developing that makes it possible to determine the optimal temperature boundary limits of those wide fractions that minimize the loading of catalyst into the reactor block.

Two new options for configuring the reaction block of the hydrotreating plant were proposed. These plants can provide differentiated hydrotreating of the feedstock, which has been optimally divided into two or three narrow fractions beforehand.

Thanks to this technology, new plants are able to increase their productivity by 1.4–1.50 times or reduce the loading of catalyst into the reactor blocks by 40%–50% under the same technological conditions as in modern industrial diesel fuel hydrotreating.

Institutional review board statement: Not applicable.

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Definitions of variables

A	constant in Equation (3)
C_{i0}	concentration of *i*-th component in raw material, mol./mol.
$C_{i\tau}$	concentration of *i*-th component in reaction mixture, mol./mol.
C_S	concentration of sulfur, mol./mol.
C_{Si}	concentration of *i*-th organosulfur component or pseudo-component, mol./mol.
$\mathrm{C}_{\mathrm{Siend}}$	final concentration of *i*-th pseudo-component, mol. /mol.
G_F	the feed of raw materials, m^3/h
G_{Fi}	consumption of the narrow fraction, mol./h
G_{kat}	loading of the catalyst into the reactors, m^3
K	kinetic characteristic, h^{-1}
k_i	reaction rate constant of the *i*-th organosulfur component or pseudo-component, h^{-}
$k_{(i,ef)}$	effective reaction rate constant, h^{-1}
l	catalyst bed height in the reactor, m
M	constant in Equation (3)
N	number organosulfur pseudo-components,-
R	criterion optimality, m^3
$R1_{F/C}$	the specific volume capacity of the catalyst (LHSV) in the first reactor, m^3 of raw materials /m^3 of catalyst per hour
$R2_{F/C}$	the specific volume capacity of the catalyst (LHSV) in the second reactor, m^3 of raw materials /m^3 of catalyst per hour
$R3_{F/C}$	the specific volume capacity of the catalyst (LHSV) in the third reactor, m^3 of raw materials /m^3 of catalyst per hour
W	flow rate, m/c
X and X+1	the numbers of the last and first narrow fractions between the light and middle wide fractions
Y and Y+1	the numbers of the last and first narrow fractions between the middle and heavy wide fractions
Z and Z+1	the number of the last and first narrow fractions between the light and heavy wide fractions
τ	reaction time, h
τ_{cond}	condition time, h
τ_R	duration of the reaction, h

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