

Research Article

Modeling the Composition of Raw Materials and Multicomponent Reaction Systems Using the Example of Hydrotreating Diesel Fuel

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Abstract

This article analyzes the schemes of reactor blocks of industrial diesel hydrotreating plants. It is shown that all variants of industrial direct-flow hydrotreating reactor plants are equivalent in terms of the required volume of the catalyst. A new model of hydrotreating raw materials is given, which considers raw materials as a complex or set narrow fractions, each of which contains a conditional organosulfur pseudo-component. The concentration of total sulfur in pseudo-components is equal to the sum of the concentrations of the aggregate or lump of organosulfur impurities in total sulfur in the corresponding narrow fraction. Based on this model, the principle of differentiated hydrotreating of diesel fuel and new schemes of reactor blocks of diesel hydrotreating plants were developed. Mathematical modeling and optimization of differential hydrotreatment were performed. The new schemes will reduce the amount of catalyst or increase the performance of hydrotreating plants compared to traditional industrial schemes of hydrotreating plants. The basic laws of differential hydrotreating of diesel fuel were formulated.

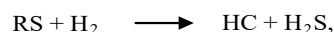
Keywords: Diesel Fuel, Hydrodesulfurization Process, Mathematical Modeling, Diesel Feedstock, Reaction Rate Constants, Industrial Reactor Blocks

1. Introduction

Mathematical modeling of chemical reactors is based on models of kinetics, hydrodynamics, momentum and heat transfer and is well developed for typical reactions of inorganic chemistry and petrochemical synthesis, when the feedstock undergoes transformation during simple or multistage reactions. It is much more difficult to adequately modeling and calculating systems with a complex composition of the feedstock, in which a large number of components are involved in the main and side reactions. Such multicomponent reaction systems include processes occurring in thermal and catalytic refining processes, such as thermal and catalytic cracking, catalytic reforming, pyrolysis, isomerization, oxidation, hydrogenation, coking and hydrogenation of wide oil fractions. Let's consider the problem of mathematical modeling of such systems using the example of hydrotreating diesel fuel. Hydrotreating of diesel fuel refers to the most large-tonnage oil refining processes.

The peculiarity of this process is its implementation in a three-phase system: liquid feed stock, hydrogen-containing gas and bifunctional solid catalysts which ensure hemolytic and heterolytic hydrogenation reactions of numerous organosulfur compounds that significantly complicates the formation of mathematical models of the process [1-

5]. During the initial period of operation of hydrotreating plants, when the quality of diesel fuel was low, an increase in the productivity of the plant was achieved by increasing the loading of the catalyst into the reactor. Since diesel fuel of the required quality in this case was produced by reducing the total sulfur content by only 5-10 times, it did not matter much that different sulfur-containing organic components of raw materials have different hydrogenation rates. It allowed using in calculations a quasi-homogeneous scheme of desulfurization process as a whole by scheme of generalized reaction



where RS, H₂, HC, H₂S are the total organosulfur substance, hydrogen, carbohydrate, and hydrogen sulfide, respectively. In this case, due to the fact that hydrogen is introduced into the hydrotreating process in a large excess (consumption of hydrogen-containing gas 200- 800 m³/m³ of raw materials), the desulfurization reaction could be considered as a pseudo first-order reaction and the kinetics of hydrotreating was described by the equation

$$\frac{dC_{RS}}{d\tau} = -kC_{RS}, \quad (1)$$

where CRS – is the concentration of the generalized aggregate of organosulfur components in the reaction system, τ – the reaction time and k – is the reaction rate constant, which, due to the accepted assumptions, is effective. As requirements to diesel fuel quality were tightened in line with environmental restrictions and the permissible sulfur content decreased from Euro-3 (350 ppm) to Euro-5 (10 ppm), schemes of hydrotreater units were improved, the amount of catalyst in the reactor unit despite the increase in its quality has increased several times, and approaches to mathematical modeling of the hydrotreating process became more complex [6-11]. The process schemes of the interconnection of equipment at the hydrotreatment plants implemented in the industry are very conservative from the standpoint of the hardware design of the reactor unit and usually represent a complex of up to four reactors operating sequentially. The volume of hydrotreating catalysts in the reactor unit is determined by the amount of diesel fuel treated and its purification depth.

The required catalyst loading is proportional to the capacity and increases dramatically (several times) with an increase in the purification depth. The design capacity of hydrotreating plants at the level of two million tons per year is achieved only with shallow treatment with a sulfur content of 350 ppm in purified fuel used for roads and agricultural machinery. For vehicles (mainly cars) according to the Euro-5 standard, the sulfur content is limited to 10 ppm which is achieved by increasing the time of hydrotreatment and, as a result, reducing the capacity of hydrotreatment plants by 3 to 4 times or by construction of additional reactors during the revamping of plants. The degree of activity of sulfur compounds in hydrogenolysis reactions is different and decreases in the series: mercaptans > sulfides > thiophenes > benzothiophenes > dibenzothiophenes. At the same time, the most difficult-to-hydrogenate compounds in the thiophene series are concentrated mainly in heavy fractions boiling above 330 °C [12-15]. While ensuring the required quality of diesel fuel hydrotreatment, the purification process as a whole is precisely limited by the interaction with hydrogen of a relatively small amount of difficult-to-hydrogenate organosulfur, while the easily hydrogenated components have already undergone hydrogenolysis. In this situation, the assessment of the composition of the initial purified diesel fuel, which is necessary for the mathematical modeling of the process [12- 17], is of particular importance.

2. Materials and Methods

2.1 Computational Procedures and Programs

Since in this article the task was to compare the different options of the reactor block formation from the standpoint of saving catalyst costs for the hydrotreating process and not an adequate simulation of the reactor, there was no need to solve it from the point of view of a difficult-to-solve hierarchical model of catalytic hydrotreating (chemistry-granule-layer-apparatus, etc.). In this regard, the operation of the reactor was examined on the basis of the following correct assumptions

- when describing the hydrotreating process, individual sulfur components are not considered, but their

complexes or lumps.

- quasi-homogeneous reaction stream within the reactor.
- constant velocities of local flow jets and hydrodynamic mode of ideal displacement in the reactor.
- isothermicity of the process.
- stationary nature of the process.
- constant activity of the catalyst.
- 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.
- the rate constants of the hydrodesulfurization reactions of the pseudo-components are effective.

Under these assumptions, the mathematical model of a hydrotreating reactor for N pseudocomponents takes the following form of a system of equations:

$$\left. \begin{aligned} \frac{dC_{S1}}{d\tau} &= -k_1 C_{S1} \\ \frac{dC_{S2}}{d\tau} &= -k_2 C_{S2} \\ &\dots \\ \frac{dC_{Si}}{d\tau} &= -k_i C_{Si} \\ &\dots \\ \frac{dC_{SN}}{d\tau} &= -k_N C_{SN} \end{aligned} \right\}, \quad (2)$$

where C_{Si} and k_i are the concentration of the organosulfur pseudo-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; when using formal models of raw materials, concentrations and reaction rate constants were introduced into the model (2) in the form of auxiliary functions. The mathematical model was calculated 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 until a given degree of purification of feedstock was achieved
- the volume of the catalyst in the reactor, ensuring the achievement of the required depth of hydrotreating of raw materials.

The same assumptions were used when comparing different configurations of reaction blocs. It is the specific features of the separation of raw materials into several narrow fractions with analysis of each of them for the content of total sulfur, for example, three (d), and - various homologous

series of organosulfur impurities, for example, disulfides, benzothiophenes and dibenzothiophenes; \blacktriangle , \blacktriangle and \blacktriangle - homologous series, e.g. disulfides, with successively increasing boiling points and decreasing reactivity chemistry in these units that made it possible to quickly compare them in terms of the effectiveness of the hydrotreating process using a fairly simple calculation program. The adequacy of the calculation of the diesel fuel hydrotreating reactor according to the developed program did not depend on the configuration of the reaction unit and was determined only by the quality of the raw material model used and the degree of its proximity to the characteristics of

the real diesel fuel being cleaned.

3. Results and Discussion

3.1 Phenomenological Models of Raw Materials of Diesel Fuel Hydrotreating Plants

Analysis of the literature data has shown that by three types of models can describe the composition of raw materials by organosulfur impurities.

The First Model is the identification of all organosulfur components and their concentrations in raw materials of hydrotreating (Figure 1). A

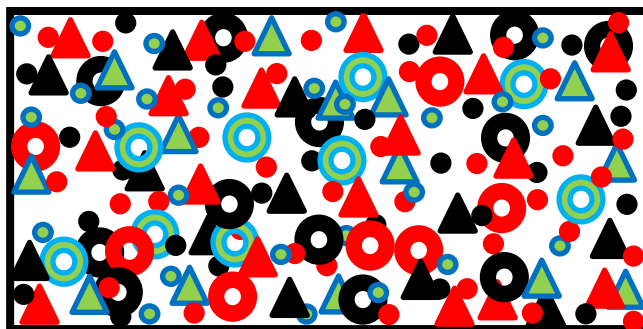


Figure 1: A Model Characterizing Hydrotreating Raw Materials by the Content of Organosulfur Impurities: The Totality of Many Different Components with Specific Concentrations in a Single Raw Material

\bullet , \circ and \circ - various homologous series of organosulfur impurities, for example, disulfides, benzothiophenes and dibenzothiophenes;

\bullet , \blacktriangle and \bigcirc - homologous series, e.g. disulfides, with successively increasing boiling points and decreasing reactivity. The identification of an extremely complete set of organosulfur components in diesel fuel according to the first model of raw materials (Figure 1a) and the development of a database of possible reaction pathways are practically impossible (for example, in the work [18] the mathematical modeling of the process of hydrodesulfurization of a catalytic cracking fluid takes into account 348 components involved in 444 reactions) due to the great scale of the task, high cost of the necessary reagents, the complication of analytical methods, and the need for expensive precision equipment

to define the concentration of dozens hundreds of individual organosulfur impurities to be determined at fractions in ppm [10, 19].

The Second Model (Figure 2), in contrast to the first, is extremely simple in analytical, experimental and computational terms, and allows us to consider only the change in total sulfur (a standard indicator of fuel quality) when modeling hydrotreating. This model has a high parametric sensitivity to the error of determining the value of the reaction rate constant: However, this model, in particular, allows us to compare the efficiency of various configurations of industrial reactor units under the same process conditions.

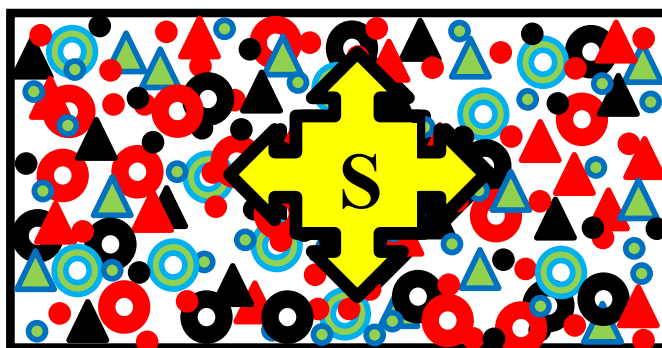


Figure 2: A Model Characterizing the Composition of Hydrotreating Raw Materials by Organosulfur Components as a Generalized Sulfur Content by Analysis for Total Sulfur S. The Symbols of Impurities are Similar to fig.1

The Third Model of the composition of raw materials for organosulfur impurities (Figure 3) is a conditional combination of some organosulfur impurities into a 2-4

pseudo-component or lump. In many cases, a feedstock model was used in the study of the hydrotreating process in which dibenzothiophene was used as the only one

generalizing hydrogenated component instead of a set of organosulfur impurities [20-22]. Most often, researchers consider the grouping of organosulfur impurities of the same homologous series as a certain conditional pseudo-component [23-25], but they do not consider the fact that

homologues with significantly different boiling points also have different reactivities. Both the form of combining impurities into one pseudo-component and the number of pseudo-components used by different researchers are quite contradictory [10-26].

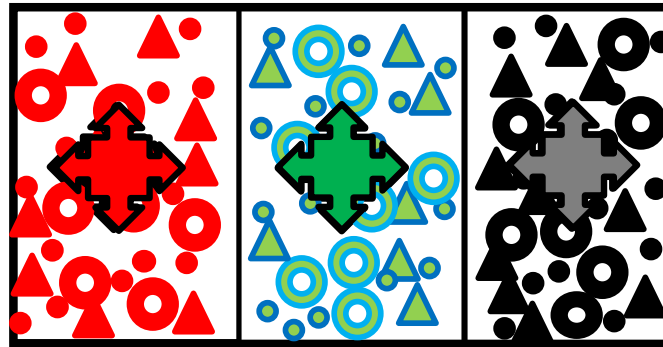


Figure 3: A Model Characterizing the Composition of Hydrotreating Raw Materials by Organosulfur Components as the Combination of Homologues as Pseudo-Components, for Example, Three. The Symbols of Impurities are Similar to fig.1.

The level of adequacy of mathematical modeling for the second and third models of raw materials can be increased if the reaction rate constant is replaced by the kinetic characteristic of the reaction rate constant [27, 28]. When multiple reactions occur simultaneously both in the feed stream and in the pseudo-component, the reactivity of the various components differs significantly from each other. In this regard, at the beginning of the process, with a short contact time, highly active components of raw materials with high reactivity are used. At the end of the process low-active components react slowly, with a low value of the reaction rate constant. To calculate the effective reaction rate constant $k_{i,ef}$ for a particular i -sh component of the reactions system (or pseudo-component), it is necessary to take a sample and determine the concentration of this component in it at the time of contact of the reaction mixture with the catalyst τ and determine the amount of decrease in the concentration of this component compared to the initial $C_{i,0} - C_{i,\tau}$; then

$$k_{i,ef} = \frac{1}{\tau} \ln \left(\frac{C_{i,0}}{C_{i,\tau}} \right) . \quad (3)$$

Regularly, the kinetic characteristic $K(\tau)=f(\tau)$ 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 $K(\tau)=f(\tau)$ 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_{cond} is characteristic of a hyperbolic type function of the form of the effective rate constants

$$K(\tau) = f(\tau_{cond}) = M / (1 + N \tau_{cond}) , \quad (4)$$

where N and M are empirical approximation coefficients of the kinetic characteristic of the experimental data set by values. All three considered models of raw materials are widely used in mathematical modeling of the diesel fuel hydrotreatment process, but they are not applicable to describe the hydrotreatment of raw materials of indeterminate composition. In this regard, we proposed.

The Fourth Model of diesel fuel for organosulphuric impurities (Figure 4) in which we considered the raw material of the hydrotreating process of determinate composition as a set of several narrow fractions, in each of which the aggregate of organosulphuric impurities is considered as a conditional pseudo-component. Its concentration in a narrow fraction can be determined using the simplest and most accessible analysis for the total sulfur content [29]. Thus, the model considers not only the qualitative and quantitative characteristics of pseudo-components, but also the localization of a specific pseudo-component in the raw material flow.

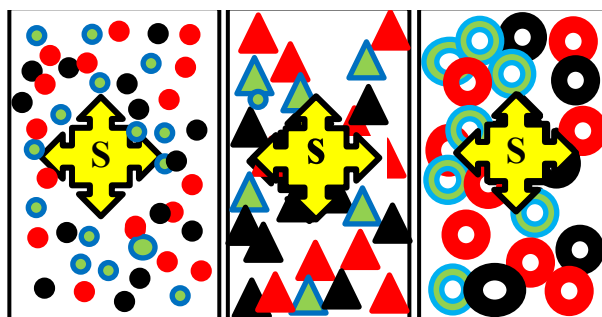


Figure 4: A Model Characterizing the Composition of Hydrotreating Raw Materials by Separation of Raw Materials into Several Narrow Fractions with Analysis of Each of them for the Content of Total Sulfur, for Example, Three. (d). by Organosulfur Components as the Combination of Homologues as Pseudo-Components, for Example, Three. The Symbols of Impurities are Similar to fig.1

Consider the effectiveness and informativeness of the fourth model using the example of the characteristics of raw materials for hydrotreating - the fraction of straight-run

diesel fuel 180-360 oC, represented by 20 narrow fractions (Table 1). The set of organosulfur components in each narrow fraction is considered as one pseudo-component.

Number	Parameters of a narrow fraction				Number	Parameters of a narrow fraction			
	Boiling temperature limits, °C	Rate constant of the hydrodesulfurization, h ⁻¹	Total sulfur concentration, ppm	Mass for raw materials, %		Boiling temperature limits, °C	Rate constant of the hydrodesulfurization, h ⁻¹	Total sulfur concentration, ppm	
1	6	180-190	1000	21	11	5	278-289	12700	11
2	5	190-199	2500	20	12	5	289-298	13700	10
3	4	199-208	4900	19	13	5	298-307	16100	9
4	5	208-218	5300	18	14	5	307-314	17000	8
5	5	218-228	6700	17	15	4	314-320	18100	7
6	5	228-238	7200	16	16	5	320-327	19000	6
7	6	238-249	8500	15	17	6	327-334	20000	5
8	5	249-260	9900	14	18	5	334-342	21200	4
9	5	260-270	10800	13	19	5	342-351	22500	3
10	4	270-278	11000	12	20	5	351-360	24000	2

Table 1. Characteristics of Hydrotreating Raw Materials - Fractions 180-360 °c.

The second and third models, when calculating the hydrotreatment of such raw materials, allow us to calculate only the time change in the concentration of total sulfur or pseudocomponents in the entire flow of the reaction mixture, and according to the fourth model, it is possible to determine the time change in the concentration of the pseudocomponent in each of the 20 local jets forming the flow as a whole (Figure 5). As the concentration of sulfur (pseudocomponent or lump) in heavier narrow fractions increases, the required duration of desulfurization of the narrow fraction increases sharply. up to the level of 10 ppm required for high-quality diesel fuel. With a known amount of substance in the local jet, the concentration of the pseudocomponent in it and the duration of its hydrogenation, it is easy to calculate the amount of catalyst needed to purify both the local jet and the total amount of diesel fuel.

The actual duration of hydrodesulfurization of diesel fuel (2-3 hours) is in good agreement with the calculated data based on the fourth model. It should be noted that with an average sulfur content of 10 ppm in the purified product, the concentration of solid hard-to-hydrogenate components (for example, dibenzthiophenes) is ten times higher than 10ppm (Figure 5). The quality of purified diesel fuel is achieved by diluting heavy narrow fractions with light narrow fractions. In the development of research, a situation was considered when several narrow fractions forming a wide fraction and hydrotreated together, for example 1 and 2, 1-3, 1-4 and so on up to 1-20 narrow fractions with corresponding components (Figure 6). The calculation results showed the presence of potential reserves for the intensification of the hydrotreating process when using the proposed fourth model of the feedstock for the distribution of organosulfur impurities in it.

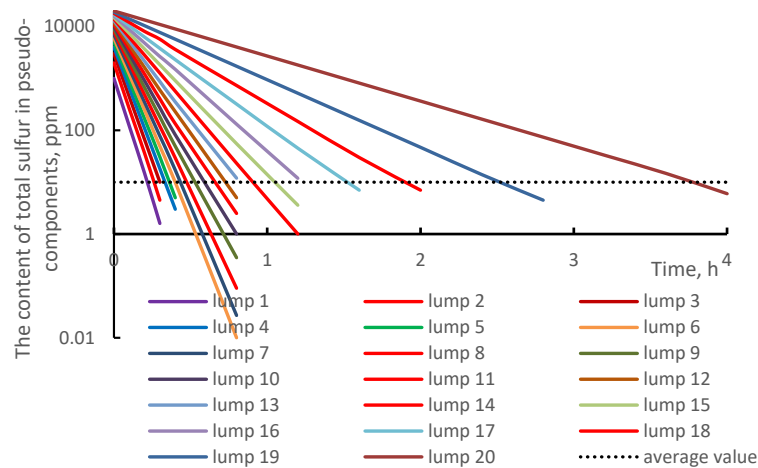


Figure 5: Kinetics of Hydrodesulfurization of 20 Narrow Fractions Containing Pseudocomponents (Lump) of Organosulfur Impurities (The Numbers of the Narrow Fractions in Accordance with Table 1 Coincide with the Numbers of Lumps).

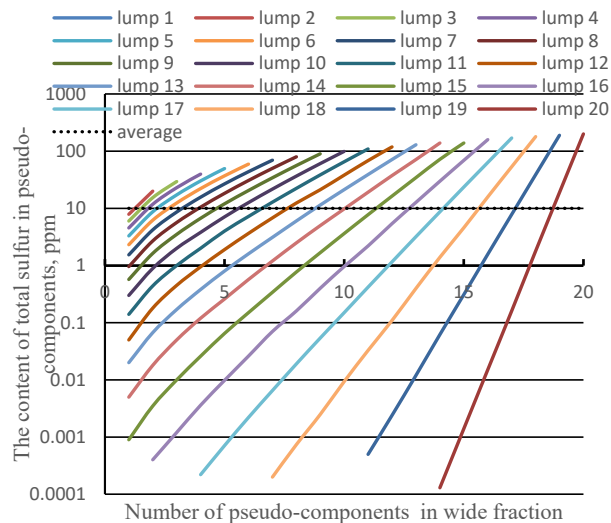


Figure 6: Composition of Hydrolysate by Pseudocomponents Depending on the Number of Light Fractions in its Forming Ranges from the First to the Twentieth (Respectively, Lumps from 1 To 20) at Purification Depth up to 10 ppm (Average - Line 21).

Substantiation of the Principle of Differential Hydrotreating of Diesel Fuel, Considering the Fourth Model of Representation of Raw Materials by the Composition of Organosulfur Impurities

The various hydrotreating units currently in operation are very conservative with respect to structural development hydrotreating units are very conservative in terms of structural development the current hydrotreating units are very conservative with respect to the structural development of process schemes and with any form of reactor unit they are equivalent to a single reactor with equal catalyst loading. The term one-reactorhydrotreatment in this part of the article refers to any typical industrial configuration of a reactor unit when all feedstock goes sequentially through one or more reactors. Only many years ago a patented method [29] of hydrotreating was proposed, in which two types of diesel feedstock are hydrogenated in two reactors in parallel and then go together to the third reactor for additional

hydrogenation. The same authors published an article [30] which showed that when hydrogenating different fractions of feedstock in different reactors at different conditions of hydrogenation, one can get high quality diesel fuel after mixing of these hydrotreated fractions.

However, in both cases, the use of two fractions of different composition did not find further development. The application of the fourth model should make it possible to justify the intensification of the diesel fuel hydrotreating process. The advantages of this approach to carrying out a diesel hydrotreating process can be easily demonstrated by the following example. Assume that diesel fuel in the amount of $G=100$ 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.

- a light (low boiling) fraction in quantity $G=80$ t/h which contains sulfur-organic components easily fully hydrogenated within 1 hour.
- a heavy (high-boiling) fraction of $G=20$ t/h containing organosulfur components which are difficult and slow to react with hydrogen within 3 hours.

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

$$G_{kat} = G_F \cdot \tau_R \quad (5)$$

where G_F – the feed of raw materials, t/h,

τ_R – the duration of the reaction, h.

If all the feedstock was in contact with the catalyst for 3 hours for complete removal of both easily slowly hydrated sulfur-organic components, the required loading of catalyst in the reactor G_{kat} will be equal to 300 tons ($100\text{t/h} \cdot 3\text{h}$) (Figure 7, a). If we carry out the hydrogenation of two fractions of feedstock separately in two reactors, then we can achieve the necessary loading of the catalyst in the first reactor 80 t ($80\text{t/h} \cdot 1\text{h}$) and in the second reactor – 60 t ($20\text{t/h} \cdot 3\text{h}$) (Figure 7, b); that is 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. Thus, in the latter case, it is possible to save 160 tons of expensive catalyst (US \$ 100,000/ton) by the reconstruction of the traditional one-reactor scheme of the reaction unit to a two-reactor scheme with separate hydrotreating of raw materials previously divided into light and heavy fractions. This reduces the investment in the purchase of a catalyst for a hydrotreating plant by \$ 16 million.

A computational analysis of two-reactor hydrotreating scheme of pre-divided model feedstock (Fig. 3), containing four conditional organosulfur components with different rates of hydrogenolysis into light (easily hydrogenated) and heavy (hardly hydrogenated) fractions has been performed. The analysis has shown that arbitrary division of feedstock into two similar broad fractions does not allow to achieve optimally high intensification of hydrotreating process and there is such boundary of division of two fractions at which the hydrotreating process can be realized at minimum catalyst loading in two reactors. For large capacity plants, each broad fraction can be hydrotreated in two or three reactors that work in series. However, in this case there was a necessity to develop a feedstock model allowing computer calculation of this promising problem.

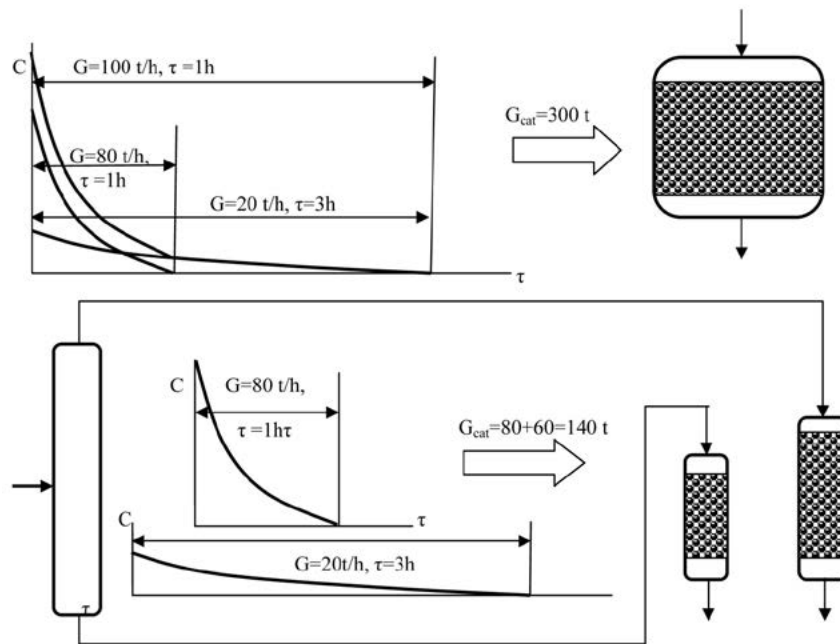


Figure 7: Illustration of the Principle of Separate Hydrogenation of Diesel Fractions.

Development of the fourth model of the composition of diesel fuel raw materials, on the basis of which it was possible to calculate the process of hydrodesulfurization of pseudo-components for any set of fixed narrow fractions (Figures

5,6), allowed to study in detail the features of differential hydrotreating of diesel fuel, previously divided into two wide fractions in the distillation column. The basic technological scheme of such a process is shown in Figure 8.

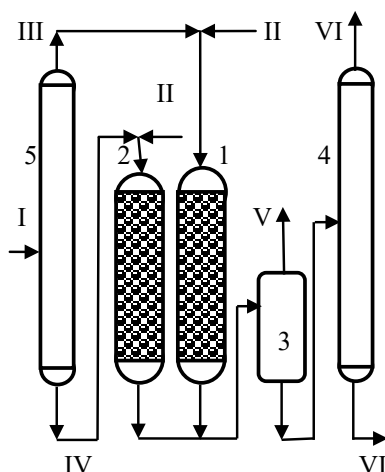


Figure 8: Basic Technological Schemes of Two-Reactor Unit.

Apparatuses: 1 – reactor R-1, 2 - reactor R-2, 3 - separator, 4 - stabilizer, 5 – distillation column. Streams: I – raw materials, II – hydrogen-containing gas (HCG), III– light fraction of raw materials, IV – heavy fraction of raw materials, V – recirculate HCG, VI - hydrocarbon gas, VII-purified diesel fuel. The results of experiments on a pilot plant for the hydrotreatment of the diesel fuel fraction 180-360 °C with a total sulfur content of 16500 ppm [31] were taken as the initial data for mathematical modeling of the separate hydrotreating of diesel fuel and the characteristics of feedstock. The concentration of total sulfur in narrow fractions was calculated by the equation:

$$CS = 5000 + 11500N/16, \quad (5)$$

where CS is the concentration of total sulfur in the narrow fraction, ppm; N is the serial number of the narrow fraction as the boiling point of diesel fuel increases; 16 - the number of narrow 6.25% v/v fractions in diesel fuel. Since the first calculations have already shown that differential hydrotreating is more efficient than the traditional direct-flow process, a number of other distributions of organosulfur impurities in raw materials were also considered in order to verify the universality of the method of separate hydrogenation of wide fractions of raw materials in two reactors. At the same time, both linear and parabolic distributions of total sulfur by pseudo-components, characteristic of diesel fractions of different oils, and pure hypothetical ones, for example, the sinusoidal distribution of sulfur, were considered (Fig. 6).

According to the experimental data given in [31], a range of reaction rate constants within 2-16.3 h⁻¹ was calculated. For narrow fractions with numbers N equal to 1, 2, 3, ..., 15,16, the values of the reaction rate constants k_i were taken as 17, 16, 15, ..., 3, 2 h⁻¹. At the first stage of modeling the process of diesel fuel hydrotreating with separate hydrogenation of two wide fractions, the effect of the boundary of separation of the feedstock on the required amount of catalyst was

considered. Each of the broad fractions was purified from sulfur to the level of 10 parts per million. The consumption of the feedstock is taken to be 100 m³/h, and the volumetric feed rate of the feedstock is 1 h⁻¹. Fractions with numbers 1, 2, ..., M were introduced into the first reactor R-1 sequentially at the fission boundary between the M-th and M+1-th fractions; fractions with numbers M+1, M+2...N were introduced into the second reactor R-2. The boundary fraction M changed its number from 1 to N; thus all 16 possible variants for the distribution of the feedstock between the two reactors were calculated.

At M = N, all feedstock was introduced into the reactor R-1, and at M = 0, all feedstock was introduced into the reactor R-2 - these calculation options corresponded to the operation of the plant with a single reactor or with two parallel reactors or with two reactors operating in series and gave the same results of calculation. Mathematical modeling of the hydrotreating process made it possible to understand the characteristic features of hydrodesulfurization of organosulfur impurities in two reactors. The R-1 reactor is characterized by an obvious increase in the required contact time and catalyst loading associated with the weighting of feedstock in R-1. At the same time, as the number of narrow fractions increases, the sulfur content in the raw materials of the R-1 reactor increases. Similar dependences for the reactor R-2 are opposite, since with an increase in the number of narrow fractions entering into R-1, the mass of the wide fraction entering R-2 decreases, and therefore, the required loading of the catalyst for this reactor decreases (Figure 8). The combined operation of two reactors of the reaction unit at any value of M is ensured when the catalyst loading is less than that required for the operation of a single reactor and equal to 231.7 m³. The minimum catalyst loading for a two-reactor hydrotreater is 134.2 m³ at M = 12 (loading in R-1 is equal to 59.0 m³ at a wide light fraction flow rate of 75 m³/h and that in R-2 is 75.2 m³ at a wide heavy fraction flow rate of 25 m³/h).

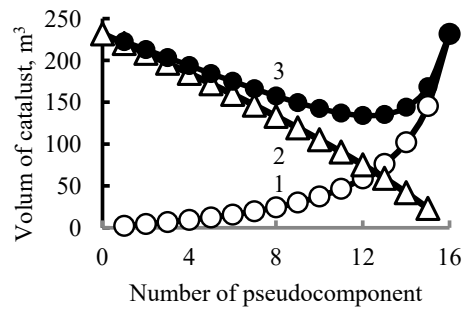


Figure 9: Dependence of the Volume of Catalyst Loaded into the Reactor Block on the Number of Pseudo-Component M at the Boundary of the Division of Raw Materials into Light and Heavy Fractions for Reactors R-1 (Line 1), R-2 (Line 2) and R-1+R-2 (Line 3).

Thus, the calculation results showed that the use of the fourth model of the composition of raw materials based on pseudocomponents of narrow fractions allows the formation of such compositions of light and heavy broad fractions allows reducing the volume of the catalyst for the implementation of the process. This result was achieved by varying the initial data over a wide range.

Optimization of Reactor Blocks of the Hydrotreating Process Based on the Fourth Model of Raw Materials

- The analysis and processing of a large array of calculated data showed that
- the loading of the catalyst into the differential hydrotreating reactor unit is 30-50% less than for traditional installations,
- the greater the range of reaction rate constants for hydrogenated components, the higher the efficiency of differential hydrotreating,
- the required volume of catalyst for differential and traditional hydrotreating installations can coincide only with the same reactivity of all hydrogenated components of raw materials

The minimum of the total loading of the catalyst into the reactor unit is considered as a criterion optimality R of the diesel fuel hydrotreating process and the numerical value of R is calculated by the equation:

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

where Z is the number of narrow fractions in the raw materials of the first reactor forming a light wide fraction; G_{Fi} is the consumption of the i -th narrow fraction, m^3/h ; C_{S0i} is the initial concentration of total sulfur (i -th pseudo-component) in the i -th narrow fraction before hydrotreating, ppmv; C_{Siend} is the final concentration of total sulfur (i -th pseudo-component) in the i -th narrow fraction after hydrotreating, ppmv; k_i is the effective rate constant of the hydrodesulfurization reaction of the i -th pseudo component in the i -th narrow fraction, h^{-1} ; $R1_{F/C}$ and $R2_{F/C}$ are the specific volume capacity of the catalyst (LHSV) in the first and second reactors, respectively, m^3 of raw materials / m^3 of catalyst per hour. Since calculations have shown that the efficiency of hydrotreating is largely negatively affected by the overloading of the reactor R-1 with heavy narrow fractions, and the reactor R-2 with light narrow fractions (Table 4), there is no doubt that it is expedient to combine a part of these fractions into the third stream of the medium wide fraction subjected to hydrotreating in a separate third reactor R-3. This fraction can be obtained in the distillation column of the hydrotreater plant (Figure 10) as a side stream. The reactor R-3 becomes an additional equipment of the unit.

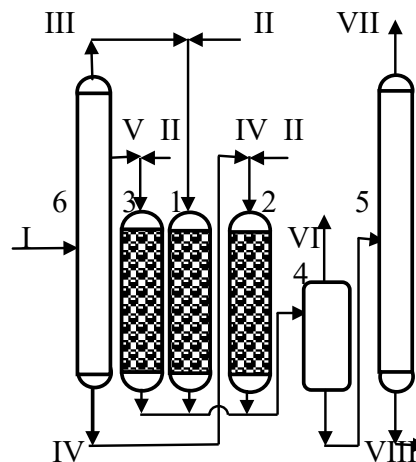


Figure 10: Basic Technological Schemes of Three-Reactor Unit.

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. 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; however, the volume of the total load in all three reactors is characterized by parabolic curve and takes a minimum value, like for a two-reactor scheme. However, if

a two-reactor unit has a single minimum of catalyst loading, many local extrema of the minimum type are formed when calculating a three-reactor unit, and 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.

As an example of mathematical modeling of the hydrotreating process in a three-reactor scheme, Figure 11 shows the distribution of total sulfur concentrations by pseudo-components in reactors and the kinetics of the process as a whole.

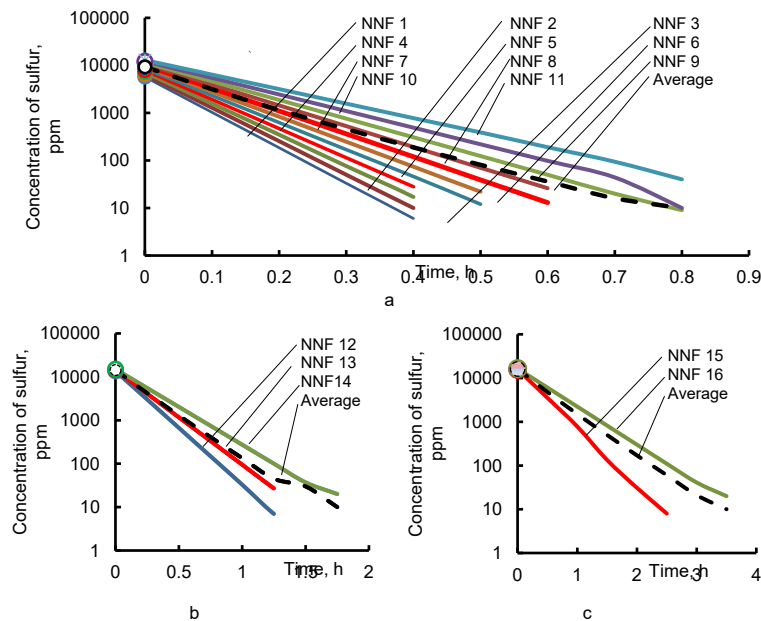


Figure 10. Kinetics of hydrodesulfurization of pseudo-components contained in narrow fractions forming reactor feedstock: R-1 (a), R-3 (b) and R-2 (c) (NNF - number of narrow fraction)

Figure 11: Kinetics of Hydrodesulfurization of Pseudo-Components Contained in Narrow Fractions Forming Reactor Feedstock: R-1 (A), R-3 (B) and R-2 (C) (NNF - Number of Narrow 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 narrow 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. An additional feature of the variability of the problems being solved for optimizing a three-reactor hydrotreatment scheme is the possibility of not only minimizing the catalyst load in a separate variant of the distribution of narrow fractions of diesel fuel over light, medium and heavy wide fractions, but also selecting such a variant of the simulated scheme, so that at a volume sufficiently close to the global minimum for the total loading of the catalyst, the scheme included close in size volumes

of catalyst in all three reactors of the scheme, which makes it possible to develop the designed reactors 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 2). 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 m³ in the first reactor to 23.1 m³ in the sixteenth reactor, totaling 108.5 m³, which is only on 2.8 m³ less that global optimum of 111.3 m³.

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, °C	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, °C	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, °C	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, °C	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

Table 2: Comparison of Characteristics of One-, Two- and Three-Reactor Units of Plants for Differentiated Hydrotreatment of Diesel Fuel.

To calculate the minimum loading of the catalyst into the three-reactor unit, the equation of the function optimality (6) is converted to the form

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

where X and Y are the numbers of the last narrow fractions that make up the light and medium wide fractions, respectively, and R3F/C is the specific volume capacity of the catalyst in the third reactor. It can be assumed that a further increase in the number of hydrotreating reactors will lead to a further decrease in the required catalyst load in the reactor block, but this will most likely be inefficient from an economic standpoint due to an increase in the cost of numerous non-standard equipments. For example, with 16 narrow fractions and their separate hydrogenation in 16 reactors, the reactor loading will vary from 2.3 m³ in the first reactor to 23.1 m³ in the sixteenth reactor, totaling 108.5 m³, which is only 2.8 m³ achieved global optimum of 111.3 m³ ...

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 a reduction in catalyst loading to 50% from the currently used 'one-reactor' variant of diesel fuel hydrotreatment. 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. Variants of two- and three-reactor schemes of

reaction blocks for hydrotreating diesel fuel, formed on the basis of the fourth model of the composition of raw materials for hydrogenated impurities based on the analysis of narrow fractions of total sulfur, are protected by patents [32, 33]. The principle of differential hydrotreating can also be useful in other polyreaction chemical processes, where targeted reactions occur simultaneously with a large number of substances that differ significantly in physicochemical properties and reactivity.

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 is formed on the basis of a set of narrow fractions with known physicochemical properties.
- A set of reacting components of a narrow fraction is considered as a pseudo-component (lump) using the fourth model of a multicomponent reaction system. 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 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, the depth of its purification and reduce the consumption of the catalyst compared to direct-flow processes.
- When dividing the feedstock 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.

4. Conclusion

It has been shown by mathematical modeling that the reactor units of industrial diesel fuel hydrotreatment units are equivalent to a single reactor, on the basis of which series or parallel reactor schemes with the same total catalyst load are formed. The development of a new model of hydrotreating raw materials makes it possible to simulate the kinetics of hydrodesulfurization of pseudocomponents not only in all raw material flow, but also in the streams of narrow fractions of the raw material. It has been substantiated that in case of differentiated hydrotreatment, when the feedstock is pre-fractionated into two or three wide, separately hydrogenated narrow fractions, it is possible to reduce the loading of an expensive catalyst by 40-50% as compared to traditional schemes of reactor units of industrial hydrotreatment plants.

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