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

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Abstract

In this article, I want to introduce new methods for calculating the hydrodesulfurization process of diesel fuel.

Mathematical models for the interpretation of the feed stock and reaction rate constants for multicomponent systems are considered. Taking into account these models, the operation of industrial reactor blocks of hydrotreatment units is analyzed and new options for their prospective implementation are presented. It has been shown that these options will make it possible to reduce the amount of catalyst in the reactors.

Keywords

Diesel fuel, hydrodesulfurization process, mathematical modeling, diesel feed stock, reaction rate constants, industrial reactor blocks.

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 feed stock, hydrogen-containing gas and bifunctional solid catalysts that provide hemolytic 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 flowsheets 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 is limited to 10 ppm, which is achieved by increasing the contact time of the feed stock with the catalyst in the hydrotreating reactors.

The degree of activity of sulfur compounds in hydrogenolysis reactions is different and decreases in the following order: mercaptans > 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 [6–9]. It is characteristic that the quality and depth of diesel fuel hydrotreatment, the cleaning process as a whole, is determined by the interaction with hydrogen of a relatively small amount of

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hardly hydrogenated organic sulfur impurities, while easily hydrogenated components have already undergone hydrogenolysis. In this situation, the assessment of the composition of the initial purified diesel fuel by hydrogenated components, which is necessary for mathematical modeling of the process, is of particular importance [6, 7, 10, 11]. The large number of these components, their different nature and reactivity complicate adequate mathematical modeling and calculation of the reaction blocks of hydrotreatment units.

2. Computational procedures and programs

Since in this work we had solved the problem of comparing different variants of hydrotreatment reactor blocs 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 operation of the reactor was studied 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 $\tau;$

• the content of total organosulfur in the feed stock 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, when analyzing the process by N organosulfur pseudo-components, takes the following form of a system of equations:

$$\frac{dC_{S1}}{d\tau} = -k_1 C_{S1N} \\
\frac{dC_{S2}}{d\tau} = -k_2 C_{S2} \\
\vdots \\
\frac{dC_{Si}}{d\tau} = -k_i C_{Si} \\
\vdots \\
\frac{dC_{SN}}{d\tau} = -k_N C_{SN}$$
(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 feed stock and the effective rate constants of the hydrodesulfurization reactions were taken from independent literature sources.

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 pseudocomponents during the process, the residence time of the reaction mixture in the reactor until a given degree of purification of feed stock was achieved, and the required volume of catalyst in the reactor. The same assumptions were used when comparing different configurations of reaction units. It is the specific features of the hydrodesulfurization 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 instead of complex programs that fully take into account the system of hierarchical modeling of the catalytic process from the catalyst grain to the reactor taking into account its placement in the reaction unit scheme.

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 is practically impossible due to the scale of the task, the high cost of the necessary reagents, the complexity of analysis methods, the need to use expensive precision equipment to determine the concentration of individual organosulfur impurities in fractions in ppm [12, 13]. Instead, the total sulfur content of the feed stock is often used in calculations as characterize the raw materials. In many cases, in the experimental study of the hydrotreatment process, there was used a feed stock model, in which dibenzothiophene was presented as the only generalizing hydrogenated component instead of a set of organosulfur impurities [14–17] (figure 1b).

Most often, researchers consider the grouping of organosulfur impurities of the same homologous series as a kind of conditional pseudo-component (figure 1c) or twolump, three-lump, four-lump kinetic model which includes corresponding groups of higher, high, low and lower reactivity portions of feed stock [18-20], but they do 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 feed stock is also very laborious.

In this regard, we propose to consider the feed stock of the hydrotreatment 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 the narrow fraction is determined using the simplest and most accessible analysis for total sulfur [21], which makes it possible to significantly simplify the constructed mathematical models for a comparative analysis of various hydrotreatment schemes. Subsequent studies have shown that it is most expedient to divide the raw material into 16 or 8 equal narrow fractions.



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 — combination of homologues as pseudo-components, 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

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 monoreactions. If one component enters into the reaction, then according to the law of action of the masses, at any time of contact of the reaction mixture with the catalyst, the calculated value of the effective reaction rate constant is constant. With the simultaneous course of many reactions, the reactivity of various components differs 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-active components react slowly, with a low value of the reaction rate constant.

To calculate the effective reaction rate constant $k_{i,ef}$ $k_{i,ef}$ for a particular i^{sh} component of the reaction 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 to the initial $C_{i,o} - C_{i,\tau}$; then

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

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, the performed processing of data [22] on the study of the diesel fuel hydrotreating process at the pilot plant (fraction 160–360 °C, total sulfur content 1.17%), as well as two fractions that make up this raw material (light fraction 160-360 °C, total sulfur content 0.92% and heavy fraction 300–360 °C, total sulfur content 1.47%), on a co-catalyst showed (table 1) that for all three fractions, the numerical values of the effective reaction rate constants k_{ef} decrease 4-5 times with an increase in the duration of the hydrotreating process, expressed in conditional hours (τ , h).

Thus, the analysis of the chemistry of hydrotreatment indicates that the hydrotreatment process as a whole with the integral method for determining sulfur should be characterized 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 be used to describe other multi-reaction systems, the patterns of which are determined as a result of the analysis of the group composition.

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 is a characteristic of a hyperbolic type function of the form

$$k(\tau) = f(\tau) = M/(1 + N\tau),$$
 (3)

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

160-300°C, 160-360°C and 300-360°C								
	Tem-	Fraction 1	60–300 °C	Fraction 1	60–360 °C	Fraction 3	00–360 °C	
τ, h	pera- ture, °C	C, %	$k_{ef}, h^{\text{-}1}$	C, %	$k_{ef}, h^{\text{-}1}$	C, %	$k_{ef}, \ h^{\text{-}1}$	
	340	0.020	3.8	0.15	2.1	0.19	2.0	
1	350	0.017	4.0	0.13	2.2	0.16	2.2	
	360	0.015	4.1	0.11	2.4	Fraction 30 C, % 0.19 0.16 0.14 0.35 0.29 0.25 0.46 0.41 0.37 0.62 0.55 0.5 - - - - - - - - - - - - -	2.4	
	340	0.035	6.5	0.18	3.7	0.35	2.9	
0.50	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	
	340	0.050	8.7	0.22	5.0	0.46	3.5	
0.33	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	
	340	0.068	10.4	0.25	6.2	0.62	3.5	
0.25	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	
	340	0.080	12.2	0.28	7.2	-	_	
0.20	350	0.071	12.8	0.25	7.7	-	_	
	360	0.060	13.7	0.22	8.4	-	_	
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	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		_	
	340	0.110	14.9	_	_	_	_	
0.14	350	0.097	15.7	_	_	_	_	
	360	0.090	16.3	_	_	_	_	

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

Let us consider mathematical modelling of the diesel hydrotreating process using the concept of 'kinetic characteristic' and expressing the composition of feed stock by sulphur-organic impurities as the total sulphur content C_S . For a steady-state process, the simplest mathematical model of a hydrotreating reactor, assuming quasihomogeneous reaction and ideal displacement mode for the flow, is expressed as

$$\frac{dC_S}{d\tau_{cond}} = -\frac{M}{1+N\tau_{cond}}C_S - W\frac{dC_S}{dl} - 0, \qquad (3)$$

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

The advantages of using kinetic characteristics over the application of the only ones natural values of reaction rate constants in mathematical modelling of hydrotreating kinetics of fractions 160–360 °C are clearly illustrated in figure 2.

When calculating the kinetic curves for complex multicomponent reaction systems on the basis of effective rate constants, the calculated concentration of the reactant in the reaction mixture corresponds to reality only in the vicinity of a kinetic time point, in which the effective rate constant of the process k_{ef} was determined earlier (for example, the black points, which belong to curves 1-5 in figure 2), whereas the group of white points, which belong to the kinetic response (curve 6 in figure 2) covers the entire hydrotreating process and equation (4) is more informative than just a set of reaction rate constants.



Figure 2 — The change in the total sulfur con-

tent 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 time ω 0.2 h (1), 0.25 h (2), 0.33 h (3), 0.5 h (4), 1.0 h (5), and with kinetic characteristic (curve (6) and O).

 \bullet — experimental data on [22]

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 determination of the k_{eff} , respectively, for three positions of the τ . At the same time, it is recommended to work in the area of sufficiently large values of $\boldsymbol{\tau}$ τ_{cond} , although this significantly complicates the experiment. So, when only $5-10 \text{ cm}^3$ of the catalyst is loaded into the microreactor it is difficult to ensure the supply of reagents (raw material and hydrogen-containing gas) in micro quantities (for example, with a volume ratio of raw materials/catalyst equal to 0.5 h^{-1} and a reaction time of 2 hours, it is necessary to ensure the consumption of diesel fuel $2.5-5 \text{ cm}^3$ per hour in the reactor while guaranteeing the stationarity 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.



Figure 3 — Concepts for reactor units of the process of hydrotreating of diesel fuel: a — single-reactor system; b — block double-reactor with parallel the supply of raw materials; c — double-reactor unit with a consistent supply of raw material.

Concentra-	Final concen-		<u> </u>	, . ,	The volume of the catalyst			
tion of sulfur	tration of sul-	Duration of reaction, h			in the system, m^3			
in feed stock, ppm	fur in purified fuel, ppm	a	b	с	a	b	с	
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	

Table 2 — Results of mathematical modeling of various reaction units of diesel fuel hydrotreating plants for different systems (figure 3, a, b, c)

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

The variety of types of layout for the reactor unit of hydrotreating plants (figure 3) requires their comparison from the standpoint of minimizing the loading of the catalyst to obtain highquality 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.

To compare different hydrotreating reactor systems (figure 3), mathematical modeling of the hydrodesulfurization process of $250 \text{ m}^3/\text{h}$ of diesel fuel with a sulfur content of 6000 ppm, the volumetric feed rate of feedstock 2 h^{-1} and the accepted effective rate constant of the hydrodesulfurization reaction 2 h^{-1} was performed [12]. The efficiency of the reaction system in ensuring the final concentration of sulfur in purified diesel fuel from 500 to 10 ppm was estimated by the total volume of the catalyst in the industrial reaction systems. 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 t 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.

3.4. Development of perspective schemes of the reactor blocs of the diesel fuel hydrotreating unit

The representation of the model of hydrotreating raw materials 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 its parts separately [24].

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) a light (low boiling) fraction in quantity G = 80 t/h which contains sulfur-organic components easily fully hydrogenated within 1 hour;

b) 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 $G_{\rm kat}$ can be calculated as

$$G_{kat} = G_F \cdot \tau_R, \qquad (3)$$

where GF — 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 and slowly hydrated sulfur-organic components, the required loading of catalyst in the reactor G_{kat} will be equal to 300 tons (100 t/h, 3 h) (figure 2a). If we carry out the hydrogenation of two fractions of feed stock separately in two reactors, then we can achieve the necessary loading of the catalyst in the first reactor 80 t (80 t/h, \cdot 1 h) and in the second reactor — 60 t (20 t/h \cdot 3 h) (figure 2b); 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.

In mathematical modeling of hydrotreating process of diesel fuel pre-fractionated into light and heavy broad fractions in separate reactors, calculation of hydrodesulphurization of several variants of model fuel as feedstock was performed. In each variant of calculation, the distribution of sulfur-organic components in each broad fraction at the time of chemical process with achievement of concentration of total sulfur at the outlet of corresponding reactor being 10 ppm and necessary volume of catalyst in each reactor and as a whole in both reactors were determined. The feed stock (fraction 180–360 °C) was divided into 16, 8 or 4 narrow fractions, from which wide fractions were formed. Eight variants of various (linear, non-linear and extreme) non-distribution functions of sulfur over narrow fractions were considered (figure 5).







Figure 5 — Options distribution of total sulfur by hydrotreating raw materials (1–8 is the number of the raw material variant according to table 3)

Calculations showed (table 3) 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 one. An increase in the number of narrow fractions increases the level of calculation accuracy. Thus, there is such boundary of division of two fractions at which the hydrotreating process can be realized at minimum catalyst loading in two reactors.

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 (figure 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 6) as a side stream. The reactor R-3 becomes additional equipment of the unit.



Figure 6 — Basic technological schemes of reactor units: a — two-reactor; b — three-reactor.
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

narrow seudo- in raw als	of nar- s by re- R-2	The total volume of the loaded catalyst in two reactors, m3, with op- tions for the distribution of total sulfur in the feedstock according to fig- ure 5							
Number of fractions (p components) materia	Distribution row fraction actor R-1 and	1	2	3	4	5	6	7	8
	1/216	252.4	247.0	375.8	184.6	331.8	332.0	514.0	434.6
	1, 2/316	239.9	239.8	358.6	181.4	318.8	319.0	488.8	414.6
	13/416	227.3	232.4	343.2	177.8	305.6	305.8	463.0	394.0
	14/516	214.7	224.6	324.4	174.2	292.2	292.2	437.2	373.0
	15/616	202.0	216.6	310.6	170.4	278.8	278.6	411.2	351.8
16	16/716	189.4	208.4	289.4	166.6	265.4	265.0	385.2	330.2
	17/816	176.9	200.2	278.6	162.8	252.2	251.4	359.6	308.8
16	18/916	164.6	192.0	254.6	159.2	239.2	238.0	334.2	287.4
	19/1016	152.8	184.0	249.0	156.0	226.8	225.0	309.8	266.4
	110/1116	141.5	176.4	221.4	153.6	215.2	212.8	286.6	246.6
	111/1216	131.5	170.0	226.0	152.4^{*}	205.2	202.0	265.8	228.6
	112/1316	123.5	165.0	194.6	153.2	198.0	193.8	249.4	214.0
	113/1416	119.4	163.2	224.0	157.8	195.8	190.0	240.8	206.0
	114/15,16	123.5	168.0	192.4	16.0	203.4	196.0	249.4	212.2
	115/16	149.5	188.0	316.4	192.6	234.8	225.6	302.4	256.0
	1/28	268.9	335.6	535.6	332.2	413.0	402.4	545.8	470.2
	1, 2/38	239.9	307.6	477.8	304.2	373.8	364.8	487.2	421.8
	13/48	211.1	279.0	420.4	276.2	334.8	326.6	428.2	372.4
8	14/58	182.9	250.6	364.4	249.0	296.6	289.4	370.4	323.0
	15/68	156.7	224.0	312.2	224.4	261.8	254.8	316.6	276.2
	16/78	136.5	203.8	272.0	207.4	235.8	228.4	275.2	239.4
	17/8	137.1	205.8	273.0	215.0	240.0	230.6	276.0	238.4
	1/24	263.7	399.0	525.2	414.8	459.6	443.4	533.8	466.4
4	1, 2/34	199.9	314.8	398.4	325.6	356.8	344.8	404.0	355.8
	13/4	148.8	247.0	375.8	184.6	331.8	332.0	514.0	434.6
* The positions of the minimum loading of the catalyst are highlighted in bold; calculations of the									

Table 3 — Summary data on the dependence of the total volume of the loaded catalyst intwo reactors for different variants of the distribution of total sulfur in the feedstock



Figure 7 — Kinetics of hydrodesulfurization of pseudo-components contained in narrow fractions forming reactor feedstock: a — R–1; b — R–3; c — R-2 (NNF — number of narrow fraction, average sulfur content in a wide fraction)

The kinetics of one of the variants of hydrodesulfurization of 16 pseudo-components of the feedstock of the process divided into three broad fractions is shown in figure 7.

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.

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 5), while the calculated volume of the total load in all three reactors also has a minimum (figure 6), like for a two-reactor scheme. However, if a tworeactor 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.

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 4).

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.

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. 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.

Conclusion

It is proposed to consider the feedstock of the hydrotreating process as a set of several narrow fractions, in each of which the aggregate of organosulfur impurities is considered as a conditional pseudo-component. Its concentration in a narrow fraction is determined using the simplest and most accessible analysis for total sulfur. It is recommended to present hydrotreating raw materials in the form of 16 or 8 identical narrow fractions, and, accordingly, organosulfur impurities — as 16 or 8 pseudo-components.

A chemical process involving a large number of simultaneous reactions, and, accordingly, many components or pseudo-components with varying degrees of activity (for example, hydrotreating diesel fuel) is more convenient and more accurate to calculate not by reaction rate constants, but on the basis of kinetic characteristics.

The kinetic characteristic is formed as a continuously changing set of reaction rate constants, which gradually decrease during the time when the reaction mixture moves through the catalyst layer in the reactor. The maximum value of the kinetic characteristic of the process $K(\tau)$ corresponds to the value of the rate constant of the hydrodesulfurization reaction of the most easily hydrogenated organosulfur component of the raw material. The minimum value $K(\tau)$ corresponds to the value of the rate constant of the most difficult-to-hydrogenate organosulfur component of the most difficult-to-hydrogenate organosulfur component of the most difficult-to-hydrogenate organosulfur component of feed.

Changesteristing of reactor writ	Reactors						
Characteristics of reactor unit	R-1	R-3	R-2				
One-reactor unit $(R = 231.7 m^3)$							
Distribution of pseudo-components	1 10						
Feedstock consumption, m ³ /h	110						
Duration of contact of feedstock with cata-	100						
lyst, h	2.31						
Catalyst volume in reactor, m ³	231.7						
Optimal two-reactor	or unit $(R = 134.2)$	2 m^3)					
Temperature limits of boiling of wide frac-							
tions, °C	180 - 315		315 - 360				
Distribution of pseudo-components	112		1316				
Feedstock consumption, m ³ /h	75		25				
Duration of contact of feedstock with cata-	0.78		3.00				
lyst, h	59.0		75.2				
Catalyst volume in reactor, m ³							
Three-re	eactor unit						
(option $1 - $ local op	otimum; $R = 123$	$3.9\mathrm{m}^3$					
Temperature limits of boiling of wide frac-							
tions, °C	180 - 270	270 - 315	315 - 360				
Distribution of pseudo-components	18	912	1316				
Feedstock consumption, m ³ /h	50	25	25				
Duration of contact of feedstock with cata-	0.49	0.97	3.00				
lyst, h	24.4	24.3	75.2				
Catalyst volume in reactor, m ³							
Three-re	eactor unit						
(option 2 — local op	otimum; $R = 119$	$0.4 { m m}^3$)					
Temperature limits of boiling of wide frac-							
tions, °C	180 - 303.7	303.7 - 348.7	348.7 - 360				
Distribution of pseudo-components	111	1215	16				
Feedstock consumption, m ³ /h	68.75	25	6.25				
Duration of contact of feedstock with cata-	0.68	2.00	3.70				
lyst, h	46.6	23.1	49.7				
Catalyst volume in reactor, m ³							
Optimal three-reactor unit							
(option 3 — global optimum; $R = 111.3 m^3$)							
Temperature limits of boiling of wide frac-							
tions, °C	180 - 292.5	292.5 - 337.5	337.5 - 360				
Distribution of pseudo-components	110	1114	1516				
Feedstock consumption, m ³ /h	62.5	25	12.5				
Duration of contact of feedstock with cata-	0.60	1.48	3.35				
lyst, h	37.4	41.9	32.0				
Catalyst volume in reactor, m ³							

Table 4 — Comparison of characteristics of one-, two- and three-reactor units of plants for differentiated hydrotreatment of diesel fuel

It has been shown by mathematical modeling that the reactor blocks 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. Analysis of a number of options for the hardware design of the reactor blocks of the diesel hydrotreating process showed that the only way to intensify the process is a system of two or three separately operating reactors with loading of light, middle or heavy fractions of pre-fractionated raw diesel fuel. Such a system provides the desired performance and quality of diesel fuel purification from organosulfur impurities at a lower load of catalyst, while accounting for 70 to 40% compared to other traditional options. While maintaining the loading of the catalyst into the reactors, this scheme allows for a 1.5-2-fold increase the productivity of the hydrotreating plant.

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Математическое моделирование процесса гидроочистки дизельного топлива от сероорганических примесей

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Аннотация

В статье представлены новые методы расчета процесса гидрообессеривания дизельного топлива.

Рассмотрены математические модели для интерпретации константы скорости исходного сырья и реакций многокомпонентных систем. С учетом этих моделей проанализирована работа промышленных реакторных блоков установок гидроочистки и представлены новые варианты их перспективной реализации. Показано, что эти варианты позволят уменьшить количество катализатора в реакторах.

Ключевые слова

Дизельное топливо, процесс гидрообессеривания, математическое моделирование, дизельное сырье, константы скорости реакций, блоки промышленных реакторов.

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