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CHARACTERIZATION OF MONITORING DATA OF A DIESEL HYDRODESULFURIZATION REACTOR WITH LANGMUIR-HINSHELWOOD MODEL: PART 1- REACTOR MODELLING

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Hydrodesulphurization is a catalytic process that uses H_2 to stabilize petroleum products by hydrogenating unsaturated hydrocarbon and hydrogenating and deeply removing sulfur and nitrogen contaminants. Usually the compounds with sulfur, the compounds with nitrogen, the alkenes and respectively the aromatics, which are hydrogenated, are considered to have a unique representation. The using conditions of a LH kinetic model for an industrial reactor are carefully analyzed. Simulation of the mathematical model for industrial reactor conditions showed that the results are consistent with the current operation of the reactor. A two-level factorial design with temperature, diesel flow rate and gas phase flow rate is used to show how these factors influence the concentration of sulfur compounds in the product. The second part of paper use a large volume of monitoring data, which highlights the influence of factors on the hydrodesulfurization process on the performance of a fixed catalyst bed reactor. These data are exploited so that they can allow the identification of those parameters of an LH model that give specificity to the process used catalyst and to the reactor operating conditions.

Keywords: Diesel hydrodesulfurization, LH kinetic model, Reactor mathematical model, Model parameters, Reactor monitoring, Data valorization

1. Introduction

Beginning with the 1990s, hydrodesulfurization was transformed, due to environmental conditions, to advanced hydrodesulfurization having the basic goal in reducing the sulphur compounds content of fuels at the pump to extremely low values (below 10 ppm according to the latest USA and EU regulations [1- 3]). It is known that hydrodesulphurization is a catalytic process where are hydrogenated

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unsaturated hydrocarbon and hydrogenated and deeply removed sulfur and nitrogen contaminants.

Generally, and specifically with diesel hydrodesulfurization, the reactive processes kinetics studies are determinant in their scale up, beginning with conceptual design and laboratory research and continuing with pilot plant study, with commercial reactor and plant design and with process improvements and optimization of operating conditions [4,5]. In our concrete case it is expected that the effects of reactor operating variables such as temperature, pressure, phases residence time, and gas/oil ratio on a catalyst's hydrotreating performance can be predicted by an adequate kinetic expression or model [6,7]. In this sense kinetic studies can be approached in two ways: apparently respectively intrinsically.

The apparent kinetics investigation way (method) considers the catalytic hydrogenation process through global reactions, for which formal kinetic relations are applied. Thus, the general reaction (1), considered to proceed with excess of hydrogen, where A is the sulfur, nitrogen, aromatic and alkene compounds lead, when $k_d >> k_s$, to the kinetic model (1), known as the power law (PL) hydrodesulfurization model.

$$A + nH_2 \underset{\underset{k_s}{\rightarrow}}{\overset{\overset{k_d}{\rightarrow}}{-}} H_{2_{n/2}} AH_{2_{n/2}} \xrightarrow[rapid]{} \mathrm{Pr}oducts \qquad (1) \qquad v_{rA} = -\frac{dc_A}{d\tau} = k_r c_A^n \qquad (2)$$

The intrinsic kinetics investigation way (method) considers the catalytic hydrogenation process by evolution of the elementary kinetic processes, which express a verified, or proposed, mechanism for global reaction (reactions). The result is a class of detailed kinetic models, to which the Langmuir-Hinshelwood (LH) model(s) also belong [8,9].

The present work focuses on: i) the expression of the reaction rate for the hydrogenation of a sulfur compound by a LH kinetic model , ii) the specification of the reactions rate expressions for the hydrogenation of all species accompanying the desulfurization of diesel fuel, iii) the coupling of the hydrogenation rate expressions through the plug flow reactor model, iv) the presentation of a set of monitoring data from an industrial hydrodesulfurization reactor and their processing so that they are interpretable by the reactor stability model (second part of paper).

2. Reaction mechanism and LH kinetic model

In development of an LH kinetic for desulfurization, the catalyst must be taken into account due to the fact that it is a determining part of the reaction mechanism. Hydrotreating catalysts are synthesized in oxide form and must be activated by turning them into sulphide form through a complex sulfidation process [10]. The active phase for the hydrotreating catalyst is believed to be CoMoS or NiMoS where Co and Ni are promoters, which take place of some Mo in MoS_2

structure [11]. For promoted or non-promoted catalyst, the basic part is MoS_2 phase, which consists of layers of Mo alternating with S layers in an overall structure near to hexagonal close packed. If it considers one catalyst site having MoS_2 structure, then the thiophen hydrogenation mechanism can be assumed [12, 13] as in figure 1.

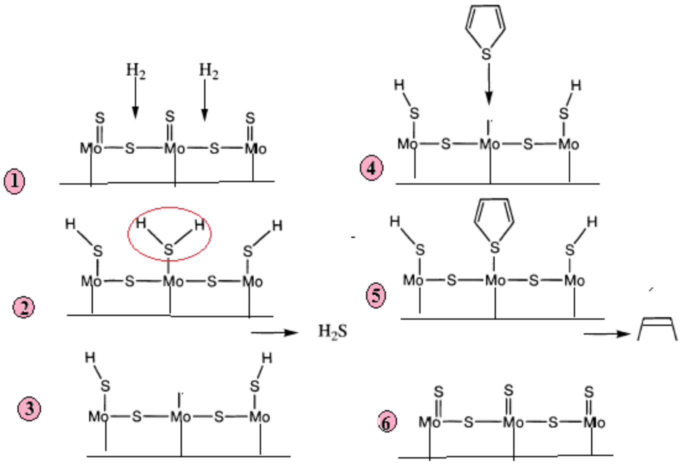

Fig. 1. Mechanism of Thiophen hydrogenation on an active site of sulfide form of MoO_3/Al_2O_3 catalyst

We identify as elementary processes of reaction mechanism: a) hydrogen acquisition by the reactive sulfur of the site (1,2), b) development of vacancy position at Mo by removing H_2S (2,3), c) fixing the thiophene at the Mo vacant position (4,5), d) rebuilding of site structure by bringing sulfur to Mo and releasing butene (5,6). By using the notation A for hydrogen, S_c for species characterizing the catalyst active site, B for hydrogen sulfide, S_{c1} for species of active site with Mo vacancy, C for thiophene and D for butene, it can write the following elementary chemical reactions, which are given by relations (3) – (6).

$$A+S_c \underset{\underset{\leftarrow}{k_{-1}}}{\overset{\overset{k_1}{\rightarrow}}{-}} AS_c \qquad (3) \qquad AS_c \underset{\underset{\leftarrow}{k_{-2}}}{\overset{\overset{k_2}{\rightarrow}}{-}} AS_{c1}+B \qquad (4)$$

$$AS_{C1}+C \underset{\underset{\leftarrow}{k_{-3}}}{\overset{\overset{k_3}{\rightarrow}}{-}} AS_{c1}C \qquad (5) \qquad AS_{C1}C \underset{\underset{\leftarrow}{k_{-4}}}{\overset{\overset{k_4}{\rightarrow}}{-}} S_c+D \qquad (6)$$

The kinetic relations (7)-(10) are associated with the elementary processes of the reaction mechanism. It observes that for each process we associate formal kinetics with unitary reaction order.

$$\frac{dc_{ASC}}{d\tau}=k_1c_Ac_{S_c}-k_{-1}c_{AS_c}-k_2c_{AS_c} \qquad (7)$$

$$\frac{dc_{ASC}}{d\tau}=k_1c_Ac_{S_c}-k_{-1}c_{AS_c}-k_2c_{AS_c} \tag{7}$$

$$\frac{dc_{ASc1}}{d\tau}=k_2c_{AS_c} \quad (8) \qquad \frac{dc_B}{d\tau}=k_2c_{AS_c} \quad (9)$$

$$\frac{dc_{ASc1c}}{d\tau}=k_3c_Cc_{AS_c}-k_{-3}c_{AS_{c1}C}-k_4c_{ASc1C} \tag{10}$$

$$\frac{dc_C}{d\tau}=k_{-3}c_{AS_{c1}C} \quad (11) \qquad \frac{dc_{S_c}}{d\tau}=k_4c_{ASc1C}-k_{-4}c_{Sc} \quad (12) \qquad \frac{dc_D}{d\tau}=k_4c_{ASc1C} \quad (13)$$

In the written kinetic relations firstly, we apply the steady-state approximation to species AS_c. The result is in relation (14). By expressing c_{S_c} and c_{ASc} as function of initial concentration of active sites (c_{Sc0}) and their coverage degree (θ), as it is shown by relations (15) and (16), it transforms the relation (14) into equation for θ (17). With obtained θ the kinetic of B (hydrogen sulfide) release becomes as in relation (19), which shows that it is important to have a catalyst with a good sulfide content simultaneously with a high hydrogen concentration in liquid phase.

$$\frac{dc_{ASc}}{d\tau}=0\,,\ k_1c_Ac_{S_c}-k_{-1}c_{AS_c}-k_2c_{AS_c}=0 \tag{14}$$

$$c_{ASc}=\theta\, c_{S_{c0}} \quad (15) \qquad c_{Sc}=(1-\theta)\,c_{S_{c0}} \quad (16)$$

$$k_1c_A(1-\theta)c_{S_{c0}}-k_{-1}\theta\, c_{S_{c0}}-k_2\theta\, c_{S_{c0}}=0 \tag{17}$$

$$\theta=\frac{k_1c_A}{k_1c_A+k_{-1}+k_2} \quad (18) \qquad \frac{dc_B}{d\tau}=\frac{k_2k_1c_Ac_{S_{c0}}}{k_1c_A+k_{-1}+k_2} \quad (19)$$

Now if we apply the steady state approximation to AS_{C1} then we obtain the fraction of site with active Mo vacancy and from here the kinetic expression of species *C* (sulfur compounds in diesel) reaction rate of. The relations below (20)-(24), where ξ represent the coverage degree of catalyst sites with Mb vacancy, shows the relationships processing of in the aforementioned sense.

$$\frac{dc_{AS_{c1}C}}{d\tau}=0 \quad (20) \qquad k_3c_Cc_{AS_c}-k_{-3}c_{AS_{c1}C}-k_4c_{ASc1C}=0 \quad (21)$$

$$c_{AS_{c1}C}=\zeta c_{AS_c} \quad (21') \qquad k_3c_Cc_{AS_c}-k_{-3}\zeta c_{ASc}-k_4\zeta c_{ASc}=0 \quad (22)$$

$$\zeta=\frac{k_3c_C}{k_{-3}+k_4} \tag{23}$$

$$\frac{dc_C}{d\tau}=k_{-3}\frac{k_3k_1c_Cc_Ac_{S_{c0}}}{(k_{-3}k_4)k_1c_A+k_{-3}(k_{-1}k_2)+k_4(k_{-1}k_2)} \tag{24}$$

The relation (24) expresses the reaction rate regarding the hydrogenation of sulfur compounds from diesel fuel. With a mechanism like that in figure 1, similar relations can be established for the hydrogenation kinetics of nitrogen compounds, respectively aromatics and alkenes, which are present in diesel fuel. Processing and concentration of the type (24) relations for the mentioned 4 species is still possible. In this sense, it is considered that: i) the product of two reaction constants is expressed as a single constant, ii) hydrogen comes into hydrogenation from the gas phase, iii) hydrogen sulfide is a kinetic inhibitor. All of these have made the kinetic model of LH hydrodesulfurization to be expressed by most authors [6, 14-19], by the relation (25). Here $i = S$ (1), N (2), A (3) respectively O (4), representing the above mentioned hydrogenating species, k_{hi} is the constant of *i* species reaction rate (h^{-1}), K_i express the equilibrium constant for reaction of *i* species, K_{H_2S} represent the catalyst adsorption constant for hydrogen sulfide , P_{H_2} gives the partial pressure of hydrogen in gas phase (at), c_i dons the *i* species concentration in liquid phase (kg/m^3), K_{H_2} shows the catalyst adsorption constant for hydrogen ($kg/(at\ m^3)$), P_{H_2S} gives the partial pressure of hydrogen sulfide in gas phase (at).

$$\upsilon_{ri} = -\frac{dc_i}{d\tau} = \frac{k_{hi}K_iK_{H_2S}P_{H_2}c_i}{1+K_ic_i+K_{H_2}P_{H_2}+K_{H_2S}P_{H_2S}} \qquad 25)$$

If in relation (25) P_{H2S} is expressed as a function of diesel sulfur species, as shown in relation (26), then it takes the form (27). It should be noted that relation (26) is a measure of catalyst inhibition by H_2S and that, in this relation, *b* considers the stoichiometry of reactions producing of H_2S and its specific interfacial equilibrium. For pressure values above 30 atm *b* can be considered constant.

$$P_{H_2S} = bc_s \qquad (26)$$

$$\upsilon_{ri} = -\frac{dc_i}{d\tau} = \frac{k_{hi}K_iK_{H_2S}P_{H_2}c_i}{1+K_ic_i+K_{H_2}P_{H_2}+K_{H_2S}bc_s} \qquad (27)$$

As is expected, all parameters from relation (27) depend, with specificity in the case of simultaneous hydrogenation, namely HDS, HDN, HDA and HDO, on operating conditions, expressed by catalyst type, pressure, phases flow rate and temperature especially.

2.1. HDS reactor model

The application of the LH kinetic model to the hydrodesulfurization reactor takes into account the flow structure through the reactor of liquid and gas phases. For cocurrent plug flow structure of the two phases, the reactor model with L-H kinetics for hydrogenation reactions, here written as assembly of differential equation system (28)- (30) and initial conditions (31), can simulate its operation well [20]. The basis of this differential equations assembly becomes from species balance relative for a control volume from reactor (Figure 2).

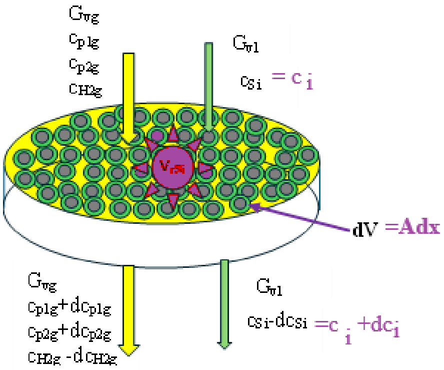

Fig.2. Schema of species balance for a control volume from the hydrodesulphurization reactor

$$\frac{dc_i}{dx} = -\frac{k_{hi}A(1-\varepsilon_g-\varepsilon_l)}{G_{\upsilon l}} \frac{K_i K_{H_2S} P_{H_2} c_i}{1+K_i c_i + K_{H_2} P_{H_2} + K_{H_2S} b c_s}, \; i=1,2...4 \tag{28}$$

$$\frac{dc_{g\,i}}{dx} = -\frac{a_i k_{hi}A(1-\varepsilon_g-\varepsilon_l)}{G_{\upsilon g}} \frac{K_i K_{H_2S} P_{H_2} c_i}{1+K_i c_i + K_{H_2} P_{H_2} + K_{H_2S} b c_s} \quad i=1,2 \tag{29}$$

$$\frac{dc_{H2G}}{dx} = -\Sigma_{I=1}^{4} \frac{\beta_i k_{hi}A(1-\varepsilon_g-\varepsilon_l)}{G_{\upsilon g}} \frac{K_i K_{H_2S} P_{H_2} c_i}{1+K_i c_i + K_{H_2} P_{H_2} + K_{H_2S} b c_s} \quad i=1,2...4 \tag{30}$$

$$x=0, c_i = c_{i0}, i=1,2...4, c_{gi} = c_{gi0} = 0, i=1.2, c_{H2g} = C_{H2g0} \tag{31}$$

In the previous relations the meaning of the new notations is as follows: x gives the current position along of the catalytic bed (m), c_{gi} is the hydrogen sulfide concentration in gaseous phase (kg/m^3), c_{g2} express gas ammonia concentration (kg/m^3), c_{H2g} shows the gas hydrogen concentration (kg/m^3), A is the reactor flow area (m^2), G_{vl} and G_{vg} represent the liquid and gas respectively volumetric flow rates (m^3/h)), ε_l and ε_g give us the fraction of liquid and respectively gas in the catalytic bed (m^3/m^3), α_1 and α_2 are mass ratios for the reactions that give H_2S and NH_3 respectively, β_i are specific mass ratios characterizing the hydrogen consumption of each hydrogenation reaction.

All kinetic and equilibrium (adsorption) constants in LH kinetics are temperature dependent, the equilibrium constants being weakly dependent on pressure even if the liquid-solid (catalyst) system is not compressible. Likewise, the volumetric flow rate of gas is a function of temperature and pressure.

In an attempt to simulate the hydrodesulfurization reactor functioning through the presented model, numerical values must be given to it, respectively expressions of temperature and pressure dependence of each of the variables that appear in its expression (28) – (31). As some of these data are strictly related to the catalyst specificity, they are quite difficult to find in case-oriented scientific research information.

From this point of view, in this paper it uses: i) literature data in order to express the temperature dependencies for $k_{hi}(T)$, $K_i(T)$, $K_{H_2S_i}(T)$, ii) data that serve the interest of model simulation, which are adopted by similarity and intuition in order to be case appropriate, iii) identification of model maximum sensitivity variables so that they can be used in the valorization of monitoring data of an industrial reactor.

3. Simulation of HDS reactor and process factors effect

We have shown that for the transposition of HDS reactor model as simulation software, all the parameters that enter must be specified as expressions or values. Since literature data regarding diesel desulfurization LH kinetics with a certain catalyst are few, it was necessary the establishing of some parameters by theirs taking intuitively or without a total identity regarding the catalyst.

Table 1

LH kinetic models' parameters in hydrotreating of some sulphur containing fuels

		HDS, K_1=K_S			HDN K_2=K_N			HDA K_3 = K_A		
	t ^{0}C	k_{h1}=k_S h^{-1}	K_S MPa	K_{H2S} MPa	k_{h2}=k_N h^{-1}	K_N MPa	K_{H2S} MPa	k_{h3}=k_A h^{-1}	K_A MPa	K_{H2S} MPa
HD	340	0.833	1.2	117.4	0.261	1.5	145.4	0.301	1.5	159.4
HD	360	1.271	1.7	100.7	0.464	1.7	125.7	0.464	1.7	137.5
HD	380	1.933	6.6	95.81	0.562	2.8	105.7	0.622	2.2	115.4
HD	400	2.691	7.9	85.63	0.753	3.7	85.55	0.813	2.9	94.37
D	340	0.897	0.9	129.2	0.291	1.1	156.4	0.331	0.9	169.4
D	360	1.471	1.5	111.7	0.453	1.8	137.8	0.534	1.6	148.6
D	380	1.835	5.9	105.8	0.662	3.1	116.2	0.692	2.7	127.3
D	400	2.541	6.9	96.6	0.823	4.1	99.55	1.037	3.2	105.7

With respect to parameters $k_{hi}(T)$, $K_i(T)$, $K_{H_2S_i}(T)$, that appear in LH kinetic models, data from the literature [6] and by them inspired [21-24] are presented in Table 1. Here the catalyst is activated NiMo/Al_2O_3, but it is worth noting that it works very closely to CoMo/Al_2O_3 or NiCoMo/Al_2O_3 catalysts [25]. We also show that HDO column data was inspired by a power law kinetic model [20]. For temperature dependence of reaction rate constant, $k_{hi}(T)$, we are obliged to use Arrhenius relation (32).

$$k_{0hi}(T) = k_{0hi}\exp(-\frac{E_i}{RT}) \qquad (32)$$

Processing data from Table 1 respect to pre-exponential factor, k_{0hi}, and activation energy, E_i, for HDS, HDN, HDA and HDO it obtains the results from Table 2. For comparison, Table 3 provides literature data for the same parameters when identification was based on the power-type (law) kinetic model [6, 20,26] and when the catalysts are in the class of the above-mentioned.

Table 2

Activation energies and Arrhenius constants from kinetic LH models

Case	Parameter	HDS	HDN	HDA	HDO
HD	k_{0h} h^{-1}	3.9992 10^4	2.185 10^4	1.368 10^4	1.418 10^4
HD	E j/Kmol	6.173 10^7	5.393 107	5.059 10^7	5.359 10^7
D	k_{0h} h^{-1}	3.415 10^4	2.013 10^4	1.939 10^4	2.109 10^4
D	E j/Kmol	5.994 10^7	5.136 10^7	4.824 10^7	5.024 10^7

Table 3

Power law models parameters in hydrotreating of some sulphur containing fuels

Case	Ref.	Reaction order n			k_{0hi} 10^{-4} h^{-1}			E_i 10^{-7} J/Kmol		
		HDS	HDN	HDA	HDS	HDN	HDA	HDS	HDN	HDA
Light Diesel	[30],[31]	1	1	1	2.585	5.28	8.06	5.17	4.13	6.35
Diesel	[32]	1	NS	NS	17.67	NS	NS	31.3	NS	NS
Diesel	[33]	1			21.32	NS	NS	54.8	NS	NS
Diesel	[34]	1	NS	1	1.855	NS	4.07	6.71	NS	5.44
Heavy Diesel	[35]	1	1.5	NS	1.223	2.89	NS	8.7	7.4	NS
Light Diesel	[36]	1.5	1	1	1.775	3.33	9.14	7.8	6.4	5.2

From Table 1 is observed that k_S, k_N and k_A increased with temperature, so the rate of HDS, HDN and HDA increased with temperature increasing. Moreover, Table 1 shows that K_{H2S} presents specificity for hydrogenation case and decreased, for all cases, with temperature. This trend indicates that the increase in temperature decreased H_2S inhibition on HDS, HDN and HDA reactions [6, 26]. From data given by Tables 1, 2 and 3 results a comparison respect to k_{0hi} and E_i parameters for LH and PL kinetic models. We thus find that: i) the parameters of the PL and LH models are slightly dependent on diesel type subjected to desulfurization, ii) in LH models k_{0hi} is slightly higher (HDS) or slightly greater (HDA) than in PL models, remaining in the range of 10^4 h^{-1}, iii) the Arrhenius pre-exponential factor, k_{0hi}, is differentiated by HDS, HDN and HDA respectively, increasing from HDS to HDA in PL model and decreasing from HDS to HDA in LH model, iv) the activation energies, with values between $4x10^6$ and $7X10^7$ J/Kmol and specificity for HDS, HDN and HDA, both in PL models and in LH models, are in the range of activation energies specific to catalytic hydrogenations of organic compounds [27, 28], v) the activation energies for HDS, HDN and HDA reactions from LH model reported to those of PL model indicate that nitrogen and H_2S adsorptions have significant inhibition effects on hydrogenation reactions (H_2S, as desulfurization reaction product competes with the organosulfur, oganonitrogen and respectively aromatic compounds for the same active catalyst sites in the reaction process [29], which in turn reduce HDS, HDN and HDA activities of the catalyst and hence activation energies).

Table 4

Temperature dependence of $K_i(T)$ and $K_{H2S}(T)$ based on data from table 1

Case	Units	Expressions
S compounds	$K_S(T)$ MPa^{-1}	$K_S(T) = 293.032 - 1.013T + 8.75*10^{-4}T^3$ (33)
	$K_{H2S}(T)$ MPa^{-1}	$K_{H_2S}(T) = 2.747 - 7.725T + 5.625*10^{-3}T^2$ (34)
N compounds	$K_N(T)$ MPa^{-1}	$K_N(T) = 46.27 - 0.188T + 1.875*10^{-4}T^2$ (35)
	$K_{H2S}(T)$ MPa^{-1}	$K_{H_2S}(T) = 1.253*10^3 - 2.56T + 1.25*10^{-3}T^2$ (36)
A compounds	$K_A(T)$ MPa^{-1}	$K_A(T) = -74.63 + 0.2T - 1.25*10^{-3}T^2$ (37)
	$K_{H2S}(T)$ MPa^{-1}	$K_{H_2S}(T) = 563.22 - 0.256T - 6.25*10^{-4}T^2$ (38)
O compounds	$K_O(T)$ MPa^{-1}	$K_A(T) = 43.711 - 0.185T + 1.825*10^{-4}T^2$ (39)
	$K_{H2S}(T)$ MPa^{-1}	$K_{H_2S}(T) = -2.33*10^4 + 75.87T - 0.061T^2$ (40)

In expressing of functions $K_i(T)$, $K_{H_2S_i}(T)$ it shows that data from Table 1 was used. These were evaluated assuming that the mentioned dependencies are described using a polynomial function of degree 2. The result is given by relations (33)-(40), which are concentrated in Table 4.

Once the temperature dependencies of characteristic parameters of the LH kinetic model have been established, we can proceed to simulation of one HDS reactor performance. For that it considers data on reactor size and the phases flow rates and phases composition in its feeding. Figure 3 shows such a simulation. What is noteworthy from figure 3 is: i) for data considered in Figure 3 simulation, a reduction in the sulphur concentration of sulphur compounds from 6000 ppm to 6 ppm can be obtained if the catalytic bed length is over 13 m, ii) a stronger evolution, at 610 ^{0}K, of S compounds concentration along of catalytic bed, can be a consequence of the catalyst specificity (fig 3. left), iii) it is observed an important influence of temperature, in the range of 590 and 610 ^{0}K, on the hydrogenation yield of S, N, A, O compounds. The last observation is in accord with industrial practice where the hydrodesulfurization reactor temperature control is one of the objectives of reactor exploitation.

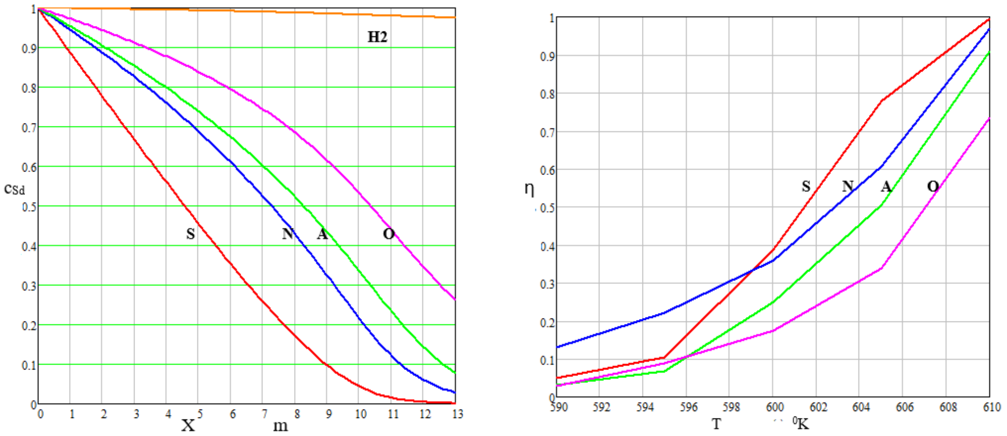

Fig. 3. Dimensionless species concentration ($c_{Sd} = c_i / c_{i0}$) versus catalytic bed length (X) at T = 610 ^{0}K and species hydrogenation degree (η) versus temperature (T) at X=13 m in LH model (S-sulfur compounds, N-nitrogen compounds, A-aromatic compounds, O -alkene compounds, H_2 – hydrogen, $G_{vl} = 100\ m^3/h$, $G_{vg0} = 30000\ Nm^3/h$, $D = 3.3$ m, $\varepsilon_g = 0.3\ m^3/m^3$, $\varepsilon_l = 0.05\ m^3/m^3$, $P = 3.5$ MPa, $b = 0.5$, $K_{H2} = 2\ MPa^{-1}$, k_i and E_i , i = S, N, A, O in table 2, $K_i(T)$ and $K_{H2S}(T)$ in table 4, $c_{10} = 5.04\ kg/m^3$ (6000 ppm), $c_{20} = 3.4\ kg/m^3$, $c_{30} = 210\ kg/m^3$, $c_{40} = 117\ kg/m^3$)

A greater concentration of the LH model for HDS reactor simulation is obtained by the fact that data showing K_{H2S} dependence on temperature can be targeted in a single relation (41). In this way, the pre-exponential factor and the activation energy for the hydrogenation of sulphur compounds, nitrogen compounds, aromatics and alkenes can have new values by supplementing data from table 1 with a more precise reference to the catalyst cases for classical diesel processing [30-32]. Thus, table 5 resulted, which in addition to the above-mentioned ones also contains specified data of the other model parameters, which are to be specified in the new HDS reactor simulation.

$$K_{H_2S}(T) = 887.098 - 1.589T + 6.25T^2 \tag{41}$$

Table 5

New Arrhenius constants (k_{0hi}) and activation energies (E_i) of LH kinetic model with others HDS reactor model specific parameters

Case	Parameter	HDS	HDN	HDA	HDO
D	k_{0hi} h^{-1}	$7.504\ 10^4$	$4.078\ 10^4$	$2.663\ 10^4$	$2.243\ 10^4$
D	E_i J/Kmol	$5.749\ 10^7$	$5.597\ 10^7$	$5.734\ 10^7$	$5.731\ 10^7$
D	$K_i(T)$	(42)	(43)	(44)	(45)
D	β_i	0.04	0.02	0.05	0.06
D	α_i	1.068	1.252	-	-
D	c_{i0} kg/m^3	5.04	3.36	210	117
D	P_{H2}, P MPa	3.3		3.5	

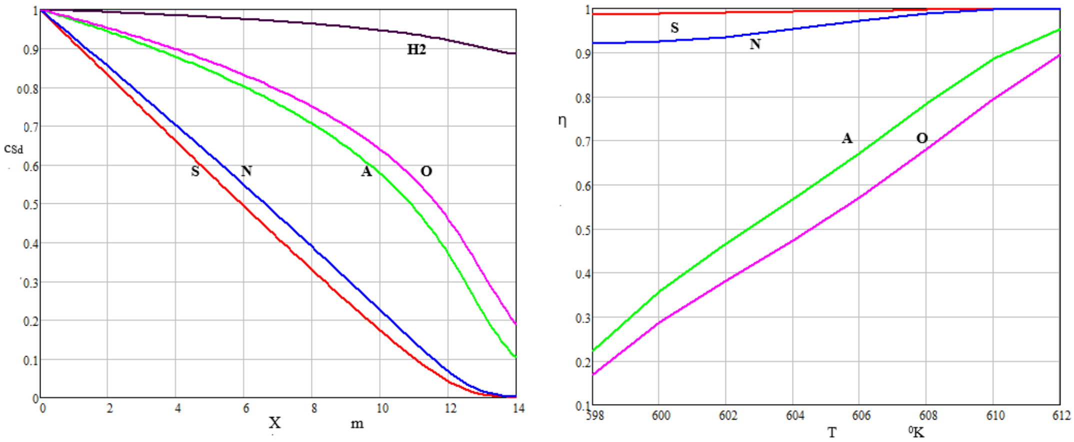

Fig. 4. Dimensionless species concentration ($c_{Sd} = c_i / c_{i0}$) versus catalytic bed length (X) at T= 610 ^{0}K and species hydrogenation degree (η) versus temperature (T) at X=14 m in LH model (S-sulfur compounds, N-nitrogen compounds, A-aromatic compounds, O -alkene compounds, H_2 – hydrogen, G_{vl} = 100 m^3/h, G_{vg0} = 30000 Nm^3/h, D = 3.3 m, ε_g = 0.3 m^3/m^3, ε_l = 0.05 m^3/m^3, P= 3.5 MPa, b = 0.5, K_{H2} = 2 MPa^{-1}, k_i and E_i , i = S, N, A, O in table 5, $K_i(T)$ in table 5 $K_{H2S}(T)$ -(41) , c_{i0} in table 5)

So, with these new data regarding the LH model parameters and considering, as in the previous case, an industrial-scale reactor, the new simulation of HDS model reactor goes to the results concentrated in figures 4 and 5.

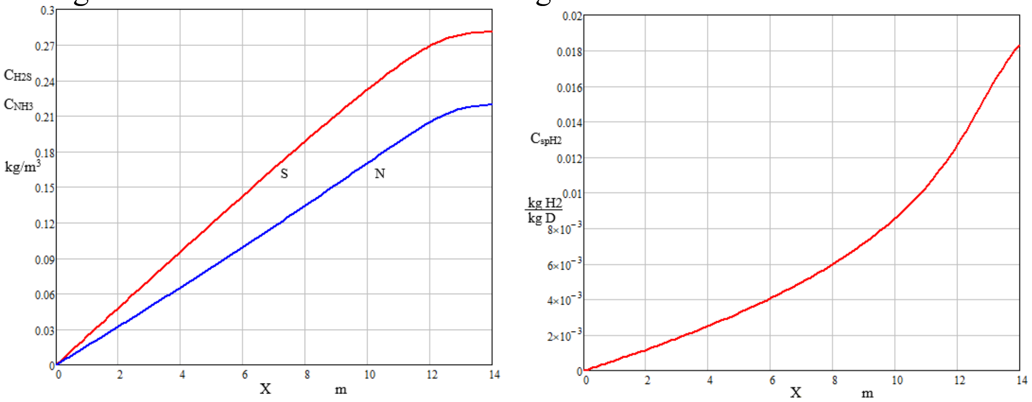

Fig. 5. Concentration of hydrogen sulphide (c_{H2S}) and ammonia (c_{NH3}) and specific hydrogen consumption (c_{spH2}) along of catalytic bed (X) in LH model at T = 610 ^{0}K (G_{vl} = 100 m^3/h, G_{vg0} = 30000 Nm^3/h, D = 3.3 m, ε_g = 0.3 m^3/m^3, ε_l = 0.05 m^3/m^3, P= 3.5 MPa, b = 0.5, K_{H2} = 2 MPa^{-1}, k_i and E_i , i = S, N, A, O in table 5, $K_i(T)$ in table 5 $K_{H2S}(T)$ -(41) , c_{i0} in table 5)

$$K_1(T) = 557.138 - 1.827T + 1.501 * 10^{-3} T^2 \quad (42)$$

$$K_2(T) = 71.708 - 0.269T + 2.503 * 10^{-4} T^2 \quad (43)$$

$$K_3(T) = -75.293 + 0.201T - 1.25 * 10^{-4} T^2 \tag{44}$$

$$K_4(T) = 99.465 + 0.279T - 1.875 * 10^{-4} T^2 \tag{45}$$

All observations made with reference to the first simulation of an industrial hydrodesulfurization reactor remain valid with reference to the second simulation. The differentiation highlighted by the second simulation consists in that it shows an increased sensitivity to temperature (figure 4 right the temperature range is 14 ^{0}K, compared to 20 ^{0}K in figure 3 right) and brings in addition those specified in figure 5. Figure 5 right shows that the gas phase accumulating the gases from the HDS and HDN reactions ends up having 0.285 kg/m^3 H_2S and respectively 0.215 kg/m^3 NH_3 at the reactor outlet. Comparing figure 5 right to figure 5 left and considering the reactor feed composition (see table 5) it is found that the specific hydrogen consumption is predominantly determined by hydrogenation of aromatics and alkenes from the diesel.

The two simulations show that the HDS reactor model where the process kinetics follows the LH model has the capacity to be used in the analysis of monitoring data of an industrial reactor.

4. Temperature, liquid and gas flow rate on reactor response

The above shows in particular the temperature (T) strongly influence on the HDS reactor response. The reactor operation shows that their performance is also strongly influenced by the processed diesel flow rate (G_{vl}) and to a lesser extent by the circulated gas flow rate (G_{vg}).

Table 6

Use of second order ortogonl plan with factors temperature (T), diesel flow rate (G_{vl}) and gas flow rate (G_{vg}) for those influence on sulfur compounds concentration in reactor exit (c_{SF})

n	T_{min} ^{0}K	T_{max} ^{0}K	$G_{vl\ min}$ m^3/h	$G_{vl\ max}$ m^3/h	$G_{vg\ min}$ Nm^3/h	$G_{vg\ max}$ Nm^3/h	X_1	X_2	X_3	c_{SF} ppm
1	-	620	100	-	-	30000	1	1	1	6.3
2	-	620	100	-	26000	-	1	1	-1	6.5
3	-	620	-	80	-	30000	1	-1	1	0.2
4	-	620	-	80	26000	-	1	-1	-1	0.24
5	600	-	100	-	-	30000	-1	1	1	367
6	600	-	100	-	26000	-	-1	1	-1	372
7	600	-		80	-	30000	-1	-1	1	110
8	600	-		80	26000		-1	-1	-1	112
9	610	610	90	90	28000	28000	0	0	0	125
10	623.4	623.4	90	90	28000	28000	1.225	0	0	0.09
11	598.8	598.8	90	90	28000	28000	-1.225	0	0	117
12	610	610	102.5	102.5	28000	28000	0	1.225	0	351
13	605	605	78	78	28000	28000	0	-1.225	0	23
14	605	605	90	90	30450	30440	0	0	1.225	125
15	605	605	90	909	25550	25550	0	0	-1.225	127

The interest is to analytically establish how the sulfur content in the processed diesel fuel (c_{SF}) depends, for the industrial reactor, on T, G_{vl} and respectively G_{vg}. In this sense, a statistical model, developed based on second order orthogonal plan with three factors, was used to express the dependence of one response y on dimensionless factors X_1,X_2 and respectively X_3. Relation (47) expresses the general form [5, 33] of the $Y(X_1,X_2,X_3)$ dependence when it uses of a second order orthogonal plan. Thus, table 6 presents the data, in dimensional and dimensionless form (46), for determining the dependence of c_{SF} on T (X_1), G_{vl} (X_2) and G_{vg} (X_3) respectively.

$$z_c = \frac{z_{\max} + z_{\min}}{2} \;,\quad \Delta z = \frac{z_{\max} - z_{\min}}{2},\quad X = \frac{z - z_c}{\Delta z} \tag{46}$$

$$y(X_1,X_2,X_3) = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 + \beta_{11}(X_1^2 - 0.73) + \beta_{22}(X_2^2 - 0.73) + \beta_{33}(X_3^2 - 0.73) \tag{47}$$

$$c_{SF}(X_1,X_2,X_3) = 91. - 99.2X_1 + 84.6X_2 - 63.1X_1X_2 + 42.9X_1^2 \tag{48}$$

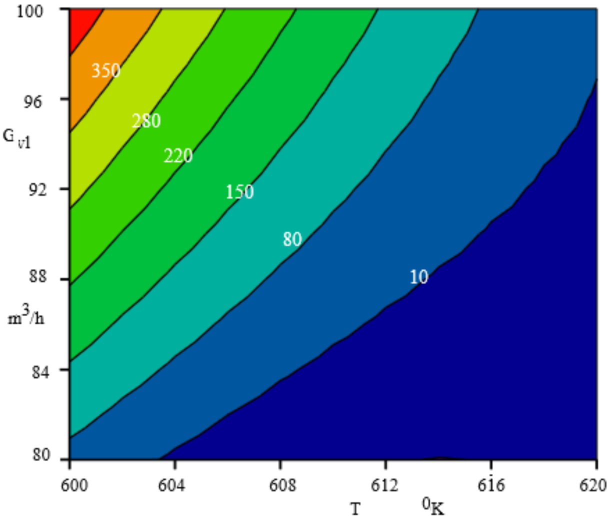

Fig. 6. Influence of temperature and diesel flow rate on the sulfur content of reactor processed diesel fuel (white color, values in ppm)

In the model simulations for determining of sulfur concentration values in the processed diesel , the reactor characterization data, respectively those that give the LH kinetics, are expressed by D = 3.3 m, H=14 m, $\varepsilon_g =$ 0.3 m³/m³, $\varepsilon_l = 0.05$ m³/m³, P= 3.5 MPa, b = 1.68, K_{H2} = 2 MPa⁻¹, k_{0i} and E_i , i = N (2), A (3), O (4) in table 5, k_{01}=7.101 10⁴ h⁻¹, E_1 =5.989 10⁷ J/Kmol, $K_i(T)$ in table 5, $K_{H2S}(T)$ -(41) , c_{i0} in table 5. A computer program was developed to determine the value of the $\beta_0 \ldots \beta_{33}$ coefficients, and to test their significance [5]. The result for expressing the dependence of $c_{SF}(X_1,X_2,X_3)$ is the relation (48). This shows that c_{SF} is independent respect to X_3 (G_{vg}) and has a complex dependence after X_1 and X_2.

Figure 6, which is a graphical transposition of relation (48), shows that there is an important range relative to the temperature (*T*) and flow rate of processed diesel (G_{vl}) in which c_{SF} remains below 10 ppm. This game temperature- diesel flow rate with c_{SF} under 10 ppm, is used in industrial reactor control. In this sense, relation (48) can be considered for predictive purposes.

5. Conclusions

The paper presents a development on the use of LH catalytic kinetics as the basis for a diesel hydrodesulfurization reactor model having plug flow and cocurrent phases circulation. The basic aim is to use this model in exploitation of monitoring data from an industrial diesel hydrodesulfurization reactor but that will be developed by the second part of paper. The present paper is structured on three levels, namely: i) consideration of the use of the LH kinetic model for the hydrogenation of sulfur and nitrogen compounds respectively of aromatics and olefins from diesel fuel, ii) establishment of the reactor model and simulation of its operation for conditions of an industrial reactor, iii) development of a procedure to express, for an industrial reactor, the analytical dependence of the hydrodesulfurization performance, expressed as the sulfur concentration in the processed diesel, on the catalytic bed temperature and on liquid and gas phase flow rate circulating through the bed.

Many comments have been on the use and processing of literature data on identification of the kinetic parameters of the LH kinetic, which characterize the operation, and the comportment of the catalyst used in the hydrodesulfurization reactor.

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