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

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Hydrodesulphurization is a catalytic process that uses H_2 to stabilize petroleum product 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 uses 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

Controlling and monitoring in diesel hydrodesulfurization (HDS) processes is a very important system for producing ultra-low sulfur diesel and for meeting increasingly stringent environmental regulations for use of fossil combustibles [1-2].

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In a given process, whether simple or extremely complex, the monitoring-control system must be understood as having in the control part the process modeling and respectively effective control [3].

Consequently, the triplet monitoring-modeling-control is responsible for the more or less optimal management of an industrial process with or not molecular-scale transformation of raw materials [4,5]. In this sense the monitoring says what we have, the process mathematical model decides what needs to be done and control does what has been decided, so that the process objective remains within the accepted characteristics. In diesel hydrodesulphurization (HDS) the effective control request to process model the optimizing of operating conditions based on monitoring key parameters to ensure efficient sulfur removal while maintaining product quality.

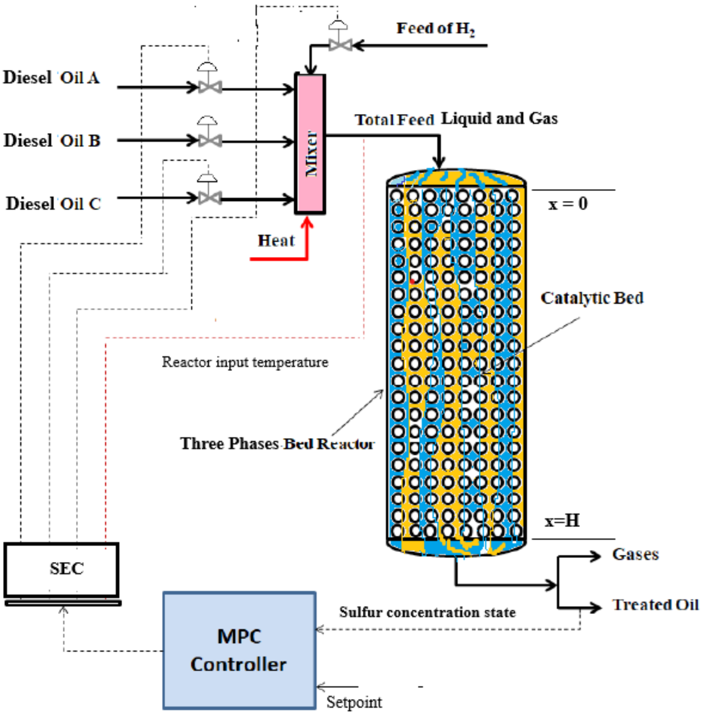

Fig.1. Coupling of monitoring (sulphur concentration state) with process model (model predictive control (MPC)) and heat and flow control in diesel hydrodesulphurization

In the case of diesel hydrodesulphurization, Fig. 1 shows the monitoring-modelling (predictive control model) and flow control system so that the monitored property (sulphur concentration in the processed diesel) remains within the set range [6]. In the scheme from Fig. 1 it considers that the control model, based on the mathematical model of the hydrodesulphurization process, is a datum in the sense that it does not require any adjustments or even reconstructions with its use. More precisely what is in Fig. 1 Set point remains nailed down.

In the case of diesel hydrodesulphurization, as a rule, predictive control models are based on simplified mathematical models, which consider that process rate is determined by the catalytic chemical reactions. In this sense, reactor models based on the fact that hydrogenation reactions of hydrodesulphurization are of the power law appear in the construction of predictive control models for this process [7]. The large number of factors involved in HDS, together with phenomena difficult to consider in simple models, such as catalyst deactivation and forced plant shutdown, require the use of monitoring data to identify the kinetic parameters that characterize the catalyst comportment at the moment.

In the first part of the work, the mathematical model was developed and tested in relation to an industrial reactor based on the fact that the kinetics of catalytic hydrogenation reactions within hydrodesulfurization follows the Langmuir-Hinshelwood model. Now, through the complex monitoring data for an industrial reactor, we show that: i) these are supported by the reactor model with LH kinetics, ii) they can be used to identify the most important parameters in the LH kinetic model so that the monitoring-modeling-control system can perform the momentary update of the model (MPC with new setpoint in Fig. 1), iii) they show the coherence of the process control during the monitoring period

2. LH Kinetics and Reactor Model

In the first paper part it was shown that among the kinetic models for hydrogenations in hydrodesulfurization process, the LH model has the greatest specificity because it takes into account the elementary processes of catalysis through MoS_2 catalyst sites [8,9]. The result of this kinetic model is expressed by relations (1), which give the species reaction rate. In this relation $i = S$ (1), N (2), A (3) respectively O (4) define the mentioned species (sulfur compounds, nitrogen compounds, aromatics and olefins), 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 ($kg/(at\ m^3)$), b gives the ratio between partial pressure of hydrogen sulfide and those concentration in liquid.

$$\upsilon_{ri} = -\frac{dc_i}{d\tau} = \frac{k_{hi} K_i K_{H_2S} P_{H_2} c_i}{1 + K_i c_i + K_{H_2} P_{H_2} + K_{H_2S} b c_s} \tag{1}$$

The coupling of this kinetics to the structure of the phase flow through the reactor as being co-current plug type, suggested in Fig. 1, leads, as established in the first paper part, to the reactor mathematical model. It is expressed by the system of differential equations (2) -(4) with the initial conditions (5) and it shows the evolution, along the catalytic bed, of the species concentration in liquid and gaseous phase.

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

$$\frac{dc_{gi}}{dx} = -\frac{a_ik_{hi}A(1-\varepsilon_g-\varepsilon_l)}{G_{\upsilon g}}\frac{K_iK_{H_2S}P_{H_2}c_i}{1+K_ic_i+K_{H_2}P_{H_2}+K_{H_2S}bc_s} \; i=1,2 \tag{3}$$

$$\frac{dc_{H2G}}{dx} = -\Sigma_{I=1}^{4}\frac{\beta_ik_{hi}A(1-\varepsilon_g-\varepsilon_l)}{G_{\upsilon g}}\frac{K_iK_{H_2S}P_{H_2}c_i}{1+K_ic_i+K_{H_2}P_{H_2}+K_{H_2S}bc_s} \; i=1,2...4 \tag{4}$$

$$x=0, c_i=c_{i0}, i=1,2...4, c_{gi}=c_{gi0}=0, i=1.2, c_{H2g}=c_{H2g0} \tag{5}$$

Here we identify by A the reactor surface area, by $\varepsilon_g, \varepsilon_l$ the volumetric fractions two phases in the bed, by a_i the conversion coefficients of transferred sulphur and nitrogen compounds from liquid to gas phase and respectively by β_i the hydrogen consumption coefficients respect to hydrogenation reactions. The model use (checking) is conditioned by specifications, as expressions, as values or as a computing procedure, of all its quantities, which in the case of LH kinetics are not few and specific to the type of catalyst. In the first paper part this problem was detailed. We bring here the relations expressing the temperature dependence for K_i , K_{H_2S} ((6)- (10)) as well as data (table 1) regarding the pre-exponential factor and the activation energy expressing the reaction rate constant of i hydrogenation reaction (11). Table 1

$$K_1(T) = 557.138 - 1.827T + 1.501 * 10^{-3}T^2 \tag{6}$$

$$K_2(T) = 71.708 - 0.269T + 2.503 * 10^{-4}T^2 \tag{7}$$

$$K_3(T) = -75.293 + 0.201T - 1.25 * 10^{-4}T^2 \tag{8}$$

$$K_4(T) = 99.465 + 0.279T - 1.875 * 10^{-4}T^2 \tag{9}$$

$$K_{H_2S}(T) = 887.098 - 1.589T + 6.25T^2 \tag{10}$$

$$k_{hi}(T) = k_{0hi}\exp\left[\frac{-E_i}{RT}\right], \; i=1,2...4 \tag{11}$$

Table 1 also contains recommendations, as numerical values, for the model variables, which have not been referred to in the previous sections. Thus, all that is needed to simulate a hydrodesulfurization reactor is available. This can be done by numerically integrating of model system of differential equations, with its placement in the vector Z, synthetically expressed by relation (12)

Table 1

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

Oil	Parameter	HDS	HDN	HDA	HDO
D	k_{0hi} h^{-1}	6.504-7.897 10^4	5.078-6.678 10^4	2.663-4.552 10^4	2.243-3.987 10^4
	E_i J/Kmol	5.749 -6.981 10^7	5.397-6.667 10^7	5.734-6.887 10^7	5.731-6.897 10^7
	β_i	0.04	0.02	0.05	0.06
	α_i	1.068	1.252	-	-
	c_{i0} kg/m^3	5.04	3.36	210	117
	P_{H2}, P MPa	3.3 3.5			
	b	0.4 – 1.9			
	K_{H2}	1.5 - 2.5			

3. Industrial Reactor Monitoring and LH Kinetic Models

As it can be seen from relations (6)-(12) the hydrodesulfurization reactions temperature is one of the very highly sensitive factors of the discussed models and therefore of the reactor control. Controlling of this factor is necessary to comply with the requirements of the technical process regulations. It is known cases when if this factor is out, with 2-5 ^{0}K, from technical prescription, then there is a decrease of over 5% in production. For a reactor which processes around 90 m^3/h it can compute that the Diesel losses of the hydrodesulfurization device goes over one million dollars per month. Many aspects with economic reference regarding the influence of factors on the productivity of diesel hydrogenation reactors are presented in the literature [10-12]. It is thus shown that near temperature the input and output data of gas and liquid the flow rate, the reactor mean internal pressure, the hydrogen purity and the Diesel quality are other process factors which must be considered by technical process regulations [13-18], so in the current monitoring procedures of HDS plants. Fig. 2 shows the HDS reactor diagram with the specification of the important geometric dimension of catalytic bed and of process variables, which were monitored for a period, namely from day 67 to day 117. As can be seen from the figure, the following independent respectively dependent variables were measured during the monitoring: i) independent variables: Diesel flow rate (G_{vl}), Diesel density (ρ_{cd}), Diesel ASTM curve, Sulphur diesel content (c_{s1} or c_{10} in (5)), Nitrogen crude diesel content (c_{s2} or c_{20} in (5)), Input pressure (p+Δp), Recycled gas flow rate (G_{vgr}), Total gas flow rate (G_{vg}), H_2 content in gas (c_{H2g0} in (5)), Input temperature (t_i), Temperature distribution around ring 1, Temperature distribution around ring 2, Temperature distribution around ring 3, Temperature distribution around ring 4; ii) dependent variables: Treated Diesel flow rate (G_{vltd}), Treated Diesel density (ρ_{ctd}),Treated Diesel ASTM curve, Sulphur diesel content (c_{s1f} or c_{Sf} in 15)), Nitrogen diesel content (c_{s2f} or c_{Nf} in (16)), Total gas flow rate(G_{vgf}), H_2 content in gas (c_{H2gf}), Exit temperature (t_e). Before the beginning of presentation concerning monitoring data on diesel desulfurization industrial reactor, extremely interesting at first glance in terms of content and analytical point of view, it must be specified how these data are to be interpreted in the sense of explaining them in terms of LH kinetic model. Thus, it was considered of interest to identify the most important LH kinetic model parameters that characterize the removal of sulfur compounds (k_{0h1}, E_1, b) and nitrogen compounds, respectively (k_{0h2}, E_2).

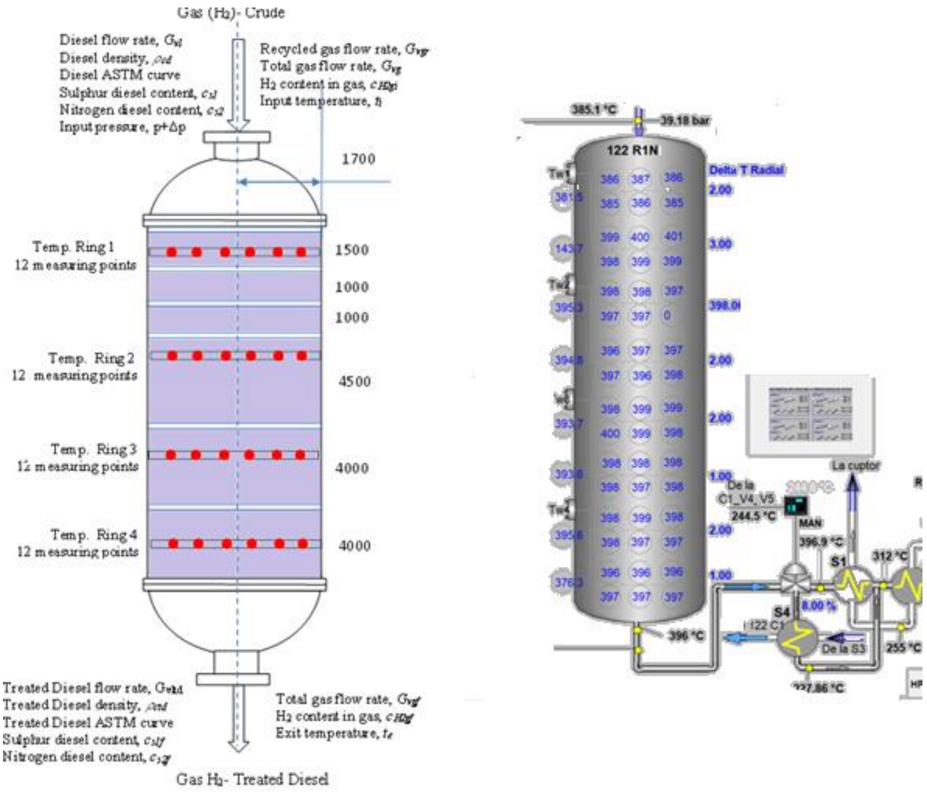

Fig. 2. Presentation of the monitored variables for an industrial hydrodesulfurization reactor (left dimensions and variables list, right –image generated with MPC for rings level temperature registration)

This is because the concentration status of these compounds in the product is monitored daily. In this sense: i) the reactor numerical model was put in a form that shows a) the concentration of sulfur compounds (13) and nitrogen compounds (14) at the reactor outlet as a function of all process factors involved in the model,

ii) the kinetic parameters k_{0h1}, E_1 and respectively b were identified by minimizing the mean square deviations [7,19] between the computed and measured concentrations values of sulfur compounds in reactor outlet (15), iii) the kinetic parameters k_{0h2}, E_2 were identified by proceeding as above(16), with reference to the reactor outlet concentrations of nitrogen compounds

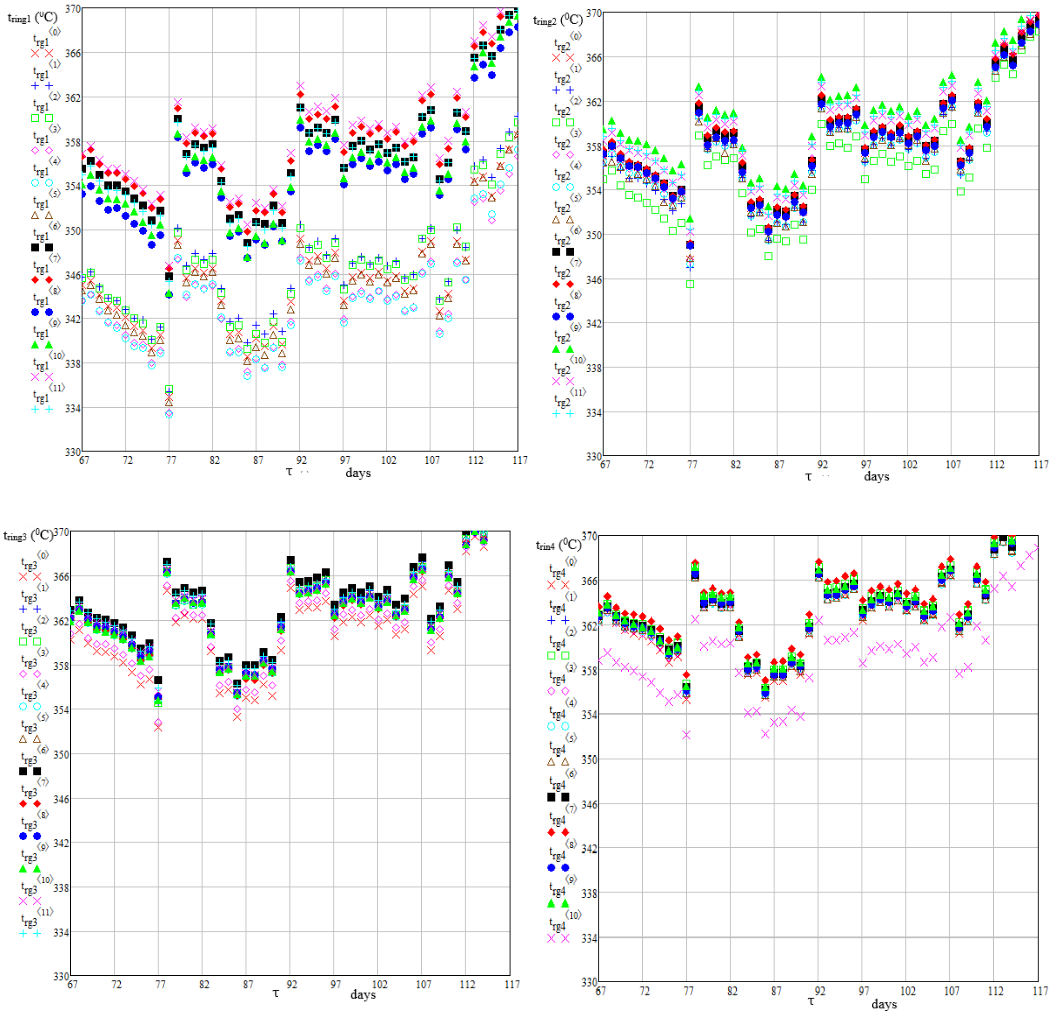

Fig. 3. State of catalyst bed temperature (°C) at 12 measurement points respect to ring 1, ring 2, ring 3 and respectively ring 4.

$$c_{S_c}(k_{01},E_1,b,T_{mc},G_{\upsilon l},G_{\upsilon g},c_{s0},c_{N0}) = (Z^1(k_{01},E_1,b,T_{mc},G_{\upsilon l},G_{\upsilon g},c_{s0},c_1,c_2,c_3,c_4.c_{g1},c_{g2},c_{H2}))_{99} \quad (13)$$

$$c_{N_c}(k_{02},E_2,T_{mc},G_{\upsilon l},G_{\upsilon g},c_{s0},c_{N0}) = (Z^2(k_{01},E_1,b,T_{mc},G_{\upsilon l},G_{\upsilon g},c_{s0},c_1,c_2,c_3,c_4.c_{g1},c_{g2},c_{H2}))_{99} \quad (14)$$

$$F(k_{01},E_1,b) = \sum_{i=1}^{49}\left(c_{S_c}(k_{01},E_1,b,T_{mci},G_{\upsilon li},G_{\upsilon gi},c_{s0i}) - c_{Sfi}\right)^2 \quad (15)$$

$$G(k_{02},E_2)=\sum_{i=1}^{49}\left(c_{N_c}(k_{02},E_2,T_{mci},G_{\upsilon li},G_{\upsilon gi},c_{N0i})-c_{Nfi}\right)^2 \qquad (16)$$

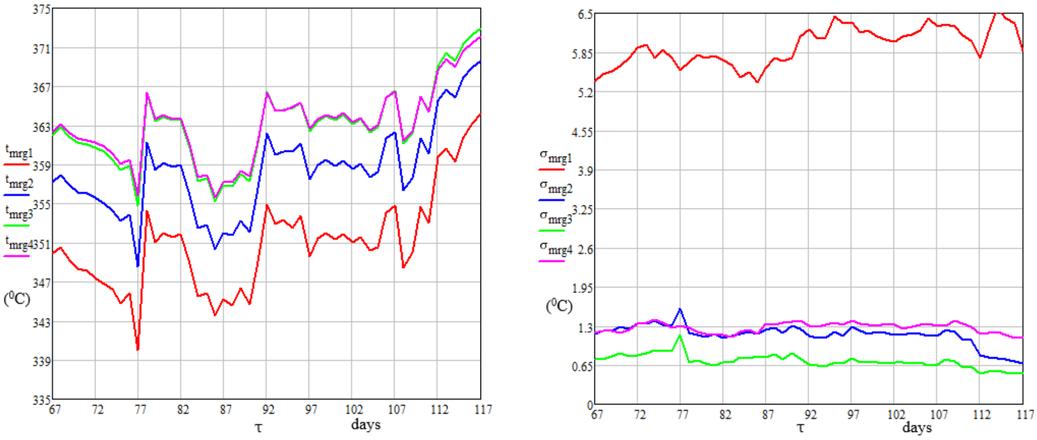

Fig. 4. Daily dynamics of mean temperatures (left) and related dispersions (right) for rings from 1 to 4.

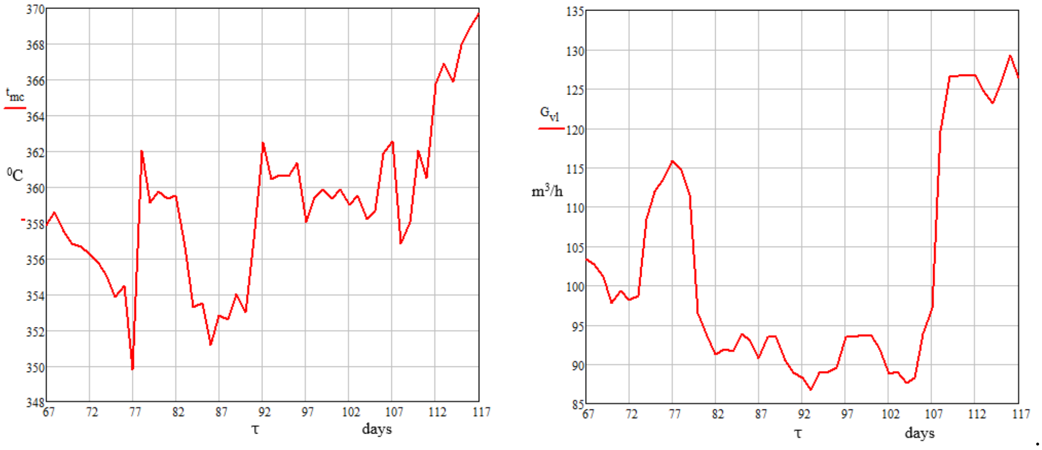

Fig. 5. Daily dynamics of temperature in the catalyst bed (left) and daily dynamics of diesel flow rate through the industrial HT reactor (right).

From what is shown, it can be deduced that for the dependencies $K_i(T)$ and $K_{H2S}(T)$ the relationships presented above were accepted. The index 99 in numerical model integration function Z shows that 100 integration steps are used for the 14 m of catalytic bed length (Fig. 2). Also, it observes that from the monitoring data, 49 days were considered, not 50 as it results from monitoring data Figs.. Taking into account that reaction temperature is the most important HDS kinetic factor, we begin the presentation of the monitoring data with Fig. 3. Here it shows the catalyst bed temperature dynamics of at 12 measurement points in the area of ring 1, ring 2, ring 3 and respectively ring 4. The mean temperature at the level of each ring and the ring temperature variance, given by Fig. 4, is the intermediary step in establishing of daily temperature characterizing the reactor operation, which is given with Fig. 5 left. So, this figure contains the values T_{mci} requested in (15) and (16) respectively. The right part of Fig. 5 contains the daily values of volumetric liquid flow rate through catalytic bed ($G_{\upsilon li,i}=1,2...49$ in (15) and (16)).

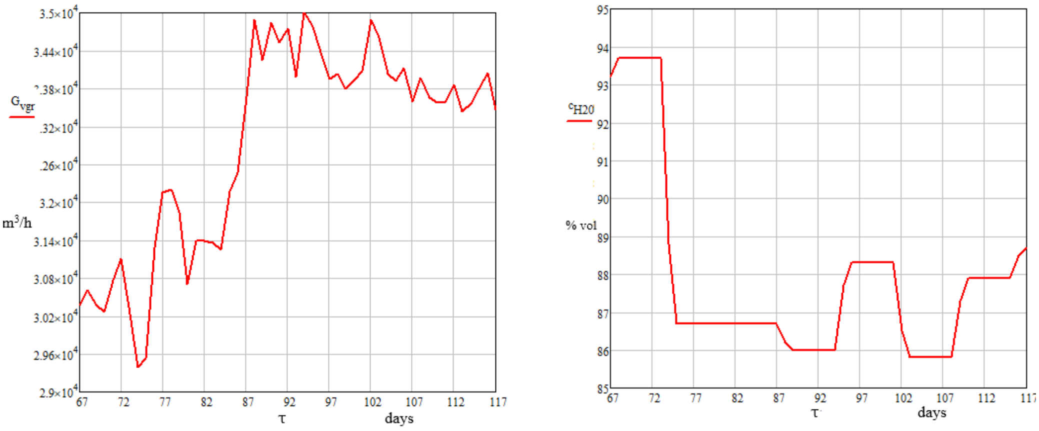

Fig. 6. Mean flow rate of recirculated gas through the catalyst bed (left) and the hydrogen gas content in reactor entrance (right) for monitoring days

With Fig. 6 left we bring through the daily state of the recycled gas flow rate, as a measure for the gas flow, which is the hydrogen support in the bed $G_{\upsilon gi,i}=1,2...49$ in (15) and (16)). The other side of Fig. 6 shows the particular importance of the hydrogen content in the gas; the hydrogen concentration at gas entrance to the catalytic bed is an initial condition in the reactor model (5). The daily state of sulfur compounds and nitrogen compounds concentration in the diesel fuel entering and leaving the HDS reactor, expressing for relations (15) and (16) by the daily values $c_{s0i}, c_{Sfi}, c_{N0i}$ and respectively c_{Nfi}, is presented in Figs. 7 and 8 respectively.

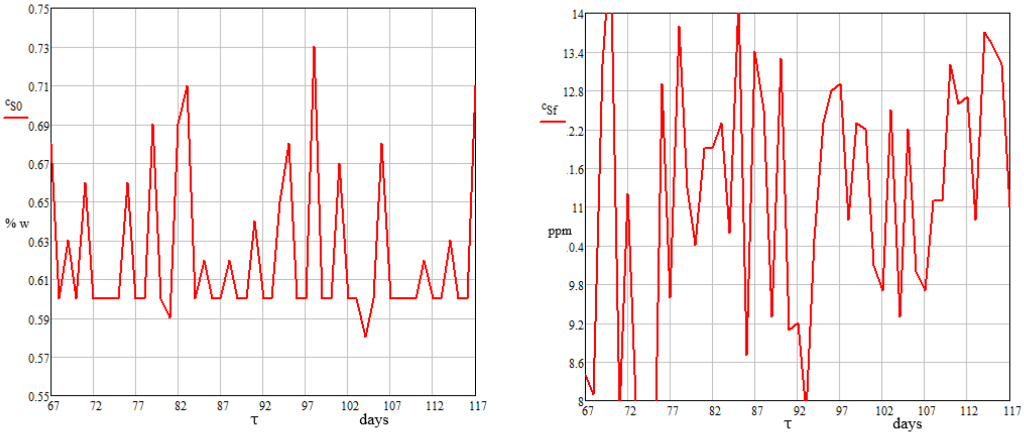

Fig. 7. Sulfur compounds concentration at HDS reactor inlet (left) respectively outlet (right) of diesel fuel for monitored days

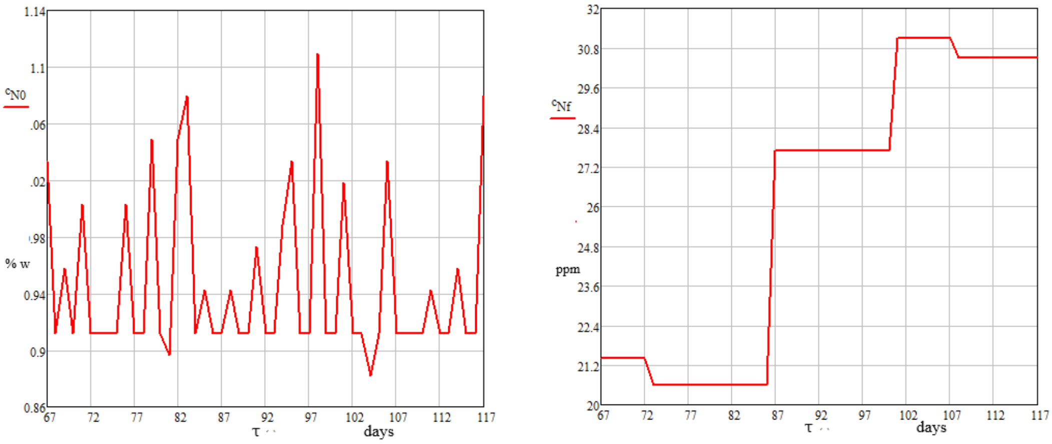

Fig. 8. Nitrogen compounds concentration at HDS reactor inlet (left) respectively outlet (right) of diesel fuel for monitored days

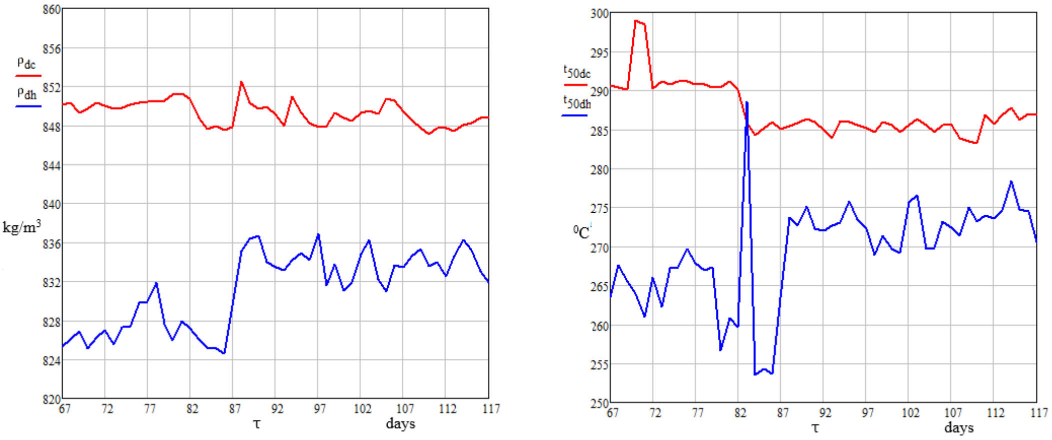

Fig. 9. Diesel density at HDS reactor inlet (red) respectively outlet (blue) and ASTM t_{50} diesel temperature at HDS reactor inlet (red) respectively outlet (blue) for monitored days

Many other monitoring data, showing dynamics of other independent and dependent variables, may be of interest for models closer to the more complex phenomenology of hydrodesulfurization. In this sense, we supplement the monitoring data with daily dynamics of i) the diesel density for reactor fed and processed diesel, respectively (Fig. 9 left) and ii) the ASTM 50% distillation temperature for the fed and processed diesel fuel (Fig. 9 right).

Before proceeding to presentation of the announced models parameter identifications, some observations are required on the monitoring data presented with Figs. (3) -(9). Here are some of these observations: i) all data presented in the aforementioned figures show that the HDS reactor operates in a stable regime; this is sustained by the fact that the daily values of the monitored variables are in line with the average or its trend, ii) there is a temperature gradient along the catalytic bed consisting of an average increase of 12 degrees between the diesel entry and exit in/from the catalytic bed (Fig. 5) and with extreme gradient of 20 ^{0}C (Fig. 5 left, day 77), iii) at the liquid and gaseous phases catalytic bed entrance occurs an arrangement of the two-phase flow structure, which is sustained by the fact that the temperature of the catalytic bed at the level of the first ring shows a much greater dispersion than those reffering to rings 2-4 (Fig. 4 right), iv) the increase in the feed diesel flow noted starting from day 103 (Fig. 5 right, day 103) is a productivity boost for reactor and in order to maintain c_{Sf} and c_{Nf} within technological limits, the increase is accompanied by an increase in temperature (Fig. 5 left, day 103) and gas flow through the bed (Fig. 6 left, day 87), v) the high gas flow rate through the catalytic bed is also strongly related to its hydrogen content; that is shown in Fig. 6 when on day 77 the hydrogen concentration in the gas drops from 95 to 87% so that the gas flow rate begin to increase consistently, vi) the trend of bed temperature increasing (Fig. 5 right), explained by some aspects such as the increase in reactor productivity, can also be associated with the slow deactivation of the catalyst, vii) the reactor response to nitrogen compounds hydrogenation (Fig. 8 left) , in conjunction with these compounds concentration in the diesel feed (Fig. 8 right), show that after day 87 it observes the efect of hidrogen concentrtion in gas (87%) and especially of decreasing of catalyst activity for this hydrogenation

Returning now to the problem of identifying the kinetic constants k_{01},E_1,b and respectively k_{02},E_2, we show that in this sense a complex numerical program was used. It was developped, as shown above, on the basis of the numerical model of the reactor with selection to express, as a function of the process factors, the sulfur (13) respectively nitrogen (14) concentration compounds, in the HDS reactor outlet stream. In the construction of the mentioned program was taken into account, the following: i) import for program use of the file with the monitored data, here given by Figs. 5 - 8; ii) the choice based on literature data [7,10,17,18,20,21, 22] of the ranges of values of Arrhenius equations parameters namely k_{01},E_1 , for sulfur compounds removing kinetic, and respectively k_{02},E_2, for nitrogen compounds case (table 2); iii) putting in program of functions $F(k_{01},E_1,b)$ and $G(k_{02},E_2)$, which minimize the mean square deviations for sulfur and nitrogen compounds respectively, and testing the $F(k_{01},E_1,b)$ behavior respect to parameter *b* (table 3); iv) applying the sensitivity procedure [23, 24] by analysis of partly derivates $\frac{\partial F(k_{01},E_1,b)}{\partial E_1}$, $\frac{\partial F(k_{01},E_1,b)}{\partial k_{01}}$, $\frac{\partial G(k_{02},E_2)}{\partial E_2}$, $\frac{\partial G(k_{02},E_2)}{\partial k_{02}}$, evolution versus k_{01},E_1 respectively k_{02},E_2 (Figs. 10 and 11) in order to establish start points in $F(k_{01},E_1,b)$ and $G(k_{02},E_2)$ minimization procedure [25], v) Use of Minimize(f, var1, var2, ...) Mathcad procedure to obtains the best values of k_{01},E_1,b, k_{02},E_2 (table 4) and the computed concentration of sulfur and nitrogen compounds in HDS reactor exit; vi) for monitoring time express graphically the daily state of computed and measured concentration for sulfur and nitrogen compounds in diesel leaving the HDS reactor (Fig. 12).

Table 2

The range of selected values for E_1, E_2 respectively k_{01}, k_{02}

E_1, E_2 ,J/kmol	$5.0\ 10^7$	$5.3\ 10^7$	$5.6\ 10^7$	$5.9\ 10^7$	$6.2\ 10^7$	$6.5\ 10^7$	$6.8\ 10^7$	$7.1\ 10^7$
k_{01}, k_{02}, h^{-1}	$4.5\ 10^4$	$4.8\ 10^4$	$5.1\ 10^4$	$5.4\ 10^4$	$5.7\ 10^4$	$6.0\ 10^4$	$6.3\ 10^4$	$6.6\ 10^4$

In the sense of the above, we show that the data from table 2 were sequenced from numerical calculation requirements associated with the sensitivity of the functions $F(k_{01}, E_1, b)$ and $G(k_{02}, E_2)$ to the parameters $k_{01}, E_1, b, k_{02}, E_2$. Likewise $k_i = k_{01} \exp(\frac{-E_i}{RT}), i = 1,2$ notes changes for the second and third decimal places of the factor that multiplies 10^X. The calculations in table 3, conditioned by the fact that F must be as small as possible, allowed the value of this parameter to be limited to subunit values in its identification together with E_1 and k_{01}.

Table 3

State of function $F(k_{01}, E_1, b)$ after *b* values for two sets of values k_{01}, E_1

b	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6
$F(2.402*10^4, 5.851*10^7, b)$	0.0058	0.0073	0.021	0.094	0.366	1.108	2.774	6.045
$F(3.402*10^4, 6.151*10^7, b)$	0.012	0.062	0.312	1.091	3.57	8.722	17.96	31.97
Acceptability	positive				negative			

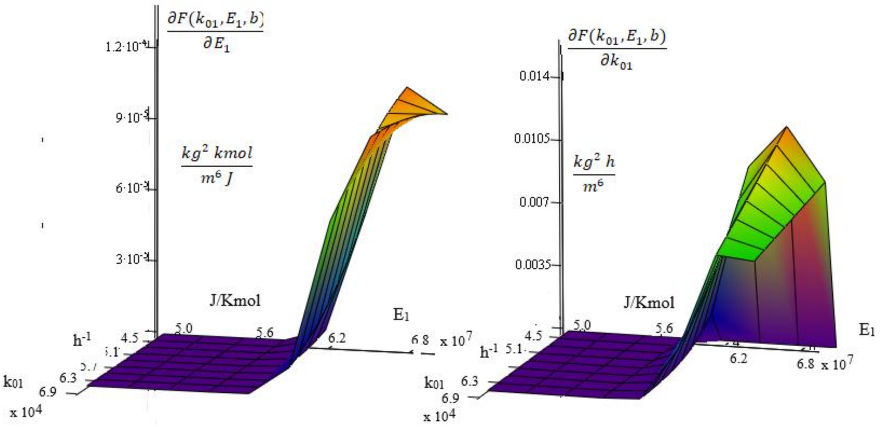

Fig. 10. Sensitivity analysis for $F(k_{01}, E_1, b)$ respect to k_{01}, E_1 parameters and with b = 0.8

The sensitivity analyses in Figs. 10 and 11 started from the general case that shows where the derivative of the function to be analyzed is active with respect to the parameter considered, then this parameter values area of the is important [24, 26]. Thus we find that in $F(k_{01}, E_1, b)$ minimizing one must search for E_1 in 5.95 - 6.75 10^7 J/Kmol (Fig. 10 left) respectively for k_{01} between 4.5 and 6.3 10^4 h^{-1} (Fig. 10 right), with E_1 in the previously specified range

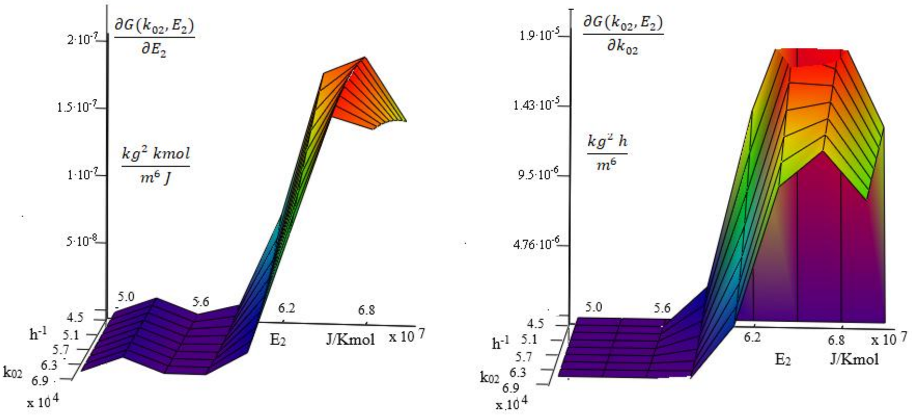

Fig. 11. Sensitivity analysis for $G(k_{02}, E_2)$ respect to k_{02}, E_2 parameters

In the case of sensitivity analysis for $G(k_{02}, E_2)$ it obtains that the range of interest for E_2 is 6.2 - 7.1 10^7 J/Kmol, whereas for k_{02} no clear range is identified (Fig. 11). Taking into account the above, the Mathcad Minimize procedure led to the identification of the parameters centralized in table 4. The activation energies and pre-exponential factors in this table are characteristics of the hydrogenation of sulfur compounds (HDS) respectively nitrogen compounds (HDN) with the catalyst used in the monitored industrial reactor.

Table 4

Identified values for the activation of energies and pre-exponential factors for sulfur and nitrogen compounds hydrogenation with the catalyst used in monitored industrial reactor

Case	Sulfur compounds hydrogenation			Nitrogen compounds hydrogenation	
Parameter	E_1 J/Kmol	k_{01} h^{-1}	b $\frac{at*m^3}{kg}$	E_2 J/Kmol	k_{02} h^{-1}
Value	6.255 10^7	4.402 10^4	0.675	6.905 10^7	3.993 10^4

The values obtained for the kinetic parameters regarding the hydrogenation of sulfur and nitrogen compounds are in the range of those in the literature regarding CoMoS catalysts, range that was taken by processing program of reactor monitoring data.

With reference to the sulfur and nitrogen content in the processed diesel, in Fig. 12, a comparison is made between the monitored (experimental) values and those calculated according to the reactor model based on LH kinetics with data from Table 4.

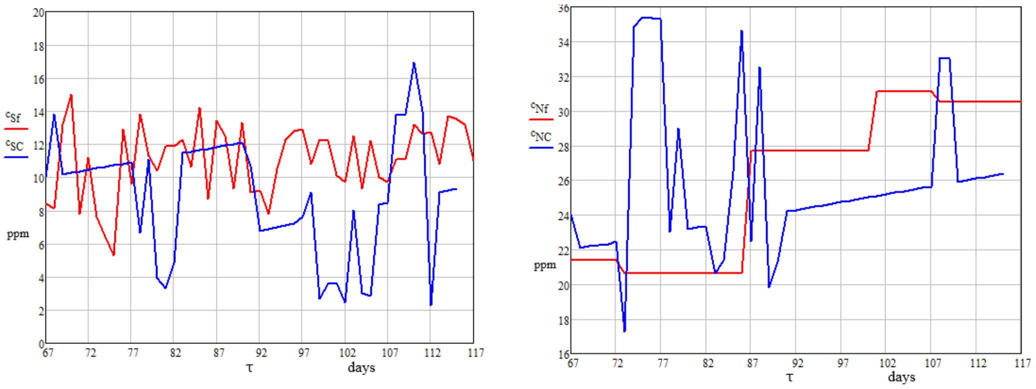

Fig. 12. Monitored (red) and model computed (blue) for sulfur concentration (left) and nitrogen (right) compounds in diesel leaving HDS reactor

From Fig. 12 it is observed that the calculated values of the concentration of sulfur and nitrogen compounds in the processed diesel adequately cover the values obtained by monitoring. In the case of nitrogen compounds concentration (Fig. 12 right) it is seen that monitoring data have small individual values (5 steps, in increase) and this fact had consequence on E_2 and k_{02} identification. The increase of this concentration, in stages (monitoring) or in overall (calculation according to the LH reactor model) may indicate the beginning of catalyst activity reduction, respect to nitrogen compounds hydrogenation.

In the case of sulfur compounds concentration in the processed diesel (Fig. 12 left) the model computed values for days 92 -107 are determined by the fact that two main model factors, namely the temperature and the flow rate of diesel, together supported low sulfur compounds concentrations. Thus, for this period, as shown in Fig. 5, the temperature was quite high (on average $360 \pm 2\ ^{0}$C and the flow rate of processed diesel was the lowest values (90 ± 3 m^3/h). It is interesting to note that after day 107 the strong increase in diesel flow rate caused the increase of sulfur content in the product and only the important increase of temperature on day 112 limits this increase. Not noticing any increase or decrease trends in both calculated and monitored sulfur concentrations, it can be considered that the activity of the catalyst for the hydrogenation of sulfur compounds remains stable for this monitoring period. The computing of mean and of standard deviation of the monitored or LH model calculated sulfur concentrations allows the expression of those from Fig. 12 right by $c_{sf} = 11.09 \pm 2.12$ ppm respectively $c_{SC} = 8.91 \pm 3.54$ ppm.

4. Conclusions

The papers is focused on the use HDS reactor model based on LH catalytic kinetics for exploitation of monitoring data from an industrial diesel HDS reactor. It was thus shown that it is necessary to express the reactor model numerically so that they highlight the influence of all the factors that can be monitored. Then, a consistent number of monitoring data on industrial reactor exploitation were brought and were systematized for graphic representations respectively for their import as exploitable files in computing program, which estimate the sensitivity of identification problem respect to the most important LH kinetics parameters of the catalyst used in HDS reactor. Activation energy of hydrogenation reactions for sulfur and nitrogen compounds, respectively the pre-exponential factors associated with these hydrogenations was considered as basic parameters of LH kinetics.

Many comments have been made on the monitoring of the industrial reactor and especially on the way of processing the monitoring data so that they allow the best identification of above-mentioned kinetic parameters of the LH kinetic models, which characterize the comportment of catalyst used in the HDS reactor.

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