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The Gasoil Hydrofining Kinetics Constants Identification

C. Patrascioiu, V. Matei, N. Nicolae

Abstract**—**The paper describes the experiments and the kinetic parameters calculus of the gasoil hydrofining. They are presented experimental results of gasoil hidrofining using Mo and promoted with Ni on aluminum support catalyst. The authors have adapted a kinetic model gasoil hydrofining. Using this proposed kinetic model and the experimental data they have calculated the parameters of the model. The numerical calculus is based on minimizing the difference between the experimental sulf concentration and kinetic model estimation.

Keywords**—**Hydrofining, kinetic, modeling, optimization.

I. INTRODUCTION

THE kinetic studies of the gasoil hidrofining are many and they are dependent of the reactant flow on the catalytic bed (bi-fazes or three-fazes). The reactor is ideal, characterized by plug flow, operated in isotherm regime.

The kinetic calculus is based on reaction time of the gaseous phase in catalytic zone. The gaseous phase is compounded by hydrogen and the feed in vaporized phase. The literature indices that the liquid phase feed may by neglected in the reaction time calculus.

The kinetic calculus has some particular forms. The Hiadar's paper considers that the reaction can be described in terms of simple first-order expression [1]. Frye and Mosby showed that the hydrodesulfurization (HDS) kinetic of the three compounds found in cycle oil feed stock followed a first order model [2]. It was proposed that the HDS reaction of petroleum distillates were also first order. The reaction of hydrodesulfurization can be described by use of two simultaneous first-order expressions, one expression for easy-to-remove sulfur and a separate expression for difficult-to-remove sulfur [1].

The hydrodesulfurization of an Arabian light atmospheric residuum could be represented as the sum of two competing first order reaction [3]. Arey et al. [4] fitted kinetic data for heavy vacuum gas oil, atmospheric residues, vacuum residue and deasphaltened residue according to this model. The reaction of hydrodesulfurization can be described using a second-order treatment [5]. Application of this model to Kuwait vacuum residue using two type of catalyst gives a liner relation. Mohammed et al [6] show that the HDS of Qaiyarah deasphaltened reduced crude followed second order kinetic. The kinetic of the catalytic HDS of the deasphaltened oil and non-asphaltenic fraction obtained from the atmospheric residue of the Greek Thasos crude oil follow second order model [7].

II. GASOIL HYDROFINING LAB EXPERIMENTS

The experimental installation is represented by a hydro-desulfurization micro-plant characterized by a catalyst bed reactor and descendent flux of the reactants and reaction products. The micro-plant is composed of the following elements: feed system (pump feed and flow rate recording), hydrogen feed (hydrogen storage, pressure reduction), catalyst bed reactor (isotherm reactor), could system, liquid - vapor separator, monitoring and control systems (Fig. 1).

The catalysts used in the lab experiments are made with Mo and promoted with Ni on aluminum support, Table I.

TABLE I
CATALYSTS USED IN THE REACTION EXPERIMENTS

Catalyst	Measurement unit	I	II	III
NiO	[% mass]	5	4.3	5
MoO3	[% mass]	14	15	16
Specific surface	[m^2 g^{-1}]		125	185
Porous volume	[cm^3 g^{-1}]		0.56	0.32
Porous medium radius	[Å]		90	40

For the first set of the experiments (catalyst I) the reaction zone volume was 50 ml, the operation pressure was of around 50 bar, and the hydrogen flow rate of 1 l/min (in normal conditions). The details of the input and output variables are presented in Table II.

TABLE II
INPUT AND OUTPUT VARIABLES

Temperature [°C]	Volume velocity [h^{-1}]	Sulf [% mass]	Sulf conversion [% mass]
340	0.84	0.0837	77.69
340	1.44	0.0771	79.45
340	2.04	0.0955	74.55
370	0.84	0.0572	84.75
370	1.44	0.0560	85.07
370	2.04	0.0635	83.08
420	0.84	0.0391	89.58
420	1.44	0.0355	90.54
420	2.04	0.0332	91.15

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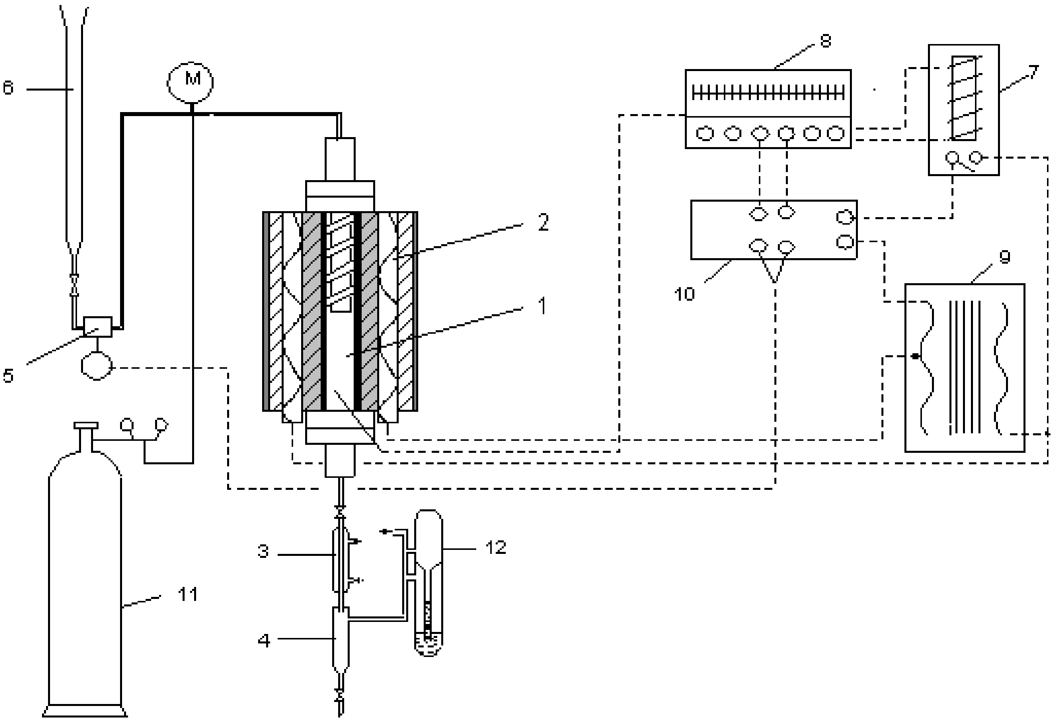

Fig. 1 Scheme of the gasoil hydrofining lab micro-plant: 1 – bed catalytic reactor; 2 – electric heating system; 3 – condenser; 4 – liquid product vessel; 5 – pump; 6 - feed vessel; 7 – electrical device; 8 – temperature controller; 10 – electric connection; 11 – hydrogen vessel; 12 - condensed products vessel

III. KINETIC MODEL

The desulfurization kinetic equation has the following form [5]:

$$-\frac{dS}{dt} = k\,S^{n}, \qquad \left[s^{-1}\right] \tag{1}$$

where *S* represents the sulfur mass concentration, *k* – reaction rate (speed), *n* – reaction order; *t* – reaction time.

As the experimental data contains both the initial and final values of the sulfur content present in the diesel fuel, it is necessary to analytically solve (1) in order to determine its unknown constants. The solution can be iteratively obtained by using the following sequence of steps:

- The separation of variables followed by the integration of each member of the following equation

$$\frac{dS}{S^{n}} = -kdt\,;$$

$$\int S^{-n} dS = -\int kdt + C\,;$$

- Match the function to integrate to the corresponding primitive from the primitive table of functions, followed by the selection of the desired primitive

$$\frac{S^{-n+1}}{-n+1} = -kt + C\,;$$

$$S^{1-n} = (1-n)(-k\,t + C)\,;$$

- The solution of the homogenous differential equation is

$$S = \left[(1-n)(-k\,t + C)\right]^{\frac{1}{1-n}}\,. \tag{2}$$

- The integration constant *C* results from the initial condition

$$S = S_0\big|_{t=0}\,. \tag{3}$$

At $t = 0$, the solution of the homogenous differential equation becomes

$$S_0 = \left[(1-n)(C)\right]^{\frac{1}{1-n}}\,,$$

and subsequently

$$C = \frac{S_0^{\,1-n}}{1-n}\,. \tag{4}$$

By combining (2) and (4), one can obtain the general solution of the differential equation

$$S = \left[-k\,t(1-n) + S_0^{\,1-n}\right]^{\frac{1}{1-n}}\,. \tag{5}$$

The kinetic model of the gasoil hydrofining reaction has two parameters: reaction order *n* and the speed reaction constant *k*. In the nest paragraph they will calculate the kinetic parameters using the experimental data.

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IV. THE KINETIC PARAMETERS CALCULUS

A. Reaction Time Problem

In order to identify the kinetic model of the process, it is necessary to determine the time of contact within the reaction. In the previous section it was shown that the raw material can only be found in a liquid phase. Therefore, in order to determine the time of contact we can consider two possible approaches:

Case 1 The time of contact is calculated from only the volumetric flow rate of the raw material;

Case 2 The time of contact is calculated from the volumetric flow rate of the hydrogen (in working conditions).

The reactor used in this model is a cylinder with a diameter of 20 mm and a volume of 50 cm^3, as in Fig. 2.

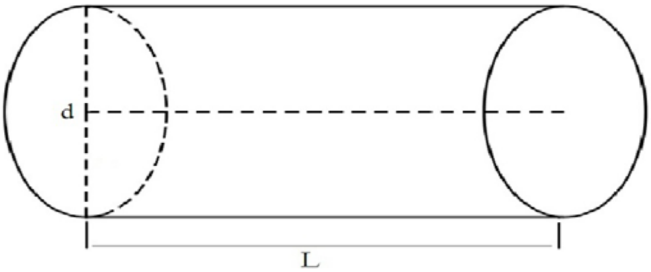

Fig. 2 The structure of the reactor

The length of the reactor is given by:

$$V_{ZR} = 50\ cm^3 = 5 \times 10^{-5}\, m^3$$

$$A = \frac{\pi d^2}{4} = \frac{3.14 \times \left(20 \times 10^{-3}\right)^2}{4} = 3.14 \times 10^{-4}\, m^2$$

$$V = L \times A \Rightarrow L = \frac{V}{A}$$

$$L = \frac{5 \times 10^{-5}}{3.14 \times 10^{-4}} = 1.59 \times 10^{-1} = 0.159\, m$$

The reaction time results from:

$$t = \frac{L}{v} = \frac{L \times A}{F} = \frac{L \times A}{\omega \times V_{ZR}} = \frac{3594}{\varpi} \qquad [\mathrm{s}] \tag{6}$$

The above variables represent:

F	- input flowrate	[m^3 h^{-1}]
ω	- volumetric velocity	[h^{-1}]
V_{ZR}	- reaction volume	[m^3]
t	- cross time of the entire reactor	[s]
L	- reactor length	[m]
v	- fluid velocity	[m s^{-1}]
A	- reactor area	[m^2]

Given that only a part of the reactor volume is free, the time of contact is correlated with the reactor free flow fraction, f_{flow}. We consider f_{flow} = 0,5, and the time of contact to be given by:

$$t = 3594 \frac{f_{flow}}{\omega}. \qquad [\mathrm{s}] \tag{7}$$

B. The Feed Characterization

The feed is a gasoil fraction, characterized by next properties: standard density 889.5 kg/m^3; molecular mass 300 kg/kmol; sulf content 0.37 % mass and the ASTM distillation curve, Table III.

TABLE III
ASTM DISTILLATION CURVE OF GASOIL

Vaporized [% volume]	Temperature [°C]
0	185
16	226
32	246
48	265
54	288
74	310

Using the UNISIM® Design petrochemical simulation program, they has been calculated the liquid-vapor equilibrium of the feed at the experimental temperature and pressure. For all experimental conditions, the calculus has indicated that feed is in liquid phase.

C. The Speed Constant Calculus Using Mono-Variable Optimization

The kinetic model contains two variables: *k* (the speed constant) and the reaction order *n*. In order to simplify the kinetic model identification, one can consider the following single variable objective function:

$$f(k) = \sum_{j=1}^{m} \left(S_j - \left[-k\, t_j (1-n) + S_0^{\,1-n} \right]^{\frac{1}{1-n}} \right)^2 \tag{8}$$

The experimental data contains pairs of variables such as (t_j, S_j), $j = 1, \ldots, m$, in which t_j is the reaction time that can be calculated using (7) from the experimental data of Table II, and S_j is the sulfur mass concentration. An analysis of the behavior of the $f(k)$ function for the particular values of $n = 1.2$ is given in Fig. 3.

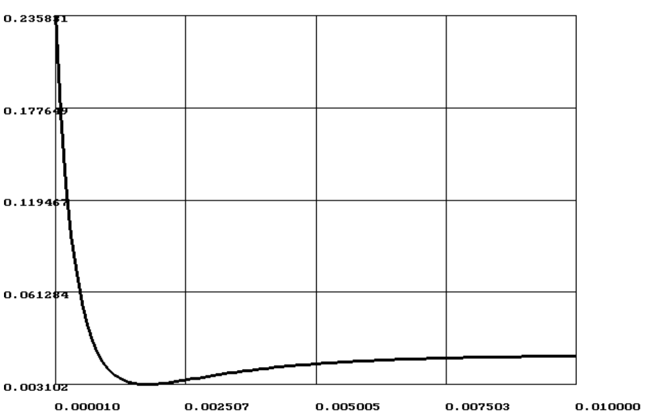

Fig. 3 Plot of the $f(k)$ function for $n = 1.2$

The numerical results contains the computation out the optimum solution after 10 successive iterations that give a value of $k = 1.7612853654 \times 10^{-3}$ for which the objective function takes the value $3.0953565128 \times 10^{-3}$. To calculate the optimum of the function (8) the authors have used the gold section algorithm [8], [9].

D.Kinetic Parameters Calculus Using Multi-Variable Optimization

In the case of considering both variables (*k* and *n*) of the kinetic model, the objective function takes the following form:

$$f(n,k) = \sum_{j=1}^{m} \left(S_j - \left[-k\, t_j (1-n) + S_0^{1-n} \right]^{\frac{1}{1-n}} \right)^2 \qquad (9)$$

In order to minimize (9), there are used an algorithm that explores on the directions of the axes of the variables, using in addition the optimization of every iterative step of the exploration [9].

The numerical solution of the calculation outputs the following values: $n = 1.8$ and $k = 5.137 \times 10^{-3}$, that are obtained after 21 successive evaluations of the objective function with an error of 10^{-4}.

As the experiments were conducted at three different temperatures, we can expect that the values of the kinetic parameters to be influenced by the thermal conditions. Therefore, for every given input temperature, the corresponding pair of variables (*n*, *k*) was determined, as shown in Table IV.

TABLE IV
THE KINETICS PARAMETERS OBTAINED BY USING MULTI-VARIABLE OPTIMIZATION

Temperature [°C]	Reaction order	Velocity constant
340	1.80	5.137×10^{-3}
370	1.55	4.854×10^{-3}
420	1.36	5.007×10^{-3}

It can be observed that the velocity parameter (k) takes an approximate constant value on the studied temperature range, with an average of about 5×10^{-3} which can be used within the model. It can also be noticed that the reaction order (*n*) depends strongly on temperature, and we find that $n(T)$ dependence could be modeled by the following second order polynomial, which constants were determined by a polynomial regression (see Fig. 4):

$$n = 1.1762 \times 10^{1} - 4.8566 \times 10^{-2}\, T + 5.6666 \times 10^{-5}\, T^{2}$$

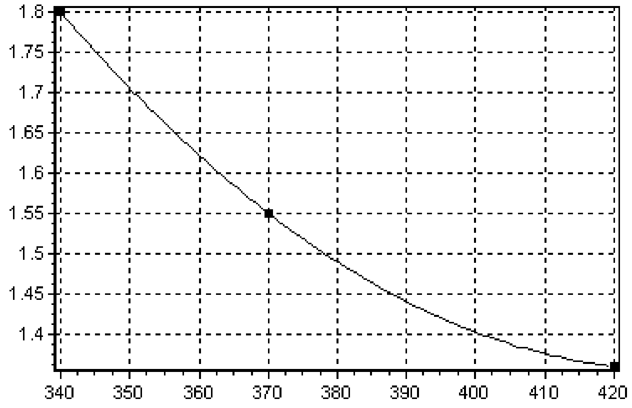

Fig. 4 The graphical regression results

V. CONCLUSION

The paper presents the experiments and the calculus of the kinetic parameters of the gasoil hidrofining reaction. There has been proposed a kinetic model of the hydrodesulfurization reaction. The hydrodesulfurization reaction has been studied in laboratory, when they have obtained some experimental data. The kinetic parameters are: reaction order n and the speed reaction constant k. They have been used two calculus modality:

a) Calculus of the speed constant using mono-variable optimization (for a value of the reaction order)
b) Calculus of the kinetic parameters using multi-variable optimization

The numerical results have indicated that the speed reaction constant is 5×10^{-3} and the reaction order depends on reaction temperature.

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