Modelling and Simulation of Gasoline Hydrofining Process

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Abstract. Gasoline hydrofining represents the catalytic treatment of commercial gasoline in order to remove sulphur and nitrogen compounds. This paper presents the authors researches concerning the mathematical modelling of the gasoline hydrofining process. In view of this purpose there was developed a software system for simulating the process. The validation of the proposed mathematical model was done analyzing the numerical results obtained from simulations. The mathematical model and software system can be used in the framework of an advanced control system for gasoline hydrofining process.

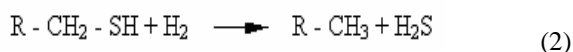**Keywords**: gasoline, hydrotreating, kinetic model, modelling, simulation

1. Introduction

Hydrogen treatment procedures for petroleum products represent nowadays a key factor in producing ecological fuels. Petroleum hydrofining reactors have a continuous development. The thermodynamic and kinetic studies are the fundamentals of mathematical modelling of hydrofining processes [1]. Aspects regarding the catalytic hydrogenation of unsaturated hydrocarbons are widely treated in literature [2], and some particular features of chemical reactors used in refineries are presented in [3].

The mathematical models for chemical reactors have various employments: dimensioning, operating, scaling, optimization and control [4, 5]. Due to the importance of the gasoline hydrofining process, the authors oriented their researches in the mathematical modelling field of this operating process.

2. Kinetic Model

The specific reactions of hydrofining mainly consist of selective hydrogenation of carbon-sulphur, carbon-nitrogen, carbon-oxygen, carbon-metal bonds and also carbon-carbon unsaturations from processed gasoline, in the presence of the catalyst formed by Ni-Mo oxides on alumina supporter. The simplified kinetic model is based on the following chemical reactions: olefins hydrogenation (1), desulphuration (2) and nitrogen removal (3):

$$R\text{-}CH=CH\text{-}CH_2\text{-}CH_3 + H_2 \longrightarrow R\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3 \quad (1)$$

$$R\text{-}CH_2\text{-}SH + H_2 \longrightarrow R\text{-}CH_3 + H_2S \quad (2)$$

$$R\text{-}CH_2\text{-}NH_2 + H_2 \longrightarrow R\text{-}CH_3 + NH_3 \quad (3)$$

The three chemical reactions are first order, the catalytic coeficient is expressed by relations like:

$$k_H = A_H e^{-\frac{E_H}{RT}} ; \quad (4)$$

$$k_S = A_S e^{-\frac{E_S}{RT}} ; \quad (5)$$

$$k_N = A_N e^{-\frac{E_N}{RT}} . \quad (6)$$

The pre-exponential factor and activation energy have the values presented in table 1 [6].

TABLE 1. The pre-exponential factor and the activation energy

Reaction	Pre-exponential factor [kg/m^3 h]	Activation energy [cal/mol]
Hydrogenation	$5 \bullet 10^9$	17300
Nitrogen removal	$4,1 \bullet 10^7$	10000
Desulphuration	$7,6 \bullet 10^5$	5850

3. Reactor Modelling

The mathematic model for hydrofining reactor is situated in the class of models for continuous tube reactors, operated in adiabatic regime. The hydrofining reactor model contains the following components:
   a) differential material balance;
   b) total material balance;
   c) differential heat balance.

The differential material balance is described by the differential equation

$$-G \cdot dc = r \cdot dV , \quad (7)$$

where G represents the total feed flowrate; c – the concentration of the referred component in the differential

equation; r – the chemical reaction rate; dV – the differential reaction zone volume.

Putting the c concentration according to the x conversion of each reaction

$$c = c_0 \cdot (1 - x), \tag{8}$$

the differential material balance becomes

$$\frac{dx}{dV} = \frac{r}{G \cdot c_0}. \tag{9}$$

Considering the hydrofining process based on the mentioned reactions from the kinetic model and noting with x_H, x_S, x_N the conversions of unsaturated hydrocarbons, of sulphur hydrocarbons and nitrogen hydrocarbons, the differential material balance has the expression

$$\begin{cases} \dfrac{dx_H}{dV} = \dfrac{k_H \cdot (1 - x_H) \cdot e^{-\frac{E_H}{RT}}}{G} \\[2ex] \dfrac{dx_S}{dV} = \dfrac{k_S \cdot (1 - x_S) \cdot e^{-\frac{E_S}{RT}}}{G} \\[2ex] \dfrac{dx_N}{dV} = \dfrac{k_N \cdot (1 - x_N) \cdot e^{-\frac{E_N}{RT}}}{G} \end{cases}. \tag{10}$$

The total material balance describes the components distribution in reactor. The raw material is assimilated to a representative hydrocarbons mixture, table 2, the calculus relations being the following:

$$Q_1 = Q_{10}(1 - x_H); \tag{11}$$
$$Q_2 = Q_{20}(1 - x_H); \tag{12}$$
$$Q_3 = Q_{30}(1 - x_S); \tag{13}$$
$$Q_4 = Q_{40}(1 - x_N); \tag{14}$$
$$Q_5 = Q_{50} + (Q_{10} - Q_1); \tag{15}$$
$$Q_6 = Q_{60} + (Q_{20} - Q_2) \tag{16}$$
$$Q_7 = Q_{70} - \frac{Q_{30}}{96}(1 - x_S) - \frac{Q_{40}}{88}(1 - x_N). \tag{17}$$

TABLE 2. The pseudocomponents from raw material

No.	Name	Medium molar mass	Concentration
1	Unsaturated	110	17,5
2	Aromatics	105	12,5
3	Sulphides	111	2500 ppm
4	Nitrates	79	40 ppm
5	Paraffins	128	42
6	Naphthenes	100	27,9
7	Hydrogen	2	-

The differential heat balance written in the vicinity of the volume element dV has the form

$$\frac{dT}{dV} = \frac{A_H \cdot c_H \cdot e^{-\frac{E_H}{RT}} \cdot (-\Delta H_H) + A_S \cdot (1 - x_S) \cdot e^{-\frac{E_S}{RT}} \cdot (-\Delta H_S)}{G \cdot c_p}. \tag{18}$$

4. Simulation Program

The simulation program was realized under PASCAL environment, using toolboxes and libraries for chemical process simulation from Petroleum-Gas University of Ploiesti [7]. The **SEuler_a** procedure was used, procedure that determine the solution of a system of first order differential equations. The logical scheme of the simulating program is presented in figure 1. The source code of PASCAL module with the mathematical model of the hydrofining reactor is presented in list 1.
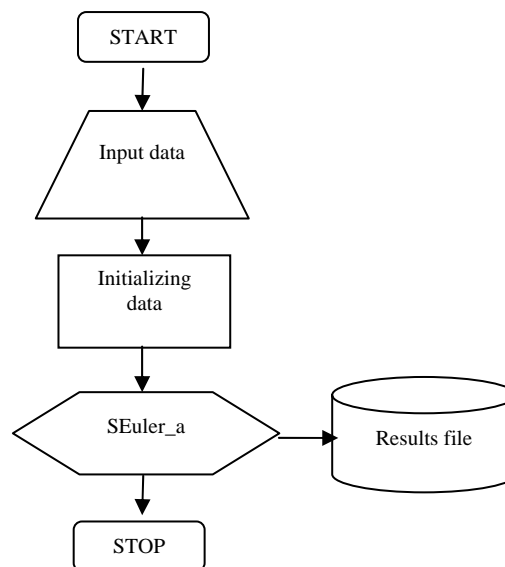

Fig. 1. The logical scheme of simulation program.

5. Numerical Results

The hydrofining reactor was simulated in real operating conditions: reactor volume $68 m^3$, inlet temperature 350ºC, operating pressure 52 bar, feed flowrate 90000 kg/h, hydrogen flowrate 2900 kg/h, and the gasoline composition presented in table 2. From figure 2 it is noticeable that the reactor volume assures high conversion of olefins hydrogenation and nitrogen removal reactions.

For the desulphuration reaction there is obtained a conversion of more than 99%, conversion that assures a final concentration of 0.2 ppm sulphur in hydrofined gasoline. The hydrofining gasoline reactor was simulated in different operating conditions. In table 3 are presented sulphur and nitrogen concentrations variations in effluent, according to inlet reactor temperature. The simulation results emphasized the fact that a growth of reaction temperature leads to a diminution of sulphur and nitrogen compounds concentrations. In figure 3 it can be seen that this diminution is more powerful in the sulphur compounds and smaller in the case of nitrogen compounds.

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List 1

The list PASCAL module containing the hydrofining reactor mathematical model

```
Procedure Model (vol:real; print:integer; var y,func:sir);
var kH,kS,kN:real;
   T:real;
begin
  T:=y[4]+273;
  for i:=1 to nc do
     begin
       conc[i]:=q[i]/Gtotal;
     end;
  kH:=5e9*exp(-17300./(1.98*T));              {kg/mc/h}
  kS:=4.1e7*exp(-10000./(1.98*T));
  kN:=7.6e5*exp(-5850./(1.98*T));
  func[1]:=kH*(1-y[1])/Gtotal;              {conversion of  hydrogenation}
  func[2]:=kS*(1-y[2])/Gtotal;              {conversion of autofining}
  func[3]:=kN*(1-y[3])/Gtotal;              {conversion of nitrogen removal}
  Q[1]:=Q0[1]*(1-y[1]);        {unsaturated}
  q[2]:=q0[2]*(1-y[1]);        {aromatics}
  q[3]:=q0[3]*(1-y[2]);        {sulphides}
  q[4]:=q0[4]*(1-y[3]);        {nitrates}
  q[5]:=q0[5]+(q0[1]-q[1]);       {paraffins}
  q[6]:=q0[6]+(q0[2]-q[2]);       {naphthenes}
  q[nc]:=q0[nc]-q0[3]/96*(1-y[2])-q0[4]/88*(1-y[3]); {hydrogen}
  if print=1 then
     begin
       write(fis_rez,vol:8:3);
       for i:=1 to 7 do
          write(fis_rez,conc[i]:12,' ');
       writeln(fis_rez);
     end;
end {model} ;
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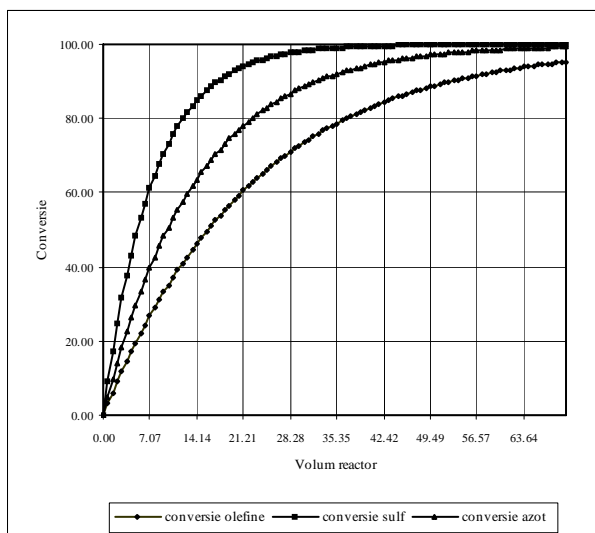

Fig. 2. The conversion variation for the three reactions.

TABLE 3. The dependency of sulphur and nitrogen concentrations in effluent, according to inlet reactor temperature

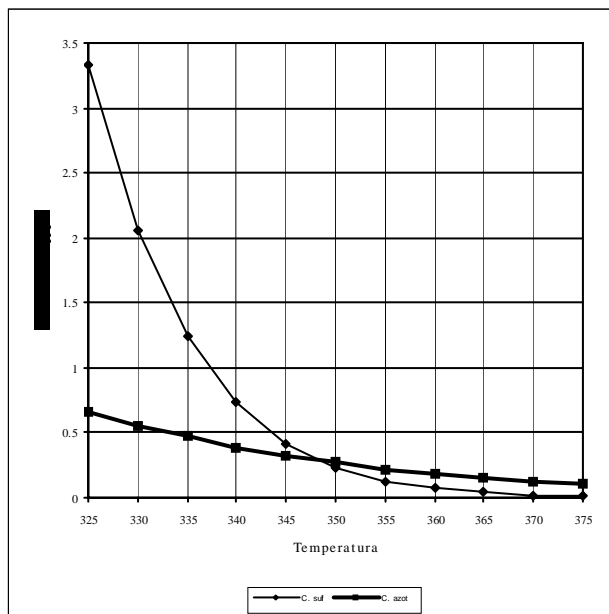| Temperature reactor ºC	Conc. sulphur, ppm	Conc. nitrogen, ppm
325	3.33	0.66
330	2.06	0.56
335	1.24	0.47
340	0.73	0.39
345	0.42	0.33
350	0.23	0.27
355	0.12	0.22
360	0.07	0.18
365	0.04	0.15
370	0.02	0.12
375	0.01	0.10

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Fig. 3. The inlet temperature influence on sulphur and nitrogen compounds concentrations.

6. Conclusions

In this paper were approached problems concerning gasoline hydrofining reactor modeling. A kinetic model of the hydrofining process was presented, based on olefins hydrogenation, autofining and nitrogen removal reactions. A mathematical model for gasoline hydrofining reactor was developed. Based on the proposed model, there was elaborated a simulation program of gasoline hydrofining process.

The simulation program was run with similar conditions to the industrial ones. The obtained results, close to the industrial data, allowed the model validation.

The proposed mathematical model can be successfully used in gasoline hydrofining process control.

References

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Notation

k_H , k_S , k_N - catalytic coefficient;

A_H , A_S , A_N - pre-exponential factor;

E_H , E_S , E_N - activation energy;

x_H , x_S , x_N - conversions;

$Q_i, i = 1,\dots,7$ - raw material of compounds.