Five-Lump Kinetic Model for the Catalytic Cracking Process

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The main objectives of the present paper are to adaptation the five-kinetic model of the catalytic cracking process and simulation the riser to predicts the FCC products yields when one of the major input variable of the process is change. The simulation and adaptation are based on the industrial data from Romanian refinery. The adaptation is realize using a computational method from Optimization Toolbox from Matlab programming language. The new model can be used for optimization and control of FCC riser.

Keywords: kinetic model, simulation, adaptation, catalytic cracking

The cracking catalytic is the most important process for secondary petroleum processing, that convert the heavy oil fractions like vacuum distillate or residues into more suitable products such as gasoline with high octane number and C_1-C_4 gases used in petrochemical industry for manufacturing of octane components by modern methods like alkylation, oligomerization and etherification [1].

The cracking catalytic process is divided into riser-reactor, regenerator and main fractionator. The fresh feed and regenerate catalyst are injected into bottom of the riser, where occurs all the endothermic cracking reactions. Numerous papers have been emphases different kinetic models to study this endothermic reactions and how economic benefits of process could be considerably increased [2-8]. Also, many studies involve the simulation of the cracking catalytic process [9-12]. In this paper, the objectives are: i)modelling the cracking catalytic riser associate with five lumps-kinetic model; ii) determination of kinetic model parameters by a special adaptation method using computational method from MATLAB and industrial data; iii) prediction the effect of operating variables on the riser temperature and product yields. The operating variables include the feedstock temperature, feedstock flow rate, regenerate catalyst temperature, regenerate catalyst flowrate. The products of interest are the gasoline, dry gas, LPG (liquefied product gas), coke, output temperature riser and feed injection riser temperature.

Experimentl part

The data for determination of the kinetic parameter of proposed model are obtained by testing an industrial cracking catalytic process presented in tables 1. The FCC industrial unit processes vacuum distillate over zeolite catalyst.

Nr test	Feedstock temperature[^{0}C]	Regenerate catalyst temperature[^{0}C]	Feedstock flow rate [kg/h]	Regenerate catalyst flow rate [kg/h]
1	292	672	126500	755880
2	272	668	122000	823540
3	296	680	109800	541560
4	302	675	136200	878060
5	321	655	127850	936830
6	275	675	131400	849400
7	276	660	115000	825670
8	292	665	132100	914100
9	320	675	120500	854490
10	264	660	121800	823460

Table 1
INDUSTRIAL RISER PARAMETERS

The riser modelof cracking catalytic process

The model of the riser contains the following components: the five-lump kinetic model, the material balance and heat balance equations.

The five-kinetic model is based on five lumps reaction schema depicted in figure 1. The expressions of the chemical reaction rates are presented in table 2.

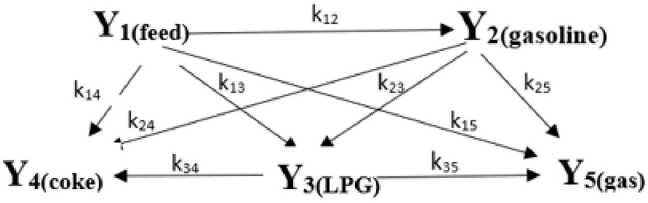

Fig.1 Five- kinetic model [13]
(Y_{1feed}-wt.fr.feedstock, $Y_{2gasoline}$-wt.fr gasoline ,Y_{3LPG}-wt.fr liquefied product gas, Y_{4gas} -wt.fr dry gas, Y_{5coke} -wt.fr coke, k_{ij}- reaction constant rate.

The effect of catalyst is quantified by an exponential deactivation function

$$f(t_c) = e^{-a_{dez} \cdot t_c} \qquad (1)$$

where: a_{dez}- the deactivation velocity constant [1/s]; t_c- catalyst residence time in riser [s].

The constants of the reaction rates k_{ij} are obtained by following relations:

$$k_{ij} = k_{ij}^0 \cdot e^{-a_{dez} \cdot t_c} \cdot \qquad (2)$$

were E_{ij} - activation energies [kcal/mol][2], R- universal gas constant [1.98 kcal/mol.°K], T- curent riser temperature [°C], T_0- reference temperature [482°C], k^o_{ij}- reaction constant rate at 482°C.

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Table 2

THE CHEMICAL REACTIONS OF THE FIVE KINETIC MODEL

Reaction	*Reaction rate*
$Y_1 \longrightarrow Y_2$	$r_{12} = -k_{12} \cdot Y_{1feed}^2$
$Y_1 \longrightarrow Y_3$	$r_{13} = -k_{13} \cdot Y_{1feed}^2$
$Y_1 \longrightarrow Y_4$	$r_{14} = -k_{14} \cdot Y_{1feed}^2$
$Y_1 \longrightarrow Y_5$	$r_{15} = -k_{15} \cdot Y_{1feed}^2$
$Y_2 \longrightarrow Y_3$	$r_{23} = -k_{23} \cdot Y_{2gasoline}$
$Y_2 \longrightarrow Y_4$	$r_{24} = -k_{24} \cdot Y_{2gasoline}$
$Y_2 \longrightarrow Y_5$	$r_{25} = -k_{25} \cdot Y_{2gasoline}$
$Y_3 \longrightarrow Y_4$	$r_{34} = k_{34} \cdot Y_{3LPG}$
$Y_3 \longrightarrow Y_5$	$r_{35} = k_{35} \cdot Y_{3LPG}$

The material balance

The riser is a plug flow tubular reactor under adiabatic conditions. To calculate the concentration profile for each lump throughout the riser height, a differential material balance can be applied along the riser, the following next equation thus being obtained [14]

$$\frac{1}{\rho_v} \cdot \frac{\partial(\rho_v \cdot Y_j)}{\partial t_c}\bigg|_z + U_v \cdot \frac{\partial Y_j}{\partial z}\bigg|_{t_c} = R_j \qquad (3)$$

where $j=1\text{-}5$, ρ_v - vaporsdensity [kg/m^3], U_v - vapors velocity[m/s], z -length of riser [m], Y_j- mass fraction for pseudocomponent of reaction[kg/kg$_{vap}$].

As shown in the following papers [2], the riser is a system without inertia, in which the first term $\frac{1}{\rho_v} \cdot \frac{\partial(\rho_v \cdot Y_j)}{\partial t_c}\Big|_z$ can be neglected. Under these conditions, the equation (2) becomes:

$$U_v \cdot \frac{\partial Y_j}{\partial z}\bigg|_{t_c} = R_j \qquad (4)$$

The vapors velocity is expressed by the relation:

$$U_v = \frac{Q_{feed}}{\rho_v \cdot A_r \cdot \varepsilon} \qquad (5)$$

where Q_{feed} is the feedstock flow rate [kg/h], ρ_v - vapors density [kg/m^3], A_r-riser cross section area[m^2], e -avoid volume fraction of the catalyst.

The heat balance.

The variation of temperature along the riser is determinate from heat balance equation on volume element of reactor ($dV_r = A_r \cdot dz$), where heat lost is neglected. There are describe by equations (6-8) and illustrated in figure 2.

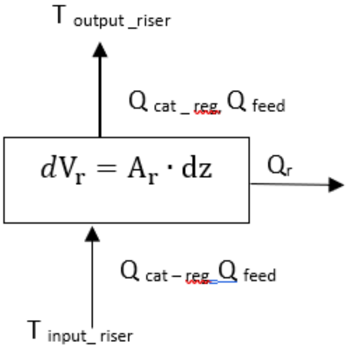

Fig.2. Heat balance on the element of riser volume

(Q_{feed}-feedstock flow rate; $Q_{cat.-reg}$-regenerate catalyst flow rate; Q_r-heat of catalytic cracking reaction)

$$Q_i = Q_{feed} \cdot \left(c_{pfeed} + a \cdot c_{pcat}\right) \cdot T_{input\_riser} \qquad (6)$$

$$Q_e = Q_{feed}\left(c_{pfeed} + a \cdot c_{pcat}\right) \cdot T_{output\_riser} + Q_r \qquad (7)$$

where: c_{pcat}- heat capacity of catalyst, [kJ/kg °C], c_{pfeed}- heat capacity of feedstock in vapor phase, [kJ/kg °C], a= Q_{cat_reg}/ Q_{feed} - catalyst feed ratio, [kg/kg].

To simplify the heat balance equation,the global heat effect of catalytic cracking reaction was considered as heat of gasoline reaction formation R_2

$$Q_r = Q_{R2} \cdot R_2 \cdot \Delta z \cdot A_r \cdot M_{Y2gasoline} \qquad (8)$$

where: Q_{R2}-heat of reaction for gasoline formation, [kJ/kg$_{gasoline}$]; R_2- gasoline formation rate, [kmol$_{gasoline}$/m^3 h]; $M_{Y2gasoline}$- molecular weight of gasoline, [kg /kmol]; Δz-height of elemental riser volume, [m]; A_r- riser area, [m^2].

From Q_i=Q_e results:

$$\frac{dT_{riser}}{dz} = -\frac{\frac{dY_{2gasoline}}{dz} \cdot Q_{R2} \cdot \Delta z \cdot A_r \cdot M_{y2gasoline}}{c_{pfeed} + a \cdot c_{pcat}} \qquad (9)$$

The material and heat balance can be described by following system of differential equations with distributed parameters:

$$\begin{cases} \frac{dY_{1feed}}{dz} = -\frac{1}{U_v} \cdot (k_{12} + k_{13} + k_{14} + k_{15}) \cdot Y_{1feed}^2 \\ \frac{dY_{2gasoline}}{dz} = \frac{1}{U_v}\left(k_{12} \cdot Y_{1feed}^2 \text{-} (k_{23} + k_{24} + k_{25}) \cdot Y_{2gasoline}\right) \\ \frac{dY_{3LPG}}{dz} = \frac{1}{U_v}\left(k_{13} \cdot Y_{1feed}^2 + k_{23} \cdot Y_{2gasoline} - (k_{34} + k_{35}) \cdot Y_{3LPG}\right) \\ \frac{dY_{4coke}}{dz} = \frac{1}{U_v}\left(k_{14} \cdot Y_{1feed}^2 + k_{24} \cdot Y_{1gasoline} + k_{34} \cdot Y_{3LG}\right) \\ \frac{dY_{5coke}}{dz} = \frac{1}{U_v}\left(k_{15} \cdot Y_{1feed}^2 + k_{25} \cdot Y_{2gasoline} + k_{35} \cdot Y_{3LPG}\right) \\ \frac{dT_{riser}}{dz} = -\frac{\frac{dY_{2gasoline}}{dz} \cdot Q_{R2} \cdot \Delta z \cdot A_r \cdot M_{Y2gasoline}}{c_{pfeed} + a \cdot c_{pcat}} \end{cases} \qquad (10)$$

No.	Pseudocomponents distribution, %gr.				
Test	Y_{1feed}-Feed(wt.fr.)	$Y_{2gasoline}$gasoline(wt.fr)	Y_{3LPG}-LPG(wt.fr)	Y_{4coke} Coke(wt.fr)	Y_{5gas} Dry gas(wt.fr)
1	0.277	0.4611	0.1168	0.054	0.0974
2	0.282	0.4521	0.115	0.0526	0.0974
3	0.322	0.4426	0.096	0.0525	0.086
4	0.303	0.4115	0.117	0.0565	0.112
5	0.264	0.4523	0.1149	0.0575	0.111
6	0.2842	0.456	0.1236	0.0526	0.0836
7	0.2429	0.4570	0.1345	0,0602	0.1054
8	0.2454	0.4608	0.1292	0.0558	0.1088
9	0.2691	0.4452	0.1305	0.0566	0.0986
10	0.2678	0.4714	0.1146	0.0573	0.0875

Table 3
REACTION PRODUCTS DISTRUBUTIONS

Results and discussions

Determination of kinetic model parameters

The products reation yields obtained from experimental data are presented in table 3.

The kinetic parameters of the model are determined by *adjustment* procedure, that starting from a set of proposed parameters, is changing these parameters until the deviation between experimental data and model data is appropriate. Determination of model parameters is an optimization procedure (minimization) where the objective function is describing by the sum of squares of deviations between industrial data and model data [15].

The proposed objective function is:

$$F_{ob} = \sum_{j=1}^{n} \sum_{i=1}^{5} \left(Y_{ij}^{exp} - Y_{ij}^{mod}\right)^2 \qquad (11)$$

where Y_{ij}^{exp}–wt.fr. of pseudocomponent j from expermental data, tabel 3; Y_{ij}^{mod}–wt.fr of pseudocomponent predicted by model; n-number of experimental data.

For the minimization of the objective function (11) it used Nelder-Mead algorithm from Optimization Toolbox from Matlab. The algorithm determines the minimum of the nonlinear, multivariable objective function without restrictions and without using the functions derivation. In table 4 are presented the values of kinetic parameters determinate by adjusted procedure.

By solving the differential equation systems (10) for data set case study the temperature and the lump profile of the five groups along the riser are presented in tabel 5, (feedstock flow rate - Q_{feed}=126500kg/h, regenerate catalyst flow rate-$Q_{cat\_reg.}$=755880 kg/h, feedstock temperature – T_{feed} =292°C and catalyst regenerate temperature - T_{cat_reg}=672°C) figure 1 and 2.

The reaction constant ratek_{ij}^{o}	Value
k_{12}^{0}	0.516
k_{13}^{0}	0.121
k_{14}^{0}	0.002
k_{15}^{0}	0.018
k_{23}^{0}	0.022
k_{24}^{0}	0.001
k_{25}^{0}	0.006
k_{34}^{0}	0.0007
k_{35}^{0}	0.001

Table 4
KINETIC PARAMETERS OF MODEL

The results have proved a typical behavior of the fluid cracking catalytic process, figure 3 and 4. Both the temperature in the reactor and the feedstock yield decrease exponentially with the riser heigh. The gasoline yield, increase fastly to a maximum value around the half of riser height and then increase is very slowly due the succesive chemical rections character, asshowed in kintetic reaction schema, respectively figure 1. LPG, dry

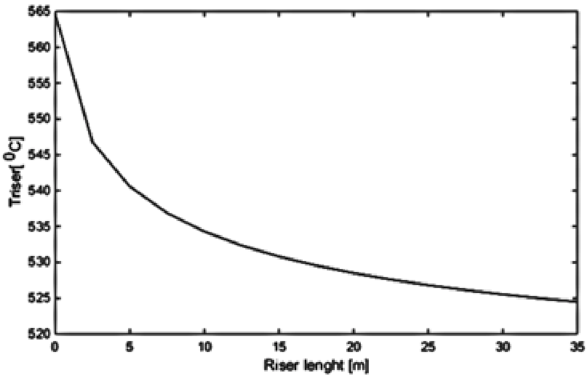

Fig.3. Temperature riser profile along the riser.

H.riser, m	Yields, wt. fr					Temperature °C
	Y_{1feed}-Feed	$Y_{2gasoline}$Gasoline	Y_{3LPG}-LPG	Y_{4coke} Coke	Y_{5gas} Dry gas	
0.0	1	0	0	0	0	564.620
2.5	0.629	0.274	0.041	0.038	0.018	546.775
5.0	0.508	0.357	0.060	0.052	0.025	540.583
7.5	0.437	0.401	0.073	0.060	0.029	536.880
10.0	0.388	0.429	0.084	0.066	0.033	534.299
12.5	0.352	0.448	0.094	0.070	0.036	532.355
15.0	0.324	0.462	0.103	0.073	0.038	530.817
17.5	0.301	0.472	0.110	0.076	0.041	529.559
20.0	0.282	0.479	0.118	0.079	0.043	528.505
22.5	0.265	0.485	0.124	0.081	0.045	527.604
25.0	0.251	0.489	0.131	0.083	0.047	526.823
27.5	0.239	0.492	0.137	0.084	0.048	526.138
30.0	0.228	0.494	0.142	0.086	0.050	525.529
32.5	0.218	0.495	0.148	0.087	0.052	524.985
35.0	0.210	0.496	0.153	0.088	0.053	524.495

Table 5
FIVE GROUPS CONCENTRATION AND TEMPERATURE PROFILE ALONG THE RISER

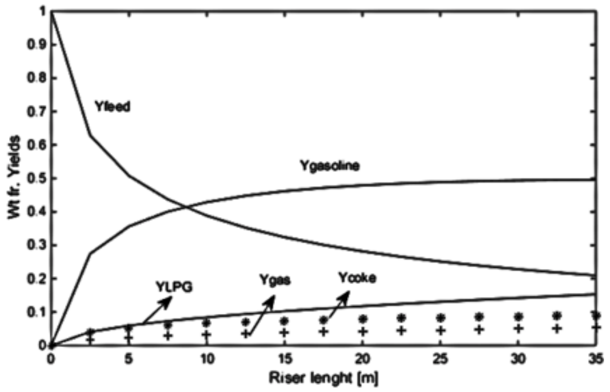

Fig.4. Profiles of the pseudo-components along the riser

gas and coke yileds increase slowly with riser length(fig. 3).

The model simulation

The riser performances were established by model simulation for the main input operating variables (feedstock flow rate - Q_{feed}, regenerate catalyst flow rate- $Q_{reg.cat.}$, and regenerate catalyst temperature - $T_{cat.reg}$).

When the feedstock flow rate is increased while catalyst regenerate flow rate, feedstock temperature and catalyst regenerate temperature are maintained constant, is leading to decreasing of the input and output riser temperature and reaction of the reaction time (fig. 5). As result, the conversion of feedstock is decreasing, as illustrated in figure 6 and yield gasoline is increasing up to the maxim value and after that starts to decrease like in figure 7. The decrease of feedstock conversion is kinetic justified due to reduction of the temperature and reaction time. As mentioned in literature [1], for a successive chemical reaction where gasoline is intermediate product, (fig. 1), the gasoline yield increases in the same time with reaction time and after a specific moment is starting to decrease because the gasoline is converted in gas.For a successive process, the decreases of the reaction temperature is leading to increasing of intermediary product yield (gasoline) as a result reduction the velocity of the conversion reaction of gasoline into gas which has an activation energy higher in the report with velocity of conversion reaction of feedstock into gasoline that has a more higher activation energies [1]. Increases feedstock flow rate influences the decreasing GPL yield and dry gas yield due to drop of the reaction time, as shown in figure 8. The slow increasing of the coke yield due gasoline yield increases is caused by lowered reaction temperature which will lead to coke reactions with activation energies smaller than the higher activation energies of the formation reaction of gases [1].

The coke yield is slowly decreasing, because the coke formation reaction has lower activation energies than feedstock conversion (fig.12) [1].

Figures 9-12 shown the influence of the regenerate catalyst temperature on the riser performance. If the feedstock temperature, catalyst flow rate and feedstock flow rate are maintained constant, then the increases of the regenerate catalyst temperature is leading to the increasing of feed injection temperature, as illustrated in figure 9. The feedstock conversion increase with the regenerated catalyst temperature due the increasing of riser temperature, as presented in figure 10. The increasing the riser temperature will reduce the gasoline yield (fig. 11) and will increase the gas yields (fig. 12), because at

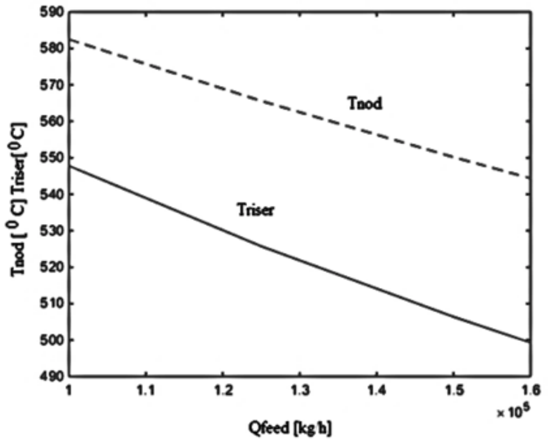

Fig. 5. The influence of feedstock flow rate on the output riser temperature and feed injection temperature.

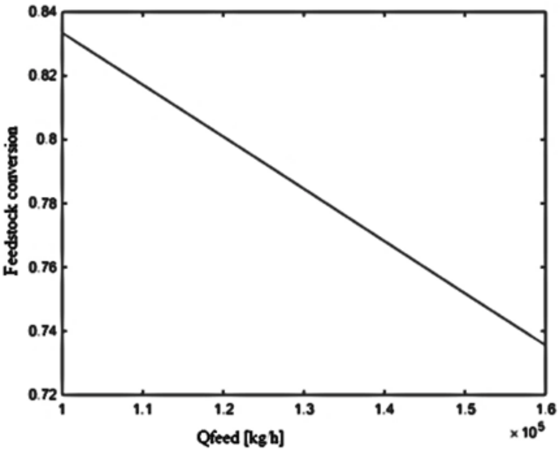

Fig. 6. The influence of feedstock flow rate on the conversion

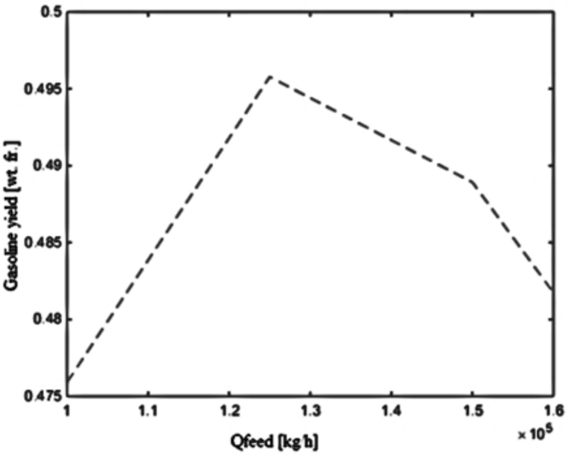

Fig. 7. The influence of the feedstock flow rate on gasoline yields

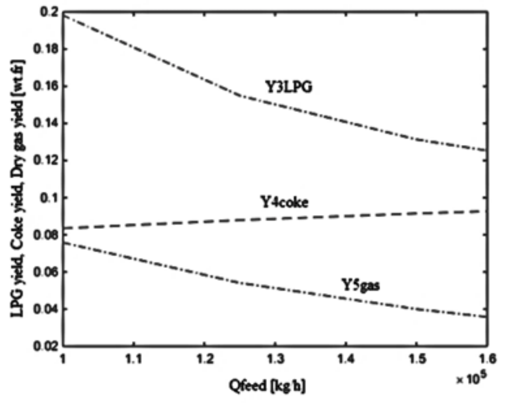

Fig. 8. The influence of feedstock flow rate on Coke, LPG and Dry gas yields

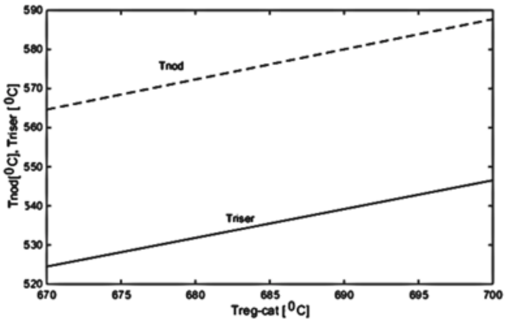

Fig. 9. The influence of the regenerate catalyst temperature on the output riser temperature and feed injection temperature.

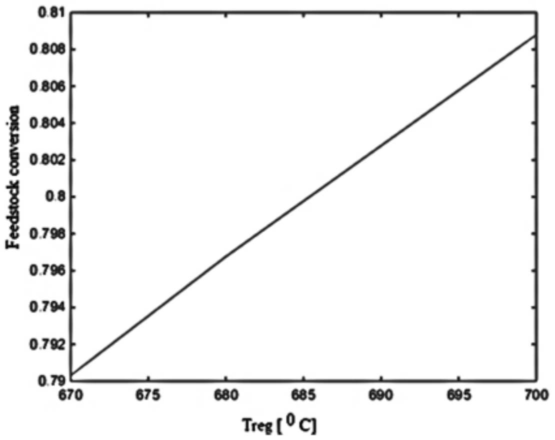

Fig. 10.The influence of regenerate catalyst temperature on the conversion.

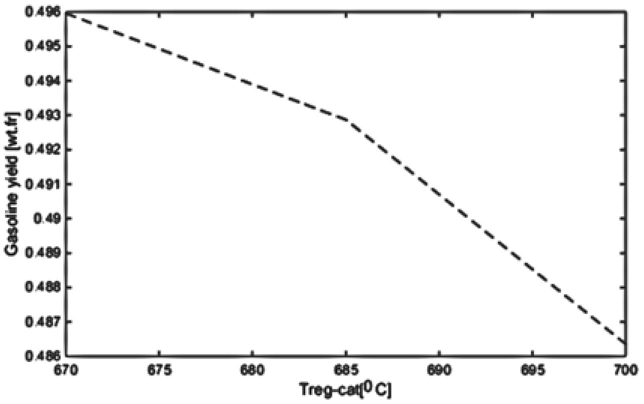

Fig. 11. The influence of the regenerate catalyst temperature on the gasoline yields

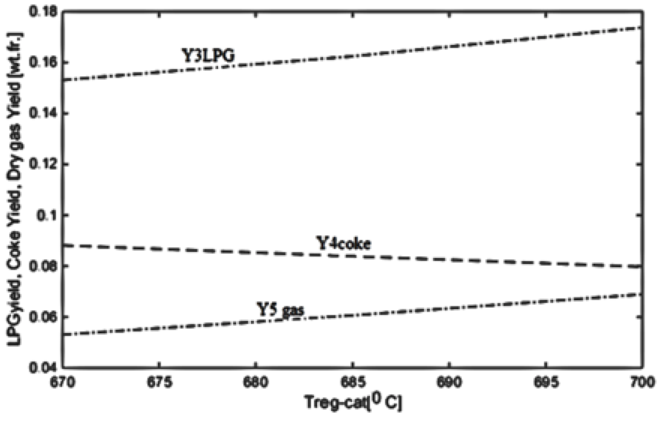

Fig. 12. The influence of the regenerate catalyst temperature on the LPG, Coke and Dry gas yields.

higher reaction temperature will be intensified the conversion reactions from gasoline to gas with higher activation energy than gasoline from feedstock with lower activation energies.

The regenerate catalyst flow rate has the same effect on the riser performance like the regenerate catalyst temperature due the similar influence on the riser temperature profile.

Conclusions

The mathematical model of riser has been elaborated based on kinetic schema with five pseudocomponents differentiated by distillation limits: feedstock, gasoline, LPG, coke and dry gas. The equations model was solved using computer code Matlab.

The kinetic parameters of model were determined by adjusting procedure for velocity constant which corresponds to the reactive scheme using o minimization procedure. It was started from a proposed set of parameters, after that are changed until the adequacy between experimental data and model is agreed. This validated model is used to highlight the effect of the main operating variables of the riser expressed through conversion performance, gasoline yield, coke yield, dry gas yield, and LPG yield. The simulation results of the riser mathematic model allow to choice the domain of operating parameters in order to allow maximum performance of cracking catalytic process.

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