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Four – Lump Kinetic Model vs. Three - Lump Kinetic Model for the Fluid Catalytic Cracking Riser Reactor

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Abstract

The paper presents the research and the results obtained by the author concerning the kinetic modeling of the riser of the catalytic cracking unit. This study is structured in four parts. The first part presents the process description and the actual kinetic model existent in the special literature. The next part contains a detailed presentation of the two kinetic models developed by the author for the catalytic cracking riser reactor (four and three lump kinetic model). The final part presents the comparison results of the three and four lump kinetic model. The results reveal the 4 lump kinetic model is more appropriate to represent the kinetic model of the catalytic cracking process, in the sense that a higher gasoline yield is thus obtained, whereas a lower quantity of coke is obtained.

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Keywords: kinetic model; fluid catalytic cracking; simulation

1. Introduction

The fluid catalytic cracking plant (FCC) ensures the conversion of the heavy fractions into a high octane number gasoline (the main element in the commercial gasoline) and olefin – rich gases (the feed stock in the petrochemical industry). The fluid catalytic cracking unit, consists of two pieces of equipment: the riser reactor, where almost the endothermic cracking reactions and coke deposition on the catalyst occur, and the regenerator reactor, where air is used to burn off the accumulated coke [1]. The regenerator is a complex system, assimilated to a reactor with perfect mixing, whose aim is the catalyst regeneration by the partial burning of the coke deposited on the catalyst. The riser reactor is the most important equipment in an FCC unit. The modeling of a riser reactor is very complex due to

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many complex reactions occurred in the riser, coupled with mass transfer resistance, heat transfer resistance and deactivation kinetics. A complete model of the riser reactor should include all the important physical phenomena and detailed reaction kinetics [2].The first kinetic model, developed by Weekman, is based on three lumps and it may be applied to any type of feedstock [3]. Starting from this model, other kinetic models were developed, based on 4- lumps [4, 5, 6], 5 –lumps [7, 8], 6 –lumps [9], 10-lumps [10], 11-lumps [11], 19-lumps [12]. Table 1 presented the most important kinetic models developed in the last 30 years.

Table 1. Kinetic models for the catalytic cracking process.

Number of lumps	Year of appearance	References
3-lump	1968	[3]
4 -lump	1989	[4, 5, 6]
5 -lump	1991	[7,8]
6- lump	1984	[9]
10-lump	1970	[10]
11-lump	1995	[11]
19-lump	1994	[12]

Nomenclature

a	contact ratio
A_r	riser cross section area
c_{pi}	heat capacity of i^{th} lump
$c_{p,A}$	heat capacity of the feedstock
$c_{p,abur}$	heat capacity of the steam
$c_{p,cat}$	heat capacity of the catalyst
E	volume fraction of the catalyst
E_j	reaction activation energy of j^{th} reaction
H_{rj}	enthalpy for j^{th} reaction
k_j	reaction velocity constants of j^{th} reaction
k_j^0	frequency factor or preexponential factor for j^{th} reaction
nc	number of lump
nr	number of reaction
r_j	reaction velocity of j^{th} reaction
R	universal ideal gas constant
Q_{mp}	feedstock flow
Q_{abur}	steam flow
Q_{rj}	mass flow of the reacted compound
t_c	catalyst residence time
T_0	reference temperature
T_{nod}	interfusion node temperature
Uv	riser vapours velocity
Y_i	weight fraction of i^{th} lump
z	spatial coordinate associated to the riser
ρ_v	density vapour

2. Models of the riser

The mathematical model of the riser contains the following components: the kinetic model, the material balance and the heat balance.

2.1. Kinetic models

Because the mathematical model of the riser will be used in a control system of the process, the author has chosen two simple, but robust models, which are the Weekman kinetic model based on 3 lumps and the Gianetto kinetic model based on four lumps.

The Weekman kinetic model is based on three lumps as follows: feedstock – A, gasoline –B, gases and coke – C, depicted in figure 1a. The expressions of the chemical reactions are presented in table 2.

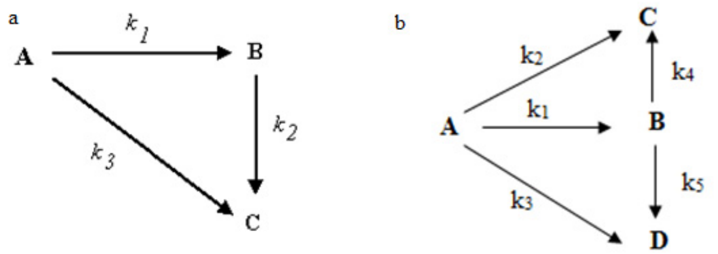

Fig. 1. a) The Weekman kinetic model; b) The Gianetto kinetic model.

Table 2. The chemical reactions in the Weekman kinetic model.

Reaction	Reaction velocity
$A \rightarrow B$	$r_1 = -k_1\, Y_A^2$
$B \rightarrow C$	$r_2 = -k_2\, Y_B$
$A \rightarrow C$	$r_3 = -k_3\, Y_A^2$

The Gianetto kinetic model is based on four lumps as follows: feedstock – A, gasoline –B, gases – C and coke – D, illustrated in figure 1b. The expressions of the chemical reactions are presented in table 3.

Table 3.The chemical reactions in the Gianetto kinetic model.

Reaction	Reaction velocity
A ⟶ B	$r_1 = -k_1 \cdot Y_A^2$
A ⟶ C	$r_2 = -k_2 \cdot Y_A^2$
A ⟶ D	$r_3 = -k_3 \cdot Y_A^2$
B ⟶ C	$r_4 = -k_4 \cdot Y_B$
B ⟶ D	$r_5 = -k_5 \cdot Y_B$

The constants of the reaction velocity k_j are obtained based on Arrhenius' law, being dependent on the temperature in the riser and the reaction activation energy E_j. In order to determinate these constants, the following relations are used:

$$k_j = k_j^0 \cdot e^{\left(\frac{E_j}{R}\right)\left(\frac{1}{T_0} - \frac{1}{T}\right)} \tag{1}$$

2.2. The material balance

The riser is a plug flow tubular reactor under adiabatic conditions. In order 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 [3]

$$\frac{1}{\rho_v} \cdot \left.\frac{\partial(\rho_v \cdot Y_j)}{\partial t_c}\right|_z + U_V \cdot \left.\frac{\partial Y_j}{\partial z}\right|_{t_c} = R_j \tag{2}$$

where $j=3$ in the case of the Weekman kinetic model and $j=5$ in the case of the Gianetto model.

As shown in the following papers [13, 14], the riser is a system without inertia, in which the first term $\frac{1}{\rho_v} \cdot \left.\frac{\partial(\rho_v * Y_j)}{\partial t_c}\right|_z$ can be neglected. Under these conditions, the equation (1) becomes

$$U_V * \left.\frac{dY_j}{dz}\right|_{t_c} = R_j \tag{3}$$

The vapour velocity is expressed by the relation

$$U_V = \frac{Q_{mp}}{\rho_v * A_r * E}, \tag{4}$$

2.3. The heat balance

The heat balance is also described by the next differential equations

$$\sum_{i=1}^{nc} Q_i cp_i \frac{dT_r}{dz} = \sum_{j=1}^{nr} (-\Delta H_{rj}) * Q_{rj}\ , \tag{5}$$

where $nc=3$ in the case of the Weekman kinetic model and $nc=5$ in the case of the Gianetto model.

The simplified assumptions taken into account for the heat balance are:

- neglecting the heat contributions of the pseudo- components represented by gasoline and gases and coke, due to small flows and heat capacities;
- neglecting the heat effect resulted by the transformation of the gasoline into gases and coke, due to the reduced conversion of the gasoline into gases and coke and the values of the enthalpy of these reactions.

The material and heat balance can be described by a system of differential equations with distributed parameters, as presented in table 4.

By solving the differential equation systems from table 4 we can obtain the temperature profile along the riser and the lump profile of the kinetic scheme along the riser.

Table 4. The kinetic models.

The model	System of differential equations	The initial conditions
3 lump kinetic model	$\begin{cases} \frac{dY_A}{dz} = -\frac{1}{U_v}\left(k_1 + k_3\right) Y_A^2 \\ \frac{dY_B}{dz} = \frac{1}{U_v}\left(k_1 Y_A^2 - k_2 Y_B\right) \\ \frac{dY_C}{dz} = \frac{1}{U_v}\left(k_2 Y_B + k_3 Y_A^2\right) \\ \frac{dT_r}{dz} = \left(-\frac{dY_A}{dz}\right) * \frac{\left(-\Delta H_{r1}\right)}{\left(Y_A c_{p,A} + Q_{abur} c_{p,abur} + a \cdot c_{p,cat}\right)} \end{cases}$	$\begin{cases} Y_A(0) = 1 \\ Y_B(0) = 0 \\ Y_C(0) = 0 \\ T(0) = T_{nod} \end{cases}$
4 lump kinetic model	$\begin{cases} \frac{dY_A}{dz} = -\frac{1}{U_v}\left(k_1 + k_2 + k_3\right) Y_A^2 \\ \frac{dY_B}{dz} = \frac{1}{U_v}\left(k_1 Y_A^2 - (k_4 + k_5) Y_B\right) \\ \frac{dY_C}{dz} = \frac{1}{U_v}\left(k_4 Y_B + k_2 Y_A^2\right) \\ \frac{dY_D}{dz} = \frac{1}{U_v}\left(k_3 Y_A^2 + k_5 Y_B\right) \\ \frac{dT_r}{dz} = \left(-\frac{dY_A}{dz}\right) * \frac{\left(-\Delta H_{r1}\right)}{\left(Y_A c_{p,A} + Q_{abur} c_{p,abur} + a \cdot c_{p,cat}\right)} \end{cases}$	$\begin{cases} Y_A(0) = 1 \\ Y_B(0) = 0 \\ Y_C(0) = 0 \\ Y_D(0) = 0 \\ T(0) = T_{nod} \end{cases}$

3. Comparison of kinetic models

For the simulation of the two kinetic models presented in this paper, the author has developed two simulators using the SIMULINK. The SIMULINK is a *MATLAB*-based software package for the process' simulation. For the simulations are used the constructive data from an industrial unit from Romania, presented in table 5, and the constants of the reaction velocity k_j and the reaction activation energy Ej from literature[13, 15, 16, 17] , table 6.

Table 5. The constructive data.

Constructive data	Value
The height riser	35 [m]
The diameter riser	1-1.4 [m]
The riser area	1.32 [m^2]

Figure 2 depicts the evolution of the riser temperature profile. As shown, the riser temperature starts to increase and ensures a good conversion in the riser. Figure 3 shows the evolution of the feedstock and the gasoline along the riser. As shown, the feedstock and gasoline conversion is better in the case of the 4-lump kinetic model than in the case of the 3-lump kinetic model. The results reveal that the 4-lump kinetic model is more appropriate to represent the kinetic model of the catalytic cracking riser. The comparison values for both kinetic models are shown in table 7.

Table 6. Kinetic parameter used for riser reactor modeling.

Kinetic model	Reaction cod	Constants of reaction velocity	Activation energy [kj/kmol]
3 lump kinetic model	A → B	0.769	10.000
	B → C	0.648	18.000
	A → C	0.055	10.000
4 lump kinetic model	A → B	12500	57359
	A → C	1950	52754
	A → D	16	31820
	B → C	2650	65733
	B → D	550	66570

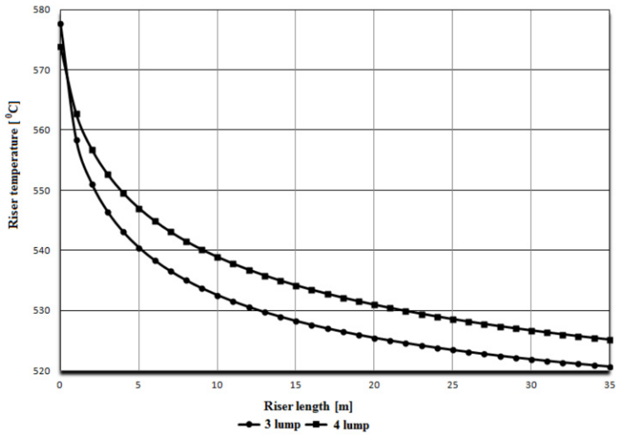

Fig. 2. The riser temperature profile for both kinetic models along the riser.

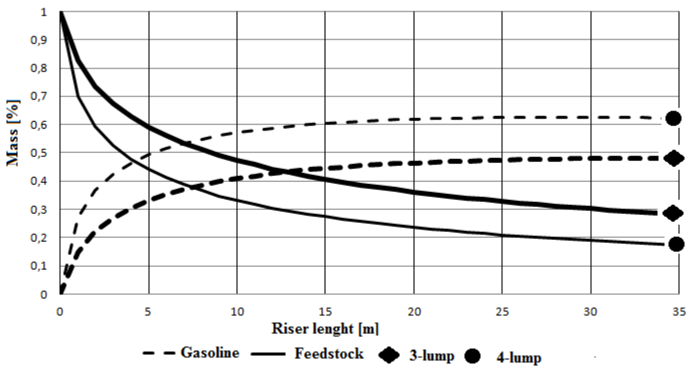

Fig. 3. The gasoline and feedstock mass fraction profile for both kinetic models along the riser.

Table 7. The comparison of values of the both kinetic models.

The lumps	3-lump	4-lump	Difference
The temperature riser	525.13	517.01	8.12
Gasoline	0.48	0.62	0.14
Feedstock	0.280	0.177	0.103

Conclusion

The purpose of this paper is to draw a comparison between the two kinetics models (four and three-lump models) associated to the catalytic cracking riser. The results evidenced that the riser temperature start is increased in the case of the four-lump kinetic model, assuring a better conversion along the riser. The feedstock and gasoline conversion is better in the case of the 4-lump kinetic model than in the case of the 3-lump kinetic model. Consequently, the results reveal that the 4-lump kinetic model is more appropriate to represent the kinetic model of the catalytic cracking riser.

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