

MATHEMATIC MODELING OF CATALYTIC CRACKING

Timur Chis¹, Renata Radulescu²

¹ Ovidius University Constanta, Applied Science Engineering Faculty, Chemical and Chemical Engineering Department, B-dul Mamaia, Constanta, **Romania**

² Oil and Gas University Ploiesti, Petroleum and Gas Engineering Faculty, Petroleum and Gas Department, B-dul Bucuresti, Ploiesti, **Romania**

e-mail: timur.chis@gmail.com

ABSTRACT

The catalytic cracking plant is one of the most important facilities in the refinery, due to ensuring the conversion of heavy oil fractions into gasoline, diesel and olefin-rich gases. The catalytic cracking process is a complex process of automatic conduction, due to the strong interactions between the process variables. That is why the mathematical modeling of this process is difficult to achieve, given the nonlinear nature of the system. This complexity increases with the increasingly restrictive requirements regarding the products obtained, the modernization of the installation and especially the reduction of operating costs. The present paper aims to present the techniques of hierarchical management of the catalytic cracking process and the numerical simulation models of this installation.

Keywords: catalytic, cracking, simulation, oil, refinery.

INTRODUCTION

The catalytic cracking plant is one of the most important plants in the refinery [1].

It ensures the conversion of heavy oil fractions into gasoline, diesel and olefin-rich gases (figure 1).

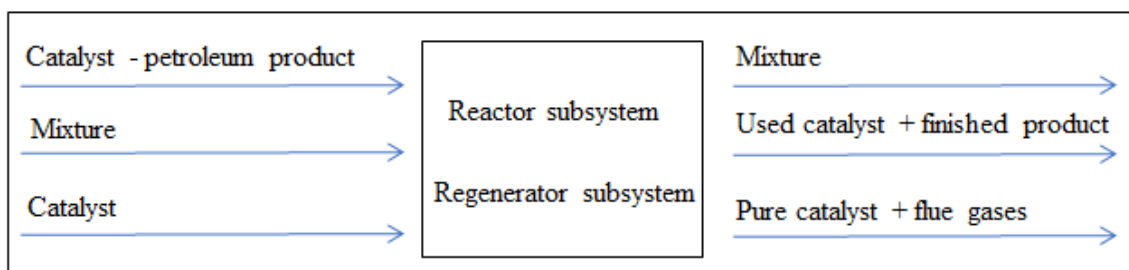


Figure 1 Decomposition of the catalytic cracking plant

This process is complex, being difficult to automate and model mathematically [2].

This complexity lies in the strong interactions between process variables, its nonlinear nature and system requirements [3].

The installation must ensure performance according to increasingly restrictive product specifications, lower and lower costs and higher operational safety. In the past, the operation of the installation had to ensure the maintenance of stability in operation, nowadays it is desired to control the processes automatically and the management on hierarchical levels, with the role of ensuring the increase of the quality of the regulation control process.

This is achieved by their converting into light hydrocarbons and gasoline with high octane research (COR) [4]. The basic raw material is vacuum distillate with distillation limits 350 - 400 ° C. Heavy diesels obtained from the atmospheric distillation plant, heavy distillates from the coking plant and sometimes residual from the atmospheric distillation are also used.

The catalytic cracking plant works with recycled diesel and using in process catalyst, steam and air.

The quality, quantity and physico-chemical properties of the products obtained depend on the physico-chemical properties of the raw material [5].

Catalysts are substances that have the property of accelerating and directing the transformation of petroleum products by decreasing the activation energy of chemical reactions. The most used catalysts in catalytic cracking plants are crystalline aluminosilicate (zeolites).

The steam is necessary to ensure an optimal mixing of the catalyst with the raw material. It is injected with the raw material into the riser supply distributor.

Steam is also used to strip the hydrocarbon vapors that are deposited on the catalyst particles.

The air provides the necessary conditions for the combustion of the coke deposited on the catalyst following the cracking reactions. It is supplied by a blower in the regenerator.

The main reaction products obtained from the cracking reaction regardless of the raw material used are: gasoline, light gases, light distillate and heavy distillate.

Gasoline is the main product of the catalytic cracking process (about 50-60% vol.). It is characterized by high research octane number (86-93 COR).

Light gases are C₃ - C₄ (70 - 80% by mass of hydrocarbons). They are used as raw material for the gas concentration and fractionation plant (GASCON).

The light distillate (light diesel) has the cetane number and ID (Diesel index) below 40. This is due to the high content of aromatic hydrocarbons.

Heavy distillate (heavy diesel) is a product of the process. It is partially recirculated (after solvent with furfuryl) in the catalytic cracking plant supply.

Because it has a high aromatic content, it can be used as a raw material for the manufacture of carbon black or electrode coke (through the coking process) [6].

MATERIALS AND METHODS

Decomposition of the catalytic cracking process

Modeling of complex chemical systems involves the decomposition of the catalytic cracking plant into subsystems.

The catalytic cracking process is a complex process of transforming refinery distillates into high quality compounds and therefore the development of fundamental kinetic models to track all components has not yet been completed, nor is it absolutely necessary.

In catalytic cracking kinetics studies, the raw material components are grouped into pseudocomponents, which represent important classes of hydrocarbons. Models which have been developed describe the global conversion of these classes of hydrocarbons function by a number of pseudocomponents.

Numerous kinetic models are known in the specialized literature [7].

First model of mathematical analysis is proposed by Weekman in 1968 [8].

Weekman managed to reduce the broad spectrum of raw materials and products to a simplified reaction system with three groups of components, namely: raw material, gasoline and gas - coke fractions.

Modeling and simulation of the reactor in steady state

a. The Weekman model.

In 1968, Weekman managed to reduce the broad spectrum of raw materials and products to a simplified reaction system with three groups of components, namely: raw material, gasoline fractions and coke gas (figure 2) [8].

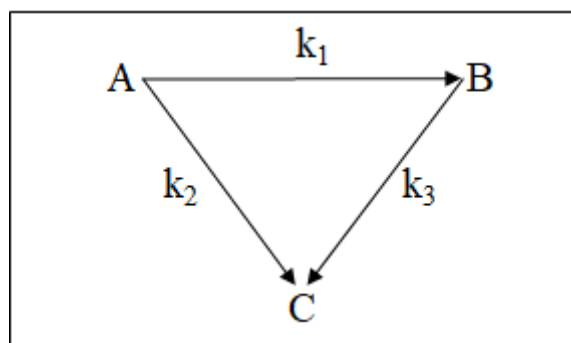


Figure 2 The Weekman model: A. the raw material (a diesel), B. gasoline, C. formed gases + coke, k_i , $i = 1, 2, 3$ reaction rate constants.

Weekman's model is valid for diesel cracking, which limits its area of application. Some of these limitations have been overcome by improvements to the model.

The equations of the Weekman model were established on the basis of the pseudo-component correlation equations, written for reactions taking place in an isothermal reactor, with piston flow for the gas phase, negligible inter particular diffusion and catalyst deactivation over time [9].

By solving the Weekman model, the amount of raw material, the yield of gasoline, the yield of gas and coke resulting from the catalytic cracking reaction are determined.

In 1979, Elnashaie and El-Hennawi presented, based on a triangular kinetic scheme, a model that combines Weekman kinetics with the hydrodynamics of two-phase fluidization theory [10].

b. The Wojciechowski model.

The model proposed by Wojciechowski and his collaborators was developed on the basis of a triangular kinetic scheme of diesel transformation similar to the Weekman kinetic scheme, but of successive parallel type.

Unlike Weekman, Wojciechowski considers all reactions to be of first-order, introduces a correction of the rate constant with respect to the degree of transformation, and proposes a hyperbolic deactivation function based on a catalyst aging theory [11].

c. The Gianetto kinetic model.

With four groups of components it was developed to more accurately describe the behavior of reactors using new catalysts, consisting of small zeolite crystals dispersed in a silico- alumina matrix (figure 3) [12].

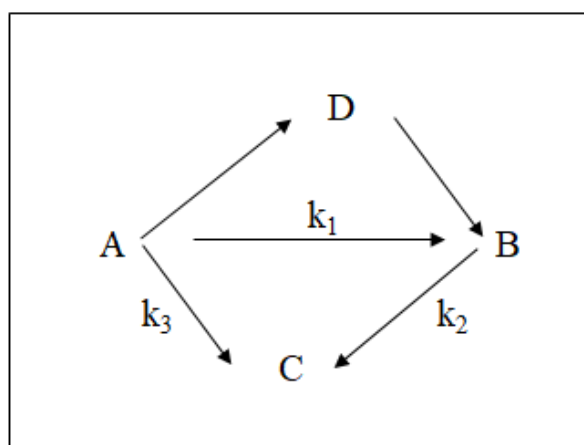


Figure 3. The Gianetto model: A the raw material (diesel), B gasoline, C formed gases + coke, D light gases

Compared to the Weekman model, this model treats coke and light gases as two components. The kinetic expressions of the chemical reactions were determined experimentally using a riser simulator.

Gianetto presented the rate constants and activation energies so that the reaction rates are calculated with expressions based on Arrhenius equation. The same model with four groups of components was used in the study of the adsorption phenomena that take place in the cracking reactor [13].

d. The 5 - component model

It was developed by dividing the gas –coke component into paraffin, aromatic and naphthenic components [14].

e. Model with 6 groups of components

For heavy raw materials, Chiyoda Chemical Engineering and Construction Co. developed a model with six groups, namely residue, light diesel, heavy diesel, gasoline, gas and coke [15].

The raw material was defined by the sum of two components: C₂ - residue and C₁ - heavy diesel.

Four components are considered for the reaction products: C₅ - light diesel, C₄ - petrol, C₃ - gas and C₆ -coke.

Statistic Refinery models proposed

The numerical model proposed by us is based by mathematical equation of the chemical process (statistical methods).

We assume that the chemical phenomenon can be approximated by the method of least squares, with a polynomial of degree I, thus we find ourselves in the situation of approximating the phenomenon by the polynomial:

$$P_n(x) = a_0 + a_1x \quad (1)$$

Input value and output parameter of equation described catalytic cracking process is presented in Table 1.

Table 1. Equation Models

Equation	Output parameter	Input value	a ₀ value	a ₁ value	The average value of the experimental points	The average value of the calculated points
1	Temperature at the exit of the riser [°C]	Density	545.75	-16.534	530.733	529.291
2	Temperature at the exit of the riser [°C]	Sulfur content	531,361	-1,585	530,733	530.799
3	Temperature at the exit of the riser [°C]	Raw material temperature [°C]	536.845	-0.03	530.733	530.879
4	Gasoline flow (kg/h)	Input product flow (kg/h)	46830	0.189	77595	78032
5	COR octane research	Sulfur content	95.508	-3.204	94.375	94.373

RESULTS AND DISCUSSION

Following the study carried out on the catalytic cracking plant, we managed to create models of linearization of the final operating parameters of the plant based on the input parameters of the operating parameters of the operating parameters.

The first equation is dedicated to the analysis of the research octane number of gasoline according to the sulfur content of the initial distillate.

The equation is:

$$COR \text{ calculating} = 95.508 - 3.204 \cdot \text{Sulfur content} \quad (2)$$

To determine the outlet temperature of the riser from the product density the equation is:

$$\text{riser outlet temperature} = 574.75 - 16.534 \cdot \text{product density} \quad (3)$$

To determine the riser outlet temperature relative to the sulfur content of the product the equation is:

$$\text{riser outlet temperature} = 531.361 - 1.585 \cdot \text{Sulfur content} \quad (4)$$

To determine the riser outlet temperature from the raw material temperature the equation is:

$$\text{riser outlet temperature} = 536.845 - 0.003 \cdot \text{Raw material temperature} \quad (5)$$

To determine the gasoline flow rate from the input product flow rate the equation is:

$$\text{petrol flow} = 46830 + 0.189 \cdot \text{Entered product flow} \quad (6)$$

All equations were tested by the t Student method and the Fisher criterion, the results being conclusive the equations are viable (Table 2).

Table 2 Analysis of statistical data based by equation determined in Table 1.

Equation	Dispersion of experimental data	Dispersion of determined data	criterion tStudent t_{a0}	criterion tStudent t_{a1}	criterion tStudent t_p	Conclusion
1	0.352	0.00245	10.496	0.301	1.761	It is significant
2	0.457	0.002194	235.907	0.25	1.761	It is significant
3	0.457	0.034	86.867	0.979	1.761	It is significant
4	$1.593 \cdot 10^7$	$2.787 \cdot 10^6$	2.238	1.508	1.761	It is significant
5	0.055	0.00897	122.259	1.457	1.761	It is significant

CONCLUSIONS

The model in 5 equations and in 8 functional parameters best describes the static behavior of the catalytic cracking installation.

Compared to all the models developed in the specialized literature, this model wants a system of linear equations that can be used for automation and automatic control of the installation.

The other models are chemical equations that do not involve 8 functional parameters (maximum 7).

As it can be seen, the installation can be controlled by implementing the measuring and control equipment with a deviation of maximum 2 degrees C which is a very good approximation to the average reading value of 530,73 degrees C (Table 3).

Table 3. Result of equation function by process date

Day of observation	Temperature at the exit of the riser [°C] Installation read	Temperature at the exit of the riser [°C] calculated density function	Temperature at the exit of the riser [°C] calculated sulfur function	Temperature at the exit of the riser [°C] calculated function of raw material temperature
1	531	529.91	530.72	530.75
2	531	529.91	530.72	530.84
3	530	529.91	530.82	530.78
4	530	529.92	530.79	530.78
5	530	529.92	530.80	530.63
6	530	529.92	530.85	530.69
7	531	529.92	530.86	530.99
8	531	529.92	530.77	531.02
9	531	529.91	530.80	530.99
10	530	529.91	530.74	531.11
11	531	529.92	530.77	531.14
12	532	529.92	530.85	531.11
13	531	529.92	530.83	530.90
14	531	529.92	530.82	530.69
15	531	529.91	530,79	530,69

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