

## Modeling and Optimization of a Semi Regenerative Catalytic Reforming of Naphtha in the Presence of Catalyst Coking

Inna V. Pchelintseva<sup>1\*</sup>, Emilia D. Ivanchina<sup>1</sup>, Ekaterina S. Chernyakova<sup>1</sup>, and Dmitry S. Poluboyartsev<sup>2</sup>

1. National Research Tomsk Polytechnic University, Tomsk, Russia

2. Joint Stock Company, Tomsk Oil and Gas Research and Design Institute, Tomsk, Russia

### Abstract

Catalytic naphtha reforming is practiced extensively in petroleum refineries and petrochemical industries to convert low-octane naphtha into high-octane gasoline. Moreover, this process is an important source of hydrogen and aromatics obtained as side products. Bifunctional Pt-catalysts used in reforming are deactivated by coking during its industrial operation. This results in a reduction of the yield and octane number. In this paper, modeling and optimization of a semi regenerative catalytic reforming of naphtha have been carried out by considering catalyst deactivation and complex multicomponent composition of a hydrocarbon mixture. Furthermore, a detailed coke formation mechanism was described. In addition, operating parameters (yield, octane number, and activity) for different catalysts were predicted and optimized. In addition, the analysis was extended to study the reactor configuration features and their influence on the process parameters. Finally, economic values were calculated, and the benefits of process improvement were demonstrated.

**Key words:** Catalytic Naphtha Reforming, Mathematical Modeling, Semiregenerative Process, Activity, Coke Formation, Product Yield.

### Introduction

Catalytic naphtha reforming process is one of the most important processes in the petroleum refining and petrochemical industry for converting low-octane naphtha into high-octane gasoline and production of aromatic feedstock. Furthermore, hydrogen is obtained as a valuable side product, which is intensively demanded in most refineries for hydrogen-consuming processes such as hydrotreating, hydrocracking etc. Moreover, the produced reformat contains aromatics, namely benzene, toluene, xylene (BTX) that are very valuable and important petrochemical material. Generally, the industrial reforming process is carried out in three or four adiabatically operated reactors at temperatures from 450 to 520 °C and total pressures between 10 and 35 atm. A preliminary hydrodesulfurized naphtha cut is used as the feed. Naphtha is a fraction of petroleum – a very complex mixture of hydrocarbons, consisting of several hundred components, mainly paraffins, iso-paraffins, naphthenes and aromatics [1-5].

There are three main groups of catalyst regeneration procedures according to which industrial naphtha reforming units are classified: semi-regenerative catalytic reformer (SRR), continuous catalyst regeneration

reformer (CCR), and cyclic catalytic reformer. SRR is the most commonly used scheme – about 60% of total capacity. In this unit, the research octane number can be achieved in the range of 85-100. This process is characterized by continuous operation over a long period; the shutdown of the SRR unit occurs once every 6-24 months due to decreased catalyst activity [1].

Catalytic naphtha reforming has already vastly improved by many researchers who investigated different aspects of this industrial process, namely developing more effective catalysts, designing efficient reactor configuration, and mode of operation or representing appropriate kinetic and deactivation model. Still, in spite of a plethora of existing papers, there is a need for more investigations in revealing and elucidating kinetic and deactivation mechanisms as well as suggesting more efficient reactor setups and mode of operation [1].

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\*Corresponding author: Inna V. Pchelintseva, National Research Tomsk Polytechnic University, Tomsk, Russia

E-mail addresses: E-mail: yakupovaiv@tpu.ru

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existing papers, there is a need for more investigations in revealing and elucidating kinetic and deactivation mechanisms as well as suggesting more efficient reactor setups and mode of operation [1].

Methods of investigating catalytic reforming processes are divided into two groups, called instrumental and kinetic models. The first group of methods includes the study of physio-chemical characteristics of catalyst, i.e. composition, structure, and texture (porosity, specific surface, etc.). The second group explains the formalized mechanism of process reactions on the catalyst surface and allows us to obtain the initial data for optimal management by determining kinetic parameters of reactions. However, there is more than one method for studying complex hydrocarbon processes, and mathematical modelling is successfully applied for catalytic naphtha reforming. Moreover, the process of a mathematical model based on its kinetic model and process parameters has been presented.

Mathematical modelling is based on the optimal ratio of experimental and computational data. Many phenomena are not available for studying, modelling, and expanding research opportunities. For example, by using a mathematical modeling method, it is possible to describe the reactivity of hydrocarbon conversion on various industrial catalysts, solve the inverse kinetic problem and determine the numerical values of the reaction rate constants, and predict the duration of the inter-regeneration cycle and the total catalyst service life. The conditions for intelligent technological installations functioning are created. The development of any industrial production is based on the close interaction of three fundamental components; they are material, technical, and intellectual components. This contributes to the high technology introduction and increases the intellectual potential of engineers. The introduction of intelligent catalyst control modules, which has been developed on the basis of prognostic models into production, allows plant operators to make technical decisions by taking into account the recommendations promptly issued by this module. The mathematical modeling methodology of multicomponent catalytic processes was developed at the Tomsk polytechnic university with the active support of the Russian refineries. For more than 30 years, within the framework of a scientific school, systematic work has been carried out to develop catalytic processes for various purposes. Using this methodology, the operating conditions of reforming, isomerization, dehydrogenation and alkylation, catalytic cracking and hydrocracking catalysts were studied, proposed, and implemented. In addition, methods for modification of them have been proposed. Ultimately, the catalyst resource has been increased by optimizing its operating conditions. The research conducted using the mathematical modeling method and intelligent systems allows developing the scientific basis for the preparation of mixed commercial fuels based on the physical and chemical laws of the transformation of the components of the mixture [6-10].

All catalysts undergo the deactivation process. Plenty of scientific work has been devoted to study this process [11,12]. For heterogeneous catalysts for reforming, isomerization and dehydrogenation processes, and deactivation as a result of deposition of coxogenic compounds on their surface

occurred. In these processes, deactivation is accompanied by self-regeneration of coke under the influence of the components of the mixture (hydrogen, water, etc.). The level of stationary (optimal) activity is established when the rates of deactivation and self-regeneration are equal to each other [13].

Our previous studies have been done on catalyst deactivation are of its reversible type. Thus, while maintaining the equilibrium reaction of coke formation and hydrogenation of the intermediate products of compaction, the level of optimal activity of the catalyst is achieved, at which its self-regeneration occurs [14]. Work under conditions of equal rates of coke formation and hydrogenation reactions, which under industrial conditions are controlled by temperature, the consumption of raw materials and recycle hydrogen-containing gas, can significantly extend the inter-regeneration run of reforming catalysts [15]. Based on the thermodynamic equilibrium conditions of the oxidation reaction of coke compounds, formed on the surface of platinum-containing dehydrogenation catalysts, the optimal modes of water supply to an industrial reactor were determined that ensured an increase in the catalyst service life by 20% [16,17].

As a work developed in this direction, studies in a narrow pressure range (12-14 atm) should be considered. The main task, in this case, is the theoretical justification for the existence of optimal conditions for the catalyst and the development of recommendations for maintaining optimal pressure with raw materials composition changing in a given interval and technological conditions.

## Materials and Methods

Methods of mathematical modeling have been intensively developing since the beginning of the 1960s [18-25]. The main idea of these methods is to study object properties on a mathematical model. The model and the object of investigation (the catalytic reforming process of naphtha) have a different physical nature, but the same properties. In general, the mathematical modeling of chemical processes and reactors can be represented in the form of a scheme (Figure 1).

Modeling catalytic naphtha reforming process is a very complex task because of some features such as catalyst bimetallic nature, feed composition complexity, a large number of reactions with different rates and deactivation processes occurring during the catalyst operation. Therefore, a model should consider both the bimetallic catalyst nature and the complexity of the feed composition as in the real technological process [26-32].

The main rule of chemical processes modeling is a sequential definition of the thermodynamic and kinetic parameters of chemical transformations (chemical phenomena), the parameters of transport phenomena (physical phenomena), and the laws of their interaction. For this purpose, experimental research data are used.

The results of the process analysis and the study of its components make it possible to construct a mathematical model as an algebraic or differential system of equations. The model study is aimed at studying its properties, while computational methods are used. The obtained model properties should be further interpreted as the study object ones, which in this case, is a chemical reactor.

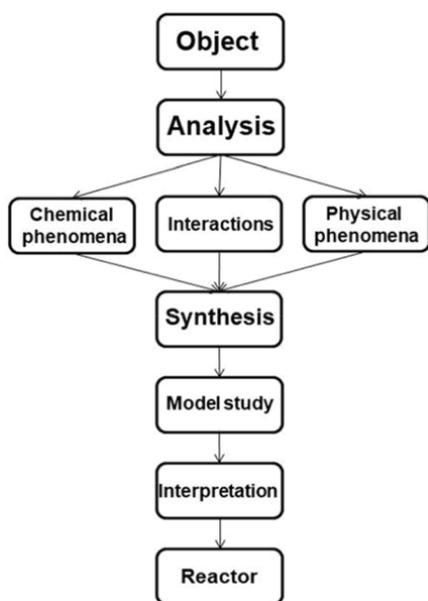


Fig. 1 Schematic diagram of chemical processes modeling.

**Mathematical Model Design of Semi Regenerative Catalytic Naphtha Reforming In Catalyst Coking Presence**

As mentioned above, catalyst coking throughout a process is the main and inevitable cause of its deactivation. But, despite this fact, the problem of catalyst coking is reversible in contrast to other irreversible reasons for catalyst deactivation such as erosion, breakage, poisoning, or aging. Therefore, deposited coke could be removed from the catalyst.

The coke formation mechanism has been studied in many investigations [33-39], but still, information about this phenomenon is insufficient due to the difficulty of obtaining direct experimental data. In addition, the platinum surface area on the catalyst is less than 1% of the total surface. However, some knowledge based on this process is obtained.

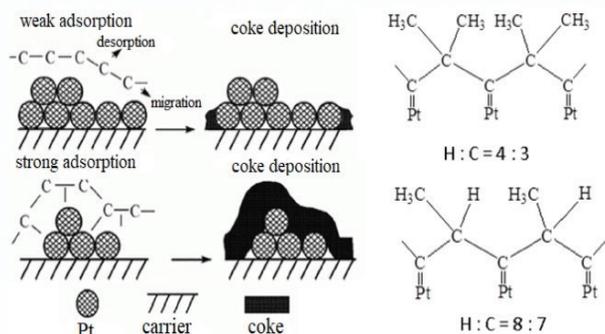


Fig. 2 Scheme of coke formation mechanism on the Pt-catalyst surface.

In Figure 2, the coke formation mechanism is shown [40]. Hydrocarbons are subjected to dissociative adsorption on the catalyst surface. Surface compounds formation that is firmly retained happened as a result. Yet, these compounds are in quasi-equilibrium with gas-phase hydrogen. These carbon-containing compounds are amorphous (reversible) coke and have an H:C ratio equals to 4:3, and it is bound to a metal function. If equilibrium is disturbed, irreversible adsorption

of hydrocarbons occurs, which leads to the graphite coke formation with a ratio of H:C = 8:7. In both cases, multiple strong bonds of some carbon atoms of reacting molecules with platinum atoms on the catalyst surface exist [40]. Even though coke is deposited in both acid and metal sites, it could be demonstrated that the main fraction of coke is formed over acid sites.

Electron microscopic analysis (Hitachi S-3400 N) of catalyst grain samples was done. These samples were obtained after the catalyst service operation life, and consequently, containing depositions of coke. It could be seen from the pictures, which the catalyst surface is covered with highly disperse coke particles of amorphous type. The carbon mass content on the surface is derived between 8 and 19%, which it allows to state that a significant amount of medium and high density coke (including graphitized coke) remains unchanged on the catalyst; in addition, it has not been removed after industrial regeneration (T = 500–550 °C).

According to Figure 3, it is obvious that the existence of the formation and hydrogenation of unsaturated intermediate products of compaction is possible. The mechanism of coke formation can be represented by the scheme of sequential reactions: hydrocarbons → resins → asphaltenes → coke, where resins and asphaltenes are unsaturated immediate compacting products (UICP). Therefore, under certain conditions, coke formation does not occur because asphaltenes (precursors of coke) can be hydrogenated to hydrocarbons or be in equilibrium with the gas-phase reaction medium. Moreover, by controlling feed temperature in the reactor, it could be possible to provide process operation mode with the existence of equilibrium of formation and hydrogenation of coke structures. But providing this process is difficult to realize in practice because obtaining the final high-octane product is required, so there is an objective need for deviations from thermodynamic equilibrium.

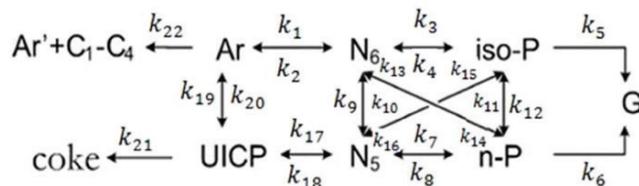


Fig. 3 Formalized reaction scheme of naphtha reforming: n-P, iso-P – normal and iso-alkanes; N-5, N-6 – methylcyclopentane and methylcyclohexanes; Ar – aromatic hydrocarbons; UICP – unsaturated immediate compacting products; G – gas.

As a result, the accumulation of unsaturated intermediate products of compaction occurs. However, the solution to a very important industrial problem – how to find the desired catalyst – is based on this contradiction.

The rate law for elementary steps is proportional to the concentration of reacting substances in the degrees showing the number of particles entering interaction [41-42]:

$$r_j = k_j \cdot C_i \tag{1}$$

where  $r_j$  is the reaction rate;  $k_j$  is the rate constant and  $C_i$  is initial concentration of components.

Kinetic model of catalytic reforming process can be written for reactions of hydrogenolysis of naphthenes and

hydrocracking of paraffins as:

$$\frac{dC_i(x)}{dt} = \sum_{j=1}^n k_j(x) \cdot C_i(x) \cdot C_{H_2} \quad (2)$$

where  $j=1, \dots, n$  is the number of a chemical reaction;  $C_i(x)$  and  $k_j(x)$  are distributions of hydrocarbons concentration and rate constants on the number of carbon atoms in a molecule  $x$ , respectively and  $t$  is space-time, h.

According to Figure 3, the kinetic model of the catalytic reforming process is performed by the following system of equations:

$$\begin{aligned} r_1 &= k_1 \cdot C_{Ar} \cdot C_{H_2} \\ r_2 &= k_2 \cdot C_{N_6} \\ r_3 &= k_3 \cdot C_{N_6} \cdot C_{H_2} \\ r_4 &= k_4 \cdot C_{iso-P} \\ r_5 &= k_5 \cdot C_G \cdot C_{H_2} \\ r_6 &= k_6 \cdot C_{n-P} \cdot C_{H_2} \\ r_7 &= k_7 \cdot C_{N_5} \cdot C_{H_2} \\ r_8 &= k_8 \cdot C_{n-P} \\ r_9 &= k_9 \cdot C_{N_5} \\ r_{10} &= k_{10} \cdot C_{N_6} \\ r_{11} &= k_{11} \cdot C_{n-P} \\ r_{12} &= k_{12} \cdot C_{iso-P} \\ r_{13} &= k_{13} \cdot C_{N_6} \cdot C_{H_2} \\ r_{14} &= k_{14} \cdot C_{n-P} \\ r_{15} &= k_{15} \cdot C_{N_5} \cdot C_{H_2} \\ r_{16} &= k_{16} \cdot C_{iso-P} \\ r_{17} &= k_{17} \cdot C_{UICP} \\ r_{18} &= k_{18} \cdot C_{N_5} \\ r_{19} &= k_{19} \cdot C_{UICP} \\ r_{20} &= k_{20} \cdot C_{Ar} \\ r_{22} &= k_{22} \cdot C_{Ar} \end{aligned} \quad (3)$$

The equation of heat balance can be written as:

$$G \frac{dT}{dV} = \frac{1}{(\rho \cdot C_p^{mix})} \sum_{j=1}^m Q_j \quad (4)$$

$$Q_j = \Delta H_j \cdot k_j(x) \cdot C_j(x) \quad (5)$$

where  $V$  is a catalyst volume in the reactors ( $m^3$ ),  $\rho$  is density ( $mol/m^3$ ),  $C_p^{mix}$  is the heat capacity of the mixture ( $kJ/mol \cdot K$ ),  $Q_j$  is the amount of heat in the  $j^{th}$  chemical reaction, and  $\Delta H$  is  $j^{th}$  reaction heat ( $kJ/mol$ ).

$$\begin{aligned} Q_1 &= \Delta H_1 \sum_x [k_2 \cdot C_{N_6} - k_1 \cdot C_r \cdot C_{H_2}] \\ Q_2 &= \Delta H_2 \sum_x [k_4 \cdot C_{iso-p} - k_3 \cdot C_{N_6} \cdot C_{H_2}] \\ Q_3 &= -\Delta H_3 \sum_x [k_5 \cdot C_{iso-p} \cdot C_{H_2}] \\ Q_4 &= -\Delta H_4 \sum_x [k_6 \cdot C_{n-p} \cdot C_{H_2}] \\ Q_5 &= \Delta H_5 \sum_x [k_{11} \cdot C_{n-p} - k_{12} \cdot C_{iso-p}] \\ Q_6 &= \Delta H_6 \sum_x [k_8 \cdot C_{n-p} - k_7 \cdot C_{N_5}] \\ Q_7 &= \Delta H_7 \sum_x [k_{10} \cdot C_{N_6} - k_9 \cdot C_{N_5}] \\ Q_8 &= \Delta H_8 \sum_x [k_{16} \cdot C_{iso-p} - k_{15} \cdot C_{N_5} \cdot C_{H_2}] \\ Q_9 &= \Delta H_9 \sum_x [k_{14} \cdot C_{n-p} - k_{13} \cdot C_{N_6} \cdot C_{H_2}] \\ Q_{10} &= \Delta H_{10} \sum_x [k_{18} \cdot C_{N_5} - k_{17} \cdot C_{UICP}] \\ Q_{11} &= \Delta H_{11} \sum_x [k_{10} \cdot C_{Ar} - k_{19} \cdot C_{UICP}] \\ Q_{12} &= -\Delta H_{12} \sum_x [k_{21} \cdot C_{UICP}] \\ Q_{13} &= -\Delta H_{13} \sum_x [k_{22} \cdot C_{Ar}] \end{aligned} \quad (6)$$

For the mathematical description of the hydrodynamics and heat model of the catalytic reforming reactor, some assumptions are accepted:

- The formalized mechanism of hydrocarbons transformation, as seen in Figure 4;
- Plug flow reactor model, and
- Adiabatic operation.

Therefore, the mathematical model of semi regenerative catalytic reforming of naphtha is presented by a system of equations of material and heat balances:

$$\left\{ \begin{aligned} G_c \frac{\partial C_i}{\partial Z} + G_c \frac{\partial C_i}{\partial V} \sum_{j=1}^m \alpha_j \cdot r_j \\ G_c \frac{\partial T}{\partial V} + G_c \frac{\partial T}{\partial Z} = \frac{1}{\rho \cdot C_p^{mix}} \sum_{j=1}^m \alpha_j \cdot r_j \left( \frac{RT}{P} \right) \cdot \Delta H_j \end{aligned} \right\} \quad (7)$$

The boundary conditions are:

$$\begin{aligned} z = 0, C_i = C_{i0}, T = T_{en'} \\ V = 0, T = T_{en'}, C_i = C_{i0} \end{aligned} \quad (8)$$

$G_c$  is a raw material flow rate ( $m^3/s$ ),  $C_i$  is a concentration of an  $i^{th}$  component ( $mol/m^3$ ),  $Z$  is a volume of raw material processed from the moment when the fresh catalyst (new catalyst, no regenerations have been done) has been loaded ( $m^3$ ),  $V$  is a catalyst volume in the reactors ( $m^3$ ),  $\alpha_j$  is a catalyst activity;  $r_j$  is a reaction rate ( $mol/m^3 \cdot s$ ),  $i$  is a component number in a mixture;  $j$  is a reaction number due to formalized scheme accepted;  $T$  is a temperature ( $K$ ),  $\rho$  is density ( $mol/m^3$ ),  $C_p^{mix}$  is heat capacity of the mixture ( $kJ/mol \cdot K$ ),  $k_j$  is  $j^{th}$  reaction constant ( $l/mol \cdot s$ ),  $\Delta H$  is  $j^{th}$  reaction heat ( $kJ/mol$ ),  $R$  is the gas constant ( $8,314 \text{ MPa} \cdot l/mol \cdot K$ ), and  $P$  is pressure ( $MPa$ ).

$$Z = G \cdot t \quad (9)$$

where  $Z$  is a volume of raw material processed from the moment when the fresh catalyst (new catalyst, no regenerations were done) was loaded ( $m^3$ ),  $G$  is a raw material flow rate ( $m^3/s$ ), and  $t$  is space-time (h).

The mathematical model of the catalytic reforming reactor unit is performed by the following equations according to equations 1 and 3:

$$\begin{aligned} G \frac{dC_{Ar}}{dV} &= r_2 + r_{19} - r_1 - r_{20} - r_{22} \\ G \frac{dC_{N_6}}{dV} &= r_1 + r_4 + r_9 + r_{14} - r_2 \\ G \frac{dC_{iso-p}}{dV} &= r_3 + r_{11} + r_{15} - r_5 - r_{12} - r_4 \\ G \frac{dC_{Ar}'}{dV} &= r_{22} + r_2 - r_1 + r_{19} - r_{20} \\ G \frac{dC_{n-p}}{dV} &= r_{11} + r_7 + r_{13} - r_6 - r_8 - r_{12} - r_{16} \\ G \frac{dC_{N_5}}{dV} &= r_{10} - r_9 + r_8 - r_7 + r_{17} - r_{18} + r_{16} - r_{15} \\ G \frac{dC_{UICP}}{dV} &= r_{19} - r_{20} + r_{18} - r_{17} - r_{21} \\ G \frac{dC_{coke}}{dV} &= r_{21} + r_{19} - r_{20} + r_{18} - r_{17} \\ G \frac{dC_G}{dV} &= r_5 + r_6 + r_3 - r_4 + r_7 - r_8 + r_{15} - r_{16} + r_{13} - r_{14} \end{aligned} \quad (10)$$

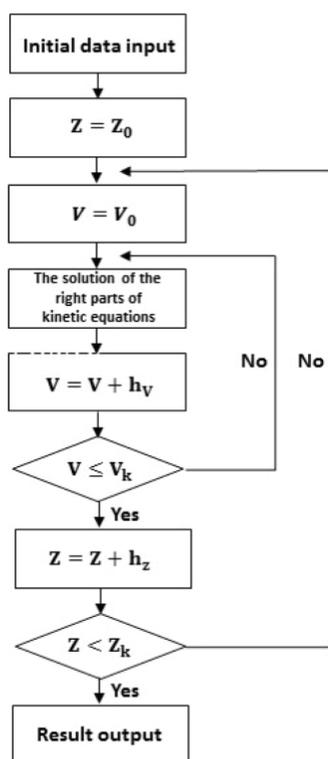


Fig. 4 Technical flowchart for the computer program.

The computer program, based on this mathematical model, has been developed. The pressure is calculated according to the general gas equation. Moreover, a technical flowchart for this problem is provided, as seen in Figure 4.

The developed reforming reactor model enables us to consider physical and chemical laws of hydrocarbons conversion on the catalyst surface and changes in the composition feedstock. By using the developed model, such parameters as current and optimal activities have been calculated. The current activity is determined by current modes of operation given by:

$$a_{cur} = W_0 - W_k (1 - a) \quad (11)$$

where  $a_j$  is the relative activity of the catalyst in each reaction according to Equation 7;  $W_0$  is the chemical reaction rate, mol/sm<sup>3</sup>·s, with and without catalyst respectively;  $a$  is the part of the volume, which is occupied by the catalyst, and it is inaccessible for reacting mixture [47].

The optimal activity ( $a_{opt}$ ) is defined by optimal process operation. The operation corresponds to the desired rate ratio of target and adverse reactions, and it also saves the equilibrium of formation and hydrogenation of coke structures. Also, the equilibrium is defined by process parameters, namely temperature, pressure, and feedstock composition. The optimal activity provides maximum process selectivity.

As a common indicator of the catalyst potential, a special criterion of effectiveness has been proposed. This criterion corresponds to the deviation of current activity from the optimal one [43]; moreover, the criterion of effectiveness is calculated using the following equation (Equation 12):

$$\Delta = \frac{\sum_{i=1}^n [a^i_{cur} - a^i_{opt}]}{\Delta_{max}} \quad (12)$$

where  $\Delta$  is a criterion of effectiveness;  $a_{cur}^i$  is the current activity;  $a_{opt}^i$  is optimal activity, and  $\Delta_{max}$  is maximum

deviation of current activity from optimal.

With this indicator of catalyst potential, it is possible to determine how effective catalyst is used on a reforming unit. This criterion also determines coke formation dynamic selectivity with different types of catalyst activity and the deviation between them. All these calculations made by mathematical model helps to increase yield and decrease coke formation dynamics during catalyst life operation, which leads to process optimization and its profitability improving.

## Results and Discussion

It was found out that a decrease in (1) the pressure range from 1,5 to 1,2 MPa at the temperature 478-481°C and (2) feedstock space velocity, which is 1,4 h<sup>-1</sup> cause an increase in yield for 1-2% mass. Moreover, at the same time, an increase in the aromatization reaction rate and decrease in the hydrocracking reaction rate depending on feedstock composition and catalyst type do not cause the increase of isomerization reaction rate.

It has been found out that the decrease in pressure is limited by the requirements for the catalyst stability due to the increase in the coke formation rate. In addition, when the temperature at the reactor entrance is 478 °C, the raw material flow rate is 64,3 m<sup>3</sup>/h, and the naphthenic feedstock the total amount of coke is evenly increased by 0,5-1,0% mass depending on pressure and catalyst type.

It is proposed that the criterion of optimality is the yield, expressed in octane-tons. It was calculated with the mathematical model, which with the naphthenic feedstock using the pressure, should vary in the range from 1,3 to 1,5 MPa [47].

Specifications of operating conditions, feedstock, and catalyst properties are presented in Tables 1 to 3.

Also, the results of the calculation of the SSR reforming process are given in Tables 3-5 and Figures 5-8. The experimental data, including the chromatographic analysis results of raw material and outlet substance compositions and technological modes of production unit operation, were obtained from the industrial SSR reforming unit of Russian refinery and used as initial data.

Table 1 Specification of operating conditions for industrial reforming units.

Parameter/Unit	Reforming unit 1	Reforming unit 2
Number of reactors	3	4
Reactors inlet temperature, °C	490	480
Mass flow rate, h <sup>-1</sup>	1.0–1.8	1.4
Pressure, MPa	2.0	1.7

Table 2 Volume percent of different components in the feed and the product.

Component	Feed (vol.%)	Product (vol.%)
Normal paraffins	45,4	11,3
Iso-paraffins	15,5	23,8
Naphthenes	29,8	5,12
Aromatics	10,2	60,4

**Table 3** Specification of catalyst properties.

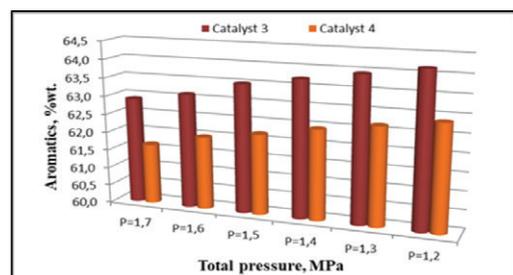
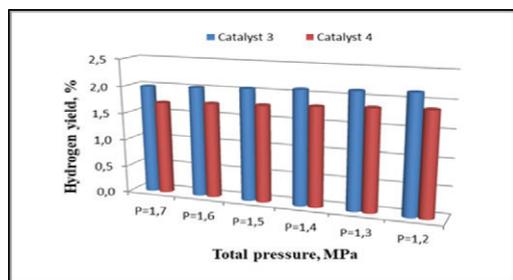
Parameter/Catalyst	Catalyst 1	Catalyst 2	Catalyst 3	Catalyst 4
Pt, wt.%	0.25	0.25	0.25	0.25
Re, wt.%	0.25	0.30	0.30	0.25
Promoted by Cl	no	yes	yes	yes
Bulk density, kg/m <sup>3</sup>	720	750	750	720

**Table 4** The evaluation of catalyst potential (Catalyst 1).

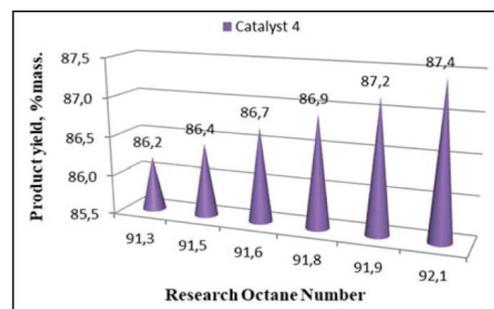
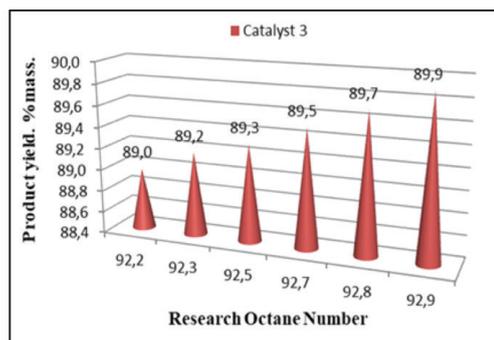
Raw material volume, t	Activity		Coke, %mass		Effectiveness Criterion, Δ
	Current	Optimal	Current	Optimal	
166253	0,76	0,86	1,84	1,23	0,71
230267	0,78	0,84	2,68	1,59	0,43
294336	0,80	0,81	3,64	2,14	0,07
315733	0,81	0,82	3,96	2,26	0,07
337826	0,81	0,83	4,23	2,42	0,14
382264	0,79	0,85	4,79	2,72	0,43
404366	0,81	0,90	5,06	2,88	0,64
426351	0,82	0,89	5,38	3,03	0,50

**Table 5** Calculation of economic efficiency due to product yield (Catalyst 2)

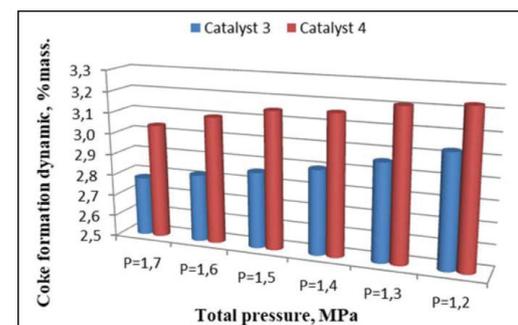
Raw material volume, millions of tons	Product yield, %mass		Raw material loss, %	Loss per year, \$
	Current activity	Optimal activity		
0,07	84,36	87,27	2,91	313 384,62
0,13	84,47	87,10	2,63	526 000,00
0,17	85,35	87,90	2,55	666 923,07
0,33	85,84	88,51	2,67	1 355 538,46
0,42	85,88	87,94	2,06	1 331 076,92
0,61	83,69	87,67	3,98	3 735 076,92
1,09	85,54	86,74	1,20	2 012 307,69
2,16	86,57	87,86	1,29	4 286 769,23



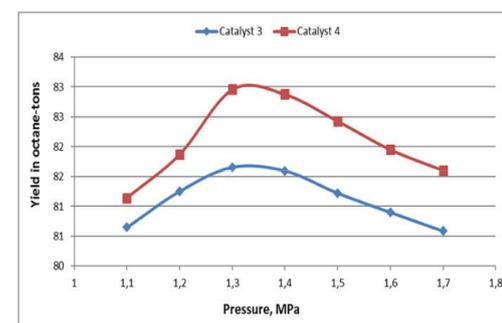
**Fig. 5** Pressure effect on the hydrogen and aromatics yield for different catalysts.



**Fig. 6** Pressure effect on the RON and product yield for different catalysts.



**Fig. 7** Pressure effect on the coke formation dynamic for different catalysts.



**Fig. 8** The dependence of yield from pressure.

**Optimization of Technological Conditions**

By using the mathematical modelling method, it has been considered how to decrease the coke formation dynamics and increase yield. In Table 4, the results of calculations of coke formation accumulation during catalyst life of operation on the current and different activities are shown. It is obvious that finding optimal conditions for catalyst gains in favor of decreasing coking can prolong catalyst life and increase product yield.

The deviation of the current activity of the catalyst from optimum during the feed cycle strongly affects [44, 45] the

process selectivity.

This fact is reflected in the economical values (Table 5).

Thus, the development of optimal conditions for process operation can improve process profitability. The next point is how to find this optimal mode of operation. It could be achieved by maintaining operation parameters such as temperature and pressure or finding a more efficient reactor configuration.

### Analysis of total pressure reducing

Operating conditions strongly affect the process characteristics, including yield, octane number, and coke formation. A few reactions such as naphthenic dehydrogenation and paraffin dehydrocyclization are favored at low pressure, while hydrocracking and hydrogenolysis side reactions are inhibited with the same conditions [45]. This fact can be successfully used in the process optimization technique.

The effect of total pressure on the product yield and catalyst coking was analyzed by using the mathematical model.

With the low pressure, the rate of paraffin aromatization increases, while the rate of hydrocracking decreases. This causes hydrogen yield and aromatics gradually increase by 0.2% and 1-2% respectively. The hydrogen yield growth results in the product yield rising. Therefore, the total selectivity of the process increases.

Despite of this positive effect on these process characteristics, low pressure contributes to the catalyst deactivation due to an increase in the coking reactions rate (Figure 7).

Thus, by reducing pressure, it is possible to increase the yield and octane number, and hydrogen and aromatic hydrocarbons due to the equilibrium shift of reactions of dehydrogenation and dehydrocyclization. Nevertheless, at the same time, reduction in pressure accelerates the coke formation process, which causes that catalyst deactivation has occurred rapidly, and its working cycle will be shortened.

In this connection, it is necessary to determine the optimal process conditions under which the maximum yield of a given quality is achieved, but coke formation does not limit the rate of target reactions. The quantity of the target product, expressed in octane-tons, is taken as an optimal criterion. Furthermore,  $\omega$ , which is yield in octane-tons, is calculated using Equation 13.

$$\omega = \frac{w \cdot RON}{100} \quad (13)$$

where  $\omega$  is yield in octane-tons;  $w$  is yield, %mass, and RON is research octane number.

The limiting condition that does not allow to reduce the pressure to a minimum is the coke formation rate. In addition, this rate increases with a decrease in pressure. The solution to this optimization problem will be to find the optimal solution (optimum), at which the maximum yield of a product of a given quality will be achieved, while not significantly exceeding the coke formation rate, leading to rapid deactivation of the Pt catalyst (Figure 8).

Therefore, it is not recommended to maintain process with pressure below 1.2 to 1.4 MPa in order to avoid rapid catalyst deactivation.

### Reactor Configuration Setup Analysis

The reactor unit is one of the most important units of the catalytic naphtha reforming process [1]. The yield and the quality

of the desired products depend on reactor configuration and design aspects. Various types of reactor configurations with different modes of operation have been suggested. These configurations could be categorized due to the entrance flow pattern of the feedstock as axial-flow and radial-flow reactors. Also, the shape of the reactors could be divided into spherical and tubular [46]. In an axial flow reactor, feed enters at one end of the reactor, flows across the catalyst bed in the direction along the axis of the reactor, and exits from the other end. In comparison with that, a radial flow reactor is designed so that the feed is distributed along the length of the reactor. Flow passes through a catalyst bed in the radial direction and then exits the system. This technique is beneficial because it has low hydraulic flow resistance, and the mixture of naphtha feed with hydrogen gas has better distribution through the catalyst bed. Radial-flow patterns can also differ in the direction of the flow: it can be direct from the periphery to the center or from the center to the periphery. Using mathematical model, the results of the main catalytic reforming indicators after the flow direction changing in the reactor were obtained. The model does not consider the geometry of the reactor and the direction of flow (and even pressure drops in the catalyst beds), but it considers the deactivation of the catalyst for different feed directions. The results of the calculation are performed in Table 6.

From the results performed, it could be concluded that the direction of flow changing has a positive result because:

- The temperature of the entrance is reduced by 9°C;
- The concentration of hydrogen is higher, about 1-2%;
- The yield is 88% in contrast to 85%.

This fact could be explained that in the second case, the flow is more uniformly distributed throughout the reactor bed, and good conversion of the reaction is achieved, which leads to higher product yield. In addition, all parts of the catalyst bed are used equally, which could help to avoid corrosion.

### Conclusions

Catalyst service life increasing is a vital task of resource and energy saving in the significant refining and petrochemical processes. A large number of studies have been devoted to the mathematical modeling of catalytic naphtha reforming. Catalyst deactivation due to coking is one of the main problems related to mathematical process description. Moreover, the process of catalyst deactivation is continuing with its self-regeneration under the influence of hydrogen. In the case when reaction rates of deactivation and self-regeneration are equal to each other, the level of stationary (optimal) activity is established.

Catalyst deactivation and problems arising are the results of many factors, and they can be solved successfully using mathematical modeling method. For now, there is no possibility to prevent the process of deactivation completely because the creation of effective technology of catalyst operation throughout its life service based on the mathematical model is the most optimal and appropriate method.

Catalytic reforming process optimization, which can be achieved by technological conditions, improve and modify reactor configuration setup. Both ways of processes of optimization contribute to an increase in product yield and a reduction in the accumulation of coke. As a result, financial costs are reduced.

**Table 6** Results of calculation of radial-flow tubular reactor characteristics with the mathematical model.

Directions of radial flow	from the periphery to the center		from center to periphery			
	Volume of raw material processed, t	199440	221760	241920	285840	307440
Hydrogen, %	80,0	81,0	84,0	83,0	81,0	83,0
Temperature in the entrance, °C	489	492	483	486	489	486
Aromatics, %mass	61,11	59,78	58,71	59,47	59,45	60,30
Coke, %mass	2,50	2,57	3,37	3,48	3,54	3,76
Research Octane Number (RON)	94,30	93,70	93,20	93,50	93,50	94,00
Product yield (on average), %mass	85		88			
Criteria of effectiveness, $\Delta$	0,18		0,06			

### Nomenclatures

CCR: Cyclic catalytic reformer

RON: Research octane number

SRR: Semi-regenerative catalytic reformer

UICP: Unsaturated immediate compacting products

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