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A mini-review

Achievements and future prospects in the scientific field of mathematical modeling of the catalytic reforming of gasoline

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Abstract: Catalytic reforming of gasoline is a pivotal industrial process among those aimed at enhancing the octane rating of motor fuels - products that are projected to maintain high demand in the foreseeable future. Extensive research has been devoted to improving the design of reforming processes, reactor configurations, and catalyst formulations. Given the complexity of catalytic reforming - which involves a multicomponent feedstock and product mixture, a bifunctional catalyst system, numerous parallel and sequential reactions, and catalyst deactivation mechanisms - mathematical modeling remains the principal tool for process investigation and optimization.

This paper provides a concise review of the evolution of kinetic modeling approaches for catalytic reforming, beginning with foundational work from 1959. Particular attention is given to the research conducted at the National Research Tomsk Polytechnic University, where a well-established scientific school has focused on developing mathematical models for petrochemical and refining processes. Using the catalytic reforming of gasoline as a case study, the paper outlines a methodological approach for constructing non-stationary models and describes the key principles underlying their development. The modeling results presented demonstrate the potential for optimizing reactor design, maintaining the balance between the catalyst's acidic and metallic functions, and minimizing coke formation on the catalyst surface.

The results of improvement of the mathematical model of catalytic reforming with a stationary catalyst bed taking into account the involvement of additional feed streams are presented.

Keywords: catalytic reforming, mathematical model, bifunctional catalyst, reactor, deactivation, coke formation, organochlorine compounds, optimisation, raw material flows

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1. Introduction

Production of high-octane fuels that meet modern environmental and operational requirements is one of the primary tasks of Russian oil refining. The catalytic reforming process is the key industrial technology for production of high-octane components of motor fuels in Russia and abroad. According to forecasts (Organization of the Petroleum Exporting Countries), in almost all regions of the world, except Europe, reforming takes and will take a significant share in production. By 2050,

the total capacity of reforming units is expected to reach 200 million tonnes per year, alkylation - 85 million tonnes per year, isomerization - 10 million tonnes per year, MTBE/ETBE - 15 million tonnes per year (Organization of the Petroleum Exporting Countries). Currently, Russia operates 51 reforming units with a total capacity of about 30 million tonnes per year.

Improving the resource efficiency of high-octane motor fuel production requires practical tools, chief among them being mathematical models grounded in fundamental knowledge of the kinetics and thermodynamics of oil refining. These models serve not only to describe but also to predict the behavior of complex processes like catalytic reforming. Similar to other petroleum refining and petrochemical operations, catalytic reforming poses significant challenges due to the multicomponent nature of the feedstock and the numerous reactions occurring on bifunctional catalysts that combine both acidic and metallic sites.

The yield and octane number of the reformate - the main product of reforming - are strongly influenced by catalyst activity (Gyngazova et al., 2010; Sharova et al., 2009). However, one of the main side reactions in this process is coke formation, which gradually deactivates the platinum-based catalyst. This ongoing catalyst deactivation, coupled with the dynamic nature of the reaction system and catalyst surface, necessitates continuous adjustments to the operating and regeneration modes of these heterogeneous precious-metal catalysts.

Against this backdrop, a critical direction in fuel processing technology is the development of strategies to extend catalyst life. This can be achieved through the applied use of mathematical modeling to simulate catalytic hydrocarbon processing under non-stationary operating conditions.

The improvement of catalytic reforming process is the subject of a large number of works aimed at modernization of technological and apparatus design, development of catalysts with improved properties, as well as creation of mathematical models of the process (Ali et al., 2005; Ancheyta, 2011; Arani et al., 2009; Belyi, 2005; Dyusembaeva & Vershinin, 2019; Elizalde & Ancheyta, 2015; Hamied et al., 2022; Hongjun et al., 2010; Hou et al., 2006; Krane, 1959; Lid & Skogestad, 2008; Petrova et al., 2021; Rahimpour et al., 2013; Ramage et al., 1980; Smith, 1959; Wei & Prater, 1962; Yusuf, Aderemi, et al., 2019; Yusuf, John, et al., 2019; Zagoruiko et al., 2014, 2021; Zaynullin et al., 2020; Ostrovskii, N. M., Sokolov, V. P., Aksenova, N. V., & Lukyanov, B. N., 1989; Reutova & Iriskina, 2000).

Among the notable achievements in the field of modeling gasoline reforming technology, the work carried out by scientists at Tomsk Polytechnic University, under the guidance of Professors A.V. Kravtsov and E.D. Ivanchina, stands out. Their scientific school has produced a substantial body of research dedicated to the catalytic reforming process, employing both newly developed and refined mathematical models. The researchers of this group have accumulated extensive expertise in modeling various oil refining processes and have made significant contributions not only to enhancing the resource efficiency of catalytic reforming but also to establishing methodological and scientific foundations for the field (Abramin, 2010; Galushin, 2004; Gyngazova, 2011; Ivanchina, 2002; Koksharov, 2023; Konstantinovich, 2016; Kostenko, 2006; Poluboyartsev, 2007; Pchelintseva, 2019; Sharova, 2010).

2. Theoretical foundations and methods of kinetic description of catalytic reforming of naphtha, taking into account non-stationarity

Catalytic reforming remains a fundamental technology for producing high-octane fuels, having undergone few radical changes over the decades (Antos & Aitani, 2004; Arab Aboosadi et al., 2011; Ciapetta & Wallace, 1972; Demirbas, 2011; Ding et al., 2013; Hui et al., 1995; Khobragade et al., 2012; Pujadó et al., 1992; Roddy, 2012). A valuable by-product of this process is hydrogen (Namioka et al., 2011; Taghvaei et al., 2012). The evolution of catalytic reforming has primarily focused on improving catalyst stability, increasing feedstock conversion rates, enhancing process selectivity, and optimizing operational conditions, particularly through pressure reduction (Rahimpour et al., 2013). Reforming catalysts serve dual functions: metallic and acidic. Maintaining the optimal balance between these functions is achieved by the continuous introduction of water and

chlorine into the reaction zone. A shift toward stronger acidic functionality enhances hydrocracking reactions, which, although beneficial in some contexts, ultimately lowers the yield of the main product, high-octane reformate (Benitez et al., 2007; Benitez & Pieck, 2010; Mazzieri et al., 2009). Naphtha, the typical feedstock for reforming, is a highly complex hydrocarbon mixture containing more than 300 individual components (Stijepovic et al., 2009). These components undergo a range of reactions, including dehydrogenation and isomerization of naphthenes; dehydrocyclization, isomerization, and hydrocracking of paraffins; and side reactions such as coke formation, which contributes to catalyst deactivation (Ancheyta-Juárez & Villafuerte-Macías, 2000; Rodríguez & Ancheyta, 2011). In kinetic modeling, a key challenge lies in aggregating these numerous components in a way that preserves sensitivity to changes in the hydrocarbon composition of the feedstock. The first major attempt to simplify this complexity was made by Smith in 1959, who proposed a model comprising three lumped component groups - paraffins, naphthenes, and aromatics - undergoing four key reactions: dehydrocyclization, isomerization, hydrocracking, and aromatization (Smith, 1959). His model consists of three group components (paraffinic, naphthenic, aromatic hydrocarbons), which enter into four reactions (dehydrocyclisation, isomerisation, hydrocracking, and aromatisation). Subsequent models have progressively increased in complexity, aiming for greater accuracy and predictive power (Arani et al., 2009; Hongjun et al., 2010; HOU et al., 2006; Hu et al., 2004; Kmak & Stuckey, 1973; Krane, 1959; Marin et al., 1983; Padmavathi & Chaudhuri, 1997; Rahimpour et al., 2003; Taskar & Riggs, 1997; Zhorov et al., 1980).

Scheme of hydrocarbon transformation on a bifunctional catalyst

Based on the analysis of chromatograms of the hydrotreated feedstock and catalyst, along with the calculation of thermodynamic parameters and examination of catalyst samples, substances were grouped according to the physicochemical properties of individual hydrocarbons. As a result, both individual components and pseudocomponents participating in the reforming process with continuous catalyst regeneration were identified. The complete list of these components is provided in Table 1.

Table 1. Hydrocarbon groups aggregated according to the results of tests and calculations (for compiling a kinetic model of the process of catalytic reforming of petrol with continuous catalyst regeneration)

№	Component	№	Component
1	ethane	2	Propane
3	i-butane	4	n-butane
5	i-pentane	6	n-pentane
7	dimethylbutanes	8	Methylpentanes
9	n-hexane	10	Dimethylpentanes
11	methylhexanes	12	n-heptane
13	trimethylpentanes	14	Dimethylhexanes
15	n-octane	16	Methylethylpentanes
17	methylheptanes	18	Dimethylheptanes
19	trimethylhexanes	20	Methyl ethyl hexanes
21	n-nonan	22	C9 and above
23	i-C9	24	Cyclopentane
25	cyclohexane	26	Methylcyclopentane
27	dimethylcyclopentanes	28	Ethylcyclopentane
29	methylcyclohexane	30	dimethylcyclohexanes
31	trimethylcyclopentanes	32	naphthenes C8

33	naphthenes C9	34	benzene
35	toluene	36	ethylcyclohexane+ethylbenzene
37	p-xylene	38	m-xylene
39	o-xylene	40	aromatic hydrocarbons C9 and higher

In a general form, the scheme of reagent transformations in the process of catalytic reforming of petrols for 40 components (Table 1), is presented in Figure 1.

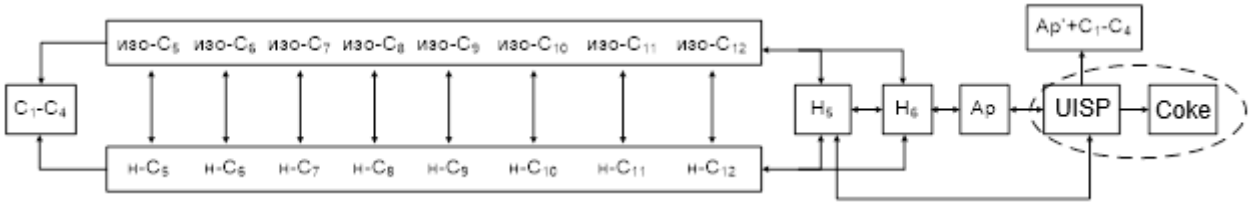


Figure 1. Formalised scheme of the mechanism of hydrocarbons transformation on Pt - catalysts: Ar, Ar' - aromatic hydrocarbons, H_6, H_5 - cycloalkanes, iso-C_5-1_2 - isoalkanes, n-C_5-1_2 - normal alkanes, UISP - unsaturated intermediate products of compaction

The proposed approach allows for the achievement of sensitivity of the model to the feedstock composition. Unlike aggregation by homological groups, the main characteristic of the target product in the production of commercial petrol-octane number is taken into account. Deactivation of catalysts plays an exceptional role in the reforming process. The study of the composition of coke deposits is one of the important tasks in studying the peculiarities of reaction progress in the reforming process. The causes of catalyst deactivation can be divided into three groups (Bartholomew, 2001; Chen et al., 2004): sulphur, nitrogen and heavy metal poisoning; thermal deactivation or aging due to a decrease in the active surface area; and coke formation. The first two causes are examples of irreversible catalyst deactivation, while the third is a reversible type of catalyst deactivation, provided the catalyst is regenerated or self-regenerated. Coke formation is the most important and controllable non-stationary process (Barbier et al., 1980, 1985; Ren et al., 2002). Predicting the dynamics of coke formation is a complex and multifactorial problem, which can be solved most effectively by mathematical modelling (Delmon & Yates, 1987; Figoli et al., 1982; García-Dopico et al., 2006). In (Bishara et al., 1984), the effect of temperature and pressure on the intensity of coke formation was investigated.

Reducing the temperature, increasing the pressure and the hydrogen/hydrocarbon ratio reduces the coke content on the catalyst. The hydrocarbon composition of the feedstock also affects the amount of coke produced. The coke content is lower when processing light naphthenic feedstock.

Samples of uncoked, regenerated, and coked industrial Pt-Sn/Al_2O_3 reforming catalyst were investigated. The studies were carried out by thermogravimetry and BET methods. The results of thermogravimetric analysis of samples of industrial gasoline reforming catalyst are presented in Figures 2-3.

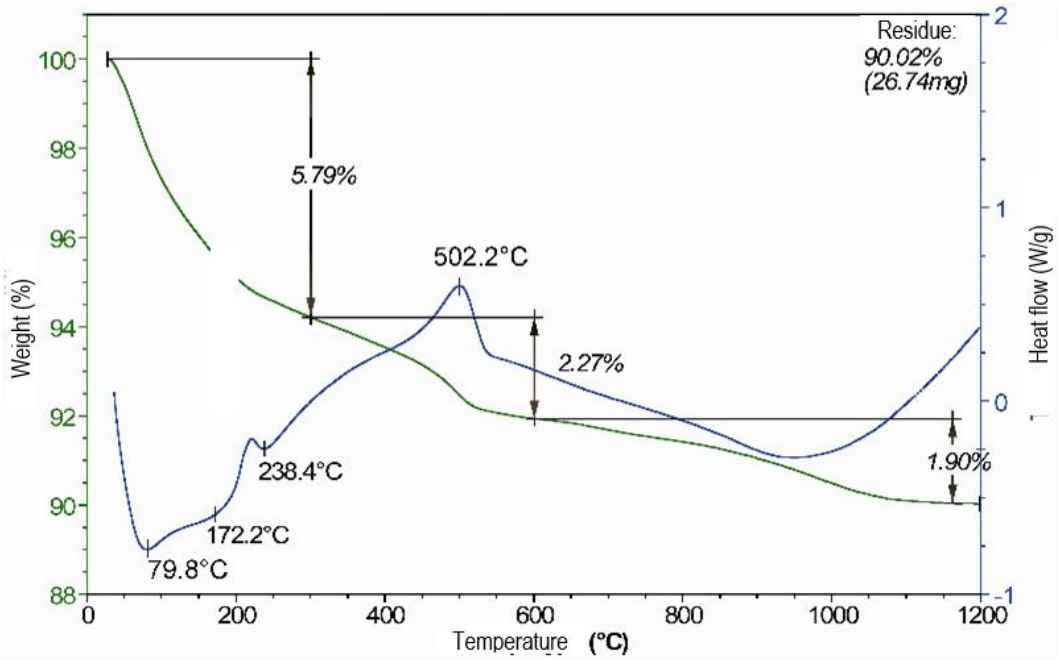


Figure 2. TG-DTA (thermogravimetric and differential thermal analysis) result of reduced Pt-Sn/γ-Al_2O_3 industrial reforming catalyst

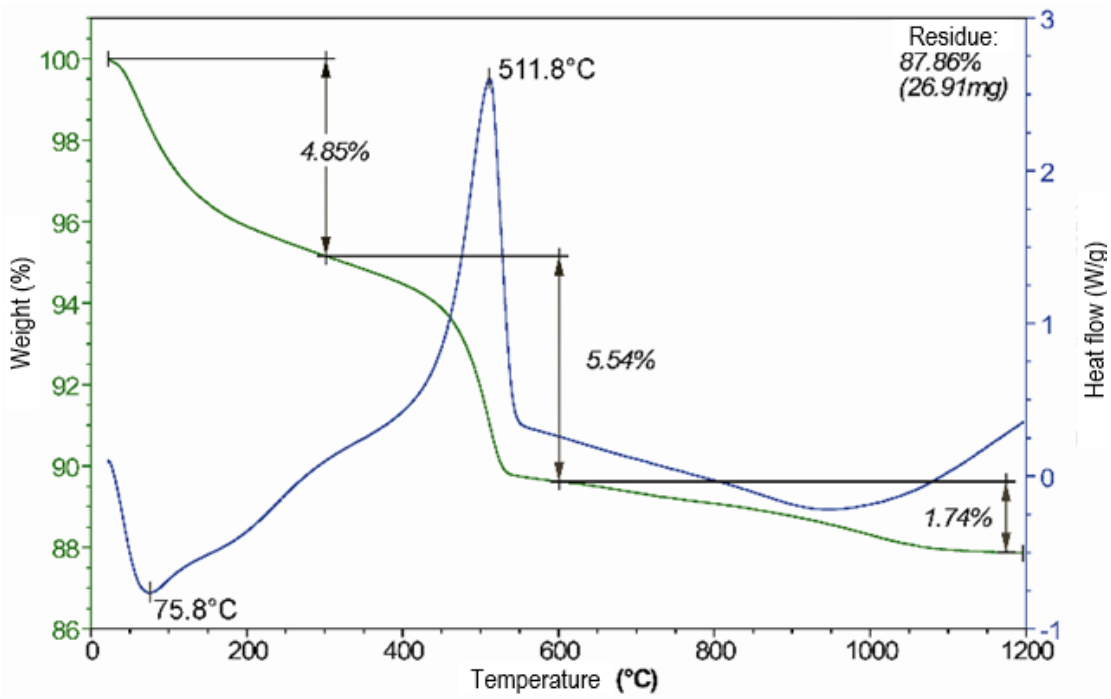


Figure 3. TG-DTA result (thermogravimetric and differential thermal analysis) of Pt-Sn/γ-Al_2O_3 encrusted industrial reforming catalyst

Thermogravimetry studies have shown that the average content of coke on the catalyst at the outlet from the reactor zone is 5-6 % wt. Coke deposits have a ‘loose’ structure, which is the so-called amorphous coke saturated with hydrogen.

The combustion of this type of coke occurs at the temperature of 450-550°C. On the reduced catalyst, the coke content varies within 1.0-2.5% wt. The results of the BET analysis are presented in Figure 4.

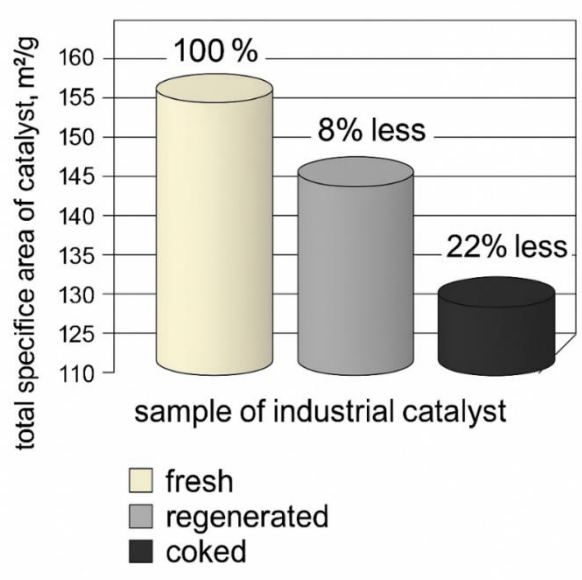


Figure 4. Results of catalyst-specific surface area analysis by the BET method

Analysis of the catalyst surface area using the BET method (Fig. 4) revealed a significant reduction in specific surface area following multiple regeneration cycles. In particular, the coked catalyst exhibited a surface area 22% lower than that of the fresh catalyst. This decline is a clear indication of catalyst degradation due to coke deposition. As a result, in reforming processes utilizing a stationary catalyst bed, both the maximum achievable depth of feedstock aromatization and the duration of inter-regeneration cycles are consistently below optimal (equilibrium) levels.

By contrast, processes employing a moving catalyst bed with continuous regeneration offer distinct advantages. These include deeper aromatization, lower system pressure, increased feedstock throughput, and higher reformate yield. However, to fully realize these benefits, it is essential to maintain catalyst operating conditions that allow the system to approach thermodynamic equilibrium, particularly for key reactions such as the formation of target aromatics and the hydrogenation of heavy by-products. Achieving this requires careful control over catalyst circulation and adjustment of the catalyst movement speed along the reactor's length, ensuring sustained equilibrium activity.

Most existing models describing catalyst deactivation in reforming are empirical. In such models, the parameters often lack clear physicochemical interpretation, as they are derived from statistical processing of large experimental datasets, typically using the method of least squares.

In the adopted formalized scheme of hydrocarbon transformations, coke was included as one of the reaction components and, therefore, the amount of coke on the catalyst can be found from the equation (1) of coke formation reaction kinetics. It was found that the activity of the catalyst in turn depends on the coke content and the catalyst circulation rate as follows (Gyngazova et al., 2011):

$$a_j = A_0 \cdot e^{-\alpha \cdot C_{coke}/h_u} \quad (1)$$

Here A_0-is a linear component determining the number of active centres; α is the poisoning factor, a non-linear component determining the different degrees of deactivation of corner and rib atoms when coke is deposited on them; for metal centres, for acid centres.

The catalyst circulation rate can be determined using the following equation:

$$h_u = \frac{u \cdot \rho_{SM}}{\phi \cdot \rho_{cat}} \quad (2)$$

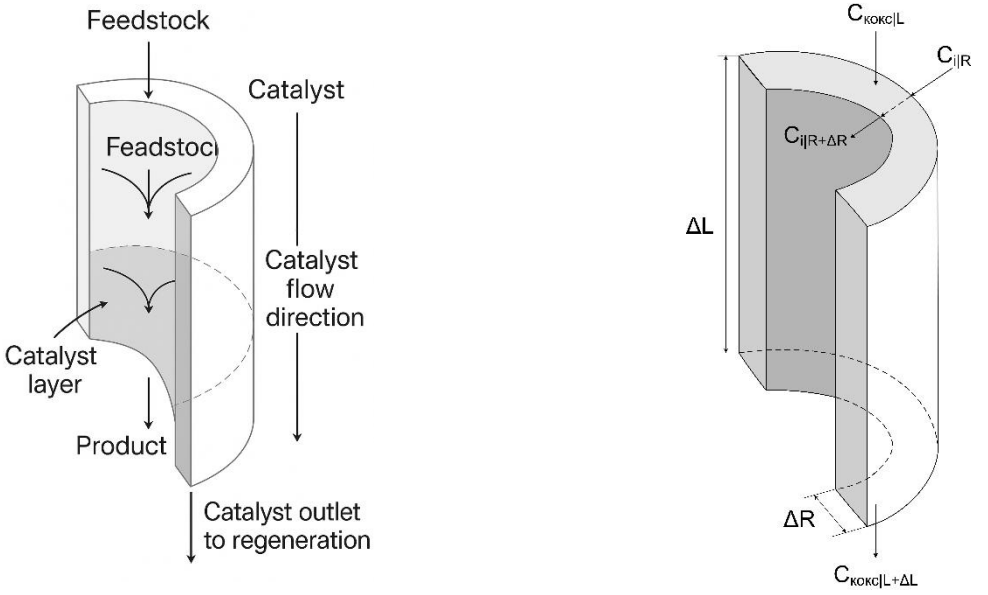
Determining the hydrodynamic regime within the contact reactor is a critical step in developing an accurate mathematical model of the reforming process. For systems utilizing a moving catalyst bed, it was established that the Reynolds number (Re) is approximately 5, while the modified Reynolds numbers for mass and heat transfer (Re_D and Re_T) are around 700 and 900, respectively. These values indicate laminar flow conditions (Re < 50), with convective transport processes dominating over diffusive transport within the catalyst bed ($Re_D > 200$, $Re_T > 200$). This suggests that the hydrodynamic regime within the reactor closely approximates ideal plug flow.

The catalyst movement velocity is significantly lower than the velocity of the main fluid stream ($\varphi << u$), allowing the associated effects on mass and heat transfer to be considered negligible.

Further calculations for industrial platinum-tin reforming catalysts show that the Thiele modulus (Φ_i) for various reaction types remains below 1, and the catalyst effectiveness factor ranges from 0.9 to 1.0. These findings confirm that internal diffusion limitations are negligible. As a result, catalytic reforming of gasoline with a moving bed operates within the kinetic regime, free from diffusion complications.

Therefore, diffusion complications are absent in the process of catalytic reforming of petrols with a moving catalyst bed, and the process proceeds in the kinetic region.

The design of a catalytic reforming reactor with a moving catalyst bed and explanations of the developed model are presented in Figure 5.



a) Reactor segment with moving catalyst bed

b) Catalyst bed, elementary volume

Figure 5. Schematic volumetric representation of the reactor with continuous catalyst regeneration

The mathematical model of the catalytic reforming process with a moving catalyst bed taking into account catalyst deactivation by coke is represented by the following equations of material and heat balances for components according to the formalised mechanism of hydrocarbon transformations:

$$G \cdot \frac{\partial C_i}{\partial z} = -u \cdot \frac{\partial C_i}{\partial r} - \varphi \cdot \frac{\partial C_i}{\partial l} + \frac{1}{l}\int_0^l W_j(l) a_j(l) dl \qquad (3)$$

$$\rho^{sm} \cdot C_p^{sm} \cdot G \cdot \frac{\partial T}{\partial z} = -u \cdot \rho^{sm} \cdot C_p^{sm} \cdot \frac{\partial T}{\partial r} - \phi \cdot \rho^{cat} \cdot C_p^{cat} \cdot \frac{\partial T}{\partial l} + \sum Q_j \cdot \frac{1}{l} \cdot \int_0^l W_j\,(l) a_j(l) dl \quad (4)$$

In the above system of equations (3) and (4), the residence time of reagents in the reaction zone, which depends on the hourly feedstock flow rate G and catalyst volume V, is replaced by the 'reduced time' z = G-t, which is equal to the total volume of processed feedstock for time t in conditions of unstable feedstock load of the industrial plant.

The concentration of components varies depending on u - the speed of the gas-raw mixture movement along the radius of the catalyst bed (raw materials are fed radially). The content of components in the mixture is also affected by φ - the speed of catalyst movement along the reactor height, since the coke content in different catalyst layers is different, and the catalyst activity changes differently along the layer height due to coke formation processes. The reaction rate Wj for the i-th hydrocarbon according to the transformation scheme depends on the catalyst motion coordinate l and catalyst activity a.

The developed mathematical model, in comparison with analogues, takes into account the catalyst movement along the reactor course and the corresponding change of its activity along the bed height, as well as the dependence of activity on the catalyst circulation ratio.

The values of kinetic parameters of the reforming process with continuous catalyst regeneration for industrial Pt-Sn/Al_2O_3 catalyst were determined for calculations using the mathematical model. It was shown that for Pt-Sn catalyst the rate of isomerisation of five-membered naphthenes into six-membered ones with subsequent dehydrogenation of cycloalkanes to aromatic hydrocarbons has the highest value. Isomerisation reactions of normal paraffins also proceed with high speed. As the molecular weight of hydrocarbons increases, the bonding energy decreases and the rate constants increase in proportion to the number of the hydrocarbon in the homologous series. The hydrocracking constants of lighter hydrocarbons are close in their values. For heavy hydrocarbons, a significant divergence is observed, with the hydrocracking constant of normal paraffins increasing faster than the hydrocracking constant of isoparaffins. Dehydrocyclisation of paraffins to five- and six-membered naphthenes occurs at approximately the same rates.

The developed model was checked for adequacy to the real process using experimental data from the industrial unit of catalytic reforming of petrol with continuous regeneration of catalyst L-35-11/1000. The results of calculation and experiment are given in Table 2 and Table 3.

Table 2. Calculation results of the process of catalytic reforming of gasoline with continuous catalyst regeneration on the mathematical model (at T=510°C, P=0,7 MPa, feedstock flow rate 160 m^3/h, catalyst circulation rate 0, 008 m^3/m^3)

Number of carbon atoms in a molecule	n-paraffins		i-paraffins		naphthenes-5		naphthenes-6		flavouring	
	calc	exp	calc	exp	calc	exp	calc	exp	calc	exp
4	1.50	1.53	0.54	0.53	0	0	0	0	0	0
5	1.49	1.51	2.57	2.49	0.21	0.22	0	0	0	0
6	1.85	1.89	5.12	5.07	0.19	0.16	0.11	0.12	5.06	5.07
7	1.33	1.37	5.16	5.11	0.13	0.09	0.09	0.07	20.07	20.09
8	0.32	0.34	1.53	1.49	0.17	0.15	0	0	26.16	26.18
9	0.03	0.04	0.20	0.20	0	0	0	0	20.34	20.35
10	0.16	0.19	0.09	0.09	0	0	0.5	0.56	5.08	5.09

Group composition										
Σ	6.68	6.87	15.21	14.98	0.7	0.62	0.7	0.75	76.71	76.78
Octane number of the catalyst by i.m.						103.2				
Product yield						90.35				

Table 3: Calculated and experimental values of coke content on the catalyst after the reactor block (calculated for experimental conditions)

Pt-Sn/γ-Al_2O_3 catalyst	**Coke, % wt.**	
	experiment	**calculation**
sample 1	5.54	5.63
sample 2	4.13	4.03

It is shown that the error of the calculated and experimental values does not exceed 3%. The proposed mathematical model can be used to perform predictive calculations when modeling the process of catalytic reforming of gasolines with continuous regeneration of the catalyst (in our case, the calculation error is determined by the error of the chromatographic analysis). Using the mathematical model, the main patterns of the catalytic reforming process in a reactor with a moving bed were studied (Figures 6-8).

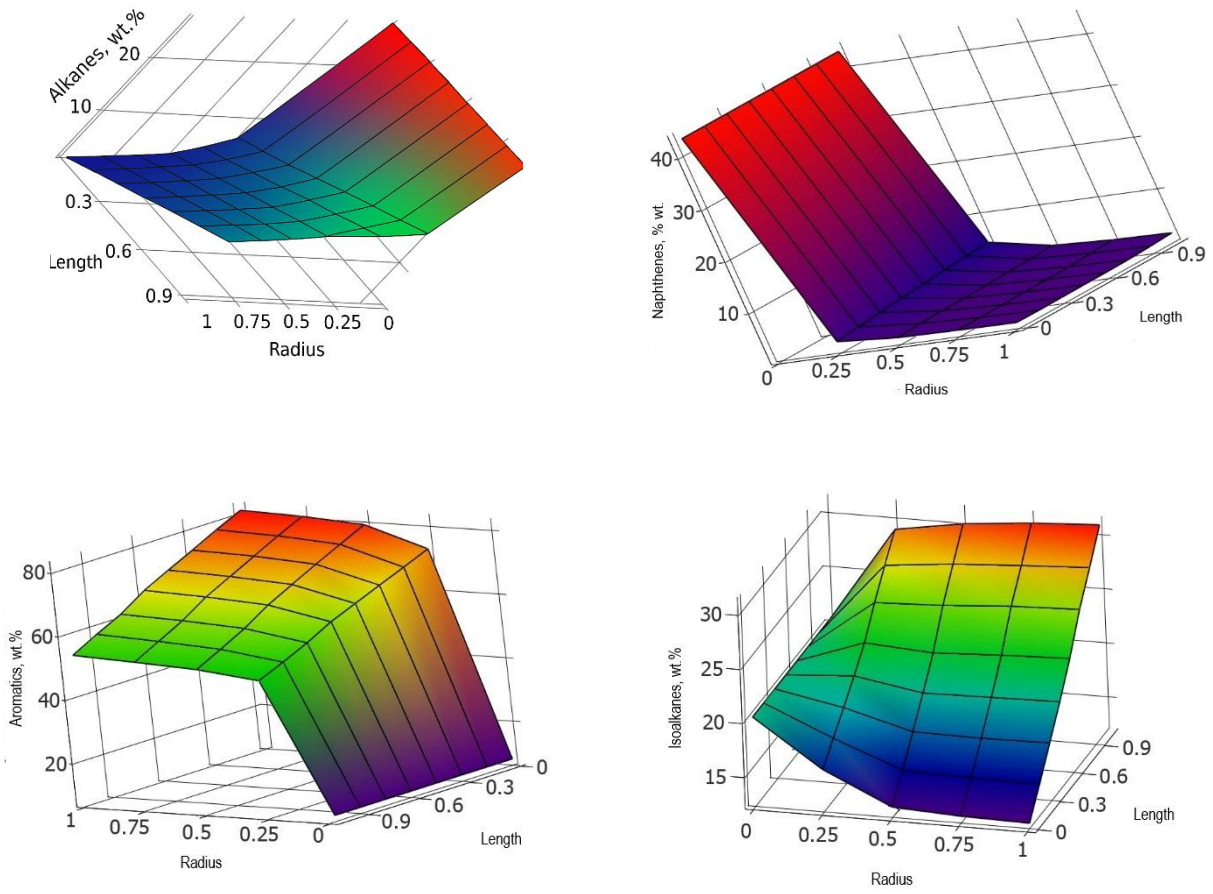


Figure 6. Changes in the concentration profile of reactants when passing through a catalytic reactor

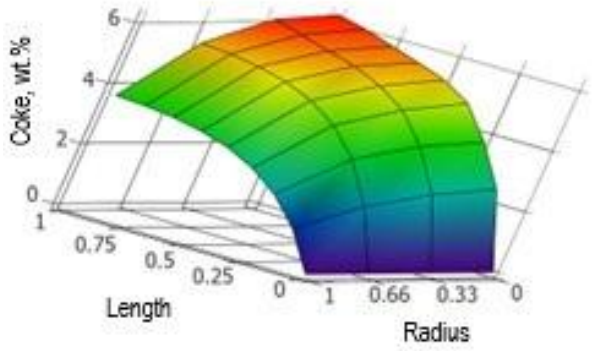


Figure 7. Profile changes of coke concentration during passage of the catalytic reactor

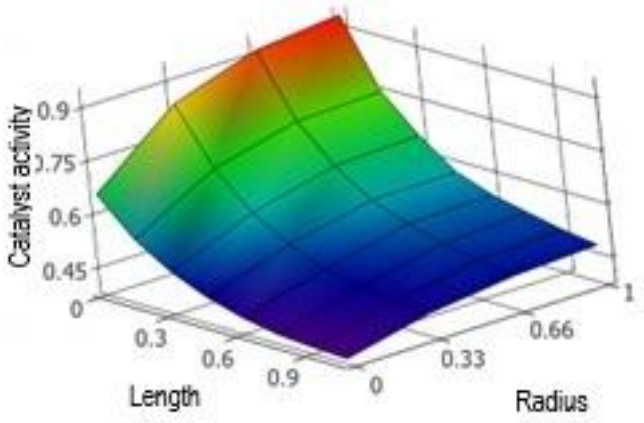


Figure 8. Changes of the profile of catalyst activity by the volume of the catalytic reactor

Research has shown that when the reaction mixture moves in the reactor at a higher rate, the conversion of components occurs at the beginning of the feedstock movement along the radius of the catalyst, since the mixture temperature and contact time are maximum (the catalyst volume decreases when moving along the radius with the same step from the periphery to the center). Along the length of the catalyst bed, there is a gradual conversion of alkanes and naphthenes and the formation of aromatic hydrocarbons and isocomponents. The concentration of coke deposits is higher at the inlet of the reaction mixture (along the radius), since in these zones, dehydrogenation of naphthenes to aromatic compounds, which are precursors of coke, occurs at a high rate. The temperature value is also maximum at the beginning of the reaction mixture movement. When the catalyst moves along the height of the reactor, a cumulative accumulation of coke on the catalyst occurs**.** At the outlet of the reactor block, the coke concentration on the catalyst is about 4% by weight in the central and 6% by weight in the peripheral parts of the reactor. Thus, the uneven distribution of the concentration profile of the reagents and temperature is the cause of the uneven distribution of coke along the radius of the reactor - the difference in coke concentrations between the extreme points is 2% by weight. The catalyst activity profile by the reactor volume is an accurate reflection of the degree of its coking. It is shown that the highest values of catalyst activity are in the upper part of the reactor, and the radial activity is lower at the points of introduction of the reaction mixture (i.e., for the real case under consideration, closer to the periphery). Figures 9 and 10 show the results of model calculations of the concentration of coke formed on the surface of the catalyst depending on its circulation rate.

It is shown that with an increase in the catalyst circulation factor, the coke content at the reactor outlet decreases. The catalyst passes the reactor at a higher speed, the active centers do not have time to deactivate, and the content of target components in the reformate increases. With a twofold increase in the catalyst circulation factor, the coke concentration decreases by about 2% by

weight, depending on the specific composition of the feedstock stream. The working range of changing the catalyst circulation factor is 0.008–0.010 m^3/m^3. To increase the octane number of the product and reduce the coke content on the catalyst, this parameter can be varied by making preliminary calculations using the model.

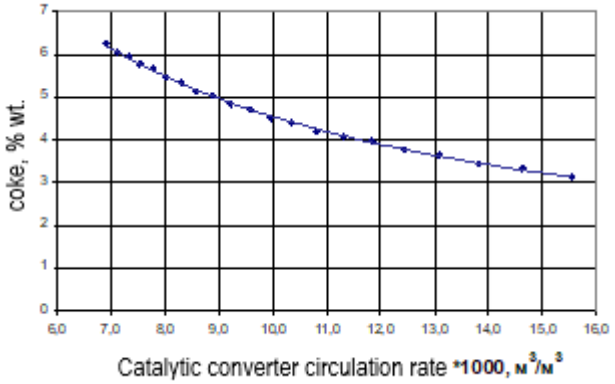


Figure 9. Dependence of the coke content on the catalyst at the outlet of the reforming reactor block on the catalyst circulation rate (according to the model)

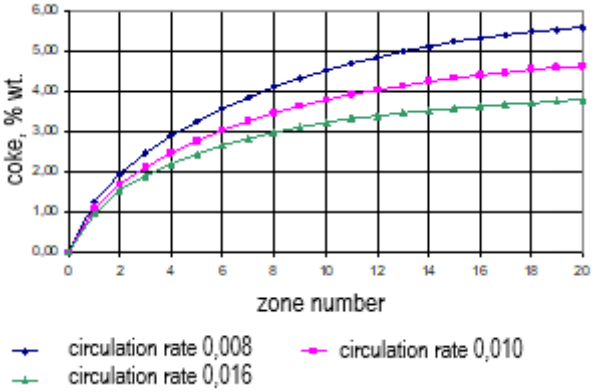


Figure 10. Change in coke content when the catalyst moves along the reactor for different values of the catalyst circulation rate: h_1=0.008 m^3/m^3; h_2=0.010 m^3/m^3; h_3=0.016 m^3/m^3 (according to the model)

Reactor design. The reactor design determines the change in the operational properties of the catalysts (activity, selectivity, and stability). In a multilayer tubular reactor with a fixed catalyst bed, the thermal scheme of the process is effectively implemented - the thermal energy of the exothermic hydrocracking reaction is used as a heat source for the endothermic reactions of naphthene dehydrogenation and paraffin dehydrocyclization (Koksharov et al., 2015; Rahimpour & Bahmanpour, 2011). The direction of movement of the gas-feedstock flow of hydrocarbons is of great importance. With radial input of raw materials, the hydraulic resistance of the flow is significantly reduced. Membrane reactors are devices that implement a combined process of chemical conversion and product separation with subsequent removal of target components to shift the equilibrium towards the formation of aromatic hydrocarbons (Arab Aboosadi et al., 2011; Choudhary et al., 2000; Iranshahi et al., 2012; Pereira et al., 2010; Rahimpour et al., 2010, 2013; Teixeira et al., 2010; Zhu et al., 2010). The catalytic reforming process is classified according to the catalyst regeneration technology into three groups: 1) with continuous regeneration and a moving catalyst bed; 2) with cyclic regeneration and a fixed catalyst bed; 3) with periodic regeneration of the catalyst located in the reactor as a fixed bed. In industry, catalytic reforming units for gasoline with a number of reactors with a moving bed from 3 to 5 are usually used. With a decrease in catalyst activity, the yield of aromatic hydrocarbons and the concentration of hydrogen in the VSH decrease. To determine the optimal number of reaction apparatuses, calculations were carried out using a mathematical model. The nature of the effect of increasing the number of reactors from 3 to 5 on such process parameters as octane number, catalysate yield, aromatic compound content, etc. was established. The calculation was carried out for the operating conditions of the process. The results of the calculation of the octane number and reformate yield are shown in Figure 11.

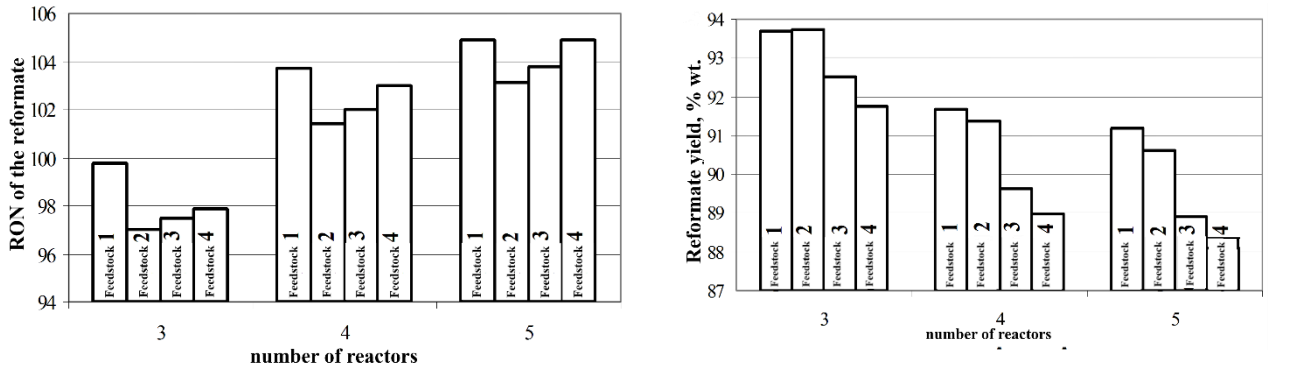


Figure 11. Effect of the number of reactors in the process flow chart of catalytic reforming with continuous catalyst regeneration on the yield and octane number of the reformate: ratio of paraffins/(naphthenes+aromatics): for feedstock 1=0.50; for feedstock 2=0.68; for feedstock 3=1.04; for feedstock 4=1.58

Based on the calculation results, it was established that an increase in the number of reactors has a beneficial effect on the process, since the temperature difference during the transition from one reactor to another decreases, the contact time increases, which entails an increase in the octane number, an increase in the content of toluene, xylene and the content of aromatic hydrocarbons in general.

On the other hand, if the process is carried out in a reactor block of five reactors using a cascade scheme, the resulting catalysate does not differ significantly in target indicators from the catalysate obtained using a four-reactor scheme (with an increase in the number of reactors from 3 to 4, the main indicator of the reformate quality - the octane number increases by 4 points, and when switching from a four- to a five-reactor scheme - by only 1 point). In turn, a cascade of 3 reactors showed the worst results, since in this case, the greatest temperature difference will be observed when moving from reactor to reactor. Therefore, despite the fact that an increase in the number of reactors and bringing the process closer to isothermal conditions has a favorable effect on the process, in this case, taking into account the economic component, the optimal number of reactors will be 4.

Further studies showed that the direction of movement of the feedstock flow in the cascade of reactors also affects the efficiency of the process. To determine the optimal direction of feedstock movement in reforming reactors with a moving catalyst bed, calculations were performed using a multi-zone mathematical model. In such a model, zones are formed by a cross-section of coaxial cylinders to account for changes in the volumetric and linear velocity of the gas-feedstock flow when moving along the radius of the reactor with radial feedstock input (Figure 12). The catalyst volume in the reactors was conditionally divided into 4 zones with the same step along the radius.

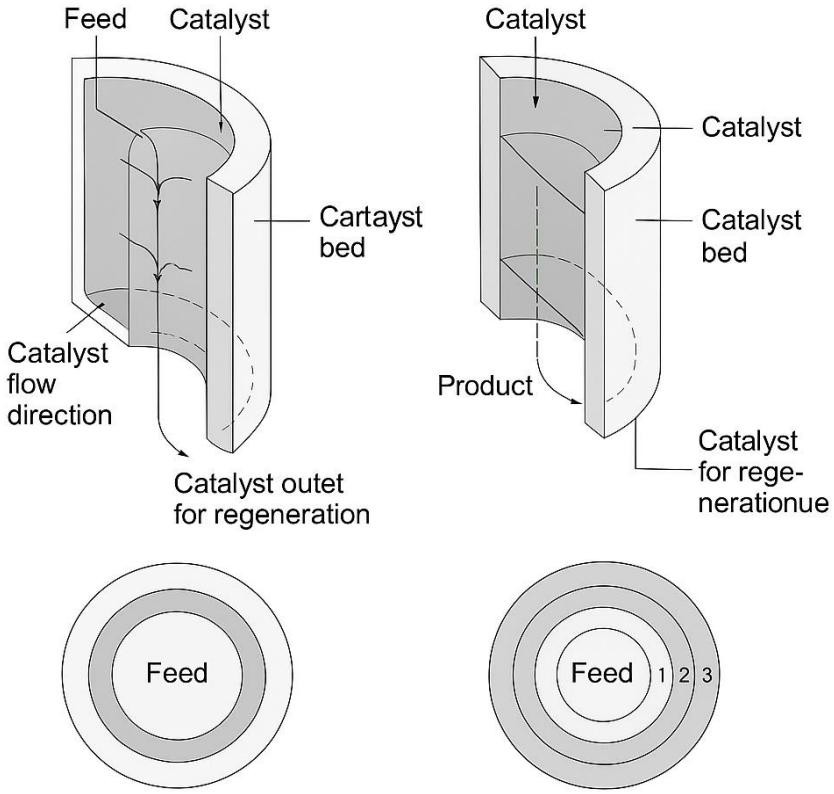


Figure 12. Schematic volumetric representation of the segments of a reactor with a moving catalyst bed for different options for the direction of feedstock movement: a) from the periphery to the center (implemented in existing installations), b) from the center to the periphery

The volume of each zone increases with radial movement from the center to the periphery (therefore, the volumetric velocity decreases), the temperature decreases, since the total thermal effect of the reforming reactions is negative, and the process is endothermic. The model is a system of equations of material and heat balances for each hydrocarbon and the entire set of reactions. Within each zone, the change in the concentration of components is written as follows in equation (5):

$$G \cdot \frac{\partial C_i}{\partial z} = -u \cdot \frac{\partial C_i}{\partial r_n} - \varphi \cdot \frac{\partial C_i}{\partial l} + \frac{1}{l}\int_0^l W_j(l) a_j(l) dl \qquad (5)$$

at z=0 C_i=0, T=0; at l=0 C_i=C_i,0, T=T_i (at the reactor inlet); at r=0 Ci=Ci,0, T=T_i, where n is the reactor zone number; z is the volume of processed feedstock, m^3; G is the feedstock flow rate, m^3/h; u is the linear flow rate, m/h; l is the length of the catalyst bed in the reactor, m; φ is the catalyst velocity, m/h; Wj is the total reaction rate, mol/(m^3 h).

The results of calculations using the model for changing the feedstock feed direction are shown in Figure 13, indicating improved aromatic yield and octane number when switching to center-to-periphery flow.

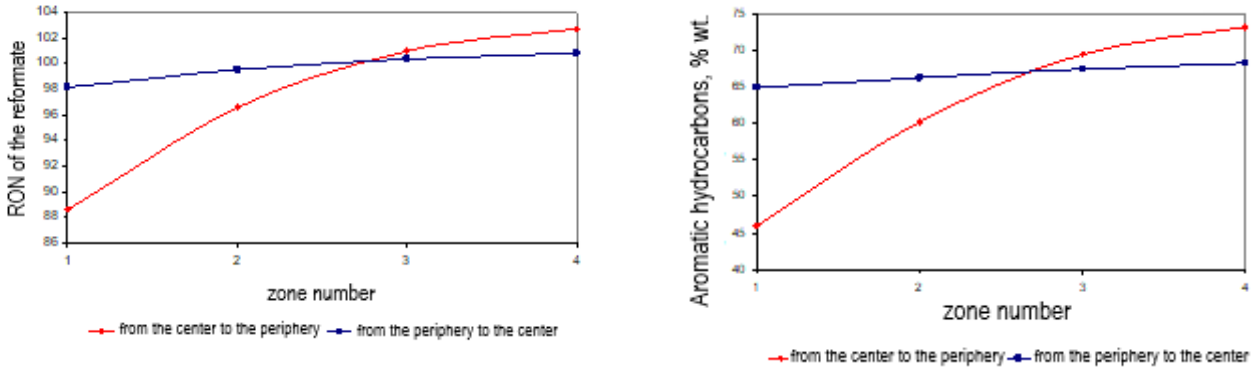


Figure 13. Change in the octane number of the flow and the yield of aromatic hydrocarbons when moving raw materials from the center to the periphery and from the periphery to the center

According to the calculations, after changing the direction of feedstock flow, the yield of aromatic compounds increases by approximately 5% by weight. Changing the direction of the gas-feedstock mixture to movement from the center to the periphery will allow obtaining a product with a higher-octane number, all other process parameters being equal (an increase in the RON of about 2 points for different compositions of the feedstock and process conditions).

Thus, to obtain a catalyzate with a given octane characteristic for a reactor with a feedstock flow direction from the center to the periphery, it will be possible to reduce the "rigidity" of the process (reduce the temperature by 10-15°C) compared to the traditional option of feedstock movement in the reactor.

Numerical studies have shown that reactor devices with a feedstock feed direction from the center to the periphery are more effective for reforming gasolines. Firstly, the non-stationarity of the coke deposition process determines that the flow from the center to the periphery leads to more uniform deactivation and, as a consequence, to a higher yield of the target product due to an increase in the degree of conversion of paraffins and cyclopentanes. Secondly, high values of the volumetric velocity in the initial zones of the catalyst when moving from the center of the reactor to the periphery (movement along the opening cone) are compensated by a higher temperature. However, the temperature profile changes quickly, since the reforming process is endothermic. In this case, the octane number of the catalyst increases by about 2 points.

Optimization of reforming process conditions to reduce coke accumulation on the surface of the Pt catalyst. The studies have shown that the high stability of the target products – aromatic hydrocarbons – under catalytic reforming conditions is the theoretical justification for choosing this criterion as an indicator of the activity level. With an increase in the coke concentration, the catalyst activity with respect to the cyclohexane dehydrogenation reaction and the number of surface Pt atoms decrease. This confirms the possibility of using the naphthene dehydrogenation reaction to aromatic hydrocarbons as a test for Pt center deactivation. When the acid centers of the support are deactivated, the rates of isomerization, cyclization, and hydrocracking change simultaneously. Deactivation of Pt centers has little effect on the isomerization rate. At the same time, a decrease in the dehydrocyclization reaction rate at the same coke concentration is noticeably higher than a decrease in the deactivation rate of isomerization reactions, and therefore cannot be explained only by the deactivation of acid centers. A decrease in the rates of dehydrocyclization reactions is a result of the complex effect of Pt and acid center deactivation. The n-paraffins/isoparaffins ratio in the product remains virtually unchanged at the same catalyst activity. The degree of cyclopentane conversion also remains practically unchanged at the same catalyst activity. When the catalyst is deactivated by coke deposits, both the metal and acid functions of the catalyst decrease, while the water-chlorine balance in the catalysis zone ensures optimal acid activity of the catalyst. The steady-state or optimal catalyst activity

corresponds to the conditions of thermodynamic equilibrium of the reaction of coke formation, hydrogenation of intermediate compaction products. In this case, the coke concentration does not increase on the metal, but its growth occurs on the surface of the carrier, and the catalyst has maximum selectivity. The formation of coke from hydrocarbons is predetermined thermodynamically.

Thermodynamic calculations indicate a general direction of hydrocarbon conversion towards the formation of graphite-like structures. The kinetics of hydrocarbon conversion, which is determined by the process mode and catalyst activity, ensures an increase in the rate of hydrogenation of intermediate compaction products and the formation of liquid hydrocarbons.

Hydrocarbon aromatization reactions are competitively associated with coke formation reactions.

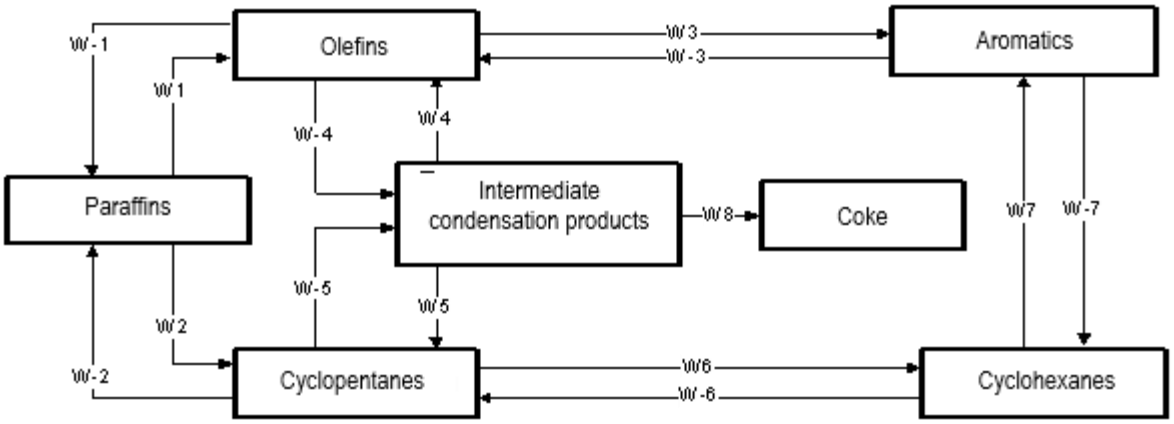


Figure 14. Hydrocarbon conversion reactions during gasoline reforming

All reactions depicted in the reaction scheme are reversible, with the exception of stage W8 (Figure 14), which results in the formation of graphite-like coke. Mitigation of coke formation can be achieved through two primary strategies: (1) increasing the ratios W3/W4 and W6/W5 to promote hydrogenation over polycondensation, and (2) directly reducing the rate of the irreversible W8 reaction.

Notably, the order of the target reforming reactions is lower than that of the coke formation reactions. Therefore, by regulating catalyst activity, it is possible to prevent the progression toward coke graphitization and subsequent pore blockage, which is especially critical since graphite-like coke embedded in the catalyst structure can only be removed through oxidative regeneration.

The equilibrium conditions for polycondensation–hydrogenation pathways are defined by the reversible reaction pairs W3–W–3, W4–W–4, and W5–W–5. At suboptimal catalyst activity (a < a_opt), coke tends to form as carbon filaments, which can still be hydrogenated back into hydrocarbons. At optimal activity (a = a_opt), two-dimensional polar particles are formed, which begin to polymerize as the activity increases further. This progression in coke structure is governed by the thermodynamic equilibrium of the polymerization reactions.

An increase in process temperature or a reduction in feedstock throughput can induce desorption of carbonaceous species into the gas phase, where they may undergo further polymerization into three-dimensional coke structures. On the catalyst surface, however, coke depolymerization occurs, leading to the formation of alkylaromatic compounds. The conditions for depolymerization depend on several factors, including the feedstock's hydrocarbon composition, reactor operating mode, and the current state of catalyst activity.

To restore catalyst activity and hydrogenate intermediate compaction products in the L-35-11/600 reforming unit, optimal hydrochlorination conditions were determined using the developed mathematical model. Under this mode, the shift in thermodynamic equilibrium for coke formation

and hydrogenation reactions was achieved by modifying the process parameters and increasing the hydrogen content in the hydrogen-rich gas.

The operating and target parameters for the hydrochlorination regime are summarized in Table 4. Under these conditions, the temperature in the reforming reactors was lowered to 420 °C, and the pressure increased to 3.0 MPa. As a result, the hydrogen concentration in the circulating gas rose to 93 vol.%, enabling favorable thermodynamic conditions for hydrogenating non-graphitized coke and reducing its content from 5.09 to 3.2 wt.%.

Table 4. Results of the calculation on the hydrochlorination process model

№ experiment	1	2	3	4
Catalyst activity, rel. units	0.58	0.6	0.57	0.37
Volume of processed feedstock, t	816000	817100	831400	856685
Hydrogen content, vol. %	93.1	76.9	75.1	83.6
Hydrogen yield, wt. % on feedstock	0.6	1.8	1.93	2.42
Inlet temperature, °C	420	498	511	507
Feedstock flow rate, m^3/h	60	60	106.4	69.9
Steam/(Naphth+Ar), rel. units	1.6	1.5	1.6	1.19
n-Steam/i-Steam in feedstock, rel. units	1.28	1	1.29	0.74
Circulation rate, nm^3/ m^3	1130	1554	1130.8	1311.4
Degree of isomerization, wt. %	44	34	51	39
Degree of aromatization, wt. %	1.48	23.65	24.26	13.33
Aromatics, wt. %	24	56.73	56.29	57.4
Coke, wt. %	3.2	5.09	5.19	5.21
Octane number, purity index	76	95.3	91.1	91.8
Reformate yield, wt. %	95	82.08	83.82	86.61

Also, when the temperature in the reforming reactors decreased, a decrease in humidity, HCl, and H_2S concentrations was observed. This effect indicates that these substances were absorbed by the catalyst surface. The main parameters of the reforming unit after the hydrochlorination operation are given in Table 5.

As a result of the hydrochlorination operation of the reforming catalyst of the L-35-11/600 unit, a positive effect was obtained, which is confirmed by obtaining an octane number analysis of 95.0 p.

Table 5. Comparison of the operating modes of the reforming unit during the hydrochlorination process

Mode parameters	Before hydrochlorination	After hydrochlorination
Input P-2, °C	498	497
Input P-3, °C	495	495
Input P-4/1, °C	493	493
ΔT P-2, °C	55	56
T P-3, °C	20	21
ΔT P-4/1, °C	7	9
ΔT P-4/2, °C	7	8
Plant loading, m^3/h	65	60

Circulation rate, nm^3/ m^3	1554	1667
Input P-2, MPa	2.6	21.5
Octane number, purity index	93.8	95.0
H_2 concentration, vol.%	76.5	76.9
HCl consumption, mg/kg	3.0	–

The obtained data show that the hydrochlorination process allows partial restoration of the catalyst activity without stopping the production of products. Before the hydrochlorination process, the product quality had a deviation from the required indicators, as a result of hydrogenation of unsaturated products of compaction, the catalyst activity increased, and a product corresponding to the required quality indicators was obtained.

Balancing of acid and metal sites on bifunctional Pt reforming catalysts

A critical condition for the optimal operation of bifunctional platinum-containing reforming catalysts is achieving a balance between their acidic and metallic functionalities. The acidic function is provided by the alumina support, which is promoted with organochlorine compounds. An excess of acid sites can lead to undesirable hydrocracking reactions, thereby reducing product yield and selectivity. Organochlorine compounds, when introduced into the reforming reactor block, decompose to form hydrogen chloride, which enhances surface acidity and promotes the selective conversion of hydrocarbons. This, in turn, deepens the conversion of feedstock hydrocarbons and increases the octane number of the reformate.

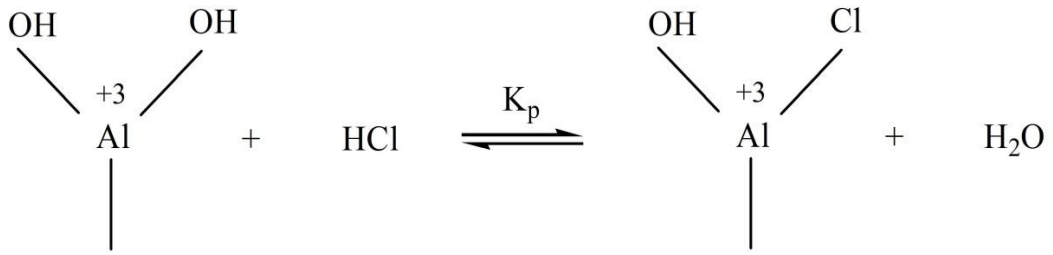
A well-developed physicochemical model of the reforming process enables the determination of optimal process conditions and feedstock compositions to ensure high efficiency through balanced acid and metal activity. Such a model allows for reactor optimization under various industrial operating conditions. Addressing the multifactorial challenge of optimizing reforming parameters - accounting for catalyst deactivation via coke deposition, fluctuations in feedstock composition and flow rate, and changes in system humidity - is made possible by regulating the feed rate of organochlorine compounds.

Based on extensive experimental and numerical studies, a working range for the organochlorine compound flow rate has been established. This range ensures a concentration of 1 to 4 ppm in the reaction mixture, depending on feedstock moisture content and reactor temperature. A non-stationary kinetic model of the industrial catalytic reforming process has been developed and successfully implemented at several industrial sites in Russia. This model supports predictive simulations of reactor performance under varying conditions of organochlorine dosing, system humidity, catalyst activity, and feedstock composition.

Implementation of the model has enabled the determination of optimal hydrochlorination conditions that promote the hydrogenation of non-graphitized coke, thereby reducing coke accumulation on the active catalyst surface by 3–4 wt.%. Process efficiency is further enhanced by optimizing the operational regime and maintaining optimal catalyst activity over time. The primary control parameters influencing catalyst performance during feedstock cycling are temperature and the organochlorine feed rate.

Experimental data show that chlorine adsorbed on the catalyst surface increases the acidity of the catalyst, thereby accelerating both the desired reforming reactions and accompanying side reactions. However, there exists an optimal chlorine loading that maximizes hydrocarbon conversion selectivity. This optimal value depends on the feedstock composition, catalyst activity, and operating conditions. The chlorine content on the catalyst is governed by the thermodynamic equilibrium of the chemisorption process, which is itself influenced by the water-to-hydrogen chloride molar ratio in the reaction zone, temperature within the catalyst bed, and the extent of catalyst deactivation due to coking, poisoning, or aging.

Research findings indicate that increased acid site activity is associated with the replacement of surface hydroxyl groups on alumina by chloride anions - an essential mechanism (6) contributing to the enhanced performance of the catalyst under reforming conditions.



(6)

Operational experience from industrial reforming units has demonstrated that insufficient chlorine levels lead to a reduction in catalyst activity, particularly in key alkane isomerization reactions, adversely affecting the quality of the resulting reformate. Moreover, the loss of chlorine from the catalyst surface accelerates the deactivation of platinum active sites, diminishing catalytic performance in paraffin dehydrocyclization and decreasing the overall selectivity of the process.

Conversely, an excessive chlorine concentration can overstimulate the acidic function of the catalyst, thereby promoting hydrocracking of paraffins. This results in reduced process selectivity, a higher proportion of light hydrocarbons - such as methane and ethane - in the circulating hydrogen-containing gas (CHG), and increased hydrogen consumption. For polymetallic reforming catalysts, the optimal chlorine content is typically within the range of 0.9–1.1 wt.%. Maintaining chlorine levels within this range is critical for maximizing process selectivity.

It is important to note that both a deficit and an excess of chlorine negatively affect the yield of stable catalyze. According to the reaction equation (8), catalyst chlorination is a reversible process, with equilibrium determined by the partial pressures of the gaseous components in the system. Specifically, hydrogen chloride present in the reaction volume reacts with hydroxyl groups on the catalyst surface, replacing them with chloride anions and forming strong covalent bonds between aluminum atoms and chlorine. This mechanism can be interpreted as chemisorption of chlorine atoms onto the catalyst surface.

The quantity of chlorine accumulated on the catalyst surface can be calculated using the following equation (7).

$$C(Cl) = \frac{A_{\max} K_p \frac{1}{M}}{1 + K_p \frac{1}{M}} \tag{7}$$

where C(Cl) is the amount of surface chlorine; Amax is the total number of active centers on the catalyst surface; Kp is the equilibrium constant of the chemical reaction; M is the molar ratio of water and hydrogen chloride in the reaction volume. After simple algebraic transformations, this equation is reduced to the following form:

$$C(Cl) = \frac{A_{\max} K_p}{M + K_p} \tag{8}$$

From equation (8) it follows that the amount of surface chlorine is inversely dependent on the ratio of water and hydrogen chloride in the system. By changing the flow rate of organochlorine compounds and water, it is possible to regulate the chlorine content on the catalyst surface. In addition, the amount of chlorine will depend on the process temperature, which affects the value of the equilibrium constant of the chemical reaction. The process temperature and the molar ratio of H_2O:HCl are the main control parameters, the change of which can affect the activity of the catalyst (Barbier et al., 1985).

The equilibrium constant of the reaction of substitution of hydroxyl groups on the surface of aluminum oxide with chlorine anions can be represented in Equation (9).

$$K_p = e^{-\frac{\Delta H - T\Delta S}{RT}} = e^{\frac{\Delta S}{R} - \frac{\Delta H}{RT}} = e^{4{,}78 - \frac{4790}{T}} \quad (9)$$

Further studies on the influence of changes in the thermal effect of hydrogen chloride chemisorption on the product yield showed that the change in the enthalpy of the reaction of substitution of the hydroxyl group by chlorine atoms depends on the bond energy between the atoms on the catalyst surface. The catalyst surface is non-uniform due to coke formation, and therefore, it can be assumed that there are active centers on its surface with different bond energies between the hydroxyl group and aluminum. In this case, hydroxyl groups that are least strongly bound to aluminum will be replaced by chlorine atoms, and therefore, the thermal effect of such a reaction will be lower than expected from calculations. A comparison of the calculated and actual product yields showed that, depending on the volume of processed raw materials and coke accumulation on the catalyst, the thermal effect of hydrogen chloride adsorption was slightly lower than theoretical (10).

$$K_p = e^{4{,}78 - \frac{3680}{T}} \quad (10)$$

Using this equation, the values of the equilibrium constant of the reaction of substitution of hydroxyl groups on the surface of aluminum oxide by chlorine anions in the operating temperature range of the L-35-11/600 unit were calculated (Table 6).

Table 6. Dependence of the equilibrium constant of the catalyst chlorination reaction on temperature (calculation on the model)

№ Experiment	Average temperature in 1 reactor, °C	*Kp*	Average temperature in reactor 3, °C	*Kp*
1	452	0.74	479	0.89
2	455	0.76	483	0.91
3	452	0.74	480	0.90
4	455	0.76	481	0.90
5	458	0.78	486	0.93
6	463	0.80	491	0.96
7	467	0.83	496	0.99
8	471	0.84	499	1.01

Further studies showed that with an increased chlorine content on the catalyst, an increase in the yield of aromatic hydrocarbons is observed, but the yield of reformate decreases by more than 1.5% by weight. In this case, the rates of chemical reactions of hydrocarbons will depend on the concentration of chlorides on the active surface of the catalyst:

$$W_i = \sum_j K_{ij} \cdot C_i \cdot \underbrace{f(f_1, f_2, f_3)}_{a_j}; \quad (11)$$

$$f_1 = \frac{D_p}{D_0}; \quad f_2 = \frac{F_{coke}}{F_0}; \quad f_3 = \frac{C^0_{H_2O} \cdot C_{H_2O}}{C_{HCl} \cdot C^0_{HCl}} \quad (12)$$

D_p, D_0 – active surface of a catalyst deactivated due to aging and a fresh one;
F_{coke}, F_0 – active surface of coked and fresh catalyst;

$\frac{C_{H_2O}}{C_{HCl}}$ – water/hydrogen chloride molar ratio.

Finally, Equations (11) and (12) express the influence of coke accumulation and surface chlorine concentration on the active surface area and catalyst performance.

Table 7. Effect of chlorine content on the catalyst on the quality of reformate

Chlorine content, % wt.	0.94	1.00	1.04
Degree of feedstock isomerization, % wt.	50	51	52
Degree of feedstock aromatization, % wt.	2.0	2.74	3.15
Reformate yield, % wt.	87.48	89.10	88.88
Hydrogen yield, % wt.	1.85	1.88	1.89
Processed feedstock, t	260000		
Cracking number, rel. units	2.3		
Hydrogen content, % vol.	85.5		
Inlet temperature, °C	483		
Feedstock flow rate m^3/h	60		
Paraffins/(Naphthenes+Arom. hydrocarbons) in feedstock, rel. units	1.32		
H2S circulation rate, nm^3/m^3	1333.3		
n-Steam/i-Steam feedstock, rel. units	0.95		

Table 7 demonstrates how variations in chlorine content on the catalyst surface affect product yield, aromatization degree, and isomerization activity.

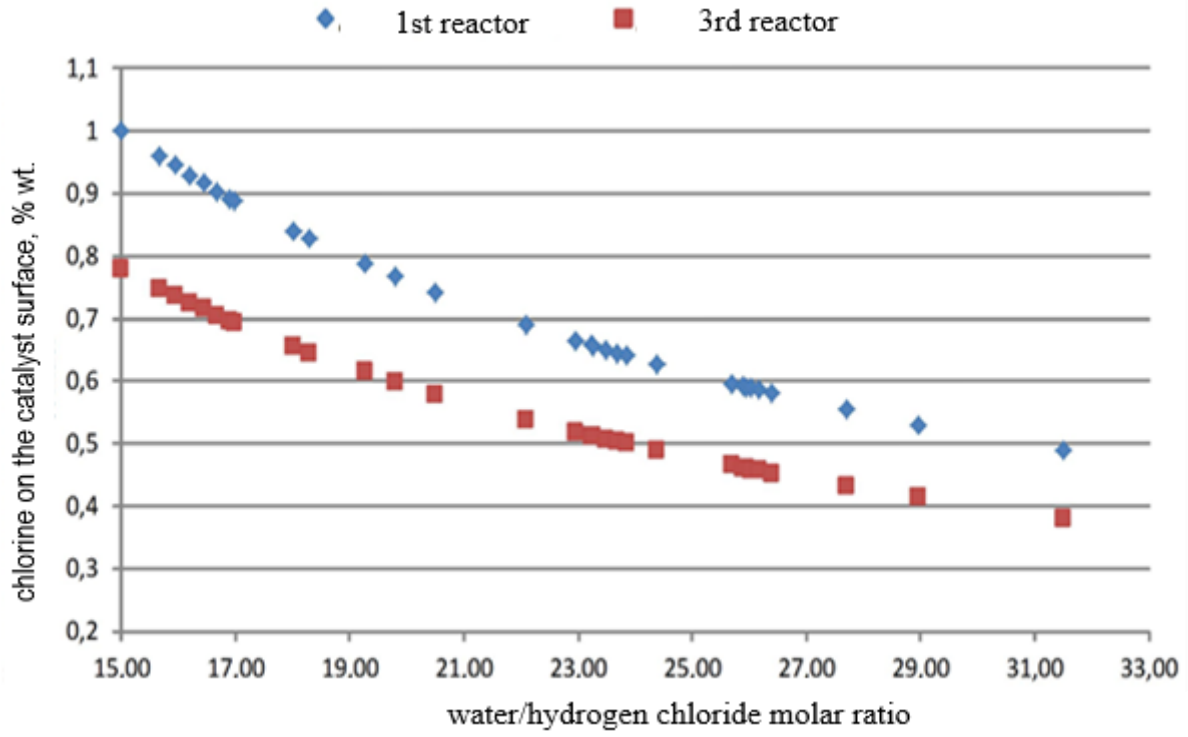


Figure 15. Chlorine concentration on the catalyst surface, wt%

Modeling results indicate that, according to the original plant configuration prior to reconstruction, introducing the organochlorine compound into the first reforming reactor results in a chlorine deficiency on the catalyst surface by the time the stream reaches the third reforming stage (Figure 15). While the optimal chlorine content on the catalyst in the third reactor should range between 0.9 and 1.1 wt.%, only 0.8 wt.% is achieved under this configuration. This deficiency reduces both the selectivity and stability of the Pt-Re catalyst, ultimately impacting the quality and yield of the main product, stable catalyst. Specifically, the observed chlorine deficit leads to a reduction in the octane number of the reformate by one unit, as measured by the research octane method.

One proposed optimization strategy involves modifying the reactor system design to inject the organochlorine compound directly into the third reforming reactor instead of the first, as illustrated in Figure 16. This change enables direct control over the chlorine concentration on the catalyst under its actual operating conditions. By regulating the humidity of the circulating H_2O:HCl stream and maintaining the required molar ratio, it becomes possible to ensure a stable balance between the acid and metallic functions of the catalyst. Under such conditions, maximum catalyst selectivity and long-term stability can be achieved.

Humidity in the reaction zone is controlled during the stripping stage of the hydrogenate in the stripping column of the hydrotreating unit. However, any disruption in the column's operating regime - without corresponding adjustments in chlorine feed rate - can result in the complete deactivation of the catalyst due to chlorine loss from its surface.

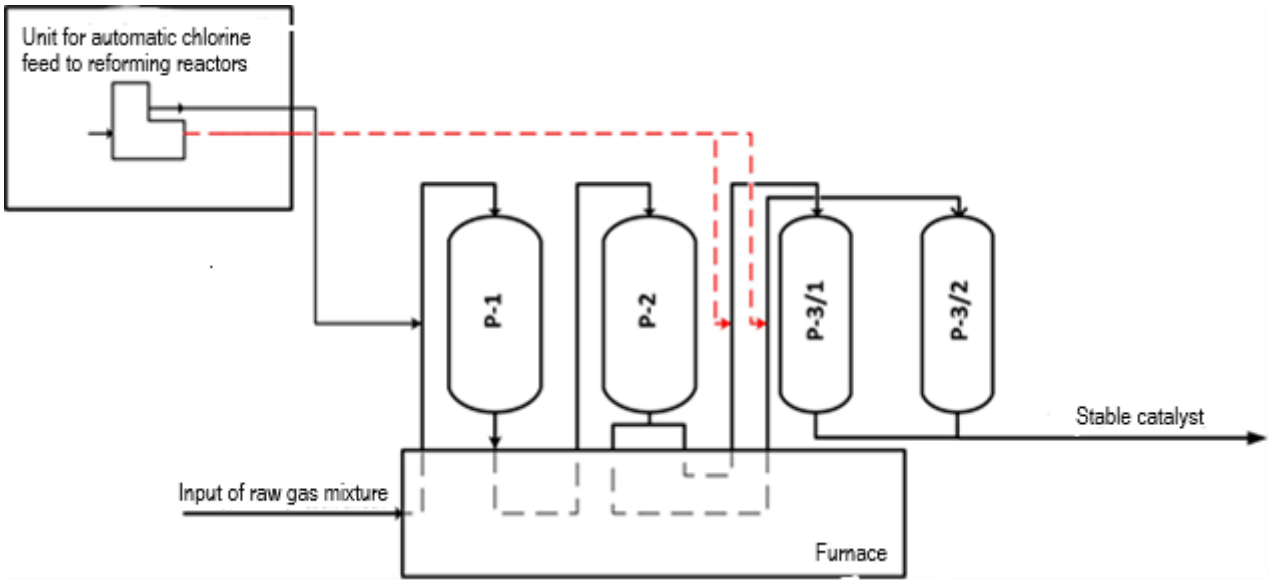


Figure 16. Scheme of chlorine feed to reforming reactors in L-35-11/600 unit: P-1 first-stage reforming reactor; P-2 second-stage reforming reactor; P-3/1.2 third-stage reforming reactor. It has been established that continuous feed of chlorine to the reaction zone is necessary to maintain balance of acid and metal activity

In an oxidizing environment, such as during the oxychlorination stage, chlorine facilitates the formation of an intermediate activated complex, denoted as $Pt\sigma_nCl_xO_\gamma L_z$. In contrast, under the reducing conditions typical of the reforming feedstock cycle, chlorine plays a critical role in maintaining the catalyst at its optimal activity level. This optimal state enables the effective hydrogenation of intermediate polymerization products - commonly referred to as amorphous coke - into hydrocarbons, thereby facilitating their removal from the catalyst surface.

The quantity of chlorine required for additional dosing into the reactors, in order to maintain the desired water-to-hydrogen chloride molar ratio and ensure optimal catalyst performance, is

calculated based on the data presented in Table 4. These values are further adjusted to account for catalyst aging and the associated decline in activity due to the progressive accumulation of coke deposits, as indicated in Table 8.

The results suggest that during the sixth feed cycle, the chlorine supply to the reforming reaction zone was suboptimal. This insufficient dosing led to a measurable reduction in catalyst activity (Figure 17) relative to conditions with optimal chlorine supply, ultimately resulting in a decline in product yield.

Table 8. Supply of chlorine to the reactor block of the L-35-11/600 unit in the sixth feed cycle

№ experiment	Humidity VSH, mg/kg	Chlorine supply, mg/kg	Temp., °C	*M**	Chlorine supply, mg/kg, including coke	Chlorine supply, mg/kg, taking into account aging	Factual yield, % mass.	Yield calc., % mass.
1	23.3	1.0	484	21.7	1.0	1.2	82.4	83.6
2	22.5	1.0	485	21.3	1.0	1.3	82.7	84.1
3	24.9	1.0	485	22.4	1.0	1.3	82.3	84.2
4	21.4	1.0	483	21.9	0.9	1.1	82.3	83.5
5	23.8	1.0	485	21.9	1.0	1.3	82.8	84.2
6	21.6	1.0	485	22.0	0.9	1.1	82.3	83.6
7	20.6	1.0	490	22.9	0.8	1.0	82.5	82.5
8	18.6	1.0	487	22.4	0.8	1.0	83.1	83.1
9	19.4	1.0	486	22.2	0.8	1.0	82.9	82.9

*M – molar ratio of water/hydrogen chloride.

Figure 17. Change in the activity of the L-35-11/600 unit catalyst in the sixth feedstock cycle

The studies described above have demonstrated the feasibility of a comprehensive approach to optimizing the dosing of organochlorine compounds into the reactors of the L-35-11/600 reforming unit. This optimization is primarily achieved by regulating key process control parameters - namely, temperature and the water-to-hydrogen chloride molar ratio. Experimental

data on chlorine surface concentration as a function of temperature suggest that the most effective chlorination of the Pt-Re catalyst occurs in the third reactor. Therefore, targeted introduction of organochlorine compounds at this stage is essential to ensure complete activation of the catalyst's acid function.

Traditionally, catalytic reforming utilizes straight-run naphtha with a boiling range of 85–180°C as its primary feedstock. However, modern refinery operations increasingly incorporate additional secondary streams, including gasoline fractions from thermal cracking processes, hydrocracking naphtha, and degassed gas condensate (Ancheyta, 2011). These alternative feedstocks are typically richer in olefinic hydrocarbons, which are prone to polymerization under reforming conditions, leading to the formation of high-molecular-weight species. These, in turn, promote coke formation, block active catalytic sites, and accelerate catalyst deactivation.

Given the broader range of feedstocks now being processed in catalytic reforming units, it became necessary to update and enhance the mathematical model for reforming processes employing fixed catalyst beds. At Tomsk Polytechnic University, using advanced analytical instrumentation, researchers conducted a detailed compositional analysis of various feedstocks, including straight-run naphtha (85–180°C), hydrocracking naphtha, and degassed condensate. It was determined that reforming feedstocks may contain olefins in concentrations ranging from 0.10 to 0.81 wt.%.

Based on a combination of experimental results and numerical simulations, the existing mathematical model was significantly refined. The updated model incorporates 200 elementary reactions involving 51 components and includes a formalized reaction network that explicitly accounts for olefin hydrogenation and polymerization pathways. Thermodynamic and kinetic parameters for these reactions were also determined, enabling more accurate predictions of reaction behavior and catalyst performance under varying feedstock compositions.

To describe the kinetic model, a matrix method was used, which makes the new scheme flexible to the changing composition of the feedstock. The updated model is implemented in the interpreted Python programming environment, and its adequacy is confirmed by calculations (Pchelintseva, 2019).

3. Conclusion

The results of the non-stationary process studies discussed above demonstrate that mathematical modeling is a powerful tool for addressing the challenges associated with catalyst deactivation. While complete prevention of deactivation is not feasible, the development of an effective catalyst management strategy offers a practical solution. The most significant technological improvements can be achieved through the controlled application of physicochemical models that account for both the reactivity of hydrocarbon fractions in the feedstock and the specific activity characteristics of the catalysts employed.

Extensive experimental and theoretical studies conducted at various industrial facilities have confirmed that optimal dosing of water, chlorine, sulfur, and other promoters in the reaction and regeneration zones plays a critical role in enhancing resource efficiency. Notably, the relative activity of the catalyst - calculated using a non-stationary physicochemical model - serves as a key indicator for balancing the acidic and metallic functions of the catalyst. This relative activity typically ranges from 0.5 to 1.0, depending on the feedstock’s hydrocarbon composition, throughput, and the operating parameters of the reactor (such as temperature and pressure).

A novel method for dosing organochlorine compounds into the reactor unit has been developed, enabling a 1.5–2% increase in the selectivity of the target aromatization reactions by precisely regulating the flow rate of the organochlorine feed. Specifically, introducing the organochlorine reagent into the final reforming reactor helps maintain the balance between the catalyst’s acid and metal activity, provided that the required H_2O:HCl molar ratio is preserved under the reactor’s operating conditions.

Overall, the industrial application of the developed mathematical reforming model has led to the establishment of optimal operating regimes that extend catalyst life, prolong the duration of inter-regeneration cycles, reduce the total number of regeneration events, and mitigate the effects of catalyst poisoning, thermal degradation, and coke formation.

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5. Author Contributions: Conceptualization and supervision, I.E.; experimental work, C.E.; data analysis and manuscript preparation, P.I. All authors have read and agreed to the published version of the manuscript.

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10. References

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Бензинді каталитикалық риформингтің математикалық модельдеу саласындағы жетістіктері мен болашағы

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Аңдатпа. Бензинді каталитикалық риформинг – мотор отындарының октан санын арттыруға бағытталған маңызды өнеркәсіптік процесс. Бұл өнімдерге деген сұраныс алдағы уақытта да жоғары болып қала бермек. Осы процесті жетілдіруге, реакторлардың конфигурациясын жақсартуға және катализатор құрамын оңтайландыруға арналған зерттеулер кеңінен жүргізілуде. Каталитикалық риформинг күрделі процесс болып табылады: онда көпкомпонентті шикізат пен өнім қоспасы, екіфункциялы катализатор жүйесі, көптеген параллель және тізбекті реакциялар мен катализатордың дезактивациясы қатар жүреді. Сондықтан бұл процесті зерттеу мен оңтайландырудың негізгі құралы ретінде математикалық модельдеу кеңінен қолданылады.
Бұл мақалада каталитикалық риформингтің кинетикалық модельдерін дамыту тарихына қысқаша шолу жасалып, 1959 жылдан бастап жүргізілген жұмыстар қарастырылады. Ерекше назар Томск политехникалық ұлттық зерттеу университетінде жүргізілген зерттеулерге аударылған. Бұл жерде мұнай-химия және қайта өңдеу процестерін модельдеуге арналған ғылыми мектеп қалыптасқан. Бензинді каталитикалық риформинг мысалында бейстационарлық модельдерді құрудың әдістемелік тәсілі көрсетіліп, олардың әзірленуінің негізгі қағидалары сипатталады. Модельдеу нәтижелері реактор құрылымын оңтайландыру, катализатордың қышқылдық және металлдық функцияларының тепе-теңдігін сақтау және катализатор бетінде кокс түзілуін азайту мүмкіндіктерін көрсетеді.
Сондай-ақ қосымша шикізат ағындарын ескере отырып, бекітілген катализаторлы риформинг процесінің математикалық моделін жетілдіру нәтижелері берілген.

Түйін сөздер: каталитикалық риформинг; математикалық модель; екіфункциялы катализатор; реактор; дезактивация; кокс түзілуі; органохлорлы қосылыстар; оңтайландыру; шикізат ағындары

Достижения и перспективы в области математического моделирования каталитического риформинга бензина

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Аннотация. Каталитический риформинг бензина является важнейшим промышленным процессом, направленным на повышение октанового числа моторных топлив, спрос на которые, как ожидается, сохранится в обозримом будущем. Ведутся обширные исследования по совершенствованию конструкции риформинговых процессов, конфигурации реакторов и состава катализаторов. Учитывая сложность каталитического риформинга, включающего многокомпонентную смесь сырья и продуктов, бифункциональные катализаторы, многочисленные параллельные и последовательные реакции, а также механизмы дезактивации катализатора, математическое моделирование остаётся основным инструментом для изучения и оптимизации процесса.
Настоящая работа представляет краткий обзор эволюции подходов к кинетическому моделированию каталитического риформинга, начиная с работ 1959 года. Особое внимание уделяется исследованиям, проведённым в Национальном исследовательском Томском политехническом университете, где сформирована научная школа по разработке математических моделей нефтехимических и перерабатывающих процессов. На примере каталитического риформинга бензина изложен методологический подход к построению нестационарных моделей, описаны основные принципы их разработки. Представленные результаты моделирования демонстрируют возможности по оптимизации конструкции реакторов, поддержанию баланса кислотной и металлической функций катализатора и минимизации коксования его поверхности.

Представлены результаты совершенствования математической модели риформинга с неподвижным катализатором с учётом подачи дополнительного сырья.

Ключевые слова: каталитический риформинг; математическая модель; бифункциональный катализатор; реактор; дезактивация; образование кокса; органохлорсодержащие соединения; оптимизация; потоки сырья.