

THE FORECASTING OF THE CATALYTIC CRACKING PRODUCTS YIELD DEPENDING ON THE FEEDSTOCK COMPOSITION AND THE CATALYST ACTIVITY

Galina Y. Nazarova, Elena N. Ivashkina, Emiliya D. Ivanchina, Alexandra A. Oreshina, Evgeny K. Vymyatnin, Vyacheslav A. Chuzlov, Igor M. Dolganov*

Fuel Engineering and Chemical Cybernetics Department, Tomsk Polytechnic University, Russia

Received August 14, 2019; Accepted October 31, 2019

Abstract

The paper presents the results of mathematical model-based predictive calculations of the processed feedstock features and regenerated catalyst activity influence on the catalytic cracking products yield, taking into account the catalyst deactivation by coke, nickel, and vanadium. It was found that when the feedstock composition, nickel (0–0.00006 wt%), and vanadium (0–0.00019 wt%) in the process feedstock change, the activity of the catalyst reaches 7.1% and 10.4% for the reactions catalyzed by zeolites Y and ZSM-5, respectively. The process target products yield (gasoline fraction and wet gas) changes by 3.62 wt% and 2.7 wt% with an increase in the ratio of saturated and aromatic hydrocarbons from 1.8 to 3.2 units.

Keywords: *Catalytic cracking, Zeolite-containing catalyst, Coke, Nickel, Vanadium, Activity, Mathematical modeling.*

1. Introduction

The catalytic cracking and hydrocracking processes implementation significantly increased the oil refining depth [1-3]. Today, various types of feedstock are processed by catalytic cracking-vacuum and atmospheric gas oils and fuel oils, coking and visbreaking gas oils, hydrocracking residues, combinations of these streams, their mixtures with plant feedstock, etc. [4-6].

Depending on the processed feedstock and the processing purpose (production of gas, gasoline or diesel fuel components), catalytic cracking technologies vary wildly by used catalysts [10-13] and from the hardware aspect viewpoint (involving in processing a feedstock with different boiling points, products recycling, involving light olefins as feedstock, multi-stage regeneration, coolers, etc.) [7-9].

Improving the catalytic cracking units efficiency is a complex and multifactorial task. Today a significant number of studies are aimed at developing new and modernizing existing catalytic cracking units and developing catalysts for heavy oil fractions, and residual feedstock processing, including those promoting yield and octane number of gasoline and gases and less suffer from heavy metal poisoning [14-17].

But the solution to this problem is complicated by the changes in the feedstock hydrocarbon composition and the catalyst activity. Further, the change in the catalyst activity largely depends on the coke content on its surface and carcass aluminum elimination and is determined by the content of aromatic hydrocarbons and resinous substances, as well as heavy metals in the fraction, thereby affecting the yield and composition of cracking products.

Nickel adsorbed on the catalyst from catalytic cracking feedstock contributes to a change in the catalyst dehydrogenation ability and consequently, to an increase in its coking degree due to the hydrogen cleavage reactions intensification (dehydrogenation, aromatization, condensation, and coke formation) and a decrease in its activity [18]. The process feedstock vanadium compounds in the presence of steam at high temperature lead to the zeolite crystalline structure destruction during dealumination, causing the active centers loss [19]. In the article [20],

the vanadium poisoning nickel inhibition mechanism is discussed, because experimental studies have shown that when nickel coexists with vanadium, the physico-chemical properties degradation and dealumination are usually reduced. According to the deactivation mechanism, a decrease in the catalyst activity under the vanadium influence occurs upon the catalyst interaction with vanadium acid formed by vanadium oxide contact with water vapor [21]. While nickel partially inhibits the destructive effect of vanadium, which leads to a decrease in zeolite carcass dealumination and the catalyst surface area, activity, and acid sites preservation.

Considering a large number of parameters that affect the process performance, the methods of mathematical modeling allow a comprehensive assessment of these factors' influence [22-26]. At the same time, it is important to take into account the combined effect of nickel and vanadium on the catalyst activity, considering the inhibitory effect of nickel, as well as the implementation of a selective approach that considers the change in the catalyst activity in the reactions catalyzed by HY and ZSM-5 catalysts, when modeling the cracking feedstock group composition.

The paper presents the results of mathematical model-based predictive calculations of the processed feedstock features and regenerated catalyst initial activity influence on the catalytic cracking products yield, considering the catalyst deactivation by coke and heavy metals.

The aim of the work is to predict the catalytic cracking products yield depending on the processed feedstock features and the regenerated catalyst initial activity of the, taking into account its deactivation by coke, nickel, and vanadium.

2. Object and methods of research

The object of the study is a vacuum gas oil catalytic cracking unit. The feedstock composition varies over a wide range, having a significant effect on catalyst deactivation, products yield, and composition.

Feedstock chemical conversion is carried out inside the riser-reactor in the microspherical zeolite-containing catalyst (HY and ZSM-5) upflow. In accordance with the experimental data, the activity of the regenerated catalyst varies in the range 74.0–84.0% and largely determines the composition and quality of the cracking products. The fresh catalyst activity after the preparation and loading stages is 2–4 points higher. In this case, the coke content on the catalyst in the cracking process before regeneration may reach 1.0% wt.

Figure 1 shows the main parameters of the catalytic cracking unit operating mode that affects the products yield and composition.

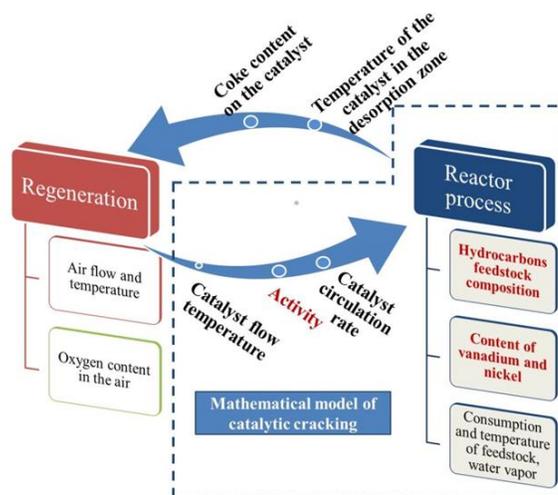


Fig. 1. The reactor and the regenerator operating conditions relationship

As a rule, with an increase in the fraction boiling temperature, the feedstock tendency to coke formation increases due to the increase in aromatic hydrocarbons and heavy metals

content in the process feedstock. In oil fractions with a boiling point above 200°C, cyclic hydrocarbons have a mixed (hybrid) structure. Typically, cyclic hydrocarbons contain paraffin side chains, but some of them contain both naphthenic and aromatic rings.

To study the processed feedstock features and the regenerated catalyst activity influence on the products yield and composition, process mathematical model-based calculations were performed [27]. The mathematical model takes into account the thermodynamic irreversibility occurrence in terms of the current chemical affinity of the reactions and catalyst regeneration at each step of the calculation **(1)**.

$$\begin{cases} \frac{dC_i}{d\tau} = \sum_{j=1}^{18} (\pm\psi \cdot (W_j - W_{-j})) \\ \frac{dT}{d\tau} = \frac{\sum_{j=1}^{18} (\pm\psi \cdot ((\Delta_r H_T^\circ)_j \cdot W_j) - ((\Delta_r H_T^\circ)_{-j} \cdot W_{-j}))}{\rho_f c_f} \end{cases} \quad (1)$$

Initial conditions: $\tau=0$; $C_i=0$; $T_0=Ti.t.$

where: C_i and C_n – the hydrocarbons i -th group concentration in the riser-reactor and regenerator, mol/L; τ and τ_{reg} – residence time in the riser-reactor and regenerator, s; j and k – the reaction sequence number; ψ – the catalyst deactivation parameter, W_j and W_{-j} – the catalytic cracking chemical reaction rates in the forward and reverse directions; k – the rate of the chemical reaction of the regeneration process; T and T_{reg} – the flow temperature in the riser-reactor and regenerator, K; ρ_f , c_f and ρ_{freg} , c_{freg} – density and heat capacity of the flow in the riser-reactor and regenerator, kg/m³, kJ/kg · K; $\Delta_r H_T^\circ$ – the chemical reaction thermal effect, kJ/mol; $Ti.t.$ – the feedstock and catalyst thermal equilibrium temperature, K.

The mathematical model considering the reversible catalyst deactivation by introducing the functions of changing the catalyst activity for the reactions catalyzed by HY and ZSM-5 zeolites, depending on the coke formed on the catalyst in the reactor concentration, determined by the processed feedstock features **(2)**:

$$A_{ZSM} = A_0 \cdot e^{-0,106 \cdot C_c} \quad A_{HY} = A_0 \cdot e^{-0,071 \cdot C_c} \quad (2)$$

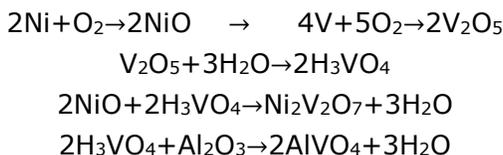
where: A_{HY} , A_{ZSM} – the catalyst current activity for reactions catalyzed by HY and ZSM-5 zeolites, respectively; A_0 – catalyst activity with a minimum coke content in the cycle (regenerated catalyst); -0.106 и 0.071 – deactivation constants determined on the basis of data on the acid sites concentration; C_c – coke content on the catalyst, % wt.

When calculating the coke content, the change in the dehydrogenating activity of the catalyst under the action of nickel for reactions proceeding with the hydrogen participation was taken into account (the assumption is made that nickel is completely deposited on the catalyst). The change in the catalyst dehydrogenation activity (A_{H_2}) was determined on the basis of the established experimental regularity of the change in hydrogen content in the cracking gas depending on the nickel content in the process feedstock **(3)**:

$$A_{H_2} = e^{1,1554 \cdot C_{Ni}} \quad (3)$$

where C_{Ni} – is the nickel content in the cracking feedstock, ppm.

The reduction in the catalyst activity depending on the combined nickel and vanadium content recording was implemented in the cycle in accordance with the reactions proposed in the article [28]. The formation of metal oxides occurs in the air stream during regeneration of the organometallic compounds Ni and V from the adsorbed catalyst surface [29]:



Next, we determine how much the amount of Al_2O_3 is reduced relative to the initial amount of Al_2O_3 , taking into account the amount of catalyst in the system.

3. The forecasting of processed feedstock features influence on the cracking products yield with consideration of changing the catalyst activity

The catalytic cracking process mathematical model application allows a comprehensive assessment of the feedstock composition and the catalyst activity effect on the gasoline fraction, wet gas, and coke yields. Moreover, not only the initial activity of the regenerated catalyst but also the change in activity along the height of the riser-reactor has a significant effect on the catalytic cracking products yield and composition. The catalyst activity at the reactor outlet depends on the regenerated catalyst activity and the concentration of coke formed on the catalyst. The coke content is determined by the thermodynamics and kinetics of the process reactions, the feedstock composition, and features and the process conditions.

3.1. The effect of resin, saturated and aromatic hydrocarbons content on the gasoline fraction, wet gas and coke yields

Model-based calculations made it possible to evaluate the effect of various hydrocarbon groups content (Tab. 1) and the catalyst activity after regeneration on the cracking products yields in the range of 0.74 - 0.84 units, *ceteris paribus*. The ratio of saturated hydrocarbons to aromatic in the feedstock varied in the range of 1.6–3.2 units, according to experimental data.

Table 1. Cracking feedstock composition for model-based calculations

Feature	Content, % wt.				
Feedstock sample number	Nº1	Nº2	Nº3	Nº4	Nº5
Saturated hydrocarbons	62.3	65.5	68.3	68.2	74.6
Aromatic hydrocarbons	33.9	31.3	29.0	27.2	23.2
Resinous components	3.8	3.2	2.7	4.7	2.2
Ratio of saturated hydrocarbons to aromatic C_{SH}/C_{AH}	1.8	2.1	2.4	2.5	3.2

Model-based calculations showed (Fig. 2) that with an increase in the ratio of saturated and aromatic hydrocarbons from 1.8 to 3.2 units and the regenerated catalyst activity from 0.74 to 0.84 units total yield of gasoline fraction and gases increases by 5.84% wt. (from 72.08 to 77.92% wt.), the yield of the gasoline fraction increases by 3.62% wt.

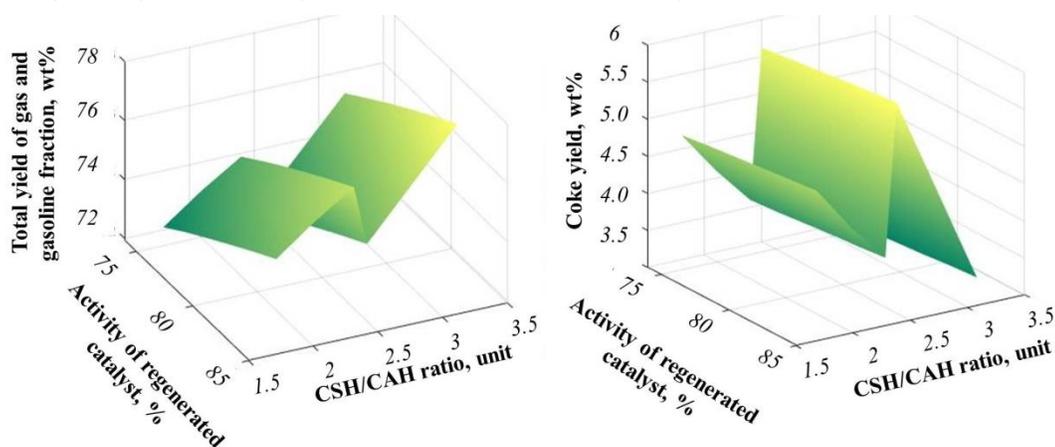


Fig. 2. The dependence of coke and total yield of gasoline and wet gas on the processed feedstock composition and the catalyst activity (model-based calculations)

The yield and content of coke on the catalyst varies from 5.84 to 3.08 and 1.05 to 0.55% wt. respectively. At the same time, for feedstock sample No. 4, there is a decrease in the gasoline fraction yield and a high yield of coke (5.25 ÷ 5.53% wt.). This is associated with high resinous compounds content in the fraction, which undergoes high condensation and coke formation, reduces the catalyst activity, thereby causing a decrease in the yield of the target product - gasoline fraction.

3.2. The effect of coke, nickel and vanadium content on the catalyst activity

Predictive calculations showed that with an increase in the nickel content in the cracking feedstock from 0 to 0.00006 wt%, with a constant vanadium content (0.00003 wt%), the coke content on the catalyst increases from 0.774 to 1.091% wt. (Fig. 3). Figure 4 shows the catalyst activity predicted calculations depending on the coke content.

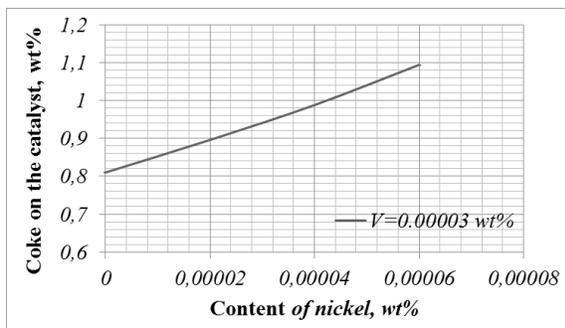


Fig. 3. The dependence of the coke content on the catalyst on the nickel content in the cracking feedstock (model-based calculations)

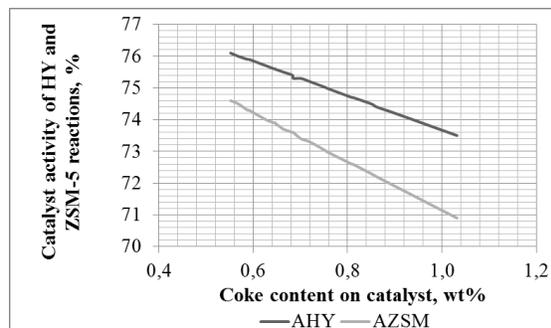


Fig. 4. The dependence of the catalysts activity in relation to the reactions catalyzed by zeolites HY and ZSM-5 on the coke content on the catalyst (model-based calculations)

The increase in coke content on the catalyst from 0.55 to 1.03% wt. leads to a decrease in catalyst activity from 76.1 to 73.5% for reactions catalyzed by zeolite Y, and from 74.6 to 70.9% for reactions catalyzed by zeolite ZSM-5, which is 7.1 and 10.4% relative to the activity of the regenerated catalyst (79.1%).

Predictive calculations of the catalyst activity loss due to dealumination taking into account the annual volume of processed feedstock (2.4 million tons) showed that with an increase in the vanadium concentration in the process feedstock by 0.00019 wt%, the catalyst activity decreases by 3.48 %. At the same time, with an increase in the cracking feedstock nickel content to 0.00006 wt%, the deactivating effect of vanadium decreases by 0.95% due to the interaction of nickel with vanadium acid.

3.3. The feedstock composition influence on the catalytic cracking products yield and composition, taking into account changes in the catalyst activity

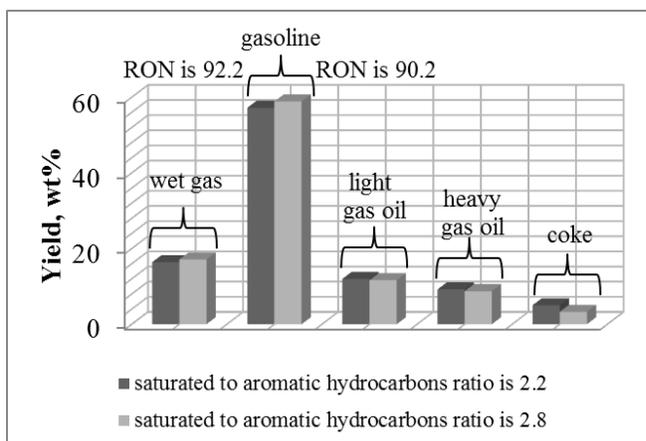


Fig. 5. The dependence of the products yield and the gasoline octane number on the catalytic cracking feedstock composition (model-based calculations)

The decrease in gasoline yield by 1.68 wt% with decreasing the saturated to aromatic hydrocarbons ratio is associated with the deactivation of the catalyst during condensation

The decrease in catalyst activity over the reaction apparatus height due to coke accumulation affects the composition and quality of catalytic cracking products at the constant activity of the regenerated catalyst (Fig. 5).

When processing feedstock with a high content of high molecular weight paraffin and naphthenes ($C_{SH}/C_{AH} = 2.8$ units), the gasoline yield is 58.87 wt%, the gasoline octane number according to the research method is 90.2 unit. The gaseous products yield for such feedstock is higher 17.13 wt% than for feedstock with a high aromatic hydro-carbons content ($C_{SH}/C_{AH} = 2.2$ units) – 16.4.

reactions, respectively. The coke yield for such feedstock is higher (5.02% wt.), relative to feedstock sample No. 4 – 3.28% wt.

As a result, with a higher concentration of aromatic hydrocarbons in the catalytic cracking feedstock, the gasoline yield is lower (57.19 wt%), gasoline has a high octane number according to the research method (92.2 unit). In addition, for such feedstock, the yields of light (12.00 wt%) and heavy (9.2 wt%) gas oils are higher than when processing vacuum distillate with a high saturated hydrocarbons content (11.64 and 8.74 wt%).

4. Conclusions

The implementation of a selective approach that takes into account the coke formation regularities upon a change in the feedstock hydrocarbon composition and the heavy metal allows predicting these factors influence on the reversible and irreversible catalyst deactivation for the reactions catalyzed by HY and H-ZSM-5 zeolites and involving hydrogen.

The processed feedstock hydrocarbon composition, in particular, the high content of resinous compounds, nickel, and vanadium, significantly affect the yield of catalytic cracking products. When the feedstock composition is changed, the coke content on the catalyst changes in the range of 0.55–1.03 wt% with constant process conditions and the regenerated catalyst activity, the catalyst activity changes by 7.1% and 10.4% in relation to reactions, catalyzed by zeolites Y and ZSM-5, respectively. The consequence of this is a significant change in the process target products yield (gasoline fraction and wet gas by 3.69 wt.% and 2.7 wt.%). In this case, the catalytic cracking gasoline fraction yield and octane features may be increased by adjusting the process conditions taking into account the feedstock composition the catalyst activity.

Acknowledgements

This research was supported by RSCF grant № 19-71-10015.

References

- [1] Sahu R, Song BJ, Im JS, Jeon YP, and Lee CW. A review of recent advances in catalytic hydrocracking of heavy residues. *Ind. Eng. Chem.*, 2015; 27: 12-24.
- [2] Lappas AA, Iatridis DK, Papapetrou MC, Kopalidou EP, and Vasalos IA. Feedstock and catalyst effects in fluid catalytic cracking – Comparative yields in bench scale and pilot plant reactors. *Chem. Eng. Journal*, 2015; 278: 140-149.
- [3] Che Y, Yuan M, Qiao Y, Liu Q, Zhang J, and Tian Y. Fundamental study of hierarchical milli-second gas-phase catalytic cracking process for enhancing the production of light olefins from vacuum residue. *Fuel*, 2019; 237: 1-9.
- [4] Al-Enezi G, and Elkamel A. Predicting the effect of feedstock on product yields and properties of the fcc process. *Petr. Sc. and Tech.*, 2000; 18(3-4): 407-428.
- [5] Sony DS, Kastagnos KP. R.U. Patent 2 391 382, 2010.
- [6] Meyers RA. The main processes of oil refining. Handbook: ed. Glagoleva OF., Lykova OP.; trans. from English 3rd ed. SPb.: TsOP "Profession", 2012; p. 944.
- [7] Xu Y, and Cui S. A novel fluid catalytic cracking process for maximizing iso-paraffins: from fundamentals to commercialization. *Fron. Chem. Science and Eng.*, 2018; 12(1): 9-23.
- [8] Gborbozoe E, Bories M, Letsch WS, Leroy P, Santner K, Ross JL. Jr. R.U. Patent 2 606 971, 2017.
- [9] Bories M, Leroy P. R.U. Patent 2 605 547, 2015.
- [10] Potapenko OV, Doronin VP, Sorokina TP, Gulyaeva TI, and Drozdov VA. Effect of the acid-base properties of additives for a cracking catalyst on the sulfur content in liquid products. *Catal. in Ind.*, 2011; 3 (2): 151-156.
- [11] Rahimi N, and Karimzadeh R. Catalytic cracking of hydrocarbons over modified ZSM-5 zeolites to produce light olefins: A review. *Appl.Catal. A: General*, 2011; 398 (1-2): 1-17.
- [12] Awayssa O, Al-Yassir N, Aitani A, and Al-Khattaf S. Modified HZSM-5 as FCC additive for enhancing light olefins yield from catalytic cracking of VGO. *Appl. Catal. A: General*, 2014; 477: 172-183.
- [13] Hussain AI, Aitani AM, Kubu M, Cejka J, and Al-Khattaf S. Catalytic cracking of Arabian Light VGO over novel zeolites as FCC catalyst additives for maximizing propylene yield. *Fuel*, 2016; 167: 226-239.

- [14] Cerqueira HS, Caeiro G, Costa L, and Ramoa Ribeiro F. Deactivation of FCC catalysts. *J. Mol. Catal. Chem.* 2008; 292: 1-13.
- [15] Caeiro G, Magnoux P, Ayrault P, and et al. Deactivating effect of coke and basic nitrogen compounds during the methylcyclohexane transformation over H-MFI zeolite. *Chem. Eng. Journal*, 2006; 120 (1-2): 43-54.
- [16] Climent MJ, Corma A, Iborra S, Epping K, Vlety A. Increasing the basicity and catalytic activity of hydrotalcites by different synthesis procedures. *Journal of Catalysis*, 2004; 225 (2): 316-326.
- [17] Lappas AA, Nalbandian L, Iatridis DK, Voutetakis SS, Vsalos IA. Effect of metals poisoning on FCC products yields: Studies in an FCC short contact time pilot plant unit. *Catalysis Today*, 2001; 65 (2): 233-240.
- [18] Magomedov RN, Popova AZ, Maryutina TA, Kadiev KhM, Khadzhiev SN. Status and prospects of demetallization of heavy oil feedstocks (review). *Petrochemistry*, 2015; 55(4): 267-290.
- [19] Etim UJ, Xu B, Ullah R, and Yan Z. Effect of vanadium contamination on the framework and micropore structure of ultra stable Y-zeolite. *J. Colloid Interface Sci.*, 2016; 463: 188-198.
- [20] Etim UJ, Xu B, Bai P, Rooh U, Subhan F, and Yan Z. Role of nickel on vanadium poisoned FCC catalyst: A study of physiochemical properties. *J. of Energy Chem.*, 2016; 25: 667-676.
- [21] Ocelli ML. Vanadium-Zeolite Interactions in Fluidized Cracking Catalysts. *Catal. Rev.*, 1991; 33: 241-280.
- [22] Yanga Q, Berrouka AS, Dub Y, Zhao H, Yang C, Rakib MA, Mohamed A, and Taher A. CFD investigation of hydrodynamics, heat transfer and cracking reactions in a large-scale fluidized catalytic cracking riser. *Appl. Math. Model.*, 2016; 40(21-22): 9378-9397.
- [23] Sedighi M, Keyvanloo K, Towfighi J. Kinetic study of steam catalytic cracking of naphtha on a Fe/ZSM-5 catalyst. *Fuel*, 2013; 109: 432-438.
- [24] Bartholomew CH, Fuentes GA. Catalyst deactivation, Elsevier, October 1997; p. 695.
- [25] Froment G. On fundamental kinetic equations for chemical reactions and processes. *Current Opinion in Chem. Eng.*, 2014; 5: 1-6.
- [26] Varshney P, Kunzru D, and Gupta SK. Modelling of the riser reactor in a resid fluidised-bed catalytic cracking unit using a multigrain model for an active matrix-zeolite catalyst. *Indian Chem. Eng.*, 2014; 57(2): 1-21.
- [27] Ivanchina ED, Ivashkina EN, and Nazarova GY. Mathematical modelling of catalytic cracking riser reactor. *Chem. Eng. J.*, 2017; 329: 262-274.
- [28] Etim UJ, Xu B, Bai P, Ullah R, Subhan F, and Yan Z. Role of nickel on vanadium poisoned FCC catalyst: A study of physiochemical properties. *J. of Energy Chem.*, 2016; 25: 667-676.
- [29] Borzaev KhKh. Catalytic processing of heavy hydrocarbons with preliminary electromagnetic exposure: a dissertation for the degree of candidate of technical sciences: special. 02.00.13. Federal State Budgetary Educational Institution of Higher Professional Education "Russian State University of Oil and Gas named after IM Gubkin"; scientific hands. I.M.Kolesnikov. Moscow, 2015; p.178.

To whom correspondence should be addressed: Dr. Galina Y. Nazarova, Fuel Engineering and Chemical Cybernetics Department, Tomsk Polytechnic University, 30, Lenin Avenue, Tomsk, 634050, Russia; E-mail: silko@tpu.ru