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## Computer modelling system application for catalytic reforming unit work optimisation

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### Abstract

Catalytic reforming of naphtha is one of the most important processes for high octane gasoline manufacture and aromatic hydrocarbons production. The application of computer modelling system “Catalyst’s Control” for monitoring of catalytic reforming unit of Achinsk oil-refinery is stated. The mathematical model-based system takes into account the physical and chemical mechanisms of hydrocarbon mixture conversion reaction as well as the catalyst deactivation. The models created can be used for optimization and prediction of operating parameters (octane number, reactors outlet temperature and yield) of the reforming process. It is shown, that the work on the optimal activity allows increasing product output with a constant level of production costs, and get the information about Pt-Re catalyst work efficiency.

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**Keywords:** catalytic reforming; monitoring, mathematical modelling; catalyst activity; product output

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### 1. Introduction

Catalytic reforming of naphtha is one of the most important processes for high octane gasoline manufacture and aromatic hydrocarbons production. The naphtha reformer is used to upgrade low octane heavy naphtha that is unsuitable for motor gasoline.

Industrial catalysts used in catalytic reforming units consist of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support, some metals such as Pt, Re, Ge, Ir,

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Sn and additive such as chlorine to increase isomerization reactions. There are several types of reactions taking place during the reforming process: dehydrogenation, isomerization, cyclization, aromatization, hydrocracking, hydrogenolysis and coke formation. Some of these reactions such as isomerization, cyclization, aromatization are desirable because of increasing the octane number. Other reactions causing the catalyst deactivation (such as coke formation and coke deposition) are undesirable.

Catalytic reforming has been studied extensively in order to understand the catalytic chemistry of the process. The first significant attempt at delumping naphtha into different constituents was made by Smith<sup>1,16</sup>. He considered naphtha to consist of three basic components: paraffins, naphthenes and aromatics.

This model is still used due to its simplicity. The model derived by Krane<sup>2,16</sup> contained a reaction network of 20 pseudo components and recognized hydrocarbons from 6 to 10 carbon atoms. Kmak<sup>4,16</sup> proposed the first model incorporating the catalytic nature of the reactions by deriving a reaction scheme with Hougen–Watson–Langmuir–Hinshelwood-type kinetics. Rate equations derived from this type explicitly account for the interaction of chemical species with the catalyst<sup>5,16</sup>. The Kmak's model was later refined by Marin and his colleagues<sup>6–9,16</sup>, who presented the reaction network for the whole naphtha. Other models were proposed by Barreto et al.<sup>5,16</sup>, Ansari and Tade<sup>6,16</sup>, Aguilar and Anchyeta<sup>11,12</sup>, Burnett<sup>13</sup>, Henningsen and Bundgaard-Nielson<sup>10,16</sup> and other researchers. A process with continuous catalyst regeneration was modeled by Lee et al.<sup>16</sup> and good agreement with plant data was reported.

As seen, most previous works on this subject were related to packed bed reactors (PBRs). In the present paper the application of mathematical modelling method monitoring of catalytic reforming installation of Achinsk oil-refinery is reported.

## 2. Experimental part

The computer-based modeling system "Catalyst's Control" created at the Department of Chemical Technology of Fuel and Chemical Cybernetics of Tomsk polytechnic university is based on the mathematical model of the benzene catalytic reforming which takes both the physical and chemical mechanisms of hydrocarbon mixture conversion reaction as well as the catalyst deactivation.

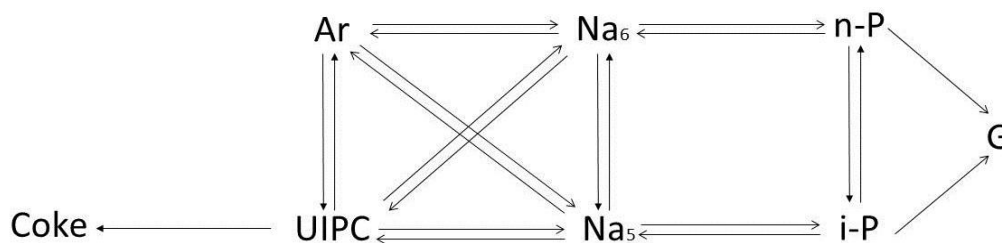


Fig. 1. Formalized scheme hydrocarbon conversions C8 – C12: G – gas; n-P – normal paraffins; i-P – isoparaffins; Na6 – cyclohexanes; Na5 – cyclopentanes; Ar – aromatic hydrocarbons; UIPC - unsaturated intermediate products of compaction

It's showed on the Figure1 that the existence of formation and hydrogenation of unsaturated intermediate products of compaction is possible. Therefore, under certain conditions coke formation doesn't occur, because resins and asphaltenes (previous substances of coke) can be hydrogenated to hydrocarbons or be in equilibrium with gas-phase reaction medium. Thus, controlling of feed temperature in reactor, it could be possible to provide process operation mode with the existence of equilibrium of formation and hydrogenation of coke structures.

But it's difficult to realize in practice, because it's required to obtain the final high-octane product, so there is an objective need for deviations from thermodynamic equilibrium. As a result, accumulation of unsaturated intermediate products of compaction occurs. However, the solution of very important industrial problem – how to find desired catalyst – is based on this contradiction.

### 3. Results discussion

Using computer modelling system, the monitoring of Achinsk catalytic reforming installation LK 6U was done. The catalyst used is R-98. As initial data the chromatographic analyzes results of raw material and outlet substance compositions were used.

The monitoring of installation was doing during the fifth work period – since 20.06.2012 to 01.05.2013.

Such catalyst work indicators as “current” and “optimal” activity were determined

The catalyst activity<sup>3</sup> is defined as:

$$A = W_k - W_0(1 - \varphi)$$

$W_k, W_0$  – the chemical reaction rate, mol/sm<sup>3</sup>·s, with and without catalyst respectively;  $\varphi$  – the part of volume, occupied by catalyst and inaccessible for reacting mixture.

The current activity depends on installation modes of operation. The optimal activity is defined by optimal process operation and corresponds to maximum process selectivity.

The amount of current activity during this work period is 0.8-0.85 points. However, a deviation from the optimal activity of 2.5 points in total can be observed. This deviation influences on the accumulation of coke (Figure 2). For example, the total amount of coke in the catalysis is 34.92 % higher than the one, which could be observed during optimal operation.

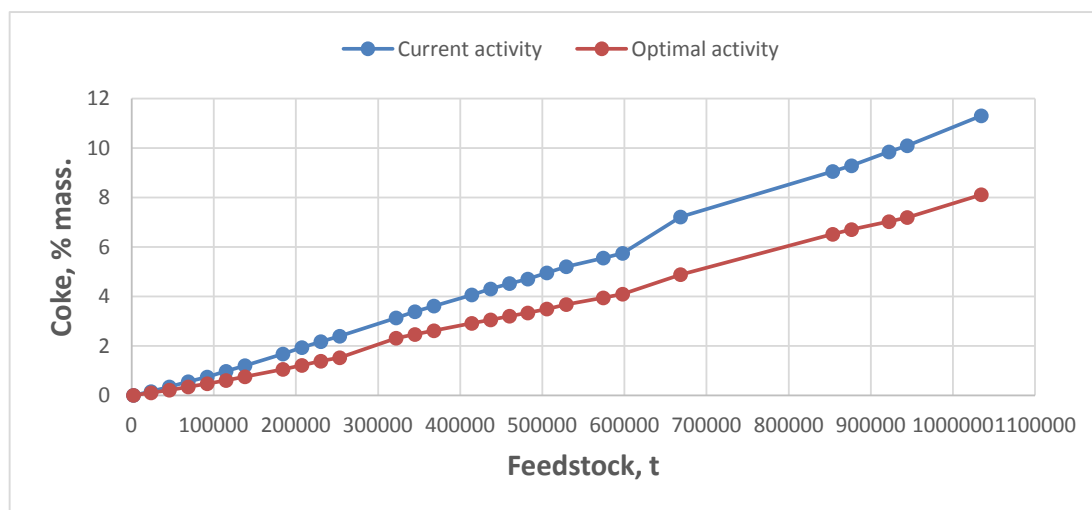


Fig. 2. Accumulation of coke in the current and optimal activity

The most selectivity of the catalyst is achieved during the working on the optimal activity<sup>14,15</sup>. According to this, as a result of “Catalyst’s Control” program application should be output product’s increasing with constant level of productions’ costs. This conclusion can be proven by analyzing the output product (Figure 3). During the end of the work period, juddering changes were observed, and the output of the product is between 81 and 84.5 % mass.

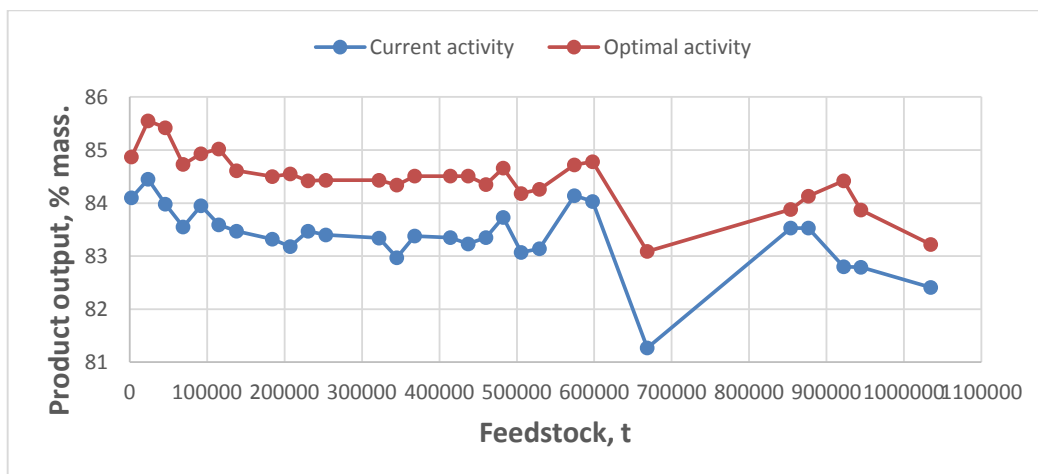


Fig. 3. Product output in the current and optimal activity

Furthermore, computer model is able to take the reactivity of the individual components into account that makes adequate evaluation of the industrial reformer operation possible. The juddering changes product output confirm changes in the composition of the feedstock in this work period, namely reduction of aromatic hydrocarbons for 19.12.12 and 09.01.13 (from 60.96 to 68.88, Table 1).

Table 1. Calculation results from Achinsk industrial catalytic reforming unit LK 6U

Date	12.12.12	19.12.12	09.01.13	06.13.13
Activity	0.75	0.77	0.94	0.79
Par/(Naft+Arom)	0.9	0.9	0.91	0.89
n-Par/i-Par Feedstock	1.09	1.1	1.05	1.02
Aromatics. % weight	60.82	60.96	68.88	62.43
Coke. % weight	5.56	5.75	7.22	9.06
Octane number	92.4	92.2	95.9	93.2
Product Output	84.14	84.03	81.27	83.53

Therefore, the current and optimal activity of the catalysis was calculated, the degree of the feedstock composition influence was evaluated. Based on these calculations it is possible to conclude that:

1. The installation work is relatively close to optimal. Insignificant deviation between the optimal and current activity was observed at the end of the work period (0.4 points) which may be associated with change in the feedstock composition.
2. The amount of coke used in the catalysis during the current activity is 34.92 % higher than the optimum value.

## References

1. R.B. Smith. Kinetic analysis of naphtha reforming with platinum catalyst. *Chem.Eng. Prog.* 1959; **55**: 6, p. 76–80.
2. H.G. Krane, A.B. Groh, B.L. Shulman, J.H. Sinfelt. Reactions in Catalytic Reforming of Naphthas. *World Petroleum Congress*. 1960: 39–53.
3. A.V. Kravtsov, E.D. Ivanchina. *Intelligent systems in chemical engineering and engineering education*. Novosibirsk, Nauka; 1996.
4. W.S. Kmak. *A Kinetic Simulation Model of the Power Forming Process*. AIChE Meeting, Houston; 1972.
5. G.F. Barreto, J.M. Vinas, M.G. Gonzalez. *Lat. Am. Appl. Res.* 1996; **26**: 1, p. 21–34.
6. G.B. Marin, G.F. Froment, J.J. Lerou, W. De Backer. *EFCE*. 1983; **2**: 27, C117, Paris.
7. G.B. Marin, G.F. Froment. Reforming of C6 hydrocarbons on a Pt-Al<sub>2</sub>O<sub>3</sub> catalyst. *Chem. Eng. Sci.* 1982; **37**:5, p. 759–773.
8. P.A. Van Trimpont, G.B. Marin, G.F. Froment. *Ind. Eng. Chem. Res.* 1988; **27**: 1.
9. G.B. Marin, G.F. Froment. *The development and use of rate equations for catalytic refinery process*. Proceedings of the 1st Kuwait Conference on Hydrotreating Processes, Kuwait, March 5–9; 1989.
10. J. Henningsen, M. Bundgaard-Nielson. Catalytic reforming. *Br. Chem. Eng.* 1970; **15**: 11, p. 1433–1436.
11. R. Aguilar, J. Ancheyeta. *Oil Gas J.* (July); 1994; p. 80–83.

12. R. Aguilar, J. Ancheyta. *Oil Gas J.* (January); 1994; p. 93–95.
13. R.L. Burnett, H.L. Steinmetz, E.M. Blue, E.M. Noble. *Petrol Chem. Am. Chem. Soc.* Detroit Meeting, April; 1965.
14. E.S. Sharova, D.S. Poluboyartsev, N.V. Chekantsev, A.V. Kravtsov, E.D. Ivanchina. Monitoring of the commercial operation of reforming catalysts using a computer simulation system catalysis in industry. *Catalysis in Industry*. 2009; **1**: 2, p. 128-133.
15. I.O. Dolganova, I.M. Dolganov, E.N. Ivashkina, E.D. Ivanchina, R.R. Romanovsky. Development approach to modelling and optimisation of non-stationary catalytic processes in oil refining and petrochemistry. *Polish Journal of chemical Technology*. 2012; p. 22-29.
16. M.S. Gyngazova, A.V. Kravtsov, E.D. Ivanchina, M.V. Korolenko, D.D. Uvarkina. Kinetic model of the catalytic reforming of gasolines in moving-bed reactors. *Catalysis in industry*. 2010; **2**:4, p. 374-380.