Available online at www.sciencedirect.com

ScienceDirect

Procedia Chemistry 10 (2014) 197 – 202

Procedia Chemistry

XV International Scientific Conference "Chemistry and Chemical Engineering in XXI century" dedicated to Professor L.P. Kulyov

Mathematical modelling method application for optimisation of catalytic reforming process

Emilia D. Ivanchina, Ekaterina S. Sharova, Inna V. Yakupova*

National Research Tomsk Polytechnic University, Lenin Avenue, 30, Tomsk, 634050, Russia

Abstract

The application of mathematical modelling method monitoring of catalytic reforming unit of Komsomolsk oil-refinery is proposed. The mathematical model-based system "Catalyst's Control" which takes into account both the physical and chemical mechanisms of hydrocarbon mixture conversion reaction as well as the catalyst deactivation was used for catalytic reforming installation monitoring. 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.

Peer-review under responsibility of Tomsk Polytechnic University

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

1. Introduction

The majority of industrial reactors and technological schemes for thermal and catalytic processes of petroleum and gas refining were designed and built in the middle of the 20th century. They are still operated at some Russian refineries. The construction of these industrial plants is based on a classical approach: laboratory apparatus – pilot testing – pilot reactor – industrial reactor[1,2-8]. As a result, oil refining and petrochemical industry obtained chemical apparatus created with a large degree of safety regardless the catalysts operational properties. Mathematical

* Corresponding author. Tel.: +7-913-117-9937.
E-mail address: yakupovaiv@tpu.ru

Peer-review under responsibility of Tomsk Polytechnic University
doi:10.1016/j.proche.2014.10.034

modelling allows choosing the optimal technological solutions that get advantage of the catalysts resources to a maximum extent.

The first mathematical models of reactor process were designed according to the “black box” type, and did not take the detailed mechanism of the subsequent reactions and catalysts adsorption properties into account.

One of the first attempts was that of Smith who tried to describe the detailed mechanism and kinetics of hydrocarbons transformation on Pt-catalysts in 1959[1, 3-8]. After that, researchers moved towards the simplified reaction network reducing the dimensionality of mathematical model by distributing by parameters depending on the number of carbon atoms in a hydrocarbon molecule. Isomers were combined into the groups of pseudo components[1, 4-8].

In the 80-s of the 20th century the studies on the mathematical modelling of the multicomponent catalytic processing of petroleum feedstock were developed. As a result of the studies on the kinetics and mechanism of the reactions proceeding on Pt-catalysts in the gasoline reforming process, as well as a detailed thermodynamic analysis, the formal mechanism was proposed for the transformation of hydrocarbons C5–C12 from different homology groups in the temperature range of 700–800 K. This scheme served as the basis for time-dependent kinetic model of the process. The advantage of this scheme is the fact that it takes into account the conversion of mono- and di-substituted naphthenes. The proposed reaction network is sensitive to changes in raw material composition containing more than 180 components.

The developed kinetic model became the basis for the computer modelling system of gasoline catalytic reforming. This software was one of the first to be implemented in a number of Russian refineries[9-11].

With the use of this simulator, calculations were carried out and recommendations were issued as to the reforming units reconstruction: in particular, the design modification of reactors internal devices with radial supply of raw materials in a stationary granular catalyst bed. Implementation of scientific results ensured the increase of the product yield by 2.5-3% with octane number of 93 points[12-16].

The developed kinetic model became the basis for the computer modelling system of gasoline catalytic reforming. This software was one of the first to be implemented in a number of Russian refineries.

2. Experimental part

The computer-based modelling system "Catalyst's Control" created at the Department of Chemical Technology of Fuel and Chemical Cybernetics of Tomsk polytechnic university was used (Figure 1). The system is based on the mathematical model of the naphta catalytic reforming which takes both the physical and chemical mechanisms of hydrocarbon mixture conversion reaction as well as the catalyst deactivation. The chromatographic analyzes results of raw material and outlet substance compositions were used as initial data.

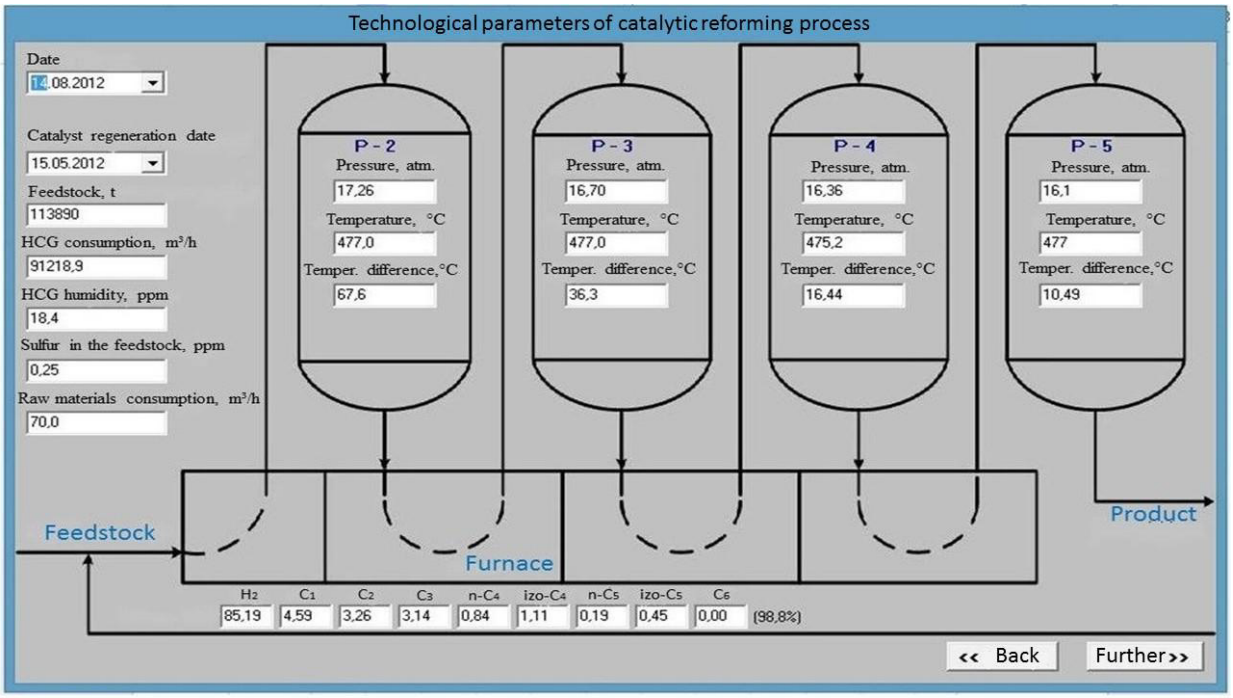

Fig. 1. Active window of the computer modeling system "Catalyst's Control"

The mathematical model of catalytic reforming[17] is performed as system of material and heat balance:

$$\begin{cases} G\left(\frac{\partial C_i}{\partial z}+\frac{\partial C_i}{\partial V}\right)=\sum_{j=1}^{m} W_j \\ G\left(\frac{\partial T}{\partial z}+\frac{\partial T}{\partial V}\right)=-\frac{1}{C_p^{mix}}\sum_{j=1}^{m} Q_j W_i \end{cases}$$

The initial conditions: Z=0, Ci=0, T=0, V=0, Ci=C_{en} (at the reactor entrance), if Z=0, T=T_{en}, where C_i - a concentration of i-th component, mol/m^3; T – temperature; Z – a raw material volume, m³; W_j – j-th reaction rate, mol/(m³·h); V - a volume of the catalyst layer,m^3; G - a raw material flow rate, m^3/h; Q_j – j-th reaction heat, J/mol; C_p^{mix} - a heat capacity of mixture, J/mol.

3. Results discussion

Using computer modelling system the monitoring of Komsomolsk catalytic reforming installation L-35-11/450K was done. The catalyst used is PR-9. The monitoring of installation was doing during the seventh work period – since 22.05.2012 to 18.03.2014.

The monitoring of each catalytic reforming installation is concluded in determination of such catalyst work indicators as "current" and "optimal" activity.

The catalyst activity[3] is defined as:

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

W_k, W_0 – the chemical reaction rate, mol/sm³·s, with and without catalyst respectively; φ – the part of volume, occupied by catalyst and inaccessible for reacting mixture.

The optimal activity is defined by optimal process operation. Work at the "optimal" activity provides maximum duration of catalyst work cycle.

The results which are presented at Figure 2 show that the amount of current activity during this work period is 0.7-1.0 points. However, a deviation from the optimal activity of 0.6 points in total can be observed. This deviation infl`uences on the accumulation of coke. For example, the total amount of coke in the catalysis is 87.73 % weight higher than the one, which could be observed during optimal operation.

Fluctuations of the catalyst's activity during the entire work period can be associated with changes in the rate of technological regime: the feed temperature to the reactor, hydrogen gas circulation rate and the variability of the composition of the hydrocarbon feedstock.

For optimal industrial conditions it's necessary to maintain the desired rate ratio of target and adverse reactions, and also save the equilibrium of formation and hydrogenation of coke structures, which is defined by process parameters (temperature, pressure, feedstock composition). Thus, the using of computer modelling system allows to explore the impact of these parameters on the process and increase product output and decrease its cost price without significant manufacturing costs.

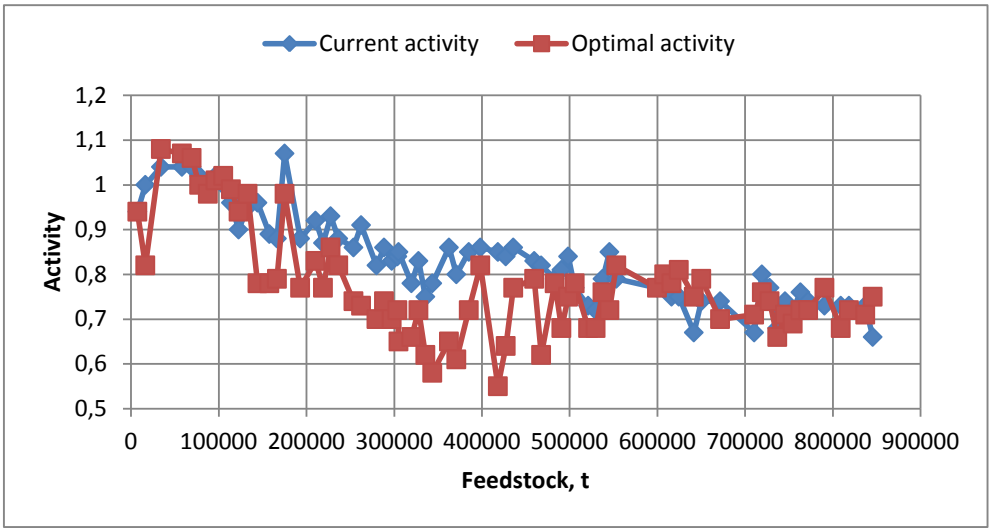

Fig. 2. The comparison of current and optimal activities of the catalyst

The most selectivity of the catalyst is achieved during the working on the optimal activity.[9-11] 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 optimal operation and the output of the product could be 3-4 % mass. higher than the one, which could be observed during current operation..

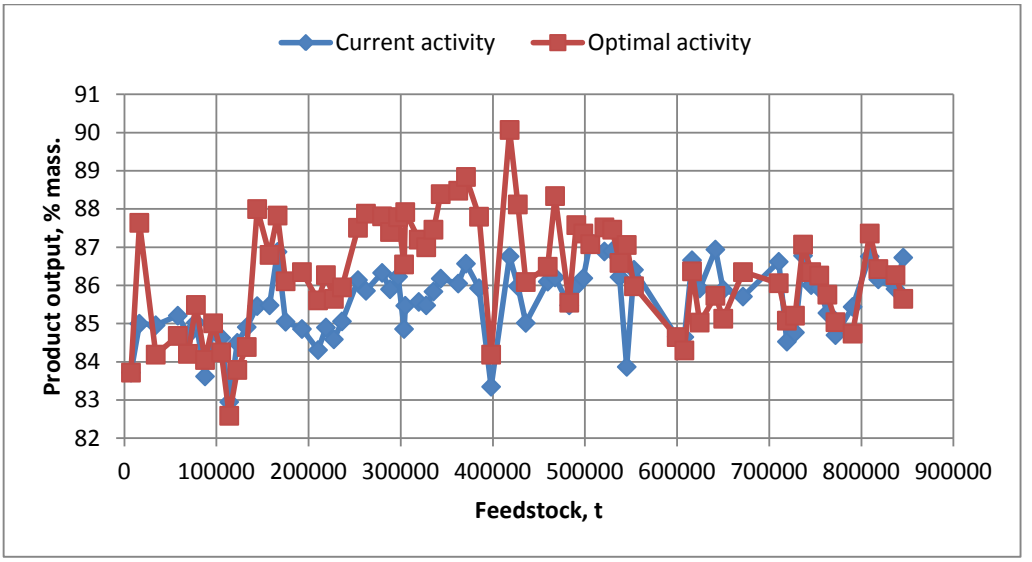

Fig. 3. Product output in the current and optimal activity

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 of activity confirm changes in the composition of the feedstock in this work period (Table 1).

Table 1. Raw material composition from an industrial catalytic reforming unit L-35-11/450K

Date	01.10.13	08.10.13	15.10.13	22.10.13	05.11.13	12.11.13
nC4	0.06	0.08	0.05	0.06	0.08	0.09
nC5	1.28	1.42	0.94	1.08	1.41	1.45
nC6	3.72	3.33	2.86	3.09	3.35	3.36
nC7	4.28	4.38	3.65	4.44	3.58	3.68
nC8	6.66	6.35	6.31	6.76	6	5.82
nC9	3.87	3.56	3.39	3.54	3.49	3.45
nC10	1.36	1.45	1.35	1.19	1.8	1.95
iC4	0.01	0.01	0	0.01	0.01	0.01
iC5	0.62	0.7	0.48	0.54	0.72	0.75
iC6	3.8	3.78	3.04	3.21	3.64	3.7
iC7	2.42	1.85	1.42	1.63	1.32	1.7
iC8	6.64	9.51	9.81	10.08	8.52	8.47
iC9	6.93	6.79	6.78	6.99	7.17	6.51
iC10	4.74	5.09	4.74	4.18	6.29	6.83
ZP	0.47	0.5	0.38	0.4	0.47	0.49
MZP	2.96	2.44	2.52	2.49	2.53	2.59
DMZP	3.6	3.37	2.9	3.26	2.65	2.98
ZG	1.2	0.58	0.83	0.73	0.53	0.69
MZG	7.01	7.52	7.36	7.65	6.35	6.39
C8H	16.06	13.46	14	14.36	12.26	12.16
C9H	7.08	6.67	7.43	6.78	7.07	7.18
C10H	0.68	0.73	0.68	0.6	0.9	0.98
BENZ	0.43	0.41	0.51	0.41	0.44	0.43
TOLY	2.73	3.21	4.02	3.56	3.28	2.98
KSIL	6.06	6.47	7.9	6.99	7.41	6.94
AP9	3.13	3.25	4.08	3.11	4.95	5.23
AP10	1.04	1.08	1.36	1.04	1.65	1.74

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 from the optimal and current activity was observed at the end of the work period (0.6 points) which may be associated with change in the feedstock composition.
2. The amount of coke deposited at the catalyst during the current activity is 87.73 % higher than the optimum value.

References

1. 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.
2. A.S. Noskov. *Two centuries of mathematical modelling.* Report at the problem seminar on 90-th anniversary of M.G. Slinko; 2005.
3. A.V. Kravtsov, E.D. Ivanchina. Intelligent systems in chemical engineering and engineering education. Novosibirsk, Nauka; 1996.
4. J. Grane. *Proceeding of the 4-th Int. Petroleum Congress*; 1961; p. 3, 34.
5. A. Aitani. Catalytic naphtha reforming. *Encyclopedia of Chemical Processing*. 2006; p. 397–406.
6. R.B. Smith. Kinetic analysis of naphtha reforming with platinum catalyst. *Chem.Eng. Prog*. 1959; **55**:6, p. 76–80.
7. D. Bommannan, R.D. Strivastava, D.N. Saraf. Modeling of catalytic naphtha reformers. *Can. J. Chem. Eng.* 1989; **67**: 405–411.
8. H.G. Krane, A.B. Groh, B.L. Shulman, J.H. Sinfelt. Reactions in Catalytic Reforming of Naphthas. *World Petroleum Congress*. 1960; p. 39–53.
9. M.S. Gyngazova, A.V. Kravtsov, E.D. Ivanchina, M.V. Korolenko, N.V. Chekantsev. Reactor modeling and simulation of moving-bed catalytic reforming process. *Chem. Eng. J*. 2011; **176-177**: 134-143.
10. 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. 2009; **1**: 2, p. 128-133.
11. 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.
12. U. Taskar, J.B. Riggs. Modeling and optimization of a semiregenerative catalytic naphtha reformer. *AIChE J.* 1997; **3**: 740–753.
13. J.H. Jenkins, T.W. Stephens. *Hydrocarbon Process.* (November); 1980; p. 163–167.
14. J. Henningsen, M. Bundgaard-Nielson. *Catalytic reforming*. Br. Chem. Eng. 15 (11); 1970; p. 1433–1436.
15. G.B. Marin, G.F. Froment. Reforming of C6 hydrocarbons on a Pt-Al2O3 catalyst. *Chem. Eng. Sci.* 1982; **37:** 5, p. 759–773.
16. G.J. Antos, A.M. Aitani. *Catalytic Naphtha Reforming*. Marcel Dekker; 2004; p.602.
17. E.D. Ivanchina, V.V. Deriglazov, I.K. Zanin. Computer modelling system using for increasing of catalytic reforming technical economic efficiency. *TPU News, Chemistry*; 2011; **319**: 3, p. 105-109.