Available online at www.sciencedirect.com

ScienceDirect

Procedia Chemistry 15 (2015) 378 – 383

Procedia Chemistry

16th International Scientific Conference "Chemistry and Chemical Engineering in XXI century" dedicated to Professor L.P. Kulyov, CCE 2015

Heavy naphtha fractions 85-155˚C recycling in the catalytic reforming industrial unit

Ekaterina S. Chernyakova, Anton G. Koksharov, Emilia D. Ivanchina, Inna V. Yakupova*

National research Tomsk polytechnic university, 30 Lenin Avenue, Tomsk, 634050, Russian Federation

Abstract

Catalytic naphtha reforming is a vital process for refineries due to the production of high-octane components, which is intensely demanded in our modern life. In these paper, the mathematical modelling method application for catalytic reforming installation of Komsomolsk oil-refinery is proposed. The mathematical model-based system "Catalyst Control" was used for catalytic reforming installation monitoring. The quality of the product from the unit was studied, with hydrocracking gasoline used as the feedstock. The impact of the feedstock on the product output was analyzed. It is shown that the feedstock replacement of catalytic reforming unit L-35-11/450K has positive impact on high-octane product output and increases the resource efficiency of the process.

Peer-review under responsibility of Tomsk Polytechnic University

Keywords: catalytic reforming, mathematical modelling, product output, heavy naphtha.

1. Introduction

Catalytic naphtha reforming is one of the key processes in the petroleum refining and petrochemical industries, which is used extensively to convert low-octane hydrocarbons of naphtha to more valuable high-octane gasoline components without changing the boiling point range. Naphtha is a fraction of petroleum, typically constitutes 15-30% of crude oil, by weight, and boils between 30°C and 200°C. This complex mixture consists of hydrocarbon

* Corresponding author. Tel.: +7-913-117-99-37;
E-mail address: yakupovaiv@tpu.ru

Peer-review under responsibility of Tomsk Polytechnic University
doi:10.1016/j.proche.2015.10.060

molecules with 5-12 carbon atoms, mainly including paraffins, olefins, naphthenes and aromatics. Other components, such as sulfur, nitrogen, oxygen, water, salt, and a number of metal containing constituents such as vanadium, nickel, and sodium are also exist.

In addition, the produced reformate in catalytic naphtha reforming process includes valuable aromatics such as benzene, toluene, and xylenes (BTX) that are very important petrochemical materials. Hydrogen is a valuable byproduct of catalytic naphtha reforming process, which in most refineries is used for hydrocracking, hydrotreating, and other hydrogen-consuming processes[1].

Naphtha reforming catalyst is a bifunctional catalyst consists of a metal function, mainly platinum, and an acid function, usually chloride alumina. The metal function catalyzes the hydrogenation and dehydrogenation reactions and the acid function promote the isomerization and cyclization reactions. In order to achieve an optimum performance of the naphtha reforming catalyst, adequate balance between these functions is needed. Improving the stability and selectivity of the catalyst as well as reducing catalyst deactivation is a vital issue for enhancing the efficiency and yield of the process[1]. Mathematical modelling allows choosing the optimal technological solutions that get advantage of the catalysts resources to a maximum extent [18-20].

Naphtha is a very complex mixture of hydrocarbons. An analysis of a typical naphtha feed revealed that more than 300 components are present in this hydrocarbon mixture. Different reactions occur between these components, including dehydrogenation and dehydroisomerization of naphthenes to aromatics, dehydrogenation of paraffins to olefins, dehydrocyclization of paraffins and olefins to aromatics, isomerization and hydroisomerization to isoparaffins, isomerization of alkylcyclopentanes and substituted aromatics and hydrocracking of paraffins and naphthenes to lower hydrocarbons. Considering all of these components and their corresponding reactions in a kinetic model is a complex problem[1].

The first significant attempt to model a reforming system has been made by Smith in 1959. His model consists of three basic components including paraffins, naphthenes, and aromatics (PNA), which undergo four reactions. In this model, which is probably the simplest model, each hydrocarbon class is considered as a single component with average properties of that class. After his model, other researchers (such as Krane, Jenkins, Froment and other) presented more complicate models with more components and reactions[1, 12-16].

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 the detailed thermodynamic analysis, the formal mechanism was proposed for the transformation of hydrocarbons C_5–C_{12} from different homology groups in the temperature range of 700–800 K. The proposed reaction network is sensitive to changes in raw material composition containing more than 180 components[2-8].

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].

2. The object of study

It is known[5,6] that gasoline fraction 85-180°C from crude oil distillation plants is the main component of feedstock for reforming units. In addition, the increase in the resource production of high-octane components of gasoline is possible due to the involvement of reforming fraction 85-155 °C (heavy naphtha) as the feedstock from the block of light fractions hydrocracker. In this paper the objects of study are the catalytic reforming and hydrocracking unit of Komsomolsk oil-refinery. The technological scheme of heavy naphtha output from the hydrocracker distillation feed unit and its addition to the catalytic reforming process with the fixed bed catalyst is shown in Figure 1.

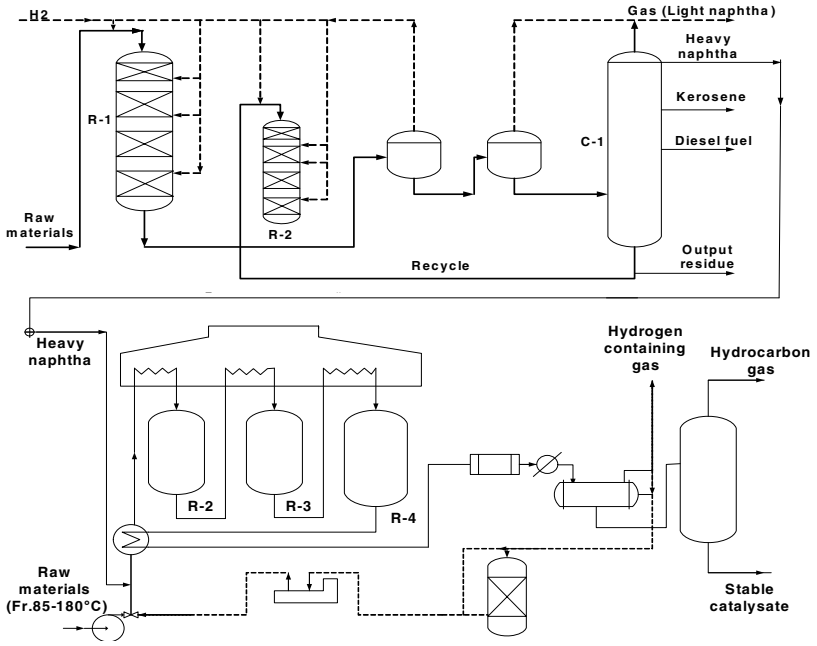

Fig.1. Technological scheme of heavy naphtha output

3. Methods

It is found[5,6] that in the reforming reactor reactions of hexatomic naphthenes dehydrogenation, dehydroizomerization of pentacyclic naphthenes and dehydrocyclization of paraffins occur, and also the reactions of izomerization, ring-opening, dealkylation, hydrocracking, and hydrogenolysis occur in the acid and metal centres:

Dehydrogenation of naphthenes:

$$C_6H_{12} \rightarrow C_6H_6 + 3H_2 \quad (1)$$

Dehydrocyclization of paraffins:

$$C_6H_{14} \rightarrow C_6H_6 + 4H_2 \quad (2)$$

Izomerization:

$$\begin{aligned} n-C_6H_{14} &\rightarrow izo-C_6H_{14} \\ C_5H_9-CH_3 &\rightarrow C_6H_{12} \end{aligned} \quad (3)$$

Hydrocracking:

$$\begin{aligned} C_8H_{18} + H_2 &\rightarrow C_3H_8 + C_5H_{12} \\ C_5H_{18} + H_2 &\rightarrow 2C_4H_{10} \end{aligned} \quad (4)$$

Hydrogenolysis:

$$C_8H_{18} + H_2 \rightarrow C_7H_{16} + CH_4 \quad (5)$$

Accounting of target and adverse reactions as a result of coke formation on the active surface allows modelling non-stationary gasoline reforming process selecting the catalysts for the reactors with radial feed injection into the fixed granular layer.

The mathematical model of catalytic reforming[17] is created as a system of material and heat balances:

$$\begin{cases} G\left(\frac{\partial C_i}{\partial z} + \frac{\partial C_i}{\partial V}\right) = \sum_{j=1}^{m} W_j \\ G\left(\frac{\partial T}{\partial z} + \frac{\partial T}{\partial V}\right) = -\frac{1}{C_p^{mix}} \sum_{j=1}^{m} Q_j \end{cases} \quad (6)$$

The initial conditions are: Z=0, C_i=0, T=0, V=0, C_i=C_{en}, if Z=0, T=T_{en}, where C_i, C_{en} is the concentration of the i-th component and in the entrance of reactor, mol/m3; T, T_{en} – the temperature and in the entrance of reactor, °C; Z – the feedstock volume, m³; Wj – the j-th reaction rate; V - the volume of the catalyst layer,m3; G - the feedstock flow rate, m3/h; Qj – the j-th reaction heat, J/mol; Cp - the heat capacity of mixture, J/mol.

The computer-based modelling system "Catalyst Control" created at the Department of Chemical Technology of Fuel and Chemical Cybernetics of Tomsk polytechnic university was used (Figure 2).

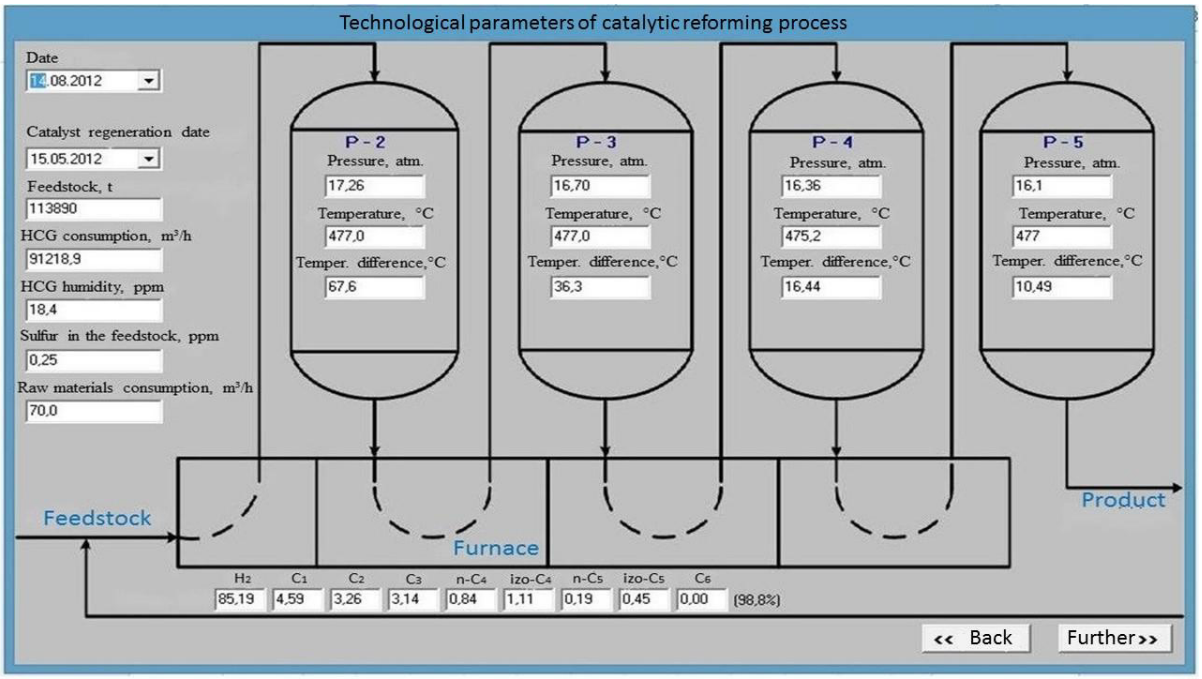

Fig. 2. Active window of the computer modeling system “Catalyst Control”

The system is based on the mathematical model of benzene catalytic reforming, which considers both the physical and chemical mechanisms of hydrocarbon mixture conversion reaction as well as the catalyst deactivation.

The chromatographic analyzes results of feedstock and outlet substance compositions were used as the initial data[9-11,17].

4. Results discussion

In this paper the quality of the product from the unit L-35-11/450K was studied, with hydrocracking gasoline used as the feedstock. The impact of the feedstock on the product output was studied. To achieve this task the composition of heavy naphtha, 85-180°C fractions, and the blending feedstock was analyzed (Table 1).

Table 1 – The feedstock composition

	heavy naphtha		feedstock without heavy naphtha		feedstock with heavy naphtha	
Component	29.12.13	09.01.14	17.01.14	02.10.14	05.02.14	05.05.14
Paraffins	8.93	8.83	21.94	22.53	20.97	21.59
Izoparaffins	34.83	36.47	34.21	33.67	34.69	34.65
Aromatics	5.98	5.40	11.85	13.79	12.58	11.09
Naphthenes	49.44	47.88	31.06	28.82	30.65	31.44
Olefins	0.36	0.45	0.25	0.71	0.24	0.36

As a result, in the mixed reforming feedstock, compared with 85-180°C fractions, reduction of paraffins content (up to 2% mass.) and insignificant increase in the naphthenic hydrocarbons content are observed. Also the content of izoparaffin hydrocarbon increases. With computer modelling system, the product output was calculated. The results of calculation are shown at Fig.3.

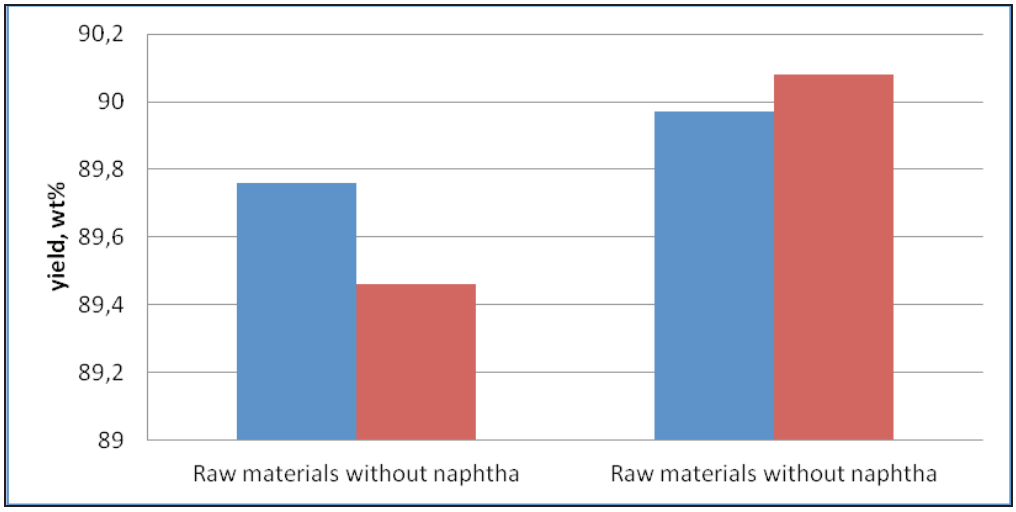

Fig. 3. The feedstock composition impact on the product output

The mathematical model is sensitive to the feedstock composition changes, and according to the obtained results it could be concluded that the heavy naphtha content in the feedstock composition increases the product output by 0,5-1% mass. In this case it is connected with concentration reduction of the paraffins of normal structure and izoparaffins concentration increase in the mixed feedstock composition because under the reforming process conditions the reactions of paraffins isomerization and dehydrocyclization play an important role. Izoalkanes dehydrocyclization reaction rate is higher than the one of normal alkanes, this leads to liquid product output increase in the feedstock with high izoparaffins content. As mentioned above, with heavy naphtha addition the izoparaffins

content increases in the mixed feedstock. This fact together with normal paraffins content reduction allows increasing the product output.

5. Conclusions

The results confirm that the feedstock replacement in the catalytic reforming unit has positive impact on the main indicators of product quality: the reformate output will be 82.71 octane tones; the octane number will be 97.6. The resource efficiency of the unit rises by 20% on account of the feedstock load increase. The research has shown that the feedstock replacement of the catalytic reforming unit L-35-11/450K has positive impact on the high-octane product output.

References

1. Mohammad Reza Rahimpour, Mitra Jafari, Davood Iranshahi, Progress in catalytic naphtha reforming process: A review. *Applied Energy* 2013; 79-93.
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 (1996). Novosibirsk, Nauka
4. J. Grane, Proceeding of the 4-th Int. Petroleum Congress, (1961), 3, 34.
5. A. Aitani, Catalytic naphtha reforming, in: Encyclopedia of Chemical Processing, 2006, pp. 397–406.
6. R.B. Smith, Kinetic analysis of naphtha reforming with platinum catalyst, Chem.Eng. Prog. 55 (6) (1959) 76–80.
7. D. Bommannan, R.D. Strivastava, D.N. Saraf, Modeling of catalytic naphtha reformers, Can. J. Chem. Eng. 67 (1989) 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, pp. 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 176-177 (2011) 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, -т. 1, No. 2-c, 2009, pp. 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, vol. 2, No. 4, 2010, pp. 374-380.
12. U. Taskar, J.B. Riggs, Modeling and optimization of a semiregenerative catalyticnaphtha reformer, AIChE J. 3 (№43) (1997) 740–753.
13. J.H. Jenkins, T.W. Stephens, Hydrocarbon Process. (November) (1980) 163–167.
14. J. Henningsen, M. Bundgaard-Nielson, Catalytic reforming, Br. Chem. Eng. 15 (11) (1970) 1433–1436.
15. G.B. Marin, G.F. Froment, Reforming of C6 hydrocarbons on a Pt-Al2O3 catalyst, Chem. Eng. Sci. 37 (5) (1982) 759–773.
16. G.J. Antos, A.M. Aitani, Catalytic Naphtha Reforming, Marcel Dekker, 2004, p.602.
17. Inna V. Yakupova, Ekaterina S. Sharova, Emilia D. Ivanchina Mathematical modelling method application for optimization of catalytic reforming process, Procedia Chemistry, Vol.10 (2014) 197 - 202.
18. Alena A. Chudinova, Anastasiya A. Salischeva, Elena N. Ivashkina, Olga A. Reutova, Konstantin S. Gulyaev, Aleksandr M. Demin, Anna Syskina. Estimation of sulfocationites application expediency as catalysts of benzene alkylation process with propylene // Procedia Chemistry. – Vol. 10 (2014) p.284-288.
19. Asem Nurmakanova, Anastasiya Salischeva, Alyona Chudinova, Elena Ivashkina, Anna Syskina Comparison between alkylation and transalkylation reactions using ab Initio Approach // Procedia Chemistry. – Vol. 10 (2014) p.430-436
20. Elena Khlebnikova, Alexander Bekker, Elena Ivashkina Hydrodynamics of reactant mixing in benzene with ethylene alkylation // Procedia Chemistry. – Vol 10. (2014) p. 297-304