

MATHEMATICAL MODEL OF ADVANCED REFINING TECHNOLOGY ADAPTED TO THE FEEDSTOCK CONDITIONS OF THE REPUBLIC OF KAZAKHSTAN

G. Nazarova^{1*}, E. Ivashkina¹, E. Ivanchina¹, G. Burumbaeva¹, A. Svarovskii¹ and G. Seytenova²

¹ *Fuel Engineering and Chemical Cybernetics Department, National Research Tomsk Polytechnic University, 30 Lenin Ave., Tomsk, 634050, Russia*

² *Mechanics and Petroleum Engineering Department, S.Toraigyrov Pavlodar State University, Pavlodar, Kazakhstan*

Received September 9, 2016; Accepted November 2, 2016

Abstract

Oil in Western Kazakhstan has significantly different in physical and chemical characteristics depending on the geographical location of oil fields, geological age and depth of burial. This has an impact on the composition and yield of light fractions in the catalytic cracking. A mathematical model of a catalytic cracking adapted to the feedstock conditions of the Republic of Kazakhstan presented in this paper. The impact of technological mode on the yield and composition of light fractions from the catalytic cracking unit was carried out using mathematical model of catalytic cracking. Patterns of change in the yield of rich gas, the light and heavy gas oil, gasoline and coke depending on the composition of the feedstock and technological mode of reactor-regenerator unit was defined.

Keywords: advanced petroleum refining; catalytic cracking; group composition of feedstock; mathematical modelling; light fraction yield; resource efficiency.

1. Introduction

Currently, in the condition of increasing of the part of recovered heavy oil, and the developing demand of high quality motor fuel, the major place in the refining industry takes processes of advanced petroleum refining, which allow producing light fraction and valuable gases from heavy oil feedstock [1-4]. In such conditions, it is required, on the one hand to provide deep researches of conditions and content of heavy oils, and, on the other hand, the developing process and catalyst and their refining and optimization of technologies operating duty device of high-refined oil and preparing oil [5-10].

The process of catalytic cracking allow to rework heavy fractions, and also vacuum distillate, which are taking in the process of vacuum distillation of fuel oil, with getting high octane diesel and gasoline fraction, and also unstripped gas, which is wealthy butane -butylene and propane-propylene fractions. Unstripped gas of the catalytic cracking is valuable feedstock for producing consumer product, especially the plastics. [11]. So most often, petrochemical plants included in the structure of gas - and oil-refining complexes.

The crude oil in Western Kazakhstan are significantly different physical and chemical characteristics, depending on the geographical location of oil fields, geological age and depth [12-14]. Such indicators as the ratio of the paraffinic, naphthenic, aromatic hydrocarbons and resins in the oil varies in a wide limit, and these indicates make much influence on the exit and property of products and coke from catalytic cracking, and therefore the efficiency of operation of industrial installations.

The use of mathematical models of processes of oil refining allows to adjust the technological regimes for operation of industrial installations with the aim of increasing the yield of light fractions and gas, and improve the quality of products from the catalytic cracking unit based on the composition of feedstock [15-17].

The work objective is to develop a mathematical model of the catalytic cracking process adapted to the raw conditions of the Republic of Kazakhstan with the ability to predict the output of light fractions, as well as propane-propylene and butane-butylene fraction.

2. Object of the research

The object of research is the catalytic cracking of vacuum distillate from blended crudes of Kazakh and West Siberian oil C-200, part of a combined installation of deep processing of fuel oil KT-1/1. As a raw material of catalytic cracking process using hydrotreated vacuum distillate (sulfur content of 0.08-0.15wt.%), FR. 350-500°C with carbon less than 0.3 wt%. Technological process realized in the riser in the upward stream of the microspheric zeolite –containing catalyst agent. (tab. 1)

Table 1. The parameters of the technological mode of the catalytic cracking reactor

The process variables	Value
Consumption of raw materials in the installation, m ³ /h	186.11
The total consumption of steam in the reaction zone of the riser, kg/h	11960.6
The total steam rate in the desorption zone, kg/h	4570.0
The temperature of the catalytic cracking, °C	522.24
The temperature at the inlet of the reactor, °C	275.64
Pressure, kgf/cm ²	1.49
The temperature of the regenerated catalyst, °C	664.46
The ratio of the catalyst : raw material	6.71

Products of the catalytic cracking unit C-200 KT-1/1 are rich gas with a high content of propane-propylene and butane-butylene fraction, a high-octane gasoline fraction (fraction of NC 205°C), light catalytic gas oil (FR.195-270°C), the fraction of 270 – 420°C and a fraction of more than 420°C and the coke burned in the process of continuous regeneration of the catalyst. The content of coke on the catalyst before regeneration is 0.4-0.72 % wt., after regeneration – 0.051-0.064 % wt.

As a catalyst cracking is used bi-zeolite catalyst, which includes from 12.0 to 60.0 wt.% zeolite Y-type, about 10% wt. ZSM-5, from 0.5 to 6.0 wt%. rare-earth elements. The weight ratio of zeolite ZSM-5:zeolite type-Y is from 0.25 to 3.0. Whereby the composition of the catalyst, in particular, the ratio of zeolite components and the technological mode of operation, the hydrodynamics features of the industrial apparatus, the composition of the feedstock determining the distribution of the main products of cracking.

3. The development of a mathematical model of catalytic cracking adapted to the raw conditions of the Republic of Kazakhstan

3.1 Laboratory investigation to determine the group composition of raw materials and products of the catalytic cracking in the processing of vacuum distillate from a mixture of Kazakhstan and West Siberian oil

To determine the group composition of heavy fractions of catalytic cracking of vacuum distillate, light gas oil (195-270°C), the fraction of 270-420°C and the individual composition of the gasoline fraction were carried out laboratory tests using the method of liquid-adsorption chromatography separation and gas-liquid chromatography using a gas chromatograph "CHROMATEC – CRYSTAL 5000" version 2 with a flame ionization detector.

Hydrocarbons of heavy fractions separated into paraffin-naphthenes fraction, the fraction of aromatic hydrocarbons and alcohol-benzene resin with the use of liquid adsorption chromatographic separation on silica gel, the physical analysis method (refractometry) and chemical-analytical method of analysis (formalin reaction) to confirm the absence of aromatic hydrocarbons in non-aromatic part of the specimen.

On the basis of data on the refractive index of the fractions of satisfied hydrocarbon of a vacuum distillate is determined by the structural-group composition of paraffin-naphthenic fraction of the vacuum distillate with C-200 installation of KT-1/1 according to the method n-d-M (tab.2).

Table 2 The structural-group composition of paraffin-naphthenic fraction

The exponent	Paraffin-naphthenic fraction
The content of carbon in the aromatic fragments (Ca)	1.103
The carbon content in naphthenic fragments (Cn)	30.571
The carbon content of the paraffinic fragments (Cp)	68.325
The average number of aromatic rings (Ka)	0.053
The average number of naphthene rings (Kn)	1.651
The total number of rings (Ko)	1.704

Definite, that vacuum distillate from catalytic cracking device are featured by high content of saturated hydrocarbons – 73.71 %. The content of aromatic hydrocarbons and alcohol-benzene resins in the raw material is from 23.31 and 3.56 % wt. Despite the high content of saturated hydrocarbons in a feedstock for catalytic cracking, vacuum distillation is characterized by high resin content, which is typical for the temperature of the end boiling point fraction 533.5°C. According to the method of structural-group composition is defined that the ratio of paraffinic hydrocarbons to naphthenic is of 2.23.

Light catalytic gas oil from the catalytic cracking unit is characterized by a high content of aromatic hydrocarbons (60.9 % wt.), the content of resinous substances in a light gas oil of catalytic cracking unit was 1.8 % wt., and saturated hydrocarbons of 37.3 % wt. The fraction of 270-420°C with a catalytic cracking unit characterized by a high content of aromatic hydrocarbons – 71.9 % wt., the resin content in the heavy gas oil is 2.6 % wt., and the content of paraffinic and naphthenic hydrocarbons is 25.5 wt%.

The results of determining the group composition of gasoline fractions from the catalytic cracking showed that the gasoline has a high content of olefin (of 17.08 % wt.), isoparaffin (27.52 % wt.) and aromatic hydrocarbons (42.44 % wt.), due to chemical transformations on the bi-zeolite catalyst of the cracking (tab. 3).

Table 3 The composition of the gasoline fraction and unstripped gas from catalytic cracking unit

Gasoline fraction		Rich gas	
The group of hydrocarbons	Content, % wt.	The group of hydrocarbons	Content, % wt.
n-paraffins	3.511	Propane-propylene fraction	36.67
Isoparaffin	27.52	Butane-butylene fraction	31.94
Naphthenes	9.48	Gaseous substance C1-C6	31.39
Aromatic hydrocarbon	42.44		
Olefins	17.08		

The high content of zeolites in the catalyst, primarily zeolite of type Y, and rare earth elements, provides primary cracking and dealkylation of aromatic hydrocarbons and naphthenes of raw materials on the acid centers of the catalyst and high speed conversion of hydrocarbon raw materials into hydrocarbons of gasoline. In the presence of zeolite Y, the influence of reactions redistribution of hydrogen with the formation of isoparaffins, aromatic hydrocarbons, and lower content of olefins in the products, which is associated with a broad porous structure of zeolite. Olefinic hydrocarbons that are in the pores of the zeolite type-Y are subjected to cyclization with the formation of naphthenic and aromatic hydrocarbons.

The high content of zeolite ZSM-5 in the cracking catalyst provides the intensity of the cracking reactions of the hydrocarbons of gasoline fraction with the formation of gases, zeolite ZSM-5 is characterized by the molecular sieve properties, that defines the constraints in the cracking of high molecular weight paraffins. Thus in the presence of zeolite ZSM-5 reduces the effect of the reaction of hydrogen transfer and isomerization contributes as olefins and paraffins, in addition, the paraffins of normal structure are subjected by cracking of aromatization. Thus,

yield of light olefins on zeolite ZSM-5 the increased due to the low speed transport of hydrogen, i.e., minimizes the saturation of olefins molecules and increases the cracking of olefins in the gases.

3.2. Thermodynamic and kinetic regularity of catalytic cracking on the bi-zeolite catalyst

On the basis of results of laboratory researches by definition of the group and structural-group of composition of the vacuum distillate catalytic cracking taking into account the thermodynamic analysis of reactions performed using the quantum-chemical calculation methods (the theory of density functional, B3LYP, 3-21-G) was composed of a formalized scheme of hydrocarbon transformations in the catalytic cracking of process [18].

In order that the model was capable of predicting the content of a propane-propylene and butane-butylene fraction unstripped gas in a formalized scheme of hydrocarbon transformations were made of the reaction of cracking of paraffins and isoparaffins, as well as the reaction of cracking of the olefins with the formation of propane-propylene and butane-butylene fractions and components of the gas.

Such a formalization of schema transformations of hydrocarbons allows to predict the yield of products from the catalytic cracking unit, group structure and octane number of gasoline, and unstripped gas the containing propane-propylene and butane butylene fractions, which is feasible in the technology of catalytic cracking in the application of the catalyst with high content of the zeolite component ZSM-5, providing to intensive of the secondary cracking reactions.

The results thermodynamic and kinetic analysis are presenting in tab. 4.

Table 4 Thermodynamic and kinetic parameters of catalytic cracking reaction

Reaction	ΔG , kJ/mol	k_{straight}	k_{straight}
Cracking of higher paraffins C ₁₃ -C ₄₀	-74.32	$7.60 \cdot 10^{-2}$	-
Cracking of higher paraffins C ₁₃ -C ₄₀ to isoparaffins	-76.82	$5.06 \cdot 10^{-1}$	-
Cracking of paraffins C ₅ -C ₁₁₊ with formation of the butane-butylene fraction	-60.79	$8.13 \cdot 10^{-2}$	-
Isomerization of paraffins C ₅ -C ₁₁₊	-2.34	$3.46 \cdot 10^{-4}$	$2.45 \cdot 10^{-4}$
Cracking of isoparaffins, C ₅ -C ₁₁₊ with formation of the butane-butylene fraction	-60.15	$1.14 \cdot 10^{-1}$	-
Cracking of olefins with formation of the butane-butylene fraction	-47.10	$2.28 \cdot 10^{-1}$	$3.48 \cdot 10^{-3}$
Redistribution of hydrogen	-111.76	17.04	
Dealkylation of naphthenes	-120.4	$2.86 \cdot 10^{-1}$	
Dealkylation of aromatic hydrocarbons	-91.68	$2.47 \cdot 10^{-1}$	
Cracking of polynaphthenic with formation of aromatics	-113.63	$2.10 \cdot 10^{-1}$	
Condensation of aromatic hydrocarbons	-594.2	$5.19 \cdot 10^{-1}$	
Polycondensation (coke production)	-594.2	$4.83 \cdot 10^{-1}$	
Cyclization of olefins to naphtene	-7.5	$1.33 \cdot 10^{-2}$	$4.44 \cdot 10^{-3}$
Condensation of aromatic hydrocarbons in gasoline	-58.44	$2.10 \cdot 10^{-1}$	
Cracking of paraffins with propane-propylene formation	-62.27	$8.13 \cdot 10^{-2}$	
Cracking of olefins with formation of propane-propylene fraction	-49.6	$4.90 \cdot 10^{-1}$	$7.49 \cdot 10^{-3}$

Kinetic parameters of reactions of the process are determined during the solution of the inverse kinetic problem. Mathematical model of the process is recorded on the basis of a formalized scheme of hydrocarbon transformations in the catalytic cracking process.

The high content of zeolite type-Y on the catalyst of the cracking and rare earth elements ensures high rate of primary cracking reactions of paraffin ($5.06 \cdot 10^{-1} \text{ s}^{-1}$) and dealkylation of naphthenic (of $2.28 \cdot 10^{-1} \text{ s}^{-1}$) and aromatic ($2.47 \cdot 10^{-1} \text{ s}^{-1}$) of hydrocarbons. In addition, the greatest speed of reaction are characterized by a redistribution of hydrogen ($17.04 \text{ l} \cdot \text{s}^{-1} \cdot \text{mol}^{-1}$), which is typical for highly porous type zeolite-Y.

Zeolite ZSM-5 provides a secondary reaction of cracking of the hydrocarbons of gasoline fraction with the formation of gaseous products. So, the reactions of cracking olefin hydrocarbons with

the formation of propane-propylene and butane-butylene fraction ($2.28 \cdot 10^{-1} \text{ s}^{-1}$ and $4.90 \cdot 10^{-1} \text{ s}^{-1}$) are characterized by high speed.

At high temperatures catalytic cracking intensively occurs reactions of coking ($4.83 \cdot 10^{-1} \text{ l} \cdot \text{s}^{-1} \cdot \text{mol}^{-1}$), the condensation of aromatic hydrocarbons of the feedstock with the formation of a complex naphthene-aromatic structures are characterized by a high rate ($5.19 \cdot 10^{-1} \text{ l} \cdot \text{s}^{-1} \cdot \text{mol}^{-1}$) than the reaction of condensation of aromatic hydrocarbons of gasoline fraction (of $2.10 \cdot 10^{-1} \text{ l} \cdot \text{s}^{-1} \cdot \text{mol}^{-1}$).

The selected level of formalization of the scheme of conversion of hydrocarbons ensures the adequacy of the mathematical description, and allows to predict the yield of products from the catalytic cracking unit, group structure and octane number of gasoline, and the maintenance of propane-propylene and butane-butylene fraction in the fat gas catalytic cracking (tab. 5, 6).

Table 5 Verification of mathematical models for adequacy

The product	The yield of products, % wt.		The group of hydrocarbons	The composition of gasoline, % wt.	
	calculated	experimental		calculated	experimental
Gasoline	42.89	42.90	n-paraffins	3.510	3.511
Rich gas	35.52	35.00	Isoparaffin	27.38	27.52
Fr. 195-270°C	8.10	8.10	Naphthenes	9.48	9.48
Fr. 270-420°C	3.40	3.40	Aromatics	42.43	42.44
Fr. > 420 °C	3.70	3.70	Olefins	17.08	17.08
Coke	5.67	5.60			

Table 6 Verification of mathematical models for adequacy

The group of hydrocarbons	Composition of rich gas, % wt.	
	Calculated	Experimental
Propane-propylene fraction	36.63	36.67
Butane-butylene fraction	31.69	31.94
Gas C ₁ -C ₆	31.68	31.39

4. Conclusion

Thus, laboratory investigation have allowed establishing the structural-group composition of the vacuum distillate refinable in the catalytic cracking process, heavy fractions, light and heavy gas oil, and the composition of the gasoline fractions from the catalytic cracking unit. Received narrow fractions will be analyzing using gas chromatography-mass spectrometry to establish the qualitative composition of raw materials and products of the catalytic cracking process.

With the use of the Density Functional Theory performed thermodynamic analysis of reactions and was evaluated the thermodynamic probability of the conversion of hydrocarbons under process conditions of catalytic cracking process. Determined that thermodynamically the most probable are the primary reaction of cracking hydrocarbons of vacuum distillate cracking of paraffins with the formation of isoparaffins ($\Delta G = -76.82 \text{ kJ/mol}$), dealkylation naphthenic ($\Delta G = -120.4 \text{ kJ/mol}$) and aromatic hydrocarbons ($\Delta G = -91.68 \text{ kJ/mol}$), the redistribution of hydrogen ($\Delta G = -111.76 \text{ kJ/mol}$) and coking ($\Delta G = -594.2 \text{ kJ/mol}$).

Formalized scheme of hydrocarbon transformations was adapted to reactions of cracking of paraffins, isoparaffins and olefins with the formation of propane-propylene and butane-butylene fraction of the unstripped gas.

Identified in the course of solving the inverse kinetic task kinetic parameters of the main reactions of cracking adequately describe the chemical conversion on the catalyst with the zeolite components. Determined that the most severe reactions are catalytic cracking reactions redistribution of hydrogen with the formation of isoparaffin and aromatic hydrocarbons ($17.04 \text{ l} \cdot \text{s}^{-1} \cdot \text{mol}^{-1}$) cracking of paraffin ($5.06 \cdot 10^{-1} \text{ s}^{-1}$) and dealkylation naphthenic ($2.86 \cdot 10^{-1} \text{ s}^{-1}$) and aromatic ($2.47 \cdot 10^{-1} \text{ s}^{-1}$) of hydrocarbons and secondary cracking reactions of the hydrocarbons of gasoline fraction with the formation of gaseous products. So, the reactions of cracking olefin

hydrocarbons ($2.28 \cdot 10^{-1} \text{ s}^{-1}$ and $4.90 \cdot 10^{-1} \text{ s}^{-1}$) with the formation of propane-propylene and butane-butylene fractions are characterized by high speed.

Thus, the established level of formalization of chemical reactions in the catalytic cracking allows to adequately describe the transformation of hydrocarbons on the catalyst bi-zeolite of cracking and to predict the composition and the yield of gasoline fraction and the content of the propane-propylene and butane-butylene fraction in unstripped gas the processing of vacuum distillate from a mixture of Kazakh and West Siberian oil.

References

- [1] Nurtazina R, Abildayev A, Nurtaza A, Aubakirova L.: Energy Security as a Political. The Social Sciences. 2015; 10(6): 845.
- [2] Yermukhan S, Azimbekova A. Actual Problems of Economics. 2014;157(7): 153.
- [3] Zhumagulov RB. Oil and gas. 2006; 2: 75.
- [4] Kang X, Guo X. Energ. Sources Part A. 2013; 35: 1921.
- [5] Usheva NV, Moizes OE, Kuzmenko EA, Kim SF, Khlebnikova ES, Dyalilova SN, Filipova TV. IOP Conference Series: Earth and Environmental Science. 2015; 27: 1.
- [6] Kim SF, Usheva NV, Moyzes OE, Kuzmenko EA, Samborskaya MA, Novoseltseva EA. Procedia Chemistry. 2014; 10: 448.
- [7] Tataurshikov A, Ivanchina E, Krivtcova N, Krivtsov E, Syskina A. IOP Conference Series-Earth and Environmental Science. 2015; 27: 1.
- [8] Jiménez-García, G, Aguilar-López R, Maya-Yescas R. Fuel. 2011; 90: 3531.
- [9] Sildir H, Arkun Y, Cakal B, Gokce D, Kuzu E. Journal of Process Control. 2012; 22: 1956.
- [10] Pevneva GS, Golovko AK, Korneev DS, Levashova AI. Procedia Chemistry. 2014; 10: 15.
- [11] Musaev S, Babaev A, Mamedov Z, Zarbaliev L. Chem Tech Fuels Oil. 2004; 40(3): 137.
- [12] Mahmotov E, Aldyyarov T, Sigitov V. Oil and gas (Almaty), 2010; 4(58): 69.
- [13] Wang X, Zhang Y, He Y, Ma Y, Wang J, Jin Y. Petroleum Refinery Engineering. 2013; 43(7): 43.
- [14] Bakirova S, Aleshin G, Shestoperova L, Koryabina N. Petroleum chemistry U.S.S.R. 1990; 29(1): 42.
- [15] Krivtcova NI, Tataurshikov AA, Ivanchina ED, Krivtsov EB. Procedia Chemistry. 2015; 15: 180.
- [16] Frantsina EV, Ivanchina ED, Ivashkina EN, Romanovskii RV. Chem Eng J. 2014; 238(1): 129.
- [17] Zagoruiko A, Belyi A, Smolikov M, Noskov A. Catal. Today. 2014; 220-222: 168.
- [18] Nazarova G, Ivashkina E, Ivanchina E, Kiseleva S, Stebeneva V. Procedia Chemistry. 2015; 15: 342.

*Corresponding author, address: Chemical Engineering Department, Tomsk Polytechnic University, 30, Lenin Avenue, Tomsk, 634050, Russia; tel.: (+7-3822) 563443; fax: (+7-3822) 563-435; e-mail: silko@tpu.ru