

# Testing of cracking zeolite catalysts using mathematical model

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**Abstract.** The testing results of the cracking zeolite catalysts using the mathematical model of catalytic cracking are given in this research. The mathematical model is based on the formalized scheme of hydrocarbon conversions according to the results of laboratory research using gas chromatography-mass spectrometry and thermodynamic analysis of the catalytic cracking reactions using quantum chemistry methods. The effect of the catalyst composition on the distribution of the catalytic cracking products, the content of propane-propylene and butane-butylene fraction in wet gas, group composition and octane number of gasoline, the content of coke on the catalyst are determined using the mathematical model of catalytic cracking.

## INTRODUCTION

Significant improvement of industrial processes of deep oil processing and catalysts for motor fuel and gas production from heavy oil fractions for the reason of growing needs of heavy oil feedstock processing is providing a substantial development of refining industry around the world for several decades [1-5]. Currently, the scientific community efforts are focused on the development of new catalysts for cracking of heavy oil fractions and improving existing catalyst compositions [6-7]. The industrial catalysts for motor fuel production provide the improving efficiency of the industrial processes depending on the production goals and are characterized by high activity and selectivity in the formation of the desired components [8-11].

The catalytic cracking technology is a universal process of heavy hydrocarbon fractions conversion. The technological mode of the catalysts operation could be different depending on the required volume and quality of petroleum products. At present, the overwhelming majority of catalytic cracking units operate using synthetic microspheric zeolite catalyst [12-14].

Extensive use and synthesis of zeolite materials allow reducing significantly the time of cracking reactions and increasing the selectivity to production of high-octane gasoline, rich gas and light gas oil yields during catalytic cracking. The Y and ZSM-5 zeolites are the most effective in catalytic cracking technology. The difference between structures of zeolites causes different distribution of catalytic cracking products.

The elementary cell of Y-type zeolite has four input windows of 0.73-1.3 nm in diameter and twelve-element oxygen rings. Si/Al ratio is in the range from 4.0 and above, zeolites with Si/Al more than 5.0 are called ultrastable. These zeolites have high acid and heat resistance and catalytic activity for cracking and isomerization reactions.

The unit cell of ZSM-5 zeolite consists of four input windows of elliptical shape and of 0.51-0.56 nm in diameter and ten-element oxygen rings. Si/Al ratio of ZSM-5 zeolite can be up to 50.0. A significant reactivity and corresponding pore size of zeolites allow carrying out selective cracking of hydrocarbons in accordance with the Deep Catalytic Cracking technology with production of low-molecular olefins [15-19].

Russian and foreign scientists investigate the effect of technological mode, reactor design, catalyst compositions, hydrodynamic mode of catalytic cracking experimentally or using the mathematical models (J.G. Carella, X. Lan, S.N. Hajiyev, A.S. Noskov, A.S. Belyi, E. Baudrez, A.G. Shumikhin, I.M. Kolesnikov, K.K. Dagde, G. Froment, V.P. Doronin, et al.). It is important to take into account the real possibilities of industrial units, technological mode and feedstock composition at the stage of planning the quality and volume of the product.

It is possible to carry out research aimed at the efficiency upgrading of the catalyst operation with reducing the coke formation on the catalyst and maintaining a high yield of light fractions (considering with the feedstock composition, technological mode of the catalyst operation, catalyst compositions, ratio of the active components, hydrodynamic characteristics of industrial installations, etc.) using the adequate mathematical model of the process [20-23].

The testing results of two types of industrial cracking catalysts during vacuum distillate conversion using a mathematical model of catalytic cracking developed at the Department of Fuel Engineering and Chemical Cybernetics of Tomsk Polytechnic University are given in this research.

The aim of this research is to evaluate the effect of the catalyst type on the yield and distribution of the main products of catalytic cracking during vacuum distillate conversion with a high content of saturated hydrocarbons.

## EXPERIMENTAL PART

### Object of research

The object of research are industrial catalysts (CAT-1 and CAT-2) used in the catalytic cracking units that are parts of KT-1/1 combined installation of deep processing of fuel oil. Vacuum distillate, obtained by vacuum distillation of fuel oil with subsequent hydrotreating, is used as feedstock of the catalytic cracking units. Table 1 shows the range of the technological mode of the cracking catalysts operation.

**TABLE 1.** Technological mode of cracking catalysts operation

Process parameter	CAT-1	CAT-2
Feedstock flow rate, m <sup>3</sup> /h	100-240	160-420
Feedstock temperature, K	533-628	513-623
Slops flow rate, m <sup>3</sup> /h	up to 55	up to 20
Steam flow rate in the grip of the lift-reactor, kg/h	1500-10000	2000-14000
Steam flow rate in the upper bubbler of desorber zone, kg/h	2000-6000	at least 1400
Steam flow rate in the middle bubbler of desorber zone, kg/h	1500-4000	at least 360
Steam flow rate in the bottom bubbler of desorber zone, kg/h	500-1000	at least 360
Temperature of the regenerated catalyst, K	913-963	903-973
Process temperature, K	500-540	495-535
Pressure, Pa	107000-152000	7800-160000
Catalyst circulation rate, ton <sub>cat</sub> /ton <sub>feed</sub>	5-10	5-10

Composite materials consisting of matrix and zeolite components are used as a catalyst in the catalytic cracking technology. Brønsted and Lewis acid sites of the matrix, whereon primary cracking of heavy hydrocarbon feedstock occurs, have high catalytic activity. The matrix components must have high acidity to provide the primary cracking of hydrocarbons.

Ultrastable high porosity Y-type zeolite (Si/Al = 4.4) and high-silicon ZSM-5 zeolite (Si/Al = 15.0) are used as zeolite components. Y-type zeolites are highly porous zeolites with faujasite structure and pore size of 0.74 nm. ZSM-5 zeolite refers to the structural type of pentasil with the system of channels intersecting at right angles: direct channels with windows size 0.51 × 0.56 nm and sinusoidal ones with windows size 0.51 × 0.55 nm. CAT-1 catalyst is characterized by a high content of zeolite components (Y and ZSM-5) – 31.5 and 12.0 % wt. relative to the catalyst CAT-2 (20 and 2 % wt.). The zeolite ratio ZSM-5 to Y is 0.381 for the CAT-1 catalyst and 0.11 for the CAT-2 catalyst. The content of rare earth elements is above (8.2 % wt.) in the CAT-1 catalyst due to higher content

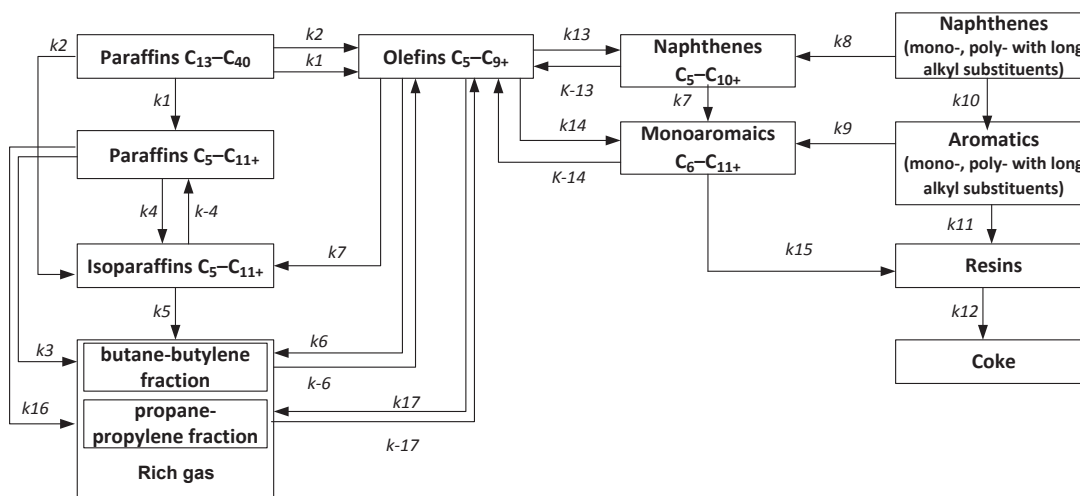
of Y-type zeolite in order to replace sodium cations and save acid sites activity after the regeneration stage. The Y-type zeolites are in decationized form in CAT-2 composition.

The composition of cracking catalysts has a major influence on the yield and composition of the products from the industrial unit together with the composition of the feedstock and technological mode of the reactor block.

In consideration of the foregoing, testing of the cracking catalyst is topical to investigate the effect of the catalyst type on the yield and composition of the cracking products taking into account the feedstock composition and technological mode of the reactor block.

## Mathematical model of catalytic cracking

The mathematical model of catalytic cracking was developed at the Department of Fuel Engineering and Chemical Cybernetics of Tomsk Polytechnic University. The mathematical model is based on the formalized scheme of hydrocarbon conversion in accordance with the results of the laboratory research by determining composition of feedstock and products and thermodynamic analysis of the catalytic cracking reactions using the methods of quantum chemistry [24-25] (Fig. 1). The scheme of hydrocarbon conversions was supplemented with the following reactions: cracking of paraffinic, olefinic and isoparaffinic hydrocarbons in order to predict the content of propane-propylene and butane-butylene fraction in wet gas during operation of the bi-zeolite cracking catalyst.



**FIGURE 1.** The formalized scheme of hydrocarbon conversions in catalytic cracking:  $k_j$  – the rate constant of the direct chemical reaction;  $k_{-j}$  – the rate constant of the reverse chemical reaction

The mathematical model of catalytic cracking is represented by a system of differential equations supplemented with the heat balance equation. The model describes a change in concentration of the reactant depending on the contact time with the initial conditions:  $\tau = 0$ ,  $C_i = C_{i0}$ ,  $T_0 = T_r$ ,  $l = 0$ , where  $i$  - the corresponding hydrocarbon,  $T_r$  – the temperature of the reaction start,  $K$ . The expressions for the reaction rate constants are written according to the mass action law.

The rate constants of the chemical reactions included in the mathematical model are defined by solving the inverse kinetic problem and represent a combination of all constants for the intermediate stages (Table 2). The resulting mathematical model is formalized and quasi-homogeneous.

The cracking reactions of paraffins are characterized by high reaction rate due to a high content of zeolite in the CAT-1 catalyst, preferably Y-zeolite and rare earth elements. Cracking of high molecular weight paraffins with isoparaffins formation ( $7.06 \cdot 10^{-1} \text{ s}^{-1}$ ) has the highest rate. The primary reactions of dealkylation of naphthenes are more intensive on the CAT- 2 catalyst ( $4.46 \cdot 10^{-1} \text{ s}^{-1}$ ). The reaction rate of dealkylation of naphthenes and aromatics, cracking of naphthenes with aromatic hydrocarbon formation on CAT-1 ( $3.92 \cdot 10^{-1}$ ,  $3.37 \cdot 10^{-1}$ ,  $3.30 \cdot 10^{-1} \text{ s}^{-1}$ ) are similar, which can be explained by a high content of Y-type zeolite in CAT-1 composition.

Thus, a high content of ZSM-5 zeolite in the CAT-1 catalyst reduces the reaction rate of hydrogen transfer ( $24.97 \text{ l} \cdot \text{s}^{-1} \cdot \text{mol}^{-1}$  – CAT-1 and  $30.91 \text{ l} \cdot \text{s}^{-1} \cdot \text{mol}^{-1}$  – CAT-2) and intensive cracking of gasoline hydrocarbons to wet gas formation with a high concentration of propane-propylene and butane-butylene fractions. Thus, the reaction rates of

paraffin cracking ( $1.11 \cdot 10^{-1} \text{ s}^{-1}$  – CAT-1 and  $1.72 \cdot 10^{-2} \text{ s}^{-1}$  – CAT-2), isoparaffin cracking ( $1.16 \cdot 10^{-1} \text{ s}^{-1}$  – CAT-1 and  $3.45 \cdot 10^{-2} \text{ s}^{-1}$  – CAT-2) with formation of butane-butylene fraction are significantly higher during the CAT-1 operation. The same pattern is observed in case of paraffinic hydrocarbons cracking with formation of propane-propylene fraction ( $1.13 \cdot 10^{-1} \text{ s}^{-1}$  – CAT-1 and  $7.77 \cdot 10^{-2} \text{ s}^{-1}$  – CAT-2).

**TABLE 2.** Kinetic parameters of catalytic cracking reactions on CAT-1 and CAT-2 catalysts (the temperature is 794 K, the pressure is 141215.8 Pa)

Reaction	Rate constant of direct chemical reaction (kpr)	
	CAT-1	CAT-2
Cracking of $C_{13}$ – $C_{40}$ high molecular weight paraffins	$1.06 \cdot 10^{-1}$	$1.11 \cdot 10^{-1}$
Cracking of high molecular weight paraffins $C_{13}$ – $C_{40}$ with isoparaffins formation	$7.06 \cdot 10^{-1}$	$5.20 \cdot 10^{-1}$
Cracking of $C_5$ – $C_{11+}$ paraffins with butane-butylene fraction formation	$1.11 \cdot 10^{-1}$	$1.72 \cdot 10^{-2}$
Isomerization of $C_5$ – $C_{11+}$ paraffins	$4.64 \cdot 10^{-4}$	$6.70 \cdot 10^{-4}$
Cracking of $C_5$ – $C_{11+}$ isoparaffins with butane-butylene fraction formation	$1.16 \cdot 10^{-1}$	$3.45 \cdot 10^{-2}$
Cracking of olefin with butane-butylene fraction formation	$3.50 \cdot 10^{-1}$	$9.51 \cdot 10^{-2}$
Redistribution of hydrogen	24.97	30.91
Dealkylation of naphthenes	$3.92 \cdot 10^{-1}$	$4.46 \cdot 10^{-1}$
Dealkylation of aromatic hydrocarbons	$3.37 \cdot 10^{-1}$	$2.21 \cdot 10^{-1}$
Cracking of poly-naphthenes	$3.30 \cdot 10^{-1}$	$6.71 \cdot 10^{-2}$
Condensation of aromatic hydrocarbons	$7.26 \cdot 10^{-1}$	$1.63 \cdot 10^{-1}$
Polycondensation (coke formation)	$6.77 \cdot 10^{-1}$	$3.73 \cdot 10^{-1}$
Cyclization of olefins to naphthenes	$1.86 \cdot 10^{-2}$	$6.44 \cdot 10^{-2}$
Aromatization of olefins	$7.34 \cdot 10^{-2}$	$1.04 \cdot 10^{-2}$
Condensation of aromatic hydrocarbons of gasoline	$2.94 \cdot 10^{-1}$	$8.99 \cdot 10^{-2}$
Cracking of paraffins with propane-propylene fractions formation	$1.13 \cdot 10^{-1}$	$7.77 \cdot 10^{-2}$
Cracking of olefins with propane-propylene fractions formation	$7.50 \cdot 10^{-1}$	$1.30 \cdot 10^{-1}$

Furthermore, olefinic hydrocarbons are the most reactive in case of cracking on the catalyst with a high content of ZSM-5 zeolite (CAT-1). The reaction rates of olefin hydrocarbons cracking with formation of propane-propylene and butane-butylene fraction are  $7.50 \cdot 10^{-1}$  and  $3.5 \cdot 10^{-1} \text{ s}^{-1}$  – on the CAT-1 catalyst and  $1.30 \cdot 10^{-1}$  and  $9.51 \cdot 10^{-2} \text{ s}^{-1}$  on the CAT-2 catalyst.

The condensation reactions of aromatic hydrocarbons (coke formation) are the most intensive on the CAT-1 catalyst due to a high content of zeolite component and developed structure of zeolite ( $6.77 \cdot 10^{-1} \text{ s}^{-1} \cdot \text{mol}^{-1}$  – CAT-1 and  $3.73 \cdot 10^{-1} \text{ s}^{-1} \cdot \text{mol}^{-1}$  – CAT-2).

### Testing of zeolite cracking catalysts using mathematical model

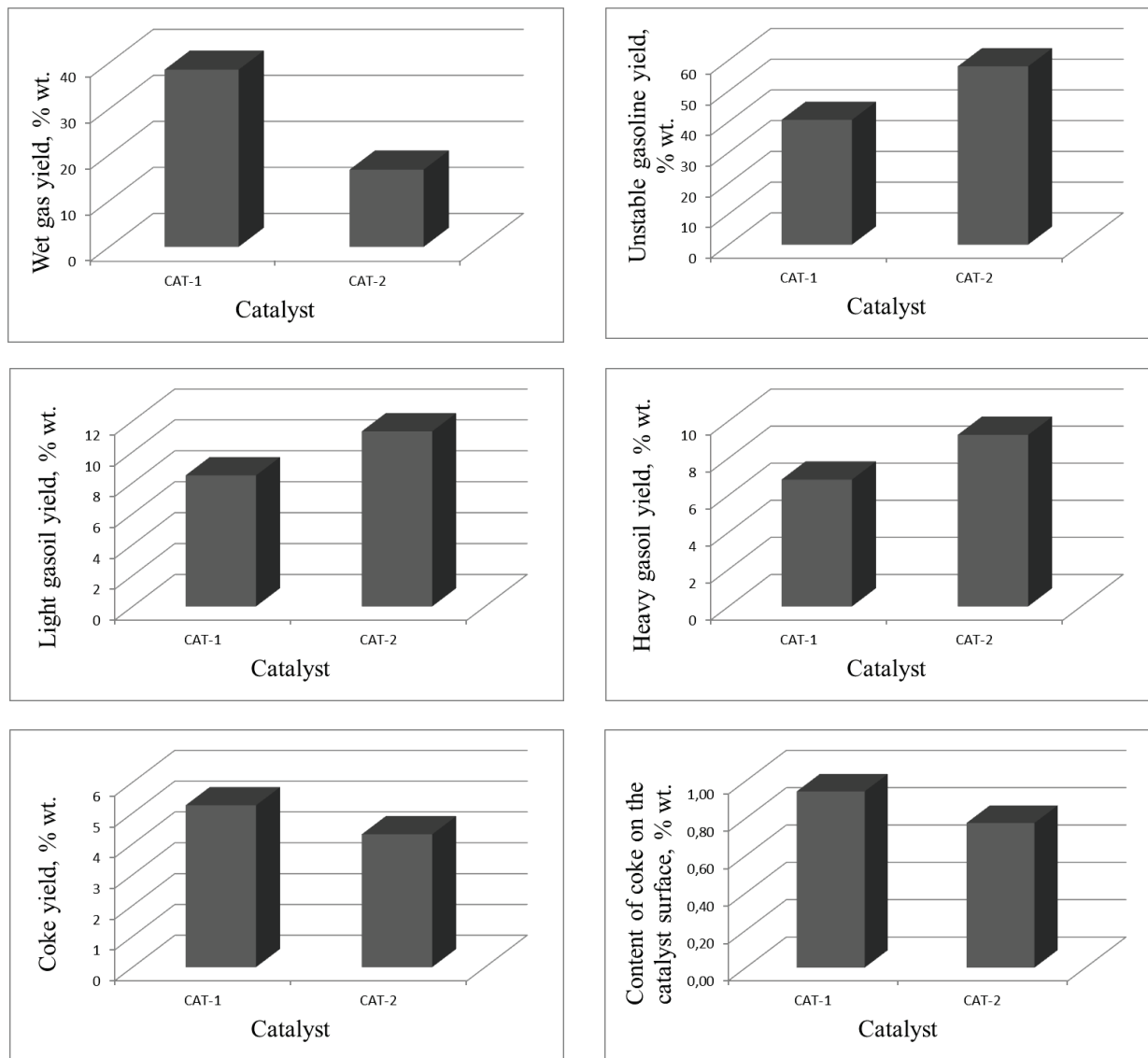
The cracking catalysts were tested to evaluate the effect of the catalyst type on the distribution of the main catalytic cracking products, content of propane-propylene and butane-butylene fraction in wet gas, group composition of gasoline from the catalytic cracking unit during vacuum distillate conversion with a high content of paraffins using the mathematical model of catalytic cracking. The calculations were performed at the constant parameters of the technological mode and composition of raw materials (Table 3).

**TABLE 3.** Composition of vacuum distillate and technological mode of catalytic cracking unit for testing cracking catalysts

Process parameter	Parameter	Composition of vacuum distillate	Value
Feedstock flow rate, $\text{m}^3/\text{h}$	378.0		
Feedstock temperature, K	577.0		
Slop flow rate, $\text{m}^3/\text{h}$	9.2	Saturated hydrocarbons,% wt.	65.4
Steam flow rate in the grip of the lift-reactor, $\text{kg}/\text{h}$	5500.0	Aromatic hydrocarbons,% wt.	31.1
Temperature of the regenerated catalyst, K	963.0	Alcohol-benzene resins,% wt.	3.5
Process temperature, K	794.0	Density, $\text{kg}/\text{m}^3$	0.904
Pressure, Pa	141215.8		
Catalyst circulation rate, $\text{ton}_{\text{cat}}/\text{ton}_{\text{feed}}$	5.56		

## RESULTS AND DISCUSSION

The composition of the cracking catalyst has a significant influence on the yield and product composition of the cracking unit. The calculation results of the product yield from the cracking unit during the CAT-1 and CAT-2 catalyst operation are shown in Fig. 2 using the mathematical model of catalytic cracking.



**FIGURE 2.** Product yields of catalytic cracking depending on the type of cracking catalyst

The yield of wet gas is significantly higher in case of the operating CAT-1 catalyst (38.53 % wt.), than in case of the CAT-2 catalyst (16.8 % wt.), due to a high content of the ZSM-5 zeolite at CAT-1 catalyst composition, which provides high selectivity of the secondary cracking reactions of gasoline hydrocarbon with wet gas formation. At the same time the coke content on the CAT-1 catalyst is above (0.94 % wt.) relative to the CAT-2 catalyst (0.78 % wt.), which is associated with a high rate of condensation reactions in the wide pores of the Y zeolite.

The content of propane-propylene and butane-butylene fractions in wet gas and gasoline composition using the CAT-1 and CAT-2 catalysts are presented in Tables 4,5 (calculations using the catalytic cracking model).

**TABLE 4.** The content of propane-propylene and butane-butylene fraction in wet gas of catalytic cracking process using the CAT-1 and CAT-2 catalysts

Component	CAT-1	CAT-2
Propane-propylene fraction, % wt.	37.07	31.50
Butane-butylene fraction, % wt.	31.75	34.35

Wet gas of the (CAT-1) cracking catalyst is characterized by a high content of propane-propylene fraction (37.07 % wt.) relative to the wet gas produced during operation of the CAT-2 catalyst (31.50 % wt. with a low content of the ZSM-5 zeolite). This product distribution is due to the chemical transformations of hydrocarbons on the surface of the microsphere bi-zeolite cracking catalyst (Table 2).

**TABLE 5.** The group composition of the gasoline fraction with the operating CAT-1 and CAT-2 catalysts

Hydrocarbons group	Content, % wt.	
	CAT-1	CAT-2
N-paraffins	2.81	4.43
Isoparaffins	22.75	30.37
Naphthenes	8.10	10.86
Aromatic hydrocarbons	48.36	34.29
Olefins	12.32	19.53
RON	93.80	91.35

Gasoline fraction is characterized by a high content of olefinic hydrocarbons (19.53 % wt.) during CAT-1 operation because the catalyst has a lower content of ZSM-5 zeolite, and for this reason the cracking reactions of olefins from gasoline with gas formation occur less. The content of aromatic hydrocarbons in the gasoline is significantly higher during CAT-1 operation (42.36% wt. – CAT-1 and 34.29% wt. – CAT-2), which is associated with a high rate of aromatic hydrocarbons dealkylation and olefins aromatization, that is characteristic in case of a high content of the high-porosity Y-zeolite.

The content of isoparaffin hydrocarbons in gasoline is above in case of CAT-2 operation that is characteristic for the low ratio of the ZSM-5/Y zeolite (0.11). Therefore, the reaction rate of hydrogen redistribution is high. The high content of aromatic hydrocarbons in gasoline in case of CAT-1 provides a high octane number (93.8 RON). The gasoline fraction during CAT-2 operation is characterized by a high content of isoparaffinic hydrocarbons (91.35 RON).

## CONCLUSION

A variety of chemical reactions involving high molecular weight hydrocarbons occurs in case of heavy oil feedstock conversion during catalytic cracking. The formalization level of hydrocarbons conversion scheme for catalytic cracking provides the adequacy of mathematical description for a wide range of process parameters. This formalized scheme of hydrocarbons conversion was supplemented with the cracking reactions of paraffin, isoparaffin and olefinic hydrocarbons to predict the content of propane-propylene and butane-butylene fraction in catalytic cracking wet gas.

The kinetic laws of catalytic cracking during operation of industrial catalysts with different contents of zeolite components were found out. The effect of cracking catalyst composition on the distribution of the main products of the process, content of propane-propylene and butane-butylene fraction in wet gas and composition of catalytic cracking gasoline using mathematical model of the process was evaluated.

A high ratio of the ZSM-5 to Y zeolite in case of CAT-1 (0.381) operation was determined to provide a high rate of the secondary cracking reaction of gasoline hydrocarbons with formation of wet gas hydrocarbon. In this case, the content of the propane-propylene fraction during CAT-1 operation is above and equal to 37.07 % wt. in comparison with the catalyst with a low ratio of zeolite components (0.11– CAT-2) (the content of the propane-propylene fraction is 31.5% wt.). Along with an increase in wet gas yield the decrease in gasoline fraction yield is observed during CAT-1 operation (93.8 RON) for the reason of intensification of the cracking reactions in the ZSM-5 zeolite pores and an increase in the coke content on the cracking catalyst due to the intensive polycondensation reactions in the Y-zeolite pores. It should be considered by the optimization of the technological mode.



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