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Thermodynamic analysis of catalytic cracking reactions as the first stage in the development of mathematical description

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Abstract

In this work thermodynamic analysis of catalytic cracking reaction involving the high molecular weight hydrocarbons was carried out using quantum chemical method of calculation realized in Gaussian software. The method of calculation is DFT (Density Functional Theory), theoretical approximation is B3LYP model, 3-21G basis. The list of catalytic cracking reactions for calculation was prepared on the basis of the theoretical data about catalytic cracking, laboratory and experimental data from the industrial unit. The enthalpy and Gibbs energy values of the main catalytic cracking reactions are presented under the process conditions. The results of this work will be used to develop a kinetic model of catalytic cracking of petroleum feedstock.

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1. Introduction

Increased proportion of extracted heavy oil dictates a need to improve existing oil refining installations and orients the industrial sector on the resource efficient use of petroleum feedstock, improvement of the environment on a global scale, while the fuel requirement (gasoline and diesel fuel) is increasing every year.

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Catalytic cracking is important processes providing advanced petroleum refining. This process is aimed at manufacturing of light oil products such as gasoline from heavy fraction of petroleum feedstock. The proportion of catalytic cracking at the Russian refinery is not more than 10%, while the foreign indicators are 27-30%.

In order to create competitive refining and petrochemical sector corresponding to the modern level of foreign refineries (the depth of oil refining is 85-95%), construction of facilities for oil refining (including catalytic cracking) is organized at the domestic enterprises for increasing the raw materials conversion level up to 82-85% by 2020¹.

During operation of industrial oil installations, it is important to consider the multifold factors that equally influence composition, quantity, and quality of the main products^{2,3,4}. The problem of improving the energy and resource efficiency of catalytic cracking can be solved by the development of adequate mathematical model based on physical and chemical regularities of catalytic cracking reactions with a high predictive ability in the advanced petroleum refining.

Approaches to formalization of the chemical reaction mechanism at the modelling of advanced petroleum process feedstock are known. The main ones are: the formation of pseudocomponent groups at the fractional composition⁵⁻⁹ and combined models that take into account the interactions of pseudocomponents – product streams (gasoline, light and heavy gasoil, liquid and dry gas) and the conversion of the main group components of the feedstock (paraffins, naphthenes, aromatics)¹⁰⁻¹⁴.

One of the first stages in mathematical description development of the refining process is the thermodynamic analysis of the alleged reactions^{15,16}. Determination of the thermodynamic regularities of catalytic cracking is possible to perform with the quantum chemical methods of calculation.

At present, software for quantum chemical calculation implementation is submitted by numerous domestic and foreign computer products with different technical possibilities. The quantum calculations, in particular via density functional theory (DFT), are an essential tool in many branches of chemical research¹⁷.

Quantum chemical methods are used for describing the alkane adsorption in nanoporous crystalline and ordered acid catalysts with different pore geometry, enthalpy of alkane adsorption and its relation with the activation energy for the monomolecular cracking of n-paraffins¹⁸. Also such methods are used to establish the mechanism of substances formation on the catalyst surface and the stages of transition states formation^{19,20}.

The aim of the work is establishment of thermodynamic regularities of catalytic cracking of petroleum feedstock using quantum chemical methods of calculation for development of catalytic cracking kinetic model.

Nomenclature

ΔH	enthalpy change during a chemical reaction, kJ/mol
ΔG	Gibbs energy change during a chemical reaction, kJ/mol
T	temperature, K
P	pressure, MPa

2. Introduction

Heavy fraction of petroleum feedstock such as vacuum distillate or residues mixture from the secondary manufacturing processes with the boiling point about 350-560°C is used as catalytic cracking feedstock. The technological process is implemented in the riser reactor. The main characterized parameters of the reactor operation are the consumption of feedstock (160-365 m³/h), the pressure in the reactor sediment chamber (0.8-1.5 kg/cm²), the temperature of the feedstock entering the reactor (240-350 °C), the temperature of the products at the outlet from the ballistic separator (495-535°C).

The products from the catalytic cracking unit are rich in gas and gasoline fractions, light gasoil (fraction of 195 - 310 °C), heavy gas oil (fraction of 310 - 420 °C).

Chemical conversions of hydrocarbon feedstock are carried on carbonium ion mechanism through chemisorption of hydrocarbon molecules to the microsphere zeolite catalyst surface²¹. This list includes:

- cracking of high molecular weight n-paraffins and isoparaffins C₁₃–C₄₀;
- cracking of medium weight n-paraffins and isoparaffins C₅–C₁₂;

- isomerization of medium weight paraffins C₅-C₁₂;
- cracking of olefins;
- hydrogen transfer;
- dealkylation of naphthenes;
- dealkylation of aromatic hydrocarbons;
- dehydrogenation of naphthenes;
- condensation of aromatic compounds;
- coke formation;
- cyclization of olefins to naphthenes.

The list of the reactions was composed using the theoretical data about catalytic cracking, experimental data from the industrial plant and laboratory and experimental data from the industrial unit.

3. Approaches and Methods

Thermodynamic analysis of the catalytic cracking reaction is one of the first stages in mathematical model developing which allows establishing the possibility of catalytic cracking reactions. Calculations to determine thermodynamic parameters of individual hydrocarbons involved in the catalytic cracking reactions of petroleum feedstock were performed using the quantum chemical methods.

The values of Gibbs energy (ΔG) reaction characterize the probability of reaction, and the value is necessary for formalization of the hydrocarbon chemical conversion scheme, which will be the foundation to the catalytic cracking kinetic model.

But there are some difficulties: since the catalytic cracking is an advanced refining process of petroleum feedstock, the thermodynamic parameters of the reactions involving the high molecular weight hydrocarbons are virtually absent in the directory. It is also important to take into account the real operating conditions of the industrial unit for calculation of the reaction thermodynamic parameters, as well as the interaction effects of hydrocarbon molecules with reaction mixture molecules.

The software which implements the quantum chemical methods of calculation of the molecule electronic structure Gaussian and provides adequacy and sufficient accuracy of calculations for chemical reaction simulation of refinery processes was used to solve these difficulties.

Comparison of quantum chemical calculation methods: ab initio methods (DFT, B3LYP) and semi-empirical (PM3) was conducted in this work. PM3 is a semi-empirical method, which uses parameters obtained from the experimental data to simplify the calculations. Thus the Schrodinger equation is solved with a certain approximation using the appropriate parameters of the systems studied. Different methods are characterized by different sets of parameters.

The ab initio (non-empirical) method of DFT implemented in Gaussian software was used for the evaluation of each individual hydrocarbon formation thermodynamic properties. Theoretical approximation was B3LYP model (Becke's DFT (B3) with theoretical approach using Lee, Yang and Parr electron correlation (LYP), 3-21G basis. The model substances participated in the chemical transformations were built in GaussView software.

Also the choice of this theory (DFT) can be explained as follows. The Schrödinger equation lays at the basis of quantum chemistry, it describes the changing of function coordinate and time for microparticles given by wave function. The solution of this problem has been initially proposed as the Hartree-Fock approximation: electronic potentials were interpreted as the sum of the electrostatic interaction of electrons with all the other electrons (repulsion) and all the surrounding nuclei of atoms (attraction). The system of this approach is described in a multi-electron wave function. The idea based on the theorem of Hohenberg - Kohn appeared with time. The main essence of this theorem is the simplification of solving the Schrödinger equation by moving from wave function to electron density function. This action reduces the computational complexity since the electron density is a function of only three coordinates and wave theory is calculated in Hartree-Fock theory as a function of n-coordinates (where n is a number of electrons). Gradient-corrected functional B3-LYP, which includes accurate result of Hartree-Fock exchange, is selected as an approximation. Thus, imprecisions of two methods compensate each other.

4. Results and Discussions

The thermodynamic parameters of the vacuum distillate catalytic cracking reactions were calculated in this work. The thermodynamic probability of each reaction was estimated by value of the Gibbs energy change ΔG during the reaction under the process conditions (temperature is 504 °C, pressure is 0.108 MPa).

Thermodynamic parameters calculated in different quantum chemical methods were compared. The literature data^{22,23} were originally used to perform the calculation of thermodynamic parameters of cracking reaction. The tabulated values of the thermodynamic parameters for low molecular weight hydrocarbons were compared with the results of calculation using ab initio DTF and semi-empirical PM3 methods (Table 1)²⁴.

Table 1. Comparison of methods of thermochemical parameters calculation

Reaction	ΔH , kJ/mol			ΔG , kJ/mol		
	Tabulated value	DTF, B3LYP	PM3	Tabulated value	DTF, B3LYP	PM3
Cracking of paraffins						
$C_5H_{12} \rightarrow C_3H_8 + C_2H_6$	77.83	81.76	82.08	-30.46	-35.88	-36.11
$C_8H_{18} \rightarrow C_4H_{10} + C_4H_8$	71.93	69.96	66.23	-55.12	-60.79	-66.62
Isomerization of paraffins						
$n-C_6H_{14} \rightarrow 2\text{-methylpentane}$	-6.08	-1.68	0.71	-1.53	0.91	9.81
$n-C_7H_{16} \rightarrow 2\text{-methylhexane}$	-6.62	-1.92	0.63	-2.4	-2.35	10.4
Cracking of isoparaffins						
$i-C_4H_{10} \rightarrow CH_4 + C_3H_8$	76.64	80.52	82.49	-44.83	-39.37	-36.93
$i-C_5H_{12} \rightarrow C_3H_8 + C_2H_6$	85.58	83.76	81.05	-26.61	-35.12	-45.56
Cracking of olefins						
$C_6H_{12} \rightarrow 2 C_3H_6$	86.84	91.47	95.96	-30.40	-33.23	-26.67
$C_5H_{10} \rightarrow C_3H_6 + C_2H_4$	100.14	105.10	116.87	-8.56	-13.56	5.82
Dealkylation of naphthenes						
$C_9H_{18} \rightarrow C_7H_{14} + C_2H_4$	86.65	107.27	115.92	-18.46	-16.50	-17.76
$C_9H_{18} \rightarrow C_6H_{12} + C_3H_6$	82.27	100.00	80.92	-17.97	-28.65	-45.32
Dehydrogenation of naphthenes						
$C_6H_{12} \rightarrow C_6H_6 + 3 H_2$	220.56	223.67	0.82	-87.81	-93.27	-311.9
$C_6H_{12} \text{ (methyl-cyclopentan)} \rightarrow C_6H_6 + 3H_2$	250.11	229.09	-4.9	-71.74	-69.62	-291.4

It was concluded that the values calculated with DTF are more reliable compared with values calculated with PM3.

Table 2. Thermodynamic parameters of n-paraffins C_{14} - C_{30} cracking reactions

Reaction	The position of olefinic link			
	From the first atom		In the middle of hydrocarbon chain	
	ΔH , kJ/mol	ΔG , kJ/mol	ΔH , kJ/mol	ΔG , kJ/mol
$C_{14}H_{30} \rightarrow C_7H_{16} + C_7H_{14}$	81.85	-46.84	70.80	-60.53
$C_{15}H_{32} \rightarrow C_7H_{16} + C_8H_{16}$	81.18	-55.15	69.60	-71.51
$C_{16}H_{34} \rightarrow C_8H_{18} + C_8H_{16}$	80.96	-58.47	69.38	-74.86
$C_{17}H_{36} \rightarrow C_9H_{20} + C_8H_{16}$	80.84	-59.50	69.33	-75.60
$C_{18}H_{38} \rightarrow C_9H_{20} + C_9H_{18}$	81.32	-58.24	69.80	-74.34
$C_{30}H_{62} \rightarrow C_{15}H_{32} + C_{15}H_{30}$	81.30	-63.46	69.38	-78.35

N-paraffin hydrocarbons are preferably cracked with the weakest bond opening located in the middle of the molecule on the basis of the calculation presented in Table 2.

The calculations demonstrate that cracking reactions of n-paraffins have endothermic effects, and reactivity of n-paraffins in cracking reactions rises with increasing the molecular weight of hydrocarbons. Moreover, the formation of unsaturated hydrocarbons with olefinic link position in the middle of hydrocarbon chain is most possible under the technological process conditions.

The calculation results of the thermodynamic parameters for the cracking reaction of n-paraffins of gasoline fraction to gaseous products are presented in Table 3.

Table 3. Thermodynamic parameters of n-paraffins C₅-C₁₂ cracking reactions

Reaction	ΔH , kJ/mol	ΔG , kJ/mol
$C_5H_{12} \rightarrow C_3H_6 + C_2H_6$	81.76	-35.88
$C_6H_{14} \rightarrow C_3H_6 + C_3H_8$	81.53	-46.43
$C_7H_{16} \rightarrow C_4H_8 + C_3H_8$	69.88	-62.27
$C_8H_{18} \rightarrow C_4H_8 + C_4H_{10}$	69.96	-60.79
$C_9H_{20} \rightarrow C_5H_{10} + C_4H_{10}$	70.16	-63.85
$C_{10}H_{22} \rightarrow C_6H_{12} + C_4H_{10}$	71.25	-60.82

The values of the Gibbs energy change and thermal effect lie in the interval $\Delta G = -35.88 \div -78.35$ kJ/mol and $\Delta H = 69.38 \div 81.76$ kJ/mol for the cracking reaction of paraffin C₅-C₃₀.

Calculations to determine the thermodynamic parameters of n-paraffin isomerization reactions of gasoline fraction were exemplified by isomerization reaction of heptane (Table 4).

Table 4. Thermodynamic parameters of n-paraffin isomerization

Reaction	ΔH , kJ/mol	ΔG , kJ/mol
$n-C_7H_{16} \rightarrow 2\text{-methylhexane}$	-1.92	-2.34
$n-C_7H_{16} \rightarrow 3\text{-methylhexane}$	1.92	1.74
$n-C_7H_{16} \rightarrow 2,3\text{-dimethylpentane}$	4.95	8.75
$n-C_7H_{16} \rightarrow 2,4\text{-dimethylpentane}$	0.88	26.53

Formation of 2-methylhexane is more thermodynamically possible than formation of 2,4-dimethylpentane. The values of the Gibbs energy change and thermal effect lie in the interval $\Delta G = -0.142 \div -2.35$ kJ/mol and $\Delta H = -1.63 \div 1.99$ kJ/mol for the isomerization reaction of gasoline fraction C₅-C₁₂. Isomerization reactions of paraffin to 2-methylparaffin have a slight exothermic effect and thermodynamic probability of reaction.

The calculation results of the thermodynamic parameters of the cracking reaction of olefins are presented in Table 5.

Table 5. Thermodynamic parameters of olefin cracking reaction

Reaction	ΔH , kJ/mol	ΔG , kJ/mol
$CH_3-CH_2-CH=CH-CH_3 \rightarrow CH_3-CH=CH_2 + CH_2=CH_2$	105.10	-13.55
$CH_3-CH_2-CH=CH_2-CH_2-CH_3 \rightarrow CH_3-CH=CH-CH_3 + CH_2=CH_2$	92.99	-27.29
$CH_3-CH_2-CH=CH-(CH_2)_2-CH_3 \rightarrow CH_3-CH=CH-CH_2-CH_3 + CH_2=CH_2$	94.15	-28.28
$CH_3-(CH_2)_2-CH=CH-(CH_2)_2-CH_3 \rightarrow CH_3-CH_2-CH=CH-CH_2-CH_3 + CH_2=CH_2$	95.45	-27.86
$CH_3-(CH_2)_6-CH=CH-(CH_2)_6-CH_3 \rightarrow CH_3-(CH_2)_6-CH=CH-(CH_2)_4-CH_3 + CH_2=CH_2$	99.89	-29.92
$CH_3-(CH_2)_7-CH=CH-(CH_2)_8-CH_3 \rightarrow CH_3-(CH_2)_7-CH=CH-(CH_2)_4-CH_3 + CH_3-C(=CH_2)-CH_3$	68.75	-67.27

According to Table 5 the cracking reactions of olefins have endothermic effect, and the thermodynamic probability rises with increasing the hydrocarbon chains in the olefin molecules. The values of the Gibbs energy change and thermal effect lie in the interval $\Delta G = -13.55 \div -67.27$ kJ / mol and $\Delta H = 68.75 \div 105.10$ kJ / mol for the above reaction.

According to the laboratory and experimental data aromatic hydrocarbons of catalytic cracking feedstock are mainly represented by the light aromatics (alkylbenzenes, methylalkylbenzenes and dimethylalkyl benzenes). The calculation results of the thermodynamic parameters for dealkylation of aromatic hydrocarbons are presented in Table 6.

Table 6. Thermodynamic parameters of aromatic hydrocarbons dealkylation

The number of carbon atoms in the substituting group	Alkylbenzenes		Methylalkylbenzenes		Dimethylalkylbenzenes	
	ΔH , kJ/mol	ΔG , kJ/mol	ΔH , kJ/mol	ΔG , kJ/mol	ΔH , kJ/mol	ΔG , kJ/mol
5	90.73	-32.26	82.50	-60.74	79.99	-36.75
10	90.53	-37.18	75.99	-62.71	74.32	-45.99
20	90.58	-42.22	73.76	-75.16	80.25	-37.70

It was determined that dealkylation reaction of methylalkylbenzenes is most thermodynamically possible. The values of the Gibbs energy change and thermal effect lie in the interval $\Delta G = -60.74 \div -75.16$ kJ/mol and $\Delta H = 73.76 \div 82.50$ kJ / mol for the above reaction.

Naphthenic hydrocarbons of feedstock are mainly represented by alkyl substituted structures according to the laboratory and experimental data. The calculations to determine the thermodynamic parameters of dealkylation and dehydrogenation of naphthenic hydrocarbons were carried out and presented in Tables 7,8.

Table 7. Thermodynamic parameters of naphthenic hydrocarbons dealkylation

Reaction	ΔH , kJ/mol	ΔG , kJ/mol
methylpentylcyclohexane \rightarrow C ₅ H ₁₀ + methylcyclohexane	42.97	-96.81
1,4-didecylcyclohexane \rightarrow 1- didecylcyclohexane + dekene-5	90.05	-68.65
1,4-didecylcyclohexane \rightarrow cyclohexane + 2dekene-5	156.07	-120.44
1,4-didecylcyclohexane \rightarrow methylpentylcyclohexane + nonene-4+pentene-5	178.31	-103.30

Dealkylation reactions of naphthenic hydrocarbons have a high thermodynamic probability, and splitting reaction of all substituents with formation of a more stable naphthenic structure is most possible. The values of the Gibbs energy change for the most possible reaction is $\Delta G = -120.44$ kJ / mol.

Table 8. Thermodynamic parameters of high molecular weight naphthenic hydrocarbons conversion reactions

Reaction	ΔH , kJ/mol	ΔG , kJ/mol
methylpentylcyclohexane \rightarrow methylpentylbenzene + 3H ₂	196.46	-119.91
1,4-didecylcyclohexane \rightarrow 1,4-didecylbenzene + 3H ₂	221.93	-124.63
C ₁₀ H ₁₈ (decaline) \rightarrow C ₁₀ H ₁₂ + 3 H ₂	252.26	-67.34
C ₁₀ H ₁₈ (decaline) \rightarrow C ₁₀ H ₁₄ (butylbenzene) + 2 H ₂	201.28	-60.25

The thermodynamic probability of dehydrogenation reactions of monocyclic naphthenes for formation of aromatic hydrocarbons is high, and the values of the Gibbs energy change lie in the interval $\Delta G = -119.91 \div -124.63$ kJ / mol for the above reaction. Cracking reactions of bicyclic naphthenes are less thermodynamically probable $\Delta G = -60.25 \div -67.34$ kJ/mol than dehydrogenation reactions of monocyclic naphthenes. Dehydrogenation reactions of

naphthenes have a large endothermic effect ($\Delta H = 196.46 \div 221.93$ kJ/mol) compared with the dealkylation reaction of naphthenes ($\Delta H = 42.97 \div 178.31$ kJ/mol).

The thermodynamic parameters of catalytic cracking reaction for development of mathematical modeling are presented in Table 9.

Naphthenic hydrocarbons are involved in the hydrogen transfer reactions which can be characterized by a high thermodynamic probability $\Delta G = -111.76 \div -241.8$ kJ/mol and negative thermal effects ($\Delta H = 2.49 \div 99.8$ kJ/mol)

The formation of coronene from naphthalene exemplifies the reactions of coke formation.

The thermodynamic probability of cyclization reactions of olefins to naphthenes is $\Delta G = -7.54$ kJ/mol, it is characterized by positive thermal effect $\Delta H = -53.8$ kJ/mol.

Table 9. Thermodynamic parameters of catalytic cracking reaction (T=504 °C, P=0.108 MPa)

Reaction	ΔH , kJ/mol	ΔG , kJ/mol
Cracking of high molecular weight n-paraffins $C_{13}-C_{40}$ ($C_{16}H_{34} \rightarrow C_8H_{18} + C_8H_{16}$)	69.38	-74.86
Cracking of high molecular weight i-paraffins $C_{13}-C_{40}$ ($CH_3-CH(CH_3)-(CH_2)_{12}-CH_3 \rightarrow i-C_8H_{18} + C_8H_{16}$)	70.55	-70.83
Cracking of medium molecular weight n-paraffins ($C_7H_{16} \rightarrow C_4H_8 + C_3H_6$)	69.88	-62.27
Isomerization of medium weight paraffins ($n-C_7H_{16} \rightarrow i-C_7H_{16}$)	-1.92	-2.34
Cracking of medium molecular weight i-paraffins ($CH_3-CH(CH_3)-(CH_2)_3-CH_3 \rightarrow i-C_4H_{10} + C_3H_6$)	62.13	-63.21
Cracking of olefins ($C_7H_{14} \rightarrow C_5H_{10} + C_2H_4$)	94.15	-28.28
Hydrogen transfer ($(CH_3)_3-C_6H_9 + C_5H_{10} \rightarrow (CH_3)_3-C_6H_3 + i-C_5H_{12}$)	99.33	-111.76
Dealkylation of naphthenes ($(C_{10}H_{21})_2-C_6H_{10} \rightarrow C_6H_{12} + 2 \cdot C_{10}H_{20}$)	156.07	-120.4
Dealkylation of monoaromatic hydrocarbons ($(C_{10}H_{21})_2-C_6H_4 \rightarrow C_6H_6 + 2 \cdot C_{10}H_{20}$)	157.8	-89.04
Dehydrogenation of naphthenes ($(C_{10}H_{21})_2-C_6H_{10} \rightarrow (C_{10}H_{21})_2-C_6H_4 + 3H_2$)	221.93	-124.63
Coke formation (polycondensation) ($12 C_{10}H_8 \rightarrow 5 C_{24}H_{12} + 18H_2$)	104.90	-597.20
Cyclization of olefins to naphthenes ($C_7H_{14} \rightarrow C_7H_{14}$)	-53.8	-7.54

According to the thermodynamic values shown in Table 9, it can be concluded that the most thermodynamically probable reactions are: cracking of paraffins ($\Delta G = -74.86$ kJ/mol), hydrogen transfer ($\Delta G = -111.76$ kJ/mol), dehydrogenation of naphthenes ($\Delta G = -124.63$ kJ/mol), dealkylation of aromatic hydrocarbons ($\Delta G = -89.04$ kJ/mol) and naphthenes ($\Delta G = -120.4$ kJ/mol), and coke formation ($\Delta G = -597.2$ kJ/mol). The isomerization reactions of n-paraffins ($\Delta G = -2.34$ kJ/mol), cyclization of olefins to naphthenes ($\Delta G = -7.54$ kJ/mol) are less thermodynamically probable.

5. Conclusions

The thermodynamic parameters of catalytic cracking reactions (enthalpy and Gibbs energy change) were determined with Gaussian software based on the method of quantum chemical modeling.

For reactions with the heavy vacuum distillate hydrocarbons from the catalytic cracking unit, thermodynamic analysis defined using quantum chemical method of calculation allowed drawing conclusions about the reaction probability according to its value of the Gibbs energy change.

Cracking reactions of paraffins, hydrogen transfer, dealkylation of aromatics and naphthenes, dehydrogenation of naphthenes, and coke formation are most thermodynamically probable. The most of the reactions of catalytic cracking have a strong endothermic effect $\Delta H = 69.38 \div 221.93$ kJ/mol.

At modeling of catalytic processes, it is important to consider not only thermodynamic regularities of chemical reactions but also the kinetic regularities of reactions. The next stage of mathematical description construction will be development of a kinetic model of catalytic cracking based on the thermodynamic analysis of the reactions and formalized hydrocarbon conversion scheme, determination and evaluation of the kinetic parameters of the catalytic cracking reactions.

Application of the catalytic cracking kinetic model will allow calculating the reactant concentration change, the quantity and composition of the products from the catalytic cracking unit, as well as providing selection of optimal technological modes depending on the production goals (for instance, increase in yield of gasoline or light gas oil), the composition and properties of the raw materials.

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