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Abstract. The paper presents the approach to the catalytic cracking modeling with consideration of the reactions' reversibility/non-reversibility depending on the current concentrations and the cracking temperature. The thermodynamic analysis of the reactions using the quantum-chemical methods allows formulating a hydrocarbons conversion scheme at the thermal equilibrium temperature between the feedstock and the catalyst. The magnitude of the current chemical attraction of reactions is a criterion of thermodynamic non-reversibility of reactions, which is determined at each stage of the calculation. It has been shown that the change in the concentrations of conversion participants and cracking temperature have a significant effect on the catalytic cracking reactions. Thus, the cyclization reactions are non-reversible up to 512.9 °C (A_{rij} =6.46 kJ/mol) during the processing of feedstock with saturated hydrocarbons to aromatics ratio is 2.1 and with further temperature increasing the contribution of reverse reactions rises. Also with increasing the saturated hydrocarbons to aromatics ratio from 2.1 to 3.2 in the feedstock, the equilibrium of the reaction shifts to low temperatures from 512.9 to 508.9 °C (A_{rij} =6.497 kJ/mol). It is connected with the fact that intensification of the exotermic reactions (alkylation, condensation, coke formation) under certain conditions is possible. It is an important factor in terms of catalyst deactivation and has an effect on the desired product yield.

1. Introduction

Wide integration of petroleum refining processes is determined by the need in light oil products and olefins productions from heavy petroleum feedstock [1-2]. A high share of catalytic cracking and advanced refining processes around the world causes a high conversion degree of petroleum feedstock at the level of 85-95%. Continuous optimization for existing and new catalytic cracking units is required taking into account the change of feedstock composition, catalysts activity and mutual influence of reactor and regenerator.

To solve the problem of optimization, scientists widely use mathematical modeling to efficiently manage an industrial unit and to forecast products quality, along with the development of new high efficient catalysts [3-9] and technological equipment [10-12]. There are various approaches to

modeling of the catalytic processes taking into account kinetics, heat transfer, hydrodynamic mode, catalyst deactivation, etc. [13-15].

A large number of research is dedicated to mathematical modeling of catalytic cracking with different detailing of hydrocarbons conversion scheme considering with the catalyst deactivation [16–19]. Specialists generally use an approach based on the fractions separation by boiling points and pseudo-components formation ignoring the conversion of hydrocarbon groups as "gas", "gasoline", and "coke" [20–26]. However, this way does not ensure the model's sensitivity to the feedstock composition, thermodynamics and kinetics of reactions involving the high-molecular hydrocarbons. Such models do not include individual reactions leading to heavy products formation with following condensation into coke, for example, cyclization, aromatization. In addition, the conversions of the reaction groups are considered in the only forward direction without using the thermodynamic potentials being the criterion of the possibility, direction and limit of the reactions.

Developed hydrocarbons conversions schemes mostly have rigid formalization, and such schemes do not consider the change in the reactions direction depending on current concentrations and cracking temperature. This fact has a significant effect on the reactions direction, yield and composition of the products along with the loss of catalyst activity due to intensive coke formation.

Thus, the aim of research is to evaluate the occurrence of thermodynamic non-reversibility of reactions at the mathematical modeling of the catalytic cracking.

2. Experimental part

Formalization of the hydrocarbons conversions scheme is the most important stage at the mathematical modeling of multi-component catalytic processes of the oil refining involving high-molecular weight hydrocarbons. This stage determines the forecasting ability of the model and ensures the required calculations adequacy in the presence of available computational power to evaluate the kinetic parameters of the reactions.

According to the principle of detailed equilibrium of classical thermodynamics any chemical transformations are thermodynamically reversible. Thus, the mathematical description of the catalytic cracking should include the principle possibility of direct and reverse transformation. A significant change in the chemical potential (in comparison with the RT value) during the reaction groups conversions is a correct criterion for the kinetic non-reversibility occurrence [27] of a certain stage in the of chemical transformations chain:

$$A_{rij} = -\Delta_r G_{ij} = \mu_i - \mu_j > RT \text{,}$$

(1)

where A_{rij} –current value of chemical attraction of reaction, J/mole, $\Delta_r G_{ij}$ – the current value of the Gibbs energy, J/mole, μ_i –current value of chemical potential: $\mu_i = \mu_{io} + RT\ln p_i$, J/mole, μ_{io} –standard chemical potential, J/mole, R –universal gas constant – 8.314 J/(mol·K), T –current temperature, К, p_i –partial component pressure, Pa.

The direction of the catalytic cracking reactions changes depending on the current components concentrations of the conversion participants and the current cracking temperature on the height of the riser. It can be quantified estimated by calculation of the current chemical attraction of reactions.

The following stages are required for accounting the change in the reactions direction at mathematical modeling of the catalytic cracking: 1) to perform a thermodynamic analysis of the catalytic cracking reactions including the most significant hydrocarbons groups participations, which were determined on the basis of structures according to chromatography-mass spectrometry, structural-group analysis and chromatography results [28,29]; 2) to form the hydrocarbons conversions scheme of catalytic cracking at the thermal equilibrium temperature between the feedstock and catalyst; 3) to develop a kinetic model of catalytic cracking taking into account the change in reactions reversibility according to the chemical attraction in accordance with figure 1.

The effect of the feedstock composition with saturated to aromatics hydrocarbons ratio 2.1 and 3.2 unit at the equal process conditions (table 1) and the catalyst circulation rate in the range of 4-8
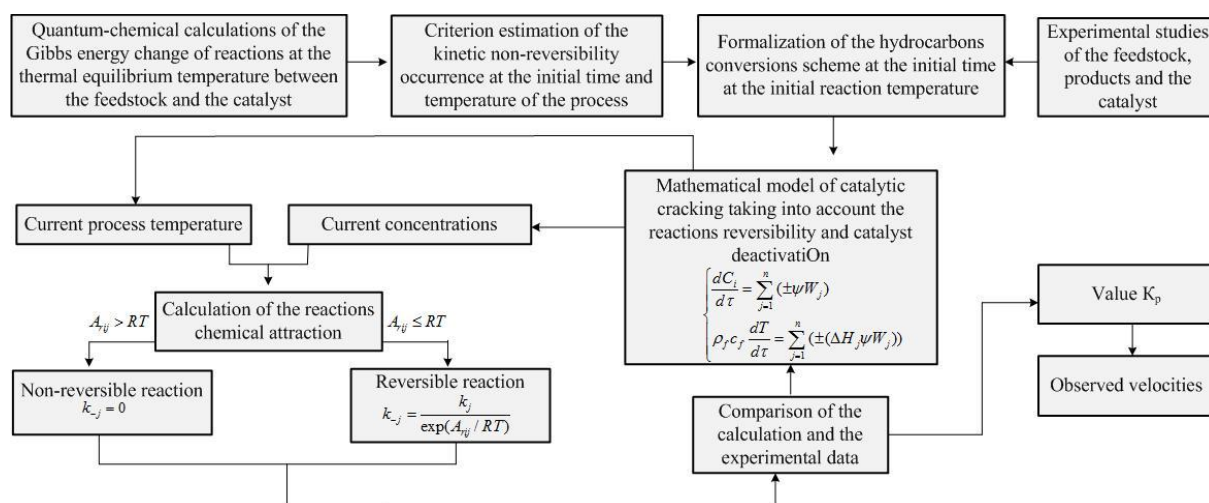
t_{cat}/ton_{feed} at the processed the feedstock with saturated hydrocarbons to aromatics ratio of 2.1unit on the current chemical attraction reactions are discovered.

Table 1. Feedstock composition and process conditions for model calculations.

Process conditions	Values
Feedstock flow rate, m^3/h /temperature, °C	378.0 /3 03.7
Cracking temperature, °C/ Riser pressure, Pa	521.0 / 141215.8
Flow temperature after regeneration, ºC / Catalyst circulation rate, t_{cat}/t_{feed}	690.6 / 5.56

3. Results and discussion

The scheme presented in figure 1 shows the stage of catalytic cracking modeling with consideration of the contribution of forward and reverse reactions under the current time and technological conditions. This approach complicates the mathematical description, but increases the calculations accuracy.
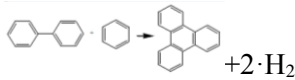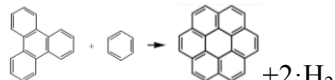

Figure 1. Flowchart for determining the observed reaction rates taking into account the reactions reversibility of the catalytic cracking: k_j, k_{-j} – reaction rate constants of forward and reverse reactions respectively; C_i – change in concentration of the i-hydrocarbons group, mol/l; τ – contact time, s; W_j – rate of chemical reaction; ψ –function of catalyst deactivation by coke and heavy metals; T – temperature flow, K; $\Delta_r H_{oT}$ – chemical reaction heat, kJ/mol; ρ_f, c_f – density and heat capacity of flow, kg/m^3, kJ/(kg·K).

Thermodynamic analysis of the catalytic cracking reactions, especially, the estimation of the thermodynamic parameters of reactions (the Gibbs energy, enthalpy and entropy change in standard conditions) and the probability of their occurrence at the thermal equilibrium temperature between the feedstock and the catalyst was performed using reference data [30] and quantum-chemical methods of calculations for reaction involving the hydrocarbons, which are not available in the reference literature (Table 2). Comparison of the thermodynamic parameters of reactions, calculated by different methods (PM3 and DFT), with reference data shows that the values calculated by Density Functional Theory (DFT method) are more reliable for the reactions of isoparaffins cracking, olefins cracking and aromatics and naphthenes dealkylation.

Also the divergence between calculated and reference data for paraffins cracking with formation of olefins and paraffins with normal and branched structure is lower using PM3 method. Using DFT method, the finding the wave function (for Hartree-Fock theory as a n-coordinates function, where n is the number of electrons) does not occur. In this case, the system energy is uniquely determined by the electron density, which depends on the three spatial coordinates, and functional which related the

electron density with the systems energy is determined. The Gradient-corrected functional B3-LYP (Becke's density functional theory (B3) model using Lee-Young-Parr (LYP) electron correlation), which includes accurate result of Hartree-Fock exchange, with basis 3-21G were used as theoretical approximation. Thus, imprecisions of two methods compensate each other. Semi-empirical methods, including PM3, solve the Schrödinger equation for atoms and molecules using certain approximations and simplifications. In addition the calculation is carried out only for the valence electrons, the integrals of certain interactions are ignored, the standard non-optimized basis functions of electron orbitals and some parameters obtained in experiment are used.
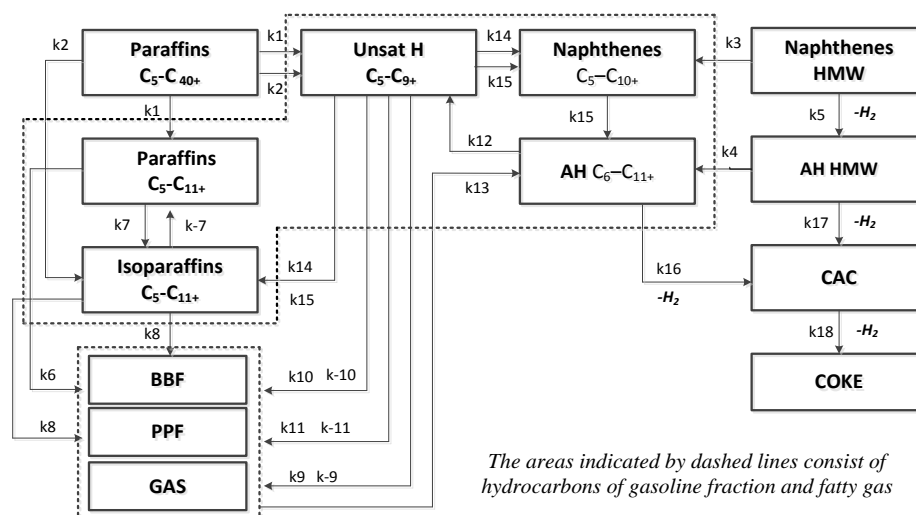
Table 2. Thermodynamic parameters of the catalytic cracking reactions.

Reactions	$\Delta_r H^o_{810-848}$, kJ/mol	$\Delta_r G^o_{810-848}$, kJ/mol
[b] Cracking of paraffins C_{14}–C_{40+}: $C_{20}H_{42} \rightarrow C_{10}H_{22} + 2\text{-}C_{10}H_{20}$	$64.7 \div 64.2$	$-(70.3 \div 76.6)$
[b] Cracking of paraffins C_{14}–C_{40+}: $C_{20}H_{42} \rightarrow$ i-$C_9H_{17} + 2\text{-}C_{10}H_{20}$	$65.3 \div 64.8$	$-(64.5 \div 70.6)$
[b] Dealkylation of naphthenes HMW [a]: $C_{17}H_{35}\text{-}C_{10}H_{17} \rightarrow C_{10}H_{18} + 2\text{-}C_{10}H_{20} + 2\text{-}C_7H_{14}$	$100.8 \div 99.7$	$-(191.5 \div 204.6)$
[b] Dealkylation of AHHMW [a]: $C_{13}H_{27}\text{-}C_{10}H_7 \rightarrow C_{10}H_8 + 2\text{-}C_7H_{14} + 2\text{-}C_6H_{12}$	$134.0 \div 133.1$	$-(143.0 \div 156.1)$
[b] Cracking of naphthenes HMW [a]: $C_{17}H_{35}\text{-}C_{10}H_{17} \rightarrow C_{18}H_{37}\text{-}C_6H_5 + C_3H_6 + 2 \cdot H_2$	$267.4 \div 266.9$	$-(138.5 \div 156.9)$
Cracking of n-paraffins C_5–C_{11+}: $C_7H_{16} \rightarrow C_3H_6 + C_4H_{10}$	$77.5 \div 77.1$	$-(36.6 \div 41.9)$
Isomerization of paraffins C_5–C_{11+}: н-$C_7H_{16} \leftrightarrow$ i-C_7H_{16}	$-(4.5 \div 4.5)$	$-(1.5 \div 1.3)$
Cracking of isoparaffins C_5–C_{11+}: i-$C_7H_{16} \rightarrow$ i-$C_4H_8 + C_3H_8$	$70.2 \div 69.8$	$-(40.2 \div 45.4)$
Cracking of UnsatH [a] C_5–C_{9+}: $C_7H_{14} \rightarrow C_2H_4 + C_5H_{10}$	$88.2 \div 78.3$	$-(22.3 \div 37.1)$
Cracking of UnsatH [a] C_5–C_{9+}: $C_8H_{16} \rightarrow C_4H_8 + C_4H_8$	$78.1 \div 77.7$	$-(35.3 \div 40.6)$
Cracking of UnsatH [a] C_5–C_{9+}: 1-$C_6H_{12} \rightarrow C_3H_6 + C_3H_6$	$77.8 \div 77.3$	$-(36.1 \div 41.4)$
Dealkylation of AH [a] C_5–C_{9+}: $C_6H_5\text{-}C_5H_{11} \rightarrow C_6H_6 + 2\text{-}C_5H_{10}$	$80.0 \div 79.6$	$-(17.3 \div 21.8)$
Diene synthesis: $1,3\text{-}C_5H_8 + C_3H_6 \rightarrow 1,2\text{-}(CH_3)_2\text{-}C_6H_{10} + 2 \cdot H_2$	$-(71.2 \div 70.9)$	$-(106.9 \div 108.6)$
Cyclization of UnsatH [a] C_5–C_{9+}: $C_7H_{14} \leftrightarrow$ c-C_7H_{14}	$-(92.2 \div 91.6)$	$-(25.1 \div 21.9)$
[b] Hydrogen transfer №1: $C_6H_{10} + C_6H_{12} \leftrightarrow \bigcirc + $ i-C_6H_{14}	$-(85.2 \div 85.3)$	$-(40.1 \div 38.1)$
[b] Hydrogen transfer №2: $\bigcirc + C_6H_{12} \rightarrow \bigcirc + $ i-C_6H_{14}	$-(169.3 \div 169.6)$	$-(162.1 \div 161.8)$
[b] Condensation of AH [a] C_5–C_{9+} with UnsatH [a] C_5–C_{9+}: $C_2H_3\text{-}C_6H_5 + 2\text{-}C_8H_{16} \rightarrow 3,4\text{-}C_3H_7\text{-}C_{10}H_6 + 2 \cdot H_2$	$-(9.59 \div 9.0)$	$-(47.2 \div 42.1)$
[b] Condensation of AHHMW [a]: (structure) $+ 2 \cdot H_2$	$(52.2 \div 48.4)$	$-(32.0 \div 36.5)$
[b] Coke formation: (structure) $+ 2 \cdot H_2$	$(4.6 \div 0.4)$	$-(130.3 \div 137.1)$

[a] HMW, AH, AH HMW, UnsatH– according to figure 2, [b] – results of quantum chemical calculations.

The reactions of cracking of high-molecular weight paraffins (–(70.3÷76.6) kJ/mol), dealkylation of aromatic hydrocarbons and naphthenes (–(143.0÷156.1)[*] and –(191.5÷204.6) kJ/mol) and cracking of high-molecular weight naphthenes (–142.0÷161.0 kJ/mol) are characterized by a high thermodynamic probability at the initial temperature range of the reaction 810÷848 K. Also, the high reactivity of hydrocarbons is observed for secondary exothermic reactions of diene synthesis (–(106.9÷108.6) kJ/mol), 2 stage of hydrogen transfer: 1) cyclization of $UnsatHC_5-C_{9+}$(–(25.1÷21.9) kJ/mol); 2) hydrogen transfer between naphthenic and $UnsatHC_5-C_{9+}$(–(162.1÷161,8) kJ/mol) and the reaction of coke formation (–(378.5÷669.0) kJ/mol). The majority of the catalytic cracking reactions are characterized by a positive thermal effect and occurred with the heat absorption. The thermal effect of the catalytic cracking can decrease at a high degree of feedstock conversion. It is connected with increasing the contribution of reactions with negative thermal effect (isomerization, cyclization, diene synthesis, hydrogen transfer, condensation).

The discovered thermodynamic regularities of the reactions are the basis of the formalized hydrocarbons conversions scheme of the catalytic cracking process at the thermal equilibrium temperature between the feedstock and the catalyst (figure 2).

Figure 2. Hydrocarbons conversions scheme of the catalytic cracking process at the range of initial temperature of reactions according to [28,29]: k_j и k_{-j} – the rate constants of direct and reverse chemical reactions, respectively; $UnsatHC_5–C_{9+}$ – olefins and dienes $C_5–C_{9+}$, Naphthenes HMW– mono- and bicyclic naphthenes with long substituents $C_1–C_{25}$ (average number of naphthenic rings – 1,7÷2,3); AH HMW– mono- and polyaromatic hydrocarbons with long substituents (average number of aromatic and naphthenic rings – 1,6÷2,8 и 1,3÷1,5); CAC– high-molecular naphthene-aromatic compounds; COKE – C/H is 0,2 до 1,5; PPF – $C_3H_8+C_3H_6$; BBF – $C_4H_{10}+C_4H_8$; GAS – $C_1–C_2$, C_{5+}.
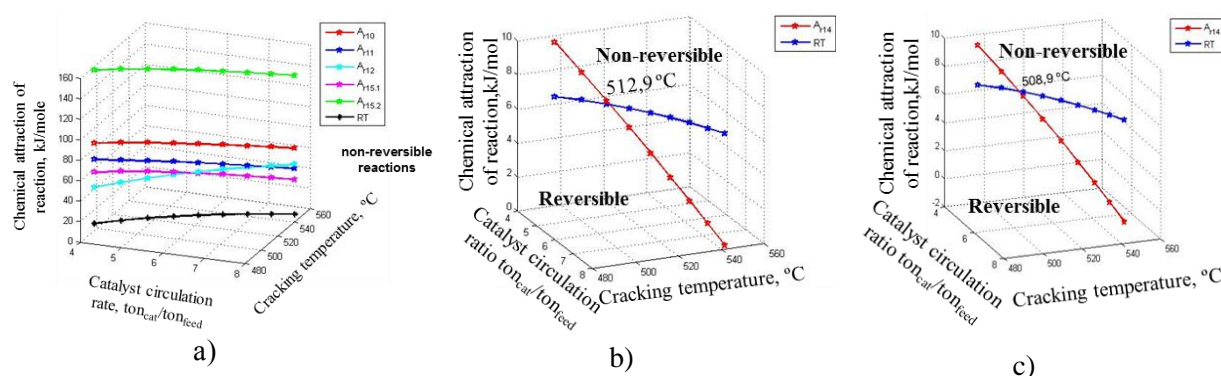
The mathematical model of catalytic cracking is presented by ordinary differential equations system of material and heat balances of reagent over the contact time for the plug-flow reactor $T_0=T_{s.r.}$ (figure 1). The main assumptions to the mathematical model are the following points: 1) the chemical transformations are carried out in accordance with the formalized mechanism, the reactions reversibility is checked and corrected at each step by the reactions chemical attraction values; 2) the statement about the kinetic non-reversibility is equivalent to the statement that the reverse reaction rate is negligible in comparison with the reaction rate in the forward direction; 3) heat exchange with the environment does not occur; 4) the kinetic model is formalized and quasi-homogeneous.

According to the formalized hydrocarbon conversion scheme the calculation of the components concentrations from the contact time of feedstock and catalyst is performed taking into account the current cracking temperature. Depending on the participants concentrations and the current temperature which changed according to the contact time changing at the riser the calculation of the

current chemical affinity is carried out for each stage at the chemical transformations chain. Then, the condition for the reactions non-reversibility is verified in accordance with (1). The determined kinetic parameters of reactions are presented in [31].
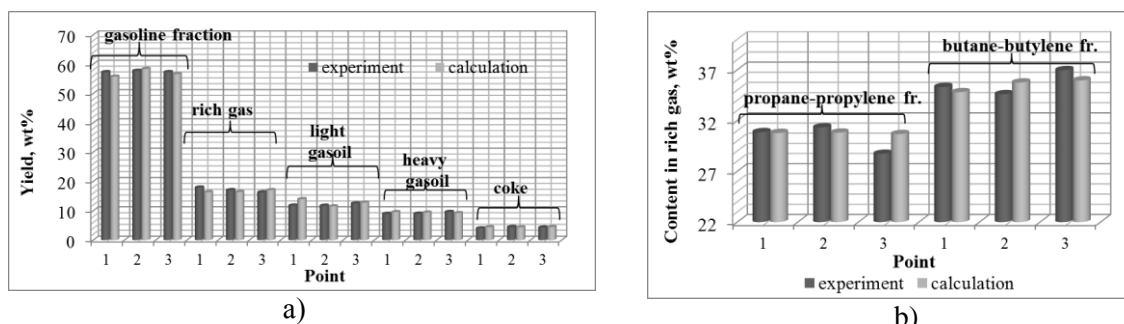
Calculations have shown that with increasing the catalyst circulation rate from 4 to 8 t_{cat}/ton_{feed}, the cracking temperature increases significantly from 497.3 to 541.7 °C, and the thermodynamic non-reversibility of the reaction (RT) changes from 6.40 to 6.77 kJ/mole. Thus, the current attraction of the chemical reactions changes due to change in the components concentrations and the current cracking temperature. It was discovered that with increasing the cracking temperature from 495.2 to 541.7 ℃ the reactions of UnsatH C_5-C_{9+}cracking with the formation of BBP and PPF, dealkylation of AH C_6-$C_{11+}$and hydrogen transfer in two thermodynamic stages are non-reversible over the entire temperature obtained, during processing the vacuum distillate with the saturated hydrocarbons to aromatics ratio is 2.1 units. This conclusion is made because the current chemical attraction values of reactions are greater extent than RT value (figure 3).

Also, the cyclization of UnsatH C_5-$C_{9+}$and isomerization reactions change their direction in this temperature range. The current chemical attraction of the isomerization reaction ($A_{rij} = -(11.4–14.3)$ kJ/mol) is much less than the non-reversibility criterion (RT = 6.4–6.8 kJ/mol).Consequently, the isomerization reaction of paraffins is strictly reversible over the entire temperature range. It was discovered that the cyclization reactions are non-reversible under temperature increasing to 512.9 °C and proceeds in the forward direction (Arij>> RT) during the processing of feedstock with saturated hydrocarbons to aromatics ratio is 2.1. With further temperature increases up to 541.7 ° C, the reactions become reversible and the contribution of reverse reactions increases (naphtenes cracking).This is typical at the high catalytic cracking temperature. Also with increasing the saturated hydrocarbons to aromatics ratio from 2.1 to 3.2 in the feedstock, the equilibrium of the reaction shifts to low temperatures from 512.9 to 508.9 °C. Such situation is associated with the naphthenes concentration increasing in the course of dealkylation reactions of high-molecular weight naphthenes.

Figure 3. Current chemical attraction of reactions depending on the cracking temperature: (a) the UnsatH C_5-C_{9+} cracking with the BBP and PPF formation, dealkylation of AH C_6-C_{11+}, hydrogen transfer; (b) the UnsatH C_5-C_{9+} cyclization during the feedstocks processing with saturated hydrocarbons to aromatics ratio is 2.1; (c) the UnsatH C_5-C_{9+} cyclization during the feedstocks processing with saturated hydrocarbons to aromatics ratio is 3.2.

a)   b)

Figure 4. Comparison between calculated and experimental data by the products yields (a) and the content of propane-propylene and butane-butylene fractions in rich gas (b).

The proposed methodology for the catalytic cracking modeling taking into account the reactions reversibility ensures the adequacy of the mathematical description (the relative error of calculations by the model is less than 10%) and allows to predict the yield and products composition, the content of propane-propylene and butane-butylene fractions in rich gas, the coke amount of depending on the feedstock composition and the technological mode of the reactor-regenerator unit. The model takes into account the thermodynamic and kinetic patterns of the process reactions, the feedstock composition, the technological mode.

4. Conclusion

Presented approach allows calculating the reactions chemical attraction depending on the current cracking temperature and components concentrations. In this way, it ensures taking into account the contribution of non-reversible and reversible reactions typical for catalytic cracking (isomerization, cyclization, hydrogen transfer, dealkylation and condensation of aromatic hydrocarbons). Carried out calculations show that, the cyclization reactions are non-reversible up to 512.9 °C (Arij =6.46 kJ/mol) during the processing of feedstock with saturated hydrocarbons to aromatics ratio is 2.1 and with further temperature increasing the contribution of reverse reactions rises. Also with increasing the saturated hydrocarbons to aromatics ratio from 2.1 to 3.2 in the feedstock, the equilibrium of the reaction shifts to low temperatures from 512.9 to 508.9 °C (Arij =6.497 kJ/mol). It is connected with the fact that intensification of the exotermic reactions (alkylation, condensation, coke formation) under certain conditions is possible. Also, accounting for reversibility of reactions can significantly affect the performance of catalytic cracking and intensify the exotermic reactions (alkylation, condensation, coke formation, etc.) due to the presence of significant temperature gradient. It is significant from the point of catalyst deactivation and has influence on the main product yield. Therefore, the reactions reversibility accounting during the study of complex chemical transformations is necessary and the accuracy of calculations by the model can be increased.

Acknowledgments

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