Mathematical modelling of catalytic cracking riser reactor
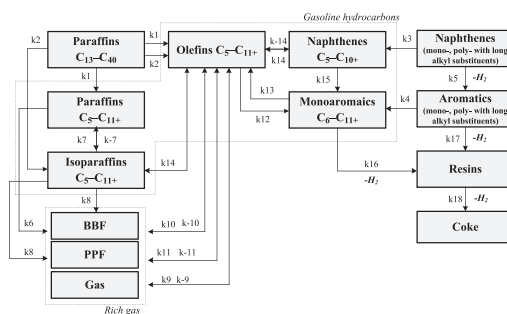
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GRAPHICAL ABSTRACT

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The quality and the yield of gasoline and light olefins from the catalytic cracking unit depend on a broad range of operation indicators including the feedstock composition, the process conditions, the type and activity of the catalyst. The aim of research is to develop the mathematical model of catalytic cracking reactor on the basis of the formalized mechanism of hydrocarbon conversion taking into account the catalyst deactivation by coke. The experimental research of the feedstock and the product of catalytic cracking using a liquid-adsorption chromatography, gas chromatography–mass spectrometry, gas-liquid chromatography and the structural-group composition methods allowed determining the list of the catalytic cracking reactions. According to the discovered reactions, the thermodynamic analysis was performed using the methods of quantum chemistry. Thermo-gravimetric analysis of the coked catalyst allowed estimating the coke structure formed on the catalyst surface. The developed mathematical model allows to predict the product yields including the content of propane-propylene (PPF) and butane-butylene (BBF) fractions, the group composition and octane number of the gasoline depending on the feedstock composition, the process conditions of reactor-regenerator unit and the catalyst activity. As a result, the high theoretical yield of the gasoline (60.4 wt.%, RON 93.5) according to requirements for the content of olefins and benzene can be achieved at the process temperature of 533 °C. This temperature is possible at the keeping the catalyst circulation ratio of 6.9 ton_{cat}/ton_{feed} at the catalyst flow temperature after regeneration (685.8 °C) with the catalyst activity of 0.79 unit and the feedstock temperature (328.0 °C). The yields of rich gas and coke are 24.0 wt% and 4.5 wt%, the concentrations of PPF and BBF are 31.5 and 34.8 wt%.

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1. Introduction

The operating efficiency of catalytic cracking units is determined by a broad range of operation indicators of non-stationary conjugate "riser-regenerator" system [1–4]. The quality and the yield of the light fractions in the catalytic cracking depend on the

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Nomenclature

PPF	propane-propylene fraction in rich gas of catalytic cracking
BBF	butane-butylene fraction in rich gas of catalytic cracking
VNII NP	All-Russia Research Institute for Oil Processing
C_5–C_{11+}	carbon number
C_{14}–C_{40}	carbon number
HMW	high molecular weight hydrocarbons of feedstock, light and heavy gas oil
MMW	medium molecular weight hydrocarbons of gasoline fraction
ΔH	heat of reaction (kJ/mol)
ΔG	Gibbs energy of reaction (kJ/mol)
C_i	concentration of the i-th component (mol/l)
τ	contact time (s)
k_j, k_{-j}	reaction rate constant (direct or reverse reactions)
W_j	reaction rate
C_e	experimental value of concentration in product (wt%)
C_c	calculated value of concentration in product using the mathematical model (wt%)
Ω	stabilizing correction: $\Omega = \alpha \lVert C_c \rVert^2$
α	regularization parameter
ψ	function of catalyst deactivation by coke

$V_{reactor}$	reactor volume (m^3)
V_{feed}	feedstock volumetric flow rate ($m^3 s^{-1}$)
V_{cat}	feedstock volumetric flow rate ($m^3 s^{-1}$)
T	flow temperature (K)
$T_{i.t.}$	initial reaction temperature (K)
ΔH_j	heat of chemical reaction (kcal mol^{-1})
ρ_f	density of flow (kg m^{-3})
c_f	specific heat of flow (kcal kg^{-1} K^{-1})
G_{cat}	catalyst consumption (kg/h)
c_{cat}	catalyst heat capacity (kJ/kg·K^{-1})
T_{cat}	catalyst temperature after regeneration (K)
G_{fs}	feedstock consumption (kg/h)
c_{fs}	catalyst heat capacity (kJ/kg·K^{-1})
T_{fs}	feedstock temperature (K)
A_Y	current relative catalyst activity to the primary reactions
A_{ZSM-5}	current relative catalyst activity to the secondary reactions
A_0	relative catalyst activity of regenerated catalyst
c_{coke}	coke yield (wt.%)
RON	octane number by the research method

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feedstock composition, the process conditions of the reactor and regenerator unit, the type and activity of the catalyst circulated continuously between the reactor and regenerator, etc.

The scientific community efforts are focused on the development of new cracking catalysts for heavy petroleum fractions and improving the existing catalyst compositions [5–9]. Thus, the vast majority of industrial catalytic cracking units use the synthetic zeolite catalysts, providing the selective cracking of heavy hydrocarbons with formation of high octane gasoline components and low molecular weight olefins.

Russian and world scientists investigate the effect of technological mode, reactor design, catalyst compositions, hydrodynamic mode of catalytic cracking experimentally or using the mathematical models [10–16]. A large number of research is dedicated to mathematical modelling of catalytic cracking with different detailing of hydrocarbons conversion scheme (depending on the required predictive power) considering with the catalyst deactivation [17–27]. It is important to take into account the reversible deactivation by coke and non-reversible deactivation by heavy metals contained in the feedstock.

Research aimed at increasing the yield of the light fractions and low molecular weight olefins taking into account a large number of process parameters in the catalytic cracking is possible to be carried out using adequate mathematical model. In the context of energy and resource efficiency it is required to minimize the coke content on the catalyst after the reactor to keep the catalyst activity, excepting it's the required amount to keep the heat balance of the system.

The aim of research is to develop the mathematical model of catalytic cracking reactor on the basis of the formalized mechanism of hydrocarbon conversion taking into account the catalyst deactivation by coke.

2. Brief description of the catalytic cracking technology

Catalytic cracking technology is implemented as a part of the combined installation of fuel oil deep processing (Fig.1). The hydrotreated vacuum distillate is used as the feedstock of catalytic cracking unit (fr. 350–550 °C). Cracking is performed in the riser flow of microspheric zeolite catalyst (Y and ZSM-5). The process temperature is 495–542 °C, the pressure is 0.08–0.2 MPa.

3. The experimental part

3.1. Analyzing the catalytic cracking feedstock and product

At the first stage of mathematical model development the group and structural-group composition of catalytic cracking feedstock and products was identified. Vacuum distillate as the prossess feedstock, light and heavy gas oil (fr. 195–310 °C and 310–420 °C) were investigated using the liquid-adsorption chromatography according to VNII NP (All-Russia Research Institute for Oil Processing) methodology and the methods of determining the structural-group composition of the petroleum fractions. Subsequently, the fractions of aromatic and saturated hydrocarbons of vacuum distillate were studied using a Hewlett Packard 6890 Gas Chromatograph System with 5973 Mass Selective Detector and GC Chemstation software.

According to laboratory research it is discovered that the content of saturated hydrocarbons in the vacuum distillate varies widely 58.2–74.2 wt% and the average paraffins to naphthenes ratio is 2.1. Paraffins of the vacuum distillate are showed by the hydrocarbons with C_{14}-C_{40} chain length. Naphthenes of vacuum distillate are presented by mono- and poly-cycloalkanes (monoalkylcycloalkanes, methylalkylcyckloalkanes, dimethylalkyl-cyckloalkanes, substituted bicyckloalkanes, etc) with C_1-C_{25} of the carbon atoms in the substituent (18.7–23.9 wt%), the average number of naphthenic rings is 2.0 units.

The content of aromatic hydrocarbons of vacuum distillate varies in a range of 25.0–38.0 wt%, and the majority of aromatic hydrocarbons is represented by monoaromatics (monoalkylbenzene, methylalkylbenzenes) with C_{10}-C_{13} chain length in the substituent (benzene, (1-buthylnonyl-), benzene, (1-propyldecyl-) etc.)., and it is discoveried that the content of resins in vacuum distillate is 2.1–6.0 wt% and the asphaltenes are absent in the catalytic cracking feedstock.

Laboratory research of catalytic cracking gasoline (fr. 28–210 °C), based on gas-liquid chromatography using "CHROMATEC-CRYSTAL