Influence of Feedstock Group Composition on the Octane Number and Composition of the Gasoline Fraction of Catalytically Cracked Vacuum Distillate

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Abstract—Thermodynamic parameters for the reactions of vacuum distillate catalytic cracking in a riser reactor have been calculated using the density functional theory. The list of the reactions has been compiled on the basis of laboratory studies on determining the group and structural-group composition of the vacuum distillate and the results of thermodynamic analysis. A kinetic model of the catalytic cracking process has been developed on the basis of a formalized scheme of the hydrocarbon conversion mechanism. By using the kinetic model derived, the effect of the group composition of four vacuum distillate samples on the octane number and the composition of the gasoline fraction of the catalytic cracking process has been assessed.

The problem of increasing the energy and resource-saving efficiency of advanced petroleum refining processes (including catalytic cracking) was covered in the works of Russian and foreign scientists in the early 1960s and remains relevant at the present stage of the development of chemical technology of fuel [1–4].

The main approach to solving optimization problems for such complex processes is the method of mathematical and kinetic–thermodynamic modeling [5–10]. For several decades at the Department of Chemical Technology of Fuel and Chemical Cybernetics of the Tomsk Polytechnic University, a trend has been developing on the modeling of multicomponent catalytic processes for the processing of light hydrocarbon feedstock and works on experimental investigation and simulation of advanced petroleum refining processes, such as catalytic cracking and hydrodewaxing, are being actively performed [11–13].

Formalization of the hydrocarbon (HC) conversion scheme is the most important step in the modeling of multicomponent processes, especially with the participation of high-molecular-weight hydrocarbons, which determines the predictive ability of the model and ensures the required adequacy of calculations with an available computing power for evaluating the kinetic parameters of reactions.

There have been many studies devoted to modeling the processes of deep processing of petroleum feedstock using the principle of technological aggregation, mainly into pseudocomponents, mainly by fractional composition [14–24]. Such an approach makes it possible to estimate the feedstock conversion and the yield of catalytic cracking products in general, but the hydrocarbon composition of the fractions of each group is diverse and does not take into account the different reactivity of hydrocarbons within individual groups.

From the viewpoint of predicting the group composition of cracking products and light fractions, studies on formalizing the HC conversion schemes in terms of group features are of current importance. In this case, the components of the reaction system are formalized in accordance with the molecular weight and structure of the hydrocarbons, excluding the least probable reactions from the scheme to simplify it. This approach is characterized by information on the mechanism of the reaction with averaged reactivity of HC groups. The complexity of the group and structurally-oriented approaches as applied to advanced petroleum refining processes consists in the determination on a regular basis of the group composition of heavy fractions of the feed stream (fractional composition 350–570°C). Therefore, combined models that take into account not only chemical reactions involv-

ing pseudo-components, but also chemical transformations of the main hydrocarbon group of the feed stream of the catalytic cracking unit are used in practice as a rule [25−37]. This approach makes it possible to predict the feedstock conversion; the group composition of cracking products; and the yield of light fractions, gas, and coke, so that the degree of catalyst deactivation can be assessed from a large number of process parameters. In this case, the conversion scheme for hydrocarbons is formalized in terms of grouping in accordance with their molecular mass, distinguishing pseudogas components, the propane−propylene and butane−butylene fractions, and coke.

It is noteworthy that the formalized hydrocarbon conversion scheme takes into account the thermodynamic features of a complex, multistage catalytic cracking process. This approach makes it possible to evaluate the influence of a large number of operating parameters of the reactor−regenerator unit and the feedstock group composition on the yield of products from an industrial plant, the group composition of the gasoline fraction, gasoline's octane number, and the concentration of propane−propylene and butane−butylene fractions in the wet gas, as well as in the long term to assess the influence of these parameters on the degree of catalyst deactivation.

The feedstock composition and the catalyst temperature and activity are determining factors in predicting the energy- and resource-efficient operation of an industrial unit. It is on these parameters that the yield and quality of the desired products, as well as the composition and amount of coke formed on the catalyst surface in a riser reactor, largely depend. The dynamics of coke buildup, in turn, determines the amount of heat released during regeneration; the circulating-catalyst temperature; and, hence, the process temperature and the composition and yield of cat-cracker light ends.

In connection with this, the purpose of the present study was to examine the effect of the group composition of a vacuum distillate on the yield of the gasoline fraction from an industrial unit using the derived kinetic model.

THEORETICAL BACKGROUND

The group composition and octane number of the gasoline fraction obtained from a catalytic cracking unit is determined by the mechanism of chemical transformations of hydrocarbons and the rate of chemical reactions of the process.

As cracking catalysts, zeolite-containing acid catalysts (zeolite content of 18−20 wt %) modified with rare earth oxides are used [38, 39]. Chemical reactions of cracking feedstock follow the carbenium-ion chain mechanism. In this case, sites of different natures can undergo interconversions; for example, Brønsted acid sites are mainly formed upon heating to 500−600°C

and, at higher temperatures, the concentration of Lewis sites increases [40]. The resulting carbocations easily enter isomerization reactions; by such transformations, the group composition of the cat cracker gasoline fraction is usually enriched in isomeric hydrocarbons and is characterized by a high octane number.

The octane number of cat cracked gasoline also increases as a result of hydrogen redistribution reactions yielding aromatic and isoparaffinic hydrocarbons. The mechanism of the hydrogen redistribution reaction on the catalyst surface with the formation of diene and saturated HC is presented in [40].

EXPERIMENTAL

A favorable feedstock [41, 42] in catalytic cracking technology is a hydrocarbon stream containing predominantly higher paraffins and naphthenes, which allows high-octane gasoline to be produced in high yields due to cracking and isomerization of paraffins, hydrogen redistribution, and dealkylation of high-molecular-weight naphthenes. At the same time, it is important to control the rate of hydrogen transfer reactions, by which a significant amount of aromatic hydrocarbons and, accordingly, coke is formed, leading to an unbalanced temperature regime in the reactor−regenerator system.

Implementation of Catalytic Cracking Technology

The technology of catalytic cracking is implemented in section S-200 of a KT-1/1 combined unit for deep fuel oil processing. The unstabilized gasoline of the S-200 section is sent for stabilization to the absorption and gas fractionation unit (section S-300) with the involvement of additional stream (visbreaker wet gas, cat cracker wet gas, reflux, hydrotreater hydrocarbon gas). Technologically, the process is carried out in a riser reactor in the ascending flow of a microspherical zeolite-containing catalyst. The main process streams of the riser reactor are shown in Fig. 1, and the operating parameters of the riser reactor are given in Table 1.

Characterization of Feedstock and Catalytic Cracking Products

In this work, the catalytic cracking feedstock was a hydrotreated vacuum distillate (300−570°C fraction).

Laboratory studies to determine the group and structural-group composition of the vacuum distillate and its catalytic cracking products (light and heavy cycle oils) were performed using a liquid adsorption chromatographic separation on silica gel ASK with a grain size of 0.2−0.3 mm according to the VNII NP method. The structural-group composition of paraffin−naphthene and aromatic hydrocarbons was determined by the $n−d−m$ and the Hazelwood methods, respectively [43, 44].