DETERMINATION OF STRUCTURAL-GROUP COMPOSITION OF CATALYTIC CRACKING RAW MATERIALS AND PRODUCTS FOR DEVELOPMENT OF MATHEMATICAL MODEL

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Increasing the oil refining depth is one of the main objectives for refining at present stage, because the proportion of hard-recoverable oil is increasing every year. Catalytic cracking has crucial significance for advanced petroleum refining at domestic refineries. This process is aimed at manufacturing light oil products such as gasoline from heavy fraction of petroleum feedstock. 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 potential in advanced petroleum refining.

There are different approaches to the formalization of chemical reactions in kinetic modelling of catalytic cracking process in the literature.

One of the first papers about kinetic modeling of catalytic creaking was a three-lump kinetic model [1], which consists of a VGO lump, a gasoline lump and a gases lump plus coke. The other kinetic models based on lumping approaches and combined approaches of lamping and hydrocarbon groups were found in the literature [2, 3]. The novelty of the work consists in development of a mathematical model which will allow to calculation of individual composition of catalytic cracking gasoline fraction.

The difficulty in modeling advanced petroleum processes of crude oil is determination of heavy fraction composition of raw materials and products which is necessary for solving the inverse kinetic problem.

The aim of work is determination of structural-group composition for catalytic cracking raw materials and product for solving the inverse kinetic problem.

At the first stage, theoretical and experimental regularities of catalytic cracking were researched and the main problems and features of industrial unit were determined.

Information about quantitative and qualitative group composition of catalytic cracking raw materials and product is required for development of catalytic cracking kinetic model.

Heavy fractions of petroleum feedstock, such as a vacuum distillate or mixture of residues secondary manufacturing processes with boiling point about 285 – 520°C, is used as catalytic cracking feedstock. In petroleum fractions with boiling point above 200 °C the cyclic hydrocarbons are of mixed (hybrid) nature. Usually cyclic hydrocarbons contain the side paraffinic chains and, simultaneously, a part of naphthenic and aromatic rings.

Mass-spectra of the catalytic cracking feedstock components were obtained in the laboratory using gas chromatography-mass spectrometry for determining qualitative composition of raw materials. Chromatography-mass spectrometer Hewlett Packard 6890 Gas Chromatograph System with 5973 Mass Selective Detector with GC Chemstation software was used as the analytical equipment. It was found that in the raw materials of catalytic cracking contain n-paraffin hydrocarbons with carbon chain from 15 to 40, monoalkylcyclohexanes, methylalkylcyclohexanes, substituted dimethylalkylcyclohexanes, bicycloalkanes, di and triterpanes, pentacyclic naphthenes, monoalkylbenzenes, methylalkylbenzenes, methylnaphthalenes, naphthalenes etc.

Laboratory investigations for determining group composition of raw materials and products (light and heavy gasoil) of catalytic cracking were performed using expedited adsorption method based on chromatographic separation on silica gel.

Liquid adsorption chromatographic separation was performed on silica gel brand ASA with a grain size of 0.2 - 0.3 mm to determine the structural-group composition flows catalytic cracking unit (from heavy gasoil pre-allocated asphaltenes). Hydrocarbon fractions were sequentially extracted by means of desorption using solvents with different polarity (hexane, toluene and hexane, a mixture of ethyl alcohol and toluene). Hydrocarbons were separated on paraffin-naphthenic fraction as well as fraction of aromatic hydrocarbons by refractive index. Measurement accuracy of refractometer IRF-22 was tested in hexane refractive index. Structural-group composition of paraffin-naphthenic fractions was determined by the n-d-m-method, for aromatic hydrocarbon fraction by the method Hazelvuda. The results of chromatographic separation on silica gel are shown in Table l.

Besides, research in determination of molecular weight in catalytic cracking raw materials and product was performed. Analyzes to determine the molecular weight of raw materials, light and heavy gas oil catalytic cracking units were carried out. The device CRYETTEWR determining the freezing point of the samples (error less than 3%) was used for molecular weight determination. Then, in terms of the calculation formulas molecular weight samples were defined (Table 1).

Table 1

The Results of Chromatographic Separation on Silica gel

Unit flow	Molecular weight, g/mol	Hydrocarbon groups, % wt.		
		Paraffins+Naphtenes	Aromatics	Resins/asphaltenes
Raw materials	382,43	61.2	35.57	3.23/0.00
Light gasoil	164,71	21.55	76.14	1.68/0.00
Heavy gasoil	234,15	19.95	70.24	8.05/1.76

The results of determination of structural-group composition of catalytic cracking raw materials and products are shown in Table 2.

Table 2

The results of determination of structural-group composition of catalytic cracking raw materials and products, %

Parameter	Raw Material		Light gasoil		Heavy gasoil	
	P+N [a]	**A** [b]	**P+N** [a]	**A** [b]	**P+N** [a]	**A** [b]
Method	n-d-m-method	method Hazelvuda	n-d-m-method	method Hazelvuda	n-d-m-method	method Hazelvuda
Ca	2.59	27.52	17.10	56.81	1.42	50.79
Cn	31.27	55.73	53.84	43.19	31.56	49.21
Cp	66.14	16.76	29.05	0.00	67.01	0.00
Ka	0.14	1.40	0.44	1.20	0.062	1.90
Kn	2.05	3.90	1.55	2.60	1.53	4.90
Ko	2.59	5.3	1.96	3.8	1.59	6.80

[a] Paraffins and Naphtenes Hydrocarbon Fractions
[b] Aromatic Hydrocarbon Fractions

According to Table 1 raw materials of catalytic cracking are characterized by a high content of paraffins and naphthenes (61.2 % wt.), the average number of rings being 2.05 % in paraffin-naphthenic fraction of raw materials (according to Table 2). Content of carbon quantity in naphthenic structures is 31.27 % in raw materials (Table 2).

Light and heavy gasoil from catalytic cracking unit contains a high proportion of aromatic hydrocarbons – 76.14 % wt. and 70.24 % wt., respectively. Heavy gasoil is also characterized by a high content of resins (8.05 % wt.) and asphaltenes 1.76 % wt. (Table 1)

Paraffin and naphthenic fractions of catalytic cracking raw materials and product obtained by n-d-m-method contain some amount of aromatic structures. It can be explained by the fact that the sorption of this structure is substantially similar with sorption of naphthenes and the small amount of this structure is washed by solvent. Content of aromatic structural is 2.59 %, 17.10 % and 1.42 % in catalytic cracking raw materials, light and heavy gasoil, respectively (Table 2). The number of naphthenic rings in paraffin-naphthenic fractions of raw materials is 2.05 % and 1.55, and 1.53 % for light and heavy gasoil.

Aromatic concentrates analysis of every sample by the Hazelvuda method showed that the average number of naphthenic rings is more than that of aromatic rings, therefore, the aromatic structure is presented by hybrid structures. The total content of rings in catalytic cracking raw materials is 5,3 units and 3.8 units and 6.8 units in light and heavy gasoil (Table 2).

Using theoretical data on catalytic cracking, experimental data from industrial plant and laboratory investigation the list of passing reactions was composed.

This list includes:

1. cracking of high molecular weight n-paraffins and isoparafins C_{13}–C_{40};
2. racking of medium weight n-paraffins and isoparaffins with formation of gaseous hydrocarbon C_5–C_{12};
3. isomerization of medium weight paraffins;
4. cracking of olefins;
5. cracking of naphthenes;
6. hydrogen transfer;
7. dealkylation of monoaromatic hydrocarbons;
8. dehydrogenation of naphthenes with formation of monoaromatic hydrocarbons;
9. condensation of aromatic compounds;
10. coke formation.

The calculations of thermodynamic parameters of vacuum distillate catalytic cracking reactions were carried out using the quantum-chemical method of calculation (program Gaussian). The thermodynamic probability of each reaction was estimated by the value of Gibbs energy change (∆G) during the reaction in the process conditions (temperature 504 °C, pressure 0.108 MPa), and formalized scheme of catalytic cracking hydrocarbons conversions was developed.

According to the created formalized scheme of hydrocarbons conversions, the kinetic model of catalytic cracking was developed. It is a differential equation system of reactant concentrations changing by contact time with initial conditions: τ=0, Ci=Ci0.

The results of this work can be used for determination of kinetic parameters obtained by the invers kinetic problem with addition of large experimental data array from industrial plant.

References

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