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REDUCTION OF THE QUALITY RESERVE WITH THE USE OF PREDICTIVE MODELS IN THE MOTOR FUEL PRODUCTION

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Abstract

The paper describes a method for reducing the margin for the quality of automotive gasoline based on the use of predictive models for the process of catalytic cracking and compounding of automotive gasolines sensitive to changes in hydrocarbon composition and physical and chemical properties of processed raw materials, as well as technological modes of operation of industrial apparatuses. Continuous calculation of the individual composition and properties of the mixing components, as well as the constant adjustment of commercial gasoline formulations in real time, allows to receive motor fuels fully complying with the modern ecological standards of EURO-5, as well as to reduce the cost of finished products by 10-12% due to a decrease in the share of high-value flows, as well as the quality margin for the octane number of commercial gasolines, the content of sulfur, aromatic hydrocarbons and benzene in their composition.

Keywords*: catalytic cracking; blending; mathematical modelling; motor fuel production; computer system.*

1. Introduction

The growing demand for motor fuels of a high class of environmental safety necessitates the development of optimal recipes [1]. Forecasting the composition of gasolines with specified properties is possible when using components for which characteristics are known: octane numbers, yield, content of aromatic hydrocarbons and olefins, etc. The efficiency of the fuel is determined by the release of energy during combustion and depends both on the properties of the individual components and on the properties of the fuel compositions, which are determined by the chemical interaction of hydrocarbons not only at the compounding stage, but also at each separate stage of gasoline components preparation (catalytic cracking, reforming, etc.).

The wide introduction of the processes of deep processing of petroleum feedstock [2], including catalytic cracking with the involvement of residues of secondary oil refining processes, provides a significant share of gasoline components in the commodity product (about 30-40%). The high content of unsaturated and aromatic hydrocarbons of cracked fuels causes limitations when they are involved in the compounding process. At the same time, the yield and quality of cracking gasoline is largely determined by the composition of the processed raw materials [3-6]. Thus, enhanced coke formation on the catalyst during the processing of highly aromatized raw materials with the involvement of secondary process residues leads to an unbalanced temperature regime, a loss of catalyst activity and a decrease in the yield of the target product-gasoline.

To optimize the process of gasoline preparation, it is necessary to take into account the influence of a large number of factors at each stage of the process for the production of gasoline components on the octane number of mixed gasoline, taking into account the hydrocarbon composition of the processed raw materials, the activity of the catalysts and their operating modes.

With the use of mathematical models of the processes of processing hydrocarbon mixtures that are complex in composition, it is possible to take into account the hydrocarbon composition of the processed raw materials, the thermodynamic and kinetic regularities of the production of gasoline components, the deactivation of catalysts, the interactions between the hydrocarbons that make up the gasoline, which cause deviations of the octane numbers from additivity [7-11].

The use of the «Compounding» system [12] in the planning of commercial gasoline production allows to reduce the percentage of involvement of expensive components (MTBE, alkylates) by increasing the share of reformate and gasoline catalytic cracking in commodity gasoline, which allows to achieve economic efficiency of the compounding process.

Continuous calculation of commercial gasoline formulations in on-line mode, taking into account the change in the composition of processed raw materials in the process of production of components of commercial gasoline, allows to receive motor fuels fully complying with the modern ecological standards of EURO-5, as well as to reduce the cost of finished products by 10-12% the proportion of expensive flows, as well as the quality margin for the octane number of commercial gasolines, the content of sulfur, aromatic hydrocarbons and benzene in their composition.

The aim of the work is to increase the efficiency of the process of compounding of gasolines taking into account the composition of the processed raw materials in the process of catalytic cracking.

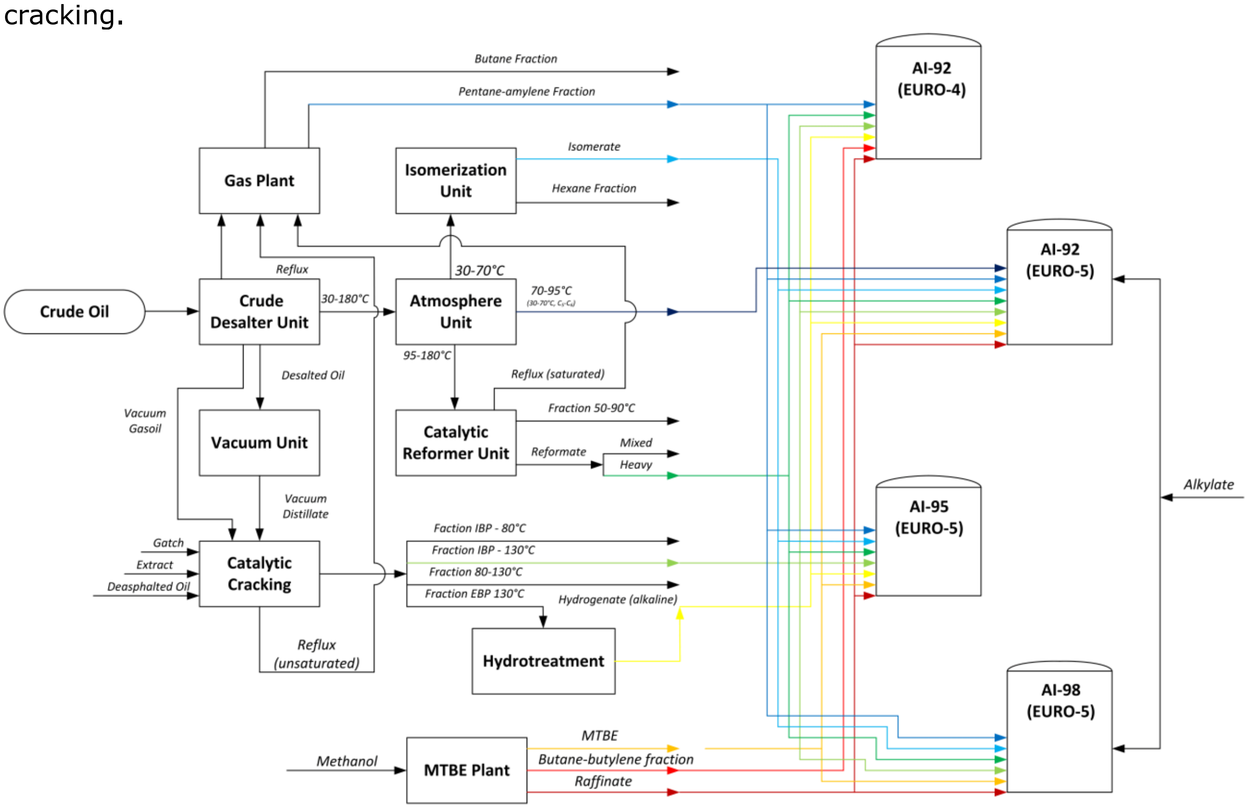

Figure 1. Block diagram of gasoline production process

2. Object of the research

The object of the current research is the flow chart of motor fuel production that consists of catalytic stage of motor fuel production and blending. The multi-stage processes of motor fuel production are performed according to the following scheme:

Catalytic cracking gasolines secondary often subjected to distillation for separation into narrower fractions to increase the octane fuel fund. Narrow fractions of gasoline (IBP -130ºC, EBP-130ºC can be used up to 100% by volume in the formulations of gasoline AI-80 and AI-92 and up to 20% in the formulations of gasoline AI-95 and AI-98.

3. Reduction of the reserve as quality with the use of predictional models in the manufacturing of motor fuels

In this work, a study was made of the effect of changing the composition of catalytic cracking gasoline on the formulation of commercial motor gasoline. To calculate the composition and properties of catalytic cracking gasolines, a computer modeling system is developed that is sensitive to changes in the composition of processed raw materials and technological modes of operation of industrial devices.

3.1 Development of the model of the catalytic cracking process for prediction the yield and composition of gasoline, taking into account the group composition of the processed raw materials

The mathematical model of the cracking process is written on the basis of the hydrocarbon transformation scheme and is represented by a system of ordinary differential equations of material and heat balance of reactants according to the contact time for an ideal displacement reactor with initial conditions $\tau=0$, $C_i=C_{i0}$. $T_0=T_{b.r.}$:

$$\begin{cases} \dfrac{dC_i}{d\tau} = W_j \\ \rho_m c_m \dfrac{dT}{d\tau} = \sum_{j=1}^{n} (\pm \Delta H_j) W_j \end{cases}$$

where dC_i – is the change in the concentration of the i-group of hydrocarbons, mol/l; τ – time of contact, s; W_j – is the rate of chemical reaction; dT – is the change in the flow temperature, K; ΔrH_j – is the thermal effect of the chemical reaction at the thermal equilibrium temperature of the feedstock and catalyst, kJ/mol; ρ_m, c_m - density and heat capacity of the flow, kg/m^3, kJ/kg · K; $T_{b.r.}$ – reaction initiation temperature, K.

The transformation scheme is formed by the results of a complex of laboratory studies to determine the composition and quality of raw materials and process products and the thermodynamic analysis of the reaction process at the cracking temperature and includes 12 pseudo-components (Table. 1).

Table 1.Characterization of hydrocarbon groups in the transformation scheme

Group in the scheme	Group in the scheme
GF Parafins	Paraffins C_{13}–C_{40+}
HMW Naphthenes	Mono and bicyclic naphthenes with long substituents C_1-C_{25} (average number of naphthenic rings - 2,1 ÷ 2,3 units)
HMW Aromatics	Mono and poly aromatic hydrocarbons with long substituents (average number of aromatic rings - 2.3 ÷ 2.8 units, average number of naphthenic rings 1.3 ÷ 1.4 units)
CAH	Condensed aromatic compounds
GF Parafins	Paraffins C_5–C_{11+}
GF Isoparafins	Isoparaffins C_5–C_{11+}
GF Olefins	Olefins C_5–C_{11+}
GF Naphthenes	Naphthenes C_5–C_{11+}
GF Aromatics	Aromatic hydrocarbons C_6–C_{12+}
PPF	Hydrocarbons C_3H_6+ C_3H_8
BBF	Hydrocarbons C_4H_8+ C_4H_{10}
Gases	Gases C_1+C_2+C_5+C_{6+}

Thus, the scheme of transformations (fig. 2) is oriented to predicting the group composition of the gasoline fraction, taking into account the reversibility of reactions in the chain of chemical transformations in accordance with [12].

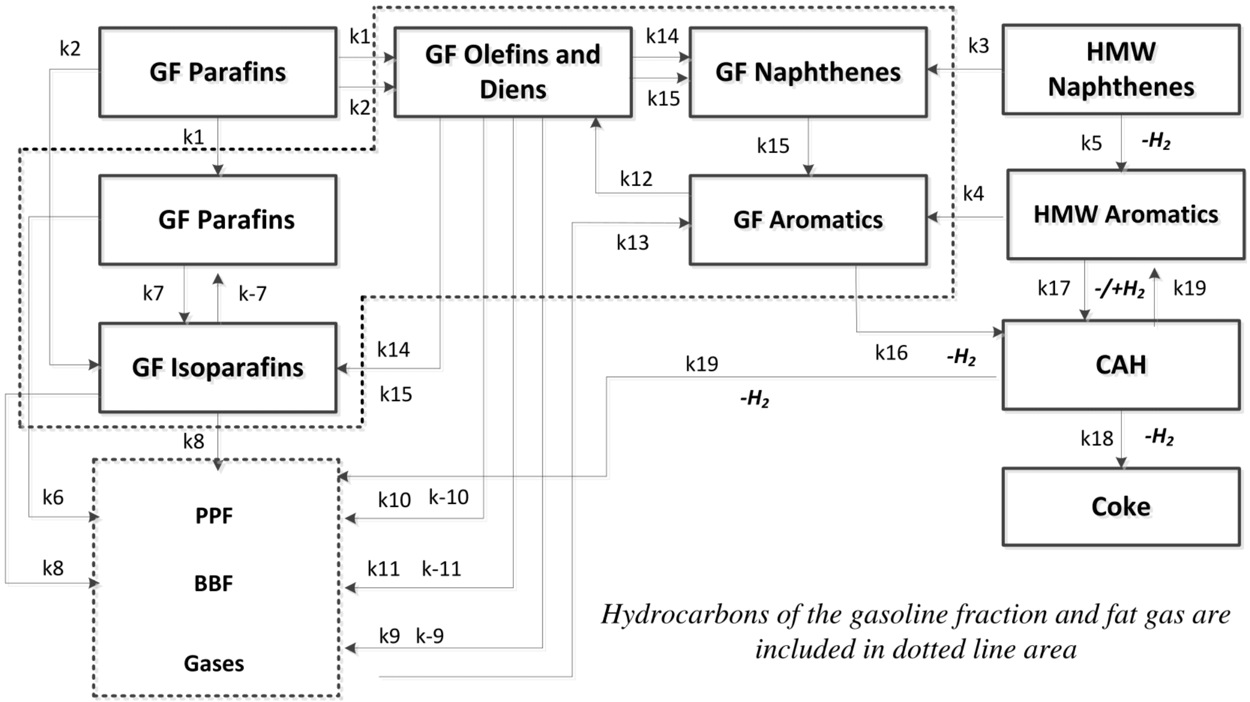

Figure 2. Scheme of hydrocarbon transformations for the catalytic cracking process and the rate constant of forward and reverse reactions at the cracking temperature 518°C

The mathematical model allows calculating the consumption and selection of products from the installation, including the output and content of coke on the catalyst, the content of PPF and BBF in the gas, the group and hydrocarbon composition of the gasoline fraction (Fig.3), depending on the composition of the feedstock and the technological mode of operation of the reactor.

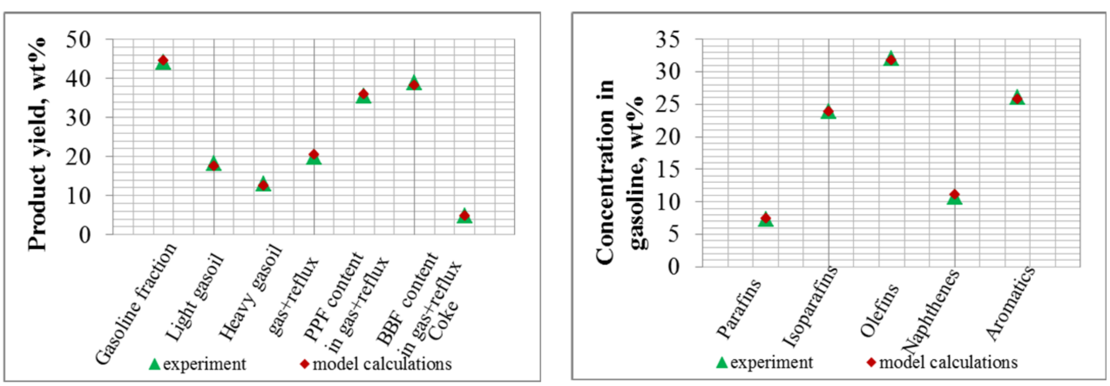

Figure 3. Verification of catalytic cracking mathematical model

The maximum relative error in the selection of products is not more than 5.0% of mass, in the group composition of gasoline cracking - no more than 4.0% of mass.

Figure 4 and Table 2 show that the composition of the feedstock has a significant effect on the yield and group composition of the target product - the gasoline fraction and coke.

When working on raw materials with a high content of saturated hydrocarbons (2.32 units), gasoline selection is higher (44.63%), gasoline, moreover, is characterized by a high content of paraffinic hydrocarbons of normal and branched structure (7.45 and 23.84 % of mass, respectively). With a higher concentration of aromatic hydrocarbons and resins in the catalytic cracking feed, the yield of coke (5.17%) is higher than when processing a vacuum distillate with a high content of saturated hydrocarbons (4.76% of mass, respectively), which causes deactivation of the catalyst and a reduction in the yield of the target product (43.81%). Gasoline is characterized by a high content of aromatic hydrocarbons and olefins (27.4 and 32.61% of mass) during the course of reactions of dealkylation of aromatic hydrocarbons, cracking and dealkylation of naphthenic and naphthene-aromatic compounds.

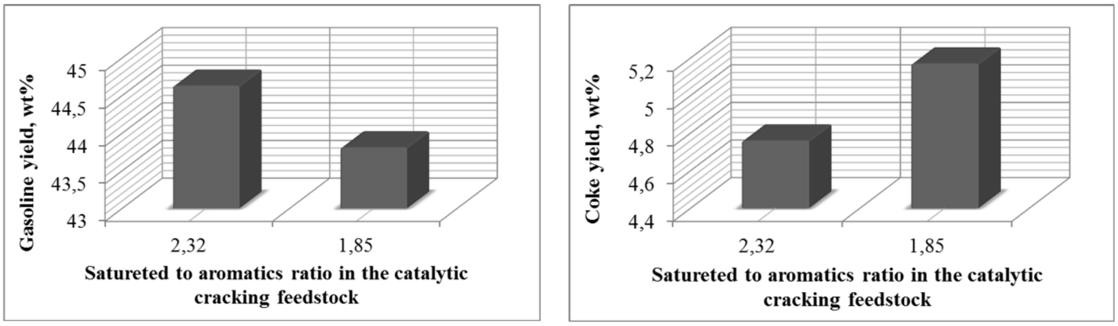

Figure 4. Selection by gasoline and coke of the catalytic process with a change in the composition of the processed raw materials

Table 2.The influence of the group composition of raw materials on the group composition of gasoline (calculation by model)

HC group	The ratio of saturated hydrocarbons to aromatic in the feedstock cracking	
	2.32	1.85
Paraffins, %mass.	7.45	7.06
Isoparaffins, %mass.	23.84	22.27
Olefins, %mass.	31.82	32.61
Naphthenes, %mass.	11.15	10.66
Aromatics, % mass.	25.74	27.40

When optimizing the process to increase the production of the gasoline fraction directed to the compounding step, it is important to take into account that the target product of the industrial plant – the gasoline fraction passes through a maximum in the range of 520 – 525°C (Fig. 5) with increasing process temperature, due to an increase in the reaction rate of hydrocarbon cracking gasoline fraction into fatty gas components.

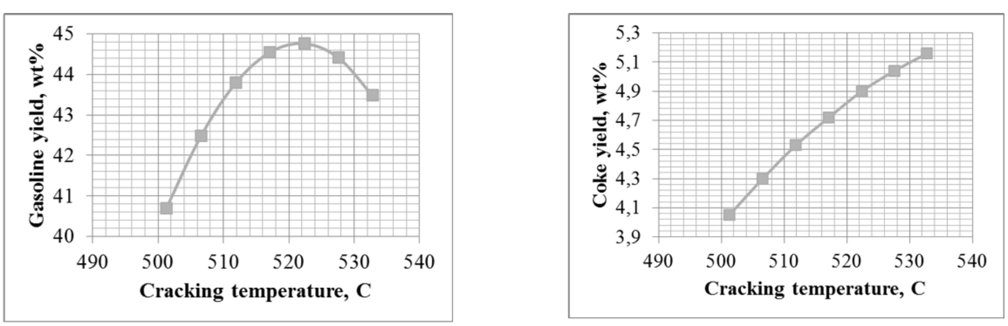

Figure 5. Gasoline and coke yield depending on the cracking temperature

Therefore, it is important to optimize the technological regime of the reactor operation depending on the composition of the processed feedstock and the temperature of the catalyst stream after regeneration in order to obtain the maximum yield of the gasoline fraction [13].

In this paper, a study was made of the effect of changing the composition of catalytic cracking fuels on the formulation of commercial motor gasoline. Calculation of the composition and properties of catalytic cracking gasoline was carried out using a developed computer modeling system that is sensitive to changes in the composition of processed raw materials and technological modes of operation of industrial devices. The calculated compositions and physico-chemical properties of catalytic cracking gasolines are presented in the Table 3.

Table 3. Estimated compositions and properties of catalytic cracking gasolines

Parameter	Gasoline fraction IBP -130°C		Gasoline fraction. IBP -130°C	
	26.04.2017	27.04.2017	26.04.2017	27.04.2017
RON	94.40	95.41	96.17	98.19
MON	87.16	88.11	87.55	89.25
Reid vapour pressure, kPa	13.11	13.40	67.73	68.20
Density of flow, kg/m^3	811.05	812.95	692.43	693.45
Flow viscosity, Pa.s	54.08	54.31	34.86	35.16
N-paraffins,%mass.	8.95	8.54	6.78	6.57
Iso-paraffins,%mass.	7.84	7.11	29.64	27.34
Naphthenes,%mass.	13.05	12.31	10.44	10.05
Olefins,%mass.	5.72	5.95	42.46	44.91
Benzene,%vol.	0.00	0.00	0.90	1.00
Aromatics,%vol.	64.44	66.09	10.61	11.07
Sulfur,%mass.	0.00	0.00	0.06	0.06

Based on the results of the calculations presented in Table 3, due to the change in the composition of the feedstock of the catalytic cracking process, the RON of gasoline of catalytic cracking oscillates in the interval of 1-2 points, the group composition changes. The influence of the composition and physicochemical properties of catalytic cracking gasoline on the formulation of commercial gasolines of various grades is shown in the Tables 4-5.

Table 4. The results of calculating the formula of gasoline AI-92-K-5

Component	26.04.2017	27.04.2017	Parameter	Value
MTBE from the installation	2.9	2.9	RON	92.09
Gasoline fraction 70-95°C	4.3	4.3	MON	85.28
Alkylate purchased	2.0	2.0	Reid vapour pressure, kPa	97.95
Pentane-amylene fraction	5.0	5.5	Olefins, %	6.65
C4 fraction raffinate	7.5	7.5	Benzene, %	0.50
Heavy reformat	32.7	32.7	Aromatic hydrocarbons, %vol.	34.83
Reformat of light straight naphtha	28.2	28.2	Sulfur, %mass.	0.0009
Gasoline fraction EBP -130°C	15.8	15.0		
Gasoline fraction IBP -130°C	1.5	1.8		
TOTAL	100.0	100.0		

Thus, the change in the hydrocarbon composition of the processed feedstock in the catalytic cracking unit leads to the need to adjust the formulation of commercial motor gasoline, taking into account the change in the composition and properties of the catalytic cracking stream as one of the main components of mixing. As a result of the increase in the RON of the IBP - 130°C, it became possible to involve a more significant amount of the 70-95 ° C gasoline fraction in the process of producing AI-92-K-5 gasoline, the share of expensive MTBE and alkylate fluxes during the preparation of «Super 98» gasoline.

4. Conclusions

1. The mathematical model of the catalytic cracking process is suitable for predicting, depending on the composition of the feedstock and the technological mode of operation of the reactor:
   - consumption and selection of products from the plant (stable gasoline, total gas and reflux selection, light gas oil, heavy gas oil, coke)
   - BBF and PPF content and total flow in the catalytic cracking of gas (gas + Reflux);
   - group and hydrocarbon composition of the gasoline fraction
   - temperature of the cracking process taking into account the thermal effect of the chemical reactions of the process.
2. Using the model of the catalytic cracking process, it is possible to predict the yield of light fractions and coke, depending on the composition of the processed raw materials and the mode of operation of the apparatus. In the future, accounting for the activity of the catalyst will allow us to evaluate the effect of the raw material composition and the technological regime of the reactor operation on the degree of its deactivation, and the regeneration operation regimes for predicting the activity of the equilibrium catalyst and reducing the loading of the fresh catalyst.
3. Complex application of mathematical models of processes of catalytic cracking and compounding of commercial gasolines makes it possible to assess the effect of changing the composition of processed raw materials and technological conditions on the composition and properties of the components of mixing and, consequently, on the formulation of motor gasolines. Thus, as a result of an increase in the RON of the IBP -130°C, it became possible to involve a more significant amount of the 70-95°C gasoline fraction in the process of producing AI-92-K-5 gasoline, the share of expensive MTBE and alkylate fluxes during the preparation of «Super 98» gasoline.

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