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Mathematical Modeling of the Gasoline Manufacturing

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Abstract

In the process of gasoline preparation, various products of hydrocarbon processing processes are used, such as catalytic reforming, isomerization, hydrocracking, catalytic cracking, liquid-phase alkylation of isobutane with olefins, as well as additives such as MTBE. Optimization of the commercial types of gasoline preparing process is a complex multi-factor task, including the stages of the catalytic processing of hydrocarbon raw materials into high-octane components and the stage of commercial gasoline components, mixing. This requires taking into account the non-additivity of the properties of commercial products. Determining the ratios of the mixing components, considering changes in the composition and properties of hydrocarbon feeds for processing, as well as the optimal technological conditions at the stages of catalytic processing of feeds, will reduce the cost of commercial products by reducing their quality stock.

***Keywords**: Mathematical modeling; Mixing; Catalytic reforming.*

1. Introduction

Improving the efficiency of the raw materials used in the process of preparing commercial types of gasoline is possible through the development and use of an intelligent computer system that improves product quality by optimizing the mix flow ratios, in accordance with the requirements of the Technical Regulations and environmental requirements.

The main goal of optimizing the process of preparing motor fuels is to predict the optimal volumes and formulations for mixing the components to produce gasoline of the required quality, considering the changes in the composition of the feedstock and technological conditions of the reforming, isomerization, alkylation and catalytic cracking processes.

To forecast the process of commercial types of gasoline preparing, an integrated computer simulation system is being developed. It describes the preparation of commercial gasoline from products of reforming, isomerization, alkylation, and catalytic cracking processes, which is suitable for predicting the performance of industrial plants. The developed system should promptly respond to the following changes:

- composition of the raw materials at the entrance to the reactor block;
- technological mode;
- catalyst activity.

The system should consider the non-additivity of mixing hydrocarbon streams with the issuance of recommendations for adjusting the formulation of gasoline for optimal consumption of components.

We predicted the optimal flow ratios considering the changes in the hydrocarbon composition of the feedstock in reforming and isomerization processes, as well as the activity of the catalysts used.

2. Object and methodology of research

The object of research is the flow chart of the production of commercial gasoline corresponding to the grades AI-92, AI-95 and AI-98 (GOST 32513-2013 Motor fuels. Unleaded

gasoline. Specifications), which includes the production processes of mixing components: catalytic reforming (with a moving and with a stationary catalyst bed), isomerization, sulfuric acid alkylation of isobutane with olefins, and catalytic cracking (Fig. 1).

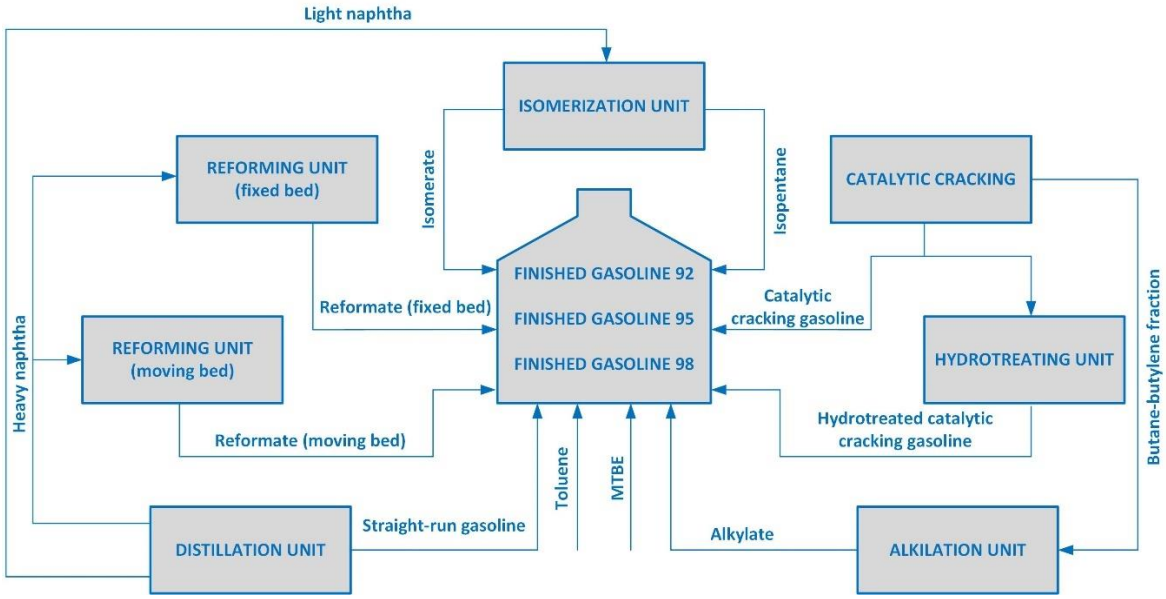

Figure 1. Scheme of the commercial gasoline production

To determine the composition and properties of commercial gasoline of various grades, the proposed mathematical model of the compounding process was used. This model considers the laws of non-additivity when mixing the octane numbers and saturated vapor pressure of mixing components. The initial data for the mixing model are the hydrocarbon compositions of the components entering the compounding. This information can be obtained from the results of the chromatographic analysis, or as an output parameter of a mathematical model of the processes of production of mixing components. In this work, the compositions of reformates from catalytic reforming units with continuous catalyst regeneration and with a stationary catalyst bed were calculated using a mathematical model [1-9]. The compositions of the remaining streams were obtained from the results of chromatographic analysis.

The main research method in this paper is the method of mathematical modeling. The mathematical model of the catalytic reforming process is represented by a system of partial differential equations that reflect the material balance for the individual components of the hydrocarbon mixture, as well as the heat balance considering changes in the temperature profile along with the height of the reactor.

$$\begin{cases} G \cdot \dfrac{\partial C_i}{\partial z} + G \cdot \dfrac{\partial C_i}{\partial V} = \sum_{j=1}^{m} a_j \cdot W_j \\ G \cdot \dfrac{\partial T}{\partial z} + G \cdot \dfrac{\partial T}{\partial V} = \dfrac{1}{\rho \cdot C_p^m} \sum_{j=1}^{m} Q_j \cdot a_j \cdot W_j \end{cases} \quad (1)$$

Initial and boundary conditions are as follows: z=0: C_i=$C_{i,0}$; T=T_0; V=0: C_i=$C_{i,0}$; T=T_0, where z is the volume of refined feedstock from the moment of fresh catalyst load, m^3; G is the feedstock flow rate, m^3/h; $z = G \cdot t$ (t is the catalyst operating time from the moment of fresh catalyst load, h); C_i is the content of i^{th} component, mol/l; V is the catalyst bed volume, m^3; a_j is the catalyst activity in j^{th} reaction; ρ is the density of mixture, kg/m^3; C_p^{mix} is the specific heat capacity of the mixture, J/(kg·K); Q_j is the heat effect of j^{th} reaction, J/mol; T is the temperature, K; W_j is the rate of j^{th} reaction, mol/(l·s); m is the number of reactions. In the above system of equations, the residence time of the reagents in the reaction zone, which

depends on the hourly flow rate of the feedstock G and the volume of the catalyst V, under the conditions of the unstable load of the industrial plant for feedstock is replaced by the "reduced time" $z = G \cdot t$, equal to the total volume of the processed feedstock during the time t.

3. Results and discussion

The adequacy of the mathematical model is checked by comparing the calculated (on the model) and experimental data with an industrial installation. The results of the verification are presented in Table 1.

Table 1. Verification of the catalytic reforming model

Component	Product composition, wt. %		Δ, rel. %
	Calc.	Exp.	
Aromatic hydrocarbons	78.02	78.09	0.09
Naphthenes C5	0.46	0.49	6.12
Naphthenes C6	0.29	0.3	3.33
N-alkanes	6.73	6.57	2.44
Isoalkanes	12.78	13.14	2.74

According to the results presented in Table 1, the model of the catalytic reforming process shows a high convergence of the calculated and experimental reformate compositions. The calculation results can be applied in modeling the stage of compounding of commercial gasoline.

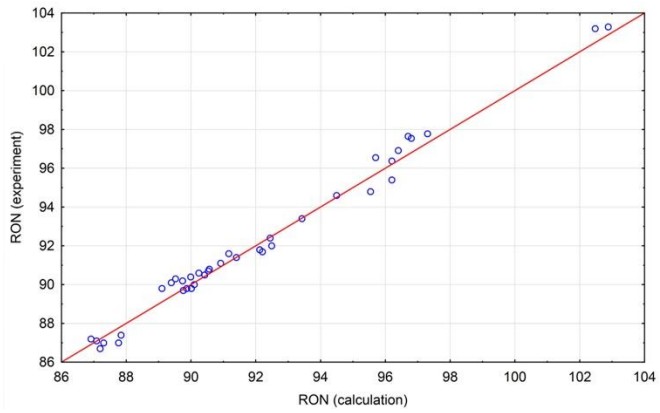

Figure 2. Verifying the calculation of octane mixing numbers

The adequacy of the commercial gasoline compounding model was evaluated by comparing the calculated octane mixing numbers with the experimental octane numbers determined for such flows as reformate (moving and stationary catalyst bed), isomerizate, alkylate, and catalytic cracking gasoline. The comparison results are presented in Fig. 2.

According to verification results, the average deviation of the calculated octane mixing number from the experimental (according to the research method) is 0.43 rel. %, the maximum deviation was 0.97 rel. %.

The reformate studied in this work differ in the content of aromatic compounds and benzene and have different octane numbers. The properties of the reformers used are presented in Table 2.

Table 2. Reformates properties

Parameter	Fixed bed of catalyst		Moving bed of catalyst	
	Reformate 1	Reformate 2	Reformate 1	Reformate 2
RON	94.74	95.75	103.54	106.32
Benzene content, vol. %.	2.12	3.22	2.33	2.17
Aromatics content, vol. %	60.76	59.73	79.57	81.83

The predictive calculation of the optimal mixing formulations for gasoline grades AI 92, AI 95, and AI 98 was carried out for a given amount of gasoline (Table 3), based on a given daily production capacity of plants (Table 4).

Table 3. The required amount of commercial gasoline production

Flow	Tones
Regular 92	7 843.92
Premium 95	3 706.20
Super 98	303.63

Table 4. Average daily production of mixing components

Flow	Tones	Flow	Tones
Catalytic cracking gasoline	1 769.58	Isomerate	835.20
Hydrotreated catalytic cracking gasoline	3 282.51	Isopentane	1 044.00
Reformate (moving catalyst bed)	2 453.40	MTBE	130.50
Reformate (fixed catalyst bed)	843.03	Straight-run gasoline	289.71
Alkylate	893.49	Toluene	182.70

When calculating the optimal mixing formulas, the following tasks were solved:
1) obtaining the gasoline of a given quality;
2) the production of the maximum amount of gasoline for each brand.

The estimated quality indicators of commercial gasoline, depending on the properties of the reformate, are presented in Table 5.

Table 5. Quality indicators of boiled gasolines depending on the properties of the reformate

Parameter	Case 1*			Case 2**		
	Regular 92	Premium 95	Super 98	Regular 92	Premium 95	Super 98
RON	92.20	95.20	98.10	92.10	95.20	98.30
Benzene content, vol. %	0.95	0.86	0.78	0.98	0.95	0.89
Aromatics content, vol. %	34.73	34.44	32.52	32.94	34.10	32.14
Olefins content, vol. %	11.02	9.96	4.60	11.12	9.65	4.26
Sulfur content, ppm	9.80	9.80	6.90	9.90	8.80	6.70

**Case 1 – Reformate 1 (fixed bed), Reformate 1 (moving bed)*
***Case 2 – Reformate 2 (fixed bed), Reformate 2 (moving bed)*

According to the data presented in Table 5, the properties of the calculated gasoline correspond to the established quality standards and have a reserve for the content of benzene and aromatic hydrocarbons. The estimated recipes for commercial gasoline are presented in Table 6.

Table 6. Design formulations of gasolines depending on the properties of the reformate

Flow, wt. %	Case 1			Case 2		
	Regular 92	Premium 95	Super 98	Regular 92	Premium 95	Super 98
Catalytic cracking gasoline	31.58	27.28	8.4	31.58	26.62	8.17
Hydrotreated catalytic cracking gasoline	13.45	13.49	12.33	13.45	13.12	11.97
Reformate (moving catalyst bed)	21.94	20.16	22.04	22.21	22.39	22.04
Reformate (fixed catalyst bed)	7.72	7.03	7.94	3.88	4.86	7.94
Toluene	0.1	2.68	3.52	1.02	2.82	4.14
Isomerate	7.3	8.11	10.98	7.4	8.33	10.98
Isopentane	8.99	9.15	11.5	9.5	9.64	11.5
Alkylate	5.9	8.06	15.07	8	8.04	14.45
MTBE	0.1	3.76	8.01	0.1	3.97	8.6
Straight-run gasoline	2.92	0.3	0.2	2.87	0.21	0.2

The calculated compositions of the mixtures vary depending on the properties of the flows used, in this case, on the properties of the reforming. Reducing the benzene content in the

reformate ensures its more complete involvement in gasoline production. The higher the octane number of reforming, the less expensive high-octane streams need to be involved.

Forecast calculations for gasoline production were carried out considering the changes in reforming properties, based on the following criteria:

- Criterion 1: the maximum yield of AI 92 gasoline;
- Criterion 2: maximum performance of AI 95 gasoline;
- Criterion 3: AI 98 maximum gasoline production.

The estimated amount of gasoline is presented in Table 7.

Table 7. Estimated release of the commercial gasoline

Gasoline grade	Criterion 1		Criterion 2		Criterion 3	
	Reformate 1	Reformate 2	Reformate 1	Reformate 2	Reformate 1	Reformate 2
Regular 92, t	7 843.92	7 843.92	7 142.70	7 460.25	7 665.57	7 830.00
Premium 95, t	2 807.49	2 807.49	3 706.20	3 443.46	3 008.46	2 757.03
Super 98, t	282.75	256.65	0.00	0.00	303.63	303.63
Total, t	10 934.16	10 908.06	10 848.90	10 903.71	10 977.66	10 890.66

According to the predicted calculation results, the highest total gasoline production is achieved if the maximum amount of AI 98 gasoline is produced using reformate 1. When using a reformate with a high benzene content and low octane number, the maximum AI 95 gasoline production (Criterion 2) is limited by the available daily MTBE production.

A comparison of the economic efficiency of the calculated and actual ratios of mixing components was performed based on the data on the relative cost of production of mixing components (Table 8).

Table 8. The relative cost of mixing components

Component	Relative cost
Straight-run gasoline	1
MTBE	5.5
Alkylate	4.9
Hydrotreated catalytic cracking gasoline	3.7
Isomerate	2.4
Isopentane	2.1
Catalytic cracking gasoline	3.2
Reformate (moving catalyst bed)	2.7
Reformate (fixed catalyst bed)	2.3
Toluene	3.4

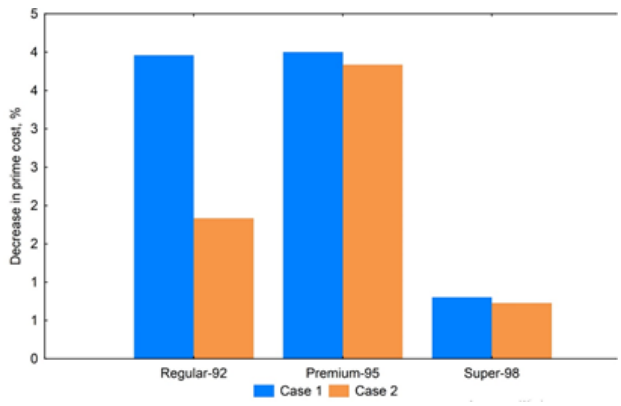

Figure 3. Reducing the cost of commercial gasoline

According to the assessment results, the proposed mixing component ratios for various brands of marketable gasoline can reduce the cost of finished products by 0.7-3.9%. The maximum benefit is achieved with the release of AI-92 gasoline since its production requires a minimum amount of expensive high-octane streams (Fig. 3).

Thus, the use of reformates with a low benzene content and a high octane number reduces the involvement of expensive high-octane streams in the production of motor fuels and also increasing the proportion of catalytic cracking gasoline.

4. Conclusions

Based on the studies, the optimal ratios were developed for mixing the material flows of industrial plants, providing a solution to the multifactorial problem of planning and increasing the efficiency of production of commercial gasoline.

The proposed solution will meet the requirements for the octane number, the content of aromatic hydrocarbons, including benzene, as well as the content of sulfur, olefinic hydrocarbons, etc.

The functionality of the system is as follows:

- tracking the gasoline mixing in a continuous mode;
- adjustment of formulations when the following factors change: the quality or volume of a batch of preparation, a schedule for the production of gasoline, technological parameters of the installations;
- calculation of the formulation considering the quality and quantity of raw materials, including considering the volume of tanks;
- the system is able to provide an interchangeable calculation of marketable gasoline in accordance with the monthly mixing plan, considering the periods of operation and the required output for a given number of days;
- the intelligent system considers the nonlinear laws of mixing octane numbers based on the values of dipole moments for polar molecules.

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