Multiobjective optimization of temperature mode in reactor unit of catalytic reforming of gasoline based on the kinetic model

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Abstract. Based on the previously developed kinetic model of catalytic reforming gasoline, the temperature regimes of catalytic reforming gasoline are optimized. Several target optimization functions are considered — output of the target product, required octane number with limitation on benzene content (high-octane component, <2% by volume), etc. The optimal input temperatures of the reaction mixture for each reactor were determined.

1. Introduction

Catalytic reforming traditionally occupies an important place in modern scheme of oil refining as one of the main sources of high-octane components in motor gasoline and individual aromatic hydrocarbons.

Such a high value of the process is associated with the volume of production of commercial gasoline and the peculiarity of their preparation. If you look at the volume of production commercial gasoline, it is about 40 million tons per year, while all the gasoline produced is sold domestically [1]. Commodity gasolines are a mixture of gasolines and high-octane components obtained at various sites of refineries. The quality of these gasoline separately is not able to meet the requirements for commercial gasoline. Therefore, gasolines are prepared exclusively by mixing different gasoline components. If you look at the production volumes of gasoline components for various processes, then catalytic reforming takes first place with a volume of 18 million tons per year, which is 45% of the total volume of commercial gasoline, followed by catalytic cracking with a volume of 10 million tons per year [2]. Today it is impossible to produce commercial gasoline without the involvement of a catalytic reforming process.

Under modern conditions, technical improvement of key refining processes to which catalytic reforming is almost reached its limit, and further improvement of their operation efficiency becomes possible only through fine process control due to detailed study of chemical transformations of complex, multicomponent systems. Such control can be achieved by multiobjective optimization of a reactor block based on a kinetic model of the process.

2. Catalytic reforming

Production of high-octane gasoline components in catalytic reforming is achieved by increasing the octane number of straight-run (pre-hydrotreated) gasoline fractions by chemical transformations on bifunctional reforming catalysts with acid and metal active centers. Usually, a gasoline fraction with boiling range of 85 - 180 ° C is used as a raw material.

Octane number depends on the hydrocarbon composition of gasoline. All hydrocarbons in gasoline, depending on the structure of the molecule can be divided into groups: paraffinic, naphthenic, aromatic (arenas). In this case, paraffin hydrocarbons can be divided into normal (linear) paraffins and branched paraffins (iso-paraffins), and naphthenic - into five-membered (cyclopentanes) and six-membered (cyclohexanes). Table 1 presents for the groups identified above, examples of structures, the range of octane numbers and the average content in raw materials and product.

Table 1. Groups of hydrocarbons according to the molecular structure.

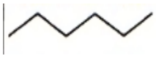
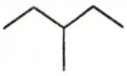
Hydrocarbon group	Molecule structure example	Octane number research method (ONRM)	Content in raw materials,% vol. (ONRM =60)	Content in product,% vol. (ONRM =95)
Normal paraffins		-30 …+60	26	14
Iso-paraffins		55…100	36	28
Cyclopentanes		75…110	30	2
Cyclohexanes				
Arenes		90…145	8 (including benzene – 0,4)	56 (including benzene – 2…4)

Table 1 shows that increasing the octane number of the gasoline is due to complete conversion of naphthenes and paraffins in partial aromatic hydrocarbons (arenes). But according to environmental requirements for commercial gasoline standard Euro 5, the content of aromatic hydrocarbons and benzene is limited and should not exceed 35 and 1% by vol. respectively [3]. In addition, in the future we can expect a tightening of these requirements.

Table 2 presents the main reactions of catalytic reforming with their relative speeds and thermal effects [4].

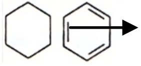
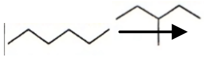
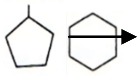
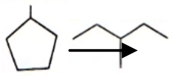
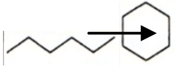
The highest rate possess cyclohexane dehydrogenation reaction and thus have a strong endothermic heat effect, these reactions are the target because it is precisely because of the conversion of naphthenes in arenes. The formation of arenes from paraffins proceeds sequentially. First, due to dehydrocyclization reactions, naphthenes are obtained, which later turn into paraffins, the stage of naphthenes formation from paraffins usually has the lowest speeds, and also has an endothermic thermal effect. Thus, the target catalytic reforming reactions come with significant heat absorption.

The production capacity of catalytic reforming does not allow for chemical increments in isothermal mode, due to the problems of maintaining temperatures in large-volume reactors. Therefore, chemical transformations in catalytic reforming are carried out in a cascade of successive adiabatic reactors displacing a variable volume with interstage heating of the reaction mixture. And as noted above, reforming is dominated by reactions with strong heat absorption, and using adiabatic reactors leads to a significant decrease in the temperature of the reaction mixture. As a result, a decrease in the rates of chemical reactions is observed hundreds of times. Figure 1 shows an example of the temperature profile in the reforming cascade [5].

Thus there is a problem of effective use of a catalyst having in its composition expensive metals (platinum).

The above-described problems of the content of arenes and benzene and the efficiency of using the catalyst can be partially solved by maintaining the optimum temperature regime of the reactor unit. Selection of the optimal temperature regime can be achieved through multi-objective optimization. But for its implementation requires a kinetic model of the process.

Table 2. The main reactions of catalytic reforming.

Reaction type	Relative speed		ΔH, kJ/mol
	C_6	C7	
Cyclohexanes dehydration 	100	120	-221,0
Paraffin isomerization 	10	13	+4,6
Cyclopentan isomerization 	10	13	+15,6
Naphthenes hydrodecyclization 	5	3	+43,9
Paraffin hydrocracking 	3	4	+56,4
Paraffin dehydrocyclization 	1	4	-40,0

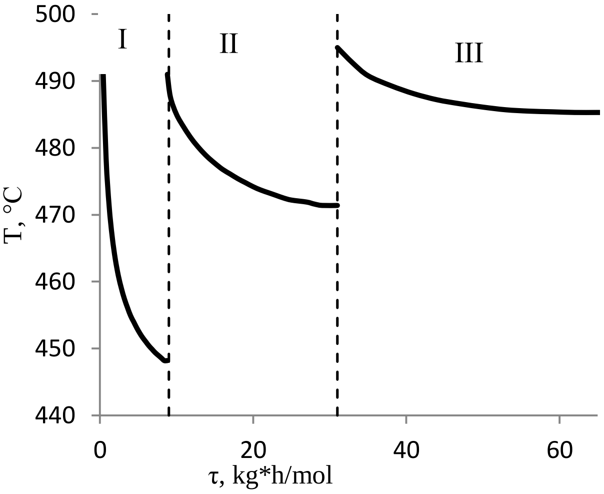


Figure 1. Reactor temperature profile. The vertical lines are zones of the reactor block I – III.

3. Kinetic model

Previously, the authors collective developed a kinetic model of catalytic reforming based on production data [5]. This model is able to predict the concentration profiles of group components within each of the reactors.

The kinetic model of catalytic reforming gasoline takes into account the possible change in a molar flow rate of a reaction mixture both with a change in initial conditions and with a change due to chemical transformations. In the kinetic model, accounting for the mass of catalyst loaded in the reactor is implemented. The basis of the kinetic model catalytic reforming of gasoline is a mathematical model in the form of a system of ordinary differential equations taking into account the non-isothermal nature of the process [6], which adds to the model an additional equation for the temperature change (1) [7, 8]:

$$\frac{dx_i}{d\tau} = u(\tau)\sum_{j=1}^{J} v_{ij} w_j, i = 1,...I;\ w_j = k_j \cdot \prod_{i=1}^{I} (x_i)^{|\alpha_{ij}|} - k_{-j} \cdot \prod_{i=1}^{I} (x_i)^{\beta_{ij}};$$

$$k_j = k_j^0 \cdot \exp\left(-\frac{E_j}{RT}\right);\ \frac{dT}{\mathrm{d}\tau} = -\frac{\sum_{i=1}^{I}(\frac{dx_i}{\mathrm{d}\tau} \times H_i(T))}{\sum_{i=1}^{I}(x_i \times C_{pi}(T))}; \tag{1}$$

with initial conditions: at $\tau = 0,\ x_i(0) = x_i^0,\ T(0) = T^0$; where u(τ) – ratio of the number moles in a mixture to the mass of the catalyst in a certain cross section of the reactor (mol / kg), v_{ij} – stoichiometric coefficients of chemical transformation schemes; J – number of stages, x_i– concentration of substances involved in the reaction, mole fraction; I – number of substances; w_j– rate j-th stage, 1/h; E_j– reaction activation energies kcal/mol; R – gas constant 0,002 kcal/(mol K); T – temperature, K; α_{ij} – negative matrix elements (ν_{ij}), β_{ij}– positive elements (ν_{ij}), k_j^0,– pre-exponential reaction multipliers, 1/h, τ- conditional contact time, (kg*h)/mol; $\mathrm{H}_i(\mathrm{T})$ - enthalpy, J/mol, $\mathrm{C}_{pi}(\mathrm{T})$ - heat capacity, J/(mol*K).

The mathematical model was developed on the basis of the catalytic reforming scheme presented in [9-12]. The values of the kinetic parameters $\ln k_j^0$, E_j given in [5].

4. Optimization criteria

Based on the purpose of the catalytic reforming process, which is increasing octane number of gasoline, the first criterion for multi-objective optimization should be such an indicator as the octane number, depending on the composition of the resulting product.

In catalytic reforming, as in any other refining process, there are side reactions that result in non-target products. Therefore, the second criterion of optimization should be the indicator of the yield of the target product.

Both criteria should aim for the maximum. An increase in the octane number is usually achieved by carrying out the process under more severe conditions, which in turn increases the proportion of adverse reactions, and as a result, decreases the yield of the target product. Thus, to achieve the maximum values of these criteria, different values of technological parameters are needed.

The composition of reforming catalysts includes such expensive components as platinum, which leaves its imprint on the cost of catalysts. In this connection, it is necessary, when optimizing the process, to select such technological parameters and sizes of reactor cascades that provide the minimum amount of catalyst for a given capacity. In this case, a proportional decrease in amount of catalysts in all reactors leads to an increase in the yield of the target product with a lower octane number. And a change in the ratio of the distribution of catalysts in the reactors may make it possible to improve the performance of the facilities. Or leave them at the same level, but with a lower total cost of the catalyst.

From environmental requirements for commercial gasoline result in two more additional optimization criteria that have character of limitations. These include the volume fraction of benzene in the composition of commercial gasoline and the volume fraction of the sum of aromatic. These restrictions do not relate directly to the reforming target product reformate, but limit the proportion of reformate introduced into composition of commercial gasoline. Therefore, these criteria should minimize.

4.1. Octane number.

Generally, this criterion will be the following:

$$Z_{ON}(X_i, ON_i) \rightarrow \max,$$

where X_i – concentrations of the components in the product mixture, ON_i – octane number of component i, Z_{ON} – octane optimization functionality.

The octane number is not an additive indicator, since the ON of the individual components differ from their octane numbers in the mixture. But for a simplified and approximate calculation of this criterion, it is possible to apply that it is additive and use the averaged octane numbers of the mixture of components in the mixture as ON components.

When

$$Z_{ON} = \sum_{i=1}^{n}(X_i \times \text{ОЧ}_i), \tag{2}$$

where n – number of components in target product.

Where in $X_i = X_i\ (X^0,\ T^0_j,\ U_j), j = 1..k$, where X^0 – initial component concentration vector; T^0_j – j – th reactor inlet temperature; U_j– molar feed rate, kmol/h/kg$_{\text{kat}}$, k – number of reactors in cascade.

$$U_j = U_j(Mkat_j,\ W_m),$$

where $Mkat_j$ – catalyst mass in the j-th reactor, W_m – raw material molar consumption.

4.2. Yield of target product.

$$Z_p = f(X^0, T^0_j, U_j) \rightarrow \max \tag{3}$$

Physically, this figure represents the fraction of the product minus cracking gases. Thus, the objective function can be described as:

$$Z_P = 1 - \sum_{i=1}^{5} X_i - \Delta X_{H2} \rightarrow \max \tag{4}$$

$X_i = X_i(X^0,\ T_j,\ U_j)$ – described by kinetics, ΔX_{H2} – changing the proportion of hydrogen in the product mixture, Z_p – product optimization optimization. Fractions can be expressed in any values (mass, molar, volume).

4.3. Amounts of catalyst in reactors

$$Z_K = \sum_{j=1}^{k} Mkat_j \rightarrow \min \tag{5}$$

Z_K – catalytic optimization functionality.

This objective function is convenient to use for optimizing the process with a given performance.

If productivity is not specified, it is more expedient to use U_j as a target function, since it gives a set of combinations of productivity and mass of the catalyst providing the same quality indicators.

$$Z_K = U = U(Mkat,\ W_m) \rightarrow \max \text{ for each reactor.}$$

4.4. Content of aromatic hydrocarbons and benzene.

Reducing the content of aromatic hydrocarbons and benzene will lead to a decrease in octane number of reformate. Thus, we have mutual direct competition between the target criteria.

$$Z_{A6} = X_6 \rightarrow \min$$

$$X_{A6} = X_{A6}\ (X^0,\ T_j,\ U_j),\ X_{Ai} = X_{Ai}\ (X^0,\ T_j,\ U_j),$$

$$Z_{Ai} = \sum_{i=6}^{11} X_{Ai} \rightarrow \min \tag{6}$$

5. Multiobjective optimization

Task of multiobjective optimization is definition of the values variable parameters that deliver unimprovable solutions to several target functions simultaneously. Unimprovable solutions of objective functions are usually called the Pareto front. The optimal values of the variable parameters are called the Pareto set [15-17].

In connection with above, the formulation of a problem in multiobjective optimization of conditions of a chemical reaction based on the kinetic model is:

- Optimization criteria vector $Z=(Z_1, Z_2, \ldots)$.
- Variable parameters in the task are temperature at the entrance to three reactors [13-14]: $X=(T_1, T_2, T_3)$. Dimension variable parameters vector of $|X|=3$.

- Mathematical model in the form of a system of ordinary differential equations, taking into account the non-isothermal nature of the process (1).

- Direct restrictions on variable parameters are determined by intervals $T_l \in [Tmin_l; Tmax_l]$, l=1,2,3.

This proposed two-goal optimization problem for catalytic reforming of gasoline was solved by an algorithm Non-dominated Sorting Genetic Algorithm II (NSGA-II) [18] in Matlab software environment [19] for optimization criteria (4) - yield of the target product minus the cracking gases and (6) decrease in the content of arenes and benzene.

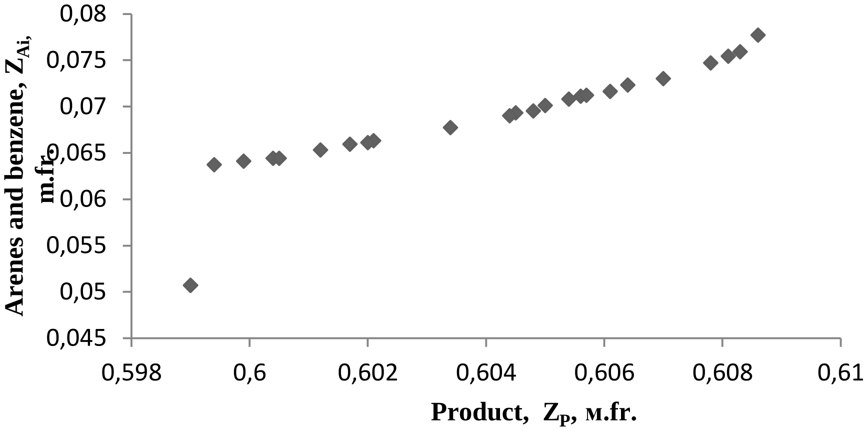


Figure 2. Pareto Front optimization in temperature regime of catalytic gasoline reforming.

Table 3. Values of temperature at inlet to the reactor and the optimization criteria.

T_1, °C	T_2, °C	T_3, °C	Z_P, м.д.	Z_{Ai}, м.д.
300	300	300	0,599	0,0507
324	393	314	0,5994	0,0637
362	394	316	0,5999	0,0641
354	395	321	0,6004	0,0644
394	391	326	0,6005	0,0644
323	399	326	0,6012	0,0653
346	400	331	0,6017	0,0659
397	398	329	0,602	0,0661
339	403	328	0,6021	0,0663
413	402	336	0,6034	0,0677
401	408	342	0,6044	0,069
373	410	348	0,6045	0,0693
422	406	348	0,6048	0,0695
376	414	349	0,605	0,0701
356	414	358	0,6054	0,0708
362	414	360	0,6056	0,0711
347	414	363	0,6057	0,0712
432	405	368	0,6061	0,0716
370	407	375	0,6064	0,0723
421	404	378	0,607	0,073
419	396	388	0,6078	0,0747
390	396	392	0,6081	0,0754
379	403	392	0,6083	0,0759
366	399	399	0,6086	0,0777

In fig. 2 and table 3 shows the solution of a two-objective problem of optimization of temperature regime in catalytic reforming of gasoline. The solution is values of three temperatures at the entrance to the reactor and corresponding values of optimization criteria. All determined values are optimal. The choice of a specific temperature regime depends on the decision maker.

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