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

K F Koledina¹,², R Z Zaynullin², S N Koledin² and A F Akhmetov ²

¹Institute of Petrochemistry and Catalysis, Russian Academy of Sciences, prospect Oktyabrya 141, Ufa, Bashkortostan, Russia, 450075
²Ufa State Petroleum Technological University, Pervomayskaya str. 14, Ufa, Bashkortostan, Russia, 450062

e-mail: koledinakamila@mail.ru

Abstract. Based on the previously developed kinetic model of gasoline catalytic reforming, the temperature regimes of gasoline catalytic reforming are optimized. Several target optimization functions are considered — yield of the main product required octane number with a restriction to benzene content (high-octane component, <2% by volume), etc. The proposed two-objective optimization problem for catalytic reforming of gasoline was solved with the Non-dominated Sorting Genetic Algorithm II (NSGA-II) in Matlab software environment. The optimal inlet temperatures of the reaction mixture are determined for each reactor.

1. Introduction
Catalytic reforming traditionally holds an important place in the modern scheme of oil refining as one of the major sources of high-octane components of gasoline and individual aromatic hydrocarbons. The reason for such a high value of the process is the output volume and the special aspects of the production of commercial gasolines.

Commercial gasoline is a mixture of gasoline and high-octane components produced at various oil refinery facilities. The quality of this gasoline alone cannot meet the requirements for commercial types of gasoline. Therefore, gasoline is produced only by mixing various gasoline components.

In terms of the production output of gasoline components, catalytic reforming holds the first place among various production processes with a volume of 18 million tons per year, which amounts to 45% of the total commercial gasoline volume, followed by catalytic cracking with a volume of 10 million tons per year. The production of commercial gasoline nowadays is impossible without the involvement of a catalytic reforming process [1, 2].

The technical improvement of key refining processes, which include the catalytic reforming, has almost reached its limit under the current conditions. Further improvement of their operation efficiency can be achieved only through delicate process control based on a detailed study of chemical transformations of complex, multi-component systems. Such control can be achieved by multipurpose optimization of the reactor block based on a kinetic model of the process.

1368 (2019) 042018 doi:10.1088/1742-6596/1368/4/042018
2. Catalytic reforming

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

The octane number depends on the hydrocarbon composition of gasoline. Depending on the molecular structure, all hydrocarbons in gasoline can be divided into the following groups: paraffinic, naphthenic, aromatic (arenes). Also, paraffinic hydrocarbons can be divided into normal (linear) paraffin and branched paraffin (iso-paraffin), and naphthenic hydrocarbons can be divided into five-membered (cyclopentane) and six-membered (cyclohexane). Table 1 provides examples of structures, the range of octane numbers and the average content in raw materials and product for the groups identified above.

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

| Hydrocarbon group | Molecular structure example | Research octane number (RON) | Content in raw materials, % vol. (RON =60) | Content in product, % vol. (RON =95) |
|-------------------|-----------------------------|-----------------------------|------------------------------------------|-------------------------------------|
| Normal paraffin   |                             | -30 …+60                    | 26                                       | 14                                  |
| Iso-paraffin      |                             | 55…100                      | 36                                       | 28                                  |
| Cyclopentane      |                             | 75…110                      | 30                                       | 2                                   |
| Cyclohexane       |                             | 90…145                      | 8 (including benzene – 0.4)              | 56 (including benzene – 2…4)       |

Table 1 shows that the gasoline octane number increases due to the complete conversion of naphthenes and partial conversion of paraffin into aromatic hydrocarbons (arenes). But according to the environmental requirements for Euro 5 commercial types of gasoline, the content of aromatic hydrocarbons and benzene is limited and should not exceed 35 and 1% by vol. respectively [3]. Also, these requirements can be strengthened in the future.

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

Cyclohexane dehydrogenation reactions have the highest rate and a strong endothermic heat effect, these are the primary reactions, as they cause the conversion of naphthenes in arenes. Arenes are formed from naphthenes gradually. First, in the course of the dehydrocyclization reaction, naphthenes are obtained, which later turn into paraffin. The stage of production of naphthenes from paraffin usually has lower speed, and also has an endothermic thermal effect. Thus, the primary catalytic reforming reactions involve significant heat absorption.

The production capacity of catalytic reforming units 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 column of series adiabatic displacement reactors of variable volume with interstage heating of the reaction mixture. As noted above, the reforming process mostly involves reactions with significant heat absorption, and the use of adiabatic reactors leads to a significant decrease in the reaction mixture temperature. As a result, the rates of chemical reactions decrease hundreds of times. Figure 1 shows an example of the temperature profile in a column of reforming reactors [5].
Table 2. Primary catalytic reforming reactions.

| Reaction type                  | Relative speed | Reaction heat $\Delta H$, kJ/mol |
|-------------------------------|----------------|----------------------------------|
| Cyclohexanes dehydration     | 100            | -221.0                           |
| Paraffin isomerization        | 10             | +4.6                             |
| Cyclopentane isomerization    | 10             | +15.6                            |
| Naphthenes hydrodecyclization | 5              | +43.9                            |
| Paraffin dehydrocyclization   | 1              | -40.0                            |

Thus, there is a problem with the efficient use of a catalyst containing expensive metals (platinum). The above-described problems of the content of arenes and benzene and the efficiency of the catalyst used can be partially solved by maintaining the optimal temperature conditions of the reactor unit. The optimal temperature conditions can be achieved through multi-objective optimization. But such optimization requires a kinetic model of the process.

3. Kinetic model

Previously, the group of authors developed a kinetic model of catalytic reforming based on production data [5]. This model can predict the concentration profiles of group components inside each of the reactors.

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

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

$$k_j = k_j^0 \cdot \exp \left(-\frac{E_j}{RT}\right); \quad \frac{dT}{d\tau} = -\frac{\sum_{j=1}^{J} \left(\frac{dx_j}{d\tau} \times H_j(T)\right)}{\sum_{i=1}^{I} (x_i \times C_{pi}(T))};$$

with the following initial conditions: at $\tau = 0$, $x_i(0) = x_i^0$, $T(0) = T^0$; where $u(\tau)$ is the ratio of the number moles in a mixture to the mass of the catalyst in a certain cross-section of the reactor (mol / kg), $v_{ij}$ is the stoichiometric coefficients of chemical transformation schemes; $J$ is the number of stages, $x_i$ is the concentration of substances involved in the reaction, mole fraction; $I$ is the number of substances; $w_j$ is the rate $j$-th stage, 1/h; $E_j$ is the reaction activation energies kcal / mol; $R$ is the gas constant 0.002 kcal / (mol K); $T$ is the temperature, K; $\alpha_{ij}$ is the negative matrix elements ($v_{ij}$), $\beta_{ij}$ is the positive elements ($v_{ij}$), $k_j^0$ is the pre-exponential reaction multipliers, 1/h; $\tau$ is the conditional contact time, (kg h) / mol; $H_j(T)$ is the enthalpy, J / mol, $C_{pi}(T)$ is the heat capacity, J / (mol*K).

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

### 4. Optimization criteria

Based on the purpose of the catalytic reforming process, which is the increase of gasoline octane number, the first criterion for multi-objective optimization should be the octane number indicator which depends on the composition of the main product.

Catalytic reforming, just like any other refining process, involves side reactions resulting in the production of off-target products. Therefore, the indicator of the yield of the main product should be the second optimization criterion.

Both of the above criteria should be as high as possible. The octane number growth is usually achieved by more severe process conditions, which in turn increase the proportion of adverse reactions, and, as a result, decrease the yield of the main product. Thus, different values of technological parameters are needed to achieve the maximum values of the above criteria.

The composition of reforming catalysts includes expensive components like platinum, which influences the cost of catalysts. For this reason, when optimizing the process, the technological parameters and the sizes of reactor cascades should be chosen that require the minimum amount of catalyst for a given capacity. Besides, a proportional decrease in the number of catalysts in all reactors leads to an increase in the yield of the main product with a lower octane number. And a change in the ratio of catalysts distribution in the reactors may allow to improve the performance of the units or leave them at the same level, but with a lower catalyst consumption.

The environmental requirements for commercial types of gasoline result in two additional optimization criteria providing certain limitations. These include the volume fraction of benzene in the commercial gasoline and the volume fraction of the total of aromatics. These limitations are not related directly to the main product of reforming - reformate, but limit the content of reformate in commercial gasoline. Therefore, these criteria should be as low as possible.

#### 4.1. Octane number.

In the general case, this criterion is as follows:
where \( X_i \) are the concentrations of components in the product mixture, \( ON_i \) is the octane number of component \( i \), \( Z_{ON} \) is the octane number optimization functionality.

The octane number is not an additive index since the \( ON \) of the individual components differs from their octane numbers in the mixture. But for a simplified and approximate calculation of this criterion, it is possible to assume that it is additive and to use the averaged blended octane numbers of components in the mixture as \( ON \) components.

Then

\[
Z_{ON} = \sum_{i=1}^{n} (X_i \times O\mathcal{N} f_i),
\]

where \( n \) is the number of components in the main product. And \( X_i = X_i(X^0, T^0_r, U_r), r = 1..k \) where \( X^0 \) is the vector of the initial component concentrations; \( T^0_r \) is the inlet temperature of the \( r \)-th reactor; \( U_r \) is the molar feed rate, kmol/h/(kg kat.), \( k \) is the number of reactors in cascade.

\[
U_r = U_r(Mkat_r, W_m),
\]

where \( Mkat_r \) is the catalyst mass in the \( r \)-th reactor, \( W_m \) is the raw material molar consumption.

4.2. The yield of the target product.

\[
Z_p(X^0, T^0_r, U_r) \rightarrow \max
\]

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

\[
Z_p = 1 - \sum_{i=1}^{5} X_i - X_{H2},
\]

\[
X_i = X_i(X^0, T^0_r, U_r)
\]

are described by kinetics, \( \Delta X_{H2} \) is the changing the proportion of hydrogen in the product mixture, \( Z_p \) is the product yield optimization functionality. Ratios can be expressed in any values (mass, molar, volume).

4.3. Amounts of catalyst in reactors

\[
Z_K = \sum_{j=1}^{k} Mkat_r \rightarrow \min,
\]

\( Z_K \) is the catalytic optimization functionality.

This target function is efficient for optimizing the process with a given production rate.

If the production rate is not specified, it is more expedient to use \( U_r \) as a target function, since it gives a set of combinations of production rate and catalyst mass providing the same quality indicators.

\[
Z_K = U(Mkat_r, W_m) \rightarrow \max
\]

for each reactor.

4.4. Content of aromatic hydrocarbons and benzene

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

\[
Z_{46} = X_{46} \rightarrow \min,
\]

\[
X_{46} = X_{46}(X^0, T^0_r, U_r),
\]

\[
Z_{Al} = \sum_{i=6}^{11} X_{Al} \rightarrow \min,
\]

\[
X_{Al} = X_{Al}(X^0, T^0_r, U_r),
\]
5. Multiobjective optimization
The task of multiobjective optimization is understood as the determination of values of variable parameters providing unimprovable solutions to several target functions simultaneously. Unimprovable solutions of target functions are usually referred to as the Pareto frontier. The optimal values of the variable parameters are called the Pareto set [15-17].

In connection with the above, the setting of the problem of multiobjective optimization of chemical reaction conditions based on the kinetic model is as follows:

- Optimization criteria vector \( Z=(Z_1, Z_2, \ldots) \).
- Variable parameters in the problem are the inlet temperatures of three reactors [13-14]: \( X=(T_1, T_2, T_3) \). The dimension of the vector of variable parameters is \( |X|=3 \).
- The mathematical model in the form of a system of ordinary differential equations considering the non-isothermal nature of the process (1).
- Direct limitations of variable parameters are determined by the intervals \( T_l \in [T_{min}, T_{max}], l=1,2,3 \).

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

Table 3. Values of inlet temperatures of the reactor and the optimization criteria.

| \( T_1, ^\circ C \) | \( T_2, ^\circ C \) | \( T_3, ^\circ C \) | \( Z_{ON} \) | \( Z_{Ai}, \% \text{ mas.} \) |
|------------------|------------------|------------------|--------------|------------------|
| 400.0            | 400.0            | 400.0            | 69.8         | 22.8             |
| 464.5            | 445.2            | 475.8            | 86.9         | 36.9             |
| 481.4            | 417.5            | 436.9            | 79.8         | 29.5             |
| 411.3            | 412.1            | 482.5            | 84.0         | 33.4             |
| 441.9            | 458.5            | 477.6            | 87.3         | 37.6             |
| 414.2            | 404.4            | 410.3            | 71.5         | 24.5             |
| 427.0            | 492.4            | 488.6            | 90.3         | 43.7             |
| 425.6            | 488.0            | 494.7            | 90.7         | 45.0             |
| 452.1            | 416.3            | 473.6            | 84.5         | 33.8             |
| 448.3            | 454.2            | 465.1            | 85.2         | 34.4             |
| 432.1            | 414.5            | 412.8            | 73.2         | 25.7             |
| 495.4            | 465.8            | 435.3            | 83.9         | 32.6             |
| 439.5            | 436.9            | 416.7            | 75.8         | 27.4             |
| 483.9            | 430.4            | 438.7            | 80.9         | 30.2             |
| 400.5            | 400.8            | 400.6            | 69.9         | 22.9             |
| 499.6            | 426.2            | 440.0            | 81.9         | 30.8             |
| 413.6            | 482.7            | 500.0            | 90.8         | 45.3             |

Figure 2 and Table 3 show the solution of a two-objective problem of temperature regime optimization in catalytic gasoline reforming. The solution is the values of three inlet temperatures of the reactors and the corresponding values of optimization criteria. All the values determined are optimal. The choice of a specific temperature regime depends on the decision-maker.

6. Conclusion
This paper presents the results of multi-objective optimization of the temperature mode of operation of the reactor block of the catalytic gasoline reforming process to reduce the content of aromatic hydrocarbons without significantly reducing the octane number of the product. The result of the work shows the possibility of achieving a positive effect in this matter without additional costs for the selection and reverse transformation of unwanted components.
The inlet temperatures of each reactor were determined, which provides reducing the content of aromatic hydrocarbons (arenes) by 18% with a decrease in the octane number of the target product by 2 points. A positive effect is achieved by preserving iso-paraffin hydrocarbons in the composition of the product, the octane numbers of which are closest to aromatic hydrocarbons. This phenomenon is explained by the thermodynamic laws of the process.

![Pareto Frontier of temperature regime optimization in catalytic gasoline reforming.](image)

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

7. References

[1] Post-release of the conference "Motor fuels 2018" URL: http://www.creonenergy.ru/
[2] RUPEC Information Analytical Center "High-octane components 2014-2020" URL: http://www.rupec.ru
[3] GOST 32513-2013 2014 Motor fuels. Unleaded gasoline. Technical conditions
[4] Akhmetov S A, Ishmiyarov M H and Kaufman A A 2009 Technology processing of oil, gas and solid fuels (St. Petersburg: Nedra) p 832
[5] Zainullin R Z, Koledina K F, Akhmetov A F and Gubaidullin I M 2017 Kinetics and Catalysis 58 279-289
[6] Nurislamova L F and Gubaidullin I M 2014 Computational Methods and Programming: New Computational Technologies 15(4) 685-696
[7] Baynazarova N M, Koledina K Fand Pichugina D A 2016 CEUR Workshop Proceedings 1576 425-431
[8] Koledina K F, Koledin S N, Shchadneva N A, Mayakova Y Yu and Gubaidullin I M 2017 Reaction Kinetics, Mechanisms and Catalysis 121(2) 425-428
[9] Taskar Uand Riggs1997 J AIChE Journal 43 740-753
[10] Padmavathi Gand Chaudhuri K K 1997 Can J Chem. Eng. 75 930-937
[11] Sotelo-Boyas R and Froment G 2009 Ind Eng Chem Res 48 1107-1119
[12] Iranshahi D, Amiri H and Karimi M 2013 Energy & Fuels 27 4048-4070
[13] Gubaydullin I M, Koledina K F and Sayfullina L V 2014 Engineering Journal 18(1) 13-24
[14] Nurislamova L F, Gubaydullin I M and Koledina K F 2015 Reaction Kinetics, Mechanisms and Catalysis 116(1) 79-93
[15] Nurislamova L F, Gubaydullin I M, Koledina K F and Safin R R 2016 Reaction Kinetics, Mechanisms and Catalysis 117(1) 1-14
[16] Koledina K F and Gubaydullin I M 2016 Russian Journal of Physical Chemistry 90(5) 914-921
[17] Koledina K F, Koledin S N, Shchadneva N A and Gubaidullin I M 2017 Russian Journal of Physical Chemistry A 91(3) 444-449
[18] Deb K, Mohan M and Mishra S 2003 Evolutionary Multi-Criterion Optimization 2632 222-236
[19] Vovdenko M K, Gubaidulin I M, Koledina K F and Koledin S N 2017 *CEUR Workshop Proceedings* **1966** 20-23

**Acknowledgments**

This research was performed due to the Russian Scientific Fund grant (project No. 19-71-00006, paragraph 3, 4), RFBR according to the research projects № 18-07-00341, 18-37-00015 (paragraph 5), RFBR according to the research projects 19-37-50021 (paragraph 4, 5).