Solution of the inverse kinetics problem for the catalytic cracking process based on a 16-component kinetic model

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Abstract. This article presents a 16-lump model of catalytic cracking of vacuum gasoil, which allows to take into account the quantity and quality of the main products of the process: gasoline, propane-propylene and butane-butylene fractions; and by-products of the process: light and heavy catalytic gasoil. To solve the direct problem of solving a system of differential equations, the Runge-Kutta method of order 4 is used, to solve the inverse problem of choosing the constants of the rate of chemical transformations, the method of direct search for minimizing the function of the sum of deviations of calculated values from experimental ones is applied. Thus, the reaction rate constants were chosen for the developed model.

1. Introduction
Catalytic cracking is the most important process for obtaining gasoline components, along with catalytic reforming. In refinery operations catalytic cracking allows to increase processing depth of oil refining at the expense of involvement in the process of heavy residue. The resulting component of gasoline is characterized by a high octane number, low content of aromatic compounds, which is very important for the production of an environmentally straight product [1]. In addition, the process products are the light propane – propylene fraction and butane-butylene fraction, which are valuable for petrochemical feedstock. Accordingly, the study and simulation of the mechanism of the process of catalytic cracking, as one of the increasing depth of oil refining, is an important and actual problem [2].

Prior to, we conducted research and analysis of existing models of the catalytic cracking process published in Russian and foreign literature [3]. Several models have been developed based on the information received [4]. This paper presents the general view and results of calculations for the sixteen lump model.

2. 16-lump kinetic model
The purpose of developing the kinetic model was to evaluate not only the quantity of the main product-catalytic cracking gasoline, but also its quality – structural, fractional composition, and octane number. Also, this model can be used to estimate the yield of valuable raw materials for petrochemical production: propane-propylene and butane-butylene fractions, as well as the quantity and quality
indicators of the fraction of light catalytic gasoil, which is a component of diesel fuel. 16-lump kinetic model

The transformation scheme used in the proposed model shown in figure 1.

![Figure 1. 16-lump kinetic model.](image)

The designations in this diagram are shown in table 1.

| The marking | Component | The Average molecular weight, kg/kmol | Belonging to the product |
|-------------|-----------|---------------------------------------|------------------------|
| Nh y₁       | Heavy naphthenes (C₂₄⁻C₄₀) | 400 | Heavy catalytic gasoil |
| Ph y₂       | Heavy paraffins (C₂₄⁻C₄₀) | | |
| Ah y₃       | Heavy aromatics (C₂₄⁻C₄₀) | | |
| Nm y₄       | Medium naphthenes (C₁₃⁻C₂₃) | | |
| Pm y₅       | Medium paraffins (C₁₃⁻C₂₃) | 200 | Light catalytic gasoil |
| Om y₇       | Medium olefins (C₁₃⁻C₂₃) | | |
| Am y₆       | Medium aromatics (C₁₃⁻C₂₃) | | |
| Ni y₈       | Light naphthenes (C₅⁻C₁₂) | | |
| n-Pl y₁₆    | Light normal paraffins (C₅⁻C₁₂) | | |
| Ol y₁₁      | Light olefins (C₅⁻C₁₂) | 100 | Gasoline |
| Al y₁₀      | Light aromatics (C₅⁻C₁₂) | | |
| i-Pl y₉     | Light isoparaffins (C₅⁻C₁₂) | | |
| DG y₁₃      | Dry gas | 16 | - |
| PPF y₁₄     | Propane-propylene fraction | 43 | - |
| BBF y₁₅     | Butane-butylene fraction | 57 | - |
| C y₁₂       | Resin + coke | 600 | - |
Differential equations of the kinetic model:
\[
\frac{dy_1}{dt} = -k_1[y_1] - k_0[y_1]
\]
\[
\frac{dy_2}{dt} = -k_2[y_2] - k_0[y_2]
\]
\[
\frac{dy_3}{dt} = -k_3[y_3] - k_{10}[y_3] - k_{15}[y_3]
\]
\[
\frac{dy_4}{dt} = k_1[y_1] - k_4[y_4] - k_{11}[y_4]
\]
\[
\frac{dy_5}{dt} = k_2[y_2] - k_5[y_5] - k_{12}[y_5] - k_{30}[y_5]
\]
\[
\frac{dy_6}{dt} = k_3[y_3] - k_6[y_6] - k_{13}[y_6] - k_{16}[y_6]
\]
\[
\frac{dy_7}{dt} = k_4[y_4] + k_9[y_9] + k_{10}[y_{10}] - k_7[y_7] - k_{14}[y_7]
\]
\[
\frac{dy_8}{dt} = k_5[y_5] + k_{18}[y_8] - k_9[y_9] - k_{20}[y_9]
\]
\[
\frac{dy_9}{dt} = k_6[y_6] + k_{17}[y_9] + k_{21}[y_{10}] - k_{22}[y_{10}]
\]
\[
\frac{dy_{10}}{dt} = k_{12}[y_{10}] - k_{24}[y_{10}] - k_{11}[y_{10}]
\]
\[
\frac{dy_{11}}{dt} = k_{15}[y_5] + k_{16}[y_6] + k_{17}[y_{10}]
\]
\[
\frac{dy_{12}}{dt} = k_{18}[y_8] + k_{21}[y_9] + k_{24}[y_{10}]
\]
\[
\frac{dy_{13}}{dt} = k_{27}[y_{11}]
\]
\[
\frac{dy_{14}}{dt} = k_{19}[y_6] + k_{22}[y_9] + k_{25}[y_{10}]
\]
\[
\frac{dy_{15}}{dt} = k_{20}[y_8] + k_{23}[y_9] + k_{26}[y_{10}]
\]
\[
\frac{dy_{16}}{dt} = k_{30}[y_5] - k_{31}[y_{16}]
\]

The separation of light paraffins into normal and isoparaffins will make it possible to estimate the octane number, since it directly depends on the structure of the carbon chain. For example, table 2 shows the values of octane numbers for normal and branched C₅–C₈ hydrocarbon structures.

| Normal and low-branched paraffins | isoparaffins |
|-----------------------------------|--------------|
| **Title**                         | **RON**      | **MON** | **Title** | **RON** | **MON** |
| n-pentane                         | 61.7         | 61.9    | isopentane | 92.3    | 90.3    |
| n-hexane                          | 24.8         | 26.0    | neopentane | 105.0   | 117.0   |
| monomethylpentane                 | 73.9         | 74.0    | 2,2-dimethylbutane | 91.8    | 93.4    |
| n-heptane                         | 0.0          | 0.0     | 2,3-dimethylbutane | 105.8   | 94.3    |
| 2-methylhexane                    | 42.4         | 46.4    | 2,4-dimethylpentane | 83.1    | 83.8    |
| 3-methylhexane                    | 52.0         | 55.0    | 2,2-dimethylpentane | 92.8    | 95.6    |
| 3-ethylpentane                    | 65.0         | 69.3    | 3,3-dimethylpentane | 80.8    | 86.6    |
| n-octane                          | -15.0        | -20.0   | 2,2,3-trimethylbutane | 112.1   | 101.1   |
| 2-methylheptane                   | 21.7         | 23.8    | 3-ethyl-2-methylpentane | 87.3    | 88.1    |
| 3-methylheptane                   | 26.8         | 35.0    | 3-ethyl-3-methylpentane | 80.0    | 88.7    |
| 4-methylheptane                   | 26.7         | 39.0    | 2,3,4-trimethylpentane | 102.7   | 95.9    |
| 3-ethylhexane                     | 33.5         | 52.4    | 2,2,4-trimethylpentane | 100.0   | 100.0   |
| 2,5-dimethylhexane                | 55.5         | 55.7    | 2,2,3-trimethylpentane | 109.6   | 99.9    |
| 2,4-dimethylhexane                | 65.2         | 69.9    | 2,3,3-trimethylpentane | 106.1   | 99.4    |
| 2,3-dimethylhexane                | 71.3         | 78.9    | 2,2,3,3-tetramethylbutane | 137.0   | 117.0   |
| 3,4-dimethylhexane                | 76.3         | 81.7    |                        |         |        |
| 2,2-dimethylhexane                | 72.5         | 77.4    |                        |         |        |
| 3,3-dimethylhexane                | 75.5         | 83.4    |                        |         |        |
3. The results of calculations on the 16-lump model

To calculate the speed constants of the 16-lump kinetic model, we used production data from the article [6], which relate to the section C-200 at the catalytic cracking unit KT-1/1 of JSC «Gazpromneft-Omsk oil refinery».

The process feedstock is a vacuum gas oil containing heavy naphthenic, paraffinic and aromatic compounds. Taking into account the production data, the initial concentrations of the components at the beginning of the reaction were calculated:
- heavy naphthenes: 0.1849 g/ml;
- heavy paraffins: 0.4065 g/ml;
- heavy aromatic compounds: 0.3129 g/ml.

Next, we calculated the concentration of products in the reaction mixture. The calculation results are given in table 3.

We used Matlab software in our calculations. The Runge-Kutta method of 4 orders (direct problem) was used to solve the Cauchy problem. The reaction rate constants were obtained from the minimum condition of the function
$$z(k_1, ..., k_{16}) = \sum_{i}^{16} |y_i - y_{exp_i}| / y_{exp_i},$$
where $y_{exp_i}$ is the concentration value of the components in the reaction mixture obtained from production data. To find the minimum of this function (the inverse kinetic problem), the direct search method was used [7,8].

| Component | Concentration, g/ml | Belonging to the product |
|-----------|---------------------|-------------------------|
| C_{Nh}    | 0.0057              | Heavy catalytic gasoil   |
| C_{Ph}    | 0.0111              |                         |
| C_{Ah}    | 0.0670              |                         |
| C_{Nm}    | 0.0039              | Light catalytic gasoil   |
| C_{Pm}    | 0.0187              |                         |
| C_{Am}    | 0.0802              |                         |
| C_{Om}    | 0.0032              |                         |
| C_{Ni}    | 0.0565              |                         |
| C_{nP}    | 0.0236              | Gasoline                |
| C_{Al}    | 0.1850              |                         |
| C_{pi}    | 0.1669              |                         |
| C_{ol}    | 0.1024              |                         |
| C_{KOKC}  | 0.0387              | Coke                    |
| C_{DG}    | 0.0498              | Dry gas                 |
| C_{PPF}   | 0.0458              | Propane-propylene fraction |
| C_{BBF}   | 0.0506              | Butane-butylene fraction |

The calculation results are shown in tables 4, 5.

| №  | $k_i$, s$^{-1}$ | №  | $k_i$, s$^{-1}$ | №  | $k_i$, s$^{-1}$ | №  | $k_i$, s$^{-1}$ |
|----|----------------|----|----------------|----|----------------|----|----------------|
| 1  | 4.7941         | 9  | 0.0060         | 17 | 0.4423         | 25 | 0.0375         |
| 2  | 5.9952         | 10 | 0.0063         | 18 | 0.2698         | 26 | 0.0050         |
| 3  | 2.5975         | 11 | 6.5347         | 19 | 0.0792         | 27 | 0.1689         |
| 4  | 6.1575         | 12 | 1.9594         | 20 | 0.2225         | 28 | 0.8340         |
| 5  | 6.9948         | 13 | 0.0063         | 21 | 0.5010         | 29 | 0.6125         |
| 6  | 3.1510         | 14 | 1.2948         | 22 | 0.0375         | 30 | 3.2744         |
| 7  | 4.8916         | 15 | 0.1240         | 23 | 0.2250         | 31 | 9.5884         |
| 8  | 1.0049         | 16 | 0.2292         | 24 | 0.0010         | 32 | 9.9996         |
4. Discussion and conclusions
As a result of the review and analysis of the literature data, a kinetic model based on a 16-component scheme of chemical reaction of the catalytic cracking process was compiled. The model allows you to estimate the quantity of main products: gasoline, propane-propylene and butane-butylene fractions; and by-products: light and heavy catalytic gasoil, as well as their structural composition, and, as a result, quality indicators. The calculation based on production data showed good convergence of the new for 16-lump model. Thus, we can count, that this model can adequately describe the process of catalytic cracking, and in the future, it will be possible to research and develop ways to improve the process of catalytic cracking.

5. References
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