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MATHEMATICAL MODELING OF KINETICS OF GASOLINE CATALYTIC REFORMING

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Introduction

Gasoline reforming process has one of the highest production volumes in modern chemical technology. Since the need of high octane gasoline increases and fuel ecological standards are getting stricter, it is essential to study the processes underlying the catalytic reforming. One of the critical requirements to modern petrol production standards is to lower the benzol and aromatic components ratio in the reformate content. Content of aromatic hydrocarbons in commercial petrol is limited to 35 %, as for benzol — its content cannot exceed 1 %. Catalytic reforming of gasoline fractions is one of the processes that define commercial petrol quality, thus it is necessary to determine the optimal parameters for the process at particular catalysts, and to study the kinetics of reactions in order to optimize the process, and obtain resultants of better quality and quantity. In other words, it is necessary to understand catalytic reforming chemistry better to increase the quality and quantity of target products. A reaction mixture has many components (up to 300) and there are a lot of chemical transformation stages they can undergo, which is quite complicated to account in a kinetic model. For kinetic models elaboration, individual hydrocarbons are grouped depending on the hydrocarbon class (lumping analysis). In a kinetic model it is acceptable to neglect stages of producing the intermediate substances that included in the resultant reformate.

Mathematical model

$$\frac{dy_i}{d\tau} = \sum_{j=1}^{J} v_{ij} w_j, i = 1,...I;\ y_i(0) = y_i^0; \quad (1)$$

$$\frac{dT}{d\tau} = -\frac{\sum_{i=1}^{n} \frac{dy_i}{d\tau} \cdot \Delta H_i(T)}{\sum_{i=1}^{n} y_i \cdot C_{pi}(T)};\quad T(0) = T^0; \quad (2)$$

$$\frac{dM}{d\tau} = \sum_{i=1}^{I} \frac{dy_i}{d\tau};\quad M(0) = M^0; \quad (3)$$

$$w_j = k_j \cdot \prod_{i=1}^{I} \left(\frac{y_i}{M}\right)^{|\alpha_{ij}|} - k_{-j} \cdot \prod_{i=1}^{I} \left(\frac{y_i}{M}\right)^{\beta_{ij}}; \quad (4)$$

$$\Delta H_i(T) = \Delta H_{298} + \int_{298}^{T} C_{pi}(T) dT; \quad (5)$$

$$C_{pi}(T) = a_i + b_i T + c_i T^2 + d_i T^3 + e_i T^4; \quad (6)$$

$$Q_1 + \Delta H_R = Q_2; \quad (7)$$

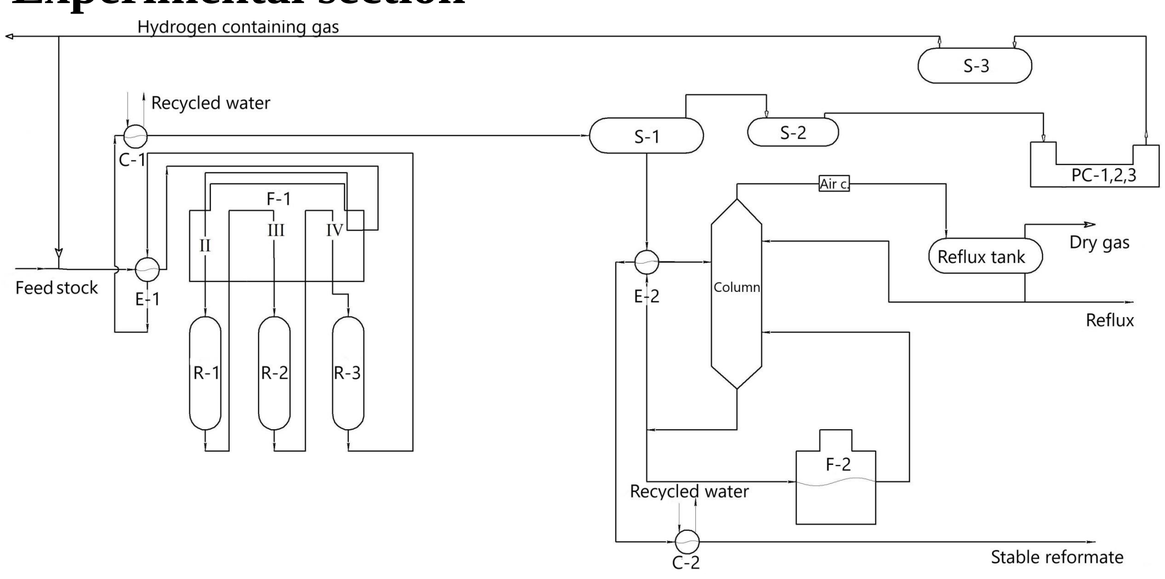
$$Z_Y = \sum_{i=1}^{I} \left| \frac{N_{Э_i} - N_{P_i}}{N_{O_i} - N_{Э_i}} \right| \cdot 100\% \quad (8)$$

$$Z_T = \sum_{m=1}^{3} \left| \frac{T_{Э_m} - T_{P_m}}{T_{O_m} - T_{Э_m}} \right| \cdot 100\% \quad (9)$$

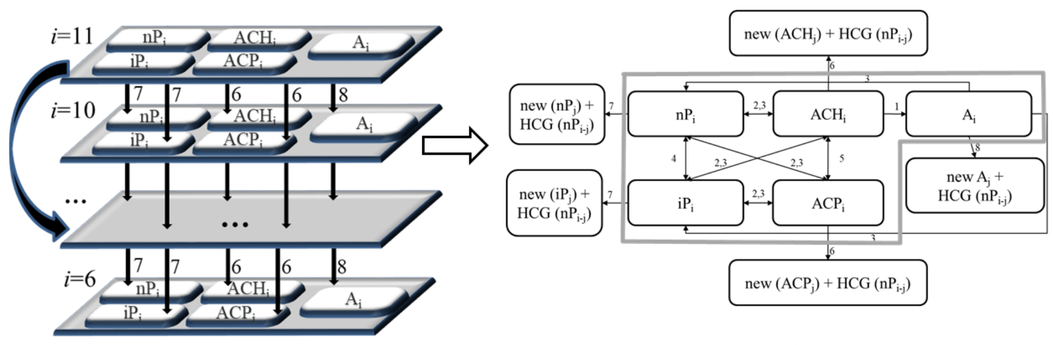
$$Z = Z_Y \cdot \mu_Y + Z_T \cdot \mu_T \quad (10)$$

For a numerical solution of direct kinetic problem (1)-(6), it is necessary to estimate coherence at each iteration. As far as this process is isometric, such evaluation can be represented by conformance* of thermal balance at each point of numerical integration. The inverse kinetic problem of restoring the parameters according to the minimization functional of calculated values from manufacturing data was resolved pursuant to the elaborated mathematical model (8)-(10) .

Experimental section



Scheme of the gasoline catalytic reforming transformations



a) b)

1 — reactions of naphthene dehydration (hydroforming process); 2 —dehydrocyclization of paraffins; 3 — hydrodecyclization; 4 — paraffins isomerization; 5 — naphthenes isomerization; 6 — naphthenes hydrocracking; 7 — paraffins hydrocracking; 8 — hydrocracking of aromatic hydrocarbons; i, j – number of carbon atoms (j < i).

Optimization of conditions of gasoline catalytic reforming

The variable parameters are mode conditions: inlet temperature T_j, $j=1, 2, 3$.

$$X=(x_1, x_2, x_3),$$

$$F(X)=(f_1(X), f_2(X), f_3(X), f_4(X), f_5(X)),$$

$$f_1(X) = ONRM(T_1,T_2,T_3) = \sum_{i=1}^{I} y_i(T_1,T_2,T_3) \cdot ONRM_i \to \max$$

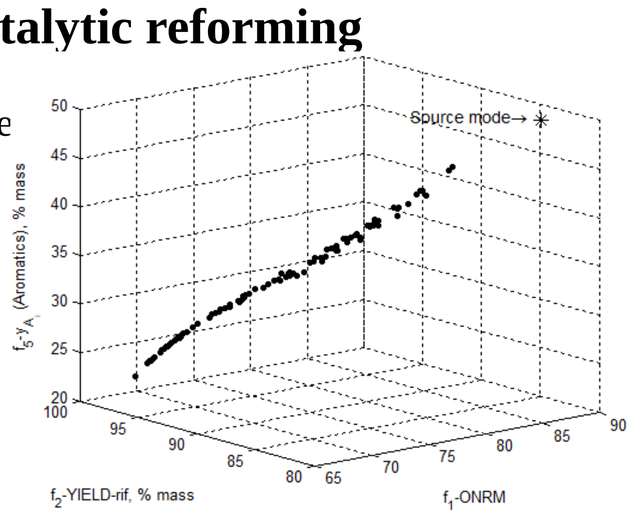
$$f_2(X) = Yield\_Rif(T_1,T_2,T_3) = 1 - \sum_{i=1}^{5} y_i(T_1,T_2,T_3) - \Delta y_{H_2}(T_1,T_2,T_3) \to \max$$

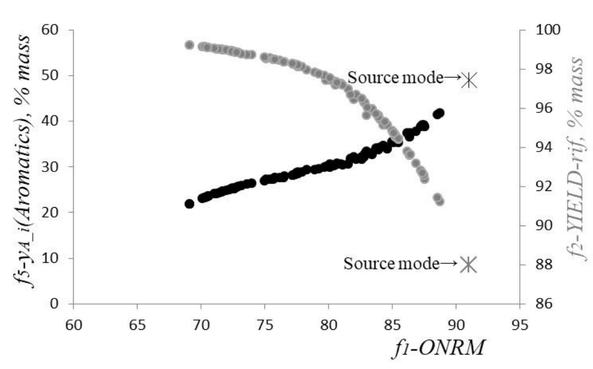
$$f_3(X) = ONRM\_ton(T_1,T_2,T_3) = ONRM(T_1,T_2,T_3) * Yield\_Rif(T_1,T_2,T_3) \to \max$$

$$f_4(X) = y_{A_6}(T_1,T_2,T_3) \to \min$$

$$f_5(X) = \sum_{i-6}^{11} y_{A_i}(T_1,T_2,T_3) \to \min$$

$$\max_{X \in D_X} F(X) = F(X^*) = F^*.$$





Conclusion

Developed a detailed kinetic model of catalytic reforming of gasoline. The individual components of the reaction mixture are grouped depending on the class of hydrocarbons. Based on the kinetic model, solving a problem of multicriteria optimization. The study of catalytic reforming kinetics and influence of temperature mode on the target product yield provides for modernization and improvement of technological process, and allows one to obtain smaller content of benzol and aromatic components in the resultant at permissible decrease of the octane number.

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