

Mathematical model of the catalytic isomerization reactor block of the pentane-hexane fraction based on the kinetic model

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Abstract. The main schemes for the conversion of the catalytic isomerization of the pentane-hexane fraction, which are probable from the standpoint of thermodynamics, are considered. Based on a literary analysis of possible transformation schemes, the mechanism of the process and based on experimental data, a mathematical model of the reactor unit of the process in UniSim Design was developed and the kinetic parameters were determined. The foundations were laid for the subsequent solution of the tasks of the multi-purpose optimization of the catalytic isomerization process of the pentane-hexane fraction.

1. Introduction

Currently, the production of environmentally friendly high-octane gasolines is a difficult problem for a number of domestic refineries. Since, apart from the ubiquitous catalytic reforming process, this requires energy-intensive processes such as catalytic cracking, alkylation and isomerization of light paraffins, as well as more stringent hydrotreating processes. In addition, strict restrictions are imposed on the content of aromatic hydrocarbons and, in particular, benzene in automobiles. at the same time saving the octane number. By structurally altering the carbon skeleton, the catalytic isomerization of light paraffins makes it possible to obtain a high-octane component of motor gasoline with a minimum content of aromatic hydrocarbons. The efficiency of this process is explained by the use of low-octane oil components as a raw material, 62–70 ° C, and catalytic reforming raffinates. The process is carried out in an environment of hydrogen in the presence of bifunctional catalysts [1, 2].

In the middle of the 20th century, when energy and material resources were not so limited, in the design and construction stages of most industrial installations, including reactors, insufficient attention was paid to the in-depth study of the mechanism of most processes. The intensive development of information technologies, such as the theory of analysis and storage of large data, parallel computing technology, artificial neural networks, etc., led to the creation of universal software systems. For example, UniSim Design, which allows you to develop a preliminary detailed kinetic model (PDKM) complex industrial processes. PDKM - is the starting point for building a kinetic model of a higher adequate level (KMVAU). What ultimately allows to solve the problem of a significant increase in the yield of the target product, while minimally spending energy and material resources [3].

In our case, the development of KMVAU solves the task of multi-purpose optimization, for example, a significant increase in the yield of iso-components, reducing the formation of gases (hydrocracking reactions) while rationally using energy and material resources.

The wide component composition of the raw materials, as well as the occurrence of a large number of parallel-sequential chemical reactions at acid and metal centers of bifunctional catalysts, often make it

difficult to describe the kinetics [4,5]. Therefore, to simplify the description of the kinetics, the intermediate stages of formation of components not present in the target products, usually not considered, which is unacceptable when it is necessary to determine the dynamic effective conditions for the conduct of industrial processes.

The reactor unit of the catalytic isomerization unit of the pentane-hexane fraction, consisting of a cascade of three reactors, was taken as the object of study. A hydrotreated gasoline fraction with a boiling point of 62-70 °C was taken as the raw material. The pressure in the reaction zone was 3.2 MPa. The inlet temperatures of the first, second, and third reactors were 147, 160, and 145 °C, respectively. At the exit of the reactors - 160, 170 and 146 °C, respectively. A bifunctional catalyst of domestic production SI-2 was used as a catalyst for the process.

Table 1 presents the component composition of the feedstock and the product of the catalytic isomerization of the pentane-hexane fraction.

Table 1. Component composition of raw materials and product.

Component	raw materials, % wt.	product, % wt.
2,2-DMC4	0.36	21.13
2,3-DMC4	2.15	6.57
2-MC5	19.32	19.58
3-MC5	14.73	11.23
Benzene	1.25	-
Isopentane	10.75	23.56
Methylcyclopentane	2.7	0.12
N-hexane	18.19	7.27
N-pentane	30.81	7.80
Isobutane	-	1.04
N-butane	-	0.87
Propane	-	0.61
Ethane	-	0.13
Methane	-	0.09

It should also be noted that a stabilization unit is available, after which the composition of the gas-product mixture is calculated.

2. Thermodynamics

The initial stage of the mathematical description of the process of catalytic isomerization of the pentane-hexane fraction is the establishment of a scheme for the reaction of hydrocarbon transformations during the process. Such a scheme should most adequately describe the experimental and industrial data with the required precision of technologists. The accuracy of the calculations and the adequacy of the mathematical model to the real process directly depend on the degree of detail of chemical transformations, reflecting the physico-chemical essence of the process [6, 7].

Isomerization reactions in the presence of bifunctional catalysts proceed through a carbonium-ion mechanism [8–10]. The basis of this is thermodynamics of the process. The result of thermodynamic analysis is a list of reactions that probably take place under given conditions [11, 12]. The probability of reactions under the technological conditions of our process was estimated by the value of the Gibbs energy ΔG (table 2).

According to Table 2, it can be seen that the isomerization, dehydrocyclization, naphthene conversion, and dehydrogenation reactions are reversible. And hydrocracking reactions are irreversible [13]. Using the law of effective masses [14], the kinetic equations of the reactions occurring during the catalytic isomerization of the pentane-hexane fraction, we write as follows (table 3).

Table 2. The equations of the reactions of catalytic isomerization of the pentane-hexane fraction and the values of thermodynamic characteristics.

Reaction	ΔH , kJ / mol	ΔG , kJ / mol
1. n-C ₅ H ₁₂ ↔ iso-C ₅ H ₁₂	-8.22	-5.76
2. n-C ₆ H ₁₄ ↔ 2-MP	-6.98	-3.77
3. n -C ₆ H ₁₄ ↔ 3-MP	-4.44	-7.60
4. n -C ₆ H ₁₄ ↔ 2,2-DMB	-18.53	-5.60
5. n -C ₆ H ₁₄ ↔ 2,3- DMB	-10.93	-0.99
6. 2-MP ↔ 3- MP	-2.54	-3.02
7. 2,2- DMB ↔ 2,3- DMB	-7.61	-4.61
8. BZ +H ₂ ↔ CH	-213.94	-52.65
9. BZ +H ₂ ↔ MCP	-197.03	-53.83
10. CH ↔ MCP	-112.34	49.10
11. n -C ₆ H ₁₄ ↔ CH + H ₂	8.57	7.82
12. 2- MP ↔ МЦП + H ₂	-66.96	-29.59
13. 3- MP ↔ МЦП + H ₂	-64.42	-26.58
14. 2,2- DMB ↔ MCP + H ₂	-78.51	-31.43
15. 2,3- DMB ↔ MCP + H ₂	-70.91	-26.82
16. MCP + H ₂ → 3- MP	-64.42	-26.58
17. n -C ₅ H ₁₂ + H ₂ → C ₃ H ₈ + C ₂ H ₆	-44.49	-49.96
18. n -C ₅ H ₁₂ + H ₂ → n -C ₄ H ₁₀ + CH ₄	-56.57	-61.66
19. n -C ₆ H ₁₄ + H ₂ → 2C ₃ H ₈	-37.94	-48.88
20. n -C ₆ H ₁₄ + H ₂ → n -C ₄ H ₁₀ + C ₂ H ₆	-45.91	-51.80
21. n -C ₆ H ₁₄ + H ₂ → n -C ₅ H ₁₂ + CH ₄	-56.14	-47.34
22. n -C ₆ H ₁₄ + H ₂ → iso-C ₅ H ₁₂ + CH ₄	-64.35	-66.71
23. 2- MP + H ₂ → iso -C ₄ H ₁₀ + C ₂ H ₆	-47.38	-49.82
24. 3- MP + H ₂ → iso -C ₅ H ₁₂ + CH ₄	-59.91	-65.95
25. 2,3- DMB + H ₂ → iso -C ₄ H ₁₀ + C ₂ H ₆	-43.44	-52.63
26. 2,3- DMB + H ₂ → iso -C ₅ H ₁₂ + CH ₄	-53.43	-65.71
27. iso - C ₅ H ₁₂ + H ₂ → iso -C ₄ H ₁₀ + CH ₄	-56.82	-57.71
28. 2,2- DMB + H ₂ → iso -C ₄ H ₁₀ + C ₂ H ₆	-35.83	-48.05
29. 2,2- DMB + H ₂ → iso -C ₅ H ₁₂ + CH ₄	-45.82	-61.11

where 2-MP - 2-methylpentane, 3-MP - 3-methylpentane, 2,2-DMB - 2,2-dimethylbutane, 2,3-DMB - 2,3-dimethylbutane, CH - cyclohexane, MCP - methylcyclopentane, BZ - benzene.

Table 3. Kinetic equations of the process of catalytic isomerization of the pentane-hexane fraction.

Reaction	Kinetic equations
30. n-C ₅ H ₁₂ ↔ iso-C ₅ H ₁₂	$W_1 = k_1 * x_1 - k_2 * x_2$
31. n-C ₆ H ₁₄ ↔ 2-MP	$W_2 = k_3 * x_3 - k_4 * x_4$
32. n -C ₆ H ₁₄ ↔ 3-MP	$W_3 = k_5 * x_3 - k_6 * x_5$
33. n -C ₆ H ₁₄ ↔ 2,2-DMB	$W_4 = k_7 * x_3 - k_8 * x_6$
34. n -C ₆ H ₁₄ ↔ 2,3- DMB	$W_5 = k_9 * x_3 - k_{10} * x_7$
35. 2-MP ↔ 3- MP	$W_6 = k_{11} * x_4 - k_{12} * x_5$
36. 2,2- DMB ↔ 2,3- DMB	$W_7 = k_{13} * x_6 - k_{14} * x_7$
37. BZ +H ₂ ↔ CH	$W_8 = k_{15} * x_8 * x_9^3 - k_{16} * x_{10}$
38. BZ +H ₂ ↔ MCP	$W_9 = k_{17} * x_8 * x_9^3 - k_{18} * x_{11}$
39. CH ↔ MCP	$W_{10} = k_{19} * x_{10} - k_{20} * x_{11}$
40. n -C ₆ H ₁₄ ↔ CH + H ₂	$W_{11} = k_{21} * x_3 - k_{22} * x_{10} * x_9$
41. 2- MP ↔ МЦП + H ₂	$W_{12} = k_{23} * x_4 - k_{23} * x_{11} * x_9$
42. 3- MP ↔ МЦП + H ₂	$W_{13} = k_{25} * x_5 - k_{26} * x_{11} * x_9$
43. 2,2- DMB ↔ MCP + H ₂	$W_{14} = k_{27} * x_6 - k_{28} * x_{11} * x_9$
44. 2,3- DMB ↔ MCP + H ₂	$W_{15} = k_{29} * x_7 - k_{30} * x_{11} * x_9$

45. MCP + H ₂ → 3- MP	W ₁₆ = k ₃₁ * x ₁₁ * x ₉
46. n -C ₅ H ₁₂ + H ₂ → C ₃ H ₈ + C ₂ H ₆	W ₁₇ = k ₃₂ * x ₁ * x ₉
47. n -C ₅ H ₁₂ + H ₂ → n -C ₄ H ₁₀ + CH ₄	W ₁₈ = k ₃₃ * x ₁ * x ₉
48. n -C ₆ H ₁₄ + H ₂ → 2C ₃ H ₈	W ₁₉ = k ₃₄ * x ₃ * x ₉
49. n -C ₆ H ₁₄ + H ₂ → n -C ₄ H ₁₀ + C ₂ H ₆	W ₂₀ = k ₃₅ * x ₃ * x ₉
50. n -C ₆ H ₁₄ + H ₂ → n -C ₅ H ₁₂ + CH ₄	W ₂₁ = k ₃₆ * x ₃ * x ₉
51. n -C ₆ H ₁₄ + H ₂ → iso -C ₅ H ₁₂ + CH ₄	W ₂₂ = k ₃₇ * x ₃ * x ₉
52. 2- MP + H ₂ → iso -C ₄ H ₁₀ + C ₂ H ₆	W ₂₃ = k ₃₈ * x ₄ * x ₉
53. 3- MP + H ₂ → iso -C ₅ H ₁₂ + CH ₄	W ₂₄ = k ₃₉ * x ₅ * x ₉
54. 2,3- DMB + H ₂ → iso -C ₄ H ₁₀ + C ₂ H ₆	W ₂₅ = k ₄₀ * x ₇ * x ₉
55. 2,3- DMB + H ₂ → iso -C ₅ H ₁₂ + CH ₄	W ₂₆ = k ₄₁ * x ₇ * x ₉
56. iso - C ₅ H ₁₂ + H ₂ → iso -C ₄ H ₁₀ + CH ₄	W ₂₇ = k ₄₂ * x ₂ * x ₉
57. 2,2- DMB + H ₂ → iso -C ₄ H ₁₀ + C ₂ H ₆	W ₂₈ = k ₄₃ * x ₆ * x ₉
58. 2,2- DMB + H ₂ → iso -C ₅ H ₁₂ + CH ₄	W ₂₉ = k ₄₄ * x ₆ * x ₉

where x_i – the concentration of components in molar fractions, x_1 is n-pentane, x_2 is isopentane, x_3 is n-hexane, x_4 is 2-MP, x_5 is 3-MP, x_6 is 2,2-DMB, x_7 is 2,3 - DMB, x_8 - benzene, x_9 - hydrogen, x_{10} - CG, x_{11} - MCP, x_{12} - propane, x_{13} - ethane, x_{14} - n-butane, x_{15} - methane, x_{16} - isobutane, k_j - kinetic rate constant of the j^{th} reaction, $l \cdot \text{mol}^{-1} \cdot \text{h}^{-1}$ ($j = 8, 9, 11-29$), h^{-1} ($j = 1-7, 10$), W_j is the speed of the j -th reaction, $\text{mol} / (l \cdot h)$.

The kinetic rate constants k_j determined using the UniSim Design software package will be used as a zero approximation in mathematical modeling of the reactor block.

3. Mathematical model

If $u(\tau)$ is the change in the mass of the catalyst, then the equation of the dynamics of a chemical reaction in the ideal displacement mode will have the form [15, 16]:

$$\frac{dx_i}{d\tau} = u(\tau) \sum_{j=1}^J \nu_{ij} w_j, \quad i = 1, \dots, I,$$

$$w_j = k_j^0 \cdot \exp\left(-\frac{E_j^+}{RT}\right) \cdot \prod_{i=1}^I (x_i)^{\alpha_{ij}} - k_{-j}^0 \cdot \exp\left(-\frac{E_j^-}{RT}\right) \cdot \prod_{i=1}^I (x_i)^{\beta_{ij}} \quad (1)$$

with initial conditions: at;

where are the stoichiometric coefficients of chemical transformation schemes; J - number of stages, x_i – concentrations of substances involved in the reaction, ppm; I - the number of substances; $-$ speed of the j -th stage, $1/h$; E_j^+ , E_j^- - activation energy of direct and reverse reactions, kcal/mol; R is the gas constant equal to $8.31 \text{ J} / (\text{mol} \cdot \text{K})$; T is temperature, K; a_{ij} - negative elements of the matrix (ν_{ij}) , b_{ij} – positive elements (ν_{ij}) , k_j^0 , k_{-j}^0 – pre-exponential factors, $1/s$, τ - contact time, $\text{kg} \cdot \text{h} / \text{mol}$.

The mathematical model (1) is a system of ordinary nonlinear differential equations with initial data [17, 18], which takes into account the flow rate of raw materials in the reactor.

To apply the resulting model, you must first conduct a comparative assessment of the kinetic parameters.

4. Conclusion

Thus, on the basis of the literature review and analysis of industrial data, a preliminary detailed scheme of chemical transformations of catalytic isomerization reactions of the pentane-hexane fraction has been established. The kinetic equations have been developed, on the basis of which an adequate mathematical model of the reactor unit of the process under investigation has been chosen. The next stage of work will be the refinement of the kinetic constants and verification of the mathematical model of the reactor in a wide range of variations in the initial reagents and process parameters. That in the subsequent stages will allow to carry out the predicted calculations, to select the optimal

technological conditions taking into account the multi-purpose optimization of the catalytic isomerization of the pentane-hexane fraction.

5. References

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