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Simulation of Light Naphtha Isomerization Process

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Abstract

An approach to modeling the isomerization process implemented in the technological scheme with the maximum normal paraffins conversion was described. The comprehensive mathematical model was designed as a powerful tool for optimization. It is based on the influence of the feedstock composition for assessment of the current catalyst activity. According to the calculations, the optimal operating parameters are determined by the refined feedstock composition.

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Keywords: isomerization, catalyst, mathematical simulation.

1. Introduction

The decrease in aromatic hydrocarbon content of gasoline can be achieved by blending reformate, alkylate and isomerate while meeting high octane rating[1]. Also the isomerization process allows refining the low octane light fractions thereby increasing the overall yield of gasoline. However the maximum conversion of low octane C_6 hydrocarbons into high octane dimethylbutanes corresponds to low process temperature which reduces the kinetic factor of reactants conversion. Currently, a great number of works are devoted to the synthesis and experimental study of new catalysts for the isomerization[9 - 11], besides a lot of attention is paid to the study of the hydrocarbons conversion mechanism during the catalytic isomerization process[14, 16]. According to[13, 19], the main problems arise in

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the study of the mechanism of carbenium ion formation, catalyst acidity role of different promoters and hydrogen in the process. Optimization and prediction of light naphtha isomerization process is a complex technological problem. The most effective solution of this problem is the use of mathematical simulation method of physical and chemical laws of the process.

2. Research object

Among the multifold of isomerization process flow diagrams the most effective is «Isomalk-2» technology with platinum oxide catalyst which has considerably higher efficiency than the Pt/zeolite catalysts, as well as high resistance in comparison with Pt/Al_2O_3-Cl systems[2, 20]. Depending on the flow structure «Isomalk-2» technology allows obtaining a product with RON from 82 to 92 points. Light straight-run gasoline fraction NBP-62 °C is used as feedstock. Complete conversion of pentane-hexane fraction is provided by two recycle process scheme for unbranched pentane and hexane (Fig. 1).

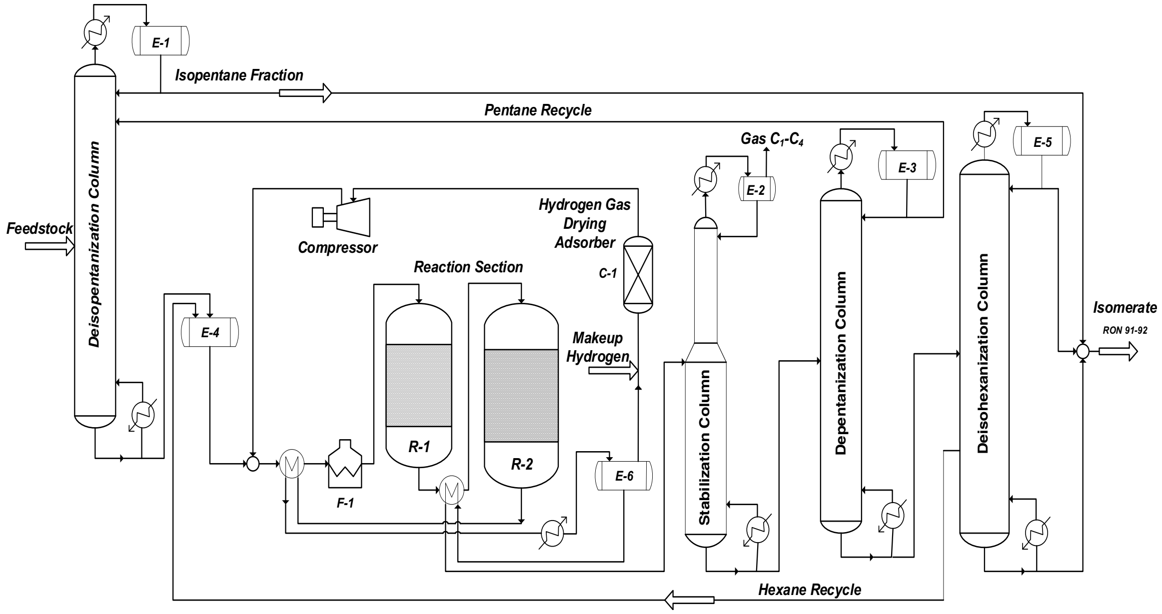

Fig. 1. Light straight run naphtha isomerization process flow diagram

The hydrotreated feedstock enters the column of the deisopentanizator for isopentane fraction separation, and then after blending with the deisohexanizator the side cut flows to E – 4, and then with makeup hydrogen passes the preheater, the combined feed successively passes the two isomerization reactors R-1, R-2. The hydrogen separation occurs in E-6 separator, after that hydrogen is mixed with the fresh hydrogen stream, and passes through the adsorption drying unit (C-1 adsorber) and is fed to the reception of the circulation compressor. The off gases C_1 - C_4 are separated in the stabilizer column. The stable isomerate enters the depentenization column for pentane fraction separation. The depentanized isomerate is then supplied to the deisohexanization column, where the mixture of unconverted unbranched C_6 hydrocarbons is separated as a side cut flow. This flow structure allows maximizing the potential of «Izomalk-2» technology. Implementation of pentene and hexane recycles can help to achieve the 91-92 point isocomponent RON.

3. Methods

According to the established methodology[3 - 5, 12] the mathematical model design is a sequential application of the thermodynamic and kinetic analysis, simulation of the reactor and chemical-technological system in general. Using the experimental data on the hydrocarbon composition of material streams and operation parameters from industrial light naphtha isomerization unit «Kinef» the effective rate constants for the chemical reactions were found by solving the reverse kinetic problem. Complete mathematical description of the process is based on the component-wise material and heat balances[6 - 8].Section headings

$$G\cdot\frac{\partial C_i}{\partial Z}+G\cdot\frac{\partial C_i}{\partial V}=\sum_{j=1}^{m}a_j\cdot r_j$$

$$G\cdot\frac{\partial T}{\partial Z}+G\cdot\frac{\partial T}{\partial V}=\frac{1}{\rho\cdot C_p^m}\cdot\sum_{j=1}^{m}Q_j\cdot a_j\cdot r_j \qquad (1)$$

if Z=0, C=0, where r=0, C=C$_0$, if Z=0, T=T$_0$, where r=0, T=T$_{in}$;

G is raw material flow rate, m^3/h; z = G*t (t is time of catalyst work from the new catalyst load, h); C$_i$ is concentration of ith component, mol/m^3; V is volume of the catalyst layer,m^3; a is catalyst activity; ρ is density of mixture, kg/m^3; Cmp is heat capacity of mixture, J/(kg*K); Qj is jth reaction heat, J/mol, T is temperature, K; r$_j$ is jth reaction rate, mol/(m^3 h).

In the multicomponent distillation calculation the number of theoretical stages, position of the feed stage, and reflux rate were selected as independent parameters. Equilibrium compositions are determined from the relations:

$$y_i^*=\alpha_i x_i/\sum_{i=1}^{b}\alpha_i x_i;\quad x_i^*=(y_i/\alpha_i)/\sum_{i=1}^{b}y_i/\alpha_i \qquad (2)$$

The equations describing the multi-component distillation are written in the following form:

$$Fx_{F,i}=Px_{P,i}+Wx_{W,i}; \qquad (3)$$

$$Gy_{n-1,i}=Lx_{n,i}+Px_{P,i} \qquad (n>f); \qquad (4)$$

$$Lx_{n,i}=Gy_{n-1,i}++Wx_{W,i} \qquad (n\geq f); \qquad (5)$$

Software implementation of the model is made in the IDE Delphi 7[4, 5]. The initial data for the calculation are the composition of the feedstock and process operating parameters. Assessment of adequacy of the calculation results to the experimental data from the industrial isomerization unit showed lower deviations of calculated values from the experimental ones comparable to the accuracy in the chromatographic analysis. The mathematical model of the isomerization process allows evaluating the impact of the feedstock composition changes, change in feed rate, fluctuations in temperature of the reactor block to improve the resource efficiency of the process and obtain a product of the given quality[4, 5].

4. Results and discussion

The composition of raw materials processed at the light naphtha isomerization unit «Kinef» varies widely, it certainly affects the quality of the products and also makes it necessary to adjust the technological parameters of the unit. Investigation of the influence of the feedstock on the quality of isomerate was performed at constant process parameters (Table 1).

Table 1. Process operating parameters

Feed rate, kg/h	36000
Inlet Reactor Temperature, °C	136
Inlet Reactor Pressure, kg/cm^2	31

The results of investigations are shown in Table 2.

According to the results which are shown in Table 2 isomerate RON can range from 2 to 2.5 points depending on the feedstock composition.

The light naphtha isomerization process is an equilibrium process, and the quality of the obtained product depends on the position of the major and side reaction equilibrium. With increasing temperature the target and side reaction speed rise. The results of predictive calculations are presented in Fig. 2.

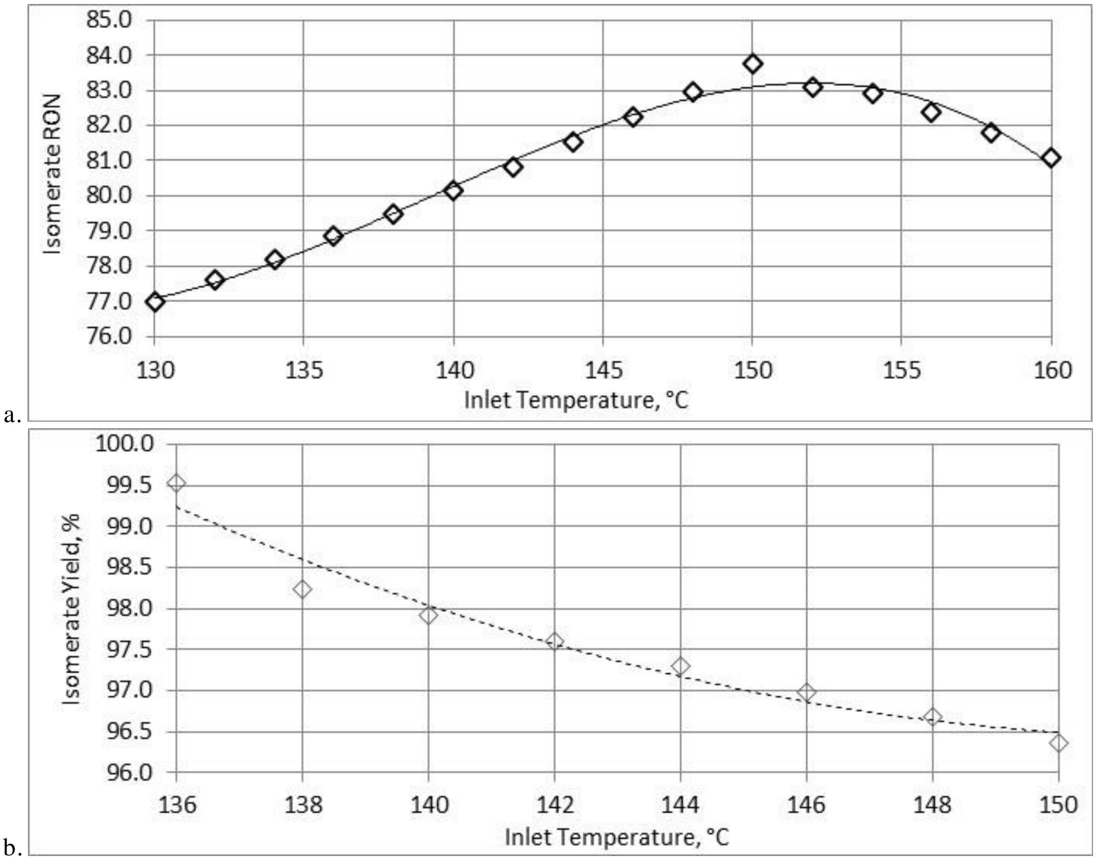

Fig. 2. (a) Temperature influence. (b) Isomerate yield.

According to the results of the studies the temperature increase at the inlet of the first isomerization reactor above 150 ° C leads to a shift of the equilibrium towards the hydrocracking side reactions (Fig. 2 B).

When the load of raw materials increases at the isomerization reactor unit, the time of contact with the catalyst raw materials decreases, and the octane number of the resulting isomerate reduces. The expected impact of the calculated load of raw materials on RON hexane isomerate is shown in Fig. 3.

Table2. The isomerate composition in dependence on different feedstock.

Component	16.12.2014	01.07.2014	17.03.2014	13.10.2014	16.05.2015	06.03.2015
n-pentane	38.60	35.87	35.41	30.84	34.20	33.15
i-pentane	13.49	9.78	12.87	18.21	12.99	12.12
n-hexane	12.49	18.48	16.32	15.31	16.34	17.37
2-MP	12.03	14.13	14.02	12.01	14.39	14.87
3-MP	6.44	7.61	7.93	6.79	8.25	8.48
2,2-DMB	0.59	0.00	0.44	0.24	0.31	0.30
2,3-DMB	1.44	1.09	1.73	1.39	1.82	1.96
n- heptane	2.80	0.00	0.00	0.00	0.01	0.00
i-C_7 sum	0.15	0.00	0.03	0.15	0.09	0.19
C_8 sum	0.00	0.00	0.00	0.00	0.00	0.00
Cyclopentane	4.15	3.26	4.06	3.82	3.92	3.72
MCP	5.15	7.61	5.33	6.48	5.63	6.35
Cyclohexane	1.37	1.09	0.35	1.36	0.69	0.00
Benzene	1.19	1.09	1.38	1.19	1.34	1.44
RON	***80.97***	***80.10***	***81.27***	***82.34***	***81.17***	***80.89***

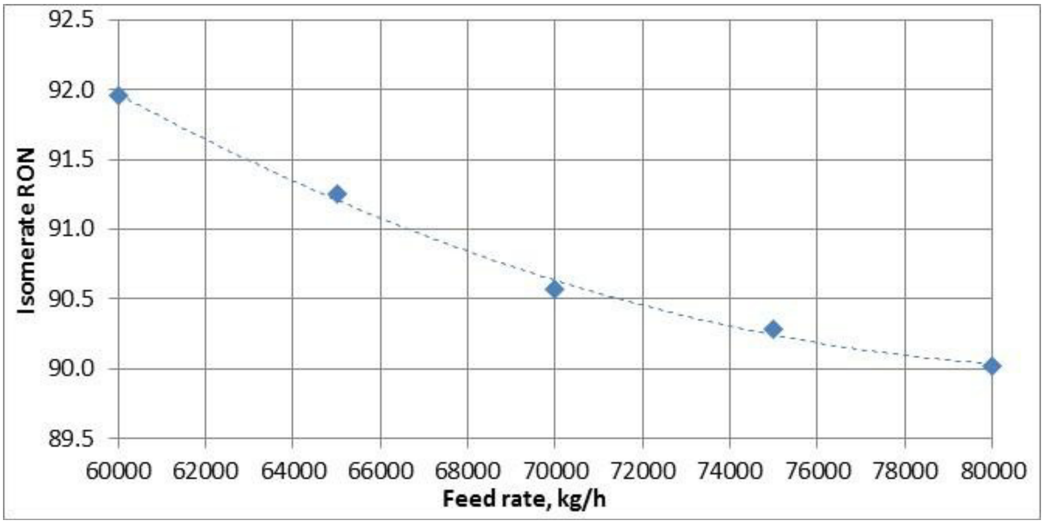

Fig. 3. The feed rate influence on isomerate RON

According to the results of the studies with increasing loading of raw materials per 2500 m / h RON isomerate reduces by 0.43 - 0.5 point depending on the feedstock composition.

5. Conclusion

1. The predicting calculations of the feedstock composition influence on the isomerate quality showed that octane rating can vary by 2 - 2.5 points depending on the feed composition.
2. The increase in the isomerization reactor block temperature results in an equilibrium displacement towards the hydrocracking side reactions and reduces the yield of isomerate.
3. The increase in feedstock charging reduces the feed contact time with catalyst: the increase in feedstock charging for every 5000 tons / h results in isomerate RON reduction by 0.43 - 0.5 points depending on the feedstock composition.
4. The transition from once-through isomerization to Izomalk-2 technology will increase the isomerate octane number by 10 - 12 points.

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