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Optimal fractionation of products of refining straight-run gasoline on zeolite catalyst with account of its deactivation

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Abstract

Flowsheet of industrial refining straight-run gasoline on zeolite catalyst includes the necessary stage of fractionation of conversion products to produce commercial gasoline, gas and heavy residue. Changes in qualitative and quantitative compositions of the catalytic conversion products under catalyst deactivation require current parametrical optimization of this stage. Objective functions that take into account catalyst deactivation and the constrains depending on the requirements for product quality and equipment specifications were developed. Optimal conditions were found to differ significantly from those designed for fresh catalyst.

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Keywords: refining straight-run gasoline; fractionation; current optimization; objective function; catalyst deactivation.

1. Introduction

Due to the one – step process and low catalyst sensitivity to sulfur, which is contained in the feed stream, it is effective to produce high octane gasoline and its components by hydrogen–free technology on zeolite catalysts[1-3].

Typical industrial technology of the process consists of a reactor unit, fractionation unit (Fig. 1) and gas preparation unit for catalyst regeneration.

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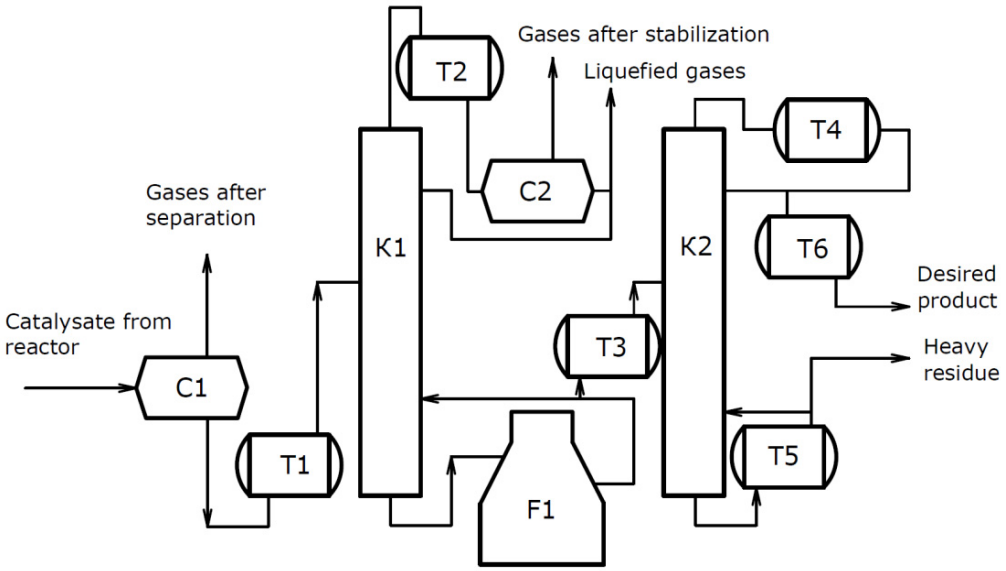

Fig. 1. Fractionation unit flowsheet

Where C1, C2 – separators;
T1, T2, T3, T4, T5 – heat exchangers;
K1 – stripping column;
K2 – distillation column;
F1 – furnace.

In hydrogen–free medium fast coke formation leading to catalyst deactivation is the key drawback of zeolite catalysts[4].

Composition of the products of catalytic conversion, which enters separation, changes because of catalyst activity reduction that requires current optimization of the fractionation unit performance during operation time.

Industrial process can be optimized by evolutionary methods with constraints on the parameters, related to the physical, structural or economic considerations, under conditions of temporary drift of the optimum operating point[5]. The authors[6-9] described examples of uses of evolutionary optimization in chemical technology for modeling and identification of parameters for optimal control of chemical engineering processes. Evolutionary methods are useful when upper and lower bounds of the independent variables are known precisely. Precise limits on the quantitative and qualitative composition of the products are generally unknown in the case of reducing catalyst activity, so it limits the possibility of using these methods.

To optimize processes without constrains on the parameters, interactive methods of the multi–objective optimization with different options of online interaction with decision makers are used[10]. These methods do not require exact bounds of parameter variations. Optimization is performed with a set of conflicting objective functions that provides consideration of all possible aspects effecting on the process behavior. In this case, there is no need to select one criterion, meeting all requirements.

Decision maker participation makes them effective for design and development of optimal control systems. Regardless of their simplicity, usage of these methods implies selection of one qualified solutions from a number of optimal ones at several stages. Decision maker is expected to have appropriate level of knowledge and qualification, which is not always available in an industrial unit.

The general technics which have been developed to optimize separation sequences included heuristic rules, based on practical experience. Heuristic rules have been found useful for optimal synthesis of homogeneous sequences, such as heat exchangers or distillation columns[11].

The main features of optimization of industrial fractionation unit under catalyst deactivation are:

- Unknown bounds of the composition change with operation time;
- Necessity to take into account structure of the flowsheet and specifications of the equipment.

The aim of the work is to develop the objective function and constrains, considering features mentioned above and to execute optimization on first principle model of the process.

2. **Experimental part**

To achieve this goal, the authors solved the following tasks:

1) The first principle model of the fractionation unit was developed in the Aspen HYSYS in accordance with the flowsheet (Figure 1);

2) The objective functions based on technological criteria were formed for the separators, the stripping and the distillation columns;

3) A list of constrains was described, which included requirements for the products quality and equipment specifications;

4) Optimal conditions were step-by-step searched for each process.

3. **Results**

To maintain the octane number of the gasoline at a fixed level, the temperature in the reactor is increased as a result of the catalyst deactivation, thereby the composition of the product, which is fed to fractionation unit[12], changes, in particular, the amount of light hydrocarbons increases significantly (Table 1).

Table 1. The concentration of light hydrocarbons in the gas fraction of the product depending on the temperature in the reactor

Concentration, wt.%	Temperature of reaction, °C			
	365	405	435	465
Hydrogen	0.004	0.004	0.06	0.024
Methane	0.24	0.76	2.67	2.01
Ethane	0.84	2.71	6.96	4.93
Ethylene	0.51	0.68	0.91	1.37
Propane	33.03	56.74	68.1	39.78

To maintain maximum yield and quality of target products, it is necessary to optimize the process parameters in the equipment of the fractionation unit.

In accordance with the structure of the flowsheet, the problem of step-by-step optimization was solved, where the optimal output parameters of the previous unit served as input in the subsequent unit.

For each unit, an objective function and a set of constraints were formed in the form of (1):

$$\max R_j(x) \tag{1}$$

$$n_j = const$$
$$x = f_j(n, P)$$
$$P_j^L \le P_j \le P_j^U$$

where $R_j(x)$ – the objective functions for the j–th unit;
x – vector of the flow rates and concentrations of the components;
n_j – design parameters of the j–th unit;
P_j – technological parameters of the j–th unit;

P_j^L, P_j^U – lower and upper bounds of process parameters according to certificate characteristics of the equipment.

The objective function takes into account the change in the composition and flow rate of the process stream as a result of catalyst deactivation. Heuristic rules for each unit of the equipments of the flowsheet used in the formation of the objective functions are given below:

• Heuristic rules for the separator C1:

1) Gases from separation should contain the maximum possible quantity of C_1, C_2, and H_2

2) The liquid leaving the separator should contain the maximum quantity of C_3, C_4 and the minimum quantity C_1, C_2, and H_2.

3) The output of the liquid from the separator should be maximum.

• Heuristic rules for the stripping column K1:

1) The stabilized flow, which enters the T3, should contain the maximum quantity of C_4;

2) The hydrocarbon gases and liquefied gases should contain the minimal amount of C_5;

3) The rate of the stabilized flow, which enters the T3, should be maximum.

• Heuristic rules for the distillation column K2:

1) The properties of gasoline should meet the state standard requirements

2) Flow rate of the gasoline, which enters the T6, should be maximum.

The objective function and a set of constraints for the separator are given below:

$$R_{opt} = \frac{G^{(l)} \cdot c_4^{(l)} \cdot c_5^{(l)}}{G^{(g)} \cdot c_4^{(g)} \cdot c_5^{(g)} \cdot (\sum c_1^{(g)}, c_2^{(g)}, H_2^{(g)})} \to \max \tag{2}$$

$P = 1{,}37$

$G_V = 154818$

$-20 \le T \le +70$

$14794 \le G_L \le 73968$

where $G^{(l)}$, $G^{(g)}$, – liquid and gas loads on the separator, respectively, (kg / h);

$c_4^{(l)}, c_5^{(l)}$ – the total concentration of butanes, pentanes, respectively, in the liquid phase of product flow, (kg–mol / h);

$c_1^{(g)}, c_2^{(g)}, H_2^{(g)}, c_4^{(g)}, c_5^{(g)}$ – concentration of methane, ethane, hydrogen, the total concentration of the pentanes, respectively, in the gas phase of product flow (kg–mol / h);

P – pressure in the separator, MPa;

T – temperature in the separator, °C;

G_V – flow rate of liquid, kg / h;

G_L – flow rate of gas, kg / h.

4. **Discussion**

The objective functions Ropt were formulated, taking into account the composition and flow rates of the streams, which leave the fractionation unit. Optimal operational conditions for the separator allow obtaining liquid stream enriched with hydrocarbon C4 and C5 for subsequent stabilization under conditions of changing activity of the catalyst.

The found optimum conditions in the separator C1 of the product flows obtained at reaction temperature of 365, 405 and 415°C,and reaction pressure of 0,15 MPa are different. Their comparison with the designed ones is shown in Table 2.

Table 2. Designed and optimal parameters in the separator C1 for product flows, obtained at different temperatures

Parameter	Design interval	Temperature of catalysate, °C		
		365	405	415
Temperature, °C	55	50	40	30
Pressure, MPa	0.9	0.5	0.8	0.9
Charge of liquid, kg/h	3407–3750	3248	3362	3524
Charge of gas, kg/h	0–343	483	369	207

5. **Conclusion**

The following conclusions may be made due to the obtained results:

1. In the given paper the algorithm of step-by-step optimization is proposed, which is based on the structure of the flowsheet and constrains on the parameters of the process under varying compositions and flow rates of product.

2. For the process of the refining of straight-run gasoline on zeolite catalysts, heuristic rules are formulated and objective functions are described taking into account changes in the activity of the catalyst.

3. The operation of the fractionation unit is optimized.

4. Significant differences are found between designed and optimal operational parameters of the unit.

References

1. Stepanov V.G., Ione K.G.; *Chem. and Tech. of Fuels and Oils*. 2000; **1**: p.8–12 (In Russian).
2. Klimov O.V, Aksenov D.G., Echevsky G.V., Meged A.A, Korsakov C.N, Adzjiev A.J.; *Ref. and Petrochem.* 2004; **3**: 19–25 (In Russian).
3. Velichkina L.M., Vosmerikov A.V., Korobitsyna L.L., Ermakov A.E.; *Ref. and Petrochem.* 2002; **11**: 19–25 (In Russian).
4. Terentiev A.I., Yurkin N.A., Hlytin A.L., Vosmerikov A.V., Barbashin Y.E. *Himicheskaya tekhnika.* 2012; **1**: 34 (In Russian).
5. Pham Q.T. URL: http://www.ceic.unsw.edu.au/staff/Tuan_Pham/Ts.pdf
6. Pham Q.T. and Coulter S.; *Proc. Int. Congress of Refrig.* 1995, **3a**: 676–683.
7. Moros R., Kalies H., Rex H.G., Schaffarczyk S.; *Computers & Chem. Engineering*. 1997; **20**: 1257–1270.
8. Li Y., Haubler A.; *Artificial Intelligence in Engineering.* 1996; **10**: 143–152.
9. Jones A.H., P.B. De Moura Oliveria ; *Proc. First IEE/IEEE Internat. Conference GA's in Engineering Systems: Innovations and Applications*, Sheffield, UK. 1995; p.141–145.
10. Miettinen, K. & Hakanen, J.; *World Scientific / Techniques and Applications in Chemical Engineering.* 2009; p. 153-188.
11. Nadgir V.M., Liu Y.A. , *AlChE Journal*. 1983, p.926-934 .
12. Agabalyan L.G., Hadzjiev S.N., Rogovskaya N.H. Golod A.N., Ione K.G., Stepanov V.G.; *Chem. and Tech. of Fuels and Oils*. 1998; **5**: 6–7 (In Russian).