

BIFUNCTIONAL Pt-Re REFORMING CATALYSTS PROPERTIES MODELLING

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Received September 9, 2016; Accepted November 2, 2016

Abstract

In this paper the industrial characteristics of the bifunctional Pt-Re reforming catalysts were studied with mathematical model. The results of the main control parameters influencing catalyst activity during operation cycle, such as the temperature, organochlorine compounds, and water amount were given. The calculation methodology development of the optimal water and chlorine supply into the reforming reactor by means of the physical and chemical nature research of this phenomenon in order to increase the industrial unit resource efficiency was proposed. The authors calculated and showed how to control the chlorine supply into the reactor for maintaining the optimum molar ratio of these components on the catalyst depending on the process temperature and varying flow rates. It was proved that the optimum organochlorine supply depends on the process temperature, system humidity, and recycled raw material volume. The methodology allows decreasing process financial costs by increasing installation work cycle.

Keywords: catalytic reforming; mathematical modeling; Pt-Re catalyst; optimal activity.

1. Introduction

The metal and acid activities balance is the most important condition for bifunctional reforming catalysts operation [1]. Organochlorine compounds fed into the reactor and transformed into hydrogen chloride promote hydrocarbon conversion selectivity increasing on the surface, and thereby the raw material processing depth increases.

The control parameters influencing catalyst activity during operation cycle are the temperature and amount of promoters fed into the reactor-organochlorine compounds and water [2-3]. The chlorine amount on the catalyst surface is determined by thermodynamic equilibrium of chlorine atoms chemisorption process and depends only on the water and hydrogen chloride molar ratio in the reaction zone, the temperature in the catalyst layer, and on the catalyst surface deactivation degree because of coke formation, poisoning and aging processes. For a resource efficiency reforming reactor increase, the method for chlorine amount calculation is necessary during operation cycle considering both the hydrocarbon raw material composition variability and catalyst activity changes.

The industrial operation experience of reforming units has shown that the chlorine deficiency leads to a catalyst activity decrease in the important alkane isomerization reactions, which has negative impact on the product quality [4-6]. The chlorine loss also promotes the platinum centers deactivation process acceleration that leads to the catalyst activity losses in the paraffin dehydrocyclization reactions and process selectivity [7]. On the contrary, an excessive chlorine amount could result in a catalyst acid activity increase and, as a consequence, paraffin hydrocracking reactions acceleration that can cause a process selectivity decrease, a light hydrocarbon proportion increase (methane and ethane) in the circulating hydrogen containing gas and higher hydrogen consumption [8-10].

A water supply increase [11] with a process temperature rise and coke accumulation on the catalyst comparing to its supply in the constant initial amount allows prolonging the catalyst operation and improving the process characteristic that may improve its efficiency. Herewith non-steady water supply mode in the reaction zone depends on the catalyst type, its chemical composition, raw material hydrocarbon composition, process technological conditions: temperature and pressure.

All these aspects determine the actuality of the optimal water and chlorine supply calculation methodology development into the reforming reactor by the research of this phenomenon physical and chemical nature in order to increase the industrial unit resource efficiency.

2. The object of study

The object of study is the industrial catalytic reforming unit L-35-11/600 with raw material capacity of 600 000 tons per year. The unit purpose is catalytic reforming of gasoline fractions (85-180°C) to obtain high-octane component for gasoline preparation or catalytic reforming of 105-127°C fractions to obtain xylenes.

The reforming unit L-35-11/600 includes the next technological blocks for:

- preliminary raw material hydrotreating;
- catalytic reforming;
- product stabilization;
- hydrogen-containing gas drying and zeolite regeneration;
- raw material;
- reforming catalyst chlorination and hydration;
- protective solution preparation and supply for hydrotreating unit equipment corrosion suppression.

In August 2014 in the L-35-11/600 unit the fresh Pt-Re catalyst RG-682 was loaded with the catalysts PK-P1, RG-582, and PR-71.

3. Methods

Mathematical modelling method was used for research calculations. A new approach based on the industrial and computational experiments combination with quantum-chemical calculation methods was applied for water effect mechanism determination of the process and theoretical base development. Water influence as a promoter and active component in the conversion reaction of coke-containing structures was assumed.

Further, the thermodynamic analysis of coke-containing structures conversion reaction with water was carried out with Gaussian'03 and HyperChem programs based on quantum-chemical modelling method.



The thermodynamic reaction characteristics for this reaction are shown in Tab. 1.

Table. Thermodynamic reaction characteristic

| ΔG_r , kJ/mol | ΔH_r , kJ/mol | ΔS_r , kJ/(mol·K) |
|-----------------------|-----------------------|---------------------------|
| -50,84 | 145 | 0,26 |

3.1. The methodology of optimal water supply calculation in a reactor

The equilibrium constant value is calculated from the equation:

$$\ln K_p = -\frac{\Delta G}{RT} \Rightarrow K_{ip} = \exp\left(-\frac{\Delta G}{RT_i}\right)$$

The equation of conversion degree dependence on the equilibrium constant:

$$K_p = \frac{P_{CO}^{28} \cdot P_{H_2}^{35}}{P_{H_2O}^{28}} = \frac{P_{com}^{35} \cdot x_{CO}^{28} \cdot x_{H_2}^{35}}{x_{H_2O}^{28}} = \frac{P_{com}^{35} \cdot n_{CO}^{28} \cdot n_{H_2}^{35}}{n_{H_2O}^{28}} \cdot \frac{1}{n_{com}^{35}}$$

where x – molar component part in a mixture.

$$K_p = \frac{P_{com}^{35} \cdot n_{CO}^{28} \cdot n_{H_2}^{35}}{n_{H_2O}^{28}} \cdot \frac{1}{n_{com}^{35}} = \frac{P_{com}^{35} \cdot (n'_{H_2O} \cdot a)^{28} \cdot (1.25 \cdot n'_{H_2O} \cdot a)^{35}}{(n'_{H_2O} \cdot (1-a))^{28}} \cdot \frac{1}{(n'_{H_2O} \cdot a + 1.25 \cdot n'_{H_2O} \cdot a + n'_{H_2O} \cdot (1-a))^{35}} = \frac{a^{63} \cdot 1.25^{35}}{(1-a)^{28}} \cdot \frac{P_{com}^{35}}{(1.25 \cdot a + 1)^{35}}$$

where: a – process conversion; n'H₂O – initial amount of water moles;

The equilibrium concentrations of CO and H₂ expressed via the initial water concentration and conversion are described by the equations:

$$n_{iCO}^* = n_{iH_2O} \cdot x_i \quad \text{where: } n_{iCO}^* \text{ - equilibrium CO amount at } T_i, n_{iH_2}^* \text{ - mol; equilibrium H}_2 \text{ amount at } T_i, \text{ mol; } n_{iH_2O}^* \text{ - equilibrium H}_2\text{O amount at } T_i, n_{iH_2}^* \text{ - mol; conversion at } T_i$$

$$n_{iH_2}^* = 1.25 \cdot n_{iH_2O} \cdot x_i$$

Amounting to the equilibrium constant expressed via ΔG and equilibrium component moles:

$$K_{ip} = \frac{P_{com}^{35} \cdot n_{iH_2O}^{63} \cdot x_1^{63} \cdot 1.25^{35}}{(n_{iH_2O} \cdot (1-x_i))^{28}} \cdot \frac{1}{(2.25 \cdot n_{iH_2O} \cdot x_1 + n_{iH_2O} \cdot (1-x_i))^{35}}$$

$$K_{ip} = \exp\left(-\frac{\Delta G}{RT_i}\right)$$

$$\frac{P_{com}^{35} \cdot n_{iH_2O}^{63} \cdot x_1^{63} \cdot 1.25^{35}}{(n_{iH_2O} \cdot (1-x_i))^{28}} \cdot \frac{1}{(2.25 \cdot n_{iH_2O} \cdot x_1 + n_{iH_2O} \cdot (1-x_i))^{35}} = \exp\left(-\frac{\Delta G}{RT_i}\right)$$

4. Experimental part

According to this methodology the equilibrium constant and conversion degree of amorphous coke-containing structure with water in the temperature range from 753 to 773 K were calculated.

The catalytic reforming unit L-35-11/600 data were used for calculations, the optimum water supply is 0.3 L/h in the beginning of the cycle, the optimum chlorine supply is 1 ppm. These water and chlorine supplies provide the optimum water/chlorine molar ratio on the catalyst (Mw/cl=20). The results are given in Table 2.

Table 2. Temperature effect on the conversion, water consumption and chlorine supply to the reforming reactor

| Temperature, K | Conversion degree X, % | Water, L/h | Optimum Cl supply, ppm | CO, ppm |
|----------------|------------------------|------------|------------------------|---------|
| 753 | 5,10 | 0,3 | 1,00 | 0,2419 |
| 756 | 5,37 | 0,33 | 1,15 | 0,2831 |
| 759 | 5,65 | 0,36 | 1,30 | 0,3280 |
| 762 | 5,95 | 0,40 | 1,45 | 0,3770 |
| 765 | 6,25 | 0,43 | 1,60 | 0,4303 |
| 768 | 6,57 | 0,46 | 1,75 | 0,4882 |
| 771 | 6,90 | 0,49 | 1,90 | 0,5509 |
| 773 | 7,13 | 0,51 | 2,00 | 0,5955 |

As it is shown in Table 2, with changing process temperature from 753 to 773K, the conversion degree varies in the range from 5.1 to 7.13 %. Therefore, at each specific temperature there is an optimum amount of water, which is necessary to supply to the reactor to maintain the maximum conversion reaction. In this case water supply changes in the range from 0.3 to 0.51 L/h. Water supply that is more or less than the optimum amount leads to a desired product yield decrease in both cases.

In addition, with water supply change it is necessary to regulate the chlorine supply into the reactor to maintain the optimum water/chlorine molar ratio on the catalyst. According to the calculation results, the optimum chlorine supply varies from 1 to 2 ppm.

4.1. The coke formation dynamic change under the conditions of the optimum water supply to the reactor unit

In this paper the changes of the L-35-11/600 unit technological mode were analyzed. From this analysis it follows that since the last catalyst RG-682A regeneration (November 2015), the unit worked on a wide fraction up to 07.02.16. The process temperature and pressure change in the range from 482°C to 493°C and from 21.5 to 24.5 kgs/m² respectively.

From 17.02.2016 until the present time the 105-127°C fraction is recycled as raw material on the unit. The process temperature changes with different raw material types are given in Fig. 1, 2.

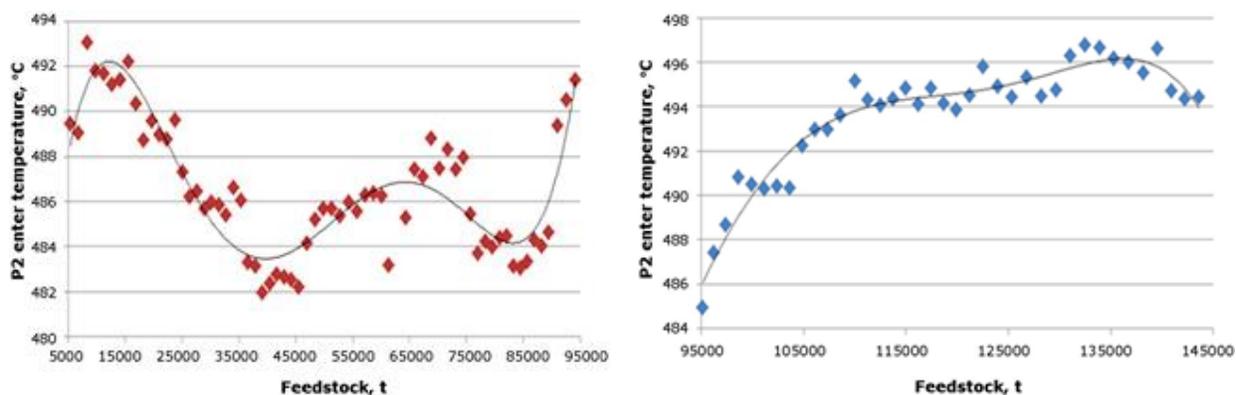


Fig. 1, 2. Process temperature changes during processing of 85-180 °C and 105-127 °C

As it is shown in Fig.1, 2, the process temperature is higher and changes in the range from 485 to 497°C in recycling the fraction. The hydrocarbon composition of the raw material is given in Tab. 3.

Table 3. Hydrocarbon composition of raw material and product

| Components | 03.12.2015 | | 05.01.2016 | | 01.02.2016 | | 04.03.2016 | |
|---------------------------|--------------|---------|--------------|---------|--------------|---------|--------------|---------|
| | Raw material | Product |
| Paraffins | 23,38 | 9,87 | 23,55 | 9,46 | 22,67 | 9,36 | 26,41 | 8,23 |
| Isoparaffins | 33,39 | 25,56 | 33,08 | 25,98 | 32,57 | 25,91 | 32,57 | 23,66 |
| Aromatics | 13,98 | 61,85 | 14,06 | 62,25 | 12,36 | 62,54 | 5,27 | 66,44 |
| Naphthenes | 28,38 | 2,34 | 28,40 | 1,87 | 31,61 | 1,87 | 35,53 | 1,49 |
| Olefins | 0,12 | 0,34 | 0,20 | 0,16 | 0,25 | 0,19 | 0,14 | 0,12 |
| Unidentified hydrocarbons | 0,75 | 0,04 | 0,71 | 0,28 | 0,54 | 0,13 | 0,08 | 0,06 |

On the basis of the data in Table 3, it could be noticed that with long distillate (85-180°C) processing raw material and product composition did not change. The iso-paraffinic and naphthenic hydrocarbons contents in the raw material were 32.5-33 % and 28-31 % wt respectively. The aromatic component changed in the range from 62 to 63 % wt. When the installation was switched to the narrow cut, in the raw material (04.03.2016) the paraffinic and naphthenic hydrocarbons contents increased to 26 and 36 % wt respectively. The aromatic 66 % wt hydrocarbon percentage prevails in the product.

With the computer program complex [15-16] «Aktiv» and L-35-11/600 unit technological data, the coke content on the catalyst and its change depending on temperature and raw material volume were calculated (Fig. 3).

Further, according to the method described in the previous chapter the optimum water supply in the reactor is calculated with the technological data. In Fig. 4 the data with humidity system at the current and optimum water supply dynamics are compared.

It can be observed from the data, that the system humidity with the optimum water supply changes from 21 to 31 ppm depending on temperature.

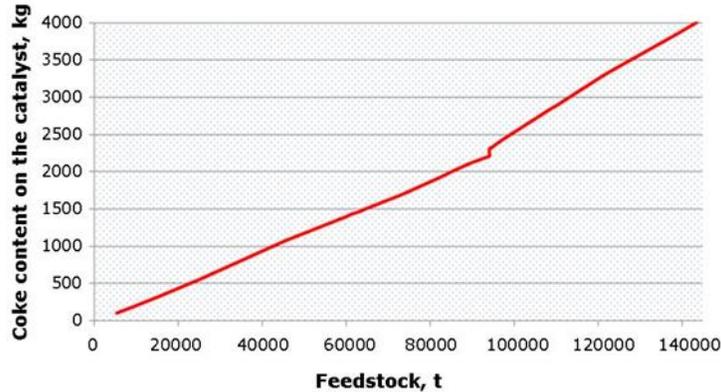


Fig. 3. Coke accumulation dynamics on the reforming catalyst at the L-35-11/600 unit in period 28.11.2015 – 31.03.2016

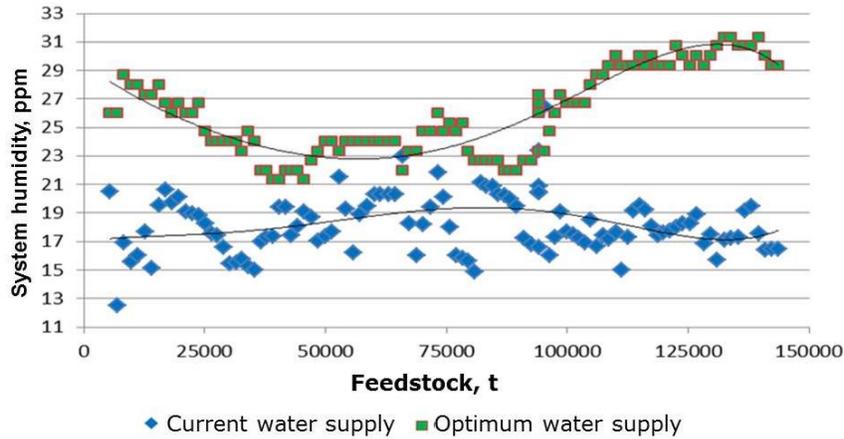


Fig. 4. System humidity comparison with current and optimum water supply

According to Tab. 2 and calculations, the differentiated water supply (at the moment of calculations about 145 thousand tons of the raw material was recycled) will reduce coke content by 300 kg compared with the current values of the current coke content under these conditions (Fig. 5).

As it was mentioned above, with the water supply change, it is necessary to regulate the chlorine supply to the reactor for the optimum water/chlorine molar ratio on the catalyst. It is shown in Fig. 6 how the chlorine content on the catalyst in the period of calculation and the optimum chlorine supply according to the calculation methodology change.

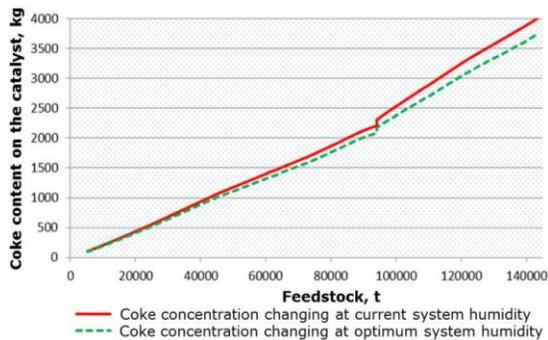


Fig. 5. Coke concentration changing on the catalyst in the current and the optimal humidity

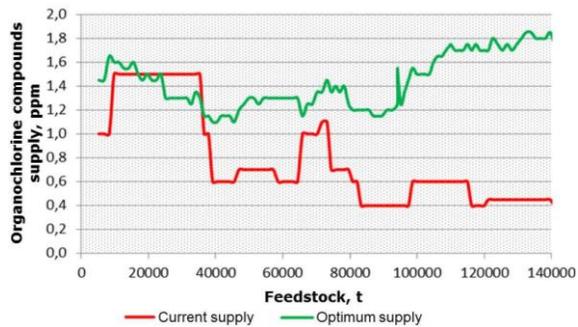


Fig. 6. Comparison of the current and optimum organochlorine supply

5. Conclusions

According to the methodology, the optimum organochlorine supply depends on the process temperature, system humidity, and recycled raw material volume.

This methodology of the optimum water and chlorine supply to the catalyst allows decreasing process financial costs by increasing installation work cycle.

Thus, the computer program complex «Aktiv» allowed:

- predicting the coke formation dynamics;
- decreasing the coke accumulation weight on the catalyst by balanced water and chlorine supply in the process area;
- decreasing process financial costs by increasing installation work cycle.

References

- [1] Rahimpour MR, Jafari M, Iranshahi D. Progress in catalytic naphtha reforming process: A review. *Applied Energy*, 2013; 103(C): 79-93.
- [2] Stijepovic MZ, Ostojic AV, Milenkovic I, Linke P. Development of a kinetic model for catalytic reforming of naphtha and parameter estimation using industrial plant data. *Energy Fuels* 2009; 23: 979–83.
- [3] Rodríguez MA, Ancheyta J. Detailed description of kinetic and reactor modeling for naphtha catalytic reforming. *Fuel* 2011; 90: 3492–508.
- [4] Ancheyta-Juarez J, Villafuerte-Macias E. Kinetic modeling of naphtha catalytic reforming reactions. *Energy Fuels* 2000; 14: 1032–7.
- [5] Frantsina EV, Ivashkina EN, Ivanchina ED, Romanovsky RV. Developing of the mathematical model for controlling the operation of alkane dehydrogenation catalyst in production of linear alkyl benzene. *Chemical Engineering Journal*, 2014; 238: 129-139.
- [6] Smith R. Kinetic analysis of naphtha reforming with platinum catalyst. *Chem Eng Prog* 1959; 55: 76–80.
- [7] Jenkins JH, Stephens TW. Kinetics of cat reforming. *Hydrocarbon Proc* 1980; 1: 163.
- [8] Froment G. The kinetic of complex catalytic reactions. *Chem Eng Sci* 1987; 42: 1073.
- [9] Dolganova IO, Dolganov IM, Ivashkina EN, Ivanchina ED, Romanovskiy RV. Development of approach to modelling and optimization of non-stationary catalytic processes in oil refining and petrochemistry. *Polish Journal of Chemical Technology*, 2012; 14: 22-29.
- [10] Yakupova IV, Chernjakova ES (Sharova), Ivanchina ED, Belyj AS, Smolikov MD. Performance Prediction of the Catalyst PR-81 at the Production Unit Using Mathematical Modeling Method, *Procedia Engineering*, 2015; 113: 51–56.
- [11] Belyi AS. Reforming catalyst of PR Family: scientific foundations and technological advancement. *Kinetica and Catalysis*, 2005; 46(5): 684-392.
- [12] Kravtsov AV, Ivanchina ED, Galushin SA, Poluboyartsev DS. The system analysis and oil-refining effectiveness increasing by mathematical modelling method – Tomsk: TPU, 2004.
- [13] Tataurshikov A, Ivanchina E, Krivtcova N, Krivtsov E, Syskina A. Mathematical modeling of diesel fuel hydrotreating. *IOP Conference Series-Earth and Environmental Science*, 2015; 27: 1-6.
- [14] Ivanchina ED, Sharova ES, Yakupova IV. Mathematical modelling method application for optimisation of catalytic reforming process, *Procedia Chemistry*, 2014; 10: 197-202.
- [15] Yakupova IV, Chernyakova ES, Ivanchina ED, Koksharov AG. Heavy naphtha fractions 85-155°C recycling in the catalytic reforming industrial unit, *Procedia Chemistry*, 2015; 15C: 378-383.
- [16] Krivtcova NI, Tataurshikov AA, Ivanchina ED, Krivtsov EB. Mathematical modelling of diesel fuel hydrodesulfurization kinetics. *Procedia Chemistry*, 2015; 15: p.180 – 186.

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