Petroleum and Coal

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COKE FORMATION REDUCTION IN THE CATALTIC REFORMING REACTORS AT THE OPTIMAL CATALYST ACTIVITY

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Received September 9, 2016; Accepted November 2, 2016

Abstract

Analysis of the catalyst operation effectiveness of the reforming process was conducted with mathematical modelling method using. The proposed method allows estimating the process unsteadiness by taking adverse reactions and the formation of reversible and graphite coke into account. The main characteristics of two reforming catalysts were calculated and compared. The criterion of effectiveness determining the coke accumulation and selectivity for the given technological conditions was used as the comparative characteristic. It was found that the coke accumulations at the current and optimal activity operation are different, vary from 2.65 % mass. for Catalyst 2 to 3.40 % mass. for Catalyst 1 and depends on the raw material volume.

Keywords: catalytic reforming; coke formation; mathematical modeling; catalyst.

1. Introduction

Catalytic reforming of naphtha is a large-capacity process which uses Pt-catalysts in significant quantities, and the total capacity of its industrial units is increasing every year. Platinum catalysts are used in hydrogenation, dehydrogenation, oxidation, isomerization, reforming processes. Due to the large surface area, platinum-supported catalysts have high activity and absorbability. In this regard, the actual direction of the chemical science development is to create a resource-efficient technology based on the applied use of mathematical models of hydrocarbon raw materials, taking the time-dependent conditions of their operation into account.

The catalytic reforming major reactions are the aromatic hydrocarbons formation reactions [1-3], which occur in the presence of $Pt/\gamma{-}Al_2O_3$ catalyst:

1) The dehydrogenation of naphthenic: $C_6H_{12} \rightarrow C_6H_6 + 3H_2 + Q$
2) The cyclopentane dehydroisomerization: $C_5H_9\text{-}CH_3 \rightarrow C_6H_{12} - Q$
$n\text{-}C_6H_{14} \rightarrow izo\text{-}C_6H_{14} - Q$
3) C_5- or C_6- dehydrocyclization of paraffins: $C_6H_{14} \rightarrow C_6H_6 + 4H_2 + Q$

Hydrocracking, hydrogenolysis and the seal reaction (condensation and polymerization) are adverse reactions, leading to the coke formation, which deposits on the catalyst surface.

Elementary reaction stages are determined by bifunctional nature of the reforming catalyst. On the one hand, they contain one metal (platinum) or several metals (for example, platinum and rhenium, or platinum and iridium), which catalyze the hydrogenation and dehydrogenation reactions. On the other hand, halogen-promoted aluminum oxide serves as a carrier, which has acidic properties and catalyzes the reaction, peculiar to the acid type catalyst. Therefore different elementary reaction stages can occur at various surface regions: metal or acidic centers. In many other catalytic reforming reactions, the major basic stage-hydrogenation and dehydrogenation of hydrocarbons. Generated in the dehydrogenation unsaturated hydrocarbons (olefins, cycloalkanes et al.) may also be converted into higher molecular compounds and thereby promote the coke formation from hydrocarbons which blocks the reactive centers [4-6].

$$C_nH_{2n+2} \longrightarrow C_nH_{2n-x} + {}^{1}/_{2}x\,H_2\uparrow \qquad (1)$$

$$C_nH_{2n+2} \longrightarrow C_n + (n+1)H_2\uparrow$$

To suppress the coke formation reaction industrial reforming processes are performed under elevated hydrogen pressure. Herewith the flavoring equilibrium depth decreasing compensates by temperature increasing, or by the fixed granular layer replacing on the moving one for continuous catalyst regeneration at reduced pressures [7-8].

Considering the coke formation mechanism (Fig. 1) the reducing of the active centers number was obtained. Hydrocarbons are adsorbed on the catalyst surface, creating the surface compounds with high hydrogen containing – the reversible coke, with H : C = 4 : 3 ratio. These compounds strongly hold on a surface, but they are in quasi-equilibrium with the hydrogen gas phase. If the equilibrium is disturbed, then a compounds with the low hydrogen containing form, connected with metal, which is irreversibly adsorbed on the catalyst surface – the graphitic coke (H : C = 8 : 7).

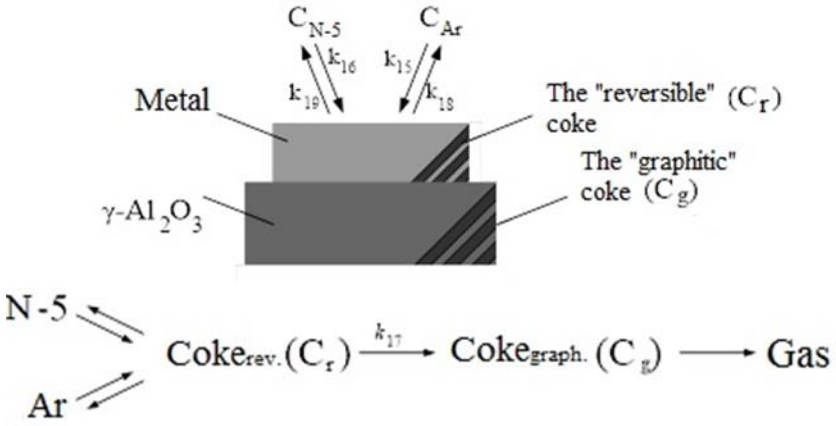

Figure 1. The coke formation scheme (CN-5 – naphthenic hydrocarbons concentration (cyclopentanes), CAr – aromatic hydrocarbons concentration, N-5 – naphthenic hydrocarbons (cyclopentanes), Ar – aromatic hydrocarbons, Cr – «reversible» coke (UIOP), Cg – graphitic coke)

It occurs in that case, when the coke formation reaction equilibrium shifts towards to the graphitic coke formation side and the C : H ratio increases. The platinum contacts properties and composition vary considerably during operation: the specific surface area is reduced due to heat treatment and coke accumulation. Herewith its porous structure changes and active sites number is reduced. The surface area reducing due to the coke formation is reversible, as the reactions occur in a hydrogen environment. But researches have shown [9-11], that this process is reversible, because catalyst works with elevated in a hydrogen-containing medium, which allows to lead the process in the optimal area, corresponding to the reaction system thermodynamic equilibrium, when the formation rates equality and intermediate seal products hydrogenation are observed (Fig. 1).

2. The object of the study

The industrial fixed-bed reforming units with preliminary hydro-treating are performed as an object of study. Units of this type (Fig. 2) are the most commonly used one. This process is characterized by continuous operation over long periods, with decreasing catalyst activity due to coke deposition. By decreasing the activity of the catalyst, the yield of aromatics and the purity of the byproduct hydrogen decreases. In order to maintain the conversion nearly constant, the reactor temperature is raised as catalyst activity declines. When the reactors reach end-of-cycle levels, the reformer is shut down to regenerate the catalyst in situ [1].The shutdown of this unit occurs approximately once each 6–24 months. The raw material undergoes deep hydro-treating of sulfur, nitrogen and other compounds.

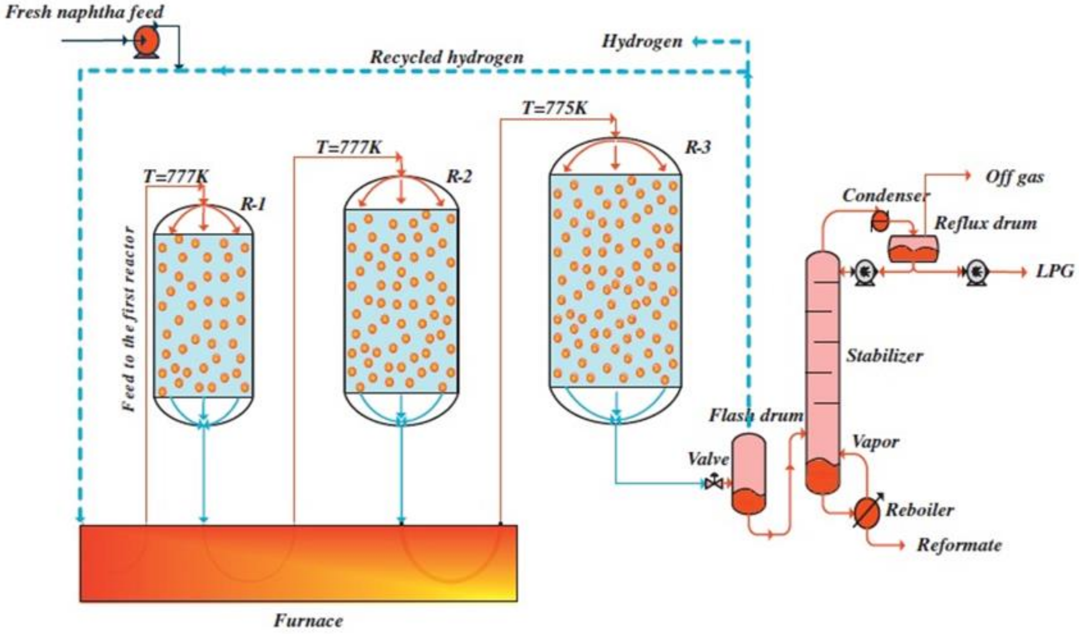

Figure 2. Technological scheme of catalytic reforming fixed-bed unit

The yield of catalytic naphtha reforming process depends strongly on the catalyst properties. During operation, the catalyst undergoes physiochemical changes, which contribute to decrease in the activity for aromatic production.

Naphtha reforming catalyst is a bifunctional catalyst, i.e. consists of a metal function, mainly platinum, and an acid function, usually chloride alumina. The metal function catalyses the hydrogenation and dehydrogenation reactions and the acid function promote the isomerization and cyclization reactions [1]. In order to achieve an optimum performance of the naphtha reforming catalyst, adequate balance between these functions is needed.

Activity, stability and selectivity are the most important catalyst characteristics [12-13]. The first two determine the reactions order and the quality, and the third is necessary for stability providing during operational stage. The modern polymetallic catalyst work with pressure P=1.5-1.7 MPa.

3. Methods

The research has been done using mathematical model which takes both the physical and chemical mechanisms of hydrocarbon mixture conversion reaction as well as the variability of the hydrocarbon feedstock composition [14-16].

The kinetic model of the coke formation and hydrogenation is presented by differential equations system:

$$\frac{dC_o}{d\tau} = k_{16} \cdot C_{H-5} + k_{15} \cdot C_{Ar} - k_{19} \cdot C_o \cdot C_{H_2} - k_{18} \cdot C_o \cdot C_{H_2};$$

$$\frac{dC_g}{d\tau} = k_{17} \cdot C_o; \qquad (2)$$

$$\text{at} \quad \tau = 0 \quad C_i = C_{i0}$$

Reforming reactor mathematical model is composed according to factors of industrial process unsteadiness involving the coke compounds depositions on the catalyst surface. The exponential dependence of the catalyst activity on the coke content has been selected as the basis:

$$A_j = \frac{a}{\exp\left(\alpha_j \cdot \left(C_r + C_g\right)\right)}, \qquad (3)$$

where A_j – the catalyst activity, equal to the ratio of reaction rates occurring at the coked and the fresh catalyst; a – entropic process factor; α_j – poisoning factor depending on the ratio of acidic and basic factors in this type of reaction; $\left(C_r + C_g\right)$ – the coke concentration on the catalyst.

Considering reforming process unsteadiness the activity can be represented [15]:

$$A = \frac{k}{k_0}, \qquad (4)$$

where: k and k_0 – target reaction rates constants in the deactivated and fresh catalyst; A–the catalyst activity.

- at $A < A_{opt}$ the «reversible» coke formation occurs;
- at $A \le A_{opt}$ the «graphitic» coke formation doesn’t occur;
- at $A > A_{opt}$ the process of «graphitic» coke formation starts to occur.

The decontamination process accounting during platinum reforming catalysts operation due to acid and metal centers coking, carried out in the model composition through the deactivation function [9]:

$$K'_{jm} = K_{jm} \cdot F_m$$
$$K'_{jk} = K_{jk} \cdot F_k \qquad (5)$$

where: K_{jm}, K_{jm} – the rates constants of stages occurring on metal and acid sites not-coked catalyst, respectively; F_m , F_k – the deactivation functions of catalyst metal and acid sites.

$$F_m = A_m \cdot e^{-b_m \cdot \left(C_r + C_g\right)}$$
$$F_k = A_k \cdot e^{-b_k \cdot \left(C_r + C_g\right)} \qquad (6)$$

where: A_m, A_k, b_m , b_k – the deactivation parameters (poisoning factor), determined from experimental data; $\left(C_r + C_g\right)$ – the coke concentrations on a catalyst (is determined from the major reaction, because coke – the reaction product).

Maintaining the steady state for a long time under non-equilibrium conditions may be carried out by the state variables adjusting (temperature, contact time). Activity decreasing is the difference between the actual and "fresh" catalyst activities. Herewith the current activity (A) is determined based on the chemical reactions rates:

$$A = W_0 - W_k\left(1 - \alpha\right), \qquad (7)$$

where: W_k, W_0 – the rate of chemical reaction with catalyst and without respectively, mol/m^3·s; α – free volume fraction occupied by the catalyst and inaccessible to the reaction mixture.

The research done have shown that the dynamics of the reforming catalyst activity change depends on the raw materials hydrocarbon composition, product octane number, the H_2/feed ratio and pressure. The impact of these factors is interrelated. There is a need to consider the integral decontamination index.

In essence activity can be expressed as the amount of desired product per time unit. It is necessary to specify the terms of its definition, which is very important in the catalysts selection.

$$W = k_0 \cdot e^{-\frac{E}{RT}} \cdot f\left(C\right), \qquad (8)$$

where: E–stock intramolecular energy measure required for the reaction; k_0 – reaction flow probability measure; $f\left(C\right)$ – raw material composition function account.

The current activity is determined by W, which is calculated according to the raw material and product chromatographic analysis data for the given technological conditions (temperature, pressure, and activity).

$$\Delta = \frac{\sum_{i=1}^{n}\left[A_{cur}^{i} - A_{opt}^{i}\right]}{\Delta_{\max}} \qquad (9)$$

Despite the large number of works devoted to the industrial reforming units work, it is not always possible to find a definite answer to the question: what the coke content on the catalyst and C/H ratios in the coke are needed for the catalyst replacing. The model developed for the catalysts selection allows to offer a single criterion of efficiency through total deviation of the current activity from the optimal one. This indicator determines the coke accumulation and selectivity for the given process conditions.

4. Results and disussion

It should be mentioned from the results shown that with considering the coke accumulation reaction reversibility, coke accumulation in the each reaction stage is limited by equilibrium, and the industrial reactors operation modes adjusting is possible by equilibrium temperature calculation taking the consumption and hydrocarbon raw material composition into account.

The approximation degree to the equilibrium, calculated on the raw material hydrocarbon composition and the reaction product at the given process conditions was compared with equilibrium approximation degree under specific conditions (the raw material composition and yield, technological conditions) of the industrial reactor unit. The results from Tab. 1 show that the product output varies between 82.96 – 88.51 %mass. The current and optimal activity deviations and the product output ones are related directly.

Table 1. The catalyst potential evaluation

Raw material volume, t	Product output, % mass.		Current indicators deviations from equilibrium, % mass.	Criteria of effectiveness, Δ
	Current	Optimal		
75234	84,36	87,27	2,91	0,23
131647	84,64	85,64	1,00	0,07
192613	85,35	87,9	2,55	0,20
307091	86,74	88,51	1,77	0,16
399460	86,54	87,52	0,98	0,06
576813	85,63	86,74	1,11	0,11

Thus, the effectiveness criteria of selection considering the unsteadiness numerically equal to the total current activity deviation from the optimal one will be different. The calculation results are shown in the Tab. 2.

Table 2. The current activity deviation from the optimal one for different catalysts

The raw material volume,t	Catalyst 1			Catalyst 2		
	Activity		Deviation	Activity		Deviation
	Current	Optimal		Current	Optimal	
75234	0.93	0.75	0.18	0.93	0.72	0.21
131647	0.88	0.71	0.17	0.88	0.68	0.20
192613	0.86	0.81	0.05	0.86	0.79	0.07
307091	0.70	0.63	0.07	0.70	0.62	0.08
399460	0.81	0.71	0.10	0.81	0.67	0.14
576813	0.70	0.64	0.06	0.70	0.63	0.07

Depends on the raw material volume the current activity deviation from the optimal one for different catalyst is from 0.06 to 0.30 conventional units.

The coke deposition on the current activity catalyst work from the optimal one also differs for different catalysts (Tab. 3) and besides, the greater the current activity deviation from the optimal one, the greater the current characteristic deviation of coke formation rate from the equilibrium evaluations. Depends on the feedstock volume the current activity coke formation deviation from the optimal one is from 2.65 % mass. for Catalyst 2 to 3.40 % wt. for Catalyst 1.

Table 3. The coke deposition deviation on the current activity catalyst work from the optimal one for different catalysts

The raw material volume, t	Catalyst 1			Catalyst 2		
	Coke, % mass.		Deviation	Coke, % mass.		Deviation
	Current	Optimal		Current	Optimal	
75234	0.70	0.40	0.30	0.51	0.29	0.22
131647	1.29	0.64	0.65	0.95	0.44	0.51
192613	1.88	0.94	0.94	1.40	0.63	0.77
307091	2.54	1.29	1.25	1.84	0.84	1.00
399460	3.25	1.59	1.66	2.33	1.02	1.31
576813	5.48	2.08	3.40	3.97	1.32	2.65

5. Conclusions

Thus, the mathematical model using for a specific industrial unit may conduct catalysts testing and choose the most optimal one.

The principal influence on the reactor work effectiveness has the current activity deviation from the equilibrium for different industrial units. Herewith the optimal activity of studied catalysts Catalyst 1 and PR-71 varies from 0.90 to 0.95 and insignificantly differs from theoretically possibly level.

The proposed criteria of effectiveness using, which is determined by current characteristics deviations from the optimal ones, provides the yield in the range 83-88.5 % mass., which in its turn influences on current characteristics deviations from the equilibrium ones on 1-4 % mass.

The current characteristics deviations from the optimal ones for different types of catalysts in fixed industrial reactor work conditions, determines by feedstock volume and may vary from 0.06 to 0.30 conventional units, and in the coke accumulation rate – from 2,65 % mass. for Catalyst 2 and to 3,4 % mass. for Catalyst 1.

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