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Optimization of higher alkanes dehydrogenation process under conditions of decreased hydrogen containing gas flow with using mathematical modeling

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Abstract

The article proposes the way of saving catalyst resource and increasing the efficiency of higher alkanes dehydrogenation process using mathematical model method. The study has indicated, that reducing hydrogen/feedstock molar ratio results in balance shear of alkanes dehydrogenation reaction to alkenes, which is proved by the results of pilot operating of the alkenes production unit at Ltd. KINEF and by the mathematical model calculations. The results of the prediction calculation of optimum process parameters at various hydrogen/feedstock molar ratios are presented.

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1. Introduction

The process of narrow fraction higher alkanes C₉–C₁₄ dehydrogenation is aimed to processing alkenes with a normal structure, being the main feedstock component of linear alkylbenzenes (LABs) production. LABs are widely used nowadays in production of both industrial and household purpose synthetic detergents. The role of detergents in a particular production and for the household is undoubtedly important and every year values of the product world output increase dynamically [1].

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By-product of the process described is high molecular polynuclear aromatics (PNA) – coke. As far as dehydrogenation process is catalytic, and as catalyst is used Pt, coating Al_2O_3 , keeping the catalyst active is the main task for chemists-technologists under conditions of intensive coke-generating [2–20].

With the purpose of reducing the rate of by-reactions, two processing methods are used: using recycle hydrogen containing gas (HCG) and demineralized water addition into the reaction medium. According to the technology, the hydrogen/feedstock molar ratio is accepted in the range of 6/1 to 8/1. Taking into account the specific character of the dehydrogenation reaction, the process is better to be kept at lower pressure, which is formed exactly by ratio hydrogen/feedstock. After decreasing molar ratio, the increase in the target product – alkenes – is observed; however, along with that, the decreasing rate of hydrogenation by-products by hydrogen and, as a result, the increasing rate of catalyst dehydrogenation by coke is observed [21–26].

The paper is aimed to the developing of the way of increasing efficiency of higher alkanes dehydrogenation process by optimization of the hydrogen/feedstock molar ratio demineralized water flow into the reactor with using mathematical model.

2. Study subject

The discussed in this paper higher alkanes C_9 - C_{14} dehydrogenation process is realized in industry using platinum catalysts, which differ in the base metal (platinum) content (0.92 - 1.06 wt.%), the catalyst support is cordierite with α - Al_2O_3 coating or γ - Al_2O_3 .

The process occurs at the temperature of 465-486 °C, the pressure of about 0.2 MPa in the HCG ambient, and the hydrocarbon feedstock is diluted by HCG. The hydrogen/feedstock molar ratio ranges from 6/1 to 8/1.

The feedstock having the following averaged composition is refined in the process, wt.%: C_9H_{20} – 0.01; $C_{10}H_{22}$ – 17.01; $C_{11}H_{24}$ – 29.89; $C_{12}H_{26}$ – 28.17; $C_{13}H_{28}$ – 20.89; $C_{14}H_{30}$ – 0.35; aromatic hydrocarbons – 1.35; isoalkane hydrocarbons – 2.33. The industrial unit process flow diagram is shown in Fig. 1.

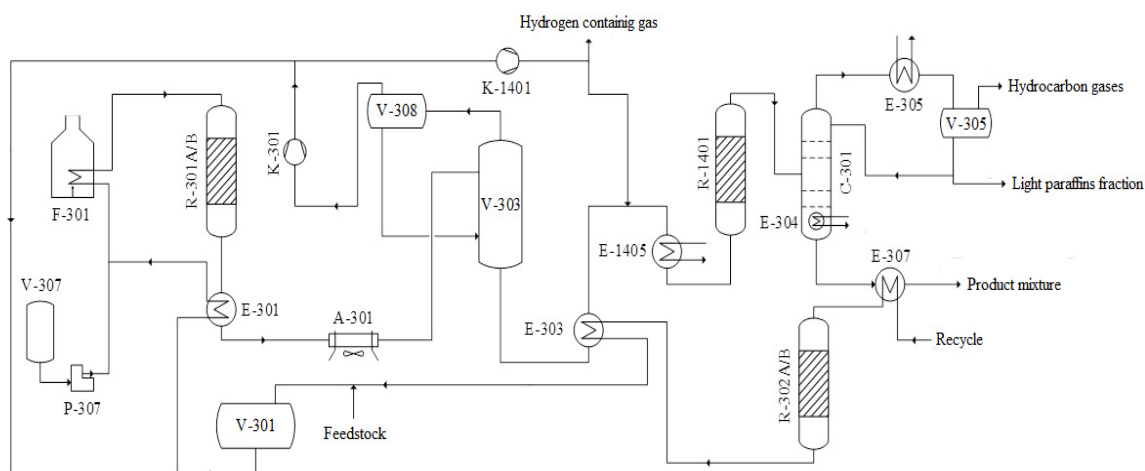


Fig. 1. The alkenes production process flow diagram: V-307 – water reservoir; V-301 – liquid alkanes storage tank; V-303, V-305, V-308 – separators; R-301 A/B – dehydrogenation reactors; R-302 A/B – absorbers; R-1401 – hydrogenation reactor; E-301, E-303, E-304, E-1405, E-305, E-307, A-301 – heat exchangers; C-301 – flash tower; F-301 – furnace for alkanes heating; P-307 – water-flow regulator; K-301, K-1401 – compressors

At the alkenes-production unit at Ltd. KINEF, Kirishi, from November til December, 2014, industrial experiment was conducted.

The experiment was conducted at decreased hydrogen/feedstock molar ratio of 6/1 at increased demineralized water flow into the reactor. During the experiment, the increase in alkenes concentration in the product flow was observed.

The experimental results are given in Table 1.

Table 1. The results of the industrial experiment at the hydrogen/feedstock molar ratio 6/1

Date	Temperature, °C	Water flow into the reactor, l/h	Concentration of alkenes in the product mixture of dehydrogenation reactor, % wt.
17.11.14	477.2	6.9	9.21
20.11.14	477.7	7.5	9.51
23.11.14	476.8	7.5	9.35
26.11.14	477.0	7.1	9.25
29.11.14	477.3	7.2	9.36
02.12.14	476.8	7.2	9.32
05.12.14	477.4	7.2	9.29
08.12.14	477.7	7.2	9.24
11.12.14	477.3	7.2	9.27
14.12.14	476.6	7.2	9.18
17.12.14	476.8	7.3	9.23

During the experiment, the temperature was maintained at the relatively same level of about 477.0 °C. The increase of alkenes concentration in the dehydrogenation reactor product flow by 0.7–1.0 % wt. was recorded, which can be recalculated for the end product LAB as productivity average increase from 168 – 173 t/day (at the hydrogen/feedstock molar ratio be 7/1) to 178 – 182 t/day (at the hydrogen/feedstock molar ratio be 6/1). However, decreasing hydrogen/feedstock molar ratio contributes to the increase in coke-generating process driving rate, which can be compensated by increasing water flow into the reaction zone. While earlier alkenes production was kept at the constant level of 4 l/h, during the experiment it was recommended to increase it up to 6.9–7.3 l/h depending on the process temperature and coke concentration on the catalyst surface area.

3. Methods

The task of controlling the activity of the catalyst of higher n-alkanes dehydrogenation process, with the purpose of increasing target product yield at the hydrogen/feedstock molar ratio of 6/1 and increasing the catalyst service life was solved in the following way: using the developed mathematical model of dehydrogenation process [26], considering coke generating from aromatic and diene hydrocarbons, and oxidizing of coke compounds by water vapour, the rate of coke generating on the catalyst coating is found:

$$\frac{dC_{coke}}{dt} = k_1 C_{C_n H_{2n-6}(\sum ar)} + k_2 C_{C_n H_{2n}(\sum ol)} + k_3 C_{C_n H_{2n-2}(\sum diol)} + k_4 C_{H_{2n}} C_{CO}$$

where $\frac{dC_{coke}}{dt}$ - change of amorphous coke concentration, mole/(m³·s);

k_1, k_2, k_3 - constants of coke-generating reactions rate, from aromatic hydrocarbons, alkenes and dialkenes, correspondently, s⁻¹;

k_4 - constant of the reaction rate of coke-generating from carbon oxide (II), $\text{m}^3/(\text{mole}\cdot\text{s})$;

$C_{C_nH_{2n-6}(\sum ar)}$ - concentration of aromatic hydrocarbons, mole/m^3 ;

$C_{C_nH_{2n}(\sum ol)}$ - concentration of alkenes, mole/m^3 ;

$C_{C_nH_{2n-2}(\sum diol)}$ - concentration of dialkenes, mole/m^3 ;

$C_{H_{2n}}, C_{CO}$ - concentration of H_2 and CO correspondently, mole/m^3 .

Dynamics of water flow into the reactor will be different at catalyst operation at hydrogen/feedstock molar ratio, equal to 7/1, and at hydrogen/feedstock molar ratio, equal to 6/1, because it is necessary to consider the rate increase of by-reactions under conditions of hydrogen deficit.

Optimum water flow is calculated from the conditions, providing reaction balance (accepted coke structure) $C_{28}H_{14} + 28H_2O = 28CO + 35H_2$ ($\Delta G_r = -50.84 \text{ kJ/mol}$).

4. Results and discussion

As the calculations based on the model have shown, demineralized water flow into the dehydrogenation reactor in amount of 4.0 – 12.0 l/h depending on the process temperature provides for catalyst activity maintaining during 340–360 operating days at the H_2 /feedstock molar ratio of 7/1. High catalyst stability (steadiness) under conditions of decreased level of hydrogen containing gas (the hydrogen/feedstock molar ratio is 6/1) is provided by optimization of the water flow into the dehydrogenation reactor, particularly, its increase up to 12–13 l/h by the end of the feedstock cycle.

Using dehydrogenation process mathematical model, recommendations on changing water flow at decreasing hydrogen/feedstock molar ratio from 7/1 to 6/1 at specified alkenes concentration in the product flow of 9.1 % wt. were developed (table 2).

Table 2. Optimum parameters of dehydrogenation process (prediction calculation using the model)

Day of catalyst operation	Molar ratio H_2 /feedstock – 6/1		Molar ratio H_2 /feedstock – 7/1	
	Temperature, °C	Flow of H_2O , l/h	Temperature, °C	Flow of H_2O , l/h
1	470.7	4.0	474.2	4.0
30	471.4	4.0	474.7	4.0
60	472.0	4.0	475.2	4.0
90	472.6	4.0	475.7	4.0
120	473.2	4.0	476.3	4.0
150	473.9	4.0	476.9	4.0
180	474.7	4.4	477.6	4.0
210	475.6	5.4	478.4	4.8
240	476.7	6.5	479.2	5.8
270	477.9	7.8	480.2	6.8
300	479.2	9.2	481.1	7.9
330	481.0	10.9	482.4	9.2
360	483.3	13.1	483.9	10.7

As a result of the conducted experiments at the industrial unit it was found, that carrying the process at decreased hydrogen/feedstock molar ratio (6/1) with additional water flow into the reactor contributes to the increase in the unit productivity on alkenes and, correspondently, on LABs by 7–12 t/day with concurrent costs reduction.

The developed recommendations are used in industry (alkenes-producing unit of the plant LAB-LABS Ltd. KINEF), which provided to carry on the process under optimum conditions and increase the yield of the target product per time unit.

5. Conclusion

Using dehydrogenation process mathematical model, considering coke generation from aromatic and diene hydrocarbons, as well as oxidizing of coke compounds by water vapour, optimum modes of water flow into the dehydrogenation reactor while reducing hydrogen/feedstock molar ratio from 7/1 to 6/1 were determined. It is shown, that high rate of catalyst deactivation can be compensated by increasing water flow to 12–13 l/h at the temperature of 482–483°C instead of 9–10 l/h at the end of the catalyst feedstock cycle.

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