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Flow Rate Influence on Loss of Catalytic Properties in Iron-and-potassium Systems

Eduard Khasanovich Karimov, Liliya Zainullovna Kasyanova,
Eldar Mirsamedovich Movsum-zade and Oleg Khasanovich Karimov

Ufa State Petroleum Technological University,
Pr. Oktyabrya, 2, Bashkortostan, Sterlitamak 453118, Russian Federation

Abstract: This article addresses influence of process parameters on deactivation of iron-and-potassium catalysts during industrial dehydrogenation of methyl-butenes to isoprene. Dependence has been detected between loss of catalytic properties of fixed catalyst bed and the volumetric flow rate of raw materials throughout the life of the catalyst; change in physical and chemical characteristics of the catalyst is shown. Correlation has been discovered between decreasing catalytic characteristics of the top half of the catalyst bed and isoprene generation, regardless of the industrial process volumetric flow rate (and as a consequence, initial temperature of the process and raw material to water vapor rate). Direction is shown for developing the technology of olefins dehydrogenation on a fixed catalyst bed by using layer-by-layer catalyst loading.

Key words: Dehydrogenation of olefins · Isoprene · Iron-and-potassium systems · Catalyst · Deactivation · Dehydrogenation technology

INTRODUCTION

Iron-and-potassium systems are successfully used in industrial dehydrogenation of methyl-butenes to isoprene that is used as a monomer [1]. Modified iron-and-potassium catalysts move the industrial dehydrogenation process to the balance in the target reaction. Shift of the balance toward target products is prevented by thermal gradient in industrial adiabatic reactors and inability to remove target products of the reaction. There are methods to overcome these obstacles that have a common principle for olefins dehydrogenation processes [2-4]. Risks of full-scale use of these solutions are related to different efficiency of the catalyst in different layers in industrial reactors-in industrial conditions, due to uneven catalyst deactivation, intensity of the reaction is shifted towards the bottom of the catalyst bed. Unlike during paraffin dehydrogenation, partial replacement of the catalyst bed with fresh (or more efficient) one during the operation is impossible [5-6]. In this regard, the question arises about proportions for loading catalysts. To solve this problem, we made a number of industrial researches that show change in catalytic characteristics of iron-and-potassium systems in different location areas within the height of the fixed bed.

Experimental Part: The complexity of identifying competent numerical dependencies causes complex influence of process parameters in a multivariate industrial process of methyl-butenes dehydrogenation to isoprene. We took volumetric rate of raw materials as the main industrial parameter. Inevitable consequence of changing selected parameter is change of the initial process temperature and the raw material flow rate to water steam rate.

For the research we chose two similar commercial units that differ from each other in using one or two reactors. Reactors of equal technological versions were loaded with iron-and-potassium catalysts (according to [7]) with equal characteristics (18.0 m^3 each). Temperature of dehydrogenation has substantial influence on the speed of the process, so when reducing intensity of dehydrogenation (conversion of raw materials not less

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Corresponding Author: Karimov, Ufa State Petroleum Technological University,
Pr. Oktyabrya, 2, Bashkortostan, Sterlitamak 453118, Russian Federation.

Table 1: The process parameters

Parameters	Value for one-reactor unit	Value for two-reactor unit
Volumetric flow rate of raw material (by liquid), hr-1	0.40 ÷ 0.60	0.17 ÷ 0.25
Raw material to steam weight ratio, t: t	1 : 6.8÷7.1	1 : 7.2÷7.6
Initial process temperature, °C	624÷652	605÷639
Reactor pressure (absolute) kgf/cm²	1.6÷2.0	1.4÷1.6
Linear flow rate (excluding catalyst bed porosity), m/sec	2.6÷3.5	1.1÷1.6

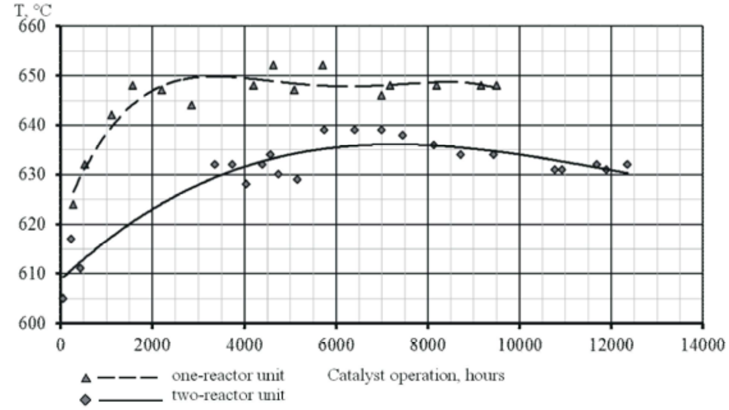

Fig. 1: Change of Initial Process Temperature

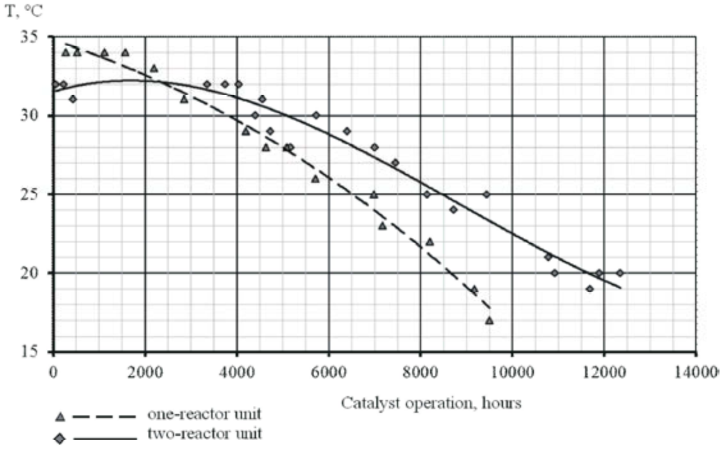

Fig. 2: Change of temperature gradient in top half of the catalyst bed

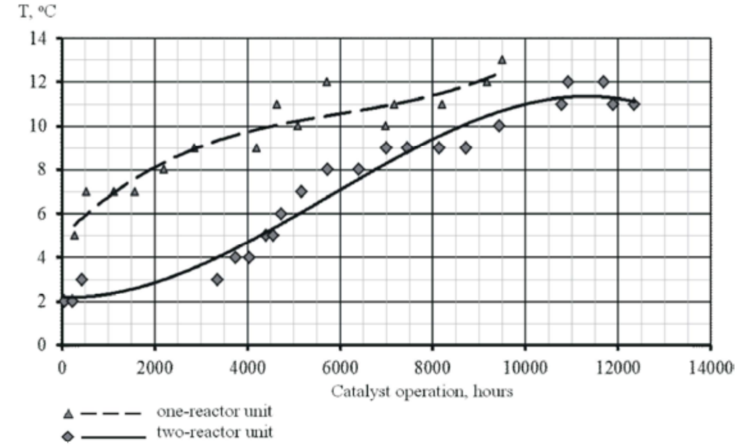

Fig. 3: Change of temperature gradient in bottom half of the catalyst bed

Table 2: Analysis of the catalyst discharged from reactors being studied

	One-reactor unit (operation 9,500 hours)			Two-reactor unit (operation 12,600 hours)		
Indicator Name	Top layers	Mid layer	Bottom layers	Top layers	Mid layer	Bottom layers
Mechanical strength, %	90.61	90.11	98.11	92.62	95.22	92.22
Specific surface, m²/g	3.86	1.60	1.71	3.30	1.68	1.63
Coke content, %	0.75	0.84	0.91	0.14	1.17	1.10
Chemical composition:						
FeO	15.3	11.6	9.2	1.23	1.12	1.45
Fe_2O_3	65.5	60.1	54.8	83.32	67.21	66.15
K_2CO_3	2.03	19.60	18.57	1.86	24.31	22.87
CeO_2	5.44	5.56	5.48	5.78	4.76	5.01
MoO_3	1.18	1.18	1.16	1.16	1.65	1.48

than 40%), we increased initial temperature of dehydrogenation (of top layer of the catalyst) while increasing operating time (Figure 1).

Decrease in catalytic properties was detected by intensity of the target reaction endothermic effect. Thermocouples were located above, in the middle of and below the catalyst bed. In each designated section of the reactor, 5 thermocouples were evenly distributed over the cross section area. The arithmetic mean value was taken for resulting temperature. Difference between temperatures of the same section did not exceed 2°C.

Process parameters for the two units are compared in Table 1. Changes in efficiency of the catalyst in each area of the reactor, depending on duration of operating time is shown in Figures 2, 3.

RESULTS AND DISCUSSION

Comparing Figures 2 and 3, we noted that shift of dehydrogenation intensity from the top half to the bottom half of the bed is clearly visible in both cases. Top layer performance decline curve in one-reactor unit is drastic and the difference between lines for one- and two-reactor units increases with increase in time of operation. Increase in the initial process temperature (Figure 1) of a two-reactor unit has a smoother characteristic and lasts for 6,000 hours. Initial temperature curve of the one-reactor unit by 2,000 hours of operation reaches the level of the average value. Up to 2,000 hours, the curve for one-reactor unit in Figure 2 has the same values of 34°C and after the initial temperature of the process stabilizes after more than 2,000 hours of operation, top half of the bed shows an decrease in activity at the rate of 4°C for 2,000 hours (16°C during operation between 2,000 and 10,000 hours).

Top bed in a two-reactor unit has stable catalytic characteristics up to 4,000 hours, when the initial temperature slowly increases, no changes in the top half of the bed were observed. The dynamics of deterioration of catalytic properties is about 3°C per 2,000 hours (13°C for operation time between 4,000 and 12,000 hours).

Work of the catalyst in the bottom half of the catalyst bed (Figure 3) of one-reactor unit is almost a mirror image of the top half and is comparable with the dynamics of loss of activity in the top layer before and after 2,000 hours of operation.

Operation of bottom half of the catalyst bed in a two-reactor unit during first 4,000 hours (with stable efficiency of the top half) has a tendency to increase dehydrogenation rate by increasing initial process temperature. This fact signifies an increase in initial process temperature commensurately to the rate of top half of the catalyst bed deactivation. Further increase in initial process temperature is limited by the rate of hydrocarbons cracking reactions. A distinctive feature of the bottom bed (compared to curves of the top layer) is to reduce the distance between the curves with increasing time of operation.

One of the main reasons for deactivation of iron-and-potassium systems in industrial environment is physical and chemical loss of potassium in the catalyst (formation of alkali displaced along the flow). KOH formation due to thermo-chemical change of active catalyst center leads to concentration of alkali and formation of monolithic solid blocks. It is rather hard to detect volume of such a defect in industrial environment, since after opening the reactor and blowing it with air, alkali develops into carbonate, which fact disturbs integrity of the lump. Unpromoted iron oxides, depending on phase composition according to [8] show low catalytic activity that decreases to 10% after 5 hours of operation.

It is worth noting that one-reactor unit developed the regulated number of isoprene (rate of catalyst usage is 2.0 kg of catalyst per 1 t of isoprene) for 8,000 hours. During this period, the top half of the catalyst bed changes dehydrogenation intensity (measured by endothermic effect of the reaction) from 34°C to 22°C (35% rel.). Two-reactor unit will have reached the regulated catalyst flow rate by 10,000 hours of operation. Intensity of top bed dehydrogenation by this period will have decreased from 32°C to 21°C (34% rel.). This is almost equal to loss of catalytic characteristics in the top half of bed during the regulated time of catalyst operation makes it possible to speak of proportional decontamination and production of isoprene.

Analysis of the catalyst discharged from the reactor under examination showed a substantial loss of potassium in the top beds of catalyst (Table 2). Concentration of potassium in the top beds of both units is almost at the same level. In bottom layers of the catalyst bed (despite shorter period of operation of one-reactor unit), potassium content in one-reactor unit is less by average value of 20% rel. Promoting agents in the analyzed samples of deactivated catalyst do not have explicit concentration.

CONCLUSION

The performed tests make it possible to visually identify kinds of curves of dehydrogenation intensity loss in top and bottom halves of catalyst bed. In case of loading two (or more) layers of multi-purpose catalysts (to shift the balance of dehydrogenation reaction), the performed studies will make it possible to make comparative evaluation of each layer separately.

It has also been proven that the flow rate decrease leads to an increase in time of stable operation of top half of catalyst bed and requires a smoother increasing initial process temperature. With that, it has been proven that by providing regulated discharge coefficient of the catalyst, loss of catalytic characteristics in the top half of the bed is proportional to development of isoprene. This fact makes it possible to talk about stability of contact gas composition in the top half of the catalyst bed until it reaches regulated production of isoprene, independently of the total operation time of the catalyst and volumetric flow rate.

Conclusions: Replacing the catalyst in the bottom bed with a more efficient catalyst (or shifting balance of the reaction by removing hydrogen similarly to as discussed in [9]) is a strategic technology development, where iron-and-potassium systems can be considered as one (at least one) of the catalyst bed. More detailed parameters for layer-by-layer use of catalysts can be originally obtained from thermodynamic and quantum calculations (by analogy to [10]).

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