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## Operational analysis of the installation for olefin production with changing of hydrogen-containing gas flow

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The dehydrogenation process of higher paraffin C9-C14 is used for the production of olefins with normal structure. From a wide range of metals, exactly platinum has the most pronounced dehydrogenation function. High conversion of paraffins into olefins can be achieved using platinum as a catalyst. The platinum content of the catalyst is at a level of 0.82–1.06 % wt., the carrier is aluminum oxide ( $\alpha$ ,  $\gamma$ -modification), where tin oxide(IV) is used as a promoting additive and content of pure metal does not exceed 0.25 %.

Rapid deactivation of coke is a problem of these catalysts. Demineralized water was introduced into a reactor, and also the process carried out in a hydrogen-containing gas, or HCG, atmosphere for the conservation of the catalyst activity at a relatively constant level. The molar ratio of hydrogen/feedstock can be equal in the range of 6–8/1, in case of obtaining the target products – olefins [1]

Catalyst life is increased up to 90 days (it is about 24.0–26.0% of the catalyst life) with the molar ratio of hydrogen / feedstock equal to 7/1 in the case of the dehydrogenation of higher paraffins, compared with the process conduct with a molar ratio of 6/1 at other equal technological parameters. It should be noted that increasing of feedstock conversion and performance of dehydrogenation reactor are observed at a lower molar ratio of hydrogen/feedstock until 6/1. Excess of demineralized water is introduced into the reactor to compensate for the HCG deficiency.

For this purpose, a program simulating process of dehydrogenation, has been upgraded. Previously, the program adequately described the operation of the installation only with a molar ratio of hydrogen / feedstock equal to 7/1. The molar ratio decrease by 6/1 generates a need for calculating the optimal flow of water into the reactor at a constant technological parameters. During the program improvement, the water supply dependence on the temperature in the reactor and on the degree of catalyst deactivation by coke with a re-

duced molar ratio of  $H_2$ /feedstock was determined. Recommendations on the water supply to the reactor were developed by means of the modeling system. Based on these recommendations with the model use, an industrial experiment was carried out on the installation for olefin production in the LTD "KINEF" Kirishi from November to December 2014.

The experiment was carried out with the reduced molar ratio of hydrogen/feedstock equaled to 6/1 with the increased supply of de-mineralized water in the reactor. Increasing the olefin concentration in the product stream on the models was confirmed during the experiment with decreasing the molar ratio of  $H_2$ /feedstock (Table 1).

**Table 1.** Comparison of the experimental data with calculation of the model

Date	Temperature, °C	Concentration of olefins in the product stream, % wt, with a molar ratio $H_2$ / feedstock equaled to:			Model deviation, abs
		7/1 (model)	6/1 (model)	6/1 (experiment)	
17.11.14	477.2	8.51	9.24	9.21	0.03
20.11.14	477.7	8.96	9.58	9.51	0.07
23.11.14	476.8	8.74	9.44	9.35	0.09
26.11.14	477.0	8.66	9.32	9.25	0.07
29.11.14	477.3	8.68	9.38	9.36	0.02
02.12.14	476.8	8.60	9.40	9.32	0.08
05.12.14	477.4	8.66	9.34	9.29	0.05
08.12.14	477.7	8.83	9.25	9.24	0.01
11.12.14	477.3	8.63	9.36	9.27	0.09
14.12.14	476.6	8.52	9.26	9.18	0.08
17.12.14	476.8	8.59	9.28	9.23	0.05

The conducted researches on the base of the models and the industrial experiments allowed us to increase the installation capacity for the target product by 0.7–1.0% by weight. However, the catalyst life for dehydrogenation of higher paraffins is remained at the same level of 360–370 days with the reduced molar ratio of hydrogen / feedstock. Conservation of the optimum catalyst activity is provided with a water flow rate in the reactor at a reduced

molar hydrogen/ feedstock ratio. The dynamics of flow changes in the reactor is carried out from 4.0 l/h to 12.0–14.0 l/h for the entire cycle with the temperature increase in the reactor.

### References

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## Comparison of HPLC, GPC and MS-TOF techniques for determination of the average molecular mass of PLA oligomer

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Poly-lactic acid (PLA) is a biodegradable aliphatic polyester produced industrially both on large and small scale. It is used for a wide variety of applications, ranging from biomedical applications to raw material for food packaging, bottles and consumables in general.

The most popular industrial production process is actually a multistep process. Firstly, lactic acid (LA) is polymerized to low molecular weight polymer (LMW PLA, < 10 kDa) by bulk Melt Polycondensation and then depolymerized and converted to the lactide, cyclic dimer of LA, in a catalytic step usually carried out at high temperature and low pressure. Finally, purified and dried lactide undergoes the Ring-Opening Polymerization for obtaining high molecular weight polymer (HMW PLA, > 100 kDa). The first step has to be carefully performed in order to optimize the extent of polymerization and minimize the multiple side reactions like discoloration, cyclization, transesterification and racemization which affect the purity of the final cyclic dimer produced from the PLA oligomers itself [1, 2].

The purpose of this study is to compare the various characterization techniques for monitoring the molecular weight of PLA oligomers.

PLA oligomer was obtained from lactic acid (PUREAC, Spain) in presence of ZnO as a catalyst and at constant temperature 160 °C.

Average molecular mass of obtained oligomer was determined by Gel Permeation Chromatography (GPC), High Performance Liquid Chromatography (HPLC) and High Resolution Mass-Spectrometry with Time-of-Flight detection (MS-TOF). GPC analysis was carried out on a PLgel 5 µm MIXED-C column (300 mm × 7.5 mm) using a series apparatus Agilent 1200