Petroleum & Coal
ISSN 1337-7027

Available online at www.vurup.sk/petroleum-coal
Petroleum & Coal 54 (3) 271-277, 2012

OPTIMIZATION OF HARDWARE DESIGN OF PARAFFINS DEHYDROGENATION PROCESS WITH USE OF MATHEMATICAL MODELING METHODS

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Received May 13, 2012, Accepted September 30 2012

ABSTRACT

A new way of reactor block of paraffins dehydrogenation efficiency improvement using a mathematical model which takes mutual influence of processes occurring in apparatus of chemical-technological system into account was proposed. Numerical evaluation of raw materials composition, process conditions and degree of catalyst deactivation influence on efficiency of apparatus of chemical industrial dehydrogenation plant.

Keywords: Mathematical model; heat exchangers and heating equipment; recycling; dehydrogenation.

1. Introduction

One of the main problems arising in the operation of existing industrial units refining and petrochemical facilities operating at high pressures and temperatures, is to ensure the optimum conditions in terms of energy and resource efficiency. To solve such problems should be with taking conjugacy thermal and reaction processes, as well as the mutual influence of modes of heat transfer and reactor equipment into account.

Today it is often the moral and physical deterioration of equipment makes the work of production inefficient. To optimize a large number of operating enterprises must be modernized with a full or partial replacement of outdated equipment, or reconstruction of the technological scheme as a whole.

Experimental studies in industrial units at a level ensuring the reliability of research is time consuming, costly and not always guarantees a significant result. The solution of this multifactorial problem of reactor and heat exchange equipment optimization can be solved most effectively by using mathematical models, based on the physico-chemical laws.

The market capacity of detergents in our country is about 1.2 million tons per year. For the production of such volumes in Russia must be present in raw material base of 100-120 thousand tons of linear alkyl benzene (LAB), while at the same time, the capacity of Russia's only LAB producer – "Kirishinefteorgsintez" constitute no more than 60 tons per year. Therefore, the task of improving the operational efficiency of industrial plants for production of LAB is relevant [1].

The aim of research is to optimize hardware design of higher alkanes process using the method of mathematical modeling.

The complex of LAB production consists of technologically connected blocks (fig. 1).

1) Pre-fractionation of a mixture of n-alkanes with the number of carbon atoms in it from 10 to 20;
2) dehydrogenation of C_{10}-C_{13} fraction using the process of dehydrogenation of alkanes and hydrogenation of diolefins;
3) hydrogen fluoride alkylation of benzene with mono-olefins to produce linear alkyl benzene;
4) sulphonation of LAB by sulfuric anhydride (SO_3) to give alklylbenzenesulphuric acid and linear alkylbenzene sulphonates (LABS).

I - n-paraffins from the unit Parex; II - n-paraffins C10-C13; III - fraction of n-alkanes C14-C17; IV - the fraction of n-paraffins C18 and above; V - hydrogen containing gas; VI - a mixture of n-paraffins and mono-olefins; VII - recycle of n-paraffins; VIII - benzene; IX - heavy alkylate; X - alkyl benzene; XI - sulfonating agent with the installation of elemental sulfur; XII - alklylbenzenesulphuric acid; XIII - lye; XIV - sodium alklylbenzenesulphuric acid.

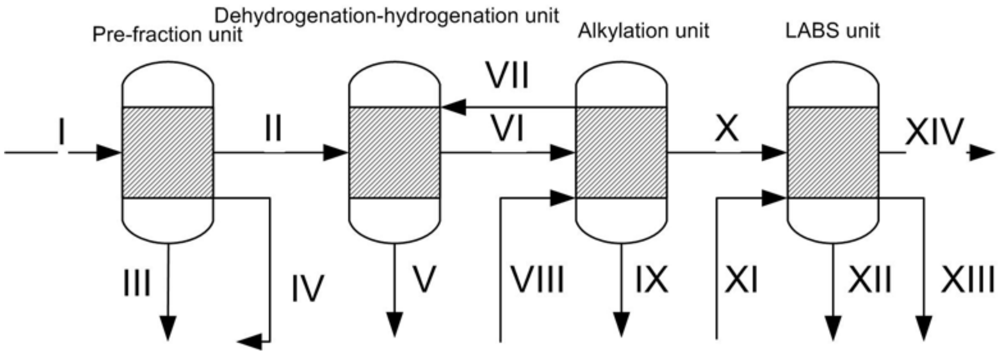

Figure 1. Scheme of LAB/LABS production

Reactor block optimization options from the position of system analysis involves the following steps:

1) identification of all possible alternative options the reactor scheme based on a priori estimates the hypotheses;
2) creation of a hypothetical, generalized structure of the of the technological scheme (HGTS);
3) analysis of the HGTS in the presence of mathematical models of processes occurring in the system;
4) optimization of HGTS by solving problem of multi-criteria analysis [2].

2. Experimental

It was determined that one of the possible ways to increase the productivity of plant is a parallel connection in the work of the second reactor of the process of dehydrogenation of higher paraffins. In 2008 experimental-industrial experiment was carried out, and causes of inefficient heat transfer equipment were found out, so to increase the productivity of plant reconstruction or replacement of heat exchanging equipment is required.

Thus, increasing of higher alkanes dehydrogenation reactor block efficiency can be achieved by:

1) selection of technological scheme optimal structure;
2) selection of optimum equipment.

For optimization of dehydrogenation process mathematical model was chosen, which is based on formalized scheme of hydrocarbon transformations and group kinetic model [3].

The developed model was supplemented with dependencies describing recycling.

We have also developed mathematical models of heat exchangers and furnaces, which are heat-balance equation.

$$T_k = \frac{Q_g Cp_r (T_e - T_i) + G_r r_e}{G_r Cp_{gr}} + T_e \qquad (1)$$

$$T_k = T_i + \frac{Q_u}{G_r Cp_{gr}} \qquad (2)$$

After that a computer modeling system «LAB-LABS» was developed which is based on time-dependent kinetic model of the process of dehydrogenation of paraffins on the basis of a formalized mechanism of hydrocarbons on Pt-catalysts conversion, as well as on mathematical models of related devices of technological scheme.

Active window of the program is shown in fig. 2.

For the purpose of testing of developed computer modeling system calculations of higher paraffins dehydrogenation process were carried. The results of the comparison of experimental and calculated data are presented in tab. 1.

Thus, the presented dependences show that the difference between the calculated with the help of a computer modeling system (CMS) and the experimental data does not exceed 10% (within experimental error), which indicates the adequacy of mathematical description which serves as the base of mathematical model.

Table 1 Computer modeling system verification results

Concentration of olefins, %mass.			Concentration of olefins, %mass.		
Experimental	Calculated	Error, %	Experimental	Calculated	Error, %
9,02	8,55	5,50	8,72	8,81	1,02
8,8	8,54	3,04	8,85	8,68	1,96
8,63	8,53	1,17	8,81	8,65	1,85
8,57	8,55	0,23	8,92	8,56	4,21
8,72	8,68	0,46	8,92	8,77	1,71
8,96	8,76	2,28	8,92	8,54	4,45
8,85	8,87	0,23	8,95	8,78	1,94
			9,21	8,8	4,66
			9,14	8,73	4,70
			9,33	8,85	5,42

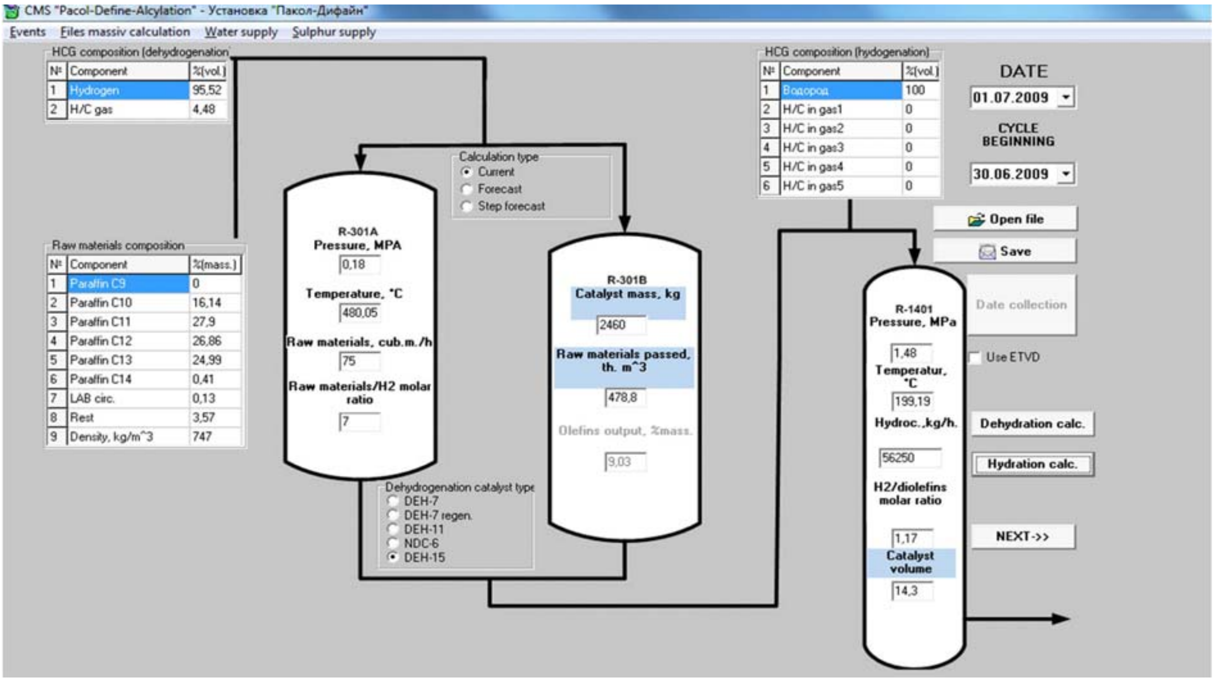

Figure 2. Active window of technological modeling system of LAB manufacturing process

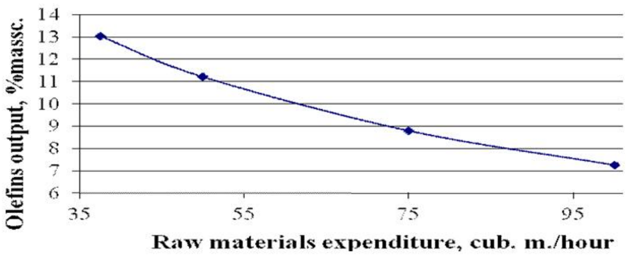

Figure 3. Dependence of olefins output on raw materials expenditure with use of CD-3 catalyst

Also, using the CCM the effect of inclusion in the parallel work of reserve dehydrogenation reactor on basic parameters of reactor block was shown. The calculation carried out takes the load of active and highly selective CD-3catalyst with different costs of raw materials into account (fig. 3).

It was established that an increase in consumption of raw materials from 75 m^3/h to 100 m^3/h in reactor or switching to double reactor scheme can increase the productivity of installation at desired product - olefins, and thus to increase the output of linear alkyl benzene (tab. 2).

Table 2 The average increase in the yield of olefins and LAB depending on the options for raw materials expenditure increasing

Vrm, m^3/h	Single-reactor scheme	Double reactor scheme	
	100	75	100
CD-2 catalyst			
$\Delta G_{olefins}$, t/day	17,68	46,85	84,27
ΔG_{LAB}, t/day	12,03	31,87	57,34
CD-3 catalyst			
$\Delta G_{olefins}$, t/day	16,16	56,04	88,03
ΔG_{LAB}, t/day	10,99	38,13	59,9

3. Results and discussion

It is shown that the maximum increase in the yield of target products is achieved when switching to double reactor scheme with a flow rate 100 m^3/hr for two reactors (increase in the yield of olefins and LAB for CD-3 catalyst by 71%).

A consequence of the transition to double reactor scheme is a significant increase in the yield of by-products (from 0,15-0,19% by weight to 0,18-0,22% wt.). To solve this problem you can increase the molar ratio of hydrogen containing gas (HCG)/ raw materials from 7:1 to 8:1. Transition to double reactor scheme would allow reduction in the total pressure in the system due to reducing the load of raw material for a dehydrogenation reactor, which will give additional reserve to increase the HCG flow by compressor in the system.

An increase in the molar ratio of HCG/raw materials from 7:1 to 8:1 allows to reduce the output of by-products diolefins by an average of 13% and reach a level which installation had while working with a load of 75 m^3 of raw material for a reactor.

To increase the expenditure of raw materials or switch to double reactor scheme is necessary to optimize the process of dehydrogenation raw materials heating and distribute the heat load between the heat exchanger and a tubular furnace efficiently, so processes and devices of reactor unit should be considered as a single interconnected system.

It was also shown that the optimization of heat exchangers and heating equipment of higher paraffins dehydrogenation unit lead to significant increase in efficiency of mono-olefins production. During the research the calculations of following options for heating of higher paraffins dehydrogenation process raw material were carried out:

1. Single pass heat exchanger shelltube (existing);
2. Multi-pass heat exchanger shelltube (reconstructed);
3. Plate heat exchanger (the ideal).

Calculation of heat exchanger and heating equipment of higher paraffins dehydrogenation unit was carried out for 9 different variants of raw materials composition for two catalysts, CD-2 and CD-3 (tab. 3).

Using the developed computer simulation system, we calculated the maximum heating temperature of existing shelltube heat exchanger. For he composition 5 (CD-2) – 350°C; for composition 5 (CD-3) - 348 °C.

The results of the existing shell and tube heat exchanger calculations showed that the lack of heat transfer surface is on average 58-59%, which is caused by a lack of flow turbulence (Re <10000) of fluids in tubes and in intertubular spacing, resulting in low values of heat transfer coefficients. Reconstruction of the existing single pass heat exchanger into multi-pass will significantly improve the heat transfer rate and reduce the shortage of surface heat transfer.

Alternatively, as variant of modernization reconstruction of the single pass heat exchanger in a 6-pass was proposed, as this variant allows to achieve maximum efficiency of heat transfer. Using CMS we calculated the maximum heating temperature of reconstructed shelltube heat exchanger.

Table 3 Variants of raw materials and products of dehydrogenation process compositions

CD-2 Date/Raw materials		CD-3 Date/Raw materials	
beginning of cycle (20.07.09)	Composition 1	beginning of cycle (20.03.10)	Composition 1
middle of cycle (30.10.09)	Composition 2	middle of cycle (25.07.10)	Composition 2
end of cycle (10.02.10)	Composition 3	end of cycle (25.11.10)	Composition 3
much paraffins (30.11.09)	Composition 4	much paraffins (20.07.10)	Composition 4
few paraffins (05.09.09)	Composition 5	few paraffins (20.11.10)	Composition 5
much circulating LAB (05.01.10)	Composition 6	much circulating LAB (10.08.10)	Composition 6
less circulating LAB (20.12.09)	Composition 7	less circulating LAB (03.07.10)	Composition 7
much hydrogen in HCG (25.07.09)	Composition 8	much hydrogen in HCG (30.04.10)	Composition 8
less hydrogen in HCG (10.08.09)	Composition 9	less hydrogen in HCG	Composition 9

Replacement of single pass shell and tube heat exchanger by a 6-way one allows to increase the maximum heating temperature of raw materials by an average of 28°C. For composition 5 (CD- 2) - 390°C; for composition 4 (CD- 3) - 386°C.

In case of shell and tube heat exchanger by plate one replacement it is possible to achieve a significantly higher maximum temperature of raw materials heating. For composition 5 (CD 2) - 434°C; for composition 4 (CD-3) - 428°C.

Thus, the replacement of single pass shell and tube heat exchanger by plate one can increase the maximum temperature of raw materials heating by an average 71°C.

It was shown that the maximum heating temperature is reached when processing of raw materials corresponding to the composition 5, the minimum temperature during the processing of raw materials corresponding to the composition number 4. It means that high content of paraffins and circulating LAB in the raw materials leads to decrease in maximum temperature of feed stream heating.

To compensate the lack of raw materials heated by heat exchanger, on plant of LAB production heat load of the tube furnace was increased by 1.5 times. The calculation results showed that the reconstruction or replacement of existing shell and tube heat exchanger increases the maximum heating temperature of raw materials, thereby reducing the excessive heat load on the furnace. Moreover, the available reserves of heat can also be used to heat the additional quantity of raw materials in case of plant productivity increasing or switching to double reactor scheme.

Using the developed computer simulation system, we calculated the maximum heating temperature of tube furnace while heating raw materials of higher paraffins dehydrogenation block for various designs of heat exchanger according to expenditure of raw materials (tab. 4). In calculating the H_2:raw materials molar ratio of was taken as 7:1.

Table 4 Maximum heating temperature of the furnace tube depending on type of heat exchanger

Heat exchanger type	The maximum heating temperature of raw tube furnace, °C / maximum raw materials expenditure, m^3/h	
	Single-reactor scheme	Doublereaktor scheme
Existing	483/80	-
Reconstructed	490/100	473/120
Plate	524/110	517/150

Thus, reconstruction of heat exchange equipment of higher paraffins dehydrogenation reactor block or its replacement can increase the productivity of installation on the desired product - olefins, and thus to increase the production of linear alkylbenzenes (tab. 5).

Table 5 Increase in the yield of olefins and LAB, depending on the variant of raw materials expenditure increasing and its composition

Vrm,m^3/h	Single-reactor scheme					Double reactor scheme		
	80	90	100	110	120	130	140	150
CD-3 catalyst								
Composition 1								
$\Delta G_{olefins}$, t/day	8,39	24,92	41,49	58,34	84,81	98,60	111,03	125,42
ΔG_{LAB}, t/day	5,71	16,96	28,23	39,69	57,70	67,09	75,55	85,33
Composition 2								
$\Delta G_{olefins}$, t/day	8,43	25,16	41,99	59,16	82,13	95,93	108,69	125,82
ΔG_{LAB}, t/day	5,74	17,12	28,57	40,25	55,88	65,27	73,95	85,61
Composition 3								
$\Delta G_{olefins}$, t/day	8,29	24,89	41,72	58,97	75,82	91,18	108,34	125,82
ΔG_{LAB}, t/day	5,64	16,94	28,38	40,12	51,59	62,04	73,72	85,61

It is shown that in the case of shell and tube heat exchanger into 6-way reconstruction maximizing the yield of target products due to increase in expenditure of raw materials will be average 41.5 t/day (ΔG_{LAB} = 28 t/day); when switching to double reactor scheme ΔG_{olef} will be average 81.5 t /day (ΔG_{LAB} =55.5 t/day). In the case of replacement of shell and tube heat exchanger by plate one, the maximum increase in the yield of target products by increasing the expenditure of raw materials ΔG_{olef} will be average 59 t/day (ΔG_{LAB} =40 t/day); when switching to doublereaktor when switching to the scheme ΔG_{olef} will be average 125.5 t/ day (ΔG_{LAB} = 85.5 t/day).

It is shown that maximizing of depth of processing to 46.9% is possible through additional recycling.

Calculations of higher paraffins dehydrogenation process for production of LAB scheme were carried out with recycle after dehydrogenation reactor. The most important indicators of dehydrogenation process quality are the yield of target products - olefins and the yield of by-products - diolefins, as well as the output of target and by-products per ton of fresh raw material.

Using the developed computer simulation system optimum ratio of recycling, ie, the proportion of stream allocated to recycle to main flow, has been determined. For CD-3 catalyst as a reference date the date 08/07/10 was selected. The results are presented in tab. 6.

Table 6 Dependence of the increase in the yield of olefins on the ratio of recycling

Yield, kg/h	Ratio of recycling						
	0	0,1	0,3	0,43	0,5	0,7	0,8
Olefins	5355,0	5440,9	5971,2	6702,8	7305,0	10816,5	15362,5
Diolefins	112,5	107,4	108,2	118,0	131,3	241,5	409,4
Olefins/ diolefins ratio	47,6	50,7	55,2	56,8	55,7	44,8	37,5

Recycling ratio equal to 0.43 for this type of raw material and catalyst activity is the best, as in this case an increase in the yield of olefins is 25.2% with an increase in yield diolefins of 4.9%. The optimum ratio of recycling is determined by identifying of maximum of monoolefins/ diolefins output ratio.

4. Conclusions

1. The establishment of mutual influence of processes and devices allows the development of models that provide versatility and value of the mathematical description for a wide variation of process conditions.

2. . Reconstruction of existing single pass heat exchangers will reduce electricity consumption by 3400 kW • h in the raw materials in the furnace heating stage. This corresponds to more than 2.5 tons of fuel oil per year. Replacing the shell and tube heat exchanger by the plate one will provide energy-efficient modes of heating equipment and reduce energy consumption at 7800 kW • hr or 5.7 tons of fuel oil per year.

3. Improving of higher alkanes process dehydrogenation efficiency is achieved by providing additional recycling of unreacted paraffins, which can increase the depth of processing of raw materials to the level of 45-46%. The optimal ratio of recycled wax depends on the composition of raw materials and the degree of deactivation of the dehydrogenation catalyst and can be 0.1-0.7.

4. Reconstruction of existing heat transfer equipment, providing raw material to the heating temperature 390 °C, improves the efficiency of production by reducing of energy consumption of raw materials in the furnace heating stage (26.7%).

5. Transition to double-reactor scheme will increase the productivity of industrial plant by an average of 71%. For CD-3 catalyst in the reconstruction of heat exchanger and an increase in consumption of raw materials up to 120 m^3/h conversion yield is increased by 82 tonnes/day. Replacing of heat exchanger by the plate one and increasing of raw materials consumption up to 150 m3/h conversion yield is increased by 126 tonnes/days. Provision of heating equipment is limited to consumption of raw materials 150 m^3/h.

List of symbols

Gr- flow rate of the total feed stream, kg/h;
C_{pr}-mass heat capacity of raw materials flow, J/kg • K;
T_i, T_k - initial and final temperatures of the total feed stream, K;
Te-temperature of total raw flow evaporation;
r_e - specific heat of vaporization total feed stream, J/kg;
Q_g – given heat, W;
Q_u - useful capacity of furnace, W;

References

[1] Kafarov V.: Mathematical modeling of the basic chemical production processes: a tutorial / V.V. Kafarov, M.B. Glebov. - M.: High School, 1991. - 399 p.

[2] Kravtsov, A. V., Fetisov, V.A. Frantsina, E.V. and other: Technology and Modeling of Reactive Processing of Higher Paraffins to Linear Alkyl benzenes: A tutorial. - Tomsk: Publishing house of Tomsk Polytechnic University, 2010. – 297. p.

[3] Dolganov, I.M., Frantsina, E.V., Afanasyev Yu., Ivanchina, E.D., Kravtsov, A.V.: Simulation of industrial petrochemical processes using object-oriented language Delphi / / Proceedings of the Tomsk Polytechnic University, 2010 - 317 tons, - № 5. - C. 53-57.