well as for manufacturing quinoline and high-boiling quinolinic bases (latudine, xylidine) [10].

In conclusion, it is necessary to note, that in modern conditions the organization of by-product coke enterprise is appropriate to compose of end products manufacturing for various branches of chemistry, including raw materials for pharmaceuticals synthesis, for growth of its economical efficiency. The real prerequisites for organization of such area in coke chemistry are the following:

- availability of active raw materials, in some cases the unique ones, in sufficient amount;
- manufacture does not require deficient and metal-intensive equipment and great capital investment; high price of marketable products ensures quick payback;
- availability of powerful treatment facilities solves the problem of neutralization and utilization of these industries waste.

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IMPROVING THE PROCESS OF HIGHER PARAFFIN DEHYDROGENATION ON THE BASIS OF NONSTATIONARY KINETIC MODEL

E.N. Ivashkina, E.M. Yuriev, A.V. Kravtsov, E.D. Ivanchina

Tomsk Polytechnic University
E-mail: MikhaylovaEN@yandex.ru

Technological modelling system of the dehydrogenation process of $C_{10}-C_{13}$ n-paraffins, in the basis of which there is a formalized mechanism of hydrocarbons transformation on the Pt-catalyst surface has been developed. According to predictive calculation, application of the developed system allows the prolongation of catalyst life due to optimization of its operation modes as well as simulation of different variants in equipment reconstruction, in particular, at transition to operation of reactors placed in parallel.

The potential demand of domestic market of synthetic detergents ащк a raw material base, which is linear alkyl benzenes (LAB) and linear alkyl benzene sulphanates (LABS), is about 100 thous. tons per year. Meanwhile, at present, OOO «KINEF». is only one LAB manufacturer in Russia. The production capacities are 50 thous. tons of LAB per year, the 70 % of which are orientated to export. The rest quantity of LAB is sufficient only for 3–4 domestic enterprises of more than existing thirty ones. In connection with the demand for LAB on Russian market the task of increasing this production capacity is urgent.

The main stages of LAB production by UOP (Universal Oil Products Company) technology are: 1) higher paraffins dehydrogenation at Pt-catalyst (Pacol process); 2) by-products hydrogenation (Define process); 3) benzene alkylation with obtained monoolefines with the use of HF-catalyst.

Nowadays, the only combination set for LAB production in Russia Pacol-Define Limited Company «KINEF» operates at excess rated capacity by 20 %. Probably, the reserves of productivity improvement (without equipment replacement) are not exhausted yet. One of the possible ways of the set productivity improvement

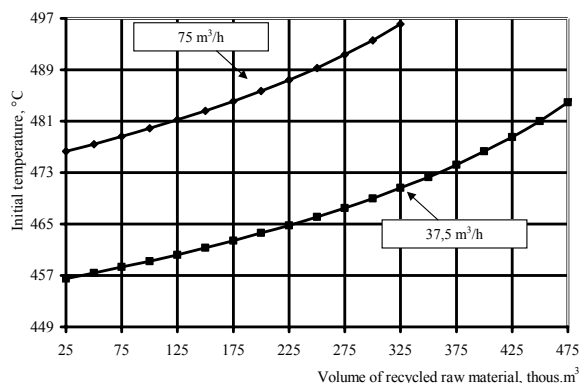is inclusion of the second dehydrogenation reactor in parallel operation (Fig. 1).

Fig. 1. *Flowchart of lines of LAB, LABS production complex: I) n-paraffins with Pareks set; II) $C_{10}-C_{13}$ n-paraffins; III) fraction of $C_{14}-C_{17}$ n-paraffins; IV) fraction of C_{18} n-paraffins and higher; V) hydrogen containing gas; VI)ямixture of n-paraffins and monoolefines; VII) recirculating n-paraffins; VIII) benzene from ЛГ-35-8/300Б set; IX) heavy alkylate; X) LAB; XI) sulfur from an elemental sulfur set; XII) LABS; XIII) alkali; XIV) LABSNa*

At present, only one dehydrogenation reactor is included into set operation, while the second reactor being a reserve one. Technical staff supposes that the reserve reactor inclusion into parallel operation allows increasing the volume of released production without fundamental reconstruction of operative equipment.

Forecasting operation of such variant of scheme for the operative set may be performed in the most efficient way applying the kinetic model developed by the authors, describing sufficiently the industrial process of higher paraffins dehydrogenation [1], and technological modeling system created on its basis (TMS) [2].

As it was showed before [3], the level of detailing the mechanism of hydrocarbon reactions on Pt-contact surface at modeling is defined by their reactivity. Hydrocarbon antiknock value or octane numbers are the indexes of reactivity for the process of benzines catalytic reforming. In this connection, at aggregation of reaction mixture components into pseudocomponents the detailing level stipulated separate consideration of mono-and disubstituted alkanets when modeling this process [4].

Formalization of main stages of higher n-paraffins dehydrogenation (gross-reactions) and the list of pseudocomponents in the model were also defined by hydrocarbon reactivity and the yield of desired products — monoolefines was chosen as the criteria.

On the ground of the created scheme of substances transformation in n-paraffins dehydrogenation the kinetic equations of chemical reactions were set up, Table 1.

The kinetic model in terms of the groups of substances in n-paraffins dehydrogenation process is presented in Table 2.

Mathematical description of dehydrogenation process is taken as a basis of the technological modeling system, which contains the following issues: current and prognostic calculation of higher paraffins dehydrogena-

tion processes (Pacol) and by-products hydrogenation (Define), material balance calculation of the set in whole, visualization of the obtained results (curves, tables).

Table 1. *Kinetic description of higher paraffins dehydrogenation process*

Type of reaction	Expression for the rate of:	
	Direct reaction	Reverse reaction
Paraffins dehydrogenation to monoolefines	$W_1=k_1C_P$	$W_{-1}=k_{-1}C_OC_{H_2}$
Monoolefines dehydrogenation to dienes	$W_2=k_3C_O$	$W_{-2}=k_{-2}C_{DO}C_{H_2}$
Coke formation from dienes	$W_3=k_3C_{DO}$	−
Dienes cyclodehydrogenation	$W_4=k_4C_P$	−
Paraffin hydrocarbons isomerization	$W_5=k_5C_P$	$W_{-5}=k_{-5}C_{IP}$
Isoparaffin cyclodehydrogenation	$W_6=k_7C_{IP}$	−
Coke formation from aromatic hydrocarbons	$W_7=k_7C_A$	−
Cracking of paraffins	$W_8=k_8C_PC_{H_2}$	−

Table 2. *Group kinetic model of higher paraffins dehydrogenation process*

Group of substances	Dependence of substance concentration on time
Paraffins	$\dfrac{dC_P}{dt}=-k_1C_P+k_{-1}C_OC_{H_2}-k_5C_P+k_{-5}C_{IP}-k_8C_PC_{H_2}$
Isoparaffins	$\dfrac{dC_{IP}}{dt}=k_5C_P+k_{-5}C_{IP}-k_6C_{IP}$
Olefines	$\dfrac{dC_O}{dt}=-k_1C_P-k_{-1}C_OC_{H_2}-k_2C_O+k_{-5}C_{IP}-k_{-2}C_{DO}C_{H_2}$
Dienes	$\dfrac{dC_{DO}}{dt}=-k_2C_O+k_{-2}C_{DO}C_{H_2}-k_5C_P+k_3C_{DO}-k_4C_{DO}$
Aromatic hydrocarbons	$\dfrac{dC_A}{dt}=-k_6C_{IP}+k_4C_{DO}-k_7C_A$
Hydrocarbon gas	$\dfrac{dC_G}{dt}=k_8C_PC_{H_2}$
Coke	$\dfrac{dC_K}{dt}=k_7C_A+k_3C_{DO}$

Here W_i is the rate of a corresponding reaction; k_i is the constant of chemical reaction rate; C_P is the concentration of paraffin hydrocarbon C_9-C_{14}; C_O is the concentration of olefinic hydrocarbon C_9-C_{14}; is the hydrogen concentration; C_{DO} is the concentration of diene hydrocarbon C_9-C_{14}; C_{IP} is the concentration of isoparaffin hydrocarbon C_9-C_{14}; C_A is the concentration of aromatic hydrocarbon C_9-C_{14}; C_G is the concentration of gaseous hydrocarbon C_4-C_7; C_C is the coke concentration; t is the time

Using the developed TMS the prognostic calculations of Pacol-Define set indexes operation were carried out at the following invariable initial data:

1) molar ratio H_2/hydrocarbons = 7:1;
2) n-paraffins volume flow for both reactors 75 m^3/h;
3) LAB generation − 180 t./day

At transition to parallel operation of dehydrogenation reactors it is necessary to consider three main constituents: hydrodynamic, kinetic and constructional (tooling backup of reactors operation).

The developed kinetic model of dehydrogenation process has inherently physical-chemical regularities of Pt-catalysts process realization with a glance of hydrodynamic constituent of reaction in contacts pores. Therefo-

re, using this model it is possible to estimate: change of process selectivity, rate of temperature rise of input into dehydrogenation reactor for supporting stated constant LAB generation, dynamics of carburizing and, hence, duration of set operation with one Pt-catalyst loading.

At parallel operation of dehydrogenation reactors the main factor, defining the change of efficiency indexes of this process, is raw materials load reduction per one reactor, and therefore, decrease of volumetric feed rate, i. e. increase in contact time of agents and catalyst. Reduction of volumetric raw materials feed rate allows decreasing temperature profile of the process, on the one hand, and as a result, increasing catalyst service life (Fig. 2).
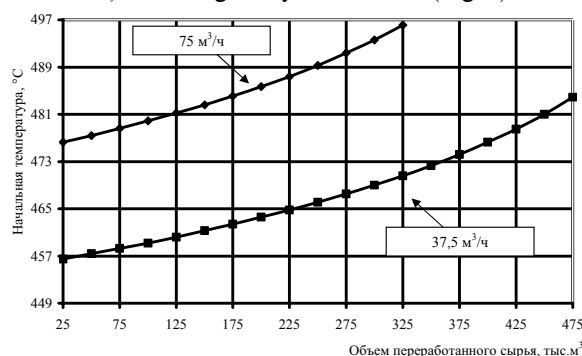
Fig. 2. *Dependence of temperature of input into dehydrogenation reactor on raw material consumption (prognostic calculation by mathematic model)*

On the other hand, it does not allow increasing LAB capacity (this index remains almost at the same level or it will be a little bit higher due to a longer contact time). The results of calculations are presented in Table 3.

Table 3. *Average content of components, wt. % (molar ratio H_2: raw material=7:1)*

Components	Raw material load, m^3/h	
	37,5	75
Olefines	10,99	8,99
Dienes	0,52	0,42
Isoparaffins	5,69	5,58
Aromatic	1,47	0,95

Therefor, for increasing process intensity the initial temperature of input into dehydrogenation reactor should be retained at prior level (as at raw material load 75 m^3/h per a reactor). Because of contact time increase, and also high temperature of reactor input the concentration of by-products (aromatic, isoparaffin and diene hydrocarbons) increases at an average on 15 wt. % and by the end of operation cycle to 50 wt. % (Fig. 3). It results inevitably in formation of such high-molecular compounds as tetralin and indan homologues, polyalkylaromatic compounds, di- and more phenylalkanets and others (at LAB generation about 200 t/day) and deterioration of a desired product biological decomposability that is inadmissible.

The transition to two-reactor scheme provides the decrease of total pressure in the system due to reduction of raw material load to one dehydrogenation reactor. It gives the additional reserve for increasing hydrogen fee-

ding into the system. Therefore, it would be reasonable in this case to increase molar ratio H_2/hydrocarbons.
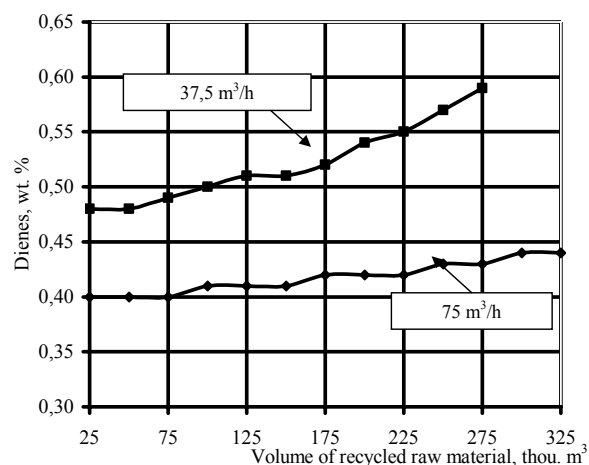
Fig. 3. *Dienes concentration depending on raw material consumption (prognostic calculation by mathematical model)*

Prognostic calculation by the model showed that the average content of desired and by-product components at ratio H_2/hydrocarbons, equal 8:1, will be reduced to the level, when the set was operating at raw material load 75 m^3/h per a reactor (Table 4, Fig. 4).

Table 4. *Average content of components, wt. % (raw materials consumption 37,5 m^3/h)*

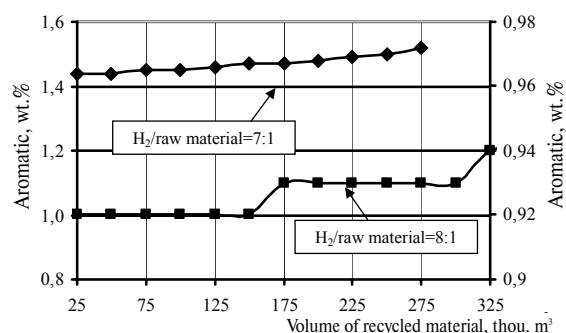| Components	Molar ratio H_2/raw material	
	7:1	8:1
Olefines	10,99	8,99
Dienes	0,52	0,39
Isoparaffins	5,69	5,58
Aromatic	1,47	0,94

Fig. 4. *Aromatic hydrocarbons concentration depending on the ratio H_2/raw material (prognostic calculation by mathematical model)*

Though LAB generation does not exceed the level 180 t/day but the duration of catalyst operation cycle increases in 2,0...2,5 times, that balances the dead time at reactors overloading.

Conclusion

The approach to the improvement of industrial technology of hydrocarbon raw material recycling into synthetic detergents, based on applied use of nonstationary kinetic model, is developed.

Using the developed technological modeling system, one of the variants of efficiency increase in higher paraffins dehydrogenation in Pt-catalysts process at linear alkylbenzenes production was considered and prognostic calculations were carried out.

According to the prognoses, at raw material load 37,5 m³/h the duration of catalyst operation cycle increases in 1,6...1,7 times in comparison with the load 75 m³/h at molar ratio H₂/raw material=7:1. In this case,

by-products concentration in the mixture increases at the average in 15 wt. %. In this case, molar ratio H₂/raw material should be increased to 8:1 for providing the prior level of undesirable compounds. It seems to be possible as the transition to the two-reactor scheme provides the decrease of total pressure in the system and gives the additional reserve for hydrogen feeding growth that allows increasing the duration of operation cycle in 2,0...2,5 times at linear alkylbenzenes generation 180 t/day.

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PERCULIARITIES OF SLUDGE FORMATION AND COMPOSITION OF OIL PARAFFIN CARBOHYDRATES IN THE UPPER–SALAT DEPOSIT

I.V. Prozorova, O.V. Serebrennikova, Yu.V. Loskutova, N.V.Yudina, L.D. Stakhina, T.L. Nikolaeva

SD RAS Institute of Oil Chemistry, Tomsk
E-mail: piv@ipc.tsc.ru

Oil examination of two wells of the Upper-Salat deposit in Tomsk region has been carried out. The oils are sufficiently different in their composition. This fact determines the peculiarities of sludge formation in them. Oil paraffin hydrocarbons are presented by homologous series of normal alkanes with the number of carbon atoms C_9-C_{30}. For the oil of 122 well with high content of solid paraffins, bur distinguished by high concentration of resinous components, the process of sludge formation begins at T=+50 °C. In the oil of 188 well the sludge formation occurs at T=+70 °C.

Oil equipment waxing represents a complex of processes, stipulating solid phase accumulation on equipment surface at oil production, transportation and storage, besides, it is a very undesirable phenomenon.

To choose the way of prevention and overcoming asphalt-tar-paraffin deposits (ATPD) it is necessary to know the composition and structure of oil deposits. Therefore, the investigation of sludge formation peculiarities of Upper-Salat deposit is of great practical interest.

The process of oil sludge formation of two wells of Upper-Salat deposit (Tomsk region) was studied by using the method of «cold rod». The temperature of oil stream varied from 30 to 70 °C, the temperature of «cold rod», imitating metal surface of pipe lines, changed from 15 to 60 °C [1]. The sludge in the oil of 118 well (bed U_1^5) is formed at oil stream temperature of 70 °C (Table). Sludge formation for oil of 122 well (bed U_1^{3-4}) starts only at the temperature of 50 °C. Generally, the

character of ATPD quantity distribution is similar for oil of two wells: at temperature reduction of oil stream of every well the amount of oil deposit increases and maximal quantity of ATPD is due to the temperature, the most approximate to oil solidification temperature of 15 °C. For the whole range of oil stream temperature the maximal amount of ATPD is formed at 30 °C of «cold rod» surface.

Surfactants, contained in tar-asphaltene components, have a lot to do in the process of sludge formation [2]. They «inhibit» paraffin hydrocarbon (PH) extraction and due to adsorption on crystal surface prevent from further growth of PH crystal lattice [3]. Quantitative distribution of tar-asphaltene components of deposits and oils of two wells was defined by the method of liquid adsorptive chromatography in a gradient variant (Fig. 1). It is stated that asphaltene compounds are absent both in oils and oil deposits.