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 m^3/h the duration of catalyst operation cycle increases in 1,6...1,7 times in comparison with the load 75 m^3/h at molar ratio H_2/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 H_2/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

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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.

Table. *Amount of asphalt-tar-paraffin deposits in oils of Upper-Salat deposit depending on the temperature of oil stream and «cold rod»*

Temperature of «cold rod», °C	Amount of ATPD, g per 100 g of oil	
	118 well	122 well
Oil stream temperature is 70 °C		
60	0	0
50	0,05	0
40	0,15	0
35	0,30	0
30	0,35	0
20	0,23	0
15	1,10	0
Oil stream temperature is 60 °C		
50	0,07	0
45	0,22	0
40	0,27	0
35	0,57	0
30	1,75	0
25	0,78	0
20	0,33	0
15	3,05	1,98
Oil stream temperature is 50 °C		
40	0,10	0
35	0,21	0
30	0,38	0,08
25	0,35	0,07
20	0,45	0,15
15	2,08	0,45
Oil stream temperature is 40 °C		
30	0,12	0,20
25	0,20	0,18
20	0,08	0,08
15	4,05	2,98
Oil stream temperature is 30 °C		
20	0,25	0,5
15	3,20	2,48

Oil and oil deposits of 118 well in comparison with the oil of 122 well are distinguished by higher content of paraffin-naphthenic hydrocarbons and lower concentrations of aromatic and tar components. The following tendencies are observed: at oil stream temperature decrease the content of saturated paraffin-nephthenic hydrocarbons in oil deposit composition increases (rel. %): from 76 to 86 for 118 well and respectively from 69 to 71 for 122 well. Besides, at oil stream temperature decrease the increase of tar components in ATPD composition is observed. It is conformed to the data already existing in scientific literature about the increase of paraffin hydrocarbon content in oil deposits as oil streaming from a bed to a surface [4].

As PH ability to form crystal structures in the presence of tar-asphaltene substances is suppressed to a considerable extent, it may be supposed that oil stream temperature decrease and increase of tar components content in oil deposit composition result in increasing a part of ATPD structure amorphism.

The correlation of sludge formation peculiarities in oils of different beds shows that the absence of ATPD formation in the oil of U_1^{3-4} bed to the temperature of 50 °C may be stipulated by increased tar components content in comparison with the oil of U_1^5 bed.

According to the scientific data, the initial period of waxing is characterized by the formation of black deposits thin layer with low-fat consistency; in which the solid phase is mainly represented by paraffin hydrocarbons [5]. Paraffin hydrocarbons of source oils and deposits were analyzed by means of GLC (at gas-liquid chromatograph «Perkin-Elmer SIGMA 2B»). Paraffin hydrocarbon composition of oils of two wells differs insignificantly (Fig. 2). Only a higher content of high-molecular paraffin hydrocarbons is recorded, starting with

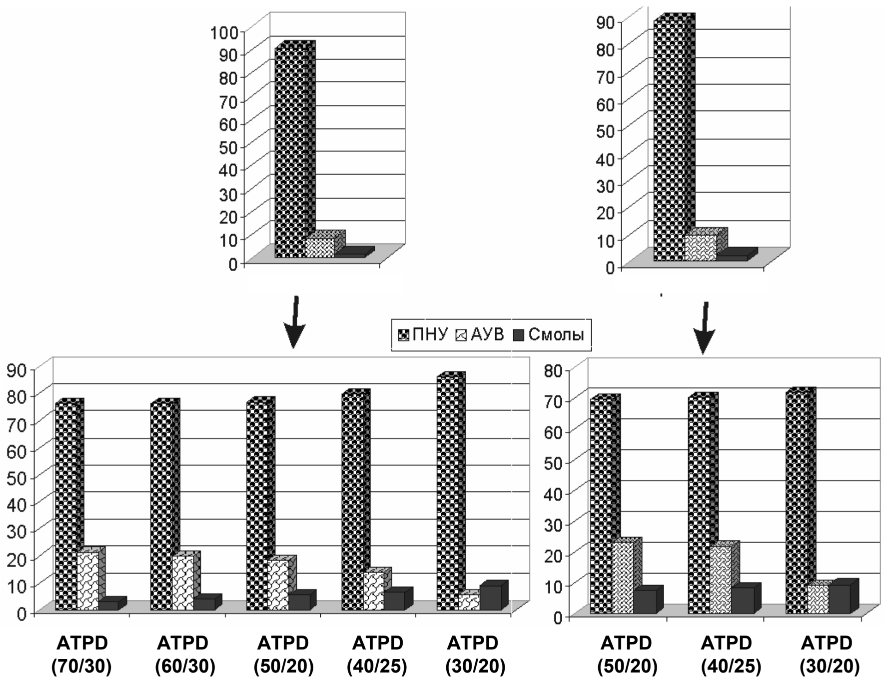

Fig 1. *Type content of oils and deposits of Upper-Salat deposit*

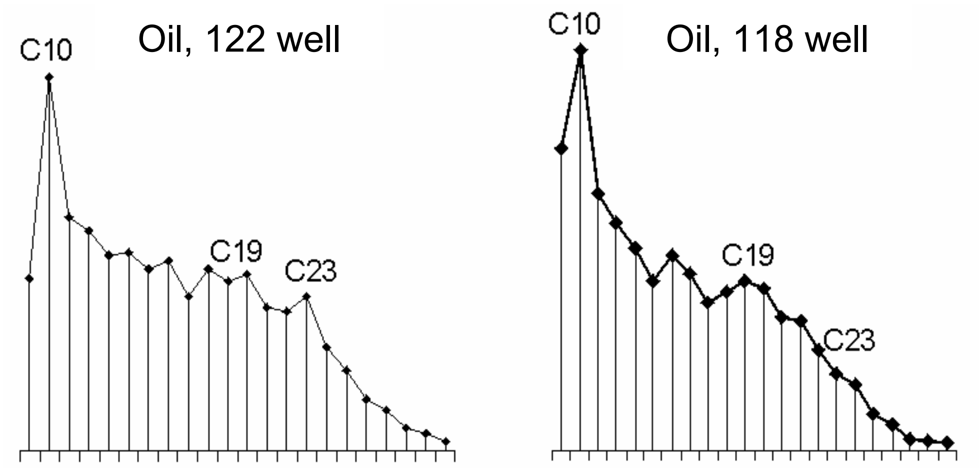

Fig. 2. *Chain-length distribution of n-alkanets of Upper-Salat deposit oils*

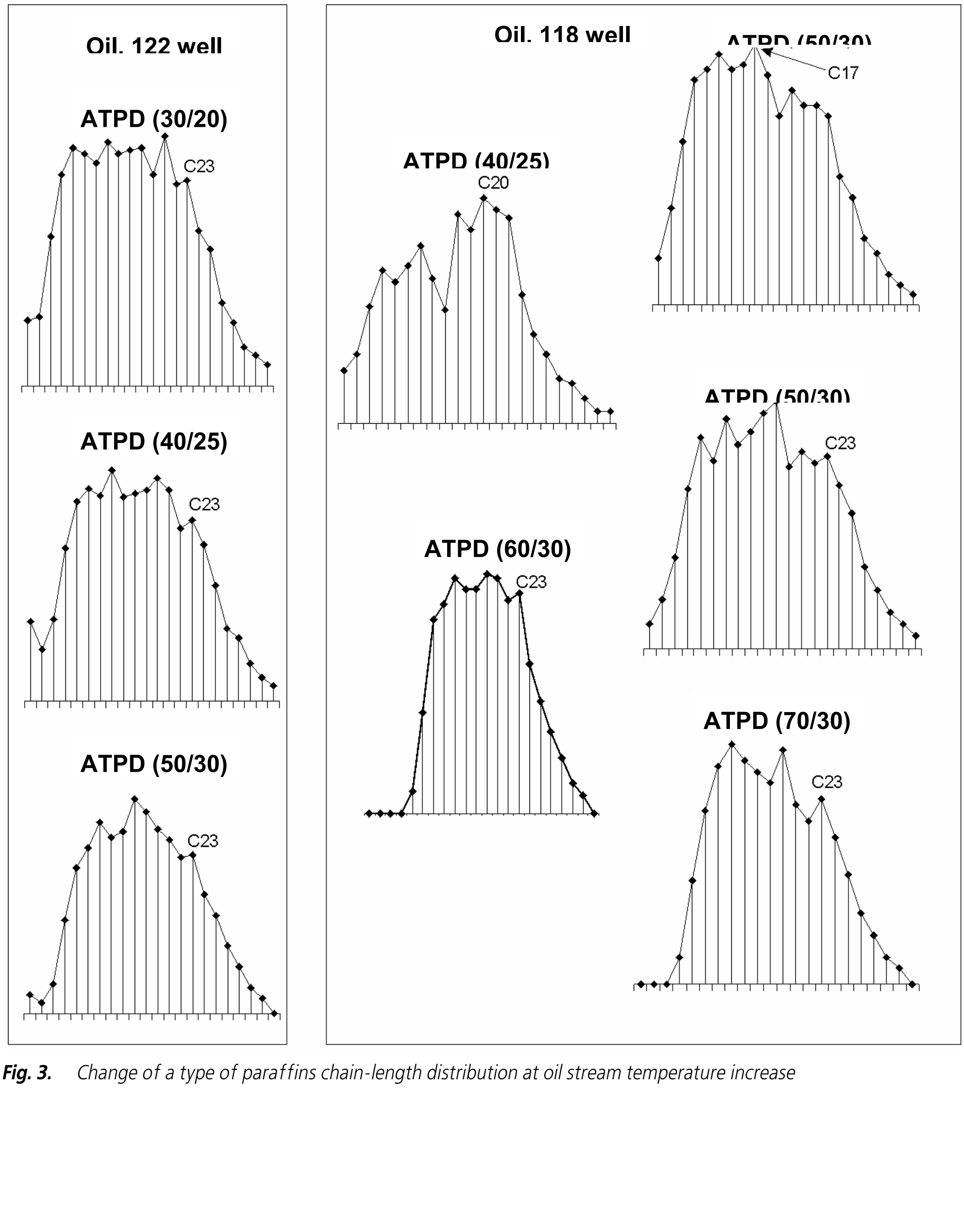

Fig. 3. *Change of a type of paraffins chain-length distribution at oil stream temperature increase*

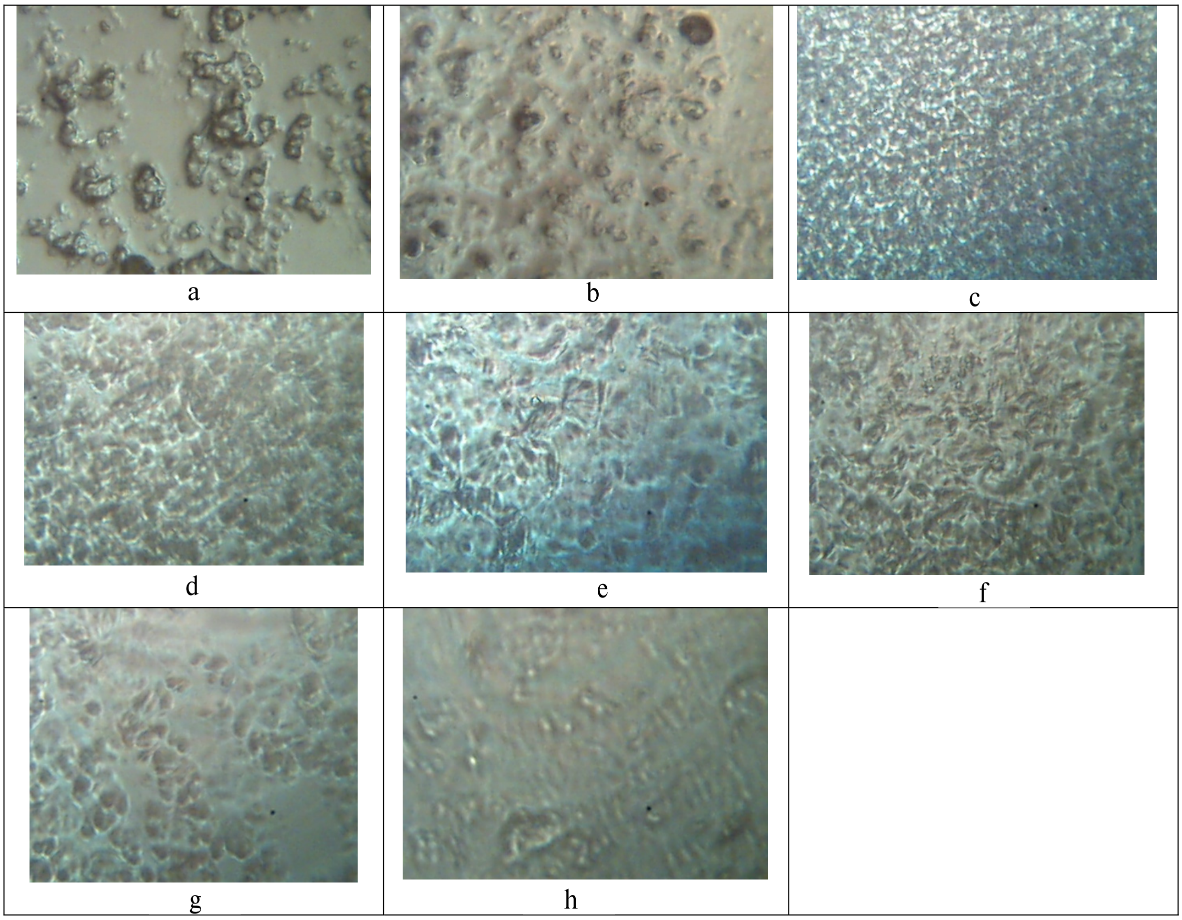

***Fig. 4**. Formation of paraffin hydrocarbon crystals in the deposit of the oil of 118 well (a–d) and 122 well (e–h) of Upper-Salat deposit at temperatures of oil stream and «cold rod»: a) 70 and 30 °C; b) 60 and 30 °C; c) 50 and 30 °C; d) 40 and 25 °C; e) 30 and 20 °C; f) 50 and 30 °C; g) 40 and 20 °C; h) 30 and 20 °C*

tricosane (C_{23}) in the oil of 122 well in comparison with the oil of 118 well.

The research on the content of oil deposits paraffin hydrocarbons showed that at oil stream temperature decrease the increase of content of low-molecular paraffin hydrocarbons takes place (Fig. 3). So for the deposits with maximal temperature of oil stream (for ATPD of the oil of 118 well it is 70 °C, for the deposit of the oil of 122 well it is 50 °C) the total lack or a very insignificant concentration of C_9–C_{12} paraffins is typical. The increase of a part of low-molecular n-alkanets in the composition of oil deposits of two wells is retraced at oil stream temperature decrease (Fig. 3). It is coordinates with the scientific data about the fact that in the ATPD composition at the beginning of deposits (in a subsurface part of a well), paraffin is mainly represented by ceresins. The latter are unable to form massive layers as their crystals are more inflexible and have a lower ability to bond than the crystals of standard paraffins. At the top of a well bore the content of these compounds are considerably lower. In the mixture of *n*-alkanets the content of light homologues increases [6].

To define crystalline modifications of paraffin hydrocarbons and the structure of oil deposit itself the micrographs of oil deposits at deposits letting down with oil at ratio 1:1 and 600 times increase were taken.

Microanalysis and study of the photos (Fig. 4) showed that spherulitic crystallization of paraffin hydrocarbons is typical for the deposits selected at 70...60 °C and containing a significant part of high-molecular paraffin hydrocarbons and minor quantity of tar components in their composition. The similar spherulites consist of closely packed laminar fibrils with thick of some angstroms and width to 1 mkm [7] (Fig. 4, *a*, *b*).

For the paraffin hydrocarbons of the deposit selected at the oil stream temperature of 50 °C, the type of crystallization remains approximate to the spherulitic one (Fig. 4, *c*). In this case, reduction of spherulites sizes and form is observed. There no vast separate fibril formations in the deposit. Homogeneity of spherulitic crystallization of paraffin hydrocarbons is attracted attention. It may be explained by the initial dispersive influence of surface-active substances, contained in tar components [8]. At oil stream temperature decrease to 40 °C the structure of oil deposit assumes more coagulation or amorphous character due to the increasing content of tar components in deposit composition (Fig. 4, *d*). The type of paraffin hydrocarbons crystallization is spherulitic.

For the paraffin hydrocarbons of the deposit, selected at the oil stream temperature of 30 °C, the increase of a part of dendritic modification of crystal structures is typical that can be explained by the raising part of low-molecular paraffin hydrocarbons (Fig. 4, *e*). The rise of a part of tar components in the composition of oil deposit increases the degree of amorphism in the ATPD structure.

For the paraffin hydrocarbons of oil deposit of 122 well of Upper-Salat deposit the similar tendency of crystal structure change at oil stream temperature decrease is observed (Fig. 4, *f–h*). The raised content of tar components in deposit composition increases the amorphism degree in ATPD structure.

Thus, the studied oils differ significantly in alkanets composition, content of tar and aromatic components that defines the peculiarities of deposit formation in them. For the oil of 122 well with high content of solid paraffins, but distinguished by higher concentration of tar components, the process of sludge formation is observed starting from the temperature +50 °C. In the oil of 118 well deposit formation occurs even at +70 °C.

Oil stream temperature decrease results in increase of a part of dendritic type of paraffin hydrocarbons crystallization and amorphism degree in oil deposit structure. The deposit formed from the oil of 118 well at 60...70 °C, is characterized by a higher content of high-molecular paraffins and slight tar component concentration, low solubility in organic solvents. By the physical properties it is distinguished by higher fragility. The deposit, formed at 30...50 °C, contains the considerable quantity of tar components and it is more soluble in organic solvents.

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INFLUENCE OF REDOX CONDITIONS AND MECHANICAL ACTION ON CHANGE IN PEAT HUMIC ACID COMPOSOTION

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Mechanical action on humic acids is shown to result in change of their composition accompanying decrease in aromaticity degree and increase in oxygen-containing fragments. Mechanical treatment of peat in oxidizing conditions increases the efficiency of extracting water-soluble components and humic acids to the maximum. Structural parameters and functional composition of humic acid molecules change at peat treatment in the redox conditions depending on the conditions.

Humic acids (HA) are the main components of peats in quantity and biological activity and correspond to high-molecular polymer compounds, stiff and insoluble in water [1, 2]. The solution of fundamental task of their investigation is added up to application of extraction, chemical, physicochemical and enzymatic methods. Using mechanochemical transformations in solid phase for developing complex macromolecules of HA is a perspective method of their deeper investigation [3, 4].

The fundamental investigation on solid-phase mechanochemical HA transformations gives the significant technological advantages to the production of bioactive substances on basis of the investigated reactions.

Previously, the preliminary data, indicating the possibility of selective mechanochemical reactions of macromolecules decomposition into definite types of bindings and production preparations from peats with primary content of substances of certain classes – carbohydrates, phenols, lipids, HA were obtained [3, 5]. Due to the system of analytical methods the composition and properties of HA, polysaccharides, polyphenols and lipids from peats, mechanoactivated in the presence of alkaline and enzymatic agents, were investigated.