UDC 661.725.81

DEVELOPMENT PROSPECTS OF BUTYL ALCOHOL PRODUCTION IN JSC «GAZPROM NEFTEKHIM SALAVAT». SYNTHESIS OF MONO GLYCOL ESTER FROM THE PROPYLENE HYDROFORMYLATION PRODUCTS

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Abstract. *The ways of development of butyl alcohol production in JSC «Gazprom neftekhim Salavat» were analyzed, towards, the isobutyraldehyde extraction from the propylene hydroformylation products and producing from it the mono glycol ester – as a component of water-dispersion paint-and-lacquer materials. The distillation of propylene hydroformylation products was carried out in laboratory. The isobutyraldehyde was extracted. The Mono glycol ester was synthesized and analyzed by methods of IR- Fourier spectroscopy and chromatography-mass spectrometry. Technological scheme for obtaining mono glycol ether was proposed.*

Keywords: *isobutyraldehyde, mono glycol ester, hydroformylation, synthesis, self-condensation, distillation*

At the moment, technologies of butyl alcohol production based on rhodium catalyst are prevailed in the world, using such technologies the ratio of normal and isobutyraldehyde (IBAL) is (10÷25):1. In Russia, the hydroformylation unit mainly based on cobalt catalyst system characterized by a ratio of normal and isomeric structure products 4:1 [1]. And so it is interesting to extract the IBAL from C_4 aldehydes mixture and convert it in higher value product, than isobutyl alcohol.

At JSC «Gazprom neftekhim Salavat» is operating butyl alcohols production unit by propylene hydroformylation in presence of cobalt carbonyls catalyst with the capacity 170 thousands t/year. According to the existing technological scheme, hydroformylation products are fed to the hydrogenation stage with a further separation of butyl alcohol by distillation. It is suggested to extract IBAL from hydroformylation products in order to produce a new product such as mono glycol ester (MGE).

MGE is a slow evaporating solvent, a coalescing additive for water-dispersion paint-and-lacquer materials. Coalescent is an organic solvent used in water based paints as a temporary plasticizer, involved in film formation. It helps the binder form a continuous film, especially if the temperature at which the coating is made, close to the minimum allowable [2 - 4].

It should be noted that in Russia these products are not produced. They are imported in order to meet a demand.

Russia buys MGE generally produced by Perstorp (Sweden) and Eastman Chemical (USA) under the trademark "Texanol."

Currently, most of the world's largest companies, owning propylene hydroformylation processes have in the oxo plant MGE producing unit.

In world practice, already known examples of petrochemical complexes which are include the butyl alcohols production unit, the acrylic acid and acrylic esters production, and MGE production unit (BASF together with the firm Yangti Petrochemical в Nanjing, China).

As it is known, JSC «Gazprom neftekhim Salavat» is going to building an acrylic acid and acrylates production unit in order to produce based on them products. One of the directions of development company is production final products, including water-dispersion paint and lacquer materials [5], for which MGE is required as one of the component. Thus, the development of the butyl alcohols production unit in JSC «Gazprom neftekhim Salavat» for the purpose of obtaining a new product – MGE from hydroformylation products is in demand by time.

To verify the possibility of obtaining MGE from propylene hydroformylation products obtained on the operating plant, planned in the laboratory by distillation extracted the IBAL from the distillate of column K-101. The sample of aldehydes mixture was taken from the butyl alcohols production unit JSC «Gazprom neftechim Salavat». Obtained MGE was directed in aldol condensation reaction by the known methodology and analyzed received products.

MGE is obtained by a condensation of three IBAL molecules in presence of an alkaline catalyst in one step to form an intermediate aldehydo-alcohol - pentaldol and follow its conversion to MGE (2,2,4-trimethyl-1,3-pentadiol monoisobutyrate). MGE which is monoester mixture, namely 1-hydroxy-2,2,4-trimethylpentyl-3-isobuyrate and 3-hydroxy-2,2,4-trimethylpentyl-1-isobuyrate. Typically, the product contains as a side product also minor amounts of 2,2,4-trimethyl-1,3-pentadiol. Also as a by-product is formed IBAL tetramer (2,2,4-trimethylpentyldiisobutyrate) used as an ester plasticizer [6].

During the initial condensation reaction of 2 molecules IBAL (I) to form the corresponding aldehydo-alcohol (II), which by accession of another molecules IBAL converted to trimmer IBAL (III),which is able to move in the taytomeric form of 2,6-diisopropyl-5,5-dimethyl-1,3-dioxane-4-ol (IV). As a result of intramolecular transfer proton H^+ in IBAL trimmer is formed a desired product as a mixture of 2 isomers of 2,2,4-trimethyl-1,3-pentadiol monoisobutyrate (V) и (VI).

As a catalysts are used LiOH, NaOH and LiOH mixture or NaOH, KOH, LiOH mixture, calcium, barium, strontium, tin oxides [6 - 9].

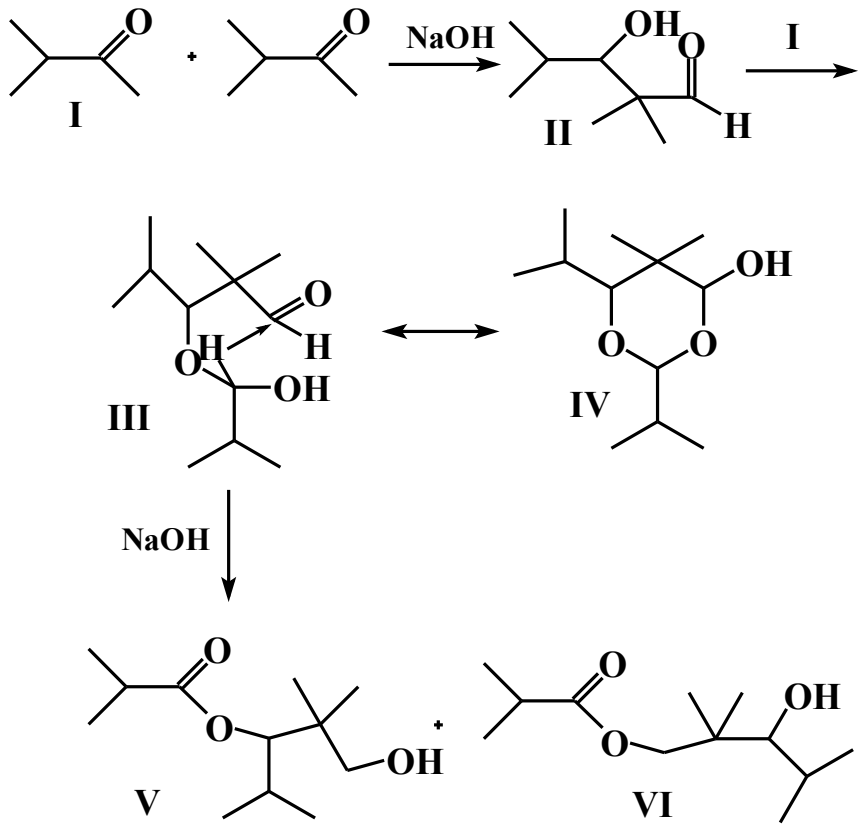

Fig. 1. The mechanism of reaction formation MGE [11]

Basically, the condensation reaction is carried out in the temperature range 65 - 105 °C, the time of the synthesis from 15 minutes to 6 hours [10].

The received condensation product separated by distillation at atmospheric pressure or under vacuum [6, 11].

The experimental part

The MGE was synthesized from IBAL in laboratory by authors of this work.

IBAL was produced from a straight and branched chain aldehydes mixture by distillation. The mixture was sampled from the operating butyl alcohols production JSC «Gazprom neftekhim Salavat» (distillate of column K-101).The composition of the mixture: IBAL 70.4 %, normal butyraldehyde 21.5 %, hydrocarbons 2.7 %, H_2O 5.3 %.

Distillation was carried out on periodic operation distillation column, equivalent of 30 theoretical plates under atmospheric pressure.

Received fractions were analyzed by methods of IR- Fourier spectroscopy and gas-liquid chromatography. The fraction containing 98.4 % wt. IBAL used for the synthesis of MGE, chromatogram of this fraction is shown in Fig. 2.

Analysis by method IR-Fourier spectroscopy confirmed that distillation product is IBAL (Fig. 3).

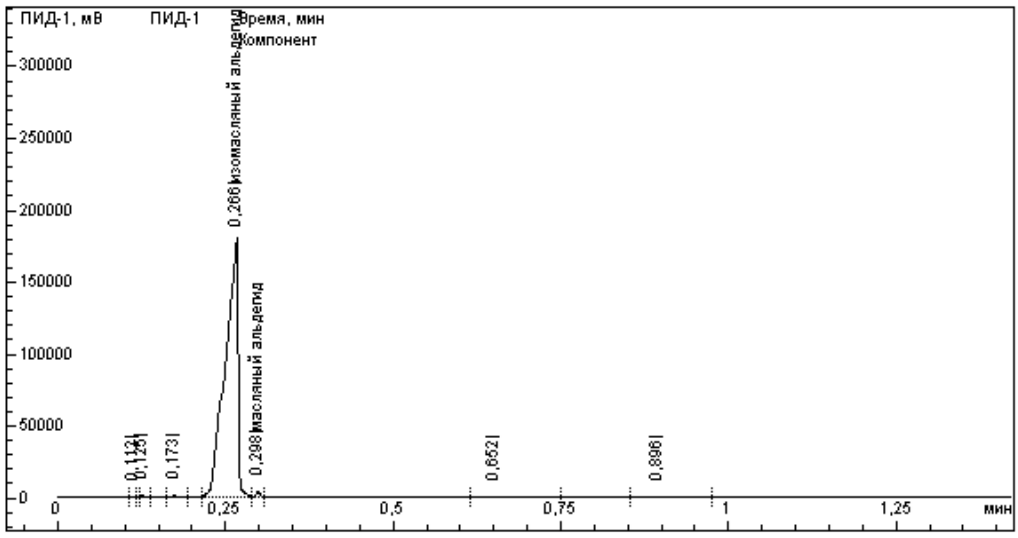

Fig. 2. Chromatogram of the product received by distillation of column K-101 distillate

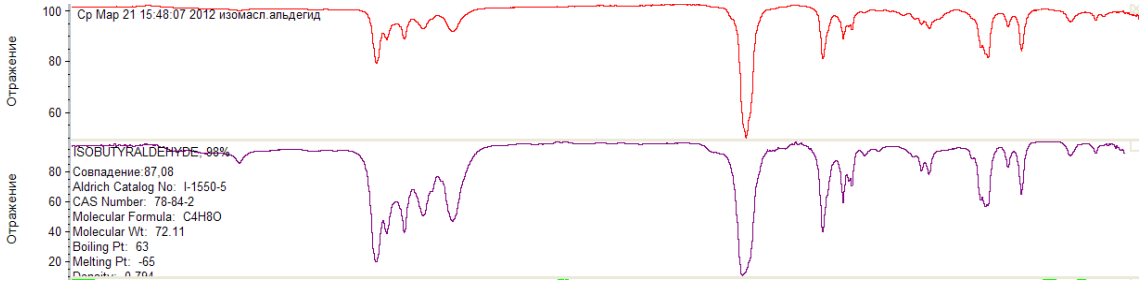

Fig. 3. IR- spectrum of the product received by distillation of column K-101 distillate in comparison with the library spectrum of IBAL

Aldol condensation of IBAL was studied in detail so as a method of synthesis of MGE was chosen one of the patented methods [6], applicable for the synthesis in laboratory.

The advantages of this methodology are its simplicity, low reaction time, using sodium hydroxide as a catalyst and low equipment requirements.

10 % aqueous solution of NaOH was placed into a four-neck flask equipped by a stirrer, a thermometer and metering pump. The contents of the flask was heated up to 60 °C. IBAL was added in a stirred solution by using the metering pump at a rate of 0.6 ml /min, the total time of dosing was 2.5 hours. The reaction mixture was stirred for 3 hours at 60 °C after completion of dosing. After completion of the reaction the organic and the aqueous layer were separated in a separating funnel. The organic phase was washed three times by distilled water in portions of 100 ml [6]. The time of layers separation is no less than 1 hour at washing the organic phase. The combined organic extracts were dried by calcined magnesium sulfate. Product was obtained as a light yellow color viscous liquid.

Structure obtained product was analyzed by methods of IR- Fourier spectroscopy and chromatography-mass spectrometry.

Analysis by method of IR-Fourier spectroscopy

Analysis was done on the infrared Fourier spectrometer Nicolet 6700 the company «Thermo Electron Corporation». The operating principle of device is based by moving of one of the interferometer mirrors change in the path difference among interfering beams.

Recorded light output at the output of the interferometer (interferogram) is the Fourier-imagery of the recorded optical spectrum.

The spectrum itself is obtained by performing special mathematical calculations on the interferogram (the inverse Fourier transformation). The obtained absorption spectrum is unique for a given substance [12].

IR-Fourier spectrometer, in additional to reading spectrums of substances allows to compare they on the database with library of IR-spectrum of compounds present in library.

Stretching vibrations of the free hydroxyl group (OH) were observed in the area of 3440 cm^{-1} on the IR-spectrum of the obtained product. The signals of the carbonyl (C=0) and ester (C-O-) groups were marked in the area 1713 and 1196 cm^{-1}, respectively (Fig. 4).

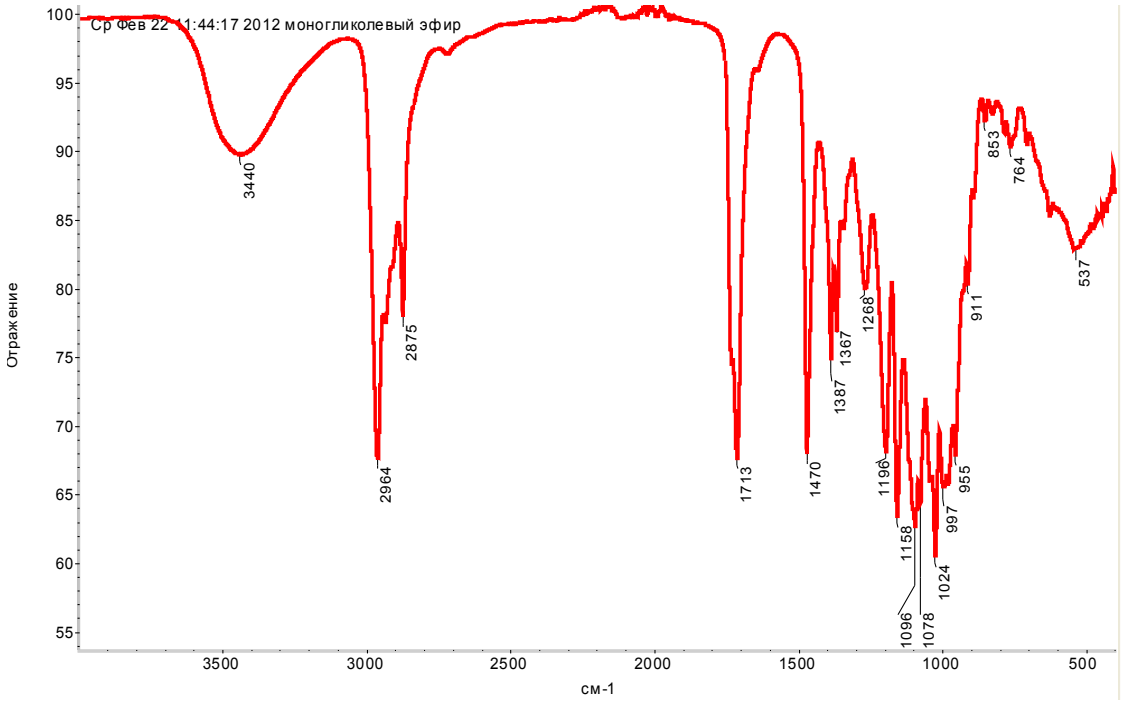

Fig. 4. IR-spectrum of IBAL aldol condensation product

A comparison of obtained IR-spectrum with spectrum of aldehyde from the library of device is confirmed the structure of the obtained product (Fig. 5).

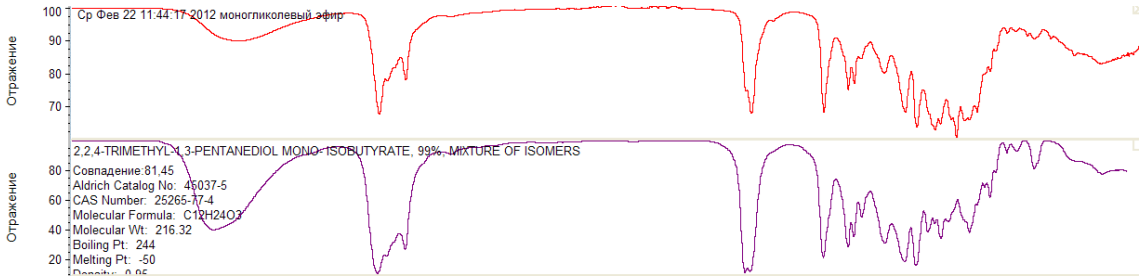

Fig. 5. IR-spectrum of IBAL aldol condensation product in comparison with spectrum of MGE from a device library

Analysis by chromatography-mass spectrometry method

Analysis was done on gas chromatography mass-spectrometer GCMS-QP 2010 Plus (Shimadzu) on a capillary column ZB-1 length of 30 meters.

The method is based on a combination of two independent methods – gas chromatography and mass spectrometry. Separation of a mixture to the components is carried out by using first, identification and structure determine of obtained individual compounds and quantitative analysis by using the second [12].

Method allows to identification isomers in the product synthesis and determines their proportion. Chromatogram of IBAL aldol condensation product is represented on Fig. 6.

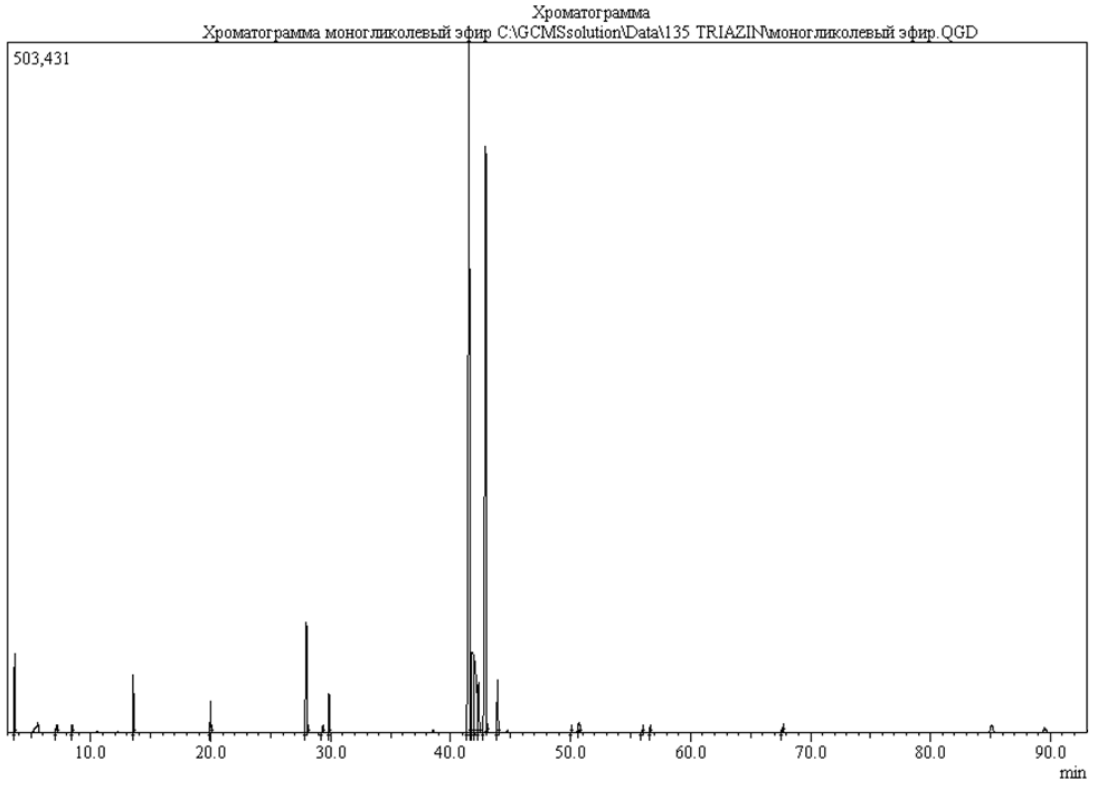

Fig. 6. Chromatogram of IBAL aldol condensation product

There are peaks both isomers of the MGE in the chromatogram 1-hydroxy-2,2,4-trimethylpentyl-3-isobuyrate and 3-hydroxy-2,2,4-trimethylpentyl-1-isobuyrate with retention times of 41,54 and 42,92 min., correspondingly (mass spectrum of isomers is represented on Fig. 7 and 8). The ratio of desired isomers in the product was 1:1, their total content in the mixture was 80 %, the others – unidentified minor components.

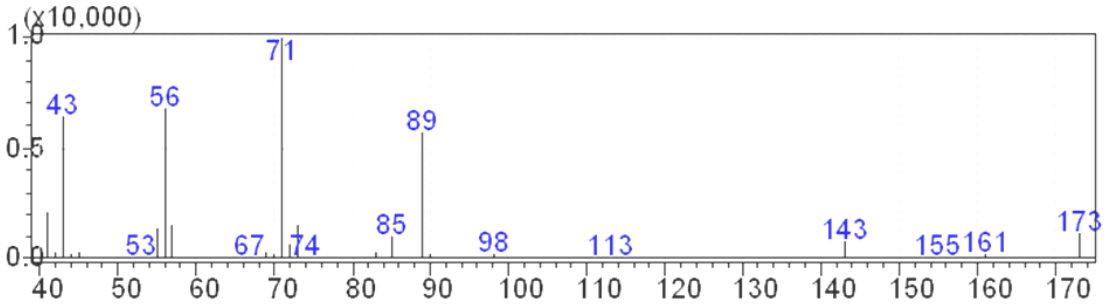

Fig. 7. Mass spectrum of 1-hydroxy-2,2,4-trimethylpentyl-3-isobuyrate

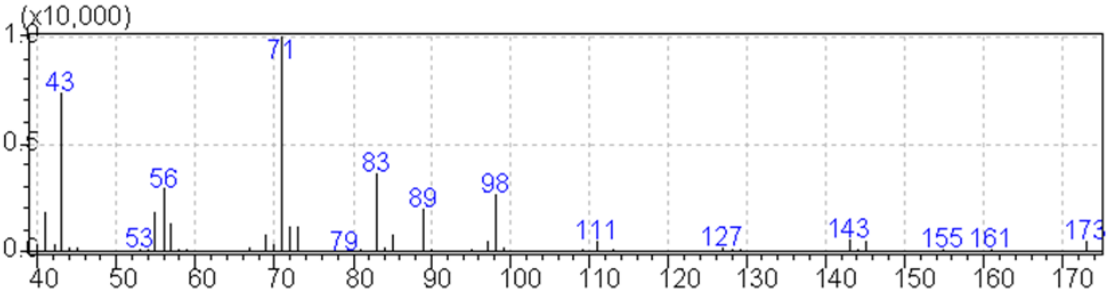

Fig. 8. Mass spectrum of 3-hydroxy-2,2,4-trimethylpentyl-1-isobuyrate

Researching by chromatography mass-spectrometer method is confirmed that the obtained product of IBAL aldol condensation is MGE, consisting of two isomers in a ratio of 1:1, the content of the desired product in a mixture of 80 %.

Technological scheme of MGE production

To MGE industrial manufacture the following technological scheme was suggested – Fig. 9.

The sample of a straight and branched chain aldehydes mixture was taken from the operating butyl alcohol production unit JSC «Gazprom neftekhim Salavat» in order to obtain MGE by distillation of sampled mixture. Existing columns K-101 and K-102 are designed to extract the normal butyraldehyde. It is suggested to extract an IBAL concentrate as a side stream of K-101, and then extract IBAL and direct to the MGE synthesis according to the following proposed scheme: azeotropic distillation column K-1 is designed to additional drying of IBAL, K-2 – for the regeneration of a separating agent. IBAL and NaOH aqueous solution, at the same time, are fed to the aldol condensation reactor R-1. Then the reaction mass is directed to the decanting tank T-1 to

separate the NaOH aqueous layer, which is recycled to the reactor R-1. Further, an organic phase from the phase decanting tank T-1 is directed to the column K-3 for the separation of unreacted IMA and returning it to the reactor R-1.A K-3 bottom product is directed to the decanting tank T-2 in order to alkali impurities washing. An aqueous phase, containing an alkali, sodium salts and dissolved organic matter is directed to purification.

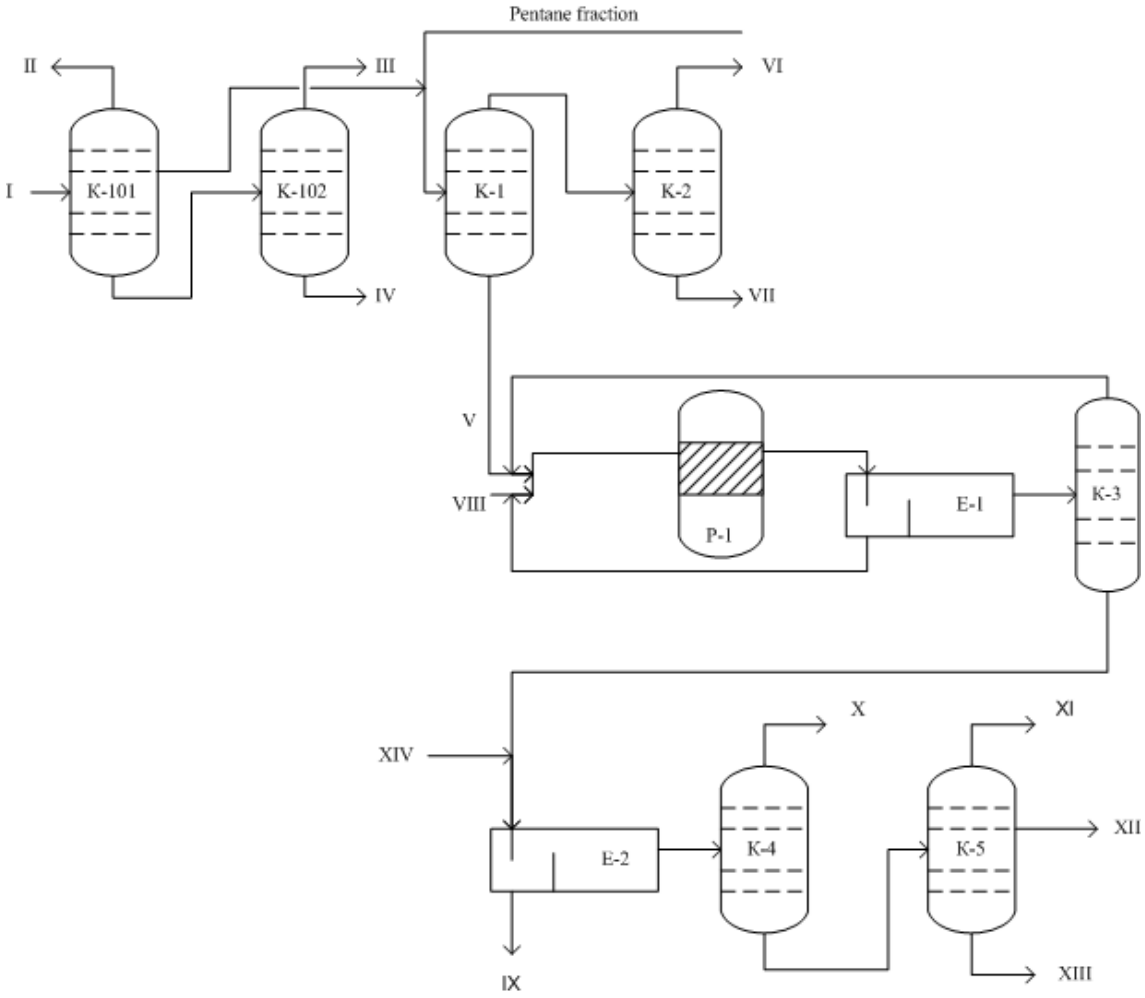

Fig. 9. Technological scheme of MGE production:

I – hydroformylation products; II – «lights», to hydrogenation;
III – desired normal butyraldehyde; IV – «heavy», to hydrogenation; V – desired IBAL;
VI – pentane fraction; VII – hydrocarbons impurity and water; VIII – NaOH aqueous solution;
IX – water to purification; X, XI – low-boiling impurities; XII – desired MGE;
XIII – high-boiling impurities; XIV – rinsing water

An organic layer from decanting tank is directed to desired MGE separation section. Column K-4 is designed to remove low-boiling by-products. Column K-4 bottom stream is fed into a feeding column K-5 to extract marketable MGE as a side stream.

Conclusions

The ways of development of butyl alcohol production in JSC «Gazprom neftekhim Salavat» were analyzed and, towards, the IBAL extraction from the propylene hydroformylation products and producing from it the MGE – product with higher value, than isobutyl alcohol.

The IBAL was extracted from propylene hydroformylation products by distillation in laboratory. The obtained product containing IBAL 98.4 % wt. The sample for distillation was taken from the distillate column K-101 operating butyl alcohol production unit JSC «Gazprom neftekhim Salavat».

The MGE was synthesized from extracted IBAL. The structure of the obtained product was proved by methods of IR- Fourier-spectroscopy and chromatography-mass spectrometry. Researching by chromatography-mass spectrometry method is confirmed that the obtained product of IBAL aldol condensation is MGE, consisting of two isomers in a ratio of 1:1, the content of the desired product in a mixture of 80 %.

Technological scheme of MGE productions was proposed with partial using of the existing equipment of operating butyl alcohol production unit JSC «Gazprom neftekhim Salavat» - such as column K-101 reconstruction (sire stream assembly).

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