

DEVELOPMENT OF TECHNOLOGY FOR OBTAINING HIGHLY CONCENTRATED ISOBUTYLENE

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ANNOTATION

The process of isobutylene hydration on sulfonic cationic catalysts is characterized by a relatively low reaction rate, the presence of a phase separation due to the mutual insolubility of water and hydrocarbons, and a high energy intensity of the process due to the need to concentrate dilute alcohol-containing solutions. However, the indisputable advantages of this method are the high degree of extraction (98–99%) of isobutylene from the hydrocarbon fraction and the high purity of the resulting monomer – 99.99 wt.% of the main substance.

Keywords: rubber, temperature, process, fraction, solution.

INTRODUCTION

Among special-purpose rubbers, butyl rubbers are the most large-tonnage, and the production of both butyl rubber and halobutyl rubbers is increasing every year, which necessitates a constant increase in the production of monomer - high-purity isobutylene with a concentration of at least 99.95 wt.%.

Traditional methods for obtaining isobutylene-containing fractions are the processes of pyrolysis of hydrocarbon raw materials, catalytic cracking, and dehydrogenation. The content of isobutylene in C₄ hydrocarbon fractions can vary on average from 15–16 wt.% in catalytic cracking fractions to 42–46 wt.% during isobutane dehydrogenation [1].

Due to the similar values of the boiling points of the C₄ components of hydrocarbon fractions, the existing industrial methods for extracting isobutylene are based on its preliminary chemical interaction with various reagents.

The main industrially developed methods for the extraction of isobutylene in the world are methods based on the synthesis, isolation and subsequent decomposition of tert-butanol on sulfonic cation-exchange catalysts [1, 2], as well as alkyl tert-butyl ethers, primarily methyl tert-butyl ether (MTBE), the production of which has been mastered at many petrochemical enterprises by now.

There is no unequivocal answer to the question of the preference of one or the other method, each of these methods has its own advantages and disadvantages.

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The process of isolation of isobutylene from hydrocarbon fractions through the synthesis - isolation - decomposition of MTBE is characterized by lower energy consumption, but this method is also imperfect. Its disadvantages are associated with the use of higher temperatures, the need for steam dilution at the MTBE decomposition stage [3], the presence of an azeotropic mixture of methanol with isobutylene, and the formation of dimethyl ether (DME) at the MTBE decomposition stage, which significantly complicates the task of isobutylene purification.

The question of choosing the technology for extracting isobutylene from the corresponding C₄ fractions arises when it comes to building a new plant. But often the task is to modernize and increase the capacity of existing production facilities. The only industrially mastered technology for the production of isobutylene of polymerization purity at the enterprises of the Russian Federation is the technology developed by NIIMSK (Yaroslavl) [1], based on the hydration of isobutylene in the presence of a molded sulfonic cationic catalyst in a reaction-extraction type reactor at a large (10–15-fold) mass excess of water in relation to hydrocarbons.

The authors of [4, 5] showed that when isobutylene is hydrated on a macroporous sulfonic cation exchanger with the introduction of a certain amount of tert-butanol into the reaction system to increase the mutual solubility of water and hydrocarbons and the process is carried out in three successive stages, a TBS solution with a concentration of up to 86 .6 wt%. Various variants of the technological process based on this approach are given. The most promising, in our opinion, are the embodiments of the process, where the reaction unit is presented in the form of two sequentially located reactors, and the process is carried out without additional supply of TBS to the reactors [6], or in the form of one reactor with several reaction zones and preliminary supply of tertiary butanol to the inlet of the first reaction zone [7, 8]. The main types of hydrocarbon feedstock for the production of isobutylene of polymerization purity are isobutane-isobutylene fractions obtained after dehydrogenation of isobutane, and butylene-containing C₄ pyrolysis fractions after extraction of butadiene-1,3 from their composition. The choice of raw materials for each manufacturer is determined by the availability or availability of a particular production method. In the process of obtaining highly concentrated isobutylene at OAO

Nizhnekamskneftekhim, only butylene-isobutylene pyrolysis fraction is used after preliminary separation of butadiene-1,3 from it and concentration of isobutylene. The process is carried out in a countercurrent mode in a cascade of reaction-extraction type reactors. The experience of operating an industrial plant shows that the proportion of side reactions of the formation of secondary alcohols and olefin oligomerization is greater when using butylene-isobutylene fraction (BIF) as a feedstock compared to IIF. This pattern takes place despite the fact that a large excess of water used in the process suppresses the side reaction of alkene oligomerization. This is due to the presence in the BIF, along with isobutylene, of butene-1, trans-, cis-butenes-2, and butadiene-1,3.

During the synthesis of TBS from butylene-isobutylene fractions under the conditions of the use of highly active macroporous cation exchangers and a slight (10–20 mol.%) excess of water, the proportion of side reactions of the formation of dimers and secondary butyl (SBA) and butenyl alcohols can increase.

EXPERIMENTAL PART

Experiments on isobutylene hydration were carried out on a laboratory setup with a flow reactor with a volume of 500 cm³ loaded with a sulfocationite catalyst in an amount of 110 g. Macroporous cationite Lewatit K 2620 from Lanxess (Bayer) and molded catalyst KU-2FPP (TU 2174-011-05766801–2003) produced by OAO Nizhnekamskneftekhim, which is a composition of polypropylene and a sulfonated copolymer of styrene and divinylbenzene; the total static exchange capacity of the catalysts is 5.2 and 3.8 mmol/g, respectively. The set temperature value was provided by the supply of coolant from the thermostat to the reactor jacket through flexible hoses. The initial reagents were supplied by dosing pumps. A mixture of water with TBS and the C₄ fraction were supplied in separate streams, which was crushed with water from an intermediate vessel.

IIF and BIF were used as the initial hydrocarbon fractions, the average compositions of which are presented in Table. one.

To improve the mutual solubility of hydrocarbons and water, a fraction of the TBS azeotrope with a water content of 11–12 wt % was used. The experiments were carried out at temperatures of 70, 80, 90°C and space feed rates of 0.96 and 1.4 h⁻¹. To maintain the components of the mixture in the liquid phase, the pressure in the system, depending on the temperature, was kept in the range of 17–20 atm.

To obtain more reliable results in each experiment, two samples of the reaction mass were taken for analysis with an interval of 30 min. Depending on the volumetric feed rate of raw materials, the first sampling was carried out no earlier than 1.5-2 hours after the plant reached the specified operating mode. Samples of the reaction mixture in the amount of 5–6 cm³ were taken into glass ampoules placed in special metal containers. The composition of the reaction mixtures was determined by three different methods on a Kristall-5000 Lux chromatograph using capillary columns with supported Al₂O₃/Na₂SO₄ and CP WAX 57 CB phases. The components of the reaction mixture were identified on a DSQ (Thermo Electron) chromato-mass spectrometer using a capillary column with a deposited CP WAX 52 CB phase.

The experimental data obtained confirm our assumptions regarding an increase in the yield of by-products when butylene fractions are used as isobutylene-containing raw materials. At the

same time, if we compare the hydration process in a flow reactor with an industrial process carried out in a countercurrent reaction-extraction mode, when BIF is used as a raw material and macroporous sulfonic cation exchangers as a catalyst, the total amount of by-products in them is commensurate, and they are represented by the same compounds.

Thus, if it is necessary to increase the productivity of existing installations for the production of highly concentrated isobutylene, the best option, in our opinion, is the joint use of reaction-extraction and flow type reactors. A schematic diagram of the design of the reactor unit of such a combined process is shown in fig. 3.

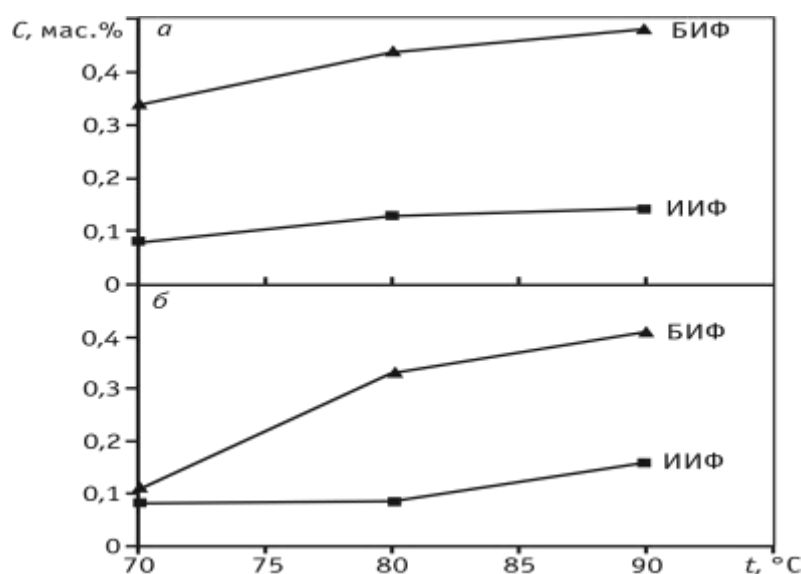


Fig 1. Temperature dependence of the concentration of dimers (wt.%) for BIF and IIF feedstock at a feedstock volumetric feed rate: a – 0.96 h⁻¹, b – 1.4 h⁻¹

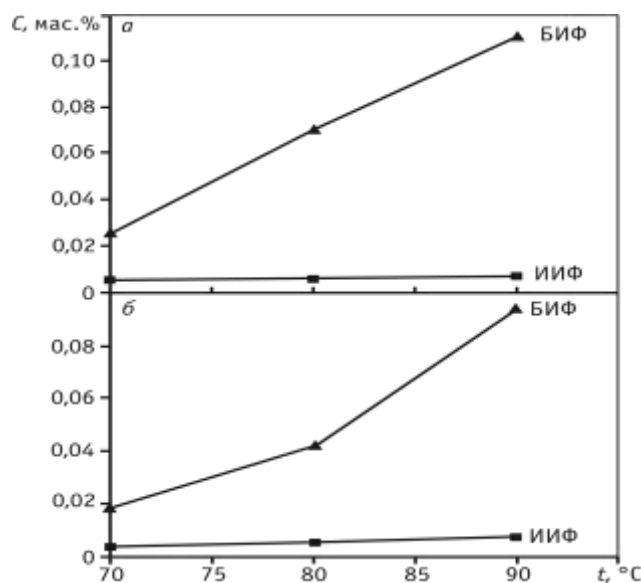
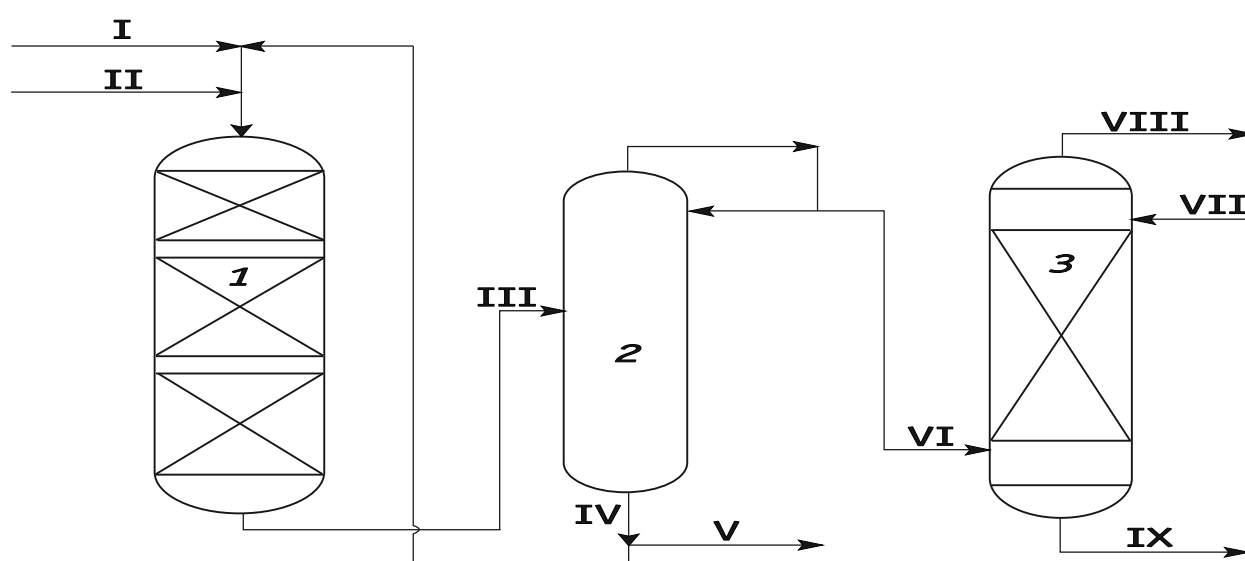


Fig. 2. Temperature dependence of the concentration of sec-butanol (wt.%) for the BIF and IIF feedstock at a space feed rate of the feedstock: a – 0.96 h⁻¹, b – 1.4 h⁻¹ isobutylene interacts with water, forming TBS.

Next, the hydrocarbon fraction (VI) after separation from the water-alcohol solution in the column (2) is sent to the reaction-extraction reactor (3), where the remaining isobutylene is recovered. The streams of the spent hydrocarbon fraction (VIII) and aqueous solutions of TBS (V and IX) are further processed according to the technological scheme of an existing production.

The implementation of such a scheme will make it possible to maintain a high degree of extraction of isobutylene from the composition of the initial BIF, to obtain a concentrated solution of tert-butyl alcohol at the reactor outlet already at the first stage, to reduce the amount of water supplied to the reaction-extraction reactor of the second stage, and, accordingly, to reduce energy consumption at the concentration stage TBS.



Rice. 3. Schematic diagram of the reactor unit for the combined process of TBS synthesis using flow and reaction-extraction reactors:

1 - flow reactor; 2 - distillation column; 3 - reaction-extraction type reactor. Flows: I - BIF; II and VII - water; III - a mixture of hydrocarbons, TBS and water; IV, V and IX - aqueous solutions of TBS; VI and VIII - C₄ hydrocarbons

CONCLUSION

For the process of obtaining polymerization isobutylene by synthesis and subsequent decomposition of TBS, C₄ fractions of various origins that do not contain diene hydrocarbons can be used. In this case, depending on the composition of the initial hydrocarbon feedstock, the rate of interaction of isobutylene with water and the yield of by-products change. Namely, when using butylene-containing fractions, there is an increased formation of oligomers and secondary C₄-alcohols, as well as a decrease in the rate of the isobutylene hydration reaction. It follows from this that the productivity of the reactor in terms of raw materials when using the BIF will be somewhat lower than when working at the IIF, and an increase in the share of by-products will adversely affect the stages of purification of intermediate process streams and the final product. In this case, the nature of the hydrocarbon feedstock is not decisive for the choice of the structure of the reactor assembly.

When modernizing and increasing the capacities of existing production facilities for isobutylene isolation of polymerization purity, the optimal solution seems to be the inclusion of an additional flow type hydration reactor in the process chain. Combining the two types of reactors will make it possible to maintain a high degree of isobutylene recovery, which is characteristic of the reaction-extraction process, to reduce the energy consumption of the process as a whole by obtaining a concentrated TBS solution at the outlet of the flow reactor, and at the same time to obtain high-purity isobutylene - at least 99.99 wt. %.

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