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PREPARATION OF PROPYLENE OXIDE FROM THE HYDROCHLORINATION OF PROPYLENE GLYCOL

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ABSTRACT
In the article, the method of determining the physico-chemical characteristics of the hydrochlorination of alcohols using the example of propylene glycol, determining the optimal parameters of the hydrochlorination of propylene glycol and developing the reaction node in the main technological scheme is given.
Keywords: propylene glycol, hydrochlorination of alcohols, propylene chlorohydrin, propylene oxide, acetic acid catalyst.

Introduction

Currently, the most commonly used product obtained by hydrochlorination of alcohols is methyl chloride. Its global consumption is more than 1 million tons per year, and a significant part is obtained as a result of liquid-phase hydrochlorination of methanol. The advantage of this method is the possibility of recycling technical hydrochloric acid, which is one of the main problems in the chlorine-organic industry [1].

Another reaction important to modern industry is the hydrochlorination of glycerol, which is one of the steps in the production of epichlorohydrin. With the development of the biodiesel industry on the world market, there was a surplus of glycerin, and its price fell sharply, and the production of synthetic glycerin was forced to close. Thus, many chemical companies began to look for new markets for its sale, including in the field of technology. One of these directions is the synthesis of epichlorohydrin [2].

Theoretıcal part

The technology of hydrochlorination of alcohol and subsequent dehydrochlorination of the resulting chlorohydrins allows obtaining other oxiranes. So, for example, it is possible to get propylene oxide from propylene glycol. As an intermediate product, pentaerythritol chlorides are used in the polymer industry, for example, in the production of pentaplast.

Until recently, ethyl chloride, obtained by hydrochlorination of ethanol, was widely used to produce tetraethyl lead, an antiknock additive for motor fuel.

Currently, tetraethyl lead is being replaced or phased out of industry in most industrialized countries. For this reason, the demand for ethyl chloride has decreased significantly. At the same time, ethyl chloride continues to be used as an ethylating agent today, for example, in the preparation of some organoaluminum compounds [3].

Also, some higher chloroalkanes are now obtained by hydrochlorination of the corresponding

ones with alcohols. In recent years, due to the continuous increase in hydrocarbon prices, more technologies have emerged that use renewable plant resources as feedstock. An example of such technology is the synthesis of epichlorohydrin from glycerol described above.

As already mentioned, propylene oxide, whose consumption exceeds 6 million tons per year and is constantly increasing, can be produced in a similar way. At this time, the raw material for the production of propylene glycol can be glycerin. Another source of propylene glycol is the processing of renewable plant resources and the subsequent production of lactic acid. Using this technology, hydrogenation of lactic acid esters produces propylene glycol in almost quantitative yield [4].

In the production of propylene oxide, it is advantageous to use hydrogen chloride and propylene glycol instead of expensive chlorine and propylene to obtain propylene chlorohydrins, which significantly reduces the cost of propylene oxide.

Currently, there are two main methods of producing propylene oxide - chlorohydrin and peroxide [5].

According to the first method, propylene and chlorine are mixed with 4-7 times excess water (1.1). At this stage, propylene is supplied in a slight molar excess of chlorine to prevent chlorine loss.

$$C_3H_6 + H_2O + Cl_2 = C_3H_7OCl + HCl \qquad (1.1)$$

To reduce the amount of side products, the reaction is carried out at 35-40 ° C, keeping the concentration of propylene chlorohydrin no more than 4-6% by weight. Excess propylene is separated and returned to the reaction [3].

In the next step, the aqueous solution of the mixture of propylene chlorohydrins is treated with excess alkali (1.2).

$$C_3H_7OCl + NaOH = C_3H_6O + NaCl + H_2O \qquad (1.2)$$

Currently, only NaOH solution is used in the dehydrochlorination stage. The most economical type of process is combined with chlor-alkali electrolytic production. Hydrolysis of propylene chlorohydrins is carried out after electrolysis with NaOH solution at a temperature of 80°C, and the resulting NaCl solution is sent for electrolysis again.

Another industrial method for the production of propylene oxide is hydroperoxide (the Chalcone process). When hydroperoxides react with alkenes (1.3), two main products are formed - a-oxide and alcohol, so all processes of this type are combined.

$$C_3H_6 + HOOH = C_3H_6O + HOH \qquad (1.3)$$

The side reaction is the parallel decomposition of hydroperoxide (1.4), which takes place in the catalyst. The process is carried out in the liquid phase at a temperature of 90-120°C and with a 2-5 times excess of propylene relative to hydroperoxide. Depending on the volatility of the hydrocarbon and the solvent, the pressure to keep the reaction mass in liquid state can reach 2-7 MPa. Under these conditions, the reaction has a fairly high rate with an amount of catalyst of 0.001-0.005 mol per 1 mol of hydroperoxide. Depending on the temperature, the concentration of the catalyst and the nature of the starting reagents, the reaction time varies from 0.3 to 2 hours. Reaction catalysts are salts and complexes of various molybdenum, tungsten, vanadium, titanium, niobium and other transition metals dissolved in the reaction mass. The choice of hydroperoxide

is determined by the practical importance of the second product, an alcohol that can be converted to the corresponding olefin by dehydration. For this reason, hydroperoxides of ethylbenzene, isobutane and isopentane have gained practical importance [6].

The chlorohydrin method has a fairly high productivity, but is characterized by the formation of by-products and large amounts of wastewater. The advantage of the peroxide method is the ability to obtain various alcohols together with the oxide, but the low yield of propylene and the simultaneous decomposition of hydroperoxide with the main reaction reduce the efficiency of the process. The main drawback of these methods is the dependence on oil for raw materials [7].

A promising new method for the production of propylene oxide from propylene glycol does not have the disadvantages considered in existing industrial processes. When developing this technology, one of the main tasks was to study the kinetics of the hydrochlorination reaction of propylene glycol, which would allow to optimize the reaction unit for the production of propylene chlorohydrins.

Experımental part

The work used the simplest monohydric alcohols such as methanol and ethanol, as well as propylene glycol, which allowed to optimize one of the stages of the promising technology for obtaining propylene oxide from renewable plant raw materials.

Hydrochlorination of propylene glycol is one of the stages of the new promising technology for obtaining propylene oxide from renewable plant raw materials.

In this case, two isomers are formed

Propylene chlorohydrin usually refers to the organic compound of the formula $CH_3CH(OH)CH_2Cl$ 1-chloropropan-2-ol. A related compound is the isomer $CH_3CH(Cl)CH_2OH$-d 1-chloro-2-hydroxypropane. Both isomers are colorless liquids soluble in organic solvents. They are classified as chlorohydrins. Both are widely produced as intermediates in the production of propylene oxide.

In the hydrochlorination process without the presence of an acetic acid catalyst, β propylene chlorohydrin is mainly formed. In the presence of an acetic acid catalyst, α propylene chloride is preferred. In this process, the catalytic effect of acetic acid is the formation of esters with propylene glycol, so that the aceto group is replaced by chlorine more easily than the hydroxyl group [8].

With the increase of process temperature, the selective production of β propylene chlorohydrin decreases, and the selectivity of obtaining α propylene chlorohydrin does not depend on the process temperature.

However, an analysis of the results of experiments conducted over a wide range of reactant concentrations at 100°C (Table 1.1) shows that the calculated value of the rate concentration varies with the change in water concentration in the water.

Table 1. shows the results of experiments studying the hydrochlorination reaction of propylene glycol at a temperature of 100°C.

Table 1. Results of the hydrochlorination reaction of propylene glycol at 100°C

№	$C_3H_8O_2$ C, mol/l	HC1 C, mol/l	H_2O C, mol/l	α-C_3H_7OC1 C, mol/l	β C_3H_7OC1 C, mol/l
1.	9.76	3,07	1,65	0,69	1.04
2	9.18	3.45	3.76	0.25	0.78
3.	8.56	4.46	9.89	0.11	0.68
4.	8.01	4.76	12.34	0.05	0.45
5.	5.98	7.09	24.41	0.03	0.32

Fig. 1 shows the principle scheme of the reaction node of the hydrochlorination of propylene glycol.

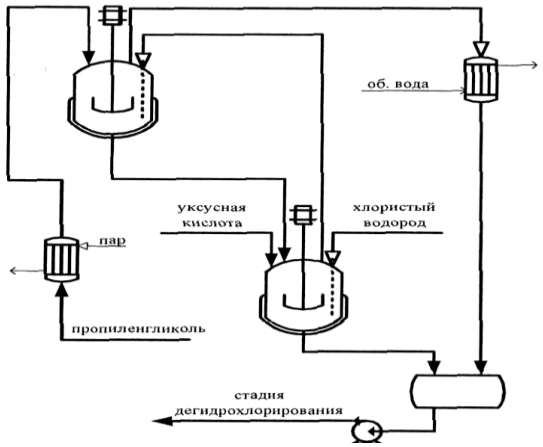

Fig. 1. The principle scheme of the reaction junction of the hydrochlorination of propylene glycol

Hydrochlorination of propylene glycol is carried out in a reactor with a cascade type mixer at a temperature of 105-110°C, which allows boiling of the reaction mixture in the liquid phase. Gaseous hydrogen chloride and propylene glycol are countercurrently supplied. The amount of acetic acid used as a catalyst in the process is 3 percent of the reaction mass.

Depending on the temperature, the concentration of the catalyst and the nature of the starting reagents, the reaction time varies from 0.3 to 2 hours.

Conclusion

1. The physico-chemical factors that optimize the process conditions for the production of propylene oxide from propylene glycol have been determined.
2. Optimum conditions for propylene glycol hydrochlorination process catalyzed by acetic acid were determined.
3. A technological scheme for obtaining propylene oxide from propylene glycol has been developed.

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ПОЛУЧЕНИЕ ПРОПИЛЕНОКСИДА ИЗ ГИДРОХЛОРИРОВАНИЯ ПРОПИЛЕНА ГЛИКОЛЯ

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РЕЗЮМЕ В статье приведена методика определения физико-химических характеристик гидрохлорирования спиртов на примере пропиленгликоля, определение оптимальных параметров гидрохлорирования пропиленгликоля и разработка реакционного узла в основной технологической схеме.

Ключевые слова. Пропиленгликоль, гидрохлорирование спиртов, пропиленхлоргидрин, оксид пропилена, катализатор уксусная кислота.

PROPİLENQLİKOLUN HİDROXLORLAŞMASINDAN PROPİLEN OKSİDİNİN ALINMASI

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XÜLASƏ

Məqalədə propilenqlikol nümunəsindən istifadə etməklə spirtlərin hidroxlorlaşdırılması prosesinin fiziki-kimyəvi xüsusiyyətlərinin müəyyən edilməsi və bunun əsasında propilenqlikolun hidroxlorlaşmasının optimal parametrlərinin müəyyən edilməsi və əsas texnoloji sxemində reaksiya qovşağının işlənib hazırlanması metodikası verilmişdir.

Açar sözlər. Propilenqlikol, spirtlərin hidroxlorlaşdırılması, propilen xlorhidrin, propilen oksidi ,sirkə turşusu katalizatoru