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Research Article

STUDY OF THE PROCESS OF OBTAINING A CATALYST FOR THE SYNTHESIS OF BENZENE BASED ON ETHYLENE FOR THE PRODUCTION OF CYCLOHEXANE

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ABSTRACT

Products of petrochemical industries are necessary for every modern person, thousands of enterprises in various industries. A result of the distillation of crude oil, cyclohexane ended up in naphtha, it was sent to catalytic reformers, where it was processed into benzene. Based on the results obtained in the laboratory for the synthesis of cyclohexane using ethylene, tests were carried out in the central laboratories Shurtan gas chemical complex. When analyzing the resulting product using gas chromatography, it was found thatabout 17.5% cyclohexane was formed. The technical parameters of the products (butadiene-1,3 and cyclohexane), synthesized by the staff of the National University of Uzbekistan and the Central Laboratory of the Shurtan Gas Chemical Complex, give approximate properties to imported cyclohexane at the JSC of the Shurtan Gas Chemical Complex.

KEYWORDS

Benzene, ethylene, cyclohexane, oil, catalyst, reaction of Dils-Alder.

INTRODUCTION

Products of petrochemical industries are necessary for every modern person, thousands of enterprises in various industries. These are varnishes, paints, solvents, polymers, detergents and cosmetics, medicines and much more. Interest in cyclohexane arose in 1938 in connection with the development of nylon by DuPont, which proposed the use of cyclohexane as the preferred raw material. After World War II, nylon production increased by 100% per year for some time, so that the cyclohexane contained in crude oil soon became insufficient. The standard crude oil that was supplied to US refineries at the time contained 1% cyclohexane. Moreover, since as a result of the distillation of crude oil, cyclohexane ended up in naphtha, it was sent to catalytic reformers, where it was processed into benzene. And subsequently, while many other substances were also converted to benzene by catalytic reforming, benzene became a good source of cyclohexane.

Cyclohexane ($C6H12$) is a cycle of six carbon atoms, each has 2 hydrogen atoms. It is similar to benzene, but it does not have double bonds. It is a colorless, water-insoluble and non-corrosive liquid with a pungent odor. It is combustible, like any product derived from oil; it is transported in tanks, tank trucks, barges and metal drums, which must have a red mark adopted for flammable liquids. The industry produces technical grade cyclohexane (purity 95% or 99%) and solvent cyclohexane (purity not less than 85%).

Cyclohexane is also used in the Shurtan gas chemical complex as a solvent for the production of various grades of polyethylene. The polymerization catalysts are dissolved in pure cyclohexane and the ethylene polymerization process is carried out; after the process is completed, the cyclohexane is recovered by distillation and returned to the process

Based on the results obtained in the laboratory for the synthesis of cyclohexane using ethylene, tests were carried out in the centrallaboratoriesShurtan gas chemical complex. Under these conditions, several methods have been tried for the synthesis of ethylene-based cyclohexane.

Ethylene dimerizes to form butene-1. Triethylaluminum is used as a catalyst. The product formed in the process is rectified, and unreacted ethylene is returned to the original synthesis process. The cis-, trans-butene-2 and butadiene-1,3 formed in this process are also separated by distillation. Purified butene-1, cis-, trans-butene-2 is subjected to dehydrogenation to obtain butadiene-1,3. The catalyst is chromium (III) oxide; activated and acid-modified Navbakhor bentonite is used as a carrier. The resulting product is purified from butadiene-1,3, but unreacted butenes are returned to the process. Cyclohexene is obtained by a 4+2 cyclocoupling reaction (Diels-Alder reaction) based on 1,3-butadiene and ethylene obtained by distillation. The catalyst is aluminum chloride and aluminum oxide is used as a carrier. The product is purified by distillation, the resulting mixture of cyclohexane, cyclohexadiene and benzene is hydrogenated on a nickel catalyst to obtain cyclohexane. Hydrogen is used for hydrogenation formed during the synthesis of butadiene-1,3.

In the process of synthesis of butene-1 in the Shurtan gas-chemical complex, a mixture of various hydrocarbons is released as a secondary product. This mixture contains 38.0 - 42.0% butadiene-1,3. This by-product is currently sold as a low quality fuel. Butadiene-1,3 was isolated from this mixture by rectification. The resulting

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product is sent for the synthesis of cyclohexane, as in the first method.

Benzene is synthesized from ethylene. At the same time, activated and acid-modified Navbakhor bentonite was used as a carrier, and chromium oxide (III) was used as a catalyst. From the mixture, benzene is purified by distillation-extraction (the extractant is dimethyl sulfoxide) and rectification. Next, hydrogenation of benzene is carried out, as in the first method, and cyclohexane is obtained.

According to the first proposed method, gaseous products obtained during the synthesis of butene-1 based on ethylene on a granular catalyst impregnated with bentonite, chromium (III) oxide at atmospheric pressure at a temperature of 550–600°C, the catalyzate was reanalyzed by gas chromatography with a yield of 8.74 mol. % butadiene-1.3. The resulting product is separated by distillation with cooling, and the remaining gas mixture is returned to the synthesis.

Table 1

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		Volume	Manually
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Last changed	l.5.1.2.21 16:35:46 by Shodmonova S (modified after loading)		
Analysis Method Last changed	C:\HPCHEM\1\METHODS\DEFUPC4.M 22.12.21 14:57:45 by Niyazov SH (modified after loading)		

Area Percent Report

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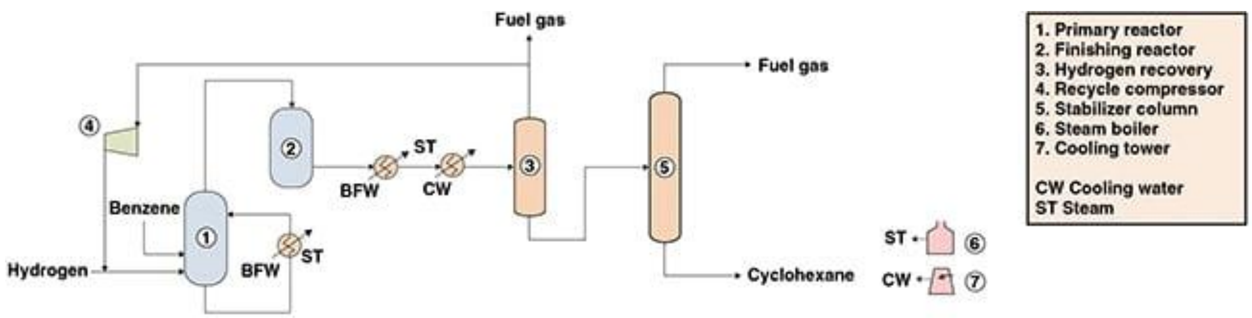

Figure 1. This flow diagram shows a process for producing cyclohexane

Reaction. Initially, benzene is fed to the primary reactor along with fresh and recycled hydrogen. The hydrogenation reaction is carried out in a bubble column reactor, in the presence of a nickel catalyst. The catalyst is maintained in a suspension with the aid of an external circulation loop. Most of the heat of reaction is removed by the vaporization of the product stream, which is further recovered via a top stream within the reactor. The remaining reaction heat is removed in the external loop, by passing the reactor reflux stream through a heat exchanger against boiler feedwater, producing low-pressure steam.

Most of the benzene feed is converted in this step. The top gaseous product stream is directed to a fixed-bed reactor, where the remaining benzene content is converted to cyclohexane. The finishing hydrogenation reaction is conducted in the presence of a solid nickel-based catalyst supported on alumina.

Hydrogen recovery. The product stream is fed to a knock-out drum operated at high pressure. Most of the cyclohexane in the feed condenses, producing two streams: one gaseous hydrogen-rich stream and a liquid cyclohexane-rich stream. The hydrogen stream is routed to the recycle compressor, where it is compressed to the pressure of the primary reactor and recycled.

Purification. In a distillation column, the liquid cyclohexane-rich stream that is recovered is stripped of lighter contaminants, such as methane, ethane and soluble hydrogen. Light-ends recovered from column's top are used for fuel, while a cyclohexane stream with a residual benzene content lower than 100 ppm is obtained from column's bottom.

As a result of the research, a catalyst was synthesized for the alkylation of benzene with ethylene based on zeolite ZSM-5 without binders. To obtain a catalyst mix 24 - 37 wt. % powdered zeolite ZSM-5 with 7 - 11

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wt. % kaolin, 53 - 60 wt. % ground silica gel and 3 - 5 wt. % of oligomeric orthosilicic acid esters. The mixture is moistened, molded into granules by extrusion, then dried and calcined in an atmosphere of air. Then the granules are subjected to hydrothermal crystallization in the reaction mixture of the composition (3,0 - 4,0)Na2O · (0,5 - 2,3)R · Al2O3× ×(60 - 80)SiO2 · (450 - 900)H2O, washed with demineralized water, treated aqueous solutions of ammonium salts to a degree of substitution of Na+ cations in the zeolite at least 97 %, again washed with demineralized water, dried and calcined. Using the synthesized catalyst, alkylation of benzene with ethylene is carried out at a temperature of 400 °C, a pressure of 2,5 MPa, a mass ratio of benzene : ethylene 18 : 1, and a bulk flow rate of benzene of 15 h - 1. The catalyst provides a high content (18,2 - 18,8 wt. %) of ethylbenzene in the alkylate

By passing a mixture of purified 1,3-butadiene and ethylene through a catalyst prepared by impregnating aluminum chloride into activated alumina at a temperature of 500-600°C. The product obtained by the Diels-Alder reaction at a temperature of 280-300°C, hydrogenation with hydrogen at a pressure of 2.0-3 MPa. When analyzing the resulting product using gas chromatography, it was found thatabout 17.5% cyclohexane was formed. Chromatographicanalysisthe product of hydrogenation of pure benzene on a nickel catalyst at a pressure of 2.0-3.0 MPa at 250-280°C gives 25.76 mol.% of the product. The results of the analysis are presented in the following tables (Tables 1 and 2).

The technical parameters of the products (butadiene-1,3 and cyclohexane), synthesized by the staff of the National University of Uzbekistan and the Central Laboratory of the Shurtan Gas Chemical Complex, give approximate properties to imported cyclohexane at the JSC of the Shurtan Gas Chemical Complex. Only for further optimization of this synthesis process, it is necessary to continue joint research to equate its technical parameters with imported cyclohexane.

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