Hydroperoxide method for the production of *para-tert*-butylphenol together with acetone

The relevance of the work. *para-tert*-Butylphenol is one of the main homologues of phenol used as a semi-product of basic organic synthesis. The scope of its application is constantly expanding, covering the production of antioxidants, pesticides, rubbers, lacquers, paints, and recently pharmaceuticals. Promising areas of use of *para-tert*-butylphenol are the production of phenolic resin 2402, used in glued leather products, as well as the production of compounds such as calixarenes and 4-*tert*-butylpyrocatechin on its basis.

In industry, the synthesis of *para-tert*-butylphenol is carried out by alkylation of phenol with isobutylene in the presence of ion-exchange resins of the KU type, and more recently using macroporous sulfocationites of the Amberlyst type at a temperature of 100-110 °C. The disadvantage of this method is the low selectivity (70-75%) of the formation of *para-tert*-butylphenol, while *ortho*- and *meta*-isomers of *tert*-butylphenol are formed along with *para-tert*-butylphenol. The latter, as is known, have boiling points close to *para-tert*-butylphenol, which significantly complicates the isolation of *para-tert*-butylphenol from a reaction mixture with a sufficiently high degree of purity. In the synthesis of *para-tert*-butylphenol by alkylation of phenol with *tert*-butyl alcohol on various heterogeneous catalysts, it is also impossible to avoid the formation of *ortho-tert*-butylphenol.

It is practically impossible to eliminate the shortcomings of the current production of *para-tert*-butylphenol noted above. At the same time, the most promising and economically preferable way to solve this problem can be considered the implementation in industrial conditions of the so-called hydroperoxide method for producing *para-tert*-butylphenol based on the oxidation of *para-tert*-butylcumene, consisting of three stages: synthesis of *para-tert*-butylcumene by alkylation of cumene with *tert*-butyl alcohol in the presence of sulfuric acid, oxidation of *para-tert*-butylcumene to tertiary hydroperoxide and subsequent acid decomposition into *para-tert*-butylphenol and acetone. This way of obtaining *para-tert*-butylphenol has not yet been implemented in petrochemical synthesis. This is primarily due to the difficulty of obtaining *para-tert*-butylcumene, the low rate and selectivity of its oxidation to *para-tert*-butylcumene hydroperoxide. In this regard, the relevance of conducting a complex of studies aimed at developing the scientific foundations of chemistry and technology for obtaining *para-tert*-butylphenol by the hydroperoxide method is beyond doubt.

The purpose and tasks of the work. To develop the scientific foundations of chemistry and technology of a method acceptable for industrial use for the joint production of *para-tert*-butylphenol and acetone based on available petrochemical raw materials.

To achieve the goal of the work, the following tasks are set:

- to analyze the methods of obtaining and chemical transformations of *para-tert*-butylcumene available in the scientific and technical literature;

- to synthesize *para-tert*-butylcumene by alkylation of cumene with *tert-butyl* alcohol;

- to investigate the regularities of the reaction of liquid-phase aerobic oxidation of *para-tert*-butylcumene to hydroperoxide in the presence of *N*-hydroxyphtalimide, to make a kinetic model and to substantiate the role of *N*-hydroxyphtalimide in the reaction of liquid-phase oxidation of *para-tert*-butylcumene;

- to study the influence of temperature, nature and concentration of the catalyst, reaction time on the selectivity of hydroperoxide formation during liquid-phase oxidation of *para-tert*-butylcumene;

- to develop a method for the isolation of *para-tert*-butylcumene hydroperoxide from oxidation products;

- to synthesize *para-tert*-butylphenol and acetone by acid decomposition of *para-tert*-butylcumene hydroperoxide and to study the main regularities of this process.

Scientific novelty. In this work, for the first time, a method for producing *para-tert*-butylphenol based on liquid-phase aerobic oxidation of *para-tert*-butylcumene to hydroperoxide and its subsequent acid decomposition was proposed and experimentally confirmed.

It was found that sulfuric acid alkylation of cumene with *tert*-butyl alcohol makes it possible to obtain only the *para*-isomer of *tert*-butylcumene with a yield of 87–89% per loaded *tert*-butyl alcohol at a cumene conversion of about 30%.

The reaction of aerobic liquid-phase oxidation of *para-tert*-butylcumene in the presence of *N*-hydroxyphthalimide and its derivatives was studied for the first time. It was found that up to the conversion of hydrocarbon 35-50%, the selectivity of the formation of tertiary hydroperoxide *para-tert*-butylcumene is more than 95-98%.

The kinetics of oxidation of *para-tert*-butylcumene to hydroperoxide by molecular oxygen in the presence of *N*-hydroxyphtalimide has been studied. Based on the study of the regularities of the formation of hydroperoxide and non-target reaction products, a kinetic model of the process was obtained that adequately describes the change in all reaction components over time.

The influence of temperature, catalyst concentration and initial concentration of *para-tert*-butylcumene hydroperoxide on the process of its acid decomposition has been studied. A kinetic model of the reaction of acid decomposition of *para-tert*-butylcumene hydroperoxide in the presence of concentrated sulfuric acid has been compiled, which adequately describes the experimental data and is used to substantiate the reaction mechanism.

Practical significance of the work. A highly selective method of obtaining *para-tert*-butylcumene by sulfuric acid alkylation of cumene with *tert*-butyl alcohol is substantiated.

In the case of liquid-phase aerobic oxidation of *para-tert*-butyl cumene in the presence of phthalimide catalysts, the conversion of hydrocarbon reaches 45% with a selectivity of 90-95% hydroperoxide formation. The process of acid decomposition of *para-tert*-butylcumene hydroperoxide to *para-tert*-butylphenol and acetone has been studied. Conditions have been found to ensure the production of *para-tert*-butylphenol with a yield of about 90%. The totality of the data obtained forms the scientific and technical basis of the oxidative method for the production of *para-tert*-butylphenol and acetone and significantly expands the prospects for the use of *para-tert*-butylphenol in the synthesis of organic compounds.

Provisions to be defended.

- a method for obtaining *para-tert*-butylcumene;
- regularities of liquid-phase aerobic oxidation of *para-tert*-butylcumene to tertiary hydroperoxide in the presence of phthalimide catalysts;
- substantiation of the mechanism and role of phthalimide compounds in the process of highly selective aerobic liquid-phase oxidation of *para-tert*-butylcumene to hydroperoxide;
- regularities of the reaction of acid decomposition of tertiary hydroperoxide of *para-tert*-butylcumene to *para-tert*-butylphenol and acetone, as well as its mechanism.