CALCULATION OF A UNIT FOR ABSORPTION OF ISOBUTYLENE IN SULFURIC ACID OF VARIOUS CONCENTRATIONS

(UDC 542.942)

A. G. Liakumovich, V. M. Sobolev, Yu. I. Michurov, and Ya. N. Prokof'ev
Sterlitamak Plant of Synthetic Rubber
Translated from Khimiya i Tekhnologiya Topliv i Masel, No. 9, pp. 5-9, September, 1965

So far the optimum conditions for the process of olefin absorption have been selected mainly either in a purely logical way by starting from experimental data which are often not related, or from a large number of experiments carried out in a pilot unit [1-3]. Optimum conditions thus selected cannot be extended to a starting material of another composition, another acid concentration or another equipment type, without considerable errors being made.

The main difficulty is to select such conditions that the process selectivity will warrant production of sufficiently pure isobutylene, the process rate will enable us to achieve both thorough extraction and high saturation of the acid, and the temperature will not give rise to noticeable formation of polymers during absorption.

A sufficiently high degree of mixing in all parts of the absorption unit is a necessary condition for the selective absorption of isoolefins. For example, in the emulsion settling tanks, where no intensive mixing takes place, the phase separation surface is overheated and considerable amounts of n-butylenes are absorbed [4]. To avoid this, it is necessary to separate the emulsion leaving the reactors in special centrifugal settlers, or to cool the emulsion to temperatures so low that the reaction will almost stop (10-15°C in 65% acid).

It is convenient to carry away the reaction heat the moment it is liberated; this may be done in several ways which may be employed separately or in combination: cooling the reactant mixture via the surface of a heat exchanger inside or outside the reactor [1], cooling the reagents — the starting material and the acid — to below the process temperature before they are supplied to the reactor [5], cooling the emulsion and recirculating the cooled emulsion of acid in hydrocarbons, evaporating part of the hydrocarbons and condensing them (C4 hydrocarbons) [4]. If 65% acid is used in the process, all the above-mentioned methods of heat removal may be employed, since acid saturated with isoolefins is only slightly corrosive [6]. Evaporating part of the hydrocarbons can be conveniently done during the settling time, since, in this case, first, the phase separation boundary, where the reaction continues, is cooled, and second, the acid phase is insulated to some extent by the gas layer, which slows down the reaction.

Since the reaction between an isoolefin and acid is reversible, the existence of an equilibrium most often does not allow us to achieve both a given degree of extraction and a high degree of saturation in a single stage. Application of several countercurrent absorption stages enables us to carry out the extraction more selectively and to achieve a high degree of absorption and a high degree of saturation of the acid. Application of several cocurrent absorption stages, too, makes it possible to carry out the absorption process selectively and at a high rate. Application of several cocurrent stages combined with countercurrent stages is convenient, if the reactors employed are made of expensive materials, for, the total reactor volume is then considerably reduced.

The purity of the isoolefin separated depends on the isoolefin to normal olefin ratio in the starting material or the reactant phase.

The higher this ratio and the isoolefin content in the starting material, the higher will be the process rate and the purity of the isoolefin separated from the extract. The economics of the process as a whole improve with the isoolefin content in the starting material, since the size of the main equipment and the reagent flows drop. Concentrating the isoolefin is certainly convenient in those cases where separate components (for example, α-butylene, isobutane, n-butane, etc.) are to be isolated from a complex mixture of isomers.
The nature of the emulsion formed is of considerable importance during extraction of isobutylene from a mixture with n-butylgnes, since, owing to turbulence, the continuous phase is mixed more intensively than the disperse phase. If the continu-ous phase consists of hydrocarbons, the intensive mixing enables us to establish equilibrium between the concentrations near the phase boundary surface and throughout the phase in a short time, i.e., to carry out the process in the hydrocarbon phase in the kinetic region. When the hydrocarbons are dis-persed, mixing is less intensive, not only because the degree of dispersion is low, but also because the viscosity of the acid is high. In this case the process is retarded by diffusion, so that this version is less suitable.

Precisely these two versions with all their shortcomings have been extensively employed in industry so far. Circulation circuits consisting of a mixing pump and a settling tank, or intensively mixed reactors, are used to achieve closer contact between the hydrocarbon phase and the sulfuric acid. Filled or other columns are used much more rarely as reactors.

In the production of highly concentrated isoolefins, the unit in which the saturated acid is freed of physically dissolved hydrocarbons deserves careful attention; these hydrocarbons, being of a structure similar to that of the refined product, reduce the isoolefin concentration by several percent. If the gas to be refined contains a large amount of normal olefins, absorption of dissolved normal olefins takes place also in the settling tanks, which reduces the concentration of the iso-olefin to be separated, since the absorbed olefins can no longer be removed in the degasifier. It is therefore necessary to shorten the acid-settling time as much as possible, and to degasify the the acid immediately after settling.

Main Experimental Data and Calculation Formulas

1. The equilibrium distribution of isobutylene over the hydrocarbon and acid phases is satisfactorily described by the following empirical equation [4, 7]:

\[ y^* = Ax^n, \]

where \( y^* \) denotes the isobutylene content in the hydrocarbon phase, \( x \) the equilibrium content of isobutylene in the acid. The concentrations are expressed in kilograms of isobutylene per 1 kg of hardly reacting hydrocarbons or per 1 kg of acid; \( A, n \) are empirical coefficients (see the table). The equation holds up to saturation of the acid with isobutylene, i.e., up to concentrations equal to 0.6-0.7 kg/kg.