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PREPARATION OF HYDROCARBONS OF HIGH PURITY BY THERMAL-DISPLACEMENT CHROMATOGRAPHY

The problem of deep purification of organic gases and vapors makes it important to develop methods for purifying starting compounds to a level at which the presence of residual impurities in them can be disregarded and, subsequently, the polymerization of pure monomers and of monomers containing strictly metered amounts of various impurities can be compared. For the deep purification of gases and liquids in laboratory practice, development chromatography has recently begun to be used successfully; its serious drawback, however, is its low productivity and the separation of components in diluted form because of the use of an inert carrier gas.

In the present work, using the isolation and purification of propylene as an example, we studied the possibility of using, for preparative purposes, a thermal-displacement variant of chromatography, the principal features of which had previously been investigated in our laboratory (^1). As applied to low-temperature mixtures of noble gases, a similar variant of separation was used in the work of E. V. Vagin (^2). The essence of the thermal-displacement method used in the present work is as follows.

The mixture to be separated is fed into an adsorption column until a certain portion of the sorbent layer is saturated. Then, along the column, beginning with the saturated section, a thermal field is moved. As a result of repeatedly recurring thermal desorption and readsorption of gases or vapors on the cold sections of the adsorption layer, at the boundary of the thermal field there rapidly forms a zone filled with the more strongly sorbed component. In front of it lies a section filled with a mixture of the components and, still closer to the outlet of the column, a section saturated with the more weakly sorbed component of the mixture. As the thermal field moves, the intermediate zone contracts and ultimately disappears completely. In the stationary state, adjacent zones of the pure components of the mixture move along the column. The formation of zones of pure components and their motion along the sorbent layer proceed by a mechanism close to that of displacement analysis.

Experimental part. The laboratory apparatus for thermal-displacement sep-

Fig. 1. Change in gas composition at the outlet from the column as the length of the hot zone increases; analysis on an adsorption column

Figure 1: Fig. 1. Change in gas composition at the outlet from the column as the length of the hot zone increases; analysis on an adsorption column

Fig. 2. Composition of the last fractions (sample 31), released when the end of the column is heated; analysis on a gas-liquid column

Figure 2: Fig. 2. Composition of the last fractions (sample 31), released when the end of the column is heated; analysis on a gas-liquid column

aration consisted of adsorption columns connected in series, filled with the same or with different sorbents. After a definite section of the adsorption layer had been saturated with the mixture of gases to be separated, the columns were gradually lowered into a furnace heated to a temperature of 200-220°. Preliminary experiments showed that a temperature below 200° does not ensure complete desorption of propylene. Separation at higher temperatures may lead to side reactions in the heated zone. At the outlet from the column, throughout the entire experiment, gas samples were taken, their composition being determined chromatographically. In analyzing light components, adsorption columns were used; for determining heavy components, gas-liquid columns.

Helium was used as the inert carrier gas; detection of the mixture components was carried out with a katharometer or an ionization detector with a Pm source (^{3}).

Fig. 1. Change in gas composition at the outlet from the column as the length of the hot zone increases; analysis on an adsorption column

The adsorbents used for thermal-displacement separation were coarse- and fine-porous silica gels and alumogels of various grades, and activated carbon. In one cycle, with a sorbent volume of 1 l and a temperature of the cold part of the column of −20 to −30°, it was possible to separate 10-20 l of the initial mixture. The composition of the initial mixtures varied within wide limits. The propylene content was 25-98%; in addition to propylene, the mixtures contained various amounts of ethane, propane, ethylene, acetylene, hydrocarbons boiling above propylene, sulfur compounds, and H_2O.

Fig. 2. Composition of the last fractions (sample 31), released when the end of the column is heated; analysis on a gas-liquid column

At first, the separating capacity of the sorbents was determined for a mixture of propylene and one or another component; it was characterized by the ratio of their retained volumes $V_{R\ \mathrm{comp}}/V_{R\ \mathrm{C_3H_6}}$. From the obtained values of $V_{R\ \mathrm{rel}}$, it was possible to select the appropriate sorbents and the sequence of their arrangement when isolating propylene from a mixture of the given composition. The functions of the sorbents used in the propylene purification process are

Fig. 3

Figure 3: Fig. 3

shown in Table 1.

Figure 1 gives chromatograms obtained in one of the experiments carried out on a column with silica gel; they show the change in gas composition at the outlet from the column as the furnace is moved.

It is evident that the less strongly sorbed components—air, ethane, ethylene, propane—are concentrated in the first fractions (samples Nos. 2-8), and then at the outlet—

Table 1

Purpose of the packing components in the adsorption column

Sorbent	Impurity removed
Activated carbon	Heavy hydrocarbons ($t^{\circ}_{\text{boil}} > 50^{\circ}$), carbon disulfide, mercaptans, acetylene, ethylene, ethane, hydrogen sulfide
Silica gel	Propane, carbon dioxide, ethane, ethylene, carbon disulfide
Alumogel	The same + hydrogen sulfide and water

During the elution from the column only propylene is detected (samples Nos. 8-30). In the very last portions of gas desorbed when the end of the column is heated, impurities appear that are sorbed better than propylene (Fig. 2).

In Fig. 3 the process of change in the impurity content in propylene is illustrated by curves plotted in the coordinates: amount of gas released from the column, in percent of the adsorbed amount—concentration of impurity, in percent of its initial concentration in the mixture.

Fig. 3. *a*—separation of propylene and hydrogen sulfide on alumogel; *b*—separation of propylene and acetylene on activated carbon

In Fig. 4 chromatograms are compared that were obtained in the analysis of a multicomponent hydrocarbon mixture and of the propylene isolated from it by the thermal-displacement method. The sensitivity of the analysis in this experiment made it possible to record impurities with concentrations down to 0.01%. The use of a highly sensitive ionization detector for analysis of the final product showed that the propane impurity, whose separation from propylene presents the greatest difficulty, is measured at 0.0003-0.0004%; in other words,

Fig. 4

Figure 4: Fig. 4

at an initial propane concentration of 75% its content can be reduced hundreds of thousands of times.

The results presented indicate the possibility of isolating pure propylene even from very poor initial mixtures.

At the same time, the experiments showed that the purification coefficients do not deteriorate when passing into the region of very low concentrations of impurities in propylene. Apparently, the proposed variant of chromatographic separation can ensure a very high degree of purification, which advantageously distinguishes it from rectification. This feature, inherent in chromatographic separation in general, is combined in the thermal-displacement variant, unlike the development method, with high productivity of the process and the isolation of components in undiluted form.

Fig. 4. Chromatogram of the initial mixture (a) and of the final product (b) on a gas-liquid (left) and adsorption (right) column

In conclusion, let us note that the field of application of the thermal-displacement method is not limited to obtaining pure propylene. In the course of our experiments, other components of the mixture were also isolated incidentally in pure form, for example propane; preliminary data are available on the successful separation of mixtures of high-boiling compounds (benzene–cyclohexane).

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Note: Figure translations are in progress. See original paper for figures.

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