A Fractionation Column Employing Adsorbents

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Midgley (1) was first to point out that a column filled with carborundum instead of glass beads was better for the fractional separation of benzene and toluene. The adsorptive capacity of carborundum in a distilling column was further studied by Miss Esther C. Farnham (2). Conclusions were drawn that the chemical as well as physical structure of the column filling specifically affects the boiling temperature-composition curves. The specific action of such materials is probably due to selective adsorption of the passing vapors.

There is a specific adsorption by silica or carbon from binary organic mixtures. Adsorption from systems of various alcohols and benzene by silica (3) reveals that the alcohol in the system is highly adsorbed at low alcohol concentrations, and benzene is preferentially adsorbed at high alcohol concentrations. If, instead of silica, carbon is used as adsorbent, the amount of alcohol adsorbed is much less, due to the fact that adhesion tension values of the alcohols against carbon are lower than those of benzene against carbon.

Without doubt, the composition of the distillate can be affected by certain solid materials as adsorbents in the column. This investigation was carried out in order to study the specific adsorption of benzene-methyl alcohol vapor by various adsorbents in a specially constructed fractional distilling column.

Experimental

Materials and Apparatus.—The general methods were employed for purifying the benzene and methyl alcohol by means of dehydration and distillation.

The following adsorbents used in this investigation were commercial products supplied by various firms as indicated: alumina, 8-14 mesh, from Alcoa Ore Co., East St. Louis, Ill.; silica gel, ½ No. 150-G-600-014, from Silica Gel Corporation, Baltimore, Md.; coconut charcoal, granulated, from Eimer and Amend, New York City; and carborundum, No. 10RA, from the Carborundum Co., Niagara Falls, N. Y.

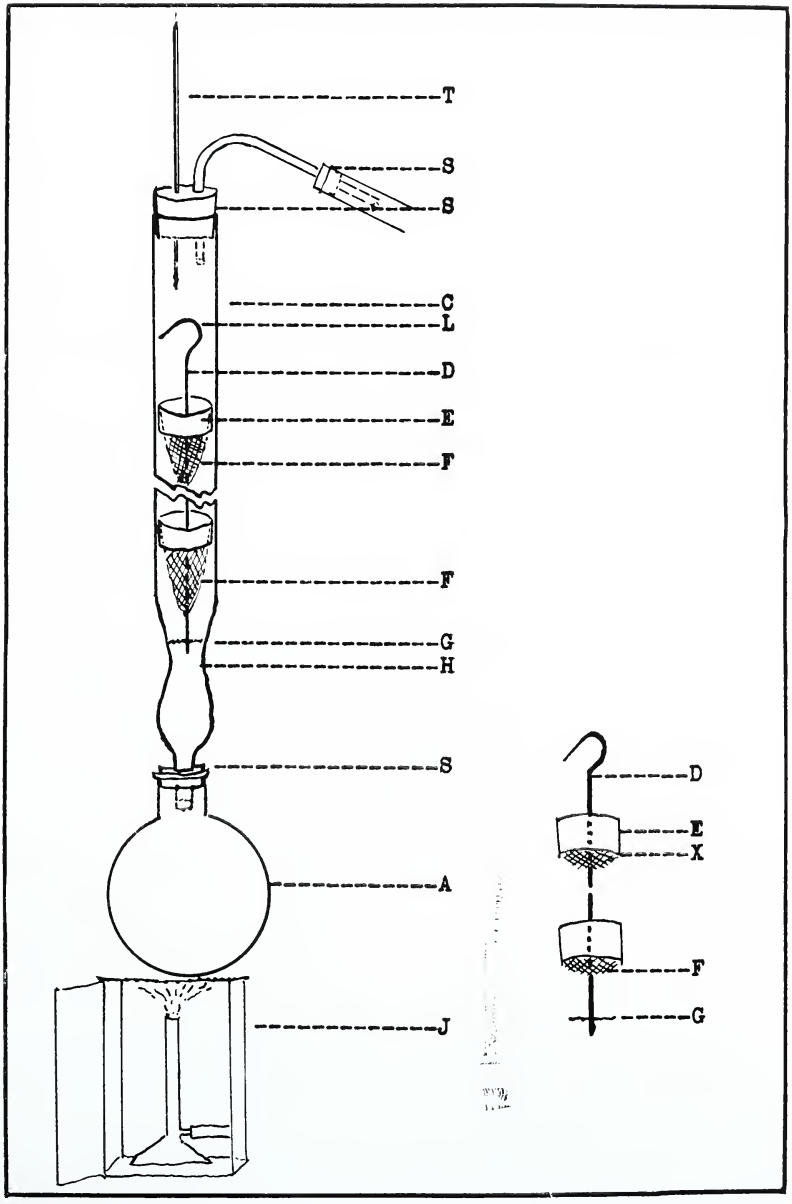
The adsorbents were activated for 8 hours at a temperature of 200°C. in a stream of air. They were immediately placed in a desiccator and used within ½ to 1 hour from the time of activation.

When an ordinary fractionation column filled with the adsorbent was used to separate the substances by distillation, it was found that the adsorbent was wetted by the condensed liquid. This rendered the adsorbent less efficient. In order to avoid this difficulty the distilling column shown in Figure 1 was designed.

The 500 cc. round-bottom pyrex flask *A* held 100 cc. of liquid to be distilled. The column consisted of a glass combustion tube *C*, 2.5 cm. inside diameter and 65 cm. long. The constriction *H* at the lower end held the coarse iron gauze disc *G*, which was tin soldered to the galvanized iron wire *D*. By this means the "ring core" was held in place.

The "ring core" was made from a galvanized iron wire *D*, 0.25 cm.

in diameter and 55 cm. in length, to which were tin soldered 20 cones *F*, 2.5 cm. long made from 30 mesh copper gauze. At the top and outside of each inverted copper gauze cone were soldered rings *E*, 1.7 cm. in



Figs. 1, 2.

diameter and 1 cm. in height made from thin sheets of galvanized iron. These rings supported the cones when filled with adsorbent.

The galvanized iron wire was bent in the shape of a hook at the top *L* to afford easy removal of the "ring core" and, at the same time, it received the condensed vapor as it dripped from the bulb of the thermometer, *T* (graduated in tenths of a degree Centigrade), thus conducting the liquid to the inner wall of the glass tube *C* and preventing the adsorbent contained in the inverted cones from becoming wet.

The cork stoppers *S* were wrapped with tin foil, and the flame from a Bunsen burner was protected with the asbestos shield *J*.

A "ring core" (Fig. 2) was first constructed in a manner similar to that described above except that in the place of cones made of copper wire gauze, a disc of iron gauze was soldered to the wire *D* and to the bottom of each ring *E*. This design was found less desirable than that shown in Figure 1 because the condensed descending liquid collected on the lower edge of the ring at *X*, causing the adsorbent contained in the ring to become wet. The "ring core" with cones, illustrated in Figure 1, showed no tendency whatever for the liquid to wet the adsorbent contained in the cones.

In order to determine the efficiency of the column, 100 cc. of a mixture of 50% by volume of 95% alcohol with 50% of water was distilled using the "ring core". The volume of the distillate collected at various temperatures was compared with a distillation carried out in exactly the same manner only without the "ring core". The rate of distillation was kept at 50 drops per minute.

Table I shows the volume of distillate collected at various temperature ranges with and without the "ring core".

TABLE I. APPROXIMATE EFFICIENCY OF "RING CORE"

Temperature Range °C.	Cc. Collected Without "Ring Core"	Total	Cc. Collected With "Ring Core"	Total
-80	45.2	45.2	48.0	48.0
80-83	1.0	46.2	.....	48.0
83-89	.2	46.4	.....	48.0
89-96	.5	46.9	.....	48.0
96-100	46.1	93.0	45.3	93.3

The volume of liquid remaining in the flask after the distillation was 3.2 cc. without and 3.0 cc. with the "ring core". The total volumes accounted for in these distillations were, therefore, 96.2 cc. without and 96.3 cc. with the "ring core".

The samples collected up to 80°C. in both cases were found to contain 93% ethyl alcohol by volume. Analysis was made by the specific gravity method.

The approximate efficiency of this "ring core" column without an adsorbent was found to be 90.10%. The Snyder's small column gave an efficiency of 73.1% (4).

Figure 3, curve 1, was obtained by plotting the figures of column 3 (Table I) against those of column 1, and curve 2 by plotting the figures of column 5 against those of column 1.

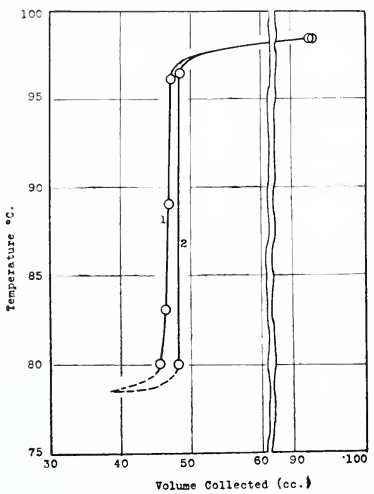


Fig. 3.

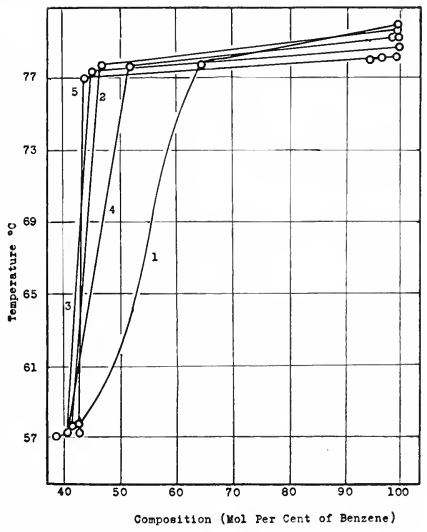


Fig. 4.

TABLE II. FRACTIONAL DISTILLATION OF 64.58 AND 35.47 MOL PER CENT OF BENZENE AND METHYL ALCOHOL RESPECTIVELY WITH "RING CORE" COLUMN USING VARIOUS ADSORBENTS.

No Adsorbent		18 Gms. Alumina		25 Gms. Carborundum		15 Gms. Cocoa-nut Charcoal		20 Gms. Silica	
Temp. °C.	Mol % C_6H_6	Temp. °C.	Mol % C_6H_6	Temp. °C.	Mol % C_6H_6	Temp. °C.	Mol % C_6H_6	Temp. °C.	Mol % C_6H_6
57.0	38.2	57.1	40.9	57.1	39.5	57.1	33.3	57.4	41.6
57.1	38.6	57.2	41.0	57.2	40.0	57.15	38.2	57.5	43.2
57.2	40.0	57.3	41.0	57.2	40.2	57.2	40.0	57.6	43.3
57.25	40.5	57.35	41.4	57.2	40.3	57.2	40.4	57.8	43.5
57.3	40.5	57.35	41.8	57.3	40.8	57.3	41.0	77.0	43.7
78.0	64.5	78.0	46.8	77.5	45.4	77.8	51.6	77.2	93.0
78.8	99.5	78.4	99.0	78.0	99.5	78.2	98.0	78.0	94.5
78.9	99.8	78.7	99.8	78.5	99.8	78.5	99.8	78.0	96.8
79.5	99.9	79.0	99.9	78.8	99.9	78.6	100.0	78.3	99.6
79.5	100.0	79.4	100.0	79.2	100.0	78.9	100.0	78.5	99.9

Procedure.—The apparatus illustrated in Figure 1 was used in all experiments. One hundred cubic centimeters of known composition of benzene and methyl alcohol was placed in the flask *A*. The cones of the "ring core" were immediately filled with activated adsorbent and put in place. The contents of the flask were heated with a constant low flame. The column was insulated with several wrappings of asbestos paper and hinged shields were used to protect the whole apparatus from draughts. The temperature for each 10 cc. portion of distillate collected was recorded and these samples were then analyzed by means of an Abbé refractometer.

Data and Results.—Table II gives the experimental results obtained when a mixture of 64.58 and 35.47 mol% of benzene and methyl alcohol, respectively, was distilled using the "ring core" fractionation column without an adsorbent and with alumina, carborundum, coconut charcoal, and silica as adsorbents.

Figure 4, curves 1-5, were obtained by plotting the data presented in Table II. The jump in temperature occurred in curve 1 (no adsorbent) when there still remained about 64.5 mol% of benzene in the distillate; curve 2 (alumina), 46.8%; curve 3 (carborundum), 45.4%; curve 4 (coconut charcoal), 51.6%; and, curve 5 (silica), 43.7%. Considering these figures and the position of the curves in Figure 4, carborundum or silica can be said to be more efficient than either alumina or charcoal in the separation by fractional distillation of the binary mixture of benzene and methyl alcohol. The jump in curve 5 is more abrupt than that in curve 3 showing that the separation is more definite when silica is used in the "ring core" in the place of carborundum. This is undoubtedly due to the specific adsorptive properties of these adsorbents.

A second series of experiments, using a mixture of 31.16 and 68.8 mol% of benzene and methyl alcohol, respectively, was performed in a manner exactly analogous to that described above. There was noted neither a decided jump in the boiling temperature nor a marked separation of benzene and methyl alcohol. When charcoal or silica was used, a sudden rise of temperature occurred at the beginning of the distillation. A much larger amount of methyl alcohol was absorbed by silica than by coconut charcoal evidently due to preferential adsorption (5).

In a third series of experiments a mixture of 10.14 and 89.8 mol% of benzene and methyl alcohol respectively was fractionally distilled. The results followed the same general course as those of the second series. Charcoal and silica again demonstrated the same irregularities as would be expected for a mixture richer in methyl alcohol.

It was noted that the curves obtained from the data of the second or third series of experiments came close together when the distillate contained about 18 or less mol% of benzene. The amount of adsorbent used was probably insufficient and became saturated with respect to methyl alcohol, thus causing the various adsorbents to behave similarly.

Summary

The distilling column described in this paper displayed two decided advantages. It not only has a high efficiency in itself, but it also affords

the study of the effect of the presence of various adsorbents in the column.

The mixture consisting of 64.5 and 35.47 mol% of benzene and methyl alcohol respectively was separated more completely on fractional distillation than either of the other two mixtures studied. The adsorbents studied in each case seemed to show individual differences in their ability to aid the separation of the mixture (benzene and methyl alcohol). Silica and carborundum acted better than either alumina or coconut charcoal, all of which are better than when no adsorbent whatever was used.

Considering the specific adsorption of adsorbents for benzene and methyl alcohol as pointed out in other investigations (3, 5, 6), the adsorbents used in this investigation behaved as would be expected.

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