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A Multicolumn Countercurrent Molecular Still

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A 10-column countercurrent molecular still, based on refluxing by gravity feeds and circulation of the liquid by means of magnetic pumps, is described. Each column consists of a concentric evaporator having a surface of 300 square centimeters, surrounded by a water-cooled condenser. The still is provided with an overflow cup at the top, a reservoir at the lower end and a pump for raising the liquid from the reservoir to the overflow cup. All the condensates move by gravity from column to column in one direction, and all the residues move similarly in the opposite direction, thus producing countercurrent refluxing of the liquid. The still is designed to operate at such a rate of evaporation that the amount of distillate from each column is slightly greater than the amount of residue from the same column. Operating on a binary mixture, the still gives a separation of the two constituents equivalent to 13 theoretical plates.

I. Introduction

Countercurrent molecular stills in which recombination of fractions is accomplished automatically by means of gravity feeds, have been described previously.[1 2] Each of these stills consists of a long column placed at a small angle to the horizontal and divided into small cells with an evaporating surface of a few square centimeters for each cell. The openings between the cells in these columns are quite large, so that mixing of the vapor between the cells takes place. Under these conditions, each cell represents merely a subdivision of the column and not an actual plate.

The multicolumn countercurrent molecular still described in this paper was designed with these objects in view:

1. To obtain a large evaporating surface so that it could be used commercially for the concentration of individual components in mixtures of liquids different in their molecular weights or vapor pressures, but having similar properties otherwise.

2. To spread the evaporating liquid in a thin film so as to reduce the hold-up.

3. To impart to the thin film a continuous motion over a rough granular surface to cause mixing and thus to prevent depletion in the light constituents.

4. To increase the efficiency of the distillation process by eliminating mixing of the vapor between cells or plates.

II. Multicolumn System

The multicolumn molecular still is a combination of refluxing by gravity feeds and of circulating the liquid by means of pumps. The still described here consists of 10 columns, but any number of columns can be used. The entire apparatus was constructed of Pyrex glass and is shown in figures 1 (diagrammatically) and 2. A single column is shown in detail in figure 3. The column consists of a central tube 2.5-cm outside diameter and 45 cm long. This tube serves as the evaporator and has a surface of 300 cm^2. The evaporator is surrounded by a condenser tube with an inside diameter of 4.1 cm, so that the distance between the evaporating and condensing surfaces across the annular space is 0.8 cm. A short ring partition at the lower end of the annular space forms two concentric annular troughs with a separate outlet from each trough. These troughs and outlets serve to separate the residue from the condensate as they flow down the evaporator and condenser, respectively. At

[1] A. K. Brewer and S. L. Madorsky, J. Research NBS **38**, 129 (1946) RP1764.
[2] S. L. Madorsky, Paul Bradt, and Sidney Straus, J. Research NBS **41**, 205 (1948) RP1918.

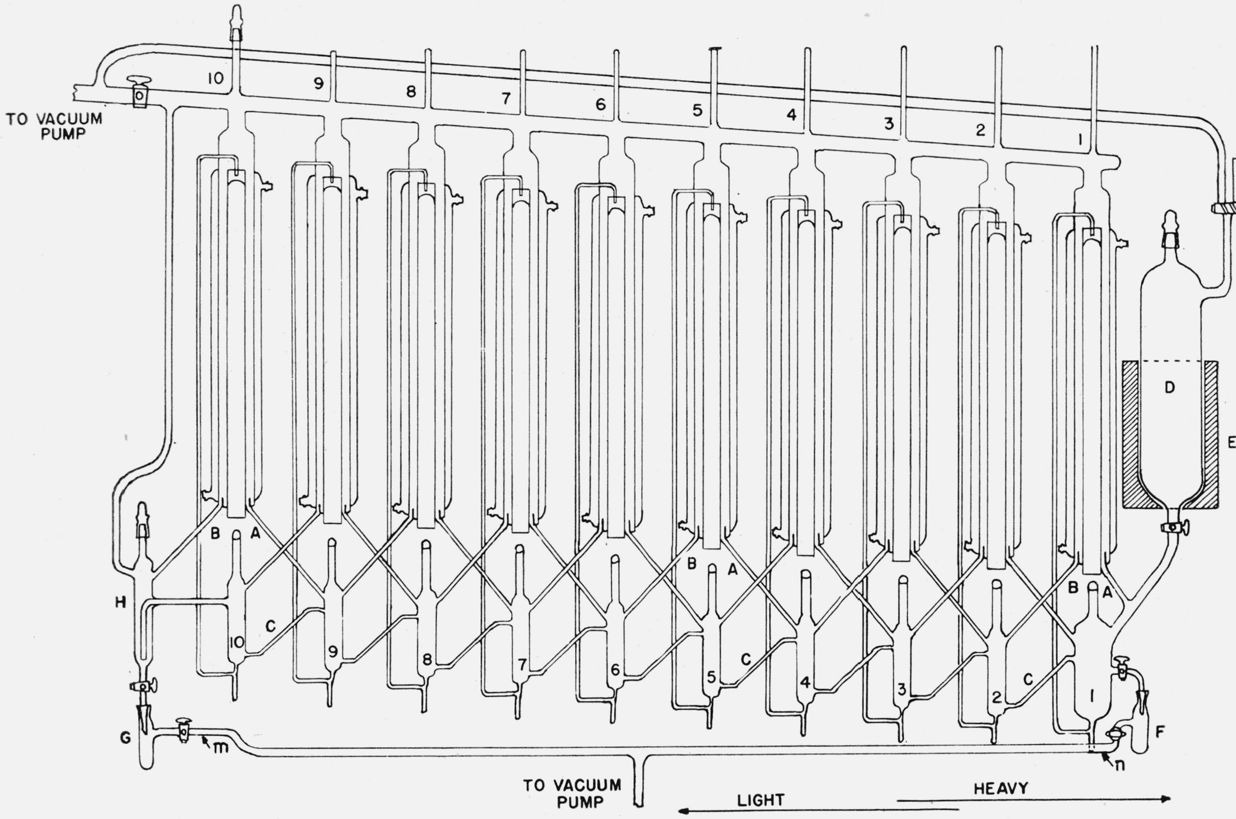

FIGURE 1. *General arrangement of the 10-column molecular still.*

A, Residue outlet; B, condensate outlet; C, overflow; D, degassing reservoir; E, heater; F, heavy fraction sample cup; G, light fraction sample cup.

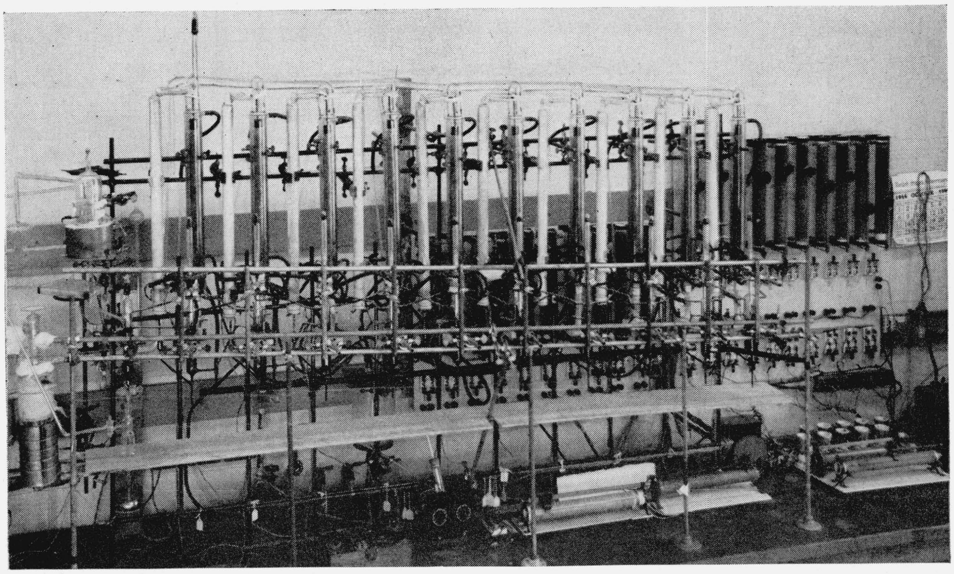

FIGURE 2. *The 10-column molecular still.*

After this photograph was taken, the degassing reservoir was transferred to the right end of the apparatus, as shown in figure 1.

the top of the evaporator is a distributing crown, or cup, provided with several notches half way down the wall of the cup. The evaporating surface is covered with a thin layer of sintered powdered glass of about 40 mesh to facilitate uniform distribution and mixing of the liquid layer.

Each column is provided at its lower end with a combination of magnetic pump and reservoir.

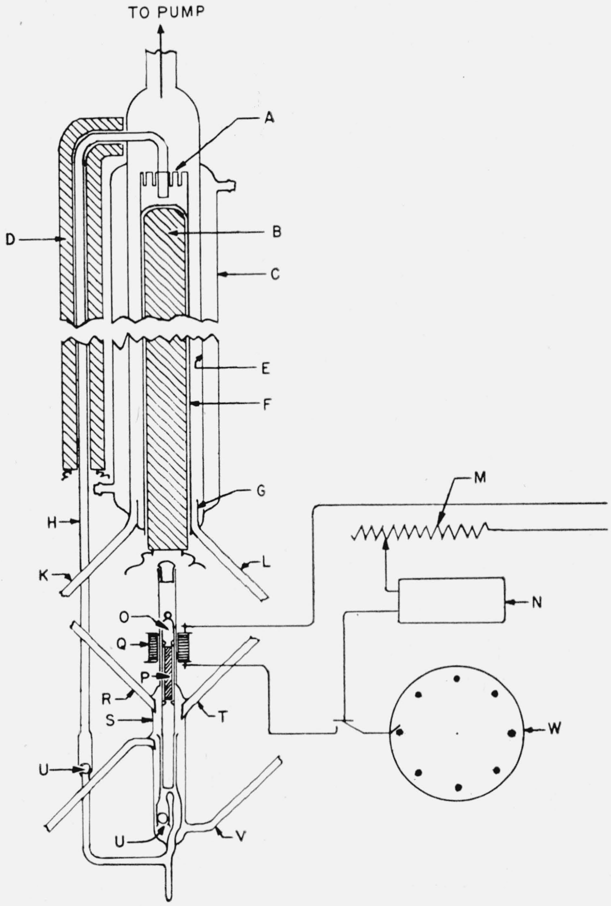

FIGURE 3. *Details of column, reservoir, and pump.*

A, Distributing crown; B, heater; C, condenser; D, preheater; E, condensing surface; F, evaporating surface; G, ring partition; H, feed line; K, condensate outlet; L, residue outlet; M, resistance; N, relay; O, piston; P, iron core; Q, solenoid; R, residue inlet; S, reservoir and pump; T, condensate inlet; U, U, check values; V, overflow; W, intermittent switch.

The liquid is pumped from the reservoir through a feed line into the distributing crown, and from there it distributes itself over the evaporator in a thin layer. In passing through the feed line, the liquid is preheated to a temperature near that of the evaporator. The evaporator is heated by a Nichrome heater fitting snugly inside of it, and the feed line is heated by another Nichrome heater surrounding it, as shown in figure 3. Both heaters are provided with slide resistances in series for the control of temperature and with thermocouples between the heaters and glass tubes. Each heater or preheater has a capacity of about 100 watts.

The columns are arranged from 1 to 10 as shown in figures 1 and 2, in an ascending order from right to left. In this arrangement the residue from each column, except the first, flows through the outlet *A* (fig. 1) into the reservoir of the adjacent lower column to the right. The residue from the first column flows back into its own reservoir. The condensate from each column, except the tenth, flows through the outlet *B* into the reservoir of the adjacent higher column to the left. The condensate from the tenth column flows into a light fraction receiver, *H* (fig. 1) and from there into the reservoir of the tenth column. In this manner, the residues or heavy fractions flow from column to column in the downward direction from left to right, whereas the condensates or light fractions flow from right to left in an upward direction.

In order to keep the system in balance, it is necessary, in the first place, to have the same pumping rate for all columns and, in the second place, to evaporate exactly half of the liquid pumped into the crown of each column. The slightest deviation from one or both of these conditions will cause a gradual accumulation of the liquid in some reservoirs and a depletion in the others. This difficulty can be overcome to some extent by constructing the pumps as uniformly as possible and by equalizing the amplitudes of the pistons in the magnetic pumps. The number of strokes per minute is the same for all the pumps, as the solenoids are operated by the same intermittent switch, *W* (fig. 3).

The evaporating rate is more difficult to control. At any rate, it would be practically impossible to control pumping and evaporating rates to a point where there would be an exact balance between the liquid streams moving in opposite directions. In order to blanket any deviation from conditions of balance, the evaporating rates in the columns were adjusted to a little over 50 percent of the amount of liquid pumped into the crown for each column. The fractions of condensates in excess of residues are allowed to flow by gravity from reservoir to reservoir in the direction from the light end (reservoir, *H*, fig. 1) to the heavy end (reservoir 1) through overflow tubes, *C*. This is made possible by staggering the reservoirs as well as the columns at an angle of a few degrees to the horizontal, sloping from reservoir, *H*, down to column and reservoir 1. This arrangement serves also the purpose of refluxing the light fractions from reservoir *H* down the series of reservoirs toward the first one.

A large reservoir, *D* (fig. 1), surrounded by a Nichrome heater, *E*, serves to degas the liquid before it is introduced into the still. This reservoir is connected to the same vacuum system as the still, but can be isolated from it by means of stopcocks, when filling it with fresh liquid. The system is evacuated by means of an oil pump backed up by a mercury diffusion pump. Sampling of the liquid can be carried out at the extreme ends of the still into cups *F* and *G* (fig. 1) without interrupting the operation of the still.

III. Magnetic Pump and Reservoir

Details of the magnetic pump [3] and reservoir are shown in figure 4. The pump consists of a piston, *A*, containing an iron core *F*, in its upper end. The core rests on asbestos wool, *K*, and is held in place by means of a sealed-in glass rod. Some mercury is placed in the piston above the iron core to give the piston sufficient weight during its fall to raise a column of liquid to the top of the distillation column. A Nichrome spring, *M*, at the neck of the piston-guide, *P*, serves to cushion the fall of the piston. The solenoid current is controlled by means of an intermittent switch, *W*, shown in figure 3. When the current in the solenoid is on, the piston moves up and draws liquid from the reservoir through check-valve, *Q* (fig. 4), into the piston-guide, *P*. When the current is off, the piston drops by gravity, closing check-valve, *Q*, and forcing the liquid through tube, *S*, and check-valve, *N*, into the delivery tube, *H*.

This type of pump is well adapted to operation in a vacuum. The glass magnetic pump described by Hickman and Hecker [4] has the shortcoming that it is almost impossible to eliminate air or any other gas once it is trapped under the piston. Another shortcoming of the Hickman-Hecker pump is that if anything goes wrong with the piston, the whole pump has to be removed for repairs by breaking. In the present pump any gas trapped in the reservoir or under the piston is easily eliminated in the operation; also, in case the piston jams or breaks, it can be corrected or replaced through a removable waxed-in cap at the top of the pump.

The reservoirs are attached to the columns by means of residue inlets, *E* (fig. 4), distillate inlets, *G*, and delivery tubes, *S-H*, also, to each other by means of overflow tubes *O*, *R*. The ends of the inlet tubes as well as the upper ends of the overflow tubes project into the inside of the res-

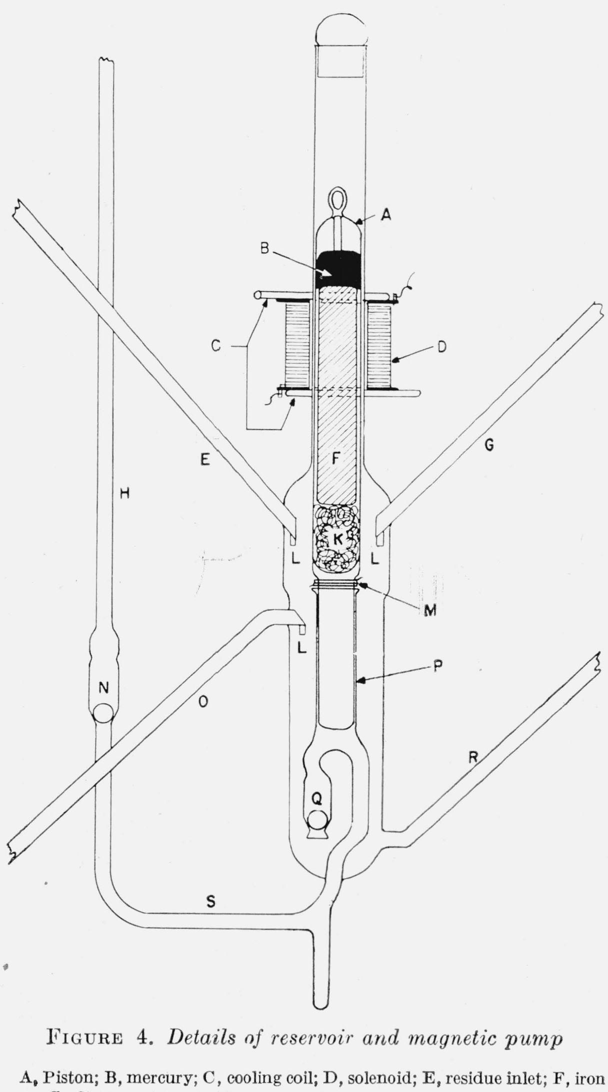

FIGURE 4. *Details of reservoir and magnetic pump*

A, Piston; B, mercury; C, cooling coil; D, solenoid; E, residue inlet; F, iron core, G, distillate inlet; S–H, delivery tube; K, asbestos wool; L, L, glass rods with ground flat ends; M, metal spring; N, Q, check valves; O, R, overflow tubes; P, piston guide.

[3] S. L. Madorsky, U. S. Patent 2,481,320 (Sept. 1949).

[4] K. C. D. Hickman and J. C. Hecker, U. S. Patent 2,126,467.

ervoir. Short glass rods, L, of uniform size and ground flat at the ends, are attached to these projections. Rates of drops of liquid falling from these rods into the reservoir serve as an indication of rates of pumping, evaporation, and overflow for each column.

In experimental tests with a binary mixture operating at a vapor pressure of 0.01 to 0.02 mm Hg, the 10-column molecular still gave at equilibrium a separation of the two constituents equivalent to 13 theoretical plates. The operation was continuous, lasting several weeks at a time and requiring very little attention. The only work involved consisted in counting the drop-rates from points L, L (fig. 4), checking heating currents and temperatures in heaters and preheaters, and making proper adjustments; also, in breaking off and sealing on again, at intervals, the sample cups, F and G, at points m and n, respectively (fig. 1), for analysis of the samples.

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