multicomponent separations. With varying holes through the column it is recommended that all trays be perforated the same and that holes be blanked off with blanking strips (see Figure 13) as required. These strips can be tack-welded to the tray and can be scattered across the tray or placed immediately adjacent to each other as in Figure 13. Scattering them across the tray is probably best; with either method in large diameter columns care should be taken to deliberately induce a small amount of vapor cross flow concurrent to the liquid flow by having more active holes on the liquid inlet side of the tray than on the outlet side. Should the service or operating conditions of the column change radically, blanking strips can be removed readily or more can be added as required.

With slight vapor cross flow concurrent to the liquid flow, hydraulic gradient is quite low. In most new tower installations trays have been deliberately tilted a slight amount toward the outlet weir to further minimize hydraulic gradient effects and to lend assurance that workmanship tolerances in fabrication do not result in occasional trays being tilted toward the inlet weir.

Recessed seal weirs, Figure 13, are recommended to minimize impact head effects, thereby permitting the trays to be perforated closer to the inlet weir. Perforations can be as close as 2 to 4 inches from the inlet weir, depending on the liquid rate per foot of weir length. Perforations can be fairly close to the outlet weir, but care should be taken to ensure having more holes on the inlet side than on the outlet side for the reasons given above.

Typical sieve trays are pictured in Figures 16, 17, and 18.

In some cases drilled trays have been obtained very economically, but generally punched trays are much less expensive. Usually punched trays of copper alloy or carbon steel can be no thicker than the hole diameter and stainless trays can be no thicker than one half to two thirds of the hole diameter, because of limitations of the punching process. As compared to the cost of bubble-cap trays, sieve trays are much less expensive.

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Liquid Thermal Diffusion of Tall Oil

Engineering
and
Process
development

A. LETCHER JONES AND ROBERT W. FOREMAN

Chemical and Physical Research Division, Standard Oil Co. (Ohio), Cleveland, Ohio

ALTHOUGH separations by liquid thermal diffusion were first observed by Ludwig (*11*) in 1856, essentially no practical applications of the principle were made until 1938 when Clusius and Dickel (*2*) separated the isotopes of chlorine in the gaseous phase. Very little work has been reported on the application of the principle to the separation of the components of organic liquid mixtures. A few papers and patents (*3, 6–10, 12*) have appeared recently, however, which show that thermal diffusion does remarkably well in separating organic liquid mixtures and that the magnitude of separation is greater than would be predicted on the basis of gaseous thermal diffusion theory.

There has not yet been developed a successful kinetic theory for thermal diffusion in liquids. It is known, however, that the mass difference principle, as developed by Chapman (*1*) for gases, does not apply to organic liquids and that more frequently than not, components of different mass separate in directions opposite to those predicted by the gaseous theory. Molecular shape or configuration appears to be a more important factor than molecular weight. It has been observed recently (*9*) that long-chain molecules, when present with more compact ring structure types, will concentrate in the hot-wall fractions regardless of their relative molecular weights.

The apparatus necessary to produce liquid thermal diffusion separations is basically simple. It consists essentially of two parallel smooth surfaces arranged vertically and separated by a narrow space, as shown in Figure 1. The space between the walls is filled with the liquid to be processed. One surface is heated, the other cooled. These conditions produce a sharp temperature gradient across the liquid. This gradient is responsible for the separations produced. Convective flow, upward along the hot wall and downward along the cold wall, results from the density difference produced by the temperature gradient.

Certain types of molecules are diffused away from the hot wall

Table I. Analyses of Tall Oil and Tall Oil Fractions

Sample	Sample, Vol. %	n_D^{20}	Iodine Number	Rosin Acids Number	Total Acids Number	Rosin Acids[a], %	Fatty Acids[b], %	Nonacids, %
Original tall oil	100	1.4938	141.5	57.8	179	31.1	60.9	8.0
First pass top	67	1.4807	149.6	31.7	185	17.1	76.5	6.4
First pass bottom	33	1.5100	126.3	85.0	164	45.8	39.8	14.4
Second pass top	40	1.4676	122.9	5.2	188	2.8	92.0	5.2
Second pass bottom	27	1.5000	159.7	62.7	167	33.8	52.5	13.7

[a] Calculated as abietic acid of M.W. = 302.
[b] Calculated as fatty acid of M.W. = 282 [average M.W. as determined in (4)].

to a greater extent than are other types. Those which move away in greater proportion enter the downward moving stream on the cold wall and thus concentrate toward the bottom of the column. The other types concentrate at the top.
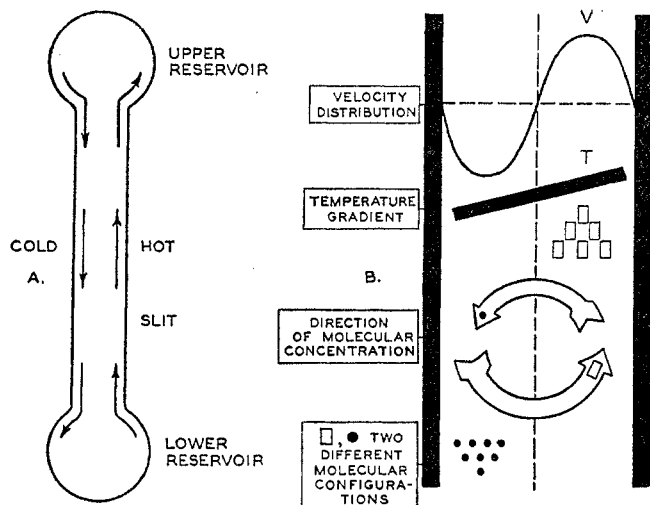

Figure 1. Apparatus

A. Thermal diffusion apparatus
B. Magnified slit section

Among the several natural fats and oils which were subjected to thermal diffusion, tall oil proved to be especially susceptible to fractionation. This vegetable oil has its origin in the tissues of resinous woods used by the paper industry as a source of pulp. When the wood fiber is heated with alkaline sulfates, the tall oil components are extracted primarily as fatty and rosin acid soaps. When the alkaline extract is acidified, an oil, consisting of a mixture of fatty acids, rosin acids, and certain nonacids such as sterols and higher alcohols, separates from the aqueous phase. This oil is known as "whole tall oil" or "crude tall oil."

Two different grades of tall oil were processed in this study. One was crude tall oil with the trade name of Liqro, the other was a double distilled product known commercially as Indusoil. Both types of tall oil appeared to be equally susceptible to thermal diffusion fractionation.

Apparatus

Two essentially identical liquid thermal diffusion columns, approximately 8 feet in length with a 90-inch rectifying section, were used in this study to separate tall oil into fractions of different chemical composition. A diagram is shown in Figure 2. These columns were constructed from ordinary borosilicate glass tubing of approximately uniform diameter. Tubes of suitable diameter were selected and arranged concentrically to provide a mean annular space diameter of 14.0 mm. and a width of approximately 1 mm. (0.043 inch). The spacing was maintained uniform by the fusion of small glass tips at 30- to 40-cm. intervals along the outer surface of the inner glass tube. The tips were

made slightly smaller than the annular space and placed at three equidistant points in a single plane, perpendicular to the axis of the tube. Small diameter glass tubing leading from the annular chamber out to stopcocks was fused in at either end of the tubes to serve as bottom and top take-offs. Charging the column was accomplished by gravity feed from an overhead reservoir into the annular space through glass tubing fused in at the center of the column. The inner tube was cooled by tap water running from the bottom to the top. The outer tube was heated by steam (atmospheric pressure) in a glass jacket which enclosed the entire column except for the feed and take-off tubes.

In addition to the thermal diffusion columns an Abbe refractometer was used for measuring refractive indexes. Conventional borosilicate laboratory glassware was used in the determinations of chemical properties and composition.

Materials

The tall oil used in this work was obtained from the Industrial Chemicals Division of the West Virginia Pulp and Paper Co. Analysis of Indusoil by standard procedures gave 60.9% fatty acids, 31.1% rosin acids, and 8.0% nonacids, which agreed with the manufacturer's specification of 50 to 60% fatty acids, 30 to 35% rosin acids, and 5 to 15% nonacids. The whole tall oil had 52% fatty acids, 41% rosin acids, and 7% nonacids (analysis by Sherwin-Williams).
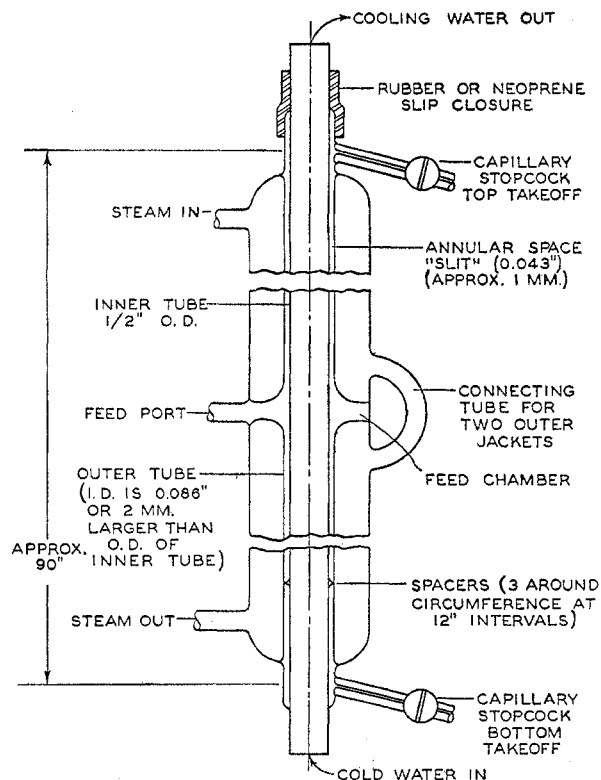

Figure 2. Glass Thermal Diffusion Column

Reagent grade chemicals were employed in the analyses of tall oil and its fractions. Among these were Hanus solution (iodine and bromine in glacial acetic acid) for iodine number determina-

tion, methyl sulfuric acid solution (100 grams of 98% sulfuric acid in 400 grams of methanol) for rosin acids determination, and 0.5 N potassium hydroxide in methanol for free acids determination.

Experimental Technique

The thermal diffusion columns were operated at a hot-wall temperature of approximately 100° C. and a cold-wall temperature of approximately 20° C. Each column was operated with a total volume take-off of 45 ml. per day and samples taken from both top and bottom every 8 hours. This low take-off volume allowed

Figure 3. Thermal Diffusion Separation of Tall Oil (Indusoil)
Top, first stage.   Middle, second stage.   Bottom, summary

near attainment of a steady state between sampling. The two identical columns were run simultaneously, with the top fraction from the first column providing the feed to the second column. Take-off ratios were two volumes to one volume for the top to bottom take-off in the first column, and three volumes to one volume for the top to bottom take-off in the second column.

The index of refraction at 20° C. of each fraction was measured. The refractive index served as a partial control on column performance and aided in establishing the proper take-off volumes and ratios. The fractions were stored in glass bottles after collection and analyses were performed on the combined samples of several take-offs.

In addition to the index of refraction measurements, chemical evaluations were made on the tall oil fractions. Iodine numbers were determined by the Hanus method as described by Jamieson (5). The rosin acid numbers, fatty acid numbers, and nonacids (or unsaponifiables) were determined by the method of Hastings and Pollak (4).

Experimental Results

The analyses of the Indusoil and the various fractions collected as described above are presented in Table I. Each value represents the average of at least two determinations. Iodine numbers were reproducible to within ±0.5 as were the rosin acids and total acids number. Percentages of rosin acids, fatty acids, and nonacids were calculated from their respective acid numbers as follows:

$$\% \text{ rosin acids} = \frac{\text{rosin acids number}}{561} \times 302$$

$$\% \text{ fatty acids} = \frac{(\text{fatty acids number} - \text{rosin acids number})}{561} \times 282$$

$$\% \text{ nonacids} = 100 - (\% \text{ fatty acids} + \% \text{ rosin acids})$$

where 302/561 represents the conversion factor for 100 grams of sample from potassium hydroxide to abietic acid, and 282/561 is the similar conversion factor for potassium hydroxide to a fatty acid of molecular weight, 282.

The fractions from the whole (crude) tall oil were analyzed by the Sherwin-Williams Co. in its Chicago laboratories. The complete analyses are shown in Table II. These are direct analyses of rosin acids, unsaponifiables, ash, and water. The fatty acid content was obtained by difference.

Figure 3, top, shows the results of the first stage of fractionation of Indusoil. The object in the center of the figure is a diagrammatic representation of the thermal diffusion apparatus. Fatty acids increase in the top fraction, while rosin acids and unsaponifiables decrease.

Figure 3, middle, shows the changes produced by running the top product from first fractionation through the apparatus a second time. The fatty acid content of the top fraction from this run increases to 92%. The rosin acids decrease to 3% while unsaponifiables do not change appreciably.

Figure 3, bottom, shows the entire fractionation. In addition, the iodine numbers of the various fractions are presented. In the first stage, the higher iodine value is found in the top fraction. When this fraction is run again through the apparatus, the higher iodine value is found in the bottom fraction. An inspection of the composition changes shows that the first time through the increase in iodine number in the top fraction is due to fatty acids because the other components decrease in percentage. On the second pass, the increase in iodine number in the bottom fraction is again due to the more unsaturated fatty acids because the rosin acid and unsaponifiable content is lower than that of the first pass bottoms. This indicates that in the presence of appreciable amounts of rosin acids thermal diffusion concentrates fatty acids of various degrees of unsaturation in the top or hot-wall fractions. In the
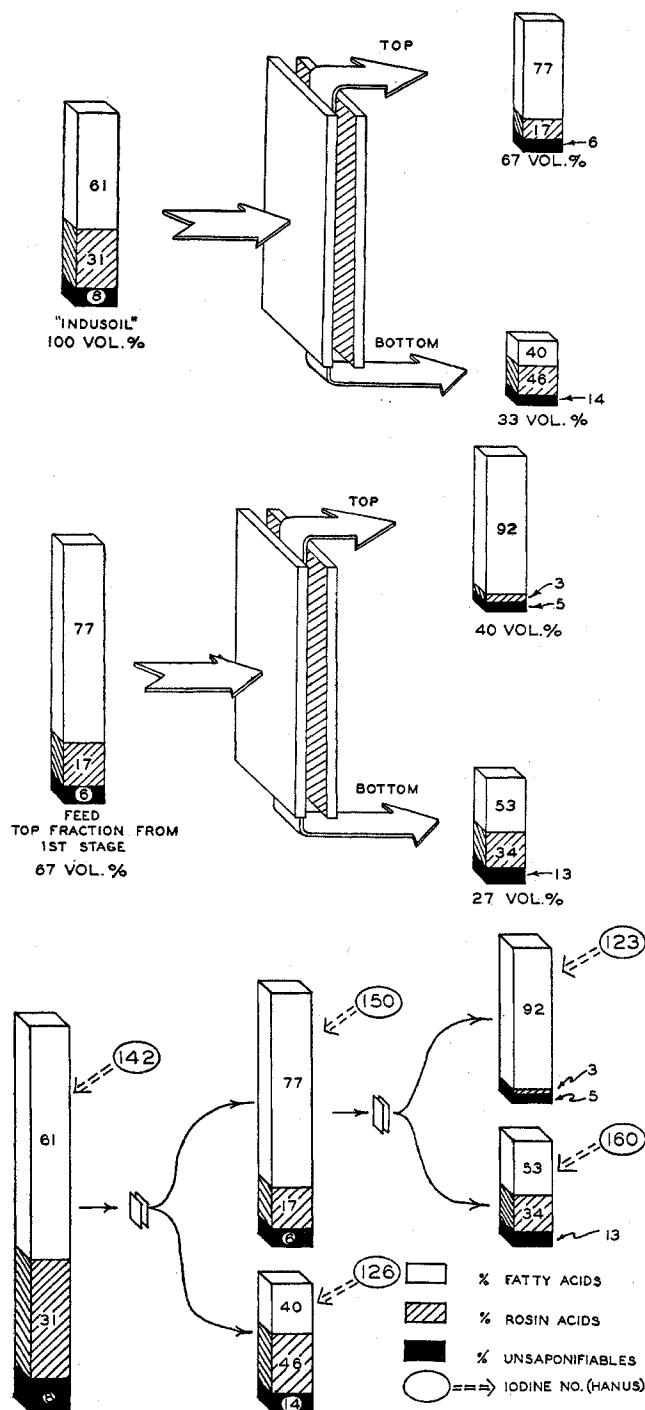
Table II. Analyses of Crude Tall Oil and Thermal Diffusion Fractions

	467-13A Feed	467-13B Overhead	467-13C Bottom	467-13D, 2nd Pass OH from OH	467-13E, 2nd Pass Bottom from OH
Rosin acids, %	40.7	23.5	54.7	8.4	45.7
Unsaponifiable, %	6.9	5.8	6.7	4.3	8.5
Fatty acids, %	52.3	70.3	38.1	86.7	45.3
Ash, %	0.2	0.1	0.1	0.04	0.1
Water, %	0.4	0.3	0.4	0.5	0.4
Wt./gal. at 75° F.	8.19	7.83	8.29	7.57	7.98
Acid value	169	173	163	180.5	159
Color (Gardner)	Dark	Dark	Dark	11–12	Dark
Viscosity (Gardner-Holdt)	V	D-E	Semisolid	A-B	Semisolid

absence of rosin acids a selection is made between the more and less unsaturated straight-chain fatty acids.

Figure 4 summarizes the thermal diffusion fractionation of crude tall oil, Liqro. The fractions were split on a 1 to 1 basis instead of 2 to 1 (top to bottom), as in the case of Indusoil. The separation pattern is the same as in the first material. Crude tall oil contains a higher percentage of rosin acids than the distilled Indusoil. This higher percentage is reflected in all of the fractions. The crude tall oil results show that thermal diffusion is equally applicable to either the crude or partially refined stocks. Iodine numbers were not measured on the fractions from crude tall oil.

Figure 5 shows the infrared absorption spectra of the first stage bottom and second stage top fraction of the crude tall oil. These spectra cover the range from 5.5 to 14 microns. They show the definite composition differences of the two fractions. The
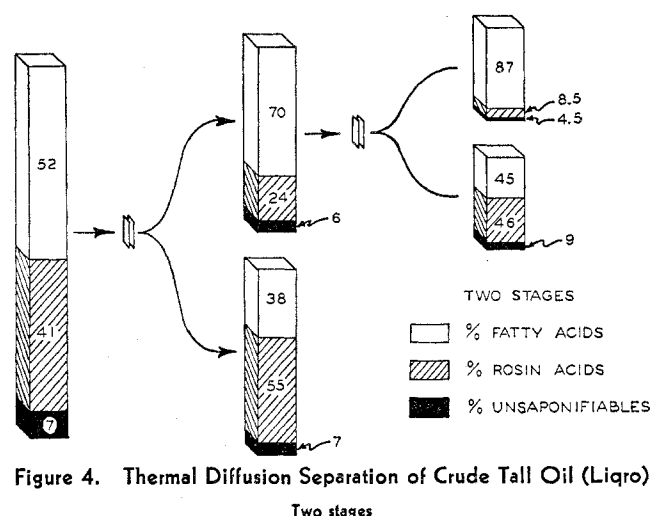

Figure 4. Thermal Diffusion Separation of Crude Tall Oil (Liqro)

Two stages

TWO STAGES

☐ % FATTY ACIDS

▨ % ROSIN ACIDS

▨ % UNSAPONIFIABLES

principal points of difference are the conjugated carbon-carbon double bond absorption at 6.25 microns, methyl branching absorption at 8.4 to 8.8 microns, and carbon-carbon double bond absorption at 12.7 microns in the bottom fraction. These absorptions are much more pronounced in the bottom fractions than in the top. The spectrum of the top fraction resembles those of straight-chain fatty acids very closely, having strong free carboxyl group absorption at 5.9 and 7.9 microns, characteristic fatty acid absorption at 10.7 microns, and long methylene chain absorption at 13.8 microns.

Discussion of Results

The analytical results presented in Tables I and II show that thermal diffusion of tall oil, in the liquid phase, concentrates free fatty acids at the top of the column and rosin acids at the bottom. This separation effect is not due to any preferential crystallization and settling of the rosin acids because the contents of the column

remain liquid at all times and undergo continuous countercurrent thermal circulation. The iodine numbers of the fractions collected from the top and bottom of the column show that the components of greater unsaturation concentrate in the upper fraction upon a first pass of tall oil through the column. A considerable difference in color is produced between the fractions, with the top being the lighter of the two. The bottom fraction partially solidifies at room temperature after removal from the column. The top fraction remains a homogeneous clear liquid under the same conditions. In addition to the rosin acids, the nonacids, which include sterols and high molecular weight alcohols, concentrate in the bottom fraction.

The refractionation of the first-pass top fraction results in a further separation of components without a significant decrease in the magnitude of separation. The composition of the second-pass fractions, however, shows a difference in the direction of separation of some of the components. The more unsaturated components in this case concentrate in the bottom fraction. This shows
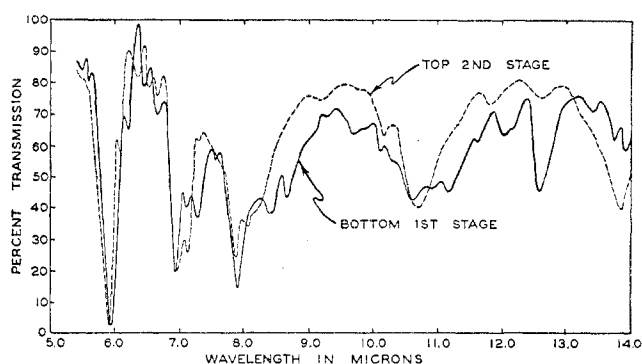

Figure 5. Infrared Spectra of Thermal Diffusion Fraction of Whole Tall Oil

Liquid state.　0.03-mm. cell.　Beckman TR-2

that the direction in which a given type of component will concentrate by thermal diffusion depends upon the nature of other components present in the liquid. In the presence of rosin acids, the unsaturated fatty acids concentrate at the top of the column, as was demonstrated by the first fractionation. With a reduced concentration of rosin acids in the second fractionation, the direction of concentration of the more unsaturated components is reversed. This observation indicates that, by a series of refractionations, thermal diffusion may be used to separate complex multicomponent systems such as tall oil into a number of fractions each having different chemical composition.

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Liquid-Liquid Extractor Design

Engineering
and
Process
development

F. DREW MAYFIELD AND WALTER L. CHURCH, JR.

Chemical Division, Celanese Corp. of America, Bishop, Tex.

IT IS well recognized that knowledge of plant scale mechanical devices for carrying out liquid-liquid extraction operations is not nearly so well developed as is the knowledge of liquid vapor contacting devices as used in absorption and distillation. The purpose of this work was to make a screening study of the type of equipment most suited to performing "clean service" liquid-liquid extractions.

It was reasoned that a multiple contacting device in which one phase was dispersed and coalesced followed by multiple repetition of this dispersing and coalescing should be the best all-purpose device. Packed columns have not been considered here for commercial application because of their limited capacity (1) and because they do not guarantee repetitious dispersion and coalescence.

The visual study reported here was made first to observe the behavior of various types of plates in liquid-liquid contacting service. The observations made in this visual study were quite encouraging in that the visual study offered explanations for most of the adverse reports in the literature on the use of perforated plate-type extractors, together with suggested means of avoiding the conditions which might have caused these adverse performances.

The original visual studies were followed by plate efficiency studies which made the whole program sufficiently successful that the conclusions and principles established in this study led to the selection of perforated (jet) plate-type extractors (the jet plates being originally thought of here in 1947) for seven different plant scale installations within 3½ years of the

Figure 1. Glass Column Operating with Varsol Dispersed in Water—8½ Inch I.D.

first plans for this study; in one case an existing ring- and disk-type extractor was cleared and equipped with jet plates in order to obtain increased efficiency and increased capacity.

An excellent review of available contemporary data on commercial extraction equipment was given recently by Morello and Poffenberger (7). Information on both commercial and laboratory scale extractors can also be derived from the recent work of Treybal (11), and practically all the recent literature on perforated plate extractors is reviewed in this latter work.

Experimental

Visual Studies. Visual studies were made of various dispersing devices in an 8½-inch i.d. column made up of 36-inch lengths of bell and spigot glass pipe (Figure 1). All studies were made with Varsol solvent (d = 0.7845 grams/cc. at 68° F.) dispersed in water, the two liquids being recirculated by means of pumps through rotameters. Various tray designs were inserted between the pipe ends in the bell and spigot joint. Trays employed (Figure 2) were as follows:

Tray 1: Perforated tray with sixty ⅛-inch holes drilled on a ¾-inch square pitch in a ¼-inch carbon steel plate (same as tray No. 3 of Figure 2 except for holes).
Tray 2: Jet tray with sixty ⅛-inch i.d. brass jets on a ¾-inch square pitch (same as Tray No. 3 of Figure 2 except for jets).
Tray 3: Jet tray with one hundred and ten ⅛-inch i.d. brass jets on ⅜-inch square pitch.
Tray 4: Cap-type tray with fifty-two ³⁄₁₆-inch holes drilled in the vertical face of a cap on a ⅜-inch vertical by ½-inch horizontal triangular pitch.
Tray 5: Cap-type tray with forty-seven ³⁄₁₆-inch i.d. brass jets in the top of the cap on ½-inch triangular pitch.

Usually, two plates were operated simultaneously on 36 inches of tray spacing. A bottom dispersal tray was employed, consisting of a round chamber with sixty ⅛-inch jets, for dispersing the Varsol; water flow was carried out of the unit through a 2-inch pipe which passed through this chamber. At the top of the column, a light phase drawoff was provided, and a heavy phase inlet nozzle was provided.

Tray Efficiency Studies. Tray efficiency studies were made in a 2-inch i.d. glass column using both ⅛-inch i.d. jets and ³⁄₁₆-inch i.d. holes in plate-type equipment (Figures 3 and 4). Each plate was equipped with one 0.62-inch i.d. downcomer. Plate spacings studied were 8, 16, and 24 inches. Trays were held in position