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ADIABATIC DISTILLATION OF DILUTE FORMALDEHYDE SOLUTIONS

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Adiabatic Distillation of Dilute Formaldehyde Solutions

I Statement of the Problem

It was the objective of this study to determine if formaldehyde solutions form azeotropes when distilled under equilibrium conditions.

II Background Literature and Discussion

Considerable confusion exists in the literature as to whether or not formaldehyde solutions form azeotropes. Many references have been found which state that azeotropes of formaldehyde have been obtained in atmospheric distillation. These azeotropes or pseudo azeotropes vary in concentration from 8[9] to 30%[10] and were obtained in a variety of equipment including rectifying columns. In a recent article Piret and Hall[11] present equilibrium data which show the distillate to be always weaker than the boiler liquor. They postulate that the apparent azeotropes reported in the literature could therefore only be obtained as a result of partial condensation, since Walker[12] has previously shown that partial condensation produced vapors which were stronger than the residue.

The explanation for the apparently conflicting data encountered in this problem undoubtedly lies in the fact, recently emphasized by Piret[1], that the fractional distillation of formaldehyde involves reaction kinetics as well as the usual problems of vapor-liquid equilibria. In the gaseous state, formaldehyde is essentially monomeric and the controlling factor is apparently the rate of solution which is determined by equilibria and kinetics of the solution reactions. This hypothesis is supported by Walker's data[2] (see Table II) on the comparative rates of solution of formaldehyde gas in water and formaldehyde solutions at different temperatures and also by previously published data on the solution reactions. The data show that the rate of solution varies directly with the temperature and inversely with the concentration of the scrubbing solution.

Bieber and Trumpler[3] have recently demonstrated that a 3% formaldehyde solution contains a small amount of monomeric formaldehyde whose concentration increases with increasing temperature and can be readily measured by the characteristic absorption of ultraviolet light having a wave length of approximately 290 millimicrons at temperatures above 50°C. They have also shown that this monomer is in equilibrium with formaldehyde hydrate, presumably methylene glycol, and that the heat of reaction calculated from the effect of temperature on equilibrium gives 14.8 kcal per mol formaldehyde gas. It was previously demonstrated that the partial pressure of aqueous formaldehyde is a function of the concentration which includes the polymeric hydrates. In view of Bieber and Trumpler's findings it would now appear that the partial pressure is a function of the methylene glycol concentration as indicated below:

$$CH_2O\ (g)\ \text{------}\ CH_2O\ \ (aq)\ \text{------}\ CH_2(OH)_2$$

Our experiments on the rate of solution of formaldehyde gas demonstrate that for formaldehyde solutions this rate decreases with decreasing temperatures. Since this is the opposite of what would be expected in dealing with normal gas-solution systems, it appears probable that the rate of the hydration reaction is the controlling factor. Wadano[5] has already demonstrated that the formation of polymeric hydrates from methylene glycol, viz.,

$$n\ CH_2(OH)_2 = \frac{1}{n}(CH_2O)_nH_2O + \frac{1-n}{n}\ H_2O$$

decreases with decreasing temperature. Accordingly, the solution is quickly saturated with monomer and will dissolve more only at a rate commensurate with the attainment of the new solvate equilibrium. This would indicate that the controlling reactions are not the hydration reactions occurring in the gas phase as postulated by Piret[1] since solution of either CH_2O or $CH_2(OH)_2$ gas would be accelerated by a drop in temperature.

Adiabatic distillation of formaldehyde solutions at total reflux clearly demonstrates that pseudo-azeotropes are formed in the absence of partial condensation. The actual concentration of the apparent azeotrope is undoubtedly a function of reactions kinetics and is determined by rate controlling factors such as column size and structure, boil-up rate, ratio of plate liquor volume to reflux volume, etc. If the distilling column is not adequately insulated, the concentration of the distillate will be raised proportionately by fractional condensation, a factor which was not appreciated by early investigators.

As azeotropes are compositions which are identical in both the liquid and vapor states, true azeotropes of formaldehyde and water do not exist. The constant boiling mixtures encountered are properly classified as apparent or pseudo-azeotropes.

III Development of the Column Design

The first phase of the problem was the development of a column which would provide true equilibrium data. Formaldehyde vapors (with water vapor) exhibit the rather unique property that water can be condensed in preference to the formaldehyde vapor. The latter must be absorbed in the condensed liquid. The first plate design which was evaluated consisted of a glass column 50 mm. in diameter containing one cap, 25 mm. in diameter with 12 vapor slots 1 x 7 mm. in area. The cap rested on the plate over a vertical chimney, and was kept in place by the plate above. The depth of liquor on this plate was only 5 mm. However, it was found that plate efficiencies were under 5% as the liquor was not deep enough to absorb the formaldehyde vapors. A single plate still was then made with the overflow pipe entered through the side of the column and held in place with a rubber stopper. By varying the height of the overflow pipe, the plate efficiency increased until an optimum of about 65% was reached at a liquor depth of 3 inches. Increasing the depth up to 12 inches did not improve the efficiency. With the 3 inch liquor depth, it was necessary to have a plate spacing of about 6 inches in order to prevent excessive entrainment. This presented a problem in supporting or securing the bubble cap to prevent its being blown off the chimney. Indentation of the column just over the cap caused surging of the liquid with an air lift which practically emptied the plate of liquor. The cap was then secured in place with three small glass rods attached to the inside of the cap and the top of the chimney. This also permitted setting the clearance of the bubble cap and the plate to provide specified vapor velocities through the slots. With a liquor depth of three inches, difficulty was also encountered with foaming and slugging of the liquid through the overflow pipe. It was necessary to extend the overflow pipe through the side of the column and up into the center. A sleeve was inserted over the end of the tube and sealed. Holes at the bottom of the sleeve permitted the liquid to enter and overflow to the lower plate but prevented the liquor from slugging over. This final design was used for a five plate column as shown in Figs. 1 and 2, which operated with an average pressure drop of 5 inches and an efficiency of 65% per plate.

Because of the property of formaldehyde-water vapors in which water is condensed preferentially, a vertical condenser could not be used immediately over the column. To operate in this manner, the water condenses and returns to the top plate of the column. The vapors become progressively richer in formaldehyde, finally reaching a concentration at which solid formaldehyde (paraformaldehyde) is deposited in the condenser, rapidly blocking it. In order to prevent this, a vertical vapor column was used, which was heated to prevent any condensation. The vapors then entered in a downward flow into vertical condensers. The water condensed preferentially and ran down the surface of the condenser in a film. The formaldehyde vapors were then absorbed in the film. The bottom of the condenser was submerged in a liquid trap to demonstrate that all the formaldehyde had been absorbed.

IV Distillation Equipment

The equipment used in this work is shown in Fig. 1 with the details of the plate shown in Fig. 2. It is as follows:

The boiler, A, is stainless steel of approximately 400 ml. capacity. The feed enters through tube B at the top, and overflows from the boiler through tube C which maintains a liquid level of 1 inch. The manifold, D, equalizes the pressure from the overflow to the top of the boiler, and has a connection at the top for the manometer, E, to measure the pressure in the boiler. The temperature of the liquor in the boiler is measured by a thermometer in well, F. The boiler is in an agitated oil bath which is maintained at constant temperature, with ± 0.5°C. by a controller and heater, G. Surmounting the boiler and connected to it by means of a spherical 30/50 glass joint, is the bubble cap section, H. The bubble cap section consists of 5 plates, 50 mm. in diameter, containing one cap, 25 mm. in diameter with 12 vapor slots 1 x 7 mm. The liquor down-flow pipes are 8 mm. tubes on the outside of the section. In the liquor overflow from the first plate is a thermometer, I, to measure the temperature of the liquor on the first plate. Around the section are two glass jackets. The inner jacket is wound with 25 feet of nichrome ribbon (one ohm per foot). The temperature of the air space between the section and the jacket is measured by a thermometer suspended in the air space. This temperature is maintained equal to that of the liquor on the first plate by adjusting the voltage of the heating element. Above the section is a long vapor line, J, which is wrapped with a heating element and insulation. Near the bottom is a thermometer and a manometer connection, L. The voltage to the heating element on the vapor line is adjusted so as to maintain the temperature at M one or two degrees above that at the base of the vapor line in order to avoid condensation. The manometer L measures the pressure of the top plate, and the difference between L and E represents the pressure drop across the section. Vertical down-flow condensers, N, are used in order that as the condensate is formed it might wash down the walls of the condenser, eliminating the formation of solid polymers. Condensate receivers, O, are arranged so that the vapors bubble through the condensate to ensure complete condensation and absorption of the formaldehyde vapors. Q is a vent for the system. P is a sample port, permitting analysis of the condensate returning to the top plate of the section. Each plate of the section has a capillary sample tube which permits withdrawing liquor from the plate to determine the plate to plate variation in formaldehyde.

V Materials Used

The formaldehyde solutions used were from two sources: (1) low methanol formaldehyde solution fresh from the production units, and (2) formaldehyde solution prepared by dissolving fresh paraform. The latter aqueous solutions were prepared by heating paraformaldehyde and distilled water at 65°C. until the paraformaldehyde dissolved and then aged at 65°C. before use.

VI Methods of Analysis

The formaldehyde in the solutions was determined by the sodium sulfite method of Lemme[6] as reported by Walker[7]. The method utilizes the condensation of formaldehyde with the sulfite ion liberating hydroxyl ions which are titrated with normal acid.

$$CH_2O\ (aq) \neq Na_2SO_3 \neq H_2O \text{ ----- } NaOH \neq CH_2(NaSO_3)OH$$

The analytical procedure is to dissolve a weighed sample containing about one gram of formaldehyde in 50 ml. of thymolphthalein neutralized 1 molar sodium sulfite solution. (Sodium sulfite solution neutralized to colorless with 1 N sulfuric acid using thymolphthalein indicator). The mixture is titrated to complete discoloration with 1 N sulfuric acid. Each ml of normal acid is equivalent to 0.03003 grams of formaldehyde and the percent formaldehyde in the sample is determined by the following equation:

$$\%\ \text{formaldehyde} = \frac{\text{acid titre x normality x 0.03003 x 100}}{\text{weight of sample}}$$

Analytical figures obtained for commercial formaldehyde solutions by the sodium sulfite method are accurate to within ± 0.02 percent. Impurities (methanol and formic acid) commonly present in formaldehyde solutions have no effect on the results. Neutral formates do not interfere[8].

VII Discussion

Distillations were carried out in the glass bubble cap column shown in Fig. 1, with a detail of the plate design in

Fig. 2. A summary of the data is shown in Table I. These data show two facts: (1) The vapors obtained from simple distillation of formaldehyde solutions (as shown by the analysis of the liquor on the first plate when the column is operating at total reflux) is always weaker than the boiler residue: and (2) rectification of the formaldehyde vapors yields a pseudo-azeotrope of about 21% in our column. The fact that vapors weaker than the residue are obtained by simple distillation agrees with partial pressure data reported by Piret and Hall[11], Walker[12], and others. Our data also show that partial condensation of the vapors between the boiler and the first plate, enriches the vapors until they are stronger than the residue. This partial condensation was accomplished by omitting the insulation between the boiler and the column. Effective insulation of this section eliminated this partial condensation.

In starting up the unit, feed is entered into the boiler, A, through tube B, and overflows into receiver R. The feed is continued until all of the unit is filled in order to maintain constant strength formaldehyde in the boiler. The feed and the overflow are then closed. Distillation is then continued with periodic samples from each of the plates and the condensate until the concentration of the formaldehyde in the reflux remains the same for a period of an hour. The column is then considered to have reached equilibrium. Samples are then taken from the boiler and each plate up the column (from the bottom up, to minimize disturbance of the equilibrium) and the reflux. The samples are obtained from the plates by drawing sufficient solution through the capillary tubes to remove the residue of the previous sample. Fresh solution is then taken. These are analyzed by the sodium sulfite method as described.

The data obtained from the operation of this column are shown in Table I. It is clearly shown that for all strength solutions, the concentration decreased from the boiler to the first plate. This effect is similar to simple distillation and agrees in a rough quantitative degree with the work of Piret and Hall[11]. This behavior of the solution could be explained by the fact that the boiler solutions are, relatively speaking, old and hydrate equilibria have become well established. On the other hand, the solution on the plates is fresh and ever-changing so that the hydrate reactions have not proceeded as far as in the boiler solution but represent a steady state dictated by operating conditions. As a consequence, the CH_2O in the solutions on the plates is more volatile. Below about 21% concentration, the formaldehyde in the vapors increased with rectification from plate to plate. Above 23% concentration, the formaldehyde in the vapors continued to decrease. Data by Pyle and Lane[13], Fig. 3, show that an apparent azeotrope of 20-21% concentration is formed in an equilibrium column. The equilibrium column was of small volume, so that with a high boil-up rate and recirculation of the condensate, it soon functioned as a single plate, giving results which were duplicated in multi-plate columns.

In run 4, the insulation was removed from the section of the column between the boiler and the first plate. Condensation was observed inside this tubing. In this instance, the concentration of the liquid on the first plate (equal to the vapors from the boiler as the system was closed and at equilibrium) was higher, 14.3 vs 10.77, than that of the liquid in the boiler. On comparison with run 2, the partial condensation resulted in an increase in concentration of the formaldehyde from 7.67 to 14.3% on the first plate.

VIII Summary and Conclusions

Adiabatic distillation of formaldehyde solutions at total reflux clearly demonstrates that pseudo-azeotropes are formed without benefit of partial condensation. As we obtained concentrations of 21-23% in our glass column, and others have reported concentrations of 8 to 30%, it would appear that the exact concentration of the pseudo-azeotrope depends upon the physical conditions, such as boil-up rate, ratio of plate liquor volume to reflux volume, etc., of the equipment being used. However, it is shown that partial condensation will further enrich the vapors, resulting in higher concentrations of formaldehyde in the distillate.

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TABLE I

ADIABATIC DISTILLATION OF DILUTE FORMALDEHYDE SOLUTIONS AT ATMOSPHERIC PRESSURE

Equilibrium Concentrations of CH_2O in per cent at Plate Indicated

Run No.	Boil-up cc/Min.	Boiler	Plate 1	Plate 2	Plate 3	Plate 4	Plate 5	Distillate
1	15	3.79	3.05	3.83	5.37	6.16	7.77	9.50
2	15	10.88	7.67	9.21	11.21	12.43	13.98	14.91
3	15	10.47*	10.41	11.26	12.33	13.64	15.13	16.98
4	15	10.77	14.3	15.86	17.22	18.78	19.85	21.1
5	15	21.11	16.80	17.64	19.03	20.13	20.37	21.52
6	15	32.1	24.07	23.6	23.6	22.9	22.8	-
7	15	54.0	40.83	37.24	34.41	32.09	30.32	28.89

* Solution prepared from paraform.

Note: Below 21% conc. drops from the boiler to 1st plate and then increases from plate to plate. Above 23% conc. drop to 1st plate is more than a theoretical plate. Conc. continues to drop from plate to plate.

TABLE II

SOLUBILITY OF ANHYDROUS FORMALDEHYDE GAS IN WATER AND FORMALDEHYDE SOLUTIONS

Concentration of CH_2O in Original Scrubber Solution	Temperature of Scrubber		
	-2 to -1°C.	25 to 29°C.	87 to 92°C.
0.0%	100	99	99
35.5%	88	98	99
41 %	73	79	93

% of formaldehyde in the gas stream which dissolved on bubbling through a definite quantity of scrubber solution.

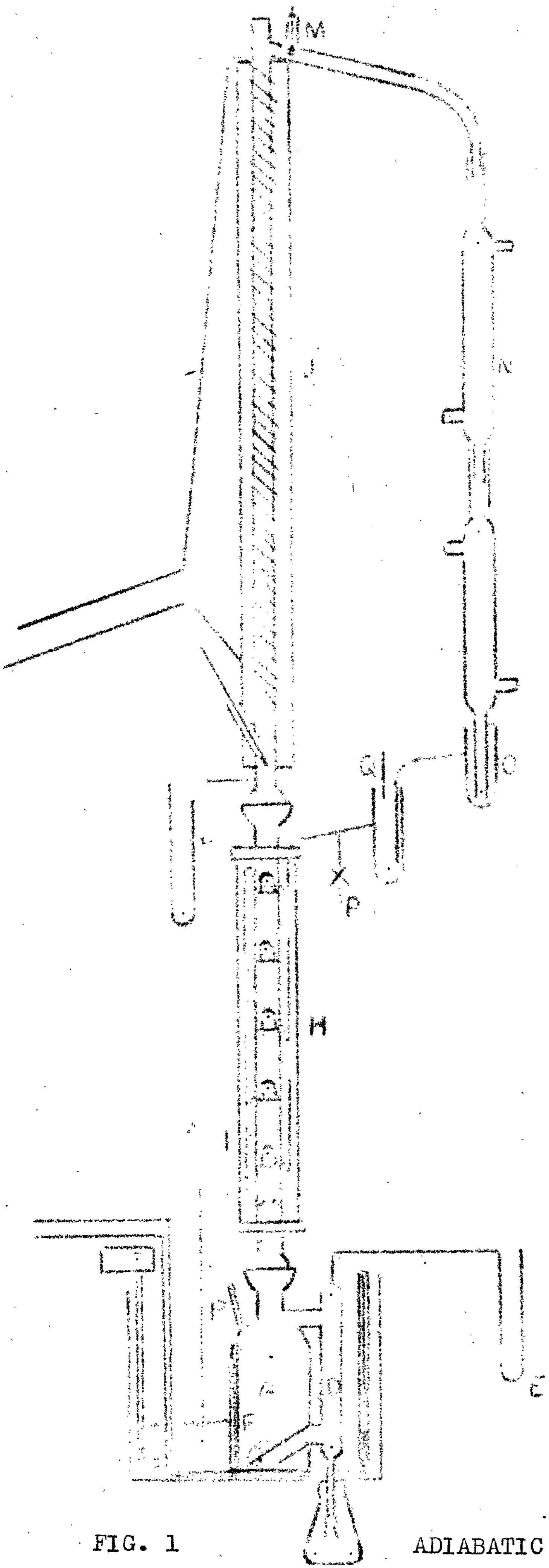


FIG. 1 ADIABATIC DISTILLATION EQUIPMENT

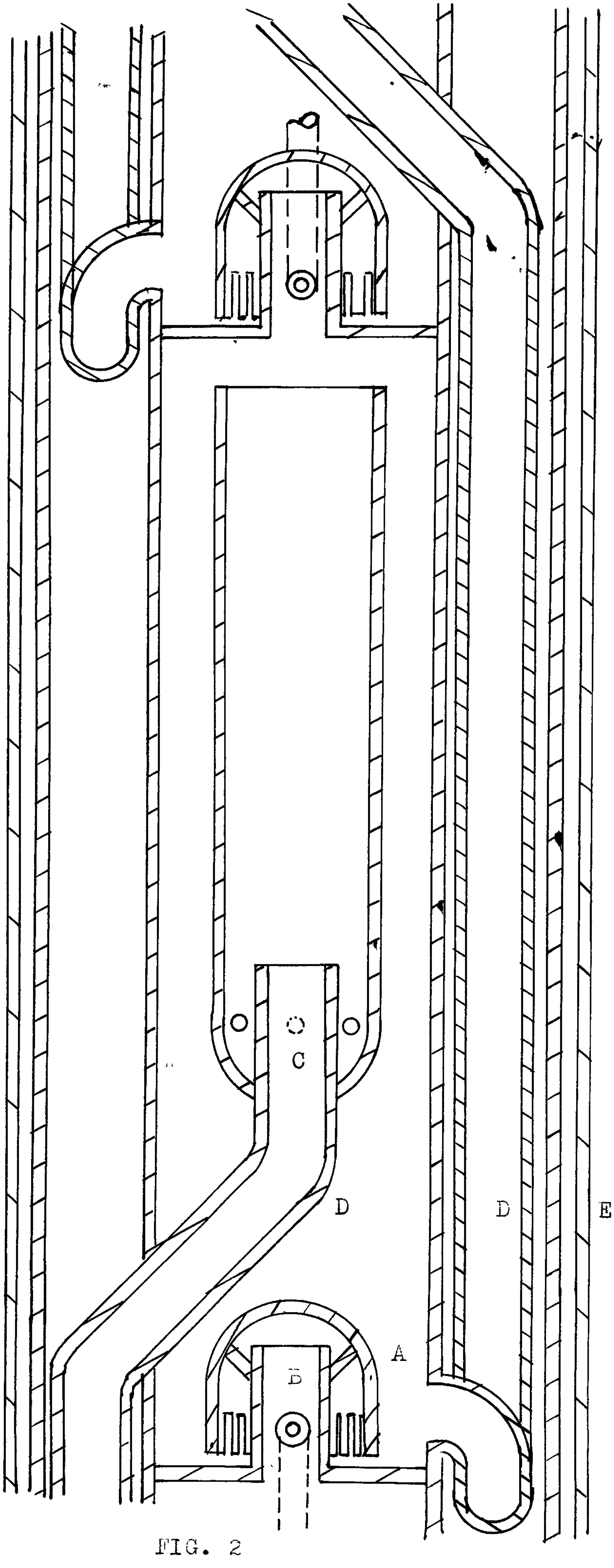
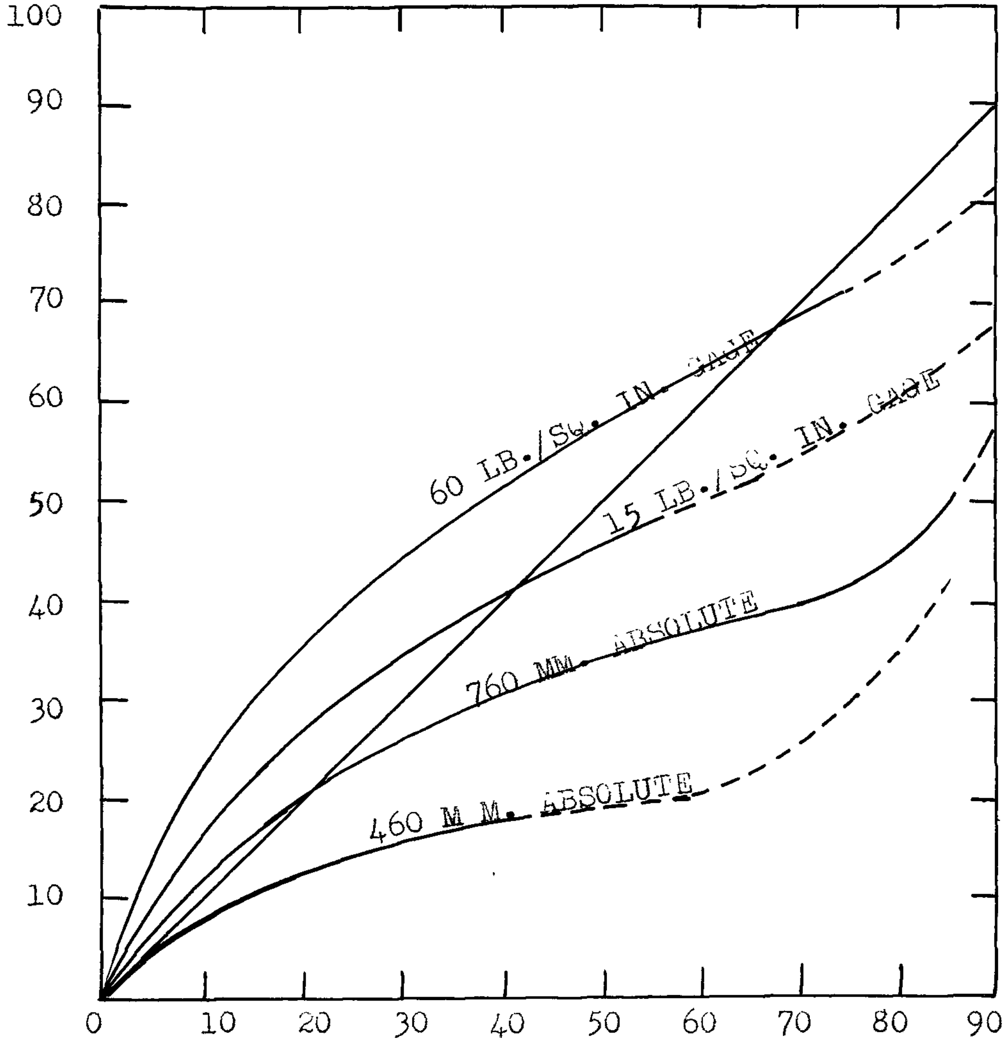


FIG. 2



WT. PERCENT HCHO IN LIQUID

FIG. 3.