HIGH PRESSURE RECTIFICATION

by

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Signature of Author
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in Charge of Research
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of Departmental Committee
on Graduate Students
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Cambridge, Massachusetts

May 21, 1936

Professor G.W.Swett,
Secretary of the Faculty,
Massachusetts Institute of Technology,
Cambridge, Massachusetts

Dear Sir:

In accordance with the regulations of the faculty, I herewith submit a thesis entitled "High Pressure Rectification" in partial fulfillment of the requirements for the degree of Master of Science.

Yours very truly,

Signature redacted

ACKNOWLEDGMENT

The author wishes to express his thanks for the advice and help of Dr.E.R.Gilliland, under whose direction this thesis was carried out, and of Mr.R.V.Lukes.

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OBJECT

The object of this thesis was to study the rectification of mixtures of the lighter hydrocarbons, as exemplified by the binary, propylene-isobutane, at pressures ranging from those now common in commercial gasoline stabilizing columns (250#/in.) up to the critical.

ABSTRACT

An experimental high pressure rectifying apparatus was designed and built and a technic for its operation developed.

The still was charged with a mixture of propylene and ise-butane and runs were made at total reflux at pressures from 228#/in.^{2} absolute to 522#/in.^{2} absolute.

Rectification became less effectual with increasing pressure. The effectiveness decreased rapidly as critical conditions were closely approached.

The maximum permissible vapor velocity diminished rapidly near the critical region and the column became exceedingly difficult to operate.

The analysis and boiling point of the bottoms calculated using the fugacity charts and fugacity rule checked the experimental values fairly well at 228#/in.^{2} absolute, but deviated considerably at higher pressures.

INTRODUCTION

Although experts are at variance as to whether the developments in cracking or in distillation have been of greater importance to the petroleum industry, there can be only the most hearty accord that each is a preeminent necessity and one whose use would be trammeled without the other. These two major phases of the oil industry have by no means assumed the static pall of standardized practice. There is too much at stake in an industry so large and traditionally so progressive. Hence, little is the respect for the status quo under the pressure of natural economic forces.

The polymerization of olefins to gasoline is one of the recent outstanding results of the struggle for competitive advantage. The coming of polymerization has created new problems in cracking and distillation. There need be no fear that the oil industry with its heralded resourcefulness and daring extrapolation will fail to arrive at practical solutions with dispatch. However, the haste with which it must work does not always permit it to arrive at a consummate design or process, let alone a sound theoretical basis which is of great importance in future work.

It is the purpose of this thesis to study one of the aforementioned phases of the oil industry, distillation, under operating conditions which heretofore have not been used commercially. The coming of polymerization has created a tremendous problem in the rectification of the lighter hydrocarbons (those which are gases under atmospheric conditions). There are three alternatives in maintaining a liquid phase with these hydrocarbons so that rectificatien may be carried out, low temperature rectification, rectification in the presence of a non=volatile solvent, and rectification under pressure. The latter method appears now to be the dominant one and will be the subject of this investigation.

It presents an interesting subject for study because of the limitations on rectification at pressures approaching and in the critical region of the components. These limitations are on completeness of separation and on capacity. The first is caused by the bowing down of the vapor-liquid equilibrium curve with increasing pressure until eventually one or more discontinuities develop in the curve and finally only a single phase can exist. The limitation on capacity is imposed by the maximum allowable vapor velocities which fall off markedly near the critical as vapor and liquid densities approach each other. The investigation also offers an opportunity to check up on the fugacity rule and fugacity charts at elevated pressures.

The limitation on separation mentioned above has been pointed out by Cummings (1,2), for the case of binary mixtures. He has shown that separation may be effected with increasing difficulty at pressures up to the critical pressure of the component with the lower critical pressure, and within limited ranges of concentration between this pressure and the maximum pressure which a two phase mixture can support (which may be higher than the critical pressure of either pure component). Above this maximum pressure, there can be only one phase, and rectification, of course, is impossible.

However, designers of oil refining equipment claim remarkable separation in the critical region (4) as e.g., obtaining a practically pure constituent in the distillate when operating above its critical pressure. It is proposed to settle this question.

Gunness (5) has recently studied the operation of a commercial stabilizing column operating at 265#/in.^{2} and has obtained good agreement between the measured boiling points on the various plates and those calculated from the liquid analysis and pressure using the fugacity charts and the Lewis and Randall fugacity rule. However, the fugacity method for calculating vapor-liquid equilibria has not been checked at pressures near the critical. This investigation will throw some light on the use of fugacities at high pressures.

The carrying out of this program narrows down to the designing and building of a suitable apparatus, the preparation of pure hydrocarbons, and successfully maintaining steady conditions during runs.

A binary mixture is used for simplicity in this first attack upon the problem. A mixture of olefin and paraffin are used (propylene-isobutane) to ensure easy analysis of product and bottoms. Runs are made at total reflux because this type of operation yields the desired data most conveniently.

SUMMARY OF PROCEDURE

A still, packed column ($\Bumpeq$ 10 plates), and condenser together with numerous appurtenances were designed (see Figure I) and built on the basis of chemical engineering principles and strength of materials. The apparatus was adequately tested and found safe at pressures far above the critical pressure of any hydrocarbon.

The still was charged with the proper amount of a mixture of propylene and isobutane and steady state runs were made at total reflux at pressures from 228#/in.^{2} absolute to 522#/in.^{2} absolute. The pressure and temperatures of bottoms, vapor at the top of the column, and reflux were recorded for each run. Samples of bottoms and product were taken and analyzed in an Orsat apparatus. The condenser cooling water rate and temperature rise were measured.

Fig 1
Diagram of Apparatus

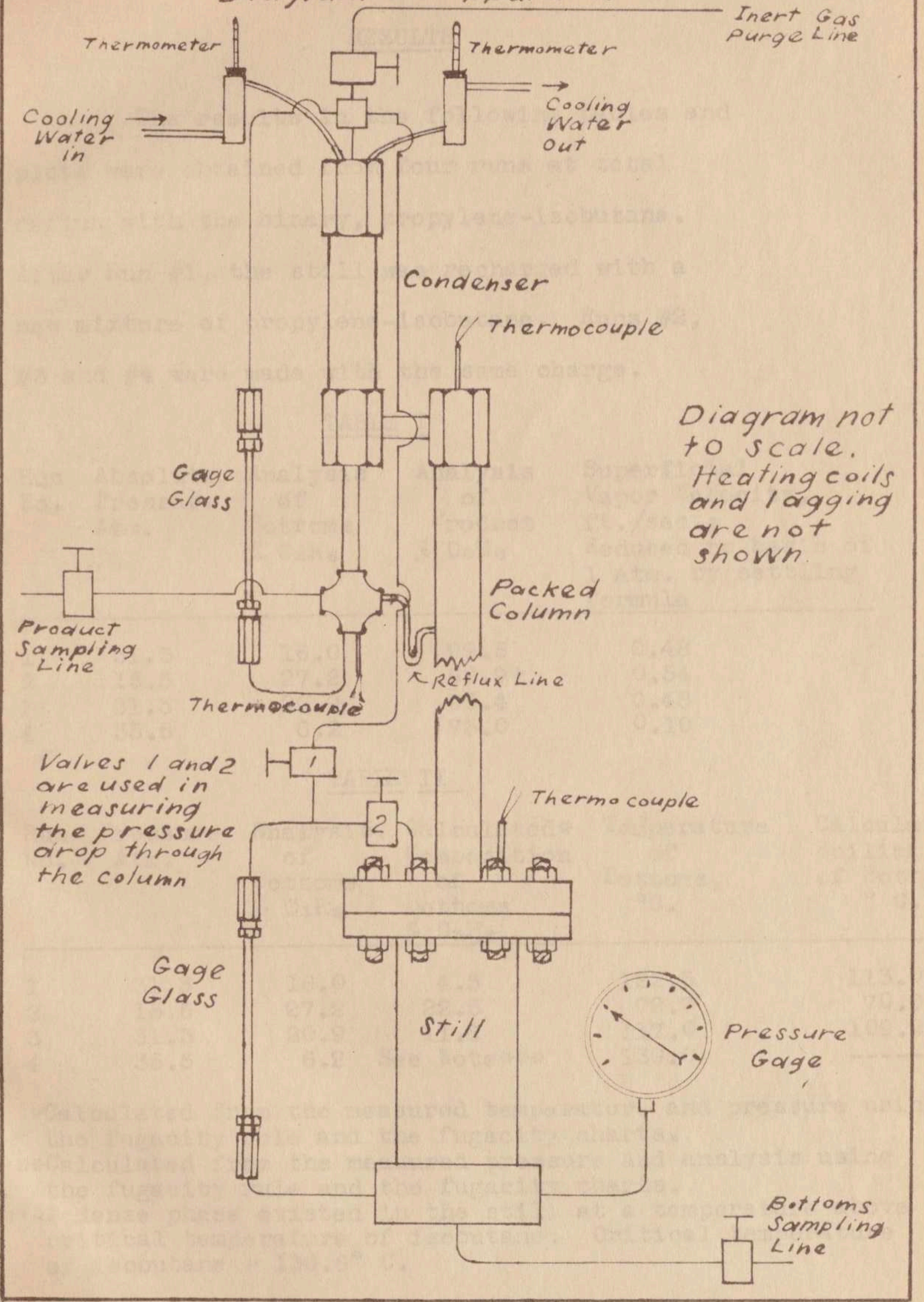

Diagram not to scale. Heating coils and lagging are not shown.

Valves 1 and 2 are used in measuring the pressure drop through the column

RESULTS

The results in the following tables and plots were obtained from four runs at total reflux with the binary, propylene-isobutane. After Run #1, the still was recharged with a new mixture of propylene-isobutane. Runs #2, #3 and #4 were made with the same charge.

TABLE I

Run No.	Absolute Pressure Atm.	Analysis of Bottoms % C_3H_6	Analysis of Product % C_3H_6	Superficial Vapor Velocity, ft./sec.; Reduced to basis of 1 atm. by settling formula
1	31.3	16.0	99.5	0.48
2	15.5	27.2	99.9+	0.54
3	31.3	20.9	99.4	0.48
4	35.5	6.2	73.0	0.10

TABLE II

Run No.	Pressure Atm.	Analysis of Bottoms % C_3H_6	Calculated* Composition of Bottoms % C_3H_6	Temperature of Bottoms, °C.	Calculated** Boiling Point of Bottoms ° C.
1	31.3	16.0	4.5	122.5	113.0
2	15.5	27.2	22.5	72.7	70.0
3	31.3	20.9	11.6	117.0	109.2
4	35.5	6.2	See Note***	139.0	-----

*Calculated from the measured temperature and pressure using the fugacity rule and the fugacity charts.

**Calculated from the measured pressure and analysis using the fugacity rule and the fugacity charts.

***A dense phase existed in the still at a temperature above the critical temperature of isobutane. Critical temperature of isobutane = 136.6° C.

Number of theoretical plates in column = 10.

(Calculated from the Fenske (3) equation).

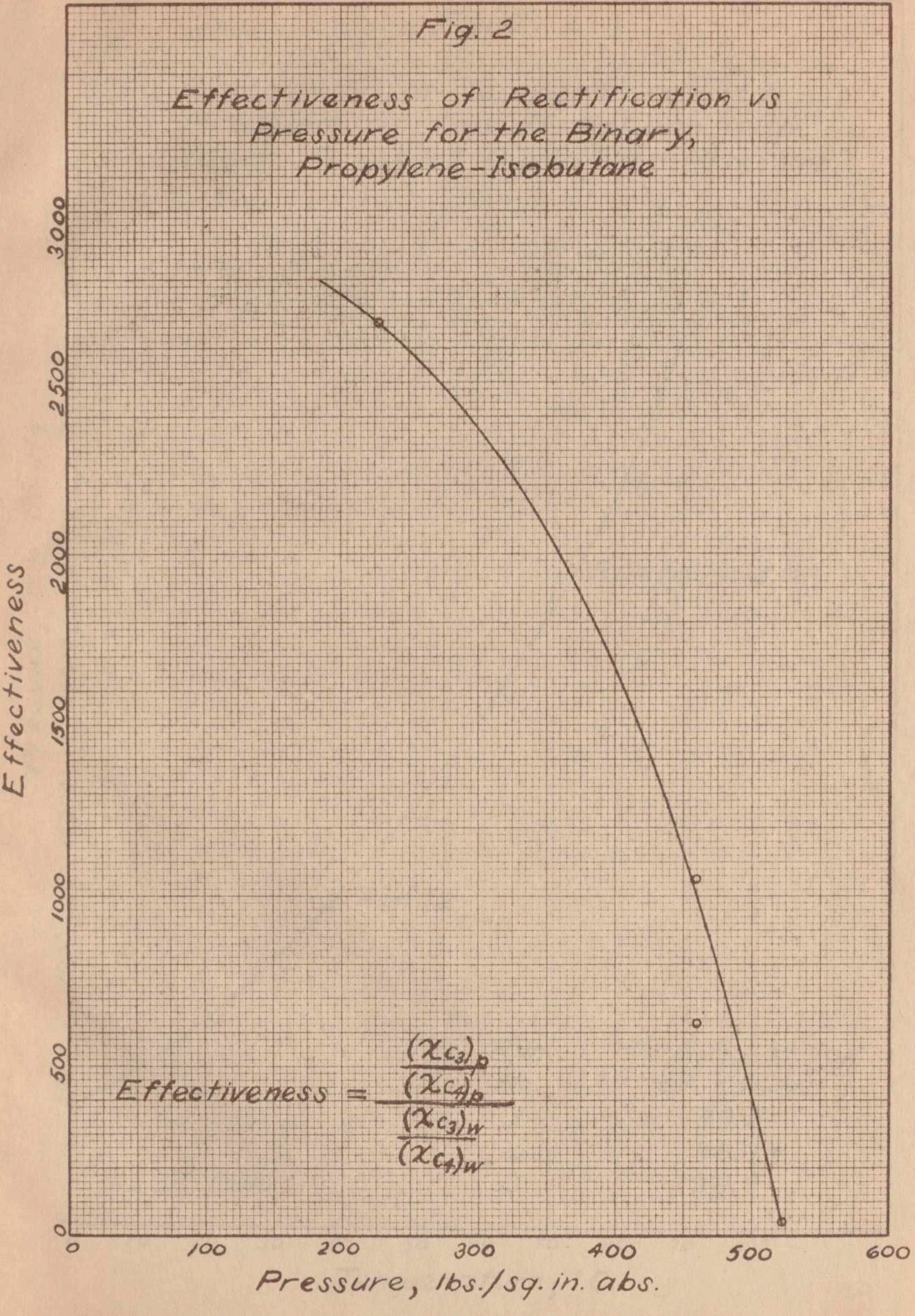

Fig. 2

Effectiveness of Rectification vs Pressure for the Binary, Propylene-Isobutane

$$\text{Effectiveness} = \frac{\dfrac{(x_{C_3})_p}{(x_{C_4})_p}}{\dfrac{(x_{C_3})_w}{(x_{C_4})_w}}$$

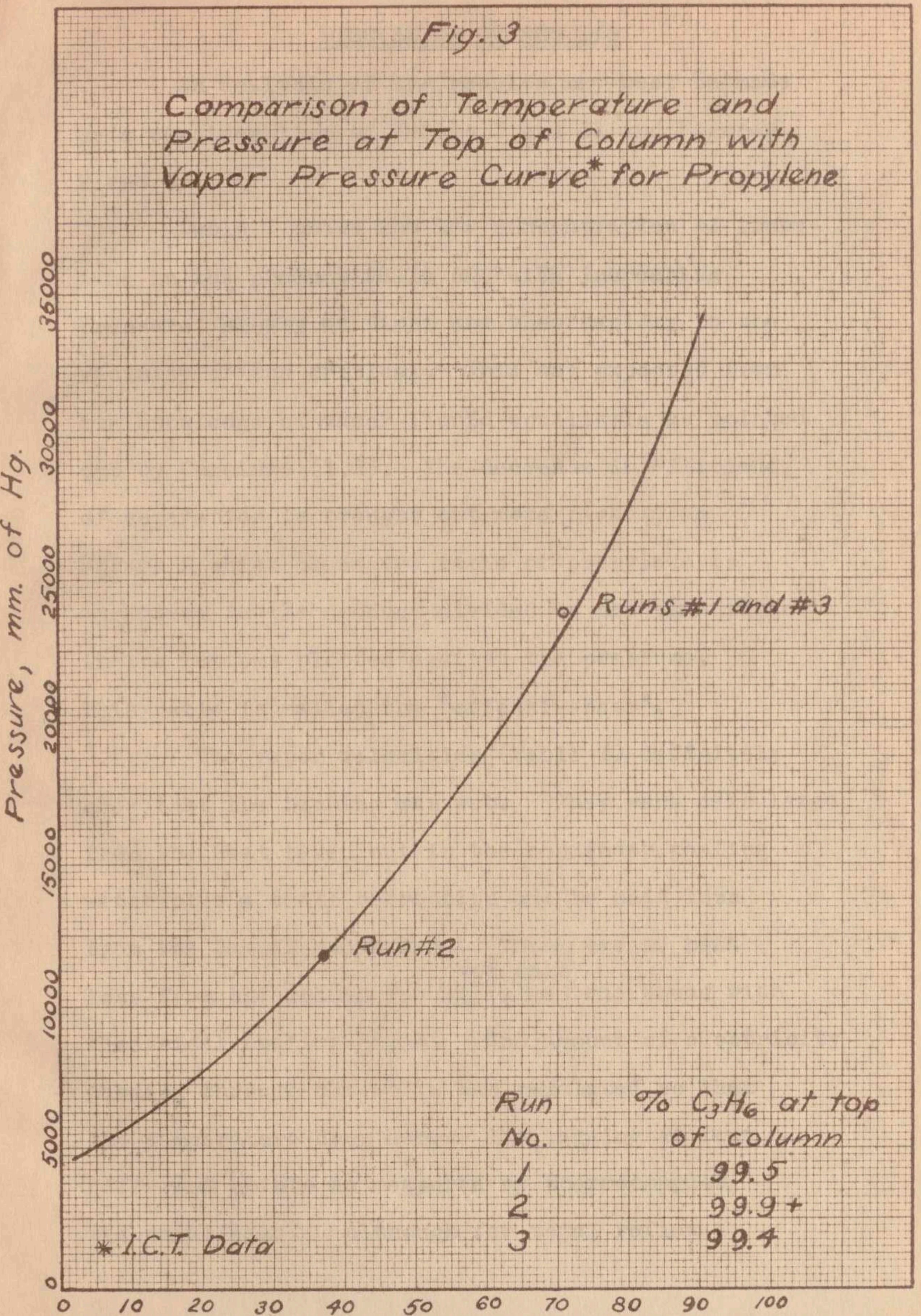

Fig. 3

Comparison of Temperature and Pressure at Top of Column with Vapor Pressure Curve* for Propylene

Run No.	% C_3H_6 at top of column
1	99.5
2	99.9+
3	99.4

* I.C.T. Data

DISCUSSION OF RESULTS

An analysis of the results may best be made by a consideration of Tables I and II and Figures 2 and 3.

Table I shows how the concentration of propylene in the product falls off with increasing pressure, slowly at first and then rapidly in the vicinity of the critical. This was expected from our knowledge of vapor-liquid equilibria as pointed out by Cummings (1,2). The decrease in efficiency of separation is brought out more clearly in Figure 2 which shows the ratio of propylene to isobutane in the product divided by the same ratio in the bottoms plotted against the pressure. This ratio is called the "effectiveness".

The vapor velocities (Table I) definitely show that the packing was wet. They were calculated from the heat taken out in the condenser cooling water plus a small correction due to heat loss from the lagged condenser. There was no heat loss from the column for it was well lagged and wound with electrical heating coils. The amount of electricity passing through the coils was regulated so that the temperature drop across the lagging at four different points as measured by thermocouples was negligible. Although for total reflux heat

heat loss from the column does not affect the operating line it was necessary to have no heat loss in the vicinity of the critical where heats of vaporization are small and the operation of the column is a delicate task.

The vapor velocities in Runs #1, #2 and #3 were not maximum vapor velocities, i.e., a slightly increased vapor velocity did not cause flooding. However, the low vapor velocity of Run #4 was just about the maximum attainable. It was run at this velocity in order to get sufficient liquid at the top of the column as read by the gage glass in order to be sure that rectification was taking place and to ensure a good sample of product. With just slightly less heat into the still nothing was obtained at the top. Thus the operation of the column was difficult at the conditions of Run #4 and it took a long time to obtain steady conditions, since they could only be obtained by minute changes in the heat supplied to the still.

In Run #4 the temperature of the still was 139.1° C. which is 2.5° C. above the critical temperature of isobutane. The pressure was 35.5 atmospheres, 0.3 of an atmosphere below the critical pressure of isobutane. Hence, a dense phase existed in the still (at least in the lower part where the thermocouple junction was and the electrical heating coil) through which heat was transferred by conduction and convection to the material in the column where there was a liquid phase and rectification was actually taking place. Of course, the heat may have been transferred to the column along the walls of the still. To make the picture complete the tenperature at the top of the column was 81° C., 11.4° C. below the critical temperature of propylene and 9.5 atmospheres below the critical pressure. According to the information that Cummings (1,2) gives, the column should have operated differently. Enough propylene should have migrated to the still to bring its temperature down below the critical temperature for isobutane and in turn enough propylene should have left the still to maintain the pressure in the column. However, the contents of the still probably formed a dense stagnant phase and there was insufficient mobility to bring about a redistribution of material in still and column.

Table II compares the measured boiling point and analysis of the bottoms with those calculated using the fugacity charts and fugacity rule. It is noted that measured and calculated values check fairly well for Run #2 at 15.5 atmospheres. At 31.3 atmospheres the values differ considerably. The boiling points check much better than the analyses.

Figure 3 shows the temperature and pressure at the top of the column for Runs #1, #2 and #3 plotted with the vapor pressure curve for propylene. The propylene at the top of the column for these runs was essentially pure (99.5%, 99.9%+, 99.4% respectively) and the temperatures and pressures should check the vapor pressure curve. The excellent agreement verifies the careful calibration of thermocouples and pressure gage.

The propylene used was prepared by the catalytic dehydration of pure isopropyl alcohol over alumina. It contained about 4.5% hydrogen in the vapor phase above liquid propylene. This hydrogen, however, merely collects at the top of the condenser as an inert gas. The isobutane was purchased from the Ohio Chemical Company. It was of a purity of 99+% and contained no unsaturateds. In Run #1 the propylene was put into the still as a liquid. Since the bottoms analysis did not check the analysis calculated from the fugacity charts it was felt that the propylene might have contained a small amount of unreacted isopropyl alcohol. Hence, the still was recharged using propylene from the vapor phase and this second charge was used for Runs #2, #3 and #4. Thus, the propylene used underwent a simple distillation. Because of the great relative volatility between propylene and isopropyl alcohol, the propylene charged would contain a negligible amount of isopropyl alcohol even if the liquid phase did contain a small amount. It is noted that measured and calculated analyses differed widely with this second charge also, indicating that the deviations in Run #1 were not caused by the presence of any isopropyl alcohol.

The number of theoretical plates in the column was calculated from the Fenske equation (3) using an average of the relative volatilities at still and top of column. The value of 10 was taken as the average of 10.6 for Run #1 and 9.5 for Run #2. It is fairly accurate even though the propylene concentration in the product was so high (99.5%) that a slight error in its analysis throws off the ratio of propylene to isobutane considerably. This is because the number of plates depends on the logarithm of the ratio of concentrations. Run #4 had concentration ratios more suitable for use in the Fenske equation but it was in the critical range and the relative volatility calculated from the fugacity charts would not be suitable. Run #3 had an unsuitable concentration ratio in the product. Ten plates are close to what would be expected for the type and amount of packing used.

CONCLUSIONS

The following conclusions on high pressure rectification were reached.

1. The effectiveness of rectification diminishes with increase in pressure, slowly at first and then rapidly as critical conditions are closely approached.

2. The capacity of a rectifying column decreases rapidly as critical conditions are approached.

3. The use of the fugacity rule and present fugacity charts in the calculation of vapor-liquid equilibria at pressures not far from the critical gives results which are only roughly approximate.

RECOMMENDATIONS

It is recommended that:

1. Rectification should not be carried out at pressures near the critical.

2. The approximate nature of vapor-liquid equilibrium calculations for high pressures by means of fugacities should be recognized.

3. A more complete investigation of high pressure rectification should be made using the same apparatus with the changes recommended in Appendix A. The proximity to the critical at which it is practical to operate should be found. A study should be made of pressure drop through the column and maximum vapor velocity with increasing pressures.

4. A comprehensive investigation of the high pressure vapor-liquid equilibria of hydrocarbons should be made.

APPENDIX

APPENDIX A

Design and Construction of Apparatus.

The apparatus used for the high pressure rectification is illustrated in Figure (1). It was built using high-pressure technique and tested strong and leakproof at 3000#/in.^{2}. The details of the construction are given below.

Still: The still consisted of a seamless steel tube 1/4" thick by 3" inside diameter by 12" long. The bottom consisted of a steel cap and the top was connected to the column by means of two flanges bolted together with eight 3/4" bolts. The connections were made tight by means of copper gaskets.

Column: The column consisted of a seamless steel tube 1/4" thick by 1" inside diameter by 72" long. It was packed with 40" of 1/4" carbon raschig rings for a preliminary calculation showed that this would give a separation of from 5% in the bottoms to 95% propylene in the product for a propylene-isobutane binary at moderate pressures. More packing would mean better separation and more difficult problems of accurate analysis of product and bottoms. Less packing would not be suitable for a mixture such as propylene-propane or isobutylene isobutane. The top of the column was closed by a cap of 2" hexagonal steel stock.

Condenser: The condenser consisted of a piece of seamless steel tubing 1/4" thick by 1" inside diameter by 14" long. It contained a cooling coil of ordinary 3/16" copper tubing 14' long and wound in the form of a compact helix. In the design of the condenser the maximum required condenser capacity was calculated as a function of pressure. It is of interest to note that the maximum required capacity goes through a maximum. This is because material capacity increases, and heats of vaporization decrease with increase in pressure.

The ends of the condenser were closed with 2" hexagonal steel caps. The two terminals of the cooling coil were soldered into the top cap. The condenser was connected to the top of the column by means of a 2" length of high pressure pipe of 1/2" inside diameter.

Reflux Line: A 16" piece of high pressure pipe 3/8" inside diameter was connected to the bottom of the condenser. A high pressure cross was connected to this pipe. A line of ordinary 1/4" copper tubing was connected from the cross to the side of the column. Thus, reflux dropped directly down from the condenser through the pipe, cross, and tubing into the column. The pipe and cross together served as a trap from which a liquid sample could be obtained. A 5/64" sharp edged orifice was located in the connection between the cross and the tubing. The height of liquid in the pipe above the orifice could be read in a gage glass, indicating the reflux rate.

Gage Glasses: Two high pressure gage glasses were used. One was connected to the bottom and top of the still to indicate the liquid level as an aid in charging the still and running the apparatus. It also served to indicate the pressure drop through the column when used in conjunction with a combination of valves and lines (see under Valves). The other gage glass was connected to the bottom and top of the reflux liquid trap. It showed the presence of reflux and the height of liquid reflux above the orifice, indicating the rate of flow.

The gage glasses were made of 12" lengths of 8 mm. soft glass capillary tubing with a bore of 1.3 mm. They were connected at each end to 1" hexagonal steel stock connectors by means of rubber packing glands. Rubber was found to be the only satisfactory packing. A gage glass was tested at 5,000#/in.^{2} without leaking through the packing glands or breaking. However, the same gage glass broke a few moments later at 1500#/in.^{2} after being subjected to intermittent pressures.

Valves and Lines: There were five high pressure valves on the apparatus. The seats were made of brass and the needles of stainless steel to insure tightness. All lines were of 3/16" high pressure copper tubing.

There was a valve in a line connected to the top of the condenser. This line was for purging inert gas out of the condenser or connecting the condenser with a supply of inert gas for the purpose of maintaining a constant pressure in the apparatus.

A line and valve were connected to the bottom of the still for the purpose of obtaining a sample of the bottoms. The line terminated in the middle of the still and 4" above the still floor level so that a good sample of boiling liquid was ensured.

A line and valve were connected to the liquid trap so that a sample of product could be obtained. The line ended in the pipe part of the trap rather than in the cross in order to insure a good sample of product and avoid any error due to stagnant liquid.

Two valves and a line were used in conjunction to obtain the pressure drop through the column. The line was connected from the top of the gage glass for the still to the top of the column. One valve was in this line; the other valve was in the line connecting the top of the gage glass to the top of the still. When the valve in the line to the top of the column is closed and the valve to the top of the still is open, the gage glass indicates the level in the still. When the valves are turned vice versa the level in the gage glass rises and the amount of rise shows the pressure drop through the column.

Lagging: The column was well lagged, The still was lagged in order that heat from an electrical heating coil would be driven into it. The condenser was lagged in order to get an accurate measure of the vapor velocity from the cooling water rate and temperature rise.

Heating Coils: The still was heated by an electrical heating coil in the lower part so as not to superheat the vapor from the still. The column was wound with electrical heating coils on the outside of the lagging in order to have no heat loss. The amount of heat was regulated until there was no temperature drop across the lagging.

Thermocouples and Pressure Gage: There was a thermocouple for measuring the temperature of the liquid in the still, one for the temperature of the vapor at the top of the column and another for measuring the temperature of the reflux in the trap as it runs through back into the column.

There were thermocouples on the column at four different points (1/8, 3/8, 5/8, 7/8 marks). One junction was on the inside of the lagging and the other on the outside. The heating coils were regulated to give no temperature difference across the lagging.

A pressure gage was connected to the still.

RECOMMENDATIONS

Gage glasses of larger bore should be used to prevent slugging.

A longer gage glass should be used for the still for the pressure drop through the column is quite large.

A larger pipe should be used to connect the column to the condenser. The pressure drop through the pipe now used is so large that it throws the orifice reading off and may limit maximum vapor velocity at the lower pressures.

APPENDIX B

PROCEDURE

The still was charged with a calculated amount of propylene and isobutane sufficient to enable critical conditions to be reached and at the same time not so much as would cause the liquid in the still to rise up into the column under any operating conditions. The amount was 14.4 oz. of isobutane and 5.6 oz. of propylene. The isobutane was charged first and then the propylene. The apparatus was evacuated and the isobutane put in under a liquid head. The propylene, of course, required no liquid head as its partial pressure in the still was greatly reduced through solution in the isobutane. The amount charged was determined from the still gage glass level and checked by weighing.

In Run #1 the still was charged with liquid propylene. After Run #1 the still was recharged. This time propylene was taken from the vapor phase of the tank and thereby the possible presence of isopropyl alcohol in the propylene was avoided. The second charge was used for Runs #2, #3 and #4.

All runs were made at total reflux. The heatingcoils on the column were regulated until there was no heat loss. When the steady state was reached the pressure and temperatures of bottoms, vapor at the top of the column, and reflux were measured. The cooling water rate and temperature rise were measured. Samples of bottoms and product were taken slowly so as not to change operating conditions during sampling. A preliminary sample of sufficient size to purge the lines was taken and discarded; then a good sample was taken. These samples were collected in aspirator bottles and analyzed in an Orsat apparatus using bromine water to absorb the propylene. The bromine was scrubbed from the gas with sodium hydroxide solution.

The pressure was regulated by means of inert gas in the condenser. Regulation by means of cooling water rate would prove unwieldy due to fluctuations in the water line pressure. Run #1 was made with a tank of city gas connected to the top of the condenser. Runs #2, #3 and #4 were made with only a small amount of city gas in the condenser as a cushion.

The apparatus was difficult to regulate in Run #4 which was made in the vicinity of the critical.

Condensation in the gage glasses prevented obtaining readings. The tops of the gage glasses were then connected to the top of the condenser in order to have an inert gas above the liquid. The gage glasses were then satisfactory.

Recommendations:

The pressure should be controlled by a small cushion of inert gas in the condenser rather than connecting the top of the condenser to a tank of inert gas. In this way steady conditions are easily maintained and there is no danger of losing some of the hydrocarbons into the inert gas tank.

A gas lock of small capacity should be used to have suitable control over the amount of inert gas added to the condenser.

Changes in the heat supplied to the still should be made slowly if steady conditions are to be made in a minimum of time, especially at the higher pressures.

APPENDIX C

Preparation of Hydrocarbons

Thanks are due to Dr. E.R.Gilliland for the preparation of the propylene. It was produced by the catalytic dehydration of pure isopropyl alcohol. The reaction was carried out at 300° C. over alumina supported on pumice. The propylene was collected in a gas holder and condensed into a tank by means of a dry ice bath. A vapor phase sample of the propylene after it was in a tank at room temperature contained 4.5 mol per cent of hydrogen.

For lack of time the isobutane was purchased from the Ohio Chemical Company. It was 99% pure and contained no unsaturateds.

However, some experimental work was done on the preparation of isobutane. Isobutylene was prepared by the dehydration of tertiary butyl alcohol with 15% sulfuric acid. The gas was scrubbed with water and dried and condensed into a tank with a dry ice bath.

The isobutylene was hydrogenated in the liquid phase at a temperature of 125° C. and 1000#/in.^{2} with a nickel catalyst. In four hours the conversion was 80%.

Hydrogenation furnishes an excellent method of obtaining pure hydrocarbons for distillation studies. The reaction is rapid until the conversion becomes quite high. However, it is not necessary to wait for complete conversion. The paraffin olefin mixture may be used directly. Any dissolved hydrogen merely collects in the condenser as an inert gas.

APPENDIX D

Summary of Data

Run No.	Pressure Atm. Abs.	Analysis of Bottomd % C_3H_6	Analysis of Product % C_3H_6	Still Temp. ° C.	Temp. at top of Column ° C.	Temp. of Reflux °C.	Heat out in Condenser cooling water, calories per min.	Height of liquid in top gage glass, cm.	Heat loss from column
1	31.3	16.0	99.5	122.5	71.0	69.8	2100	20.3	Negligible
2	15.5	27.2	99.9+	72.7	37.4	36.6	2900		"
3	31.3	20.9	99.4	117	71.0	69.6	2200		"
4	35.5	6.2	73.0	139.1	81.1	71.6	210	12.0	"

APPENDIX E

Sample Calculations

Calculation of number of plates - Run #3

Temperature of bottoms = 117.0° C.

Pressure = 31.3 atm.

For propylene: $T_R = \dfrac{390}{365.4} = 1.067$

$$P_R = \frac{31.3}{45.0} = 0.696$$

From liquid fugacity chart of E.R.Gilliland and R.V.Lukes $fp = 42.0$

From vapor fugacity chart of W.C.Kay $\dfrac{f\pi}{\pi} = 0.800$

$$f\pi = 0.800 \times 42.0 = 25.05$$

$$K = \frac{fp}{f\pi} = \frac{42.0}{25.05} = 1.677$$

Likewise for isobutane:

$$K = 0.912$$

$$\alpha_{\text{bottoms}} = \frac{K_{C_3}}{K_{C_4}} = \frac{1.677}{0.912} = 1.84$$

Likewise at the top of the column:

$$\alpha_{\text{top}} = 1.84$$

$$\alpha_{\text{average}} = \frac{\alpha_{\text{bottoms}} + \alpha_{\text{top}}}{2} = \frac{1.84+1.84}{2} = 1.84$$

$$\frac{(X_{C_3})_p}{(X_{C_4})_p} = \alpha_{av}^{t+1} \left(\frac{(X_{C_3})_w}{(X_{C_4})_w} \right)$$

$$\frac{0.994}{0.006} = (1.84)^{t+1} \left(\frac{0.209}{0.791} \right)$$

t = 9.55 theoretical plates.

Calculation of vapor velocity reduced to a basis of 1 atmosphere - Run #1:

Heat taken out in condenser cooling water = 2100 calories/min.

Heat loss from condenser to room =

$$\left(\frac{\Delta t}{\frac{1}{hA} + \frac{1}{kA_m}} \right) \left(\frac{252}{60} \right) \text{ calories/min.}$$

$$= \left(\frac{90}{\frac{144}{2 \times \pi \times 3.5 \times 20} + \frac{144}{12 \times 0.04 \times \pi \times 2.5 \times 20}} \right) \left(\frac{252}{60} \right) = 170 \text{ calories/min.}$$

Total amount of heat removed in condenser =

2100 + 170 = 2300 calories/min.

The vapor velocity will be calculated for the upper part of the column where there is essentially pure propylene.

Temperature = about 70° C.

$\Delta H = 2RT \ln \frac{D_e}{D_v}$, for D_e and D_v see Fig. (4)

$$\Delta H = 2 \times 1.99 \times 343 \times 2.3 \log \frac{0.400}{0.080} = 2195 \text{ calories per gm. mol}$$

Diameter of column = 2.54 cm.

$$\text{Vapor velocity} = \left(\frac{2300}{2195}\right) \overset{\text{Mols per min.}}{\frac{42}{60}} \quad \overset{\text{Gms. per sec.}}{\frac{30.5}{0.080 \text{x} .785 \text{x} 6.45}} = 0.0594 \text{ ft./sec.}$$

$$\text{Velocity} = K \sqrt{\frac{D_e - D_v}{D_e}}$$

$$.0594 = K \sqrt{\frac{0.400 - 0.080}{0.080}}$$

$K = 0.0297$

On a basis of 1 atmosphere

$$V = 0.0297 \sqrt{\frac{0.600 - 0.00230}{0.00230}} = 0.48 \text{ ft./sec.}$$

Calculation of composition of bottoms - Run #2:

Temperature = 72.7° C.

Pressure = 15.5 atm.

From Fugacity charts,

$K_{C_3} = 1.702$

$K_{C_4} = 0.796$

Assume mol fraction of C_3 is 0.225

$$y_{C_3} = K_{C_3} X_{C_3} = 1.702 \times 0.225 = 0.383$$

$$y_{C_4} = K_{C_4} X_{C_4} = 0.796 \times 0.775 = \frac{0.617}{1.000}$$

∴ assumption was correct.

Calculation of boiling point of bottoms - Run #2

Assume boiling point = 70° C.

From fugacity charts,

$K_{C_3} = 1.642$

$K_{C_4} = 0.765$

$$y_{C_3} = K_{C_3} X_{C_3} = 1.642 \times 0.272 = 0.446$$

$$y_{C_4} = K_{C_4} X_{C_4} = 0.765 \times 0.728 = \frac{0.556}{1.002}$$

∴ assumption was correct.

Nomenclature used sample calculations

α = relative volatility = $\frac{K_{C_3}}{K_{C_4}}$

A = area

A_m = log mean area

D_e = density of liquid

D_v = density of vapor

f_p = fugacity of liquid

f_π = fugacity of vapor

ΔH = heat of vaporization

k = thermal conductivity

K = equilibrium constant = $\frac{f_p}{f_\pi}$

l = thickness of lagging

P = pressure

P_R = reduced pressure = $\frac{P}{P_{critical}}$

R = universal gas constant

T = absolute temperature

T_R = reduced temperature = $\frac{T}{T_{critical}}$

t = number of theoretical plates

Δt ,= temperature difference

Subscripts

C_3 = propylene

C_4 = isobutane

p = product

w = bottoms

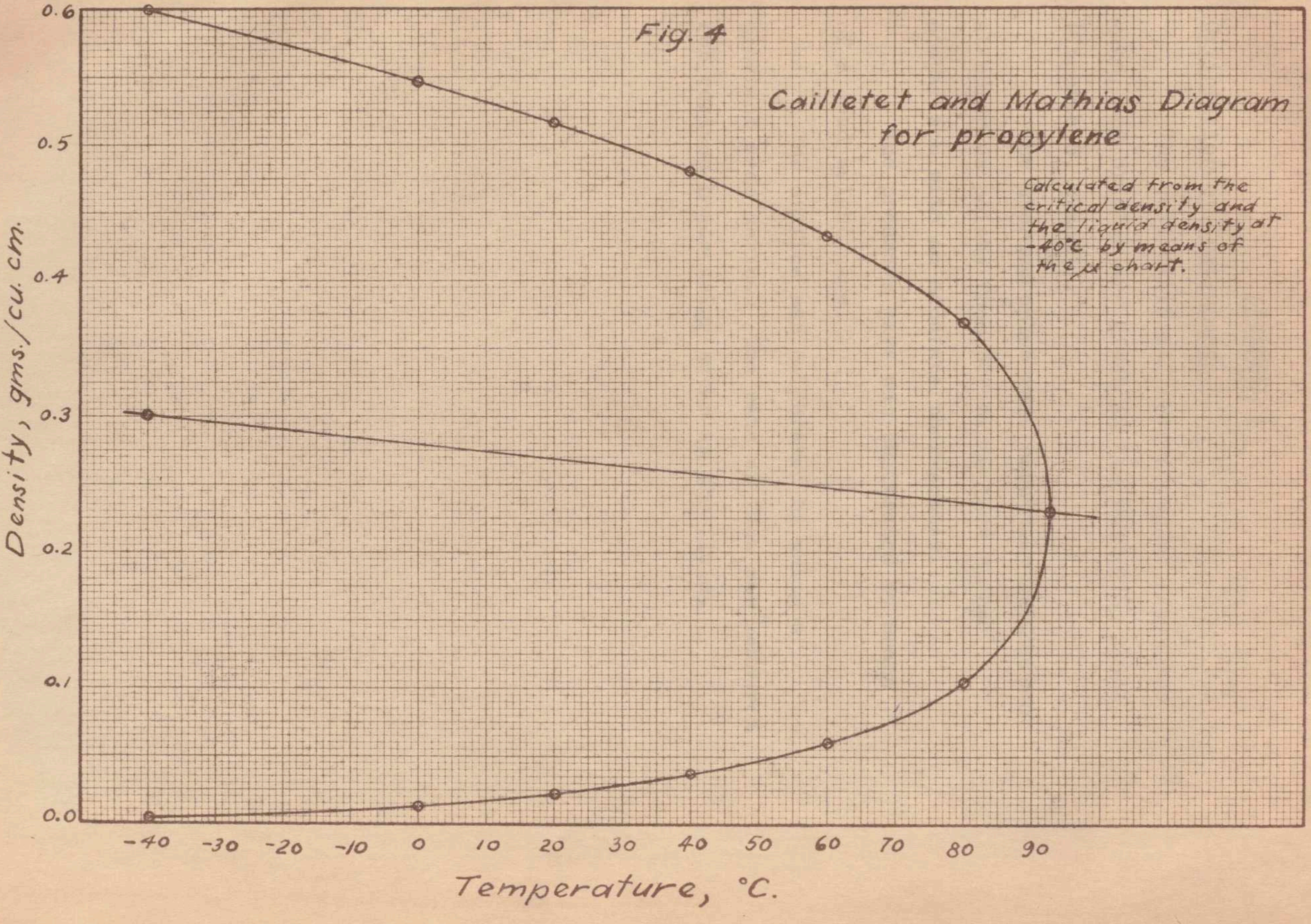

Fig. 4

Cailletet and Mathias Diagram for propylene

Calculated from the critical density and the liquid density at -40°C by means of the μ chart.

APPENDIX F

Calibration of Instruments

The calibrationsof thermocouples, pressure gage, and orifice are given in the following plots (Figures 5, 6 and7).

The thermocouples were carefully calibrated at numerous points from 30° C. to 160° C. by comparison with an accurate thermometer.

The pressure gage was calibrated by means of a dead weight gage.

The orifice was calibrated by using a constant head device. The rate of flow was measured for various heads using water as the fluid.

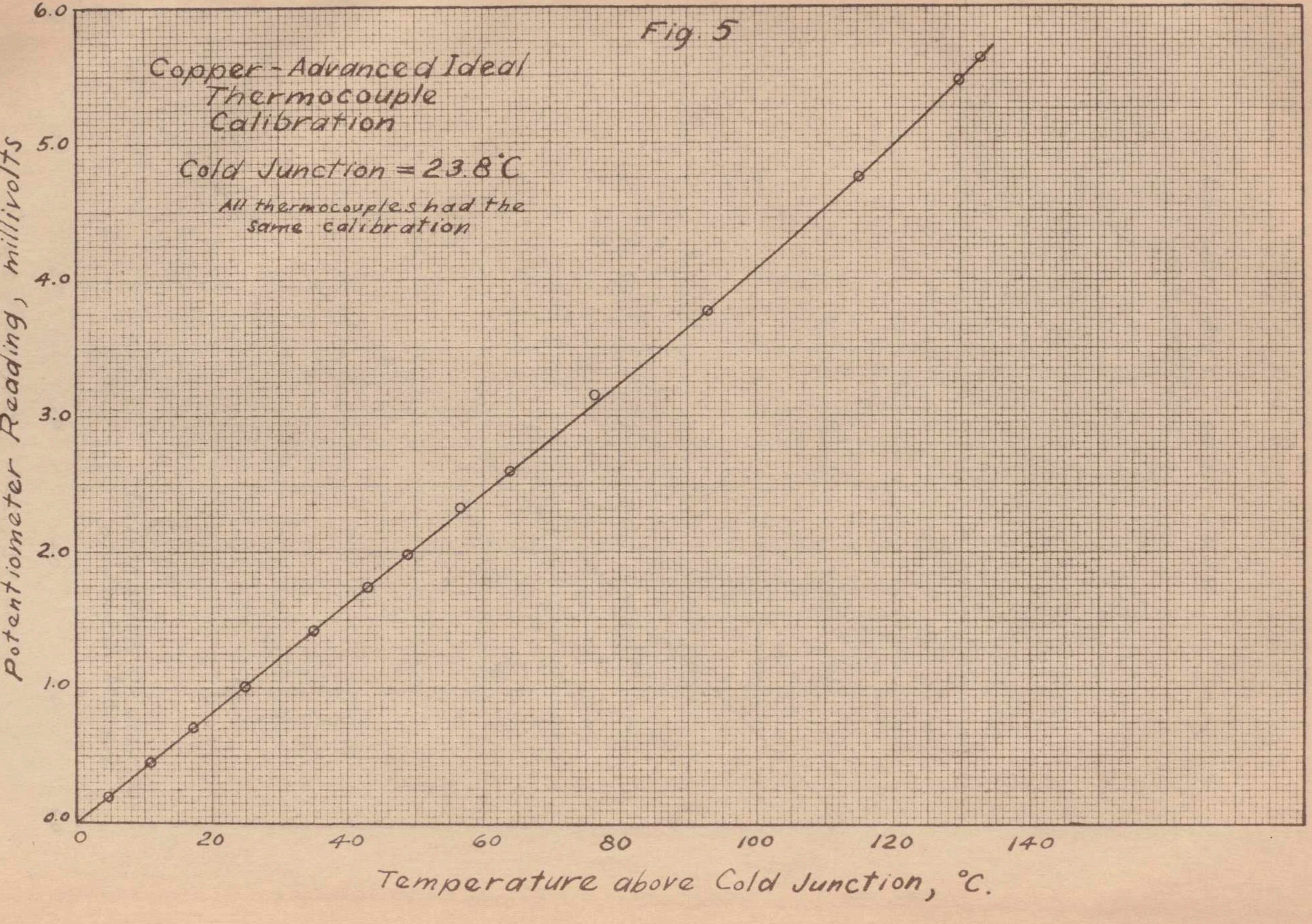
Fig. 5
Copper - Advanced Ideal
Thermocouple
Calibration
Cold Junction = 23.8°C
All thermocouples had the
same calibration
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0
20
40
60
80
100
120
140
Potentiometer Reading, millivolts
Temperature above Cold Junction, °C.

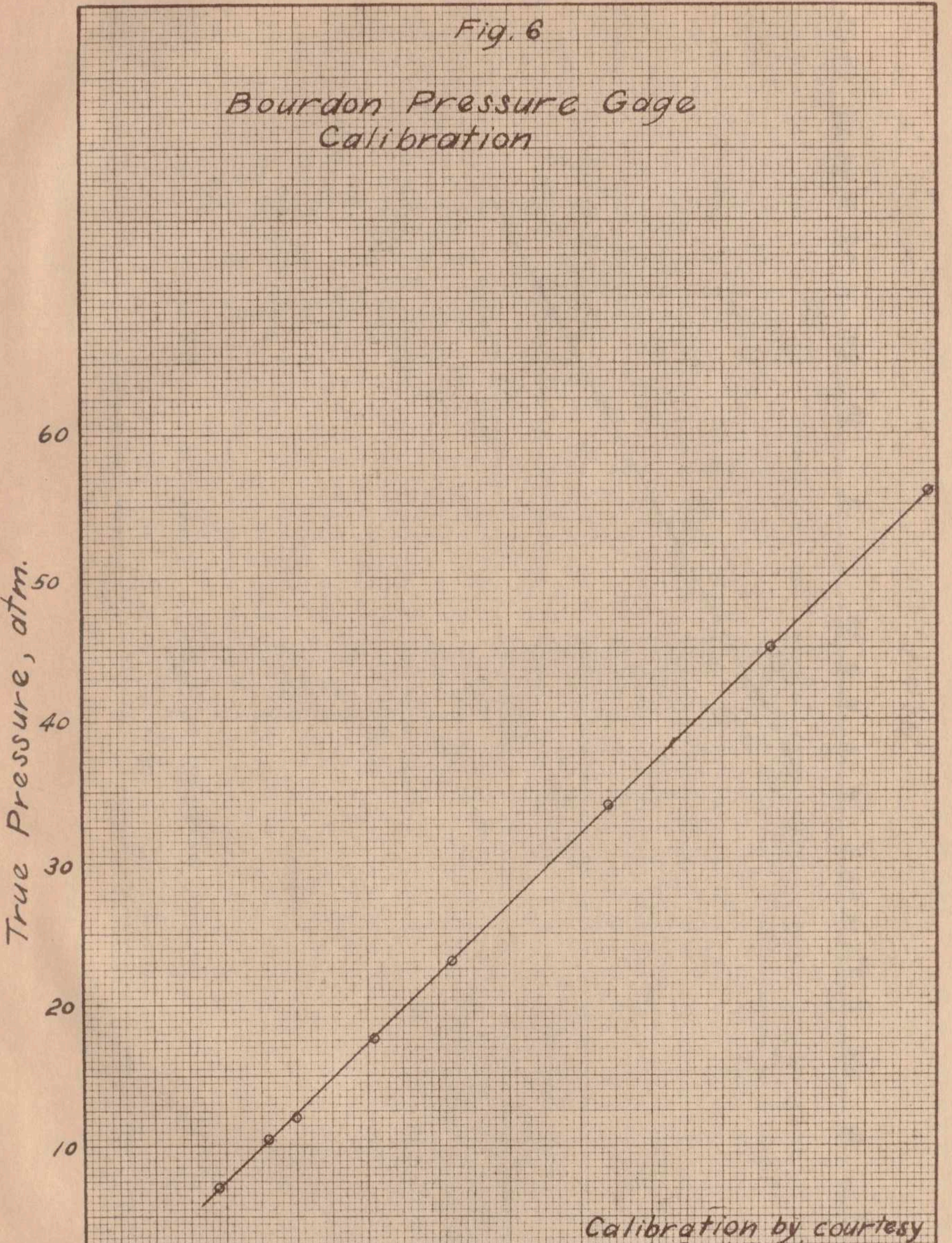

Fig. 6

Bourdon Pressure Gage Calibration

Calibration by courtesy of Paul S. Morgan

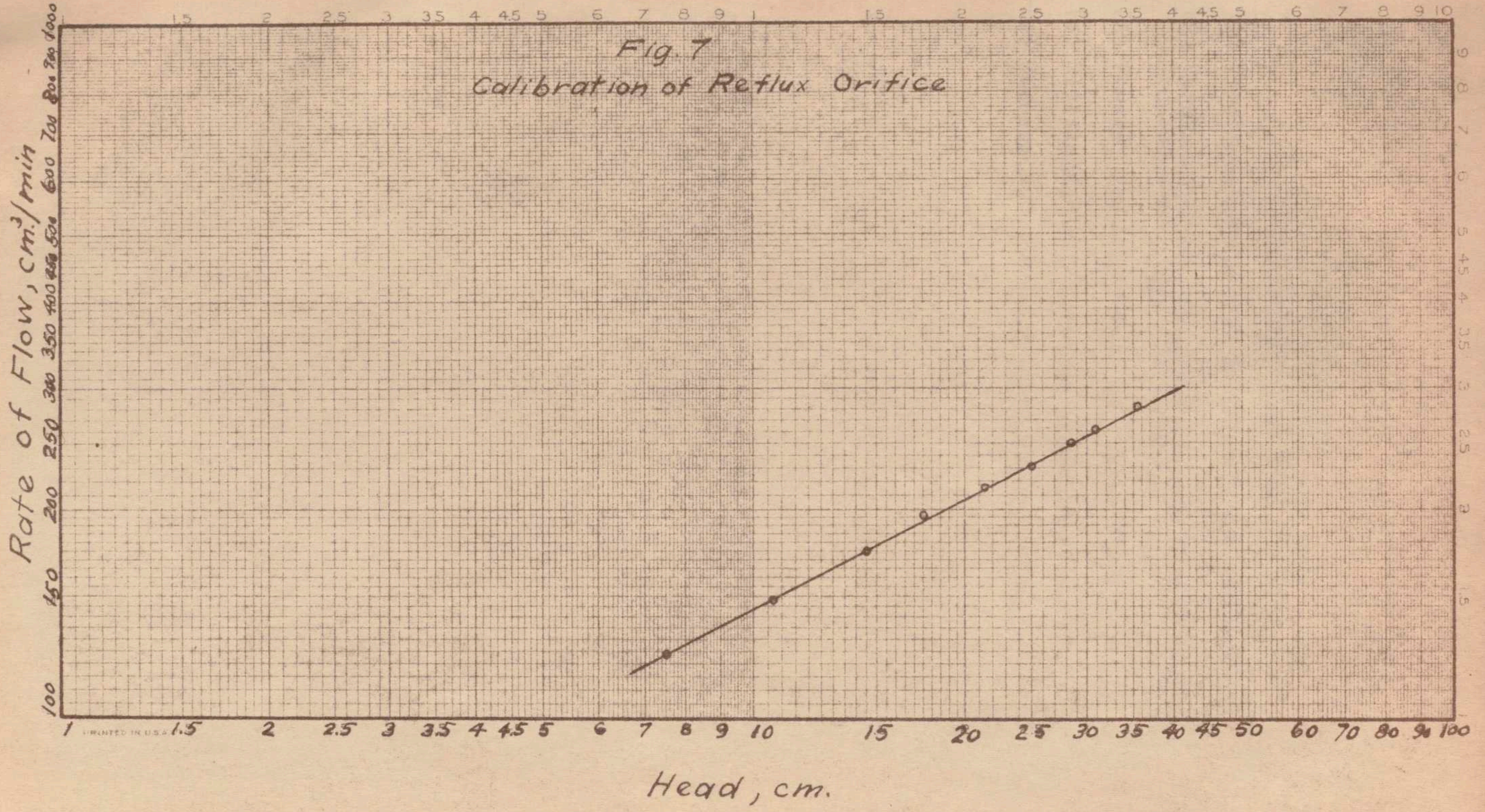

Fig. 7
Calibration of Reflux Orifice

APPENDIX G

Literature Citations

(1) Cummings, L.W.T., Ind.Eng.Chem., 23, 900 (1931).

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(5) Gunness, R.C., Sc.D. Thesis, M.I.T., 1936.