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RECONSTRUCTION OF A MODEL L
PODBIELNIAK FRACTIONAL DISTILLATION APPARATUS

by

Raymond Bauer

Thesis submitted to the faculty of the
Missouri School of Mines and Metallurgy
in partial fulfillment of the requirements for the
Degree of

MASTER OF SCIENCE
in
Chemical Engineering

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I. INTRODUCTION

An important phase of engineering is quality control of a process, and in quality control, analytical chemistry is the main tool used to produce answers. Many instruments are invented and developed to analyze samples whose results control a process, an example in the petroleum refining industry was the need for a special apparatus to analyze for the composition of a mixture of low molecular weight hydrocarbons. There are two methods of analyzing for composition, (1) separate the material into its component substances and measure the quantity of each, or (2) devise a test for each component which is independent of the other components in the mixture and is dependent on the amount of substance in the mixture.

The method of analysis depends on the physical and chemical properties of the components and on the phase of the sample. The most difficult phase to handle is the gaseous phase because of its unrestrained volume. The most common method of measuring a quantity of gas is to measure the pressure and temperature of a definite volume. Physical properties measured to determine composition are spectral properties, dielectric constant, mass, and thermal conductivity. Methods of separating gas mixtures into their components are absorption, adsorption, diffusion, distillation, and chemical properties. The gas mixtures most difficult to separate are those whose components are chemically similar. Until recently the only known technique for separating chemically similar components of gas mixtures was to liquify the gases and separate the components by fractional distillation. Most gases condense at very low temperature, therefore to separate gas mixtures by fractional distillation it is necessary to maintain a low temperature in the apparatus. Low temperatures are achieved by such coolants as liquid air, liquid carbon dioxide, or the expansion of refrigerants such as freons.

The technique of low temperature fractional distillation of gas mixtures was originated about 1900. Today the fractional distillation apparatus most used is the Podbielniak. Podbielniak (14) developed his apparatus for the petroleum industry whose refineries needed a method to analyze mixtures of low boiling hydrocarbons in order to control the processing of crude oil to gasoline. The Podbielniak low temperature fractional distillation apparatus separates mixtures of low boiling hydrocarbons by rectification at atmospheric pressure; collects the fractions in evacuated containers; and determines the quantity of each fraction by measuring the pressure of a constant volume at a constant temperature. The present Podbielniak models are instrumented to automatically control the analysis of a sample added to the column. The difficulties in designing a Podbielniak apparatus are the insulation of the column, the precise control of the separation, and the measuring and recording of the quantities of the fractions.

The purpose of this thesis was to reconstruct a Model L Podbielniak Fractional Distillation Apparatus to provide equipment suitable for the study of batch multicomponent distillation. The apparatus will also serve as an analytical instrument. The equipment was instrumented to automatically control the distillation, but an operator is needed to select fractions and insure the proper functioning of the controls.

Samples of hydrocarbon mixtures of known composition were analyzed to prove the successful operation of the reconstructed apparatus.

II. LITERATURE REVIEW

This review is presented in four parts, (1) the history of low temperature fractional distillation, (2) the theory of differential distillation, (3) the description of low temperature fractional distillation apparatus, and (4) other means of analyzing mixtures of chemically similar gases.

History

The history of the development of low temperature fractionation is described in chronological order and classified according to the developments.

Original Uses of Low Temperature Distillation. In 1884 Olszewski originated the separation of gas mixtures when he purified ethylene; shortly afterwards Kuenen purified ethane, and Dewar separated Helium from "Bath Gas" by low temperature distillation.(27) In 1901 Travers published his book on the physical properties of gases, in which he described the separation of the rare gases of air by repeated simple batch distillation at low temperature and pressure.

Analytical Distillation. In 1915 Burrell and Robertson(2) used fractional distillation for the first time as an analytical tool to obtain the composition of a natural gas sample. The gas samples were separated into individual hydrocarbons or into binary fractions which were then analyzed by slow combustion. The only need for low temperature distillation was the analyses of mixtures of low molecular weight hydrocarbons in the petroleum industry. In 1926, Shepherd (26) attempted to use an improved Burrel type apparatus to determine the gasoline content of natural gas, but the apparatus was not suitable for routine use.

Analytical Rectification. Podbielniak (9) in 1925 originated a low temperature rectification column for analytically separating low molecular weight hydrocarbon mixtures. Frey and Yant (7) used a packed column to separate a sample of the four carbon atom fraction of the gaseous hydrocarbons obtained from the carbonization of coal. In 1929, Davis (4) developed a spiral column to increase the number of theoretical plates in the column, but the spiral drastically reduced the capacity of the column.

Practical Analytical Methods. In 1928, Podbielniak (10, 11, 12) presented a precise and practical method of analyzing mixtures of low boiling hydrocarbons. In 1929, Podbielniak (13) described the theory and apparatus for low temperature fractional distillation analysis.

Improvements. In 1931, Podbielniak (14) reported a revised method of gas analysis. He described the apparatus, the procedure, the calculations, and the accuracy of the results. In 1933, he (15) reported, (1) the relative efficiencies of fractional distillation columns, (2) the effects of distillation rate, reflux ratio, and hold-up in the column, (3) the thermal insulation of columns, and (4) the types, size, and shapes of packings used. Also Podbielniak (16) published a paper on automatic controls for low temperature fractional distillation apparatus.

Podbielniak formed a company which manufactures and markets analytical distillation apparatus. He and his company (17, 18, 19) have reported many advancements in analytical distillation in the literature and in many instruction manuals issued by the company. The development of analytical fractional distillation from a technique to a science must be largely attributed to the work of W. J. Podbielniak.

Theory

The purpose of the following section is to acquaint the reader with the theories of batch distillation which are found in the literature. Fractional distillation is defined as the separation of two or more volatile components of a liquid by vaporization, caused by the addition of heat, condensing the vapors in such a way that fractions of varying boiling points are obtained, and repeating the above process until the desired separation is obtained. Mass transfer is accomplished because the vapors of a mixture in equilibrium with its liquid have a different composition than the composition of the liquid. In continuous distillation the composition at any location in the still remains constant, but in differential distillation the composition of the more volatile component at any location in the still decreases as time increases. Fractional distillation analyses are obtained by differential or batch rectification in a column.

Differential Distillation. The theory of differential distillation begins with an equation derived by Rayleigh (20) from a differential material balance, assuming (1) no rectification, (2) no hold-up, and (3) a total condenser. Rayleigh's equation is not applicable to a packed column because rectification and hold-up occur in the column. Rayleigh's differential equation is,

$$-y\ dW = -d\ (Wx) \tag{1}$$

and the integrated form of the equation is,

$$\ln \frac{W}{W_o} = \int_{x_o}^{x} \frac{dx}{y - x} \tag{2}$$

where:

W = weight of the liquid in the kettle at any instant.

W_o = W at time zero.

x = weight fraction of the more volatile liquid component in the kettle at any instant.

x_o = x at time zero.

y = weight fraction of the more volatile component in the vapor in equilibrium with the liquid in the kettle at any instant.

For certain types of packings hold-up is negligible and disregarded in deriving a representative equation. Bogart (1) derived an equation for batch rectification which is solved by using the McCabe-Thiele (1) diagram to obtain the concentration of a component in the distillate as a function of the concentration of the component in the still pot; then the reciprocal of the difference of the above concentrations is plotted against the concentration in the still pot and the graph is integrated to yield a relationship between the concentration in the still pot and the quantity of distillate.

Bogart's differential equation is:

$$P = - M_f \frac{(x_p - x_f)}{(x_p - x)^2} \frac{dx}{d\theta} \qquad (3)$$

where:

M_f = total number of moles in the kettle at the start of the distillation.

P = rate of product withdrawal.

x = mole fraction of the more volatile component in the liquid in the kettle at any time.

x_f = mole fraction of the more volatile component in the liquid at the start of the distillation.

x_p = mole fraction of the more volatile component in the distillate at any time.

θ = time.

Also, Bogart's equation can be integrated to yield the time of distillation.

$$\theta_t = \frac{M_f (x_p - x_f)}{V} \int_{x_w}^{x_f} \frac{d_x}{(1 - O/V)(x_p - x)^2} \qquad (4)$$

where:

O = molar rate of liquid product returned to the column.

V = molar rate of vapors leaving the column.

x_W = mole fraction of the more volatile component in the liquid in the kettle at the end of the distillation.

θ_t = total time of distillation.

Another equation for batch rectification was derived by Rose and Welshan (22). Their equation was derived to establish maximum sharpness of separation, and minimum number of plates. Rose's equation combined the integrated form of the Rayleigh equation with the Fenske equation. Fenske's equation is,

$$\frac{y}{1-y} = E\frac{x}{1-x} \tag{5}$$

and Rose's equation is,

$$\ln L = \frac{1}{\alpha^n - 1}\left[\ln x - \alpha^n \ln (1-x)\right] + C \tag{6}$$

where:

x = mole fraction of the more volatile component in the still when total moles in the still are L.

y = mole fraction of the more volatile component in the vapor n plates above the still.

α = vapor pressure ratio of the two components.

n = number of theoretical plates.

C = constant of integration.

$E = \alpha^n$ = overall fractionating factor.

L = total moles in still at any time.

Rose emphasized the important variable, overall fractionating factor, for it determined whether maximum sharpness of separation was best obtained by increasing the reflux ratio or by increasing the number of plates in the column. For a given distillation the per cent of total charge distilled was plotted against the overall fractionating factor; then for any separation desired the value of the factor was read from the graph and the number of theoretical plates were calculated using the definition of overall fractionating factor. Also Rose et. al. (22) have derived equations for the case when hold-up is not negligible.

$$L = K \frac{x^p}{(1 - x)^{p+1}} - \frac{H(\alpha^n - 1)}{n \ln \alpha} \left[\frac{1}{(1 - x)^{p+1}} \right] \quad (7)$$

where:

H = total moles of hold-up of all components in the column proper (exclusive of hold-up in the condenser).

n = equivalent number of theoretical plates in the column.

x - mole fraction more volatile component in the still pot when L moles remain in the still pot.

L = total moles in pot at any time.

K = integration constant.

α = vapor pressure ratio of the two components, assumed to be constant over range involved in any given distillation.

$p = \frac{1}{\alpha^n - 1}$

Reflux Ratio. The reflux ratio is the ratio of the quantity of overhead vapors returned to the column as a liquid to the quantity of distillate product removed. By returning enriched liquid to the column the overhead vapors become more concentrated in the more volatile component. The larger the reflux ratio the sharper the separation. Analytical fractionations are run at very high reflux ratios (18). When all overhead product is returned to the column, it is said to be operating at total reflux. Total reflux (21) is one limiting condition. The other limiting condition is the minimum reflux ratio necessary to obtain the desired separation and recovery when the column contains an infinite number of plates. Reflux ratio is an important economic variable when distilling large quantities, but in analytical distillation reflux ratio (23) is only a variable for obtaining sharp separations. The limiting factors in analytical distillation are, the packing, the size of the sample, and the time of distillation.

The Height Equivalent to a Theoretical Plate. Column packings are rated by the height of packing equivalent to a theoretical plate which is determined experimentally.

Sample Size. Sample size is determined experimentally. The quantity of sample is a balance between the time for distillation and the accuracy of the analysis.

Time of Distillation. For a given column and sample size the time for distillation or the maximum rate of distillation is determined by the desired sharpness of separation. Podbielniak (15, 17) reports a standard test to determine maximum flow rates at which flooding occurs. Standard tests are used so that different column designs can be compared.

Hold-up. Hold-up is a factor which occurs only in differential distillation. Hold-up is the quantity of material needed to wet the packing and fill the column. For each column hold-up is a constant depending on the column dimensions, the packing, and the design of the reflux chamber. Although hold-up is a constant for each column, the ratio of hold-up to quantity in the still pot varies with the time of distillation and the sample size, and this ratio is an important variable (18, 23). Colburn (3) reports hold-up is sometimes beneficial in obtaining sharpness of separation, but Rose (22) and Podbielniak (18) report hold-up to be detrimental to sharp separations of components in analytical fractionations. Later Rose (23) reports the effect of hold-up is a function of the reflux ratio. At low reflux ratios hold-up causes an increased sharpness of separation, but at high reflux ratios hold-up causes decreased sharpness of separation.

Multicomponent Mixtures. Multicomponent mixtures are samples containing more than two components. The equations of Rayleigh, Bogart, and Rose, already discussed, are for binary mixtures. The same ideas are applied to derive equations for multicomponent mixtures, but a series of simultaneous equations result and their solutions become too laborious for routing use. The use of the equations for multicomponent mixtures are described by Robinson and Gilliland (21).

Assumptions. Since the purpose of fractional distillation analysis is to separate the mixtures into its individual components, one can assume that at any time the separation is essentially between a binary mixture and all less volatile components can be neglected. The above assumption is acceptable when analyzing a mixture of low boiling hydrocarbons (18). Any two components that have a relative volatility near unity will behave as one component in the above method of analysis. The calculations can be evaluated at total reflux because the column is operated at very high reflux ratios, and distillate is withdrawn at a very slow rate. The theory for low temperature analytical distillation is used for improving column efficiency and automatic control of the distillation.

Apparatus

Since Podbielniak's work represents all important recent advancements in low temperature analytical fractionating apparatus, a summary of his publications comprises this section of the literature review. The apparatus is described in three sections, (1) the column, (2) the distillate receiving system, and (3) the controls.

Columns. The columns are discussed as (1) original models, and (2) improvements of columns to yield the modern column. Podbielniak's (14) original column was a 3.8 millimeter inside diameter, pyrex tube, 77 centimeters in length, with one end connected to a 60 milliliter pyrex sample bulb. See Figure 1. The tube, excluding the

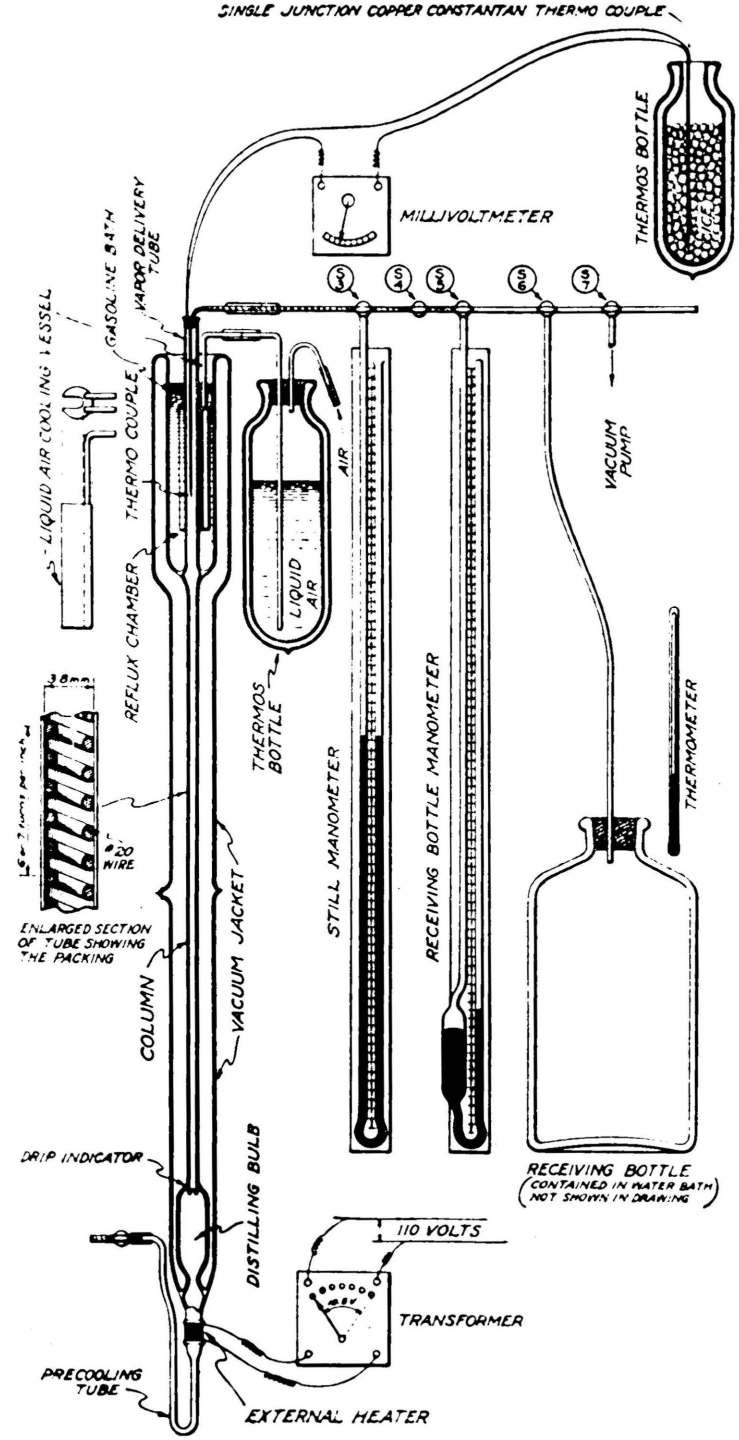


Figure 1. General Diagram Of Apparatus With Regular Type Fractionating Columns.

Podbielniak, W. J.: Apparatus and Methods For Precise Fractional-Distillation Analysis, Ind. Eng. Chem., Anal. Ed., 3, 180 (1931).

bulb, was sealed in a silvered vacuum jacketed pyrex cylinder which also contained the reflux chamber. A spiral stainless steel wire of uniform cross-section was inserted from the sample bulb to the reflux chamber; as the only packing used in the column. The reflux chamber was concentric polished metal cylinders that fitted around the tube and between the vacuum jacket. See Figure 1. A resistance wire was wrapped around the sample bulb to supply heat to the column.

Podbielniak (15, 17, 18) reported the following improvements on his distillation columns: (1) the tube was separated from the vacuum jacket to prevent breakage, and to allow interchangeable tubes (Figure 2); (2) the sample bulb was not sealed to the pyrex tube, but was connected by ground glass joints (Figure 3); (3) the reflux chamber was redesigned to allow air to circulate through the reflux chamber and along the length of the column, and this air flow stabilized the temperature gradient up through the column; (4) a variety of packings were tested and the Heli-Grid type (Figure 4) was developed to provide columns equivalent of 75 to 100 theoretical plates; (5) the vacuum jackets were improved by including a flexible pyrex bellows in the inner tube of the jacket, and the bellows reduced the strain of the inner tube from 1800 pounds to 35 pounds (Figure 5); and (6) a cartridge heater was inserted into a well in the sample bulb to replace the external heater. Present columns contain all the improvements discovered over a period of twenty years. Figure 6 is a detailed drawing of a modern column.

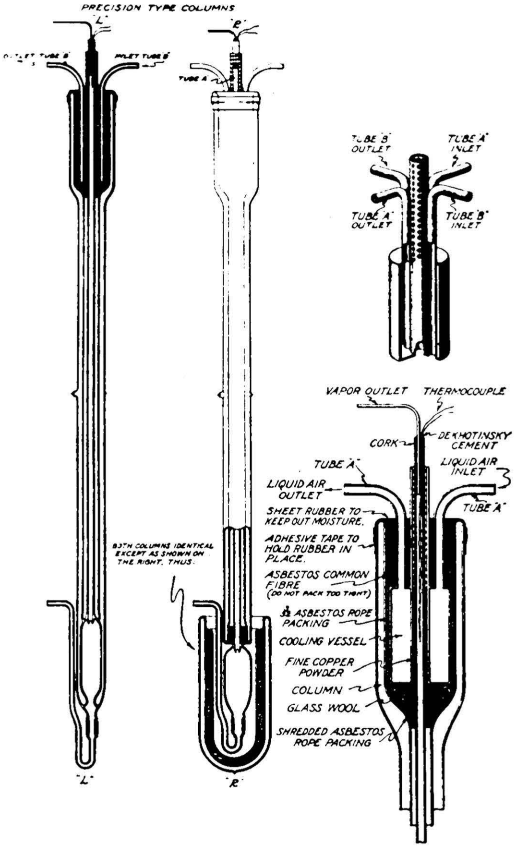


Figure 2. Precision Type Columns.

Podbielniak, W. J.: Apparatus And Methods For Precise Fractional-Distillation Analysis, Ind. Eng. Chem. Anal. Ed., 3, 180 (1931).

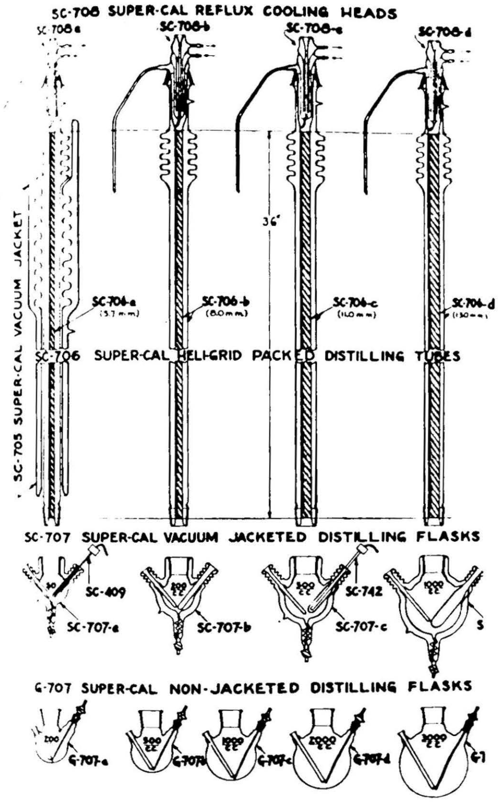


Figure 3. Super-Cal Type Of Fully Adiabatic Vacuum-Jacketed Fractionating Column System.

Podbielniak, W. J.: Apparatus And Method For Precise Fractional Distillation Analysis, Ind. Eng. Chem. Anal. Ed., 13, 641 (1941).

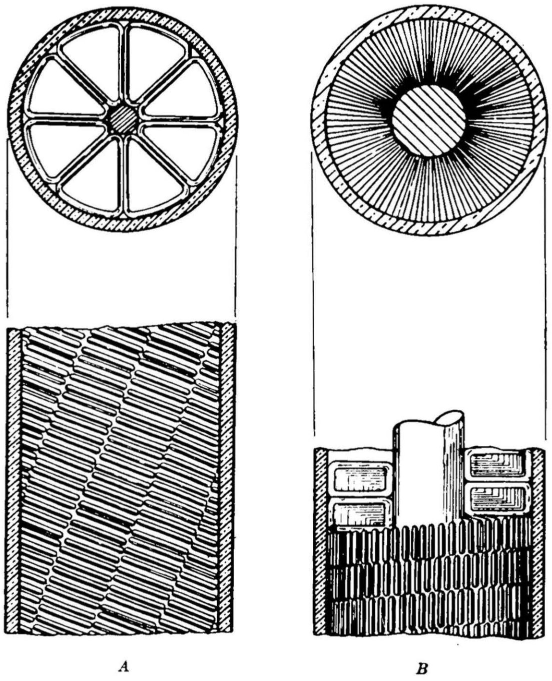


DIAGRAM OF HELI-GRID PACKINGS

A. Assembly of sector-section coils twisted around central core
B. Staircase assembly of rectangular section coils around central core

Figure 4. Diagram Of Heli Grid Packings.

Podbielniak, W. J.: Apparatus And Methods For Precise Fractional-Distillation Analysis, Ind. Eng. Chem. Anal. Ed., <u>13</u>, 642 (1941).

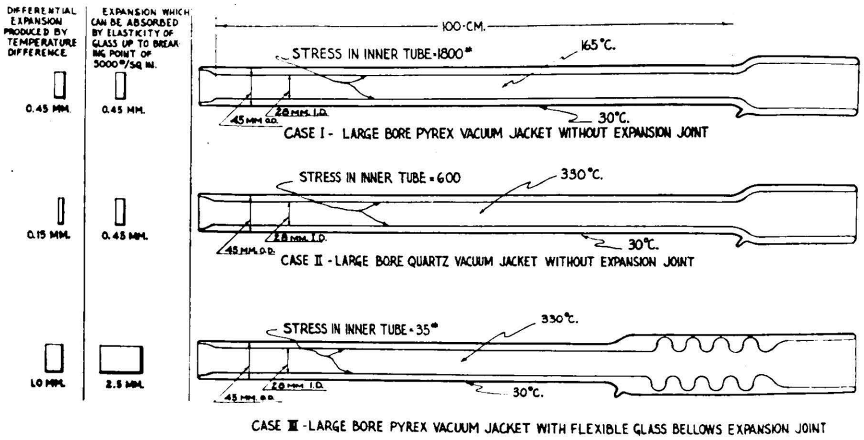


Figure 5. Differential Thermal Expansions and Resulting Stresses in Vacuum Jackets.

Podbielniak, W. J.: Apparatus and Methods for Precise Fractional-Distillation Analysis, Ind. Eng. Chem. Anal. Ed., 13, 640 (1941).

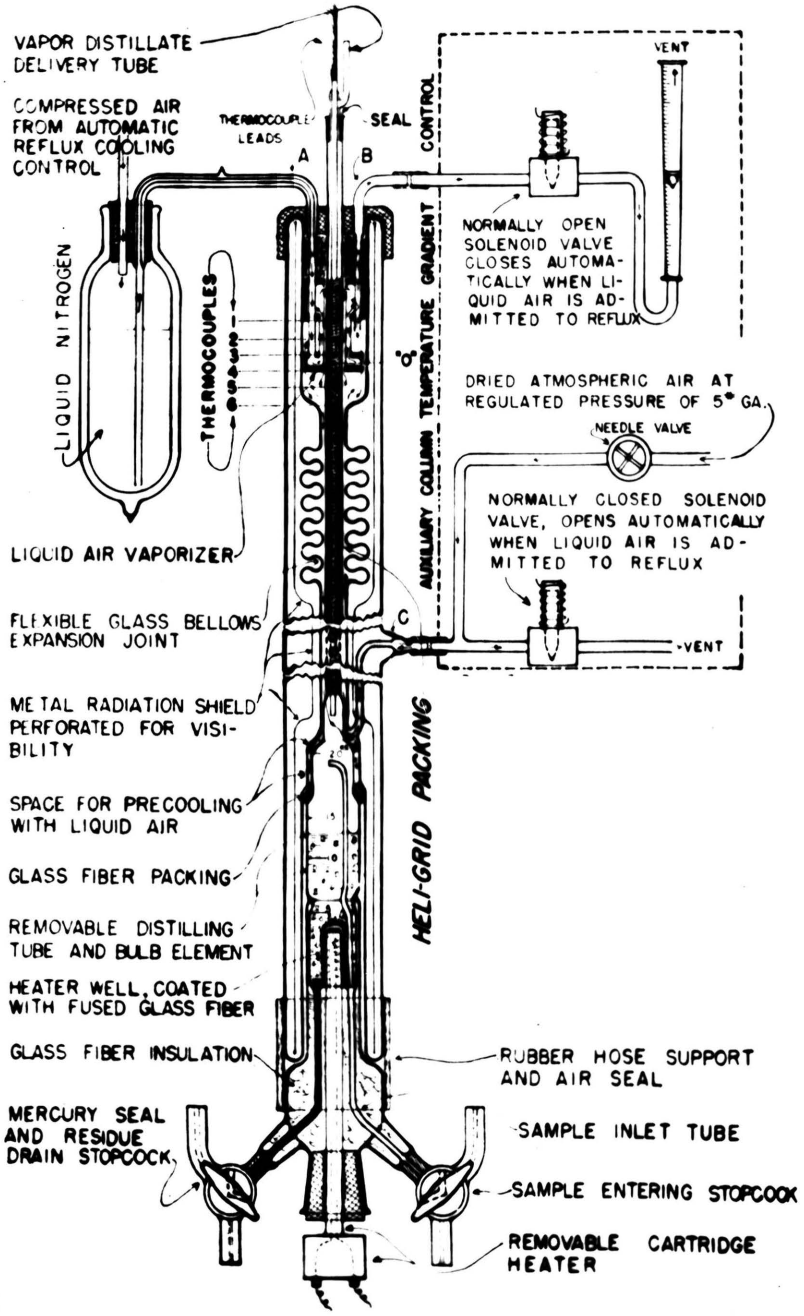


Figure 6. Diagram Of Super-Cal Low Temperature Column, With Connected Column Temperature Gradient Control Device.

Podbielniak, W. J.: Low Temperature Fractional Analysis Of Liquids And Gases, Pet. Ref., 30, No. 5, 154 (1951).

The Receiving System. The distillate receiving system(14) collected the distillate in the vapor phase at room temperature and the distillation pressure. The receiving system consisted of one gallon or larger glass bottles of known volume enclosed in a constant temperature water bath. The bottles were connected to a glass manifold by copper tubing. The column also was connected by copper tubing to the manifold (Figure 7) which controlled the vapor flow to the controls valves and to any receiving bottle.

Controls. The controls are discussed in three sections, (1) temperature, (2) pressure, and (3) flow. The measuring and controlling means are discussed in each section. Since controls vary for different distillation ranges, only controls for low temperature fractionating apparatus are reported. Figure 8 illustrates the automatic control of Podbielniak's(16) apparatus.

Temperature. The temperature of the vapor leaving the columns indicated the component boiling at the distillation pressure. Podbielniak(16) reported using a copper-constantan thermocouple as a temperature sensing element in the reflux chamber. The thermocouple was connected to a recording potentiometer which produced the distillation diagram. The temperature was controlled by maintaining a constant pressure in the column. An improvement to temperature control by Podbielniak(17, 19) was the addition of a controlled air stream flowing along the length of the tube and through the reflux chamber. The air stream

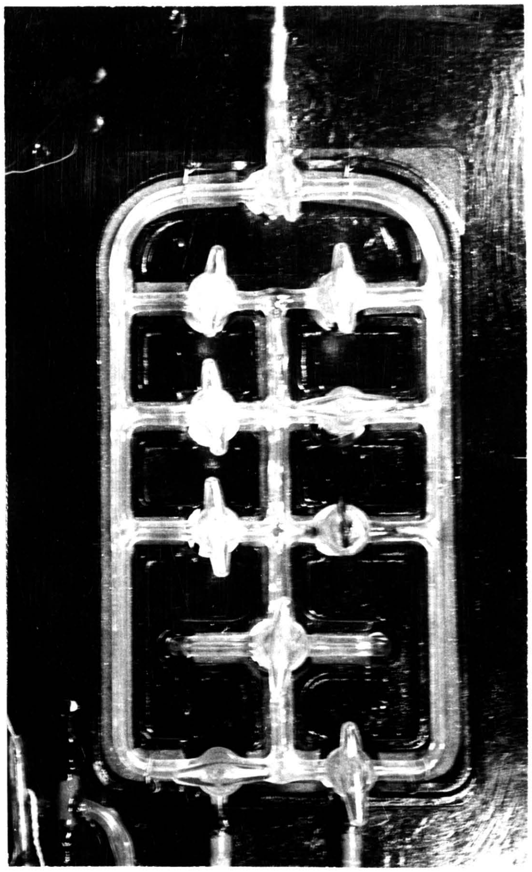


Figure 7. Glass Manifold.

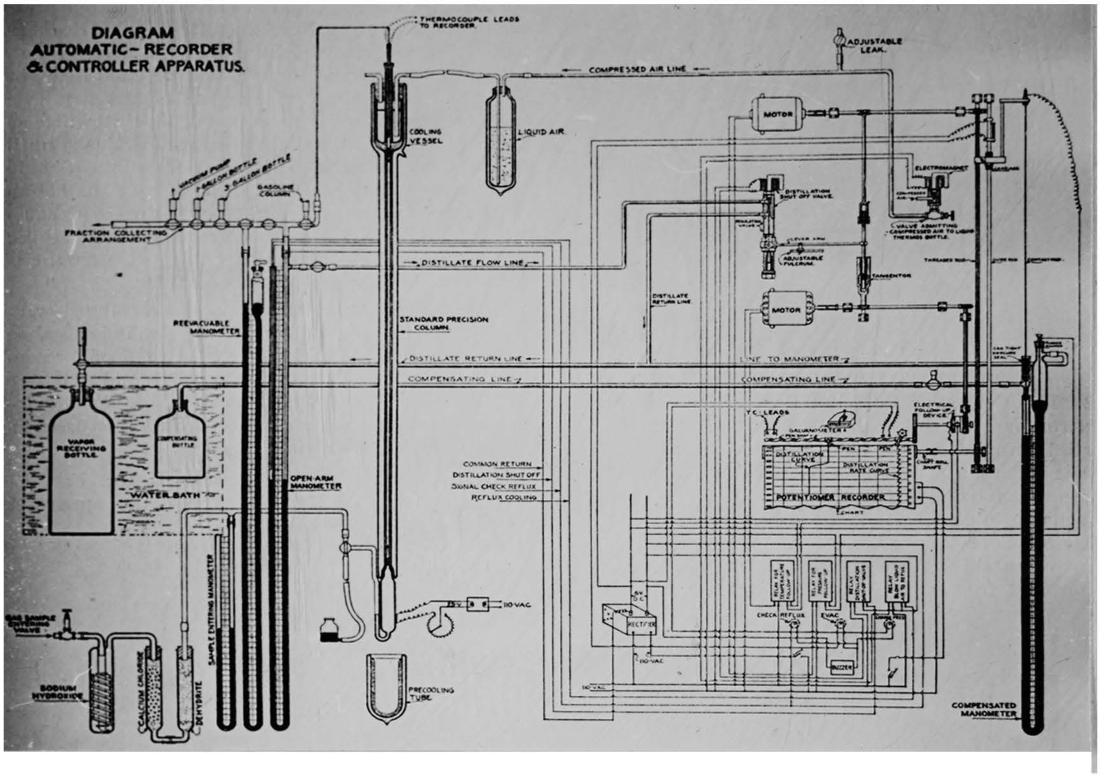


Figure 8. Diagram Of Automatic Recorder And Control Apparatus.

Podbielniak, W. J.: Apparatus And Methods For Precise Fractional-Distillation Analysis, Ind. Eng. Chem. Anal. Ed., 5, 174 (1933).

stabilized the thermal gradient along the column and reduced the temperature lag in the reflux chamber.

A thermal conductivity cell for indication of the component being distilled replaced the thermocouple because the cell eliminated erroneous indications due to supercooling in the reflux chamber. Since the thermal conductivity cell was used in conjunction with a potentiometer, the supplementary controls needed no modifications.

Pressure. The pressure in the column was measured by an open, mercury filled manometer which also controlled the flow of coolant to the reflux chamber and the position of the distillation shut-off valve. Heat was added to the sample bulb to maintain a constant pressure in the column. Methane through n-butane was distilled at atmospheric pressure and five carbon atom hydrocarbons and heavier hydrocarbons were distilled at partial vacuum.

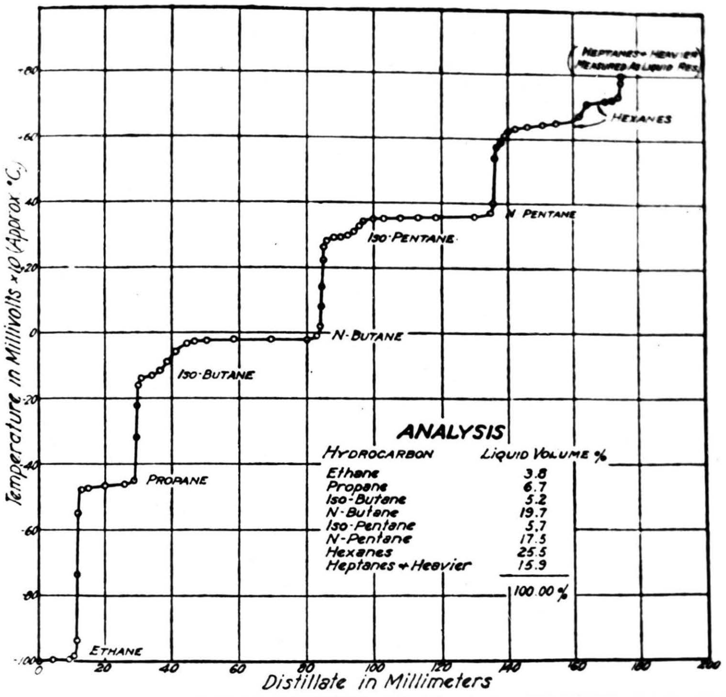
Flow. Flow was the most difficult variable to control. The flow was measured by a closed manometer which measured the rise in pressure in the distillate receiving bottles. A closed manometer was used to eliminate the variance in atmospheric pressure. The closed end of the manometer was connected to a compensating bottle of large volume to decrease the effect of compression in the closed side of the manometer. The height of the mercury in the compensating manometer controlled the rolling of the potentiometer strip chart. The motion of the chart along with the motion of temperature recording produced the distillation diagrams. See Figure 9. The flow was controlled by two valves, the distillation shut-off valve and the rate valve. The shut-off valve was closed if the distillation pressure was too low and prevented vapor from leaving the column. The shut-off valve opened when the pressure in the column became equal to the distillation pressure. The distillation rate valve, which controlled the flow rate of distillate, was a needle valve positioned by a mechanical lever. See Figure 8, page 23. The rate valve opened as the pressure in the compensating manometer increased, and the rate valve closed as the temperature of the exit vapor increased.

Schneider (24) introduced a hydraulic system for opening and closing the shut-off valve and the rate valve. The hydraulic system eliminated the mechanical linkages previously used; thereby increasing the life of the apparatus.

A detailed description of the theory and operation of automatic control for a model L low temperature fractional distillation apparatus is located in Appendix I.

Substitute Analyses

There are two alternate methods of analyzing a mixture of chemically similar gases. They are mass spectrometry, and vapor phase chromatography. Both of the methods are recent developments which are replacing analytical fractional distillation.



ANALYSIS

Hydrocarbon	Liquid Volume %
Ethane	3.8
Propane	6.7
Iso-Butane	5.2
N-Butane	19.7
Iso-Pentane	5.7
N-Pentane	17.5
Hexanes	25.5
Heptanes + Heavier	15.9
	100.00 %

Figure 9. Typical Analysis of Natural Gasoline Using Precision-Type Column.

Podbielniak, W. J.: Apparatus and Methods for Precise Fractional-Distillation Analysis, Ind. Eng. Chem. Anal. Ed., 3, 183 (1931).

Mass Spectrometry. The mass spectrometer (6) is an instrument which measures and separates gases by ionizing the gas molecules and passing the ions through a magnetic field. The force exerted on the ion is determined by its charge to mass ratio, for example, a single positively charged methyl ion and a double positive charged ethyl ion are separated as one component and measured at the same focusing band. Since one substance, like normal butane, can produce 24 different positive ions of which some are identical to ions from other substances, in the mixture, the evaluation of the analysis is very complicated; but due to the large number of bands available for readings, a system of simultaneous equations can uniquely represent an analysis. A computer is needed to evaluate the data.

Vapor Phase Chromatography. Vapor phase chromatography (8, 5) is differential sorption of a mobil vapor or gaseous phase by a fixed liquid or solid phase. The sample in the vapor phase enters a column and is eluted through the column by an inert gas, preferably helium. The components in a sample leave the column as pure components inversely proportional to their selective sorptivity. The emerging components are measured by a thermal conductivity cell and recorded on a strip chart potentiometer.

The vapor phase chromatography method of analysis has the lowest capital investment, is the easiest equipment to maintain, and operate, and produces the answers in less time than other methods. Vapor phase chromatography is not as precise as analytical fractional distillation or mass spectrometry; but as equipment and procedure improve, the method promises to be more precise. Vapor phase chromatography is already replacing other methods of gas analysis.

III. EXPERIMENTAL

The experimental section is written in seven parts which are classified as follows:

1. Purpose of Reconstruction,
2. Plan for Reconstruction,
3. Materials,
4. Apparatus,
5. Procedure,
6. Data and Results, and
7. Sample Calculations.

Purpose of Reconstruction

The purpose of this investigation was to reconstruct a Model L Podbielniak Fractional Distillation Apparatus to provide equipment suitable for the study of batch multicomponent distillation. The apparatus can also serve as an analytical instrument for determining the percentage of low molecular weight hydrocarbons in mixtures. Known hydrocarbon samples were analyzed to prove the successful operation of the reconstructed equipment. No attempt was made to convert this Model L apparatus to a modern Podbielniak fractionating apparatus, because all the main components, the column, the instrument, and the controls would have to be replaced, and the cost of the replacement would be as much as the cost of a new model. Another reason for not converting to a modern fractional distillation apparatus was that other methods of analyzing mixtures of chemically similar gases are quicker and more economical; therefore one must remember this thesis is the construction of a Model L Podbielniak Fractional Distillation Apparatus. The equipment was given to the Missouri School of Mines and Metallurgy by the Socony Mobil Oil Refinery in East St. Louis, Illinois.

Plan for Reconstruction

The plan for reconstruction was to evaluate the initial condition of the apparatus, to plan a work schedule for reconstruction of the equipment, to calibrate the components, and to test the apparatus with known samples of hydrocarbon mixtures.

Evaluation of Apparatus. The equipment needed to be completely rehabilitated. All iron parts were coated with rust. The insulation on the connecting wires was brittle and upon disassembly it would crumble leaving the bare wire exposed. The apparatus had collected dust for nine years before reconstruction started. The operation of the apparatus was the author's primary objective; therefore the evaluation began by classifying the apparatus into three categories, (1) parts that needed cleaning, (2) parts that needed repairing, and (3) parts that needed replacement, or additional non-existing parts.

Reconstruction Schedule. The first job was to locate the companies selling the materials and parts requiring purchasing. For each item to be purchased letters were sent to three companies stating the specifications and quantity of the items, and requesting cost and date of delivery information. Next, the location of the apparatus was chosen. After locating the apparatus cleaning reagents were selected, and new parts were designed. Finally parts were cleaned, repaired, and built in the order they were needed for reconstruction of the apparatus. New items were purchased as quickly as possible.

Calibration. The receiving bottles were calibrated by filling them with tap water at 25 °C. The precision of the calibration was 0.1 per cent. The volumes of the receiving bottles are tabulated in Table II.

The copper-constanan thermocouple in conjunction with the Brown recording potentiometer was calibrated at two temperatures, zero degrees centigrade and -79 °C. Zero degree temperature was obtained by an ice bath, and -79 °C was obtained by the sublimation of dry ice. The precision of the temperature range was 2 °C over an 81 degree range, which was within an acceptable limit.

Testing. Hydrocarbon samples of known composition containing C_1 to C_5 compounds were analyzed to determine the limitations of the apparatus. Also accurate analyses would prove the successful reconstruction of the apparatus.

Materials

The following materials were used for the reconstruction or operation of the apparatus. All specifications necessary to use or purchase the materials are listed. The quantity, the specifications, the supplier, and the use of the material are listed.

Alcohol, Ethyl. USP, absolute grade, 200 proof, serial No. 32843. Quantity - one liter. Manufactured by Industrial Chemical Company, Tuscola, Illinois. Used to fill column at end of distillation.

Alumina. Activated, technical grade, 10 mesh; quantity - one pound. Obtained from Cenco Company, Chicago, Illinois. Used to dry air for the controls on the apparatus.

Epoxy Resin. Steelcote's Epo-Lux 150. Quantity - one quart, with catalyst. Supplier - Plastic Parts and Sales, St. Louis, Missouri. Used as a vacuum sealing material around manifold connections.

Hydrocarbon Samples. Specification: C_1 through C_5 mixtures of hydrocarbons of known composition. Obtained from Socony Mobil Oil Refinery, East St. Louis, Illinois. Used to test the reconstruction of the apparatus.

Liquid Nitrogen. Purity 95 per cent. Obtained from Socony Mobil Oil Refinery, East St. Louis, Illinois. Liquid nitrogen storage container was supplied by Socony Mobil. Used as reflux coolant.

Lupersol DDM. Quantity-four liquid ounces. Supplier - Plastic Parts and Sales, St. Louis, Missouri. Used as catalyst for polyester plastic resin.

Mercury. Distilled. Quantity - ten pounds. Supplier - Fisher Scientific, St. Louis, Missouri. Used as manometer fluid.

Polyester Resin. Selection No. 5119. Quantity - 1/2 gallon. Supplier - Plastic Parts and Sales, St. Louis, Missouri. Used to water proof the plywood water bath, and also as a vacuum sealing material for the manifold connections.

Stopcock Grease. Spectro-Vac, type II, batch 303. Low vapor pressure. Quantity - 2 ounces. Supplier - Robert R. Austin, Ph.D. Pasadena, California. Used as vacuum sealing material for stopcocks.

Apparatus

The model L Podbielniak fractional distillating apparatus described in this section consisted of the column, the distillate receiving system, the manifold, the controls, the air supply and control, the vacuum pump, the sample apparatus, and the accessories. The main parts of the apparatus are described in the following paragraphs. The assembled parts are described and supplemented with illustrations.

Column. The pyrex column dimensions were 3.8 millimeters inside diameter and 120 centimeters in length. A single coil stainless steel wire extended 105 centimeters from the sample bulb to the reflux chamber of the column and was the only packing used. One end of the column was connected to a 15 milliliter pyrex sample bulb which was connected by a U-tube to a three way stopcock. See Figure 10. The column was separate from the insulating jacket. The pyrex vacuum jacket containing a polished metal radiation shield surrounded the pyrex column and the reflux chamber, but did not surround the sample bulb. See Figure 5, Case 1, page 19. The reflux chamber was the same type as shown in Figure 2, page 16. The heater for the column was added by the author. He wrapped an 85 ohms nichrome wire coil 7/32 of an inch in diameter around the sample bulb. The column is part of the original equipment.

Receiving System. The author built the distillate receiving system. Six, four liter empty chemical reagent bottles were used as receiving containers. Copper tubing, 3/32 outside diameter, was passed through corks that stoppered the bottles, and the corks and tubing were sealed gas tight with polyester resin. A water bath of 3/4 inch, five ply, plywood, inside dimensions 22 inches long, 15 inches wide, and 16 inches high was built and painted with four coats of polyester plastic resin. A plastic coated shelf containing six three inch diameter holes was supported by the bottles, and fastened in place by four plastic coated adjustable blocks of wood bolted in each upper corner to the side of the box by quarter inch bolts fastened with wing nuts. See Figure 11. The shelf fastened the bottles in place by resisting the bouyant forces.

The manifold was constructed of ten glass stopcocks interconnected with glass tubing. The stopcocks were assigned letters and all ports

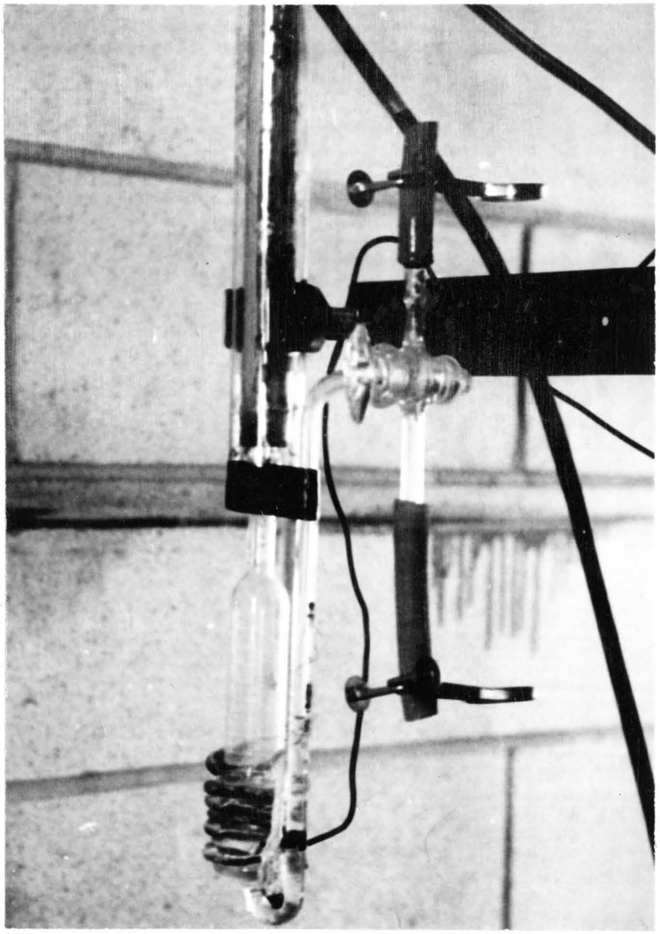


Figure 10. Column Stopcock.

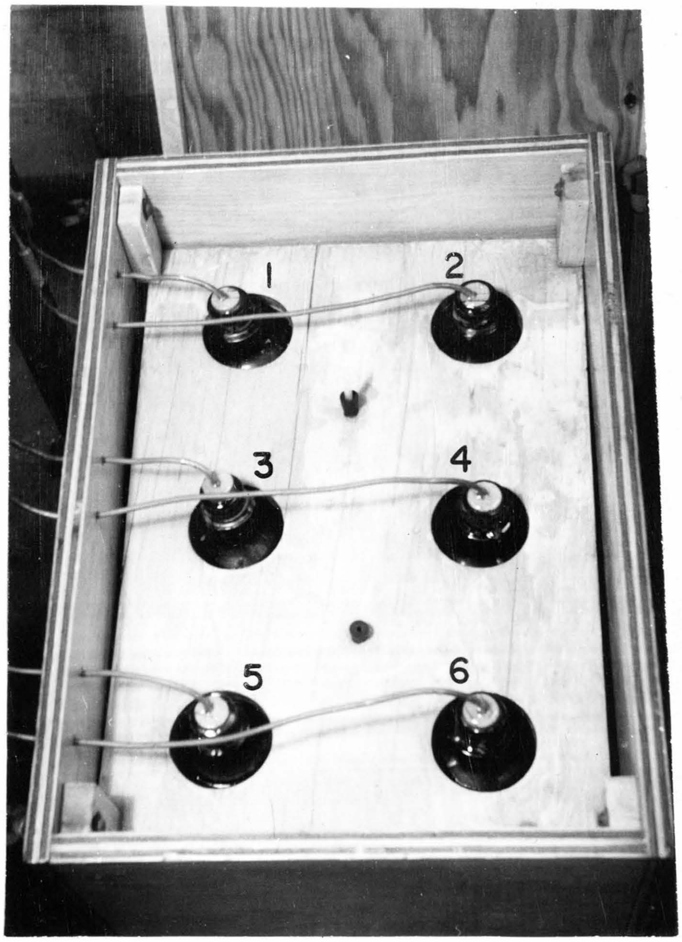


Figure 11. Water Bath.

leaving the manifold were assigned numbers to facilitate the description of the procedure. See Figure 12, page 38. The manifold was connected as shown in Table I, page 39.

Controls. The author used the same control system as described in Appendix I.

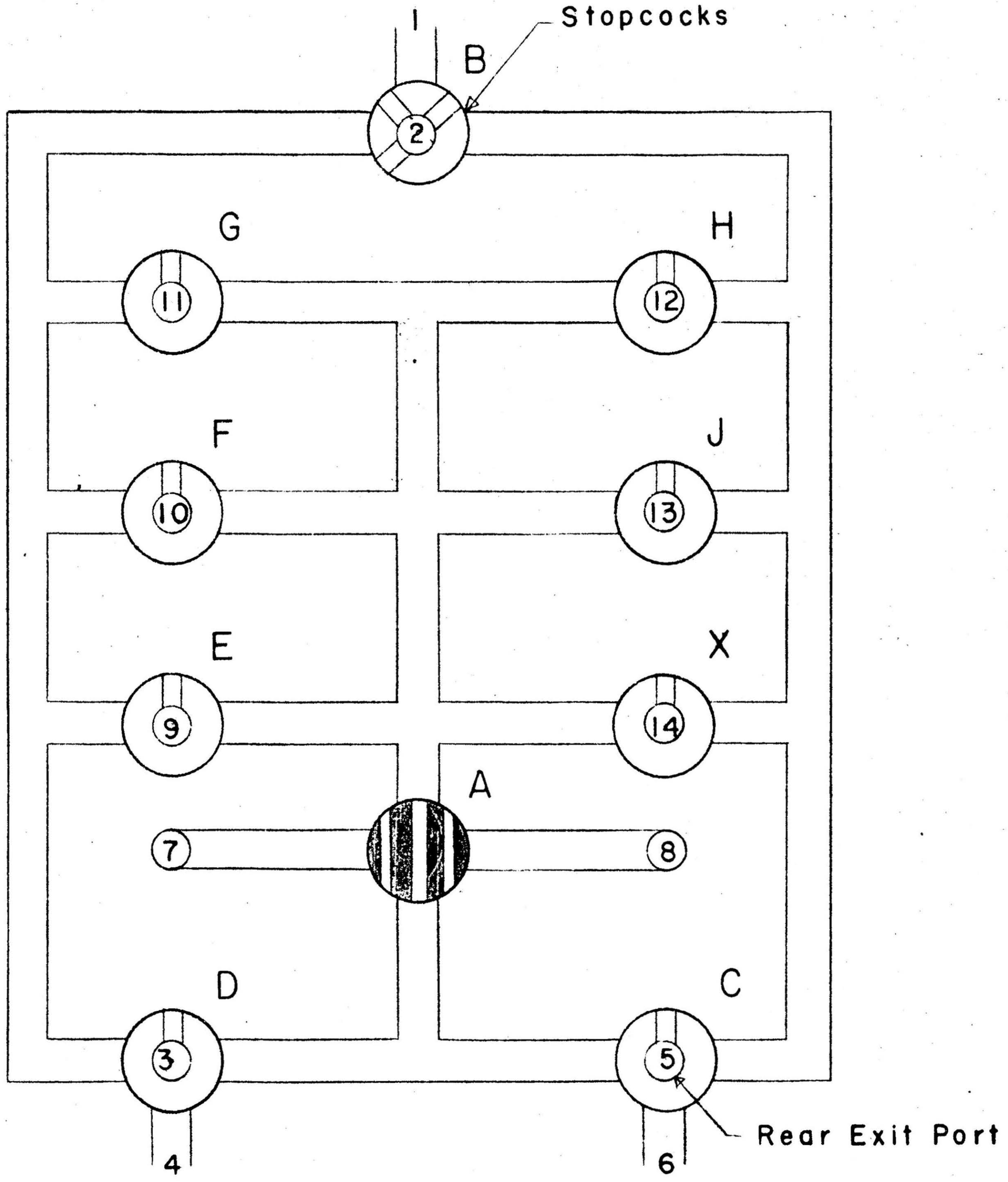
Assembly. All parts were bolted on the panel board or frame of the apparatus except the water bath containing the receiving bottles and the vacuum pump. See Figures 13 and 14. The parts were connected with copper tubing by soldering or sealing with polyester plastic resin coated with Epo-Lux flexible film to insure vacuum tight seals. Removable connections, such as the connections to the thermos bottle, were made with rubber tubing.

Flow Diagram. A schematic flow diagram (Figure 15) shows the connection of the vapor lines.

Wiring Diagram. A wiring diagram (Figure 16) shows the electrical connections for the controls.

Procedure

Before operating the apparatus one should be thoroughly familiar with the parts, their locations, the flow diagram, the electrical diagrams, and the procedure. A service manual for the Brown Recorder, flow and wiring diagrams, and a copy of the procedure should be located with the apparatus. Experience in operating the apparatus was necessary before efficient operation and accurate, reproducible results were obtained.



NOTES:

1- Capital Letters Indicate Stopcocks and Numbers Indicate Exit Ports

2- All Stopcocks except A Have Rear Exit Port

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ROLLA, MISSOURI

Schematic Flow Diagram of The Manifold

SCALE:	None	DATE	CASE NO: 58
DRAWN BY:	R. B.	5/12/58	FILE NO: 490
CHECKED BY:	JHe	5/13/58	FIGURE NO: 12
APPROVED BY:	JHe	5/13/58	SHEET NO: 1

TABLE I

Flow Connections to The Manifold

Port	Connected to	Stopcock
1	Distillation Column	B
2	Distillation Shut-Off Valve	B
3	Column Manometer	D
4	Open	D
5	Vacuum Pump	C
6	Open	C
7	Open	A
8	Rate Valve	A
9, 10, 11, 12	Receiving Bottles 3, 2, 1, and 4 respectively	E, F, G, and H respectively
13	Compensating Manometer	J

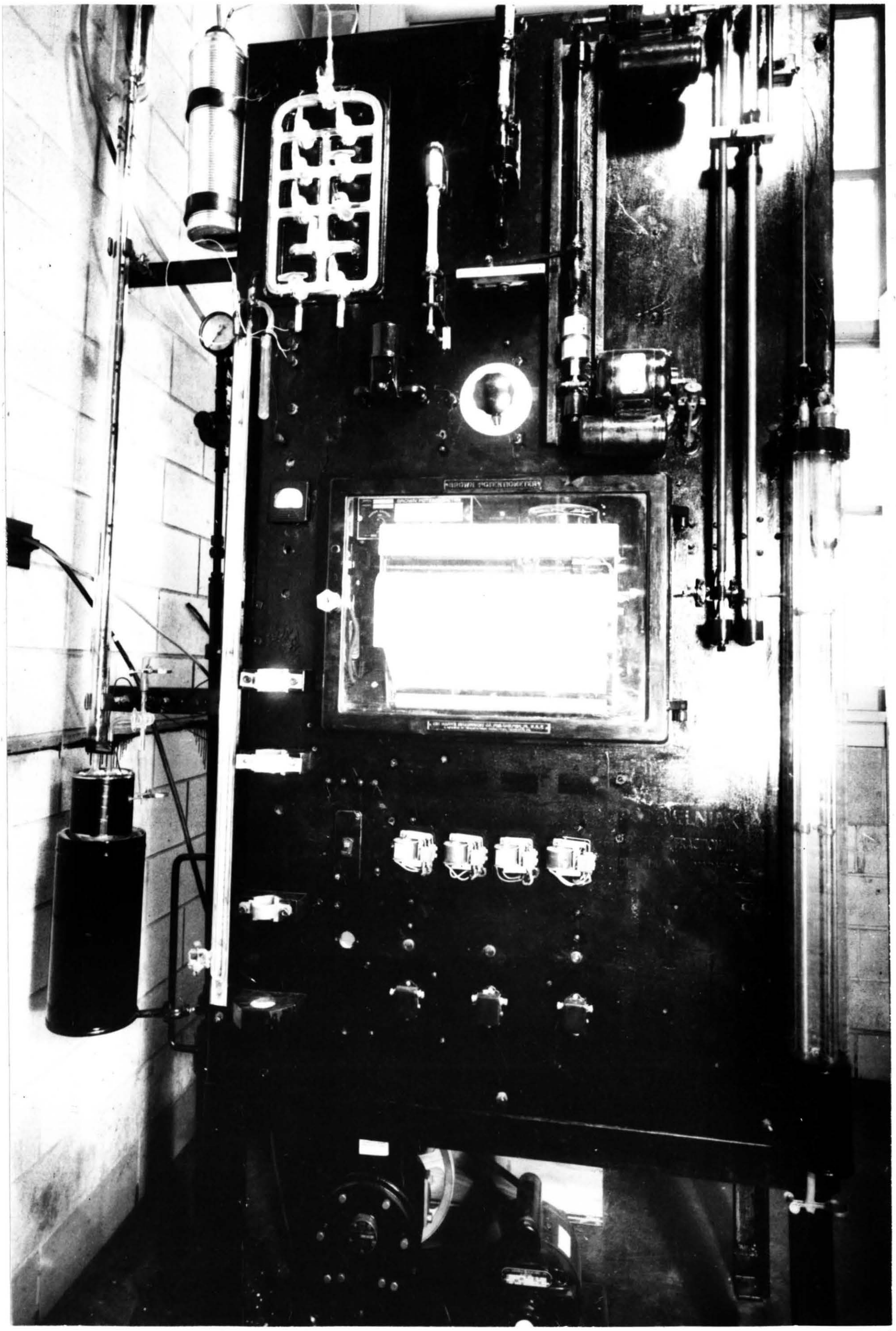


Figure 13. Front View of The Reconstructed Apparatus.

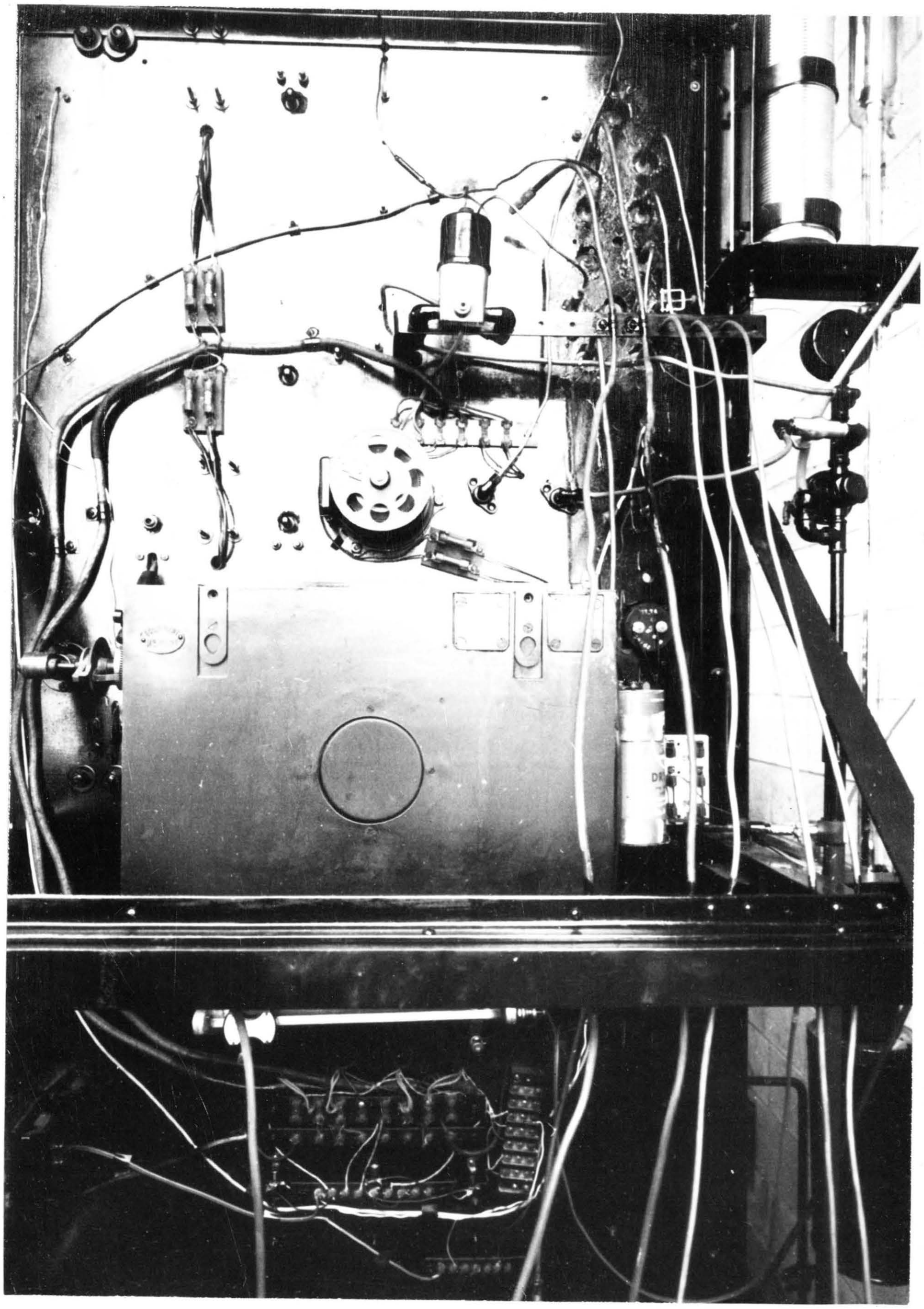
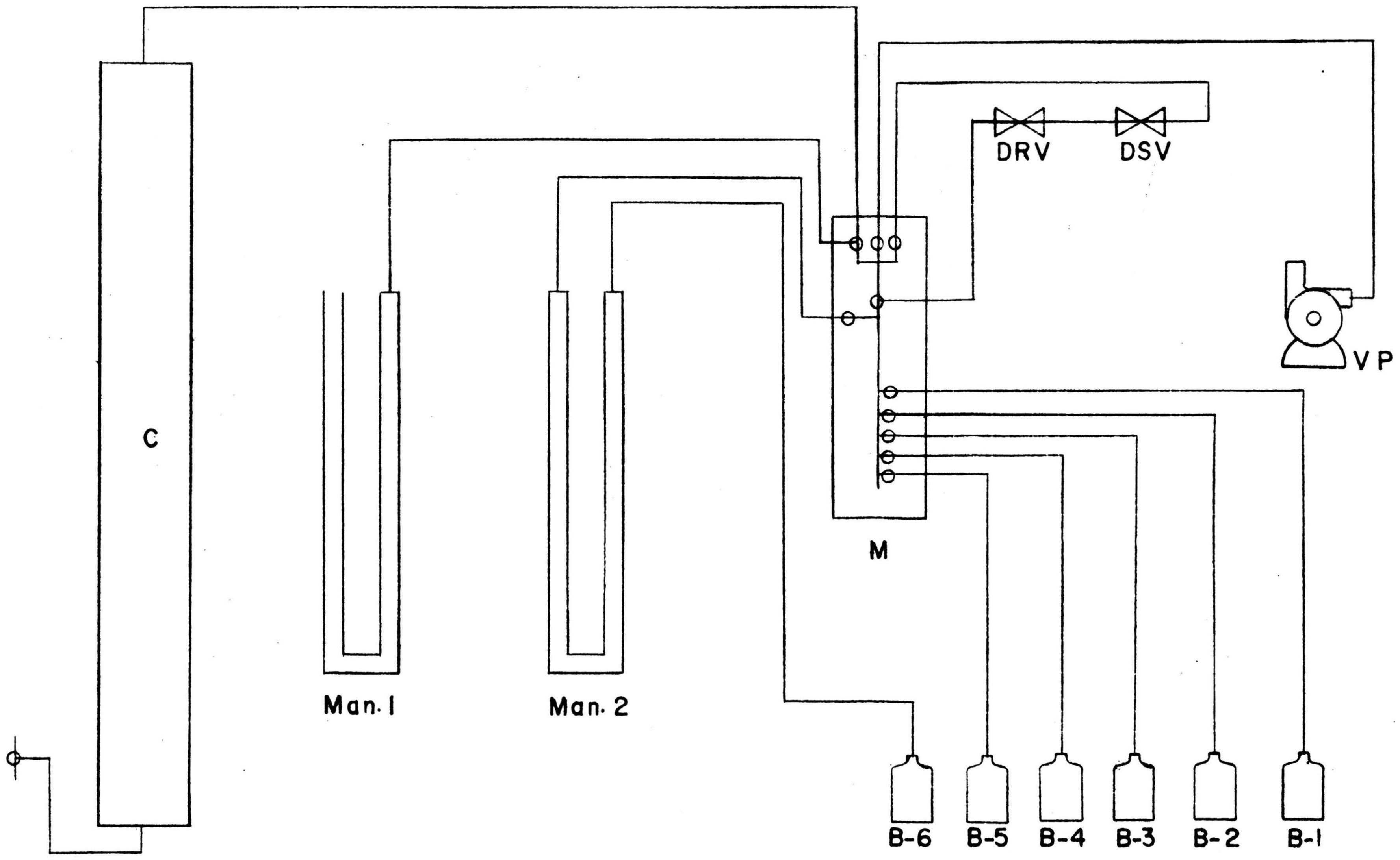


Figure 14. Back View of The Reconstructed Apparatus.



LEGEND

B-1 to 5 -	Distillate Receiving Bottles
B-6 -	Compensating Bottle
C -	Column
DRV -	Distn. Rate Valve
DSV -	Distn. Shut-Off Valve
M -	Manifold
Man. 1 -	Column Manometer
Man. 2 -	Compensating Manometer
VP -	Vacuum Pump
o -	Stopcocks

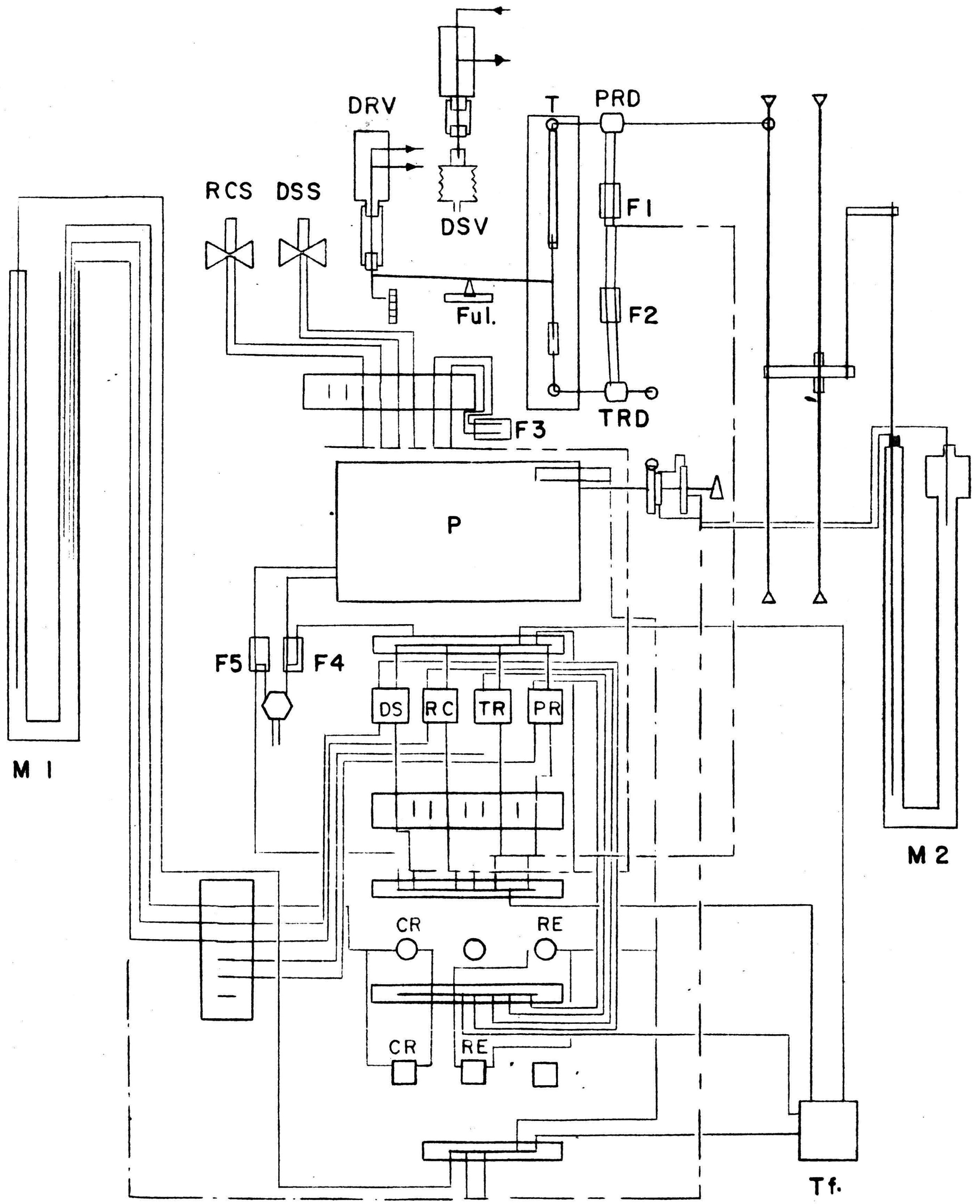
Reconstructed Podbielniak Model L
Low-Temperature
Fractional-Distillation Apparatus

DEPARTMENT OF CHEMICAL ENGINEERING
MISSOURI SCHOOL OF MINES & METALLURGY
ROLLA, MISSOURI

Schematic Flow Diagram

SCALE: None
DATE
DRAWN BY: R.B 5/13/58
CHECKED BY: 5/14/58
APPROVED BY: 5/14/58
CASE NO: 58
FILE NO: 490
FIGURE NO: 15
SHEET NO: 1

Figure 15. Schematic Flow Diagram.



LEGEND

Symbols

- ○ Gear Connections
- ○ Signal Lights
- ☐ Signal Buzzer
- ☐ Relay
- ⬡ Main Switch
- △ Bearings
- △ Bushing
- Terminal Strip
- Terminal Connector
- Solenoid Valve
- 6 Conductor Cable
- 4 Conductor Cable
- 2 Conductor Wire
- 1 Conductor Wire

Letters

CR	Check Reflux
DRV	Distn. Rate Valve
DS	Distn. Shut-Off
DSS	Distn. Shut-Off Solenoid
DSV	Distn. Shut-Off Valve
F1to5	Fuses
Ful.	Fulcrum
M 1	Column Manometer
M 2	Compensating Manometer
P	Potentiometer
PR	Press. Rise
PRD	Press. Rise Drive
RE	Re-evacuate
Tf.	Transformer
TR	Temp. Rise
TRD	Temp. Rise Drive
T	Tangentor

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Wiring Diagram of
Reconstructed Apparatus

SCALE: None DATE
DRAWN BY: R.B. 3/13/58
CHECKED BY: 5/14/58
APPROVED BY: 5/14/58
CASE NO: 58
FILE NO: 490
FIGURE NO: 16
SHEET NO: 1

Figure 16. Wiring Diagram of Reconstructed Apparatus.

Preparation for Start-Up. In preparing for start-up the procedure was as follows.

Evacuating the System. The procedure was as follows,

(1) The vacuum pump was turned on;

(2) Stopcock C (See Figure 12, page 38) was opened to connect the vacuum pump through port 5 to stopcock A which was opened to the receiving bottles and compensating manometer through stopcocks E, F, G and J. Stopcock H remained closed and bottle 4 (Figure 11) was not evacuated;

(3) When the compensating manometer was evacuated, stopcock C was opened to stopcock B which was opened to all its ports and enabled the column, the column manometer, rate, and distillation shut-off valves to be evacuated;

(4) Bottles 1 and 2 were removed from the system by closing stopcocks F and G.

Check for Leaks. If a leak occurred as indicated by a drop in mercury level in the column manometer, each part of the system connected to the manifold was evacuated separately in connection with the column manometer and tested as mentioned above. The part of the system that leaked was pressurized (by a rubber squeeze-bulb connected to the column's sample bulb) and each joint in that part of the system was tested with a soap solution. All leaks were sealed before operating the apparatus.

Column Cooling. The column was cooled by immersing the sample bulb in liquid nitrogen contained in the Dewar flask as shown in Figure 17, and by cooling the reflux chamber by manual actuation of the reflux control.

Standardization of Potentiometer. The switch lever on the slidewire was moved to the extreme left "Bal." position with the thumb, and with the index finger the knurled disc above the switch was turned until the step of the galvonometer step table indicated by a Black arrow contacted the galvonometer pointer. The mechanical zero was also checked. While the motor ran, the switch on the slidewire was pushed to the center "Zero" position, and the zero adjusting screw on the front of the galvonometer was turned, so that the step of the galvonometer step table indicated by the Black arrow contacts the galvonometer pointer. The potentiometer should be standardized before each analysis.

Check Water Bath. The water bath should be checked to insure that the water level remains above the shelf level. Loss of water by evaporation had to be replaced. The thermometer in the water should be read and the temperature recorded on the strip chart. The temperature should also be recorded at the end of an analysis. The author found no variation in water temperature during a run.

Adjust Starting Pressure in Receiving Bottles. The following procedure was carried out in numerical sequence,

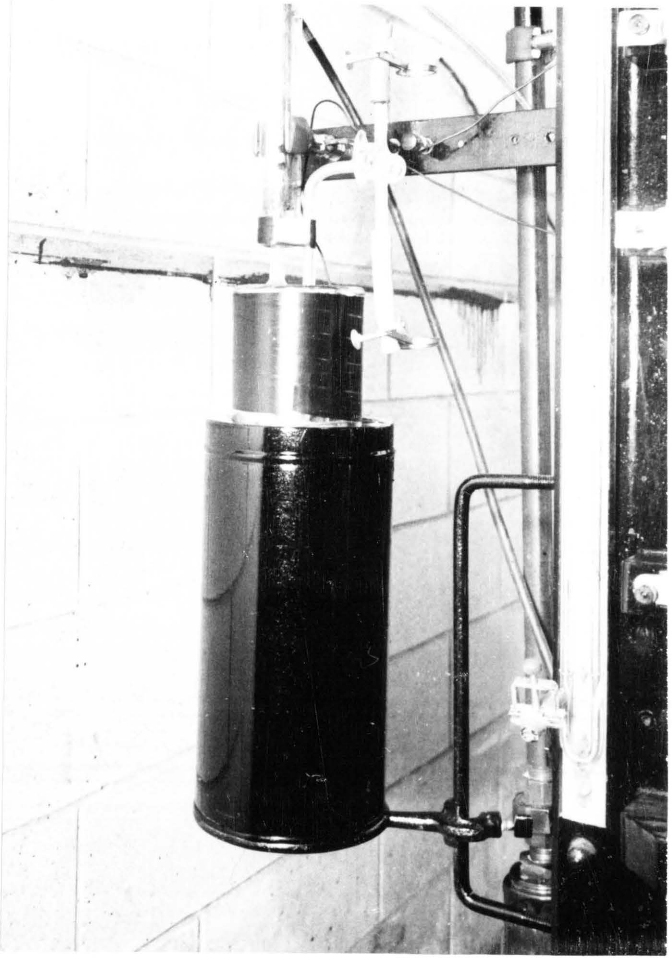


Figure 17. Sample Bulb Cooling.

(1) The wing bolt in the contact rod carriage was loosened and the carriage was lowered to the lowest possible position;

(2) The main electrical switch was turned on;

(3) The wing bolt on the sleeve connecting the chart shaft to the drive shaft was loosened to prevent chart travel;

(4) Air was admitted slowly into bottle 3 and the compensating manometer (by turning stopcock 4 to connect bottle 4 with stopcocks E and J) until the mercury in the compensating manometer contacted the contact rod;

(5) Stopcock H was closed and the chart drive motor raised the contact rod until the electrical circuit through the mercury was broken;

(6) After the starting pressure was adjusted the wing bolt loosened in "step 3" above was tightened. And now, any additional rise in pressure in the receiving system was recorded on the strip chart.

Sample Precautions. A few precautions were followed to insure that the sample entered into the column represented the sample in the sample container. One should remember that the samples were stored as liquids under pressure, and the vapors in equilibrium with the liquid were a different composition; therefore if a container leaked, the sample was being fractionated, and its composition changed. A sample was always withdrawn from the bottom of its container because the liquid was a more representative sample than the vapor in equilibrium with the liquid.

Sample Entrance. Since the samples were stored at high pressure (over 200 pounds per square inch) direct entrance of the sample into the column would break the sample bulb's connecting U-tube. The sample pressure was reduced by expanding the liquid sample into the sample entrance apparatus; then transferred from the entrance bottle into the column. A detailed sample entrance procedure is included in Appendix II.

Start-Up. The following steps were performed in numerical sequence,

(1) The Powerstat dial was rotated to position "4". The ammeter read 0.6 amperes;

(2) The Dewar flask was lowered slowly until the pressure in the column manometer rose at the rate of one centimeter per minute;

(3) The main electrical switch on the panel board was turned to the on position;

(4) The potentiometer switch was turned to the on position;

(5) The air supply valve was rotated 1/8 of a turn;

(6) The air pressure regulator valve was set, so that the pressure gauge read ten pounds per square inch;

(7) The reflux cooling needle valve was positioned, so that the pressure in the column manometer would drop five millimeters

of mercury when the manual reflux button switch was closed for an instant;

(8) The distillation shut-off contact wire in the column manometer was positioned to contact the mercury when the distillation pressure reached 760 millimeters of mercury;

(9) The manifold stopcocks were in the correct position from entering the sample, so that total reflux occurred in the column;

(10) After total refluxing the sample for twenty minutes, rotate stopcock <u>A</u> of the manifold, so that port <u>8</u> was connected to stopcocks <u>E</u> and <u>J</u>;

(11) After "step 10" the controls automatically distilled the sample.

<u>Automatic Operation of the Apparatus.</u> During the operation of the apparatus all explanatory remarks were written on the distillation diagram, and these remarks were used later to interpret the diagram.

The automatic operation of the apparatus is described by Podbielniak in the literature, which is included in Appendix I. Modifications to Podbielniak's procedure are described in the following paragraphs.

<u>Reflux Cooling Control.</u> Reflux cooling was accomplished by blowing liquid nitrogen into the reflux chamber in intermittent puffs. Liquid nitrogen was stored in a thermos bottle and was forced by air pressure into the reflux chamber. A solenoid operated valve controlled the flow of air to the thermos bottle.

The solenoid was actuated by using the mercury in the column manometer as a switch; as described in Appendix I. A needle valve in series with the solenoid valve regulated the pressure to the thermos bottle. Three, 1/16 inch diameter holes were drilled into the copper tubing connecting the thermos bottle and the solenoid valve to provide a release for back pressure developed by the evaporation of liquid nitrogen. Without the leak holes the flow of liquid nitrogen to the reflux chamber could not be controlled.

Column Heater Control. The heat input to the column was controlled by varying the voltage across the heater circuit. See Figure 19. The heat input was measured by an ammeter assuming constant voltage across the circuit. A knife switch connected the ammeter in series or parallel with the column heater resistance. A 45 ohm rheostat was used as a parallel resistor, that enabled the accurate measurement of the amperage at high and low heat input.

Increase Heat Input. The operation of the reflux cooling control produced a particular sound which was repeated about once a minute when the solenoid valve was actuated. The absence of the sound indicated the reflux cooling control was not being actuated which was caused by a low distillation pressure. A drop in distillation pressure was due to insufficient heat input. The Powerstat dial was increased one division to correct the trouble.

Distillation Shut-Off Control. The distillation shut-off valve was closed by expanding the bellows with air. When the distillation valve closed the rubber tubing which enclosed the valve stem was compressed. When the air flow to the bellows stopped the rubber tubing expanded collapsing the bellows by forcing the air through the brass fitting connecting the bellows to the copper tubing, and opening the distillation shut-off valve. The air flow to the bellows was controlled by a solenoid valve which was actuated through a relay by the contact wire in the column manometer; as described in Appendix I.

Re-evacuation. The receiving bottle and the column manometer were re-evacuated when the pressure in the compensating manometer approached 300 millimeters of mercury. The procedure for re-evacuation was performed in numerical sequence,

(1) Stopcock *A* was rotated to close port *8* and to connect stopcocks *E* and *J* to *C*. When port *8* was closed the column was at total reflux;

(2) Receiving bottle *3* and the compensating manometer were evacuated by rotating stopcock *C*, so that it connected to stopcock *A*.

(3) Stopcock *C* was closed after evacuating the receiving system;

(4) The "Adjust Starting Pressure in Receiving Bottles" procedure was repeated;

(5) Stopcock A was rotated to the original position before re-evacuation.

Reduce Pressure. The distillation pressure was reduced to lower the boiling points of the components being distilled. If the boiling point of a component was below room temperature, the component would not condense after it left the column. The distillation pressure was reduced when pure normal butane began to leave the column which was indicated by the temperature of zero degrees centigrade on the strip chart. The reason for reducing the pressure at normal butane rather than a C_5 hydrocarbon was to facilitate the location of the cut point of the C_5 compounds.

The procedure for reducing the pressure was performed in numerical sequence,

(1) Stopcock A was rotated 45 degrees so that the column was at total reflux;

(2) The Powerstat dial was rotated to the off position;

(3) The Dewar flask around the sample bulb was raised slowly until the mercury in the column manometer began dropping;

(4) The contact wires in the column manometer were lowered as fast as the mercury dropped until the distillation shut-off wire was positioned so that it contacted the mercury when the distillation pressure was 300 millimeters of mercury;

(5) Before the distillation was continued ethanol was added to the sample bulb, as explained in Appendix II;

(6) The Powerstat was rotated to position "6";

(7) The Dewar flask was lowered slowly until the pressure in the column manometer rose at the rate of one centimeter per minute;

(8) The column was totally refluxed for ten minutes;

(9) Stopcock A was rotated 45 degrees back to its original position before reducing the pressure.

Shut-Down of Apparatus. The analysis was completed when the temperature recorded on the potentiometer strip chart reached 30 degrees centigrade. The shut down of the apparatus was performed in numerical sequence,

(1) The Powerstat dial was rotated to the off position;

(2) The main electrical switch was pushed to the off position;

(3) The ethanol was removed from the column as described in Appendix II;

(4) The thermos bottle was disconnected from the reflux chamber;

(5) The air supply valve was closed;

(6) The vacuum pump was switched off.

Data and Results

All the data, from which the results are calculated, are recorded on the distillation diagram produced by the recording potentiometer. The operator determined the cut point between fractions and calculated the results. Also the data from the calibration of the receiving bottles are tabulated in Table II.

Production of Distillation Diagram. The reconstructed apparatus produces the data in the form of a diagram (Figure 18) drawn by the equipment during the analysis. The vertical lines are produced by the roll of the strip chart, and the horizontal lines are drawn by the motion of the pen. The distillation rate was recorded by a second pen that produced a horizontal pip every 90 seconds. The vertical distance between the pips represents the amount of distillate product per 90 seconds.

Determination of the Cut Point. The method of determining the cut point was obtained from Socony Mobil Oil Refinery. The method is illustrated on Figure 18. A rectangle is constructed to enclose the portion of the curve which is not vertical, and the intersection of the diagonal of the rectangle and the distillation curve is the cut point. One assumes that all material distilled above the cut point is the higher boiling component, and that all material below the cut point is the lower boiling component. This method was experimentally found to be precise. The chart travel was read directly in millimeters from the distillation diagram and tabulated in Table III.

TABLE II

Calibration of Receiving Bottles

Bottle Number	Volume, ml			
	Bottle	Lines	M[a]	Total
1	3994	15	45	4054
2	3990	16	45	4051
3	3994	14	45	4053
4	3995	16	45	4056
5[b]	3926	15	45	3986
6	3980	15	45	4040

a. Available Gas Volume in Compensating Manometer.

b. not in use.

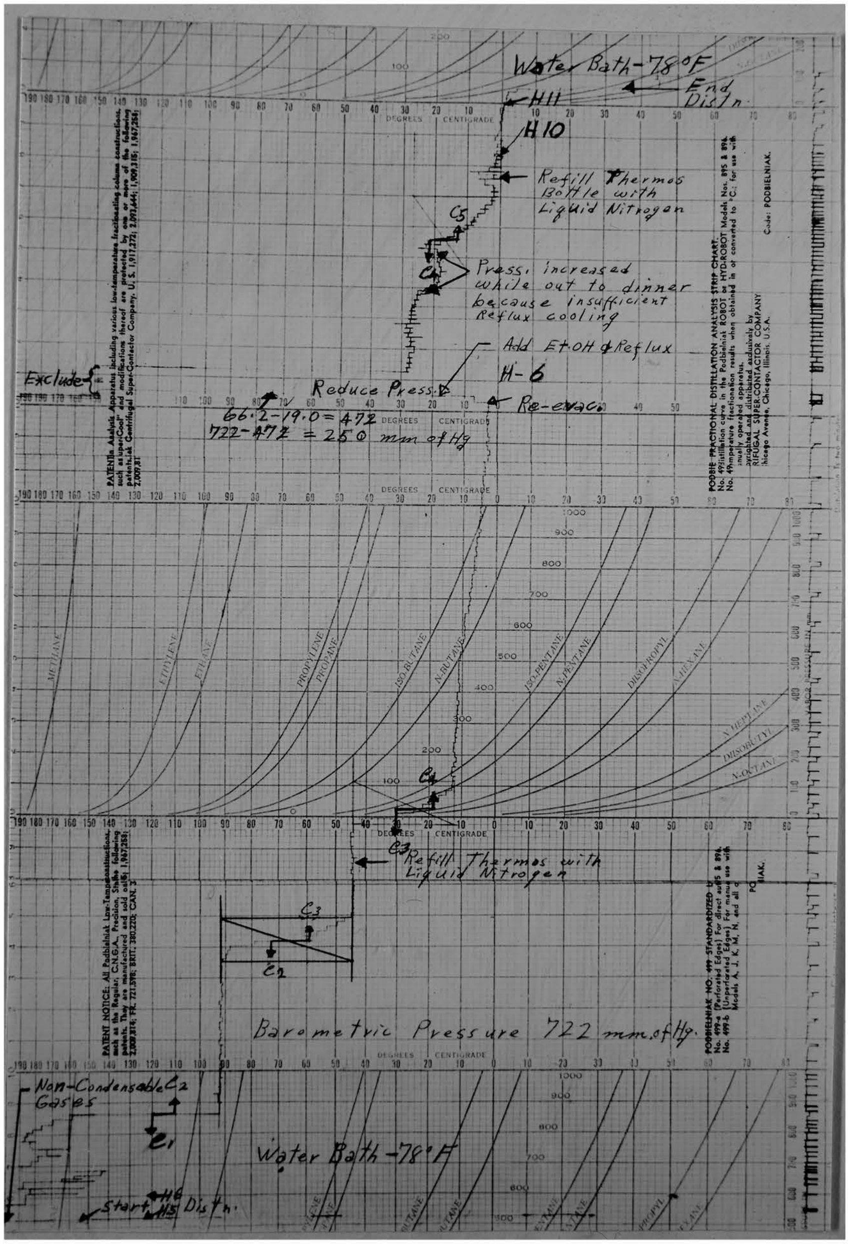


Figure 18. Distillation Diagram.

TABLE III

Analyses of Samples

Fraction	Chart Travel, mm		Composition Mole %		
	Test 1	Test 2	Test 1	Test 2	S.A.[a]
Sample 1					
C_3	96	269	36.9	36.8	28.5
C_4	150	442	57.7	60.6	70.9
C_5	14	19	5.4	2.6	0.6
Total	260	730	100.0	100.0	100.0
Sample 2					
C_1	16	33	2.0	6.1	1.6
C_2	103	56	13.0	10.3	11.5
C_3	270	161	34.1	29.6	32.4
C_4	350	244	44.1	44.9	45.4
C_5	55	50	6.9	9.2	9.1
Total	794	544	100.1	100.1	100.0

a. S.A. refers to the mass spectroscopy analyses obtained from Socony Mobil Oil Refinery.

Sample Calculation

$$\text{Composition of fraction} = \frac{\text{Chart Travel of Fraction}}{\text{Total Chart Travel}} \times 100.$$

Example: Sample 2, Test 2.

$$\text{Composition of } C_3 \text{ Fraction} = \frac{161}{544} \times 100 = 29.6\%.$$

IV. DISCUSSION

The discussion is divided into (1) discussion of the apparatus, (2) discussion of the procedure, (3) discussion of the data and the results, (4) limitations, and (5) recommendations.

Discussion of the Apparatus

The apparatus is discussed in the same order as it was described in the experimental section.

Column. The column is very fragile where the sample bulb is connected to the three way stopcock by means of a glass U-tube. Any time the stopcock is rotated the force exerted is multiplied through the U-tube which acts as a lever arm. The stopcock cannot be rigidly fixed; for then the thermal stresses would break the U-tube connection to the sample bulb. A solution to the above problem is shown in Figure 6, page 20. The sample bulb is enclosed in the vacuum jacket and the stopcocks are connected to eliminate the U-tube. The single coiled wire packing is not efficient enough to obtain sharp separations in a reasonable time required for a test. The column packing is rated by Podbielniak (17) at two inches per theoretical plate; while the new Heli-Grid packings are rated at four tenths of an inch per theoretical plate at total reflux of 200 ml per hour. Since the distillation tubes are removable from the vacuum jacket, tubes with different packings could be constructed to replace the present tube. An efficient packing would greatly reduce the time for an analysis.

Receiving System. The receiving system, consisting of six, four liter glass bottles contained in a water bath, was designed to collect a complete sample in separate fractions so that re-evacuation need not occur during a test. Since the volume of the bottles vary, only No. 3 bottle was used because a constant relation between the chart travel and quantity of distillate in the receiving bottle was desired. One bottle was used to increase the response to the increase in pressure in the receiving system. Since only No. 3 and the compensating bottles were used, the size of the receiving system and the water bath could be reduced. A water bath smaller than the existing bath could be located under the potentiometer, and this location is preferred because additional working area would be available in the rear of the apparatus.

The author had no need for a toppler pump to remove the distillate from the receiving bottles for further analyses. If one wishes to withdraw distillate for additional analyses, he can connect an evacuated container to port 7 of the manifold and direct the flow of the distillate into the container by correctly positioning stopcock A. The purpose for additional analyses would be to determine the amount of impurities in each fraction.

Reflux Cooling Control. The automatic reflux cooling control did not function satisfactorily during the analysis of the first sample. A screw clamp was used to close the rubber tubing connecting the solenoid and the copper tubing which connected to the thermos bottle. The flow of air to the thermos bottle and the flow of liquid nitrogen to the reflux chamber were regulated by closing the screw clamp. The setting of the clamp was critical, and either too much or too little liquid nitrogen was forced into the reflux chamber. The difficulty was that the air pressure in the thermos bottle could not be regulated by the clamp; hence the flow of liquid nitrogen to the reflux chamber was practically uncontrolled. The reflux cooling control was rebuilt. A stainless steel needle valve was inserted in the air line before the solenoid valve, and the solenoid valve was connected directly to the copper tubing, which connected to the thermos bottle, by brass ferrule type fittings. The needle valve regulated the air pressure to the thermos bottle and the automatically operated solenoid valve controlled the flow of air to the thermos which forced liquid nitrogen into the reflux chamber. The flow of liquid nitrogen was controlled within precise limits over a wide range of flow by regulating the needle valve. No difficulties with the reflux cooling control were experienced after the needle valve was installed.

Distillation Shut-Off Control. The reconstruction of the distillation shut-off control was delayed because a suitable bellows necessary to pneumatically actuate the shut-off valve could not be purchased. Bellows manufacturers were contacted, but they replied that they could not supply the bellows. The instrument companies contacted replied they could supply a precisely constructed bellows at the price of 30 dollars. The author finally thought of using a bellows from an automobile's thermostat for temperature regulation. The bellows from the thermostat was modified, tested, and found to operate satisfactory. The time for automatically closing the distillation shut-off valve is less than a second, but the time required for the valve to open is less then five seconds. The delay in opening the valve is caused by the slow leaking of air through the brass fittings connecting the bellows to the copper tubing air supply line. Since the time delay in opening the valve is not detrimental to the distillation, no attempt was made to change the control.

Distillation Rate Control. The distillation rate control did not function effectively. The malfunctioning was not caused by the components of the rate control. The cause was the slow response of the potentiometer which was due to either the improper location of the thermocouple or a mechanical difficulty in the potentiometer. Positioning of the thermocouple in the column is very important. If the thermocouple contacts the column wall, the heat capacity of the wall prevents a quick response to a change of temperature.

The galvanometer pointer sticks against the step table frame, and occasionally is not positioned by an unbalanced circuit caused by a temperature change in the reflux chamber. The step table is worn and needs replacement.

Heater Control. The heat input is easily manually varied by positioning the Powerstat dial, and is accurately measured by the ammeter, but only an unknown portion of the heat generated in the heater coil is transferred to the liquid in the column. By relocating the sample bulb in the vacuum jacket and by inserting a cartridge type heating element into the column, the heat input into the column is more significant because less heat is lost to the surroundings.

Discussion of The Procedure

The author's procedure was determined from his experience with the apparatus and from the procedure reported by Podbielniak (14). The limited operating experience by the author prohibits him from commenting about the procedure, but his difficulties in operating the apparatus are discussed to caution future operators.

Sample Entrance. The difficulty in transferring the sample from its container into the entrance bottle is caused by the high vapor pressure in the sample container. The needle valve of the sample container can only be opened very little, or else the high pressure blows off the neoprene tubing connecting the entrance bottle to the container, and the sample is lost. Also, if the valve of the sample container is opened too much, the sample will emerge as a liquid, and fractionate along the length of the neoprene tubing. The neoprene tubing also adsorbs some of the liquid hydrocarbons causing the vapors in the entrance bottle not to be a representative sample. The difficulty could be eliminated by connecting the sample container directly to a large metal bomb with pipe, and by expanding the sample into the bomb to reduce its pressure. No difficulties were experienced while transferring the sample from the entrance bottle into the column.

Column Flooding. When the apparatus is functioning correctly, the operator has little to do after the sample is added to the column; therefore the chances of making an operating mistake are few. The most common mistake is to flood the column. The cause of column flooding is excessive heat input which is manually controlled by positioning the Powerstat dial. When the column floods liquid is trapped in the reflux chamber. The vapor pressure of the entrapped liquid is high enough to actuate the reflux cooling control, which then cools the reflux chamber and supercools the entrapped liquid. The supercooled liquid does not boil and the distillate flow to the receiving bottle ceases. Column flooding is detected by the sound emitted by the repetitive actuation of the reflux cooling control, and is confirmed by seeing through the peep holes in the radiation shield the liquid flowing down the column. When the column is functioning correctly no liquid is seen by looking through the peep holes.

Pressure Reduction. The first procedure for reducing the column pressure was to force the contact wires in the column manometer into the mercury until the reflux cooling control was actuated. If the contact wires were pushed down the column manometer too fast, the repetitive reflux cooling supercooled the reflux chamber. A long period was necessary to warm the supercooled reflux chamber by the condensation of vapors rising through the column. During this time no product was leaving the column, and the time for a test was increased. The present procedure for reduction of the column pressure eliminated the above difficulty.

Ethanol Entrance. After the pressure was reduced ethanol was added to the column. Air was admitted to the column along with the ethanol for sample two, test two. The entrance of ethanol to the column is a technique which is developed by practicing, and the author's inefficient technique caused the addition of air into the column. If the vacuum were applied to the column's three way stopcock by connecting port 6 of the manifold to the top part of the column stopcock, the suction of ethanol into the column's stopcock could be controlled easier than when the vacuum is applied with a rubber squeeze bulb, and air would not be admitted to the column.

Discussion of The Data and The Results

The data are read from the strip chart and are tabulated in numerical form. The interpretation of the strip chart is discussed in the following paragraphs along with the analyses of samples one and two.

Diagram Interpretation. The interpretation of the distillation diagram is dependent upon the experience of the operator. During the analyses many operating errors are indicated on the distillation diagram, if they occur; and the following information which is later helpful in interpreting the diagram is written on the strip chart by the operator; (1) a sharp drop in temperature indicates flooding of the column, unless the distillation pressure is reduced; (2) A sharp drop in temperature caused by reducing the distillation pressure is written on the strip chart to distinguish the temperature drop from the error above; (3) when the distillation curve has a large negative slope, the temperature in the reflux chamber is slowly decreasing due to a drop in distillation pressure, caused by insufficient heat input; (4) additional data such as, the barometric pressure, the differential pressure on the column manometer, the position of the Powerstat dial, the time of re-evacuating the receiving system, and the water bath temperature are written on the strip chart.

Sample 1. Two tests of sample one were made. The first test was made to prove that the apparatus functioned properly. The sample size was about one gaseous liter at room conditions. The second test was made to confirm the operational procedure used in the first test, and to compare the time of distillation between the tests with the size of the samples analyzed. The sample size of the second test was about 2.7 gaseous liters at room conditions. The analysis of the first sample required close attention by the operator because the reflux cooling control occasionally functioned improperly. Before analyzing the second sample the reflux cooling control was improved to its present design by the addition of the needle valve.

The results of the first sample varied more than expected from the results determined at Socony Mobil Oil Refinery. The variance was discussed with Socony's analyst and the conclusion reached was that improper sampling at the Refinery caused the excessive variance.

Sample 2. After the reflux cooling control was re-designed, the control functioned correctly, and the existing procedure, as described in the experimental section, was used. Again two tests of sample two were made. The first test proved the apparatus and procedure were correct. The sample size was about 2.5 gaseous liters at room conditions. The sample size of the second test was varied to about 1.7 gaseous liters to determine its effect on the time required for analysis. Sample sizes were estimated from the volume they occupied in the sample entrance apparatus which was calibrated in liters. No attempt was made to determine the exact sample size. The second sample contained hydrocarbons from C_1 through C_5 so that the operating limits of the equipment could be specified for future samples. Due to supercooling of the reflux chamber when the distillation pressure was reduced, the time of the analysis was increased by an hour. Information comparing the size of the sample and the time for analysis would be incorrect because every test had many time delays caused by an inexperienced operator.

Analysis of Error. The results of sample two check within three per cent with the Socony analysis except for one value. The mole per cent of the C_5 fraction for the first test was low because high heat input flooded the column. When the column was flooded, a small quantity of liquid pentane remaining in the column was held up in the reflux chamber, and the ethanol vapors reaching the thermocouple measured a high temperature indicating the end of the analysis. The mole per cent of the C_1 fraction in the second test was high. The erratic distillation curve indicates faulty operation of the equipment. The cause of the erratic conditions was undetermined.

Other operating errors were recorded on the distillation diagram. See Figure 18, page 56. The first error happened when the distillation pressure was reduced. The reflux chamber was supercooled by excessive reflux cooling. The low temperature on the distillation diagram indicates this error. The next error was located at the portion of the curve marked "Exclude", and was caused by introducing air into the column along with the ethanol. The last error indicated by the distillation curve was insufficient reflux cooling which caused an increase in the boiling point temperature due to an increase in distillation pressure. Adjusting the needle valve controlling the air pressure to the thermos bottle corrected the insufficient reflux cooling. An evaluation of the precision of the analysis would be meaningless because of the many different operating errors caused by the inexperience of the operator.

Limitations

The limitations of the apparatus were not completely quantitatively determined, but the author will present a qualitative statement about the limitations.

Samples. Samples containing C_1 through C_5 hydrocarbons can be analyzed with the present apparatus. Samples containing C_6 hydrocarbons cannot be introduced into the column accurately because the C_6 components condense in the entrance bottles.

Sharpness of Separation. In a reasonable time the apparatus can only accurately separate hydrocarbon compounds whose boiling points differ by ten degrees centigrade. If automatic control of the analysis is used, the accurate separation is limited to fractions containing very high percentage of compounds with the same number of carbon atoms. The automatic control is limited by the slow response of the potentiometer.

Time of the Analysis. The time required for an analysis varied between four to eight hours depending on the sample size and the number of fractions in a sample. The smallest sample (one liter of gaseous sample) required four hours, when automatic control was used, and would require more time if a sharper separation was desired. A sample consisting of 2.5 gaseous liters at room conditions required six hours to analyze when automatic control was used and no time consuming operating errors were made.

Accuracy. The accuracy of the analysis is dependent upon the size of sample analyzed. The accuracy of an analysis was within three per cent of the known result. The significance of the accuracy obtained is restricted due to the few results upon which it is based.

Recommendations

The recommendations are divided into two groups: (1) improvements and (2) future uses of the apparatus.

Improvements in the Apparatus. The response of the potentiometer should be improved. The galvonometer pointer of the potentiometer sticks against the step table frame, and occasionally is not positioned by an unbalanced circuit caused by a temperature change. The step table is also worn and needs replacement along with the galvonometer coil to which the pointer is attached. Parts for the Brown mechanical potentiometer are difficult to purchase because the company no longer manufactures spare parts; therefore a new recording potentiometer would be required. The author cannot justify the expense of a new instrument for the existing apparatus.

A stainless steel rod 1/8 of an inch in outside diameter and four feet in length should be obtained to replace the contact rod in the compensating manometer. A longer rod would eliminate the "Adjust Starting Pressure in Receiving Bottles" procedure, and stainless steel would prevent rusting.

Future Use of the Apparatus. The time of analysis prohibits the use of the equipment in a laboratory experiment, but the apparatus could be used in a special problem course. Subjects for investigations are determination of the accuracy and precision of analyses for a definite range of hydrocarbons, evaluation of column packings, and determination of an exact optimum sample size. One who attempts to design a problem for the use of the equipment should remember the long time required for a test. The apparatus is difficult to operate frequently in a school because of the difficulties in obtaining samples and liquid nitrogen.

V. CONCLUSION

The reconstructed Podbielniak model L low temperature fractional distillation apparatus automatically separates mixtures of C_1 to C_5 hydrocarbon compounds into fractions containing a very high percentage of compounds with the same number of carbon atoms, and quantitatively measures the mole per cent of each fraction in the mixture to within three per cent of the spectrometric analysis received from Socony Mobil Oil Refinery.

VI. SUMMARY

The purpose of this project was to reconstruct a Podbielniak model L analytical distillation apparatus donated to the school by the Socony Mobil Oil Refinery, East St. Louis, Illinois.

The initial condition of the apparatus was evaluated and a plan for reconstruction was established. The equipment was reconstructed, the necessary components were calibrated, and the operation of the reconstructed apparatus was tested with known hydrocarbon samples.

The equipment consists of a pyrex column with a coil wire packing, enclosed in a vacuum jacket containing a polished metal radiation shield; a distillate receiving system composed of four liter glass bottles in a water bath; and automatic controls for the distillate flow rate, reflux cooling, and the production of a distillation diagram on which the analyses are recorded. The parts of the equipment are mounted on a panel board. The column is connected to the receiving system and the controls by copper tubing.

The equipment automatically separates the hydrocarbon mixtures into fractions containing a very high percentage of compounds with the same number of carbon atoms. The apparatus analyzed the samples to within three per cent of the results obtained from the Socony analyses. The time of an analysis varied from four to eight hours depending on the size of the sample and the number of fractions in the sample.

From the above results the author concluded the reconstructed apparatus functioned satisfactorily.

VII. APPENDICES

APPENDIX I

The following words are extracted from W. J. Podbielniak's (16) "Apparatus and Method for Precise Fractional-Distillation Analysis". Podbielniak presents the description and operation of the controls for a model L low temperature fractional distillation apparatus. The author has added some detailed description of the reconstructed apparatus not included in the above article.

Description of Apparatus and Operation

The general appearance of the automatic apparatus is shown in Figure 13. For aid in description, a diagram of the combined fractionation unit and recording and control mechanism, Figure 8, is presented.

Cooling of Reflux and Heating of Still. Liquid nitrogen must be admitted to the reflux chamber of the fractionating column in intermittent puffs in such manner as to maintain the column pressure as constant as possible at the desired value, as indicated on the distillation pressure manometer. Both the admission of liquid nitrogen and the heating of the still must be so conducted thatthe reflux-liquid just wets the column packing wires without excess hold-up.

A fine iron or stainless-steel wire, insulated throughout except at its extreme lower end, is inserted into the open arm of the distillation pressure manometer so that its uninsulated extremity is a few millimeters above the point where mercury will rise at the desired distillation pressure. A return wire is sealed into the manometer near the bottom or inserted through a rubber tubing connection deep into the mercury of the right arm. As soon as the pressure increases sufficiently to cause the mercury of the manometer to make electrical contact with the point of the inserted wire, a circuit is completed through a low-voltage rectifier, through two wire contacts in the mercury, through the mercury and through a sensitive telephone type relay. The relay in turn operates a specially designed compact electromagnet valve which permits compressed air to blow liquid nitrogen into the reflux cooling vessel from a thermos bottle full of the refrigerant, as illustrated in the diagram. The exact regulation of compressed air admission to the thermos bottle is controlled by a small needle valve, and by a permanent fine leak, as illustrated. The introduction of liquid nitrogen into the reflux cooling vessel, using the direct cooling tubes, almost immediately lowers the pressure, whereupon the mercury in the distillation pressure manometer leaves the electrical contact, the relay circuit is broken, and the solenoid valve closes to cut off admission both of compressed air to the thermos bottle and of liquid nitrogen to the cooling vessel. Residual pressure in the thermos bottle is immediately dissipated by means of the leak already mentioned.

If the supply of liquid nitrogen should become exhausted, or the cooling vessel should plug up, or anything else should happen to interfere with the cooling, the column pressure will of course continue to rise in spite of the action of the automatic mechanism. Eventually the mercury will rise sufficiently to reach the bottom end of another wire to operate a second low-voltage circuit including a buzzer and a trouble signal labeled "check reflux". The buzzer will summon the operator, while the light instructs him where to look for the cause of the trouble.

The supply of heat to the still may be controlled either manually or automatically. In manual operation, the operator will check the heat regulation whenever he happens to come to the apparatus and this will usually suffice. The requirement for heat increases normally, and if care be taken not to apply too much heat to the column at any time (as may be ascertained by watching the behavior of the liquid streaming down the column packing, for a minute or two) the worst that may happen from operator's prolonged inattention is a slowing up of effective distillation rate, without any detrimental effect to the accuracy of the results. Insufficient heat supply cannot cause a partial vacuum in the column, because of the functioning of another device described in the following paragraph.

Control of Distillation Pressure. The column pressure tends to remain constant, because of the action of the reflux cooling mechanism described in the preceding section. However, it rarely happens that the supply of heat at the still and the cooling of the reflux balance so nicely that there will not be sudden large drops in column pressure or continued partial vacuum. Such abnormal conditions, if permitted, would of course destroy both the sharpness of fractionation and the accuracy of the reflux temperature readings. It has, therefore, been found necessary to insert still another contact wire in the distillation pressure manometer which functions like the other contacts already described, to actuate a relay, whenever the distillation pressure falls about 4 mm below the distillation pressure. In this case the relay shuts an electromagnet valve in series with the distillate flow line from the fractionating column, thus completely stopping distillation, until the pressure again rises to break contact and to open the valve.

In this way column or distillation pressure is forced to stay between adjustable upper and lower limits. The exact adjustment of the various contacts involved is not critical, although certain definite positions for them have been worked out and found to result in smoothest action and greatest economy in the use of refrigerant. The two electromagnet valves for compressed air control and for distillate flow control, respectively, emit different sounds. As a result the operator can actually hear how well and how smoothly the regulatory mechanism is functioning and can immediately detect a wrong note, although he may be concentrating on some other task.

This distillation shut-off valve also acts as an accessory to the actual distillation-rate regulating valve described below. In other words, at breaks, where there is a tendency for column pressure to drop violently, the distillation shut-off valve shuts off the column for fairly long intervals at a time (because of slow comeback of pressure at breaks), thus giving the column a chance to fractionate out the last traces of the lower-boiling component remaining in the sample. Any operator of the low-temperature fractionating apparatus will appreciate that this valve duplicates human operation in this particular function, but more precisely and with 100 per cent dependability.

Recording and Plotting of Boiling Point and Quantity of Distillate. The fractional-distillation curve, which summarizes the results obtained by low-temperature fractionation is a plot of two series of observations: (1) reflux temperature and (2) pressure in the initially evacuated system receiving the distillate in vapor form. The ordinary temperature recorder, however, plots temperature against time. It was, therefore, necessary to develop means to operate the chart roller of the instrument in exact proportion to the pressure of the vapor-receiving system. A Bourdon-type gage with gear mechanism was not suitable because of its lack of precision and dependability. As will be appreciated by operators of the low-temperature fractionating apparatus, even the enlarged bulb-type barometric manometer used in the Standard Precision model must be read carefully, estimating to tenths of a millimeter, in order to develop the full accuracy of the apparatus.

The mechanism finally adopted as most accurate, dependable, and generally satisfactory consists of a combination of (1) a long slender contact rod with its lower extremity almost but not quite touching the mercury in one arm of a special manometer; (2) a special enlarged-bulb large-bore manometer with a gas-tight mercury-seal stuffing box on the arm in which the rod is inserted, and with the enlarged bulb and connection to vapor-receiving system on the other arm; (3) a carriage provided with a split nut to fit around a vertical threaded rod and with a clamp for the slender contact rod already listed; (4) a low-voltage source and relay circuit completed whenever the contact rod touches the mercury; and (5) an electric motor actuated by the relay when the contact rod touches the mercury and which, through a train of suitable gears and the rotation of the vertical threaded rod in the carriage nut, simultaneously and in exact proportion raises the contact rod and rotates the temperature recorder chart until contact is broken between the contact rod and the mercury. By this action, the contact rod practically floats on the surface of the mercury with barely a 0.1-mm gap, while the temperature recorder chart unrolls in proportion with the rise of mercury and thus plots the fractional distillation curve with much greater exactness than is possible by the method of manual readings of pressure and temperature.

The question of compensation for variation of atmospheric pressure immediately suggests itself, since the manometer used is not of the barometric type. The solution to this problem was found by using a small mercury-seal packing box around the contact rod and by conducting a small tube from this arm of the manometer to a bottle of about 2 gallon (7570 cc) capacity immersed in a constant-temperature water bath. This bottle is initially opened to the atmosphere before analysis is begun and then shut off. Nitrogen may be used in this part of the system to prevent oxidation of mercury. Since the mercury-seal stuffing box is absolutely gas-tight for moderate pressure differences, the left arm of the manometer will remain at constant pressure even if the barometer varies 10 mm or more during the analysis. The capacity of the compensating bottle is made about 2 gallons (7570 cc), in order to minimize the change in pressure in the bottle due to change of mercury level in the manometer.

Finally, it is necessary carefully to calibrate the manometer for nonuniformity of bore and to prepare a chart for correction of the fractional distillation curve both for nonuniformity of bore and for the change in pressures of the vapor-receiving system and of the compensating bottle caused by the change of mercury level in the manometer. The correction chart is used only to correct distances between cut points on the finished distillation curve and its use entails little extra labor. It is possible to prepare correction charts for any combination of manometer and volumes of vapor-receiving bottle system and of compensating bottle, and results corrected with such charts are more accurate than is possible by manual readings and plotting. The chart is made to unroll in the ratio of approximately 1.8 (exact ratio determined by calibration) to the pressure rise in order to give a very open scale on the paper for accurate estimation of cut points. See Figure 18. It should be noted that the abrupt drops in temperature in the butane plateau and beyond are due to lowering of distillation pressure in the usual manner. It has not been found necessary to introduce any device for automatically correcting temperatures for pressure, as the chart can be interpreted without such correction. Re-evacuations are indicated on the chart by long inked lines perpendicular to the pressure axis and followed either by resumption of the plateau or by an abrupt shift of temperature due to change of pressure as just explained.

Distillation Rate Control. In the development of an automatic recording and control apparatus, considerable difficulty was experienced in solving the problem of regulating the distillation rate in approximately inverse proportion to the tendency of the temperature to rise. In other words, according to well-known fractional distillation theory and experience, the rate of distillation should be approximately inversely proportional to the instantaneous tangent of the fractional-distillation curve at any point. (In the case of this apparatus, distillation rate is inversely proportional to reflux ratio.) The manual operator solves the problem by changing the distillation rate in steps and his greatest exercise of skill and judgment consists in the way he makes these changes to get the sharpest breaks in least total time for the distillation.

It was found necessary to develop both a specially externally leakproof very small capacity regulating needle valve and an electrical contact follow-up device to take motion off the temperature-indicating parts of the recorder and to correlate this motion with the motion of the mechanism already described for unrolling the chart roll in such manner that the regulating valve would open (and close) inversely as the tangent of the fractional distillation curve.

In order to be able conveniently and in a practical manner to take motion off the temperature-indicating parts, the recorder must necessarily be of the potentiometer type rather than the millivoltmeter type. In the case of the Brown potentiometer recorder, the spiral pen shaft indicated in the diagram revolves in exact accordance with the rise of temperature. Onto this shaft is therefore fastened an electrical contact follow-up device, very similar to the chart-rolling mechanism already described in that a relay-actuated motor simultaneously keeps the follow-up (more properly, run-away) contact piece out of electrical contact and also operates proportionately one end of a device called the "tangentor". The other end of the tangentor is actuated by the chart-rolling motor. The tangentor itself is simply a male-threaded member engaging a corresponding female threaded member, both constructed so that the male member can travel only a limited distance either upward or downward before it slips out of threads and simply rotates until the relative direction of motion of the two parts is reversed, when the threaded parts again engage.

It will be noted that, essentially, the tangentor takes motion at one end corresponding to the rise of pressure in the vapor-receiving system; while at the other end it takes motion corresponding to the rise of temperature in the reflux. Depending upon the relative speed of rotation of the two motions, the male member of the tangentor moves up or down within its limits of travel, simultaneously opening or closing the regulating needle valve through the means of an arm and fulcrum arrangement. In other words, the opening of the valve is inversely proportional to the tangent of the distillation curve. A sharp rise in the fractional distillation curve, as it is being continuously and instantaneously plotted on the chart, almost immediately closes the valve. A small rise begins to close the valve. When the curve flattens out, the valve opens gradually. The regulation is truly proportional and may be made as sensitive as desired by the use of suitable gear ratios.

It is obvious that the distillation rate cannot be permitted to become zero at any point or the distillation would stop permanently at that point. Therefore, a micrometer adjustment is provided on the valve stem for the exact setting of a definite low rate to provide a minimal flow of distillate at breaks no matter how sharp. Also, there must be some means of regulating the maximum opening of the valve at plateaus; otherwise the capacity of the column might be exceeded. This requirement is met by a variable fulcrum on the arm connecting the tangentor and valve. These adjustments need be changed only when the distillation pressure is changed and to secure different degrees of accuracy or different total times of distillation.

The regulating valve must necessarily be made with great precision. The needle is of the actual dimensions of a medium-sized sewing needle with a seat of corresponding dimensions. In order to compensate completely for the disturbing force developed through difference in atmospheric pressure and in the pressure of the vapor receiving system, two flexible metallic bellows are incorporated in the valve construction as shown. The regulating valve is in series and immediately connected with the electromagnet shut-off valve.

In order to assist in the adjustment of the regulating valve and also to have a complete record of the functioning of the regulating means and of the entire automatic apparatus, an auxiliary pen on the recorder (towards the right of the chart) is made to jog every 75 seconds through a gear and cam mechanism operated by the recorder motor, as shown in Figure 13. This curve (Figure 18) shows the remarkably sensitive and more than human response of the regulating valve to every slight wiggle of the reflux temperature.

Certain noncontinuous functions, such as the actual entering of the sample, change of distillation pressure, re-evacuation of distillate receiver, use of fraction-collecting burets, etc, cannot be made completely automatic without undue complication of apparatus. Automatic signals are therefore incorporated in the apparatus so as completely to free the human operator from the necessity of attending the apparatus until the robot operator summons him by a loud buzz and then further indicates the reason for the summons.

The signals used are the following, as indicated over the corresponding trouble lights:

Reduce Distillation Pressure. When reflux temperature approaches room temperature, an electrical contact on the frame of the recorder operates to sound the buzzer and to light the red trouble light bearing the label as stated.

Re-evacuate. When the pressure in the vapor-receiving system reaches the maximum permissible for the hydrocarbon distilled, or when it approaches distillation pressure, an electrical contact device located on the smooth guide rod next to the threaded rod is actuated by the rise of the contact rod carriage to sound the warning buzzer and to light another red trouble light.

Check Reflux. This signal summons the operator when, for any reason, the cooling of the reflux becomes imperative.

Discussion

Figure 18 illustrates the results secured with automatic operation in the analysis of a natural gas. The presence of air or nitrogen is evidenced by the unduly low temperature and disturbances in the first portion of the methane plateau. The distillation rate or jog curve indicates the extremely sensitive and truly proportional regulation of distillation rate effected by the automatic control. As a result, the breaks of the curve are extremely sharp, considering that the curve is plotted on a pressure scale almost double the actual pressure rise. The chart itself is a standard 12-inch roll chart available for use with the Brown potentiometer recorder. (The recorder itself has been considerably modified.) Similarly, sharp curves may be secured for the distillation of natural gasoline, motor fuel, absorption oil, or other samples suitable for analysis in the low-temperature fractionating apparatus.

The automatic apparatus is inherently more positive and accurate than the human operator, as shown in Table IV which gives a comparison of various analyses run in duplicate both by the robot and by a skilled human operator.

The saving of time on the part of the operator using automatic operation is very material. During its period of operation, the apparatus is from 80 to 90 per cent automatic, and the operator is free to do other work so long as he is within hailing distance of the automatic operator. The automatic apparatus plots the complete distillation curve in finished form and thereby saves the operator about an hour's time in plotting his readings and drawing the distillation curve. Automatic operation is inherently more efficient, so that the total time of distillation required to get results of any required accuracy is decreased considerably over that possible with even the most skilled human operation. For similar reasons the consumption of liquid nitrogen is reduced 15 to 20 per cent.

In spite of the number and complexity of the functions it performs, the automatic apparatus is neither a very complicated nor a

TABLE IV

Typical Check Analyses with Automatic Control and Recording Apparatus

	Automatic Operation				Manual Operation
	First Run		Second Run		
Methane and lighter	64.99		64.95		65.1
Ethane	16.60		16.53		16.7
Propane	11.53		11.44		11.5
Isobutane	1.14		1.18		1.0
n-Butane	2.93		3.05		...
Pentanes	1.51	2.81	1.60	2.85	... 2.8
Hexanes and heavier	1.30		1.25		
	100.00		100.00		100.0

delicate mechanism. The component parts (except the potentiometer recorder) are mostly gears, bearings, electric motors, telephone-type relays, etc, which in themselves are sturdy and not likely to cause trouble. The needle-regulating valve is not subject to action which would tend to damage in any way. The electromagnet valves are of very simple construction. Leaks must of course not be present, as they would destroy the accuracy of the apparatus. However, the presence of leaks would be indicated on the plotted distillation curve. The practical usefulness of automatic operation would be considerably diminished if more trouble developed through it than naturally occurs with the distillation unit, but experience in the author's laboratory has shown that this possibility is not an actual one.

Influence on Standardization. The automatic recording and control apparatus represents a standardization of factor 3 for low-temperature fractionations. The operator merely decides approximately what total time of distillation he desires and fixes a few adjustments on the controlling apparatus, with the assurance that the operation will give him a near approach to the best results possible for the particular fractionating unit and for the total distillation time used. The printed curve chart is unbiased, includes a check on the functioning of the distillation control in the form of a distillation time rate curve, and is in ideal form for inspection and criticism and for future reference. The curve is a complete record of the distillation and even reveals the possible poor functioning of the automat due to improper adjustments, leaks, or other troubles. Analyses run on the same sample in different laboratories by different operators but with the same apparatus and main adjustments should yield practically identical curves and results.

It remains to consider the standardization of decisions and functions not taken care of by the automatic apparatus which may be listed as follows:

1. Design of fractionating unit proper
2. Size of sample
3. Entering sample
4. Completing distillation
5. Automatic adjustments
    a. Contacts in distillation pressure manometer
    b. Distillation regulating valve adjustments
    c. Compressed air needle-valve adjustment
6. Choice of distilling tube and bulb on fractionating column of distillation unit
7. Manipulation of mercury seal and supply of heat to distilling bulb
8. General preparation and maintenance of distillation unit, involving evacuation, checking for leaks, cleaning, greasing stopcocks, etc.

9. General preparation and maintenance of automatic recording and control unit involving cleaning contacts, oiling and greasing, when required, servicing, etc.

10. Miscellaneous

Fractionating unit design 1 has been discussed above. Any instrument, whether automatic or not, will require such preparation and care as are outlined in 8 and 9. The comparatively simple functions 3, 4, and 7 are readily standardized, and 2, 5, and 6 may be standardized by the preparation and use of a suitable standardization chart, taking into account the accuracy required, total time of distillation, etc. In this way substantially complete standardization of the low-temperature fractionating apparatus and its operation may be effected.

Detailed Description of Parts

The following additional descriptions of the parts not included in Podbielniak's article are presented here for the assistance of future operators.

Reflux Cooling. The following components comprised the reflux cooling controls.

Column Manometer. Glass U-tube. Specifications: 4 mm inside diameter, 100 cm long, mounted on a wooden meter stick. Mercury used as a manometer fluid. Obtained from Podbielniak Company, Chicago, Illinois, as part of the original apparatus. Used to measure and control the distillation pressure.

Contact Wire. Insulated thermocouple wire. Specifications: Iron wire, No. 30 B. S. gauge, asbestos insulated. Supplied by Leeds and Northrup Company, Philadelphia, Pa. Used as contact wire in column manometer.

Needle Valve. Specifications: Stainless steel, 1/4 inch ports, standard pipe threads. The valve was donated by Socony Mobil Oil Refinery, East St. Louis, Illinois. Used to regulate air pressure to the thermos bottle.

Solenoid Valve. Specifications: Steel, 1/4 inch ports, standard pipe threads, contained 1/8 inch needle valve in outlet port. Solenoid requirements: continuous operation, 110 volts, 50 to 60 cycles, temperature rise 40°C, air cooled. Obtained as part of the original apparatus. Used to control air flow to the thermos bottle.

Thermos Bottle. Specifications: pyrex, constricted neck, double walls, evacuated, fully silvered. Capacity - 845 ml, length 11-1/2 inches, O.D. - 3 1/4 inches. Supplier - Schaar and Company, Chicago, Illinois. Used to store liquid nitrogen.

Dewar Flask. Specifications: pyrex, fully silvered, evacuated double wall container, capacity 665 ml, cylindrical shape. Supplier - Schaar and Company, Chicago, Illinois. Used to cool the sample bulb as shown in Figure 2, page .

Column Heater. The following components comprised the column heater control.

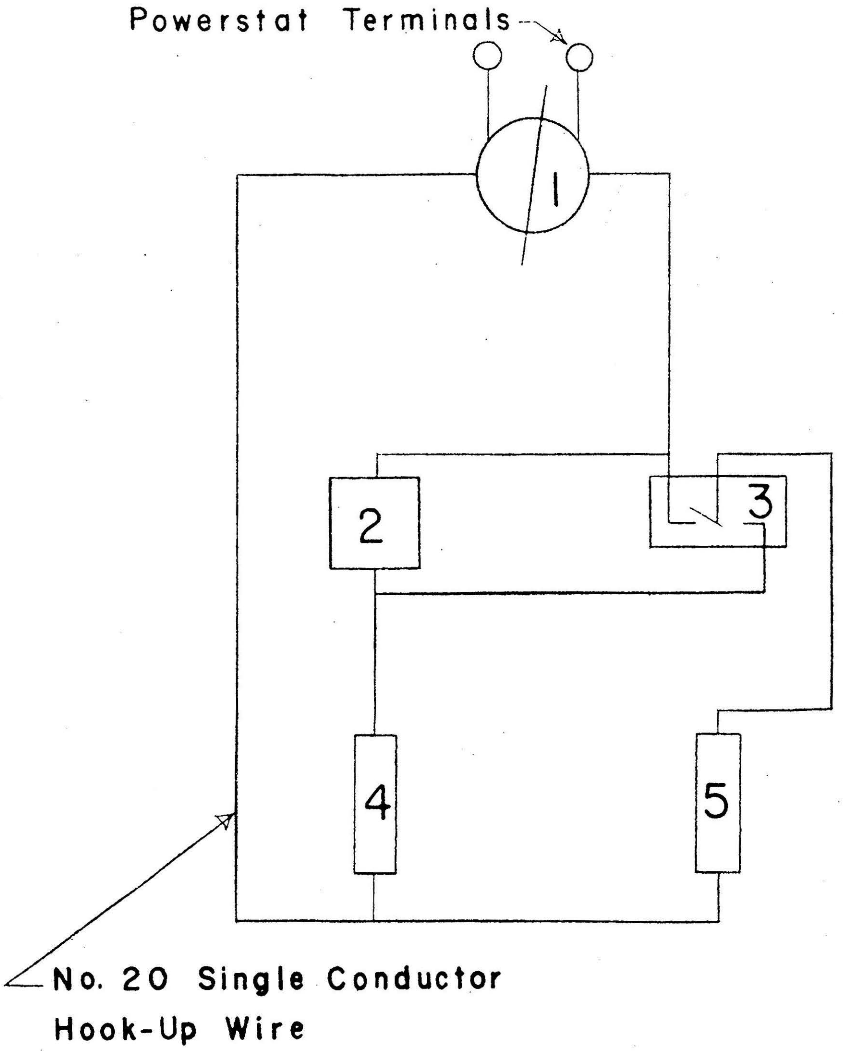
Ammeter. Tripolett. Glass front panel meter. Specifications: A. C. meter, double iron repulsion type, jeweled bearings and hardened alloy steel pivots, metal dial face finished in white enamel, enclosed in molded plastic case. Size 2-1/2 inch square. Range - 0 to 2 amps. Accuracy - 2 per cent full scale. Supplier: Allied Radio Corporation, Chicago, Illinois. Used to indicate heat input to column.

Nichrome Heater Coil. No. X3090. Specifications: 30 B. S. gauge wire, 7/32 O.D. coil, 85 ohms, 90 watts maximum. Manufactured by Waage Manufacturing Company, Chicago, Illinois. Used to supply heat to the sample bulb.

Parallel Resistor. Rheostat. Specifications: Nichrome wire wound on ceramic base, air cooled, 3 amps, maximum, 45 ohms. Supplier: Cenco Company, Chicago, Illinois. Used to allow accurate amperage measurements at high and low heat input.

Powerstat. Type 116. Specifications: Primary - 115 volts, 50 to 60 cycle, out range 1 KVA maximum, 7.5 amp maximum, 0 to 135 volts. Manufactured by the Superior Electric Company, Bristol, Conn. Used to control heat input to column heater.

Switch Knife. Single pole, double throw. Specifications: 15 amps, 125 volts. Supplier: Cenco Company, Chicago, Illinois. Used to connect the ammeter in series or parallel with the column heater. See Figure 19.



LEGEND

1 - Powerstat
2 - Ammeter
3 - Double Throw Switch
4 - 45 Ohm Variable Rheostat
5 - Nichrome Wire Column Heater

DEPARTMENT OF CHEMICAL ENGINEERING
MISSOURI SCHOOL OF MINES & METALLURGY
ROLLA, MISSOURI

Schematic Circuit Diagram of The Column Heater

SCALE: None DATE
DRAWN BY: R.B RB 5/12/58
CHECKED BY: JHE 5/13/58
APPROVED BY: JHE 5/13/58

CASE NO: 58
FILE NO: 490
FIGURE NO: 19
SHEET NO: 1

Distillation Shut-Off Control. The following components comprise the distillation shut-off control.

Bellows Assembly. The metal bellows was obtained from the thermostat of a 1950 model Buick automobile. The frame of the thermostat was removed and a 1/4 inch brass ferrule type, male fitting was soldered to the stem of the thermostat. The bellows was connected to the solenoid valve by 1/4 inch copper tubing. The assembly was built by the author. The bellows was used to actuate the distillation shut-off valve by pneumatic means.

Distillation Shut-Off Valve. Specifications: Brass, 1/16 inch ports, soldered connections, neoprene seat, stainless steel valve stem. Obtained as part of original apparatus. Used for stopping the flow of vapors from the column.

Solenoid Valve. Same as described under reflux cooling control.

Recording. The following components produced the distillation diagrams.

Potentiometer. Brown mechanical recording potentiometer, Model 1161, Serial No. 152064, Power requirements, 110 volts, 60 cycle. The potentiometer was part of the original apparatus. Used to record temperature.

Thermocouple. Copper-constantan. Specifications: No. 30 B. S. gauge wire, asbestos insulated, welded junction. Donated by Socony Mobil Oil Refinery, East St. Louis, Illinois. Used as sensing element to messure the temperature in the reflux chamber.

Chart Drive. The chart drive mechanism was identical to the original control described by Podbielniak.

Air Supply and Control. The air was obtained from the supply line in the laboratory. The line pressure was 60 pounds per square inch gauge which was too high for use at the apparatus. The following components comprised the pressure regulation and control equipment.

Air Drying Chamber. Constructed from standard pipe and fittings as shown in Figure 20. A piece of wire screen was inserted in the bottom reducing bushing to support the activated alumina adsorbing agent.

Globe Valve. Specifications: Brass, 1/4" ports, standard pipe thread connections. Supplier: Crane Company, St. Louis, Missouri.

Needle Valve. Specifications: All brass, 1/8 inch I P male threaded connections, V-shaped needle. Supplier: Fisher Scientific, St. Louis, Missouri.

Pressure Regulator. Hoke-Phoenix diaphram valve. Specifications: 1/4 inch ports, standard pipe threads, 2 inch rubber diaphram. Distributor: Fisher Scientific Company, St. Louis, Mo.

Water Trap. Constructed from standard pipe fittings as shown in Figure 21.

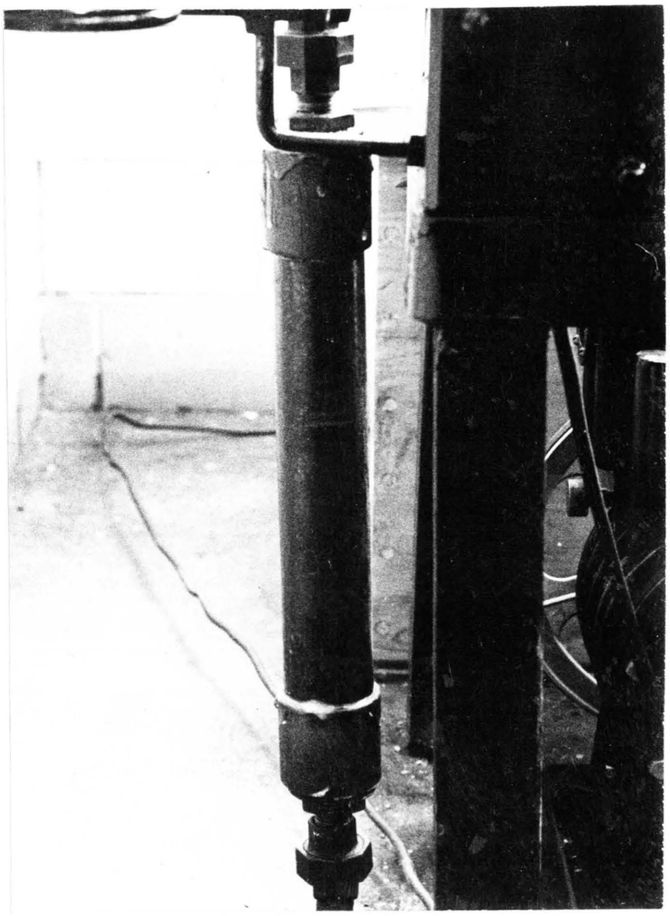
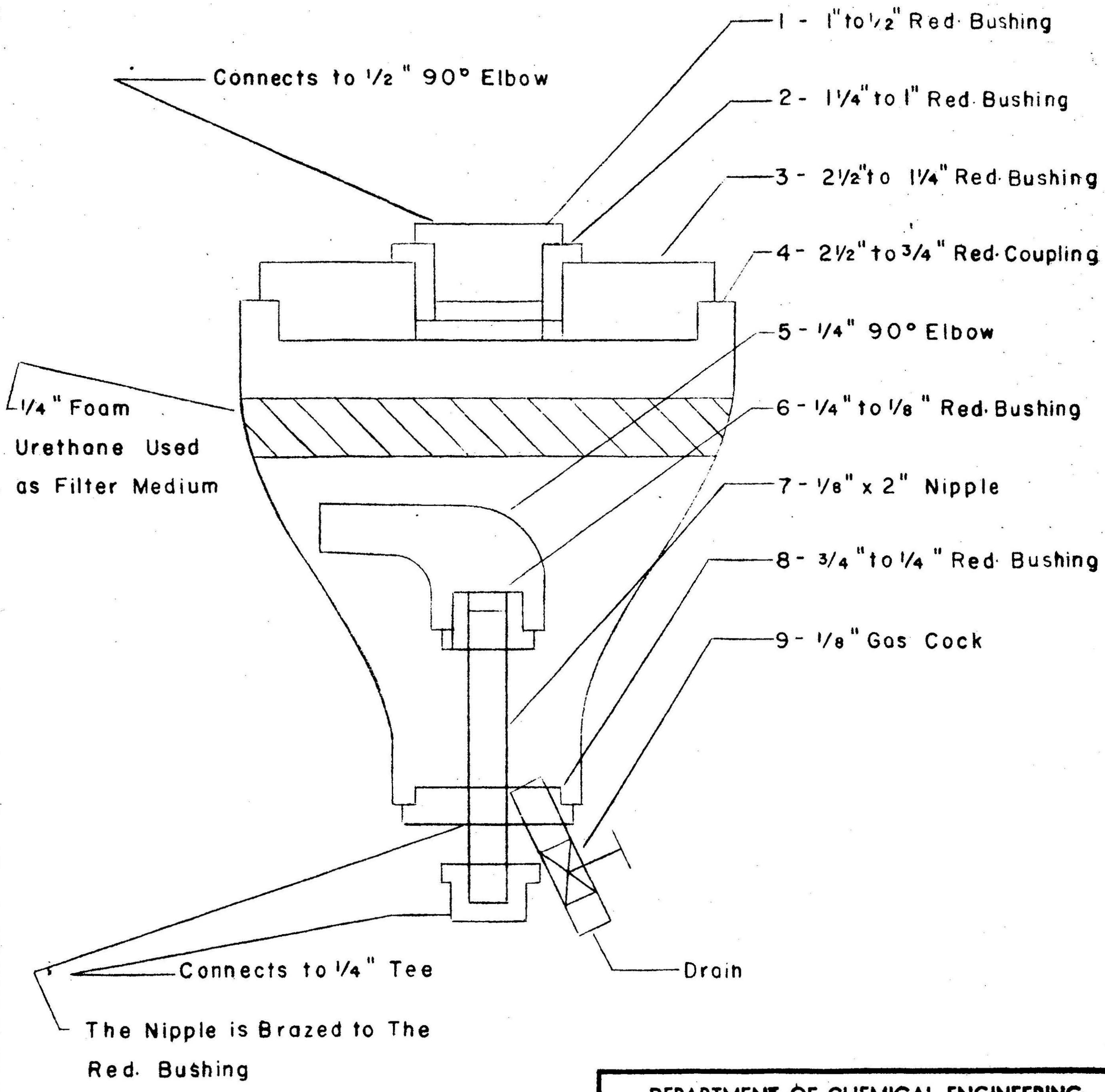


Figure 20. Air Drying Chamber.



DEPARTMENT OF CHEMICAL ENGINEERING
MISSOURI SCHOOL OF MINES & METALLURGY
ROLLA, MISSOURI

Schematic Drawing of
Water Trap

SCALE: None
DRAWN BY: R. B. B
CHECKED BY: JHC
APPROVED BY: JHC

DATE
5/12/58
5/13/58
5/13/58

CASE NO: 58
FILE NO: 490
FIGURE NO: 21
SHEET NO: 1

Assembly. The component parts were assembled with 1/2 inch pipe, and standard fittings.

Vacuum Pump. Pump, Dual-Seal, Serial No. 9944. Specifications: less than 0.1 micron of mercury pressure, continuous operation. Manufactured by W. M. Welch Manufacturing Company, Chicago, Illinois. Used to evacuate the column and receiving bottles.

Sample Apparatus. The sample container was constructed from schedule 80-, 1-1/2 inch pipe, 1/4 inch pipe nipples, and 1/2 inch stainless steel, needle valves, as shown in Figure 22.

The sample entrance apparatus was constructed from two one-gallon bottles, sealed by rubber stoppers and connected with rubber tubing so that the solution can be siphoned back and forth between the bottles as shown in Figure 23. The bottle connected to the three way stopcock was named the entrance bottle and the other was named the auxiliary bottle. The bottles were filled with a five per cent water solution of sodium sulfate. The three way stopcock directed the vapor flow either into the entrance bottle or to the atmosphere. The sample apparatus was borrowed from Socony Mobil Oil Refinery, East St. Louis, Illinois. Used to introduce samples from the containers into the column.

Accessories. Accessories such as bolts, nuts, paint, pipes, screws, and rubber tubing were obtained from the supply room of the Chemical Engineering Department or from the school warehouse. Copper tubing and hook-up wire were obtained from outside sources.

Figure 22. Sample Container.

Figure 23. Sample Entrance Bottles.

Copper Tubing. Specifications: 3/32 of an inch O D, 1/32 of an inch wall thickness, 25 foot coil. Donated by Lewin-Mathes Corporation, St. Louis, Missouri. Used to connect receiving bottles to the manifold.

Wire. Specifications: (1) No. 20 stranded, one conductor, tinned copper hook-up wire, black polyvinylchloride insulation. 25 feet. (2) No. 22 stranded cable, four conductor tinned copper hook-up wire, color coded, polyvinylchloride insulation. 25 feet and (3) No. 18 stranded, 2 conductor, copper wire, brown rubber insulation. 25 feet. Supplier: Allied Radio Corporation, Chicago, Illinois. The wire was used to construct the electrical circuit of the apparatus.

APPENDIX II

Appendix II contains the detailed procedure not included in the Experimental section.

Sample Entrance. The procedure is divided into two parts, (1) transfer of sample from the sample container to the entrance bottle, and (2) transfer of vapors from the entrance bottle to the column. Photographs of the operation are included to clarify the description.

Part One. The procedure is described in numerical sequence,

(1) Fill the sample entrance bottle with solution from the auxiliary bottle, and place the bottles as shown in Figure 24;

(2) Connect the bottom port of the sample container to the rubber tube of the entrance bottle;

(3) Turn the three way stopcock of the entrance bottle to vent to the atmosphere;

(4) Open slightly the needle valve at the bottom of the sample container, so that the liquid sample leaving the container is vaporized;

(5) Turn the stopcock to vent the vapors into the sample entrance bottle;

(6) After 2000 milliliters of vapor have entered the entrance bottle (when the solution level is at second tape marking ring) rotate the stopcock 45 degrees, so that all ports are closed;

Figure 24. Transfer of Sample from The Sample Container to The Entrance Bottle.

(7) Disconnect the sample container from the rubber tube; and

(8) Close the valve on the sample container.

Precaution: Part One operation should be performed in a well ventilated area posted with no smoking signs.

Part Two: Procedure is performed in numerical sequence,

(1) Check to insure that the manifold stopcocks are in the following positions:

Stopcock	Position
A	Open to stopcocks C, D, E, and J.
B	Connect port 2 to port 1 and stopcock D, but not C.
C, F, E, and H	Closed
D	Open to stopcock B
E	Open to stopcocks A and J
J	Open to stopcocks A and E;

(2) Place entrance and auxiliary bottles as shown in Figure 25;

(3) Connect rubber tube of entrance bottle to drying tube containing Ascarite, and connect the drying tube to the bottom part of the column's three way stopcock, which is opened only to the top and bottom ports.

(4) Connect the top port of the column's three way stopcock to port 6 of the manifold with rubber tubing;

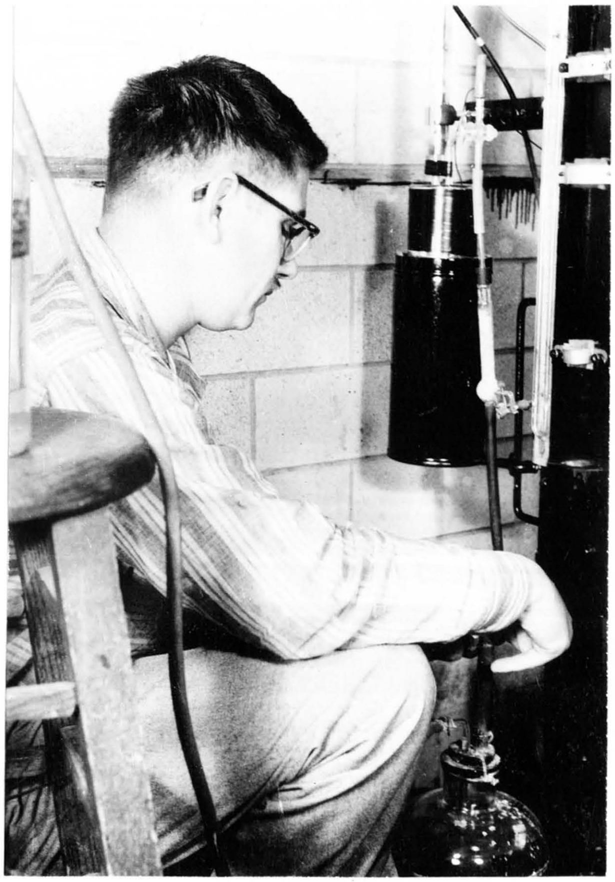


Figure 25. Transfer of The Sample from The Entrance Bottle into The Column.

(5) Apply vacuum to the line connecting the entrance bottle and the column by rotating stopcock C of the manifold to open to port 6;

(6) After evacuating, rotate the column's three way stopcock 90 degrees, so that the column's sample bulb immersed in liquid nitrogen is connected to the entrance bottle's line and the vacuum is disconnected;

(7) Close vacuum stopcock C of the manifold;

(8) Rotate entrance bottle stopcock slowly 45 degrees so that the sample bulb is connected to the entrance bottle, the difference in liquid level between the sample bottle and auxiliary bottle forces the vapors into the sample bulb where they are condensed, and the entrance of the vapors is controlled by positioning the entrance bottle stopcock so that the pressure in the column manometer does not rise more than ten centimeters;

(9) Close the entrance bottle stopcock when the level of the solution in the bottle is 1/4 inch from the rubber stopper;

(10) Rotate the column stopcock 45 degrees to close all three ports;

(11) Disconnect the entrance apparatus and the vacuum line and remove the equipment from the working area, and the distillation is ready to begin.

Ethanol Entrance. At the end of the distillation all pentane vapors are forced out of the distillation column, so that the end of the distillation can be determined. Ethyl alcohol is added to fill the column with vapors; thereby maintaining the distillation pressure as the pentane is distilled from the column. Since ethanol boils at 55 degrees centigrade at 300 millimeters of mercury, a sharp rise in temperature recorded on the strip chart indicates the end of the distillation.

The procedure is performed in numerical sequence,

(1) The top port of the column's stopcock was connected to a rubber squeeze bulb by rubber tubing;

(2) The bottom port of the column's stopcock was immersed into 50 milliliters of alcohol contained in a 150 milliliter beaker.

(3) The column's stopcock was rotated, so that only the top and bottom ports were connected;

(4) The alcohol (free of air) was drawn above the level of the stopcock by applying vacuum with the squeeze bulb; see Figure 26;

(5) The column stopcock is rotated slowly 90 degrees connecting the bottom port and the column;

(6) After a small quantity (approximately five milliliters) enters the column the stopcock is rotated back to the position in "step 3", and the alcohol above the stopcock is drained into the beaker.

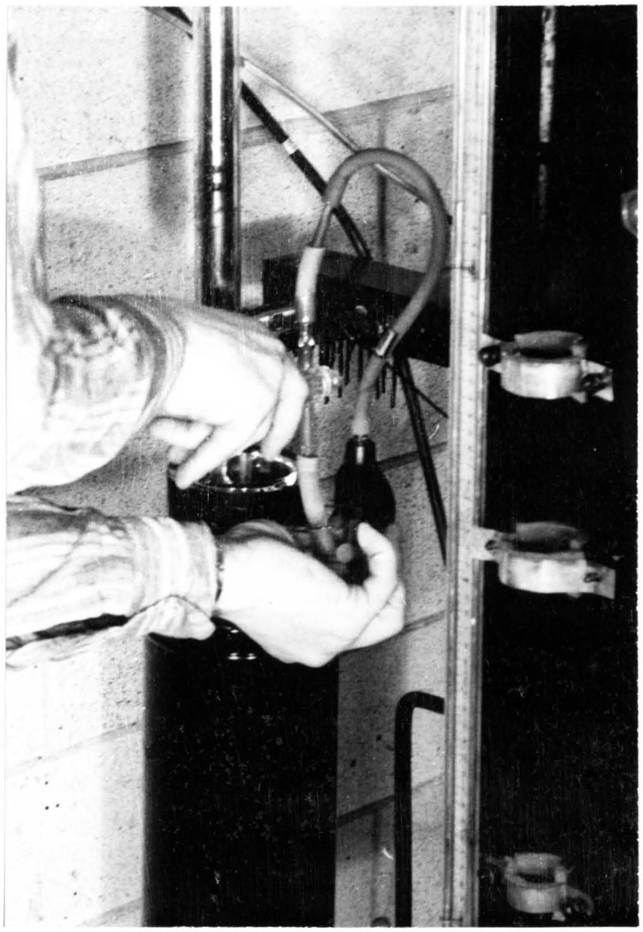


Figure 26. Entrance of Ethanol into The Column.

(7) The stopcock is rotated 45 degrees, so that all ports are closed;

(8) The squeeze bulb and beaker are removed from the stopcock ports.

Ethanol Removal. When the distillation is completed the alcohol is removed from the column according to the following procedure,

(1) The bottom port of the column's three way stopcock is connected to a 250 milliliter glass, side tube, filter flask with rubber tubing;

(2) The filter flask is connected to port 6 of the manifold;

(3) Stopcock C is opened to port 6;

(4) The column's stopcock is rotated, so that only the sample bulb and the bottom port are connected, and the ethanol is transferred to the filter flask;

(5) The column's stopcock is rotated clockwise 90 degrees;

(6) Stopcock C is rotated 90 degrees counterclockwise, and the filter flask is disconnected;

(7) Stopcock B is rotated clockwise 180 degrees, so that air is drawn through the column to remove the ethanol vapors.

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Raymond Bauer