

THE INFLUENCE OF VARIOUS MOLECULAR STRUCTURES
ON THE ELIMINATION MAXIMUM OF FATTY ACIDS

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Thesis submitted to the Graduate Faculty of the
Virginia Polytechnic Institute
in candidacy for the degree of

DOCTOR OF PHILOSOPHY

in

Chemical Engineering

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June, 1955

Blacksburg, Virginia

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I. INTRODUCTION

The vacuum distillation of heat-sensitive substances such as organic oils, dyes, and drugs requires special equipment from that available for atmospheric distillation. Study in the resulting field, high vacuum distillation, has subsequently led to the development of such equipment. Three types of high vacuum distillation and distillation equipment are recognized: conventional distillation, unobstructed-path distillation, and molecular distillation. Conventional vacuum distillation employs standard equipment under relatively high vacuum conditions. For unobstructed-path distillation, the equipment is modified so that the vapor path between the evaporating and condensing surfaces is clear.

When the vapor path is unobstructed and the condenser is separated from the evaporator by a distance less than the mean free path of the evaporating molecules, the phenomenon is called molecular distillation. Molecular distillation is the limiting type of high vacuum distillation with the absolute pressure range approximately 1 to 7 microns of mercury. The use of the centrifugal molecular still permits the distillation of organic substances which might suffer thermal decomposition even under the conditions of the conventional high vacuum still. Against the

advantages of prevention of thermal decomposition and shorter time requirements must be placed the poor separatory power of distillation and the necessity of numerous redistillations. The molecular still is valuable not because it gives good separation but because distillation is accomplished 50 to 250 degrees centigrade below temperatures of conventional atmospheric distillation.

In ideal molecular distillation, equilibrium does not exist between the vapor and the liquid, no molecules reenter the distilland after once being vaporized. Under these ideal conditions, Langmuir's equation predicts that the quantity of a given material distilling at a given temperature is proportional to P/\sqrt{M} where P is the vapor pressure and M is the molecular weight. Previous investigations at the Virginia Polytechnic Institute and other laboratories substantiate the importance of molecular weight and structure. Since most of these investigations have been only exploratory, insufficient work has been done to permit any conclusions of major importance.

The purpose of this investigation was to determine the effects of various molecular structures of fatty acids on their distillation characteristics when distilled in a laboratory-size centrifugal molecular still. Saturated

(C₁₅, C₁₆, C₁₇, C₁₈, C₁₉, and C₂₀) and unsaturated (C₁₈ with one, two, and three double bonds) fatty acids were used in the study. Such effects as the chain length, presence of double bonds and their position in the molecule, and cis-trans and positional isomerism were studied.

II. LITERATURE REVIEW

A review of the available literature was made to gain an understanding of the development and operation of molecular distillation. The terminology, development, theory, performance, and evaluation of still performance of molecular distillation will be considered.

Terminology of Molecular Distillation

The terminology of molecular distillation and differences between ordinary distillation, normal high-vacuum distillation, and molecular distillation are considered through definition and explanation of the special nomenclature of the field.

Distillation. Carey⁽²⁹⁾ defines distillation as "the separation of the constituents of a liquid mixture by partial vaporization of the mixture and separate recovery of vapor and residue. The more volatile constituents of the original mixture are obtained in increased concentration in the vapor; the less volatile in greater concentration in the liquid residue." In general, the term, distillation, is applied to any vaporization process in which the vapor evolved is recovered, usually by condensation.

High-vacuum Distillation. Hickman⁽⁵¹⁾ defines three broad classes of high-vacuum distillation according to the method and equipment employed: (1) conventional or nearly conventional apparatus, generally consisting of a boiler, fractionating column, and condenser, operated under high vacuum; (2) unobstructed-path distillation operated under high or nearly high vacuum; and (3) molecular distillation or "projective distillation" where the vapor path is unobstructed and the condenser is separated from the evaporator by a distance less than the mean free path of the evaporating molecules. Thus, only one class of high-vacuum distillation can actually be considered as true molecular distillation while the others are merely approaches to molecular distillation.

Molecular Distillation. Molecular distillation received its name from the fact that vaporization is carried out under such vacuum that almost every molecule travels toward the condensing surface unhindered by the presence of other molecules. There is a minimum return of once-vaporized molecules to the main body of the liquid. As in other high-vacuum distillation, only the molecules at the evaporating surface enter into the process, and, at any given instant, all other molecules in the bulk of the distilland need not be considered as part of the distilling process except as they replace the evaporating molecules⁽¹⁷⁾.

Trouble arises with the "spontaneous refusal of liquids to evaporate at rates and temperatures appropriate to them" due to the repressive "skin" layer of surface molecules. This has resulted in the development of falling-film and centrifugal molecular stills to prevent the sudden explosion of the repressive skin as in the vacuum pot still.

Basic Differences in Distillation Processes. In conventional distillation processes⁽²⁹⁾, distillation begins at a well-defined temperature, the material being distilled has a definite boiling point, and the distillation process is accomplished by ebullition or boiling of the distilland. A dynamic equilibrium exists between the liquid and vapor phases causing a large proportion of the molecules evaporating from the liquid surface to return to the same liquid surface.

On the other hand, in high-vacuum distillation processes, there is no well-defined temperature at which distillation begins. Some distillation occurs at any temperature as long as a thermal gradient exists between the condenser and the evaporator. Due to the high vacuum maintained during the process, there is effectively no superincumbent air pressure on the material being distilled and, consequently, there is no well-defined boiling point or attending ebullition of the distilland. The distilling vapor molecules pass directly from the vaporizing surface to the

condensing surface without having to pass through a barrier of gas molecules. The number of distilling molecules returning to the liquid phase can be considered insignificant in comparison to conventional distillation. As a consequence, dynamic equilibrium between vapor and liquid cannot exist during high-vacuum distillation. Molecular distillation has therefore also become known as "nonequilibrant" distillation.

High Vacuum. Hickman⁽⁵¹⁾ considered "high vacuum" as the existence of a pressure of residual gas so low that further reduction does not change the performance of the apparatus. Andersen⁽¹⁾ has also suggested a more restrictive meaning for high vacuum than it has in ordinary usage in that "high vacuum" should be considered to exist only when the pressure is sufficiently low that the mean free path of the vapor molecules in the residual gas is of the same magnitude as the size of the container. It is apparent that what might constitute high vacuum in one piece of equipment does not necessarily constitute high vacuum in another. For example, in a vessel one foot in diameter, the absolute pressure may be as much as 0.2 micron while for a vessel ten feet in diameter, the pressure must be less than 0.02 micron. Such a definition of high vacuum would limit it to molecular distillation as vessels in this field are generally of the magnitude of the mean free path of the distilling molecules.

The units of pressure adopted for high-vacuum work are millimeters of mercury and microns of mercury, one millimeter equal to 1000 microns. Molecular distillation is generally conducted at pressures of 1 to 7 microns of mercury with industrial molecular distillation employing an absolute pressure of about 3 microns as the economical level below which the added cost of vacuum equipment and operation is not warranted by the benefits that result.

Distillability. The rate of distillation of a substance is roughly proportional to its concentration and its vapor pressure for conventional distillation. For molecular distillation, the rate of distillation is proportional to the product of the number of molecules and the probability that any molecule will distill⁽⁴³⁾. This probability or tendency to distill is called the "distillability". The "distillability" has also been defined "as the ratio of the number of molecules of a given species leaving the distilling surface in any small interval compared with the number of similar molecules remaining undistilled in the surface layer during the same interval"⁽⁵⁴⁾.

Mean Free Path. Glasstone⁽⁴⁹⁾ defines the mean free path of a molecule as the average distance a molecule moves between two successive paths or successive collisions. Since molecular distillation tends to reduce collisions between molecules

(increase the mean free path) by use of high vacuum, the theory of the mean free path is most important in this field.

Maxwell's expression⁽⁴⁹⁾ for the calculation of the mean free path is:

$$l = \frac{V}{\pi \sqrt{2} N \sigma^2}$$

where:

- l = mean free path, centimeters
- N = Avagadro's number, 6.06×10^{23}
- V = volume of one gram mol of the gas at the existing pressure, cubic centimeters
- σ = average diameter of a gas molecule, 2×10^{-8} centimeters
- π = a constant.

This expression takes into account the relationship between relative velocity and actual velocity when a number of molecules all in motion are present, but is limited by the assumption of an average diameter for all the gas molecules.

Distilland, Distillate, and Residue. In molecular distillation, the feed mixture to be distilled is referred to as the "distilland". The "distillate" is that portion of the "distilland" removed as vapor and condensed, and the "residue" is the undistilled portion of the "distilland".

Development of Molecular Distillation

Although molecular distillation had been, until the past two decades, a laboratory technique used exclusively for research, it has since been extended to the processing of industrial chemicals at rates approximating a million gallons annually⁽⁶¹⁾. Numerous bibliographical references^(40,41,59,85) to the development of molecular distillation are available.

Historical. The need for a better type of still for recovery of organic chemicals became evident to chemists in the period from 1910 to 1925, when substances of higher molecular weights and boiling points were coming under study⁽⁵²⁾. Bronsted and von Hevesy⁽⁴⁾ appear to have designed the first molecular still in 1922 to separate the isotopes of mercury. The first application of molecular distillation to organic chemicals, and the first comprehensive statement of the potentialities of the operation were made by Burch^(25,26) in England. Both Waterman⁽⁸⁸⁾, who applied molecular distillation to labile substances in Holland, and Washburn⁽⁸⁷⁾, who employed the technique in the United States, were responsible for important early developments in molecular distillation.

Following the pioneer laboratory development of molecular distillation in the early 1920's, the Eastman Kodak Company undertook considerable development work in the 1930's in

relation to a high-vacuum process for the drying of photographic film. This work led to the development of high-vacuum condensation and fractionating pumps, the lack of which had hindered the progress of molecular distillation. In 1934, the Eastman Kodak Company joined with General Mills, Incorporated, to organize a joint subsidiary, Distillation Products, Incorporated, for the processing of oil soluble vitamin concentrate by molecular distillation. The first industrial use of molecular distillation was the separation of vitamins A and E from marine and vegetable oils.

Types of Stills and Their Development. As more efficient stills were developed from the crude pot stills employed by the first experimenters, it became evident that molecular distillation would find valuable applications beyond the relatively narrow confines of the vitamin industry. The development of the molecular still has progressed through three prominent stages⁽⁵²⁾: (1) the pot still with a "boiling" flask similar to that employed in conventional distillation but operating under high vacuum and with a condenser relatively close to the "boiling" flask, (2) the falling-film still where the distilland is metered to the vacuum chamber, degassed, and allowed to pass in a thin film down the walls of the evaporator, and (3) the centrifugal still where the distilland is metered to

and passes over a rotor generally housed in a bell jar and supported on a shaft to the motor drive. Table I, page 13, shows the transition from the earliest pot still to the centrifugal stills giving the approximate dates when each type of still was developed and the film thicknesses and times of thermal exposure encountered in each still.

Distillation Products, Incorporated, has offered for sale large centrifugal stills designed to handle 50 to 250 gallons per hour of oils or heavy chemicals⁽⁶⁴⁾. These stills utilize a rotating evaporator five feet in diameter. Separatory distillation is reputed to be from two to three times better than that obtainable from a pot-type still.

Applications of Molecular Distillation. Molecular distillation has rendered distillable a whole category of substances, natural and synthetic, which could not be distilled otherwise because of thermal decomposition at the high temperatures required. The range of usefulness of the molecular still is for organic chemicals of molecular weights between 250 and 1200 with a lower range if much oxygen, sulfur, or halogens are present in the molecules⁽⁶²⁾.

It would be impracticable to attempt to give a complete list of all the specific applications of molecular distillation which have been reported. However, a list of materials to which the

TABLE I

Transition from Pet Still to Centrifugal Still

Approximate Date	Type of Still	Approximate Distilland Thickness ^a	Molecular Thickness ^b	Approximate Time of Exposure
1922	Laboratory Pet Still	1-5 cm	5×10^7	1-5 hr
1928	Laboratory Tray Still	0.1-1 cm	5×10^6	5-60 min
1930	Laboratory Falling-Film Still	0.1-0.3 mm	5×10^4	10-50 sec
1935	Industrial Falling-Film Still	1-3 mm	5×10^5	2-10 min
1936	Laboratory Centrifugal Still	0.01-0.02 mm	3×10^3	0.04-0.08 sec
1940	Industrial Centrifugal Still	0.03-0.06 mm	1×10^4	0.1-1 sec
1942	High-Speed Centrifugal Rim Still	0.001-0.005 mm	4×10^2	0.001-0.005 sec

^a Assuming similar throughput for same unit area of all stills.

^b Assuming that the molecule of glyceride fat has an effective diameter of 15 Å.

Hickman, K. C. D.: "Science in Progress," p. 217. Yale University Press, New Haven, Connecticut, 1945. Fourth Series.

technique has been applied might be classified under the following headings⁽⁴¹⁾:

Vegetable, animal, and marine oils for edible and drying
oil purposes

Solid fats

Petroleum oils and jellies

Long-chain hydrocarbons

Aromatic hydrocarbons and derivatives

Vegetable and fruit waxes

Carbohydrates

Vitamins

Sterols and sterol esters

Hormones

Saponins

Amino acids, polypeptides, and derivatives

Condensation polymers

Phthaloyl esters

Dyes

Drugs

Miscellaneous substances such as digitonin, cholanic acid,
querbrachol, fungoid growths, and others.

Further information on the application of molecular distillation can be found in the abstracts of Detwiler and Markley^(41,42)

and Todd⁽⁸³⁾, and the bibliographies of Hickman⁽⁵⁹⁾, Blasco⁽³⁾, Burch⁽²⁷⁾, Fawcett⁽⁴⁶⁾, Burrows⁽²⁸⁾, and Waterman and van Vlodrop⁽⁸⁸⁾.

Theory of Molecular Distillation

In considering the theory of molecular distillation, several factors are of importance: the rate of distillation, the film thickness, the thermal hazard, the limitations encountered, and the mean free path considerations involved.

Rate of Distillation. For conventional distillation, the rate of distillation of any individual substance is roughly proportional to its concentration and its vapor pressure. In molecular distillation, heat is supplied to the distilland as under equilibrium conditions but the majority of the molecules leaving the evaporator are collected almost immediately on the condenser. Therefore, the rate of heat input at a constant temperature and the shape of the still are not significant variables as in the case of conventional distillation. In molecular distillation, the rate of distillation is proportional to the product of the number of molecules and the probability that each molecule will distill. This tendency to distill has been termed the "distillability". Embree⁽⁴⁵⁾ gives a more exact but less

illuminating definition of the "distillability" of a substance as being "proportional to its rate of distillation divided by its concentration". He states that "the rate of distillation of a substance is proportional to the product of its concentration and its distillability". Expressed algebraically this becomes,

$$V = kND$$

where:

V = rate of distillation, mols per second

k = proportionality constant

N = concentration, mol fraction

D = distillability.

If the distilland is considered to be an ideal solution, the partial pressure, p , of the substance considered may be taken as the product of N and P , the concentration and the

vapor pressure of the pure substance, respectively. The rate of distillation by Langmuir's equation then becomes,

$$n = NPA \sqrt{\frac{1}{2 MRT}}$$

where:

- n = rate of distillation, mols per second
- N = concentration, mol fraction
- P = vapor pressure, dynes per square centimeter
- A = area of distilling surface, square centimeters
- M = molecular weight
- R = ideal gas constant
- T = temperature, degrees Kelvin.

For any one still this term becomes $n = kNP / \sqrt{T}$ when the constant terms are considered. The distillability for this case is then proportional to P / \sqrt{T} . As an approximation, the distillability may be considered to vary directly with the vapor pressure of the substance since the changes in $1 / \sqrt{T}$ are small as compared to changes in P .

Bronsted and von Hevesy⁽⁴⁾ found that the rate of distillation of the components of a mixture was inversely proportional to the square root of the molecular weights of these components as indicated by the Langmuir equation. Washburn et al⁽⁸⁷⁾ observed

that the equation was valid for solutions if no recondensation occurred on the evaporating surface. The actual rate of distillation will always be less than the theoretical because of the return of some molecules to the evaporating surface.

Langmuir⁽⁶⁹⁾ found that under even the worst conditions, reflection, or return of the molecules to the evaporating surface, will not be greater than 90 per cent so that the actual rate can never be less than 10 per cent of the calculated rate. Burch and van Dijk⁽²⁷⁾ postulated and Fawcett⁽⁴⁶⁾ verified the theory that if the residual gas pressure were made sufficiently low that molecular distillation occurred, further reduction of pressure would effect no change in the rate of distillation.

Surface Layer and Film Thickness. A most important factor in molecular distillation is the surface of the distilling liquid⁽⁶²⁾. It must be remembered that only this surface is involved in the distillation. Momentarily, none of the other molecules in the still need be there. Their only purpose in the still is to replenish the surface layer. While only the molecules that are at the surface are needed for distillation, all of the molecules waiting their turn in the still are at the same temperature and thus, exposed to thermal decomposition. From this consideration, the reasoning behind a desire for a thin film thickness is evident.

A formula⁽⁵⁹⁾ for the relationship between the rotor speed and film thickness for centrifugal stills may be expressed as:

$$\log u = K \frac{1}{\log L}$$

where:

u = velocity, revolutions per minute

K = proportionality constant

L = film thickness, millimeters.

This formula was determined through a study of the spiral streams caused by feeding colored and colorless oils slightly off rotor center and at the rotor center, respectively. Since the colored oil was applied eccentrically, it formed a small separate stream within the main colorless stream and the composite pattern of alternate colored and colorless spirals proceeded outward from the center of the rotor. The thickness at any position was determined to be directly proportional to the distance between the spirals and inversely proportional to the area of the particular portion of the rotor considered. The persistence of the spiral pattern across the rotor is interpreted as indicating that the distilland is present in such a thin film that the evaporating surface at any moment represents the composition of the film beneath. The diffusion is so rapid that all of the

molecules will come to the surface at some time during the travel across the rotor. According to Fawcett⁽⁴⁶⁾, a concentration gradient will be set up through the film if the rate of evaporation is greater than the rate of diffusion to the outer layer. A concentration gradient will be of importance in decreasing the efficiency of the process because (1) the gross rate of evaporation will decrease as the more volatile constituents are stripped out and the vapor pressure decreased, and (2) the fractionating power will decrease since excessive quantities of the less volatile will appear in the distillate and the more volatile will appear in the residue.

Thermal Hazard. The greatest advantage of high-vacuum distillation is the ability to distill successfully substances of high molecular weight which are thermally unstable at temperatures which would be required by conventional distillation. The thermal hazards become increasingly more important as the size of the molecule becomes larger. The quantity of distilland being heated and the time of heating contribute to the thermal exposure. Hickman and Embree⁽⁶⁶⁾ have developed a "hazard index" concept and have tabulated the thermal exposure of various stills, Table II, page 21. According to the hazard index, the decomposition hazard, D, is the product of the

TABLE II

Thermal Exposures of Various Stills

Kind of Still	Pressure mm Hg	Time	Temperature ^a °C	Relative Thermal Coefficient ^b	Relative Decomposition Hazard
Simple Flask	760	1 hr	360	2 ²³	1.5 x 10 ¹²
Claisen Flask	10	1 hr	270	2 ¹⁴	3.0 x 10 ⁹
Wide-Neck Pet Still	1	1 hr	220	2 ⁹	9.2 x 10 ⁷
Petroleum Flash Still	1	1 min	220	2 ⁹	1.5 x 10 ⁶
Molecular Pet Still	0.001	1 hr	130	1	1.8 x 10 ⁵
Molecular Falling-Film Still	0.001	1 min	130	1	3.0 x 10 ³
Molecular Centrifugal Still	0.001	1 sec	130	1	5.0 x 10 ¹
Molecular Centrifugal Still	0.001	0.02 sec	130	1	1.0

^a Boiling points of dibenzylphthalate, for example.

^b Assuming that the hazard doubles with each 10 °C rise.

Hickman, K. C. D., and N. D. Embree: Decomposition Hazard in Vacuum Stills, Ind. Eng. Chem.,
40, 135 (1948).

time, t , in seconds of exposure and the pressure, p , in microns of mercury, or:

$$D = t \times p.$$

It will be noted that the thermal hazard encountered with thin-film distilland in the centrifugal molecular still is far less than with any other type of still.

Limitations of Molecular Distillation. In ideal molecular distillation, equilibrium does not exist between the vapor and the liquid and no molecules reenter the distilland after being vaporized. As indicated by the Langmuir equation, the quantity of a given material distilling at a given temperature is proportional to P/\sqrt{M} where P is the vapor pressure and M is the molecular weight. The relative quantities of two or more substances distilling from a mixture are,

$$P_1/\sqrt{M_1} \quad , \quad P_2/\sqrt{M_2} \quad , \quad \dots \quad P_n/\sqrt{M_n}.$$

This property of molecular distillation makes it possible to separate, by a single distillation, two substances having $P_1/\sqrt{M_1} = P_2/\sqrt{M_2}$. In many molecular distillation operations, where the vapor pressure and/or the molecular weight of the constituents do not differ radically, distillation simply increases the concentration of one constituent rather

than giving a sharp separation. The molecular still is valuable not because it gives good separation but because distillation is accomplished at temperatures from 50 to 250 degrees centigrade lower than temperatures encountered in conventional distillation⁽⁶³⁾.

Azeotropic mixtures which cannot be readily separated in an ordinary still may be separated by molecular distillation if their molecular weights are different. The degree of separation effected is due to the fact that although the constituents are evaporating simultaneously, they are each evaporating at different rates.

Mean Free Path Considerations. Vaporized molecules leaving the evaporating surface will necessarily be delayed in reaching the condensing surface or may even return to the distilland if they suffer collisions with other molecules. Any delay of the emergent molecules in reaching the condenser would result in distillation becoming more equilibrant and one would expect reduced distillation rates. Hickman⁽⁵²⁾ measured the change in rates of distillation with changes in the pressure of the residual gas and found that collisions had less effect than might be expected. Table III, page 24, gives the mean free paths and relative rates of distillation for various residual

TABLE III

Comparison of Pressure, Free Path, and Rate
of Distillation in a Molecular Still

Pressure of Residual Air in 2 Cm Gap	Two Cm Gap is Approximate Multiple m of Free Path	Comparative Distillation Rate with Saturation Pressures of		Number of Molecules Reaching Condenser Without Collision
		1μ	10μ	
μ		%	%	%
0.5	0.2	100	100	80
4.0	3	77	89	—
7.0	5	63	81	0.005
10.0	7	53	72	—
25.0	17	35	42	—
50.0	33	20	27	—

Hickman, K. C. D.: Molecular Distillation, "Chemical Engineers' Handbook"
(J. H. Perry, Editor), p.656. McGraw-Hill Book Co., Inc., New York,
N. Y., 1950. 3 ed.

gas pressures. It will be noted that the rate of distillation is reduced by less than 40 per cent for a change from 80 to 0.005 per cent in the number of molecules reaching the condenser without collision.

Various formulas for the mean free path of like molecules and molecules in the presence of unlike molecules have been developed. Maxwell's expression for the calculation of the mean free path has been considered in a previous section on terminology of molecular distillation. The calculation for large nonspherical molecules using this and other formulas gives mean free paths which are likely to be in error. There is some indication that oil molecules as amyl phthalate and amyl sebacate have "undeflected mean free paths" several times longer than those calculated by classical theory⁽⁵²⁾.

Variables Affecting Molecular Distillation

In molecular distillation, the rate of distillation of any component and the degree of separation of the components of a mixture depend on a number of interdependent variables in the design and operation of the still⁽⁴⁷⁾. Meaning can only be given to experimental results from the laboratory distillation of substances when arbitrary distillation conditions are fixed by close control of the variables affecting distillation. These variables include operating pressure, temperature of distilland, film thickness, splashing, rotor speed, angle of inclination of rotor surface, temperature of condensing surface, and distance between evaporator and condenser.

Operating Pressure. In true molecular distillation, the rate of evaporation is independent of pressure. Once the residual gas pressure in the still equals the vapor pressure of the distilland at the temperature of operation, further reduction in pressure effects no further increase in the rate of distillation. If the residual gas pressure within the still is allowed to exceed the vapor pressure of the distilland, a reduction in the rate of distillation will occur. As the pressure in a still rises, operation will approach equilibrant

high-vacuum evaporation rather than molecular distillation with the distillation rate becoming a function of the vapor pressure alone.

Bull⁽¹⁸⁾ reports several tests performed to study the effect of operating pressure on the distillation of 1,4-diethyldiamino-anthraquinone. An appreciable effect was noted in the shifting of the elimination maximum. For absolute pressures of 2, 6, 25, 50, and 100 microns of mercury, elimination maxima of 144, 152, 158, 173, and 177 degrees centigrade were obtained.

Temperature of Distilland. The measurement of the temperature of the actively distilling surface of the distilland presents a problem which has not been satisfactorily solved. There exists a temperature gradient of about five degrees centigrade through the distilland in a falling-film still⁽⁴⁶⁾. The temperature gradient is probably less in the centrifugal still because of the decrease in film thickness. There is also a temperature gradient from the center of the rotor to the outer rim which varies with the feed temperature and heat applied on the rotor. The customary practice has been to control the average temperature of the distilland by use of a source of heat at a constant rotor temperature and a constant temperature difference between the evaporator and the condenser. The average temperature of

the distilland of a centrifugal molecular still may be estimated by inserting a thermocouple in the collecting gutter.

Increasing the temperature of distillation increases the vapor pressure of the distilland and, hence, the rate of distillation. However, it should be recalled that the increase in distilling temperature causes a secondary effect of reducing the mean free path which would ordinarily be expected to reduce distillation. In general, this slight reduction in the rate of distillation will be much more than compensated by the increase resulting from increased vapor pressure. According to Fawcett⁽⁴⁶⁾ the highest gross distillation will occur at the highest possible temperature short of decomposition even though the distillation may shift from the molecular to the non-molecular type.

Film Thickness of Distilland. The exact effect of the film thickness on molecular distillation is unknown. Recent still design has attempted to reduce the film thickness in order to insure that diffusion will take place sufficiently fast to make the surface or distilling layer representative of the fluid beneath.

The theory of the surface layer and calculations for film thickness have been considered in the section on the theory of molecular distillation.

Splashing. Splashing will affect the degree of separation obtainable in molecular distillation since substances of lower volatility will be carried into the distillate. One of the chief reasons for the use of a thin film is to assist in the prevention of splashing of the distilland. The maintenance of a thin film on the rotor will not, by itself, insure the absence of splashing, but it does aid greatly in degassing of the distilland.

Improper degassing and too rapid evaporation have been mentioned⁽⁵⁹⁾ as the major causes of splashing. Too rapid evaporation will likely occur if the heat input to the distilland and the subsequent temperature of distillation is higher than necessary for proper distillation.

Rotor Speed. Hickman⁽⁶¹⁾ found that increasing the rotational speed of the evaporator from 100 to 3000 revolutions per minute quadrupled the amount of distillate collected on the condenser. It was first supposed that friction was the cause or that the metallic rotor was reacting with the electrical heating coil behind. Neither of these was found to be the reason for increased distillation. The real reason proved to be the changing radiative properties of the oil in thin layers. When an oil is spread sufficiently thin, it will, for all practical purposes, cease to emit radiation. Bull⁽¹⁶⁾ reports that

rotor speeds of 1000, 2000, 3000, and 5000 revolutions per minute had no effect on either the shape of the elimination curve or the position of the elimination maximum.

Angle of Inclination of Rotor Surface. Tests made by Coli⁽³⁶⁾ using rotors with angles of inclination of rotor surface of 52-1/2, 60, 67-1/2, and 75 degrees indicated no overall effect on the separation. A difference might have been expected with the difference in gradient of the distilland on the rotor but was not evidenced.

Temperature of Condensing Surface. The primary consideration of the condensing surface is that it be at a temperature sufficiently below that of the distilling surface to prevent any revaporization of the distillate on the condenser^(49,87). Any further reduction in the condenser temperature will not improve either the rate of distillation or condensation. Commercial units are generally not provided with any external means of cooling the bell jar condensing surface^(60,67). Often cooling coils or baffles are provided inside the bell jar to assist in condensation or in special fractionation of the distillate by partial condensation.

Distance Between Evaporator and Condenser. The mean free path considerations have been discussed in a previous section. In general, variations of the gap between the evaporator and

the condenser do not produce any very noticeable variations in still performance provided that the gap does not become much larger than the mean free path⁽⁴⁶⁾. It is also possible that the gap may be reduced to such an extent that the distillation rate will be decreased. Distillation tests made using linseed oil with gaps varying from one to six centimeters showed no significant change. A gap of 0.5 centimeter resulted in decreased distillation. The closeness of the condenser to the evaporating surface tended to permit the return of some of the vaporized molecules to the distilling surface which would not have returned otherwise.

Evaluation of Still Performance

The fractionating ability of molecular stills is best evaluated in terms of the theoretical molecular plate. The distillation of individual substances is usually illustrated by means of individual and composite elimination curves. The use of a solvent constant yield oil in molecular distillation studies is also discussed.

Theoretical Molecular Plate. The unit of separation that a single passage can theoretically achieve is considered to represent one theoretical molecular plate⁽⁶⁴⁾. A separation equivalent to one theoretical molecular plate is assumed to

occur when the condenser is infinitely close to the evaporator, distillation is sufficiently slow that the composition of the evaporating surface is representative of the main bulk of the distilland, and the vapor molecules emerge sufficiently far apart from one another in time and space that there are no collisions in travel. The maximum difference in composition of distilland and distillate vapor would occur under such conditions. The Langmuir equation could then be used to determine the separation of binary mixtures as proportional to the ratio of the partial pressures and to the square roots of the molecular weights of the constituents.

The concept of the theoretical molecular plate in centrifugal molecular distillation is somewhat analogous to the theoretical plate in equilibrant distillation although the concept becomes complicated by the progressive travel of the film across the rotor. In the well-stirred pot still, it is assumed that every element of the evaporating area is of identical composition. In the centrifugal still, however, succeeding areas cannot be identical in composition except at an infinite ratio of evaporation to throughput.

Industrially, centrifugal molecular stills have been reported as giving separations of 0.80 to 0.95 theoretical molecular plate⁽⁶⁵⁾. Such separations are two to three times

better than that obtainable from nonfractionating pipe or pot stills. Stills using fractionating barriers, partial condensers, and other devices for giving better separation can be described as having separating ability of multiples of the theoretical molecular plate.

Analytical Distillation. In conventional distillation, the boiling point⁽⁵⁵⁾ of a substance is the temperature at which its vapor pressure is equal to a specified pressure. This pressure is generally controlled by the gas in the apparatus other than the vapor, so that the boiling point is the temperature at which the vapor overcomes the pressure of the residual gas. Below this temperature no distillation occurs; above it, distillation is vigorous.

Under molecular conditions there is by definition no foreign gas, and distillation takes place whenever there is a difference of temperature between the distilland and the condenser. Increase in the absolute temperature and in the temperature difference increases the rate of distillation, but there is no abrupt transition such as boiling available for observation and record. Direct measurements of the rates of distillation are applicable chiefly to pure compounds and afford little information concerning mixtures of dissolved substances.

Fortunately, it is possible to "systematize" the course of molecular distillation so that a property of the constituents of the distilland, analogous to a boiling point, can be measured and used for identification purposes. This can be done most easily for a type of distillation which has reached a position of some importance - the elimination of small quantities of substances such as dyes or vitamins from a large bulk of less volatile fluid, generally an oil.

The method employed depends on two simple postulates:

(1) it is assumed that the trace of impurity (potent material) has no affinity for the solvent and (2) that it does not become preferentially located in or excluded from the distilling surface. It then follows that the quantity of potent material evaporated at any moment will be proportional to its mol concentration in the bulk of the distilland.

Two kinds of "rates of distillation" may be defined. The first is the intrinsic rate of distillation, or the "distillability" previously termed the ratio of the number of molecules of a given species leaving the distilling surface in any small interval compared with the number of similar molecules remaining undistilled in the surface layer during the same interval. The second is the rate of elimination or the rate at which the

material appears in the receiver. In the distillation of a substance at constant temperature, the distillability will remain constant with the lapse in time. The rate of elimination will decrease exponentially, approaching zero when nearly all the potent material has been evolved.

In order to hasten the elimination of the potent material, it is usually customary to raise the temperature as distillation proceeds. The distillability then increases progressively, but the rate of elimination, which at first rises in like manner, soon falls off to nearly zero because substantially all of the potent material has evaporated.

The Elimination Curve. Much can be learned from molecular distillation by this latter method. A mixture is exposed for distillation for a certain time at each of a series of temperatures, and the amount present, of the substance being considered, is measured in each fraction⁽⁴³⁾. These yields, plotted against the temperatures at which the fraction had been distilled, provide a distillation curve which Hickman⁽⁵³⁾ has called the "elimination curve". This type of curve has the general form shown in Figure 1, page 36.

The amounts of the substance in each fraction increase as the temperature increases until the yields finally reach a maximum and then decrease rapidly to zero because the supply of

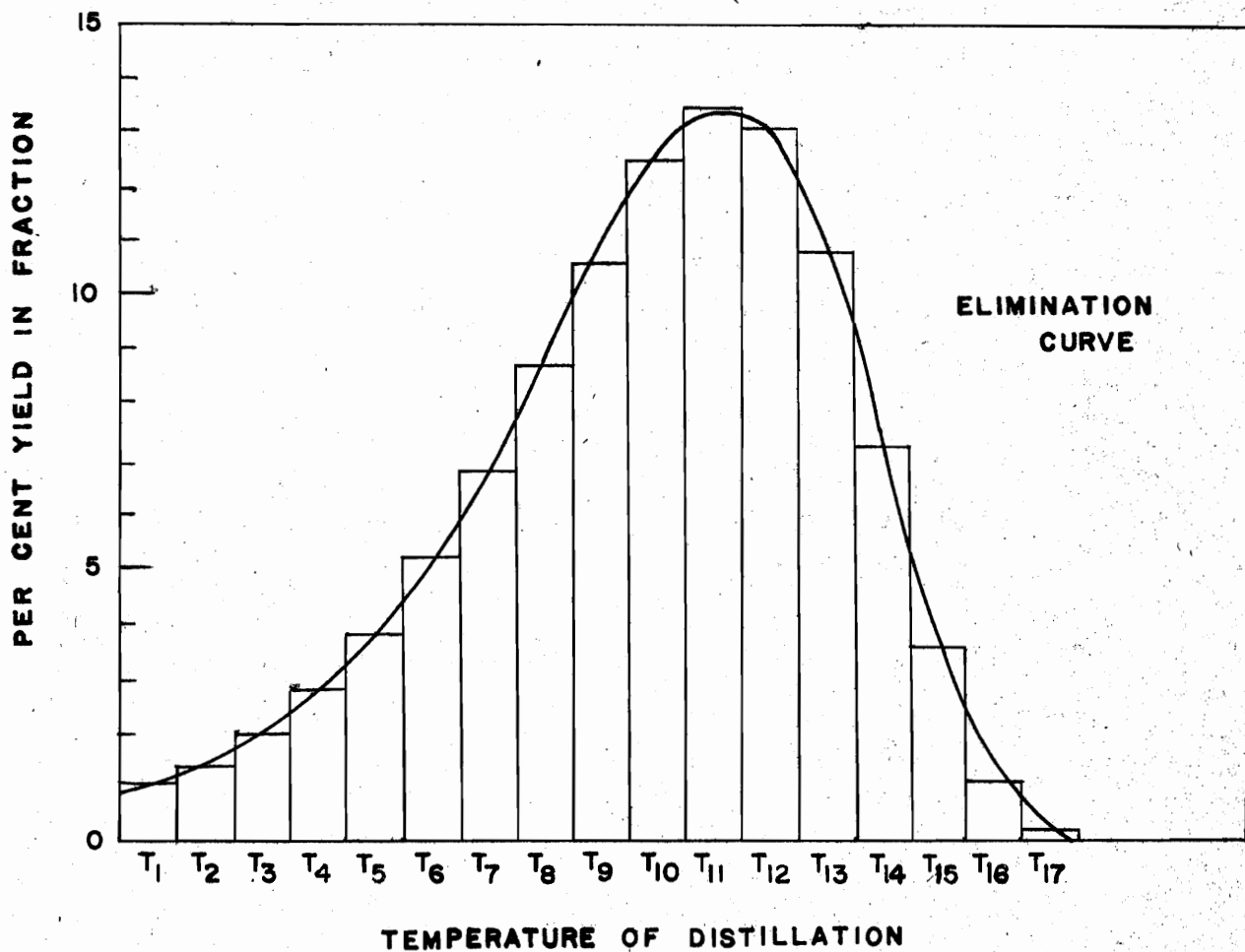


FIGURE 1. YIELD VS. TEMPERATURE CHART AND ELIMINATION CURVE

EMBREE, N.D.: THEORY OF ELIMINATION CURVE, IND. ENG. CHEM. 29, 975 (1937).

the substance in the distilland becomes nearly exhausted⁽⁴³⁾. The elimination curve has an easily recognized shape and a maximum which can be located to within a few degrees.

The exact shape of the elimination curve and the location of the elimination maximum is determined by the exact procedure employed in the distillation⁽⁵⁵⁾. For example, if the distilland is exposed at equal time intervals at each temperature and if the temperature is raised so that the distillability is increased by an equal factor at each step, a curve similar to Curve A, Figure 2, page 38, will be obtained. Embree⁽⁴⁴⁾ has shown that this same type of curve can be closely approximated by calculus, Curve B, Figure 2.

The elimination curve is significant in that its shape is independent, within the limits of previous assumptions, of the kind of substances distilled⁽⁵⁵⁾. It is the result of a standardized technique applied to the operation of the still during the distillation of any kind of molecule. If an experimental curve has a shape differing from the normal, it may be indicative of (1) faulty distillation, Curve D, Figure 2; (2) a substance not obeying the assumptions; or (3) a mixture of substances answering one identifying test.

Thus, the shape and position of the elimination curve may be used to reveal many of the properties of a substance and the

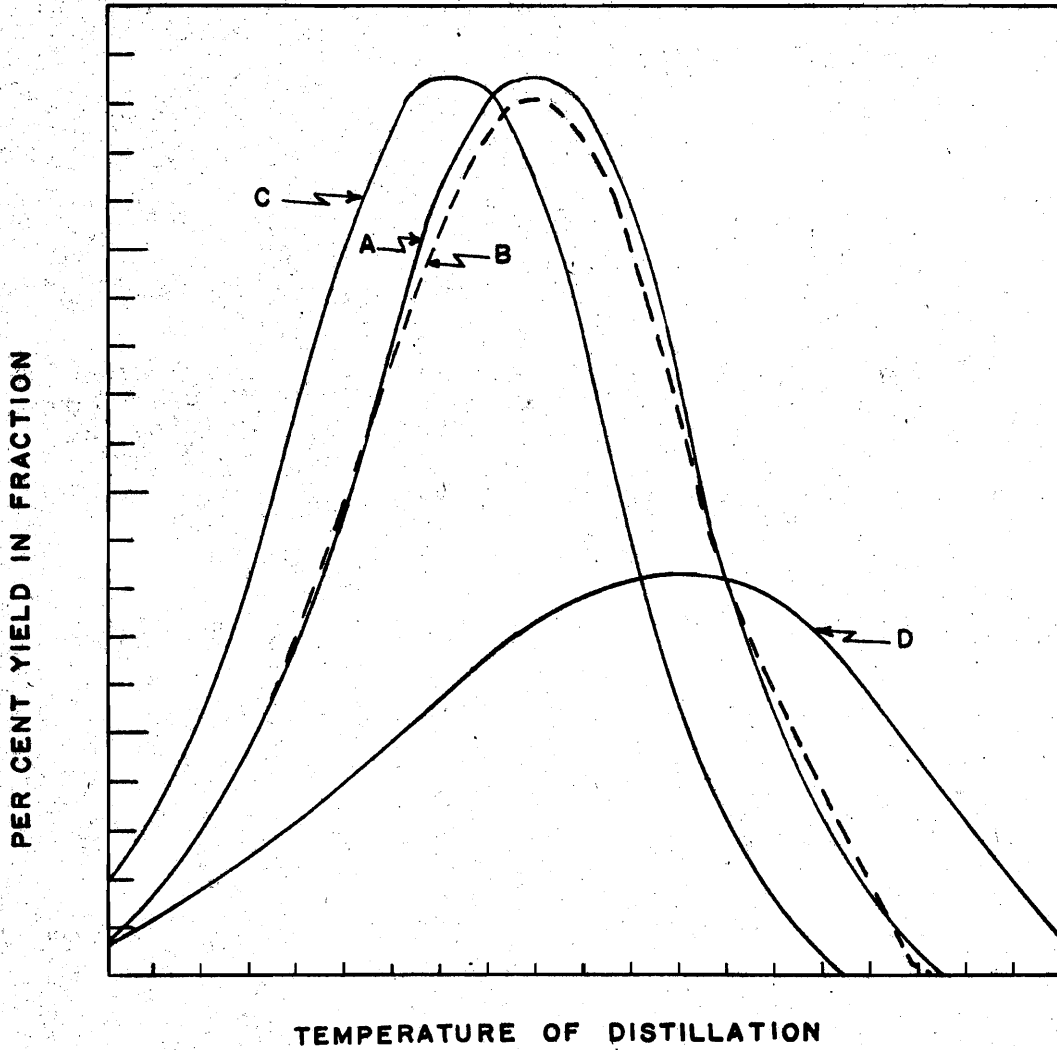


FIGURE 2. ELIMINATION CURVE

- A. EXPERIMENTAL VALUES
- B. EVALUATED BY CALCULUS
- C. TIME INCREMENTS TWICE THAT OF "A"
- D. FAULTY DISTILLATION - POOR SURFACE RENEWAL

HICKMAN, K.C.D.: APPARATUS AND METHODS, IND. ENG. CHEM. 29,
971 (1937).

kind of treatment it has received. A further study of the effects of several operational variables is valuable in consideration of the use of the elimination curve.

Effect of Distillation Time. The position of the elimination curve is greatly affected by the length of time during which the substance distills at each temperature in the series⁽⁴⁵⁾. Figure 3, page 40, shows elimination curves determined for the same substance with distillation times of 1, 2, and 4 minutes at each temperature. The curves show that increasing the time of distillation shifts the maximum of the elimination curve to lower temperatures.

Effect of Initial Temperature. The temperature at which the elimination maximum occurs is a definite property of the substance, if the distillations are always carried out so that the material is distilled for the standard length of time at a temperature series so chosen that the distillability increases by the same factor at each higher temperature⁽⁴⁴⁾. The temperature at which distillation is started has no effect on the temperature of the distillation maximum but raises the relative yields at the various temperatures as shown in Figure 4, page 41.

Effect of Heat of Vaporization. Distillability is almost proportional to the vapor pressure⁽⁴⁵⁾. Hence, for

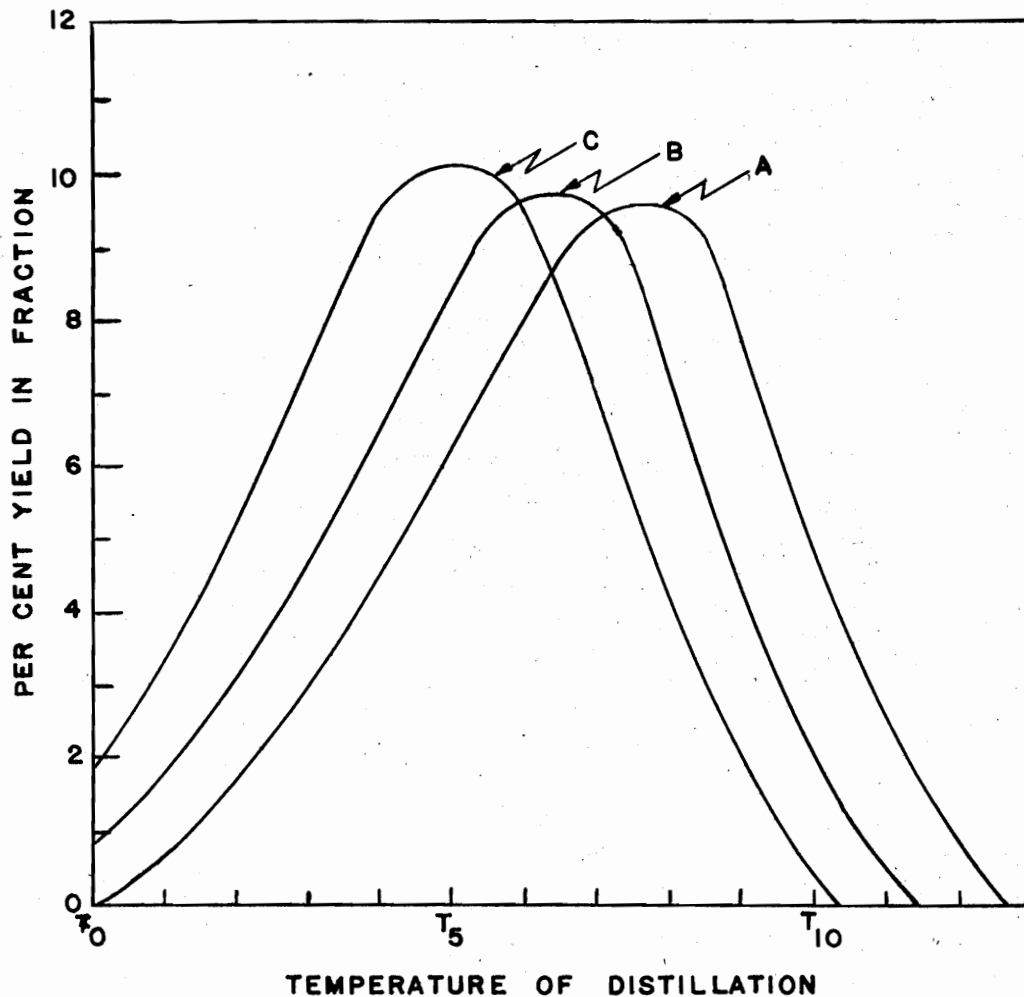


FIGURE 3. EFFECT OF TIME OF DISTILLATION ON ELIMINATION CURVES

- A. DISTILLATION FOR 1 MINUTE AT EACH TEMPERATURE.
- B. DISTILLATION FOR 2 MINUTES AT EACH TEMPERATURE.
- C. DISTILLATION FOR 4 MINUTES AT EACH TEMPERATURE.

EMBREE, N.D.: THEORY OF ELIMINATION CURVE, IND. ENG. CHEM. 29, 978 (1937).

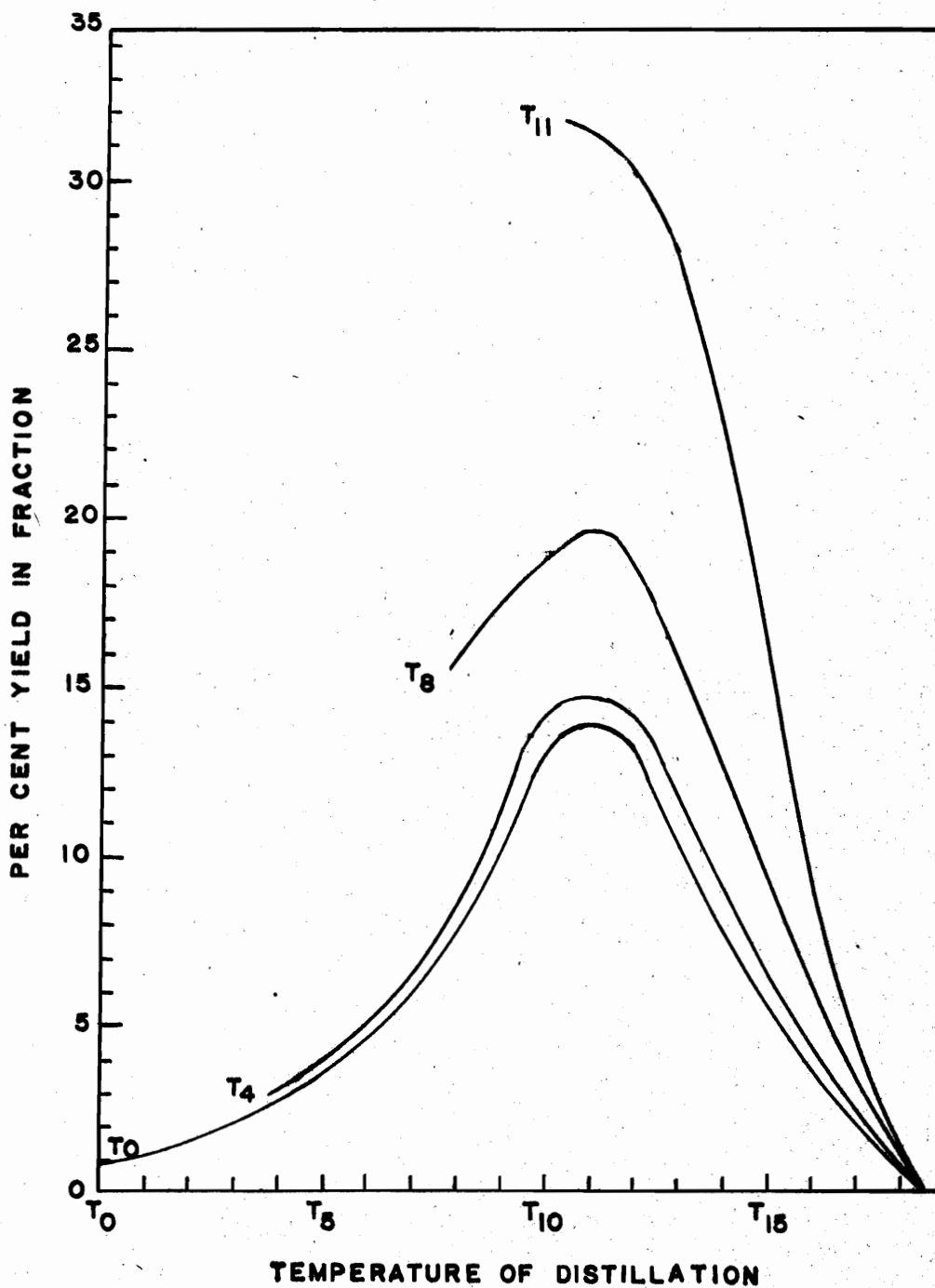


FIGURE 4. EFFECT OF INITIAL TEMPERATURE ON ELIMINATION CURVES

EMBREE, N. D.: THEORY OF ELIMINATION CURVE, IND. ENG. CHEM. 29, 978 (1937).

substances with a high heat of vaporization, the distillability will increase rapidly with temperature, and the elimination curve will be narrow and steep in comparison with substances with a low heat of vaporization which have broader and flatter elimination curves. Typical curves for two substances, one with a high and the other with a low heat of vaporization, are shown in Figure 5, page 43.

Effect of Solvent Distilling Over with Potent Material.

In many distillations, it is desirable to have a small amount of the solvent distilling over with each fraction to aid in drainage or washing of the distillate from the condenser surface⁽⁴⁵⁾. Figure 6, page 44, shows the typical difference in the elimination curves when two per cent of the total solvent distilled over with the potent material in each fraction.

Effect of Use of an Arithmetic Series of Temperatures.

If the distillation is carried out at an arithmetic series of temperatures instead of a series chosen so that the distillability increases by a constant factor at each temperature, the elimination curve will have a somewhat different shape⁽⁴⁵⁾ as shown in Figure 6, page 44.

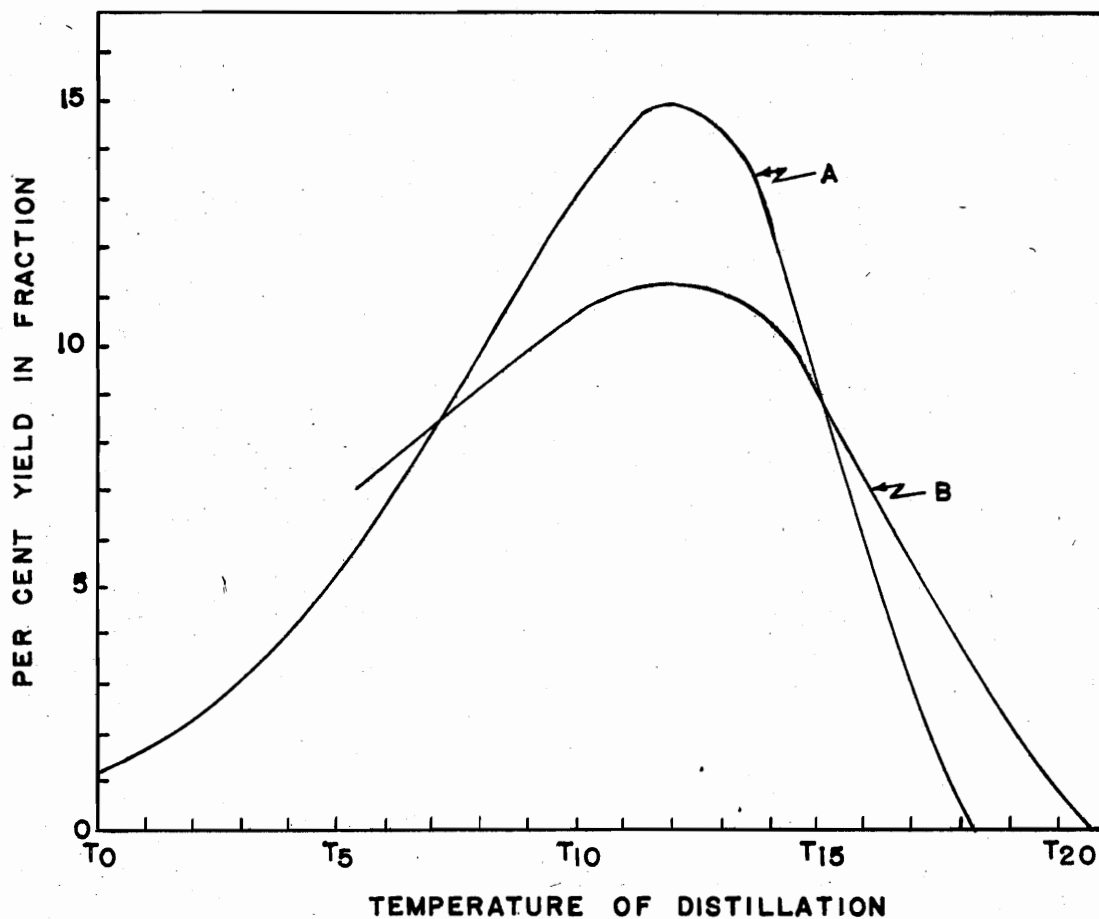


FIGURE 5. EFFECT OF HEAT OF VAPORIZATION ON ELIMINATION CURVES

- A. SUBSTANCE WITH HIGH HEAT OF VAPORIZATION.
- B. SUBSTANCE WITH LOW HEAT OF VAPORIZATION.

EMBREE, N.D.: THEORY OF ELIMINATION CURVE, IND. ENG. CHEM. 29, 978 (1937).

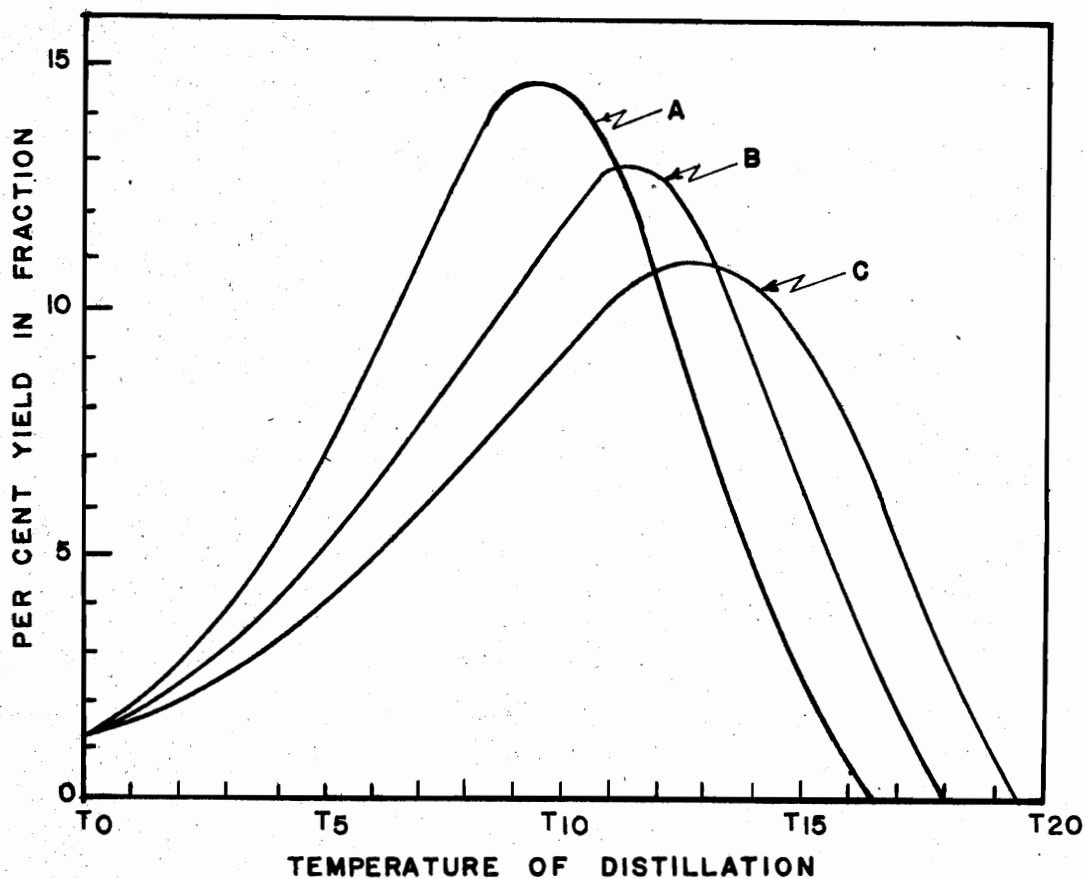


FIGURE 6. ELIMINATION CURVES FOR VARIOUS CONDITIONS

- A. TWO PER CENT OF SOLVENT DISTILLING IN EACH FRACTION.
- B. NO SOLVENT DISTILLING WITH POTENT MATERIALS.
- C. DISTILLATION WITH AN ARITHMETIC SERIES OF TEMPERATURES.

EMBREE, N.D.: THEORY OF ELIMINATION CURVE, IND. ENG. CHEM. 29, 979 (1937).

Effect of Continuous Distillability Change. In some cases it might be desirable to have the distillability increase continuously instead of by increments. This condition might exist when a still is being supplied with a greater amount of energy than is necessary to maintain a constant temperature or if the distilland is allowed to flow as a column that is heated at the bottom as might be the condition in a falling-film still. If the distillability is increased continuously for one-minute distillation increments, a curve similar to Curve A, Figure 7, page 46, might be obtained. If the temperature is increased more slowly, for instance, 2- or 4-minute periods, Curves B and C result. The shifting of the temperature of the maximum to a lower value is similar to that encountered by merely increasing the distillation time for constant temperature (constant distillability) increments as shown in Figure 3, page 40.

The Elimination Maximum. Under standardized conditions of molecular distillation, the elimination curve of any individual substance depends on its distillability. Under such conditions, the position of the maximum is reproducible with a precision of one degree centigrade. Hickman⁽⁵⁶⁾ suggests that "this position

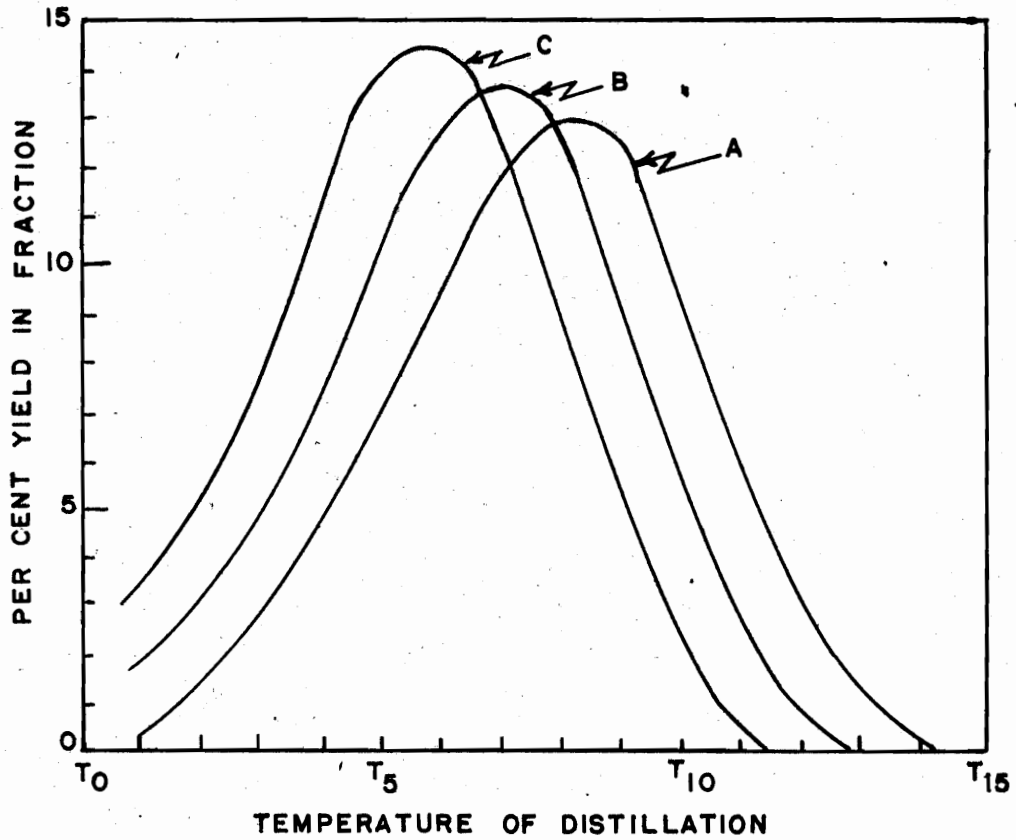


FIGURE 7. ELIMINATION CURVES FOR CONTINUOUS DISTILLABILITY CHANGE

- A. DISTILLATION FOR 1 MINUTE AT EACH TEMPERATURE.
- B. DISTILLATION FOR 2 MINUTES AT EACH TEMPERATURE.
- C. DISTILLATION FOR 4 MINUTES AT EACH TEMPERATURE.

EMBREE, N. D.: THEORY OF ELIMINATION CURVE, IND. ENG. CHEM. 29, 979 (1937).

is as valuable an attribute of a substance as the boiling point would be if it could be determined at a higher pressure".

Any group of substances can be arranged with the distillabilities in serial order when the conditions of distillation are standardized⁽⁵⁶⁾. The elimination maximum will occur for each substance in a fixed relative order with definite temperature intervals between the maxima. Changing the conditions will then shift all the maxima up or down the temperature scale but will not seriously alter the separation or the relative order except between substances of widely different latent heats.

Composite Elimination Curves. When a mixture of two or more potent materials is distilled, entirely abnormal shaped curves are often encountered⁽⁵⁸⁾. The mixture is generally very difficult to resolve. It is necessary to apply repeated fractionations by ordinary molecular distillation and then to compare the elimination curves from the redistillation of the extreme fractions. The probable resolution of binary mixtures has been studied by Hickman⁽⁵⁸⁾ by constructing composite curves representing the addition to one substance, quantities of a second substance varying from 1/4 to 4 times the quantity of the first. The elimination maxima of the two substances varied by 5, 10, 20, and 40 degrees centigrade. Figure 8, page 48, shows the composite curves for the variations.

RATIO OF SECONDARY TO PRIMARY SUBSTANCE IN BINARY MIXTURE

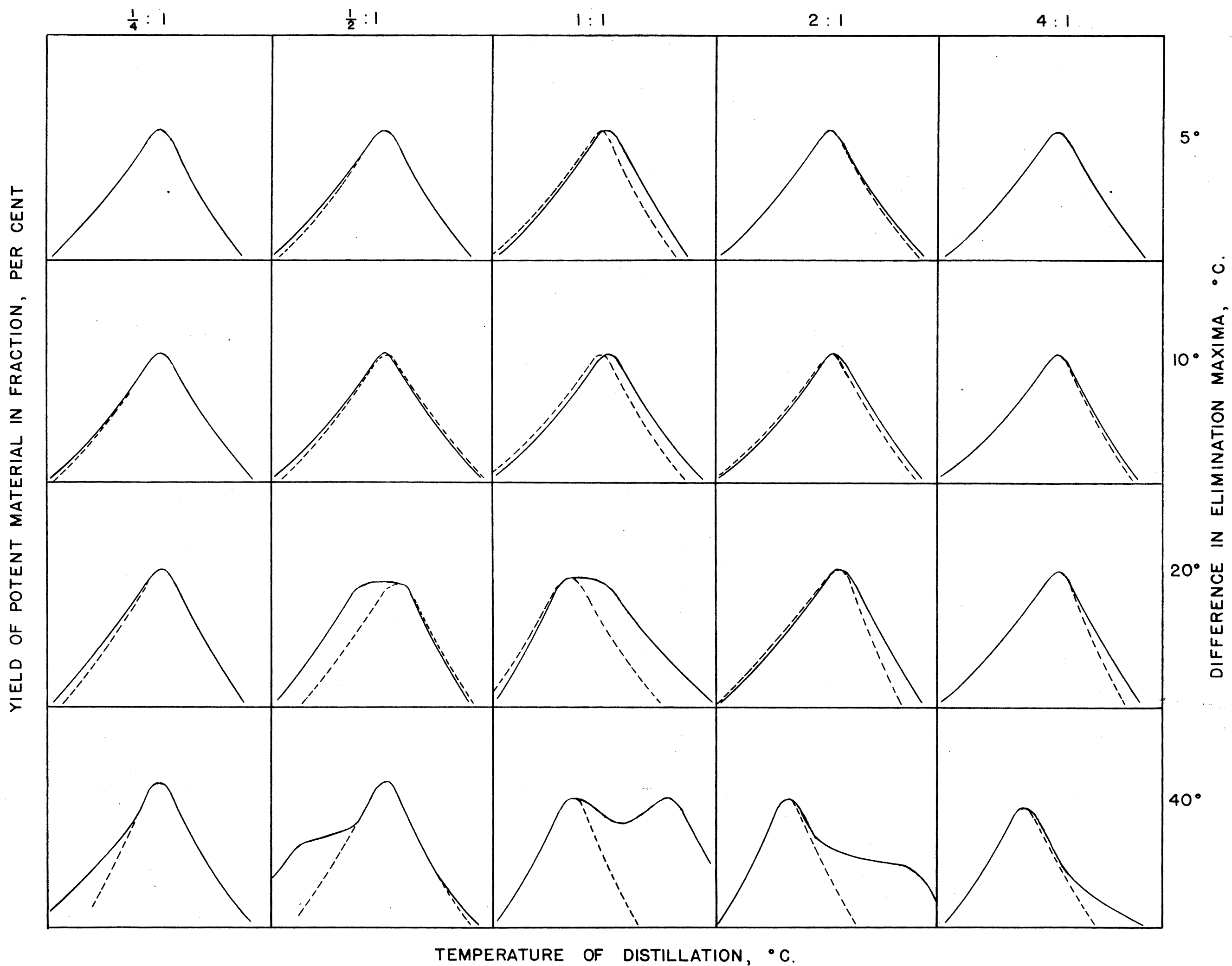


FIGURE 8. COMPOSITE CURVES FOR VARIOUS TYPICAL COMPOUNDS

HICKMAN, K.C.D.: APPARATUS AND METHODS, IND. ENG. CHEM., 29, 974 (1937).

Hickman suggests the second substance can be detected if present in one-half the quantity or more and boiling at least 10 degrees from the main constituent. When smaller quantities of nearer distilling materials are present, the only effect often is to shift the position of the maximum to a false location. The remedy is to fractionate the parent material and secure curves for the head and tail fractions of the primary elimination curve.

Constant-yield Oil. It has previously been stated that it is often desirable for a small portion of the solvent to distill with the potent material in each fraction to provide for drainage of the distillate from the condenser. This is absolutely necessary in many cases where distillation is carried out to identify rather than separate a constituent⁽⁵⁷⁾. In these instances, it is imperative that the drainage error be kept uniform. When only small traces of the potent material are distilled during a temperature increment, the material may collect as a mist on the condenser which will not drain adequately and the result is large error in the elimination curve of that substance.

The potent material should therefore be dispersed in a medium which yields a constant volume yield of distillate for each succeeding temperature interval to keep the drainage

uniform⁽⁵⁷⁾. The volume of distilland should not be reduced by more than half by the end of distillation, however.

Since it is not the nature of most oils to distill at a constant rate over even small temperature ranges, it is usually necessary to prepare a constant-yield oil by blending equal fractions of oil obtained from numerous repeated molecular distillations.

Baxter's Triglyceride Constant-yield Oil. Constant-yield oils (CYO) have been prepared by blending various nonreactive solvents, such as heavy petroleum fractions. Baxter et al⁽²⁾ have described in detail one such oil, a pure triglyceride or mixture of glycerides. The yields of the various fractions obtained from the distillation of such a constant-yield oil are presented in Table IV, page 51. It can be seen that the sixteen fractions varied in amount of oil distilled from 1.7 to 7.3 grams. However, the mixture was considered as yielding sufficiently constant fractions in the middle temperatures (140 to 230 degrees) to be of value in reducing drainage error.

Bull and Demakis's Mineral Oil Blend. Bull⁽²⁰⁾ and Demakis⁽³⁸⁾ used a constant-yield oil made by blending 7 volumes of light and 3 volumes of extra-heavy mineral oil. The blend was nearly colorless and distilled in the

TABLE IV

Data on Constant-Yield Mixture T-175

Fraction	Temperature	Residual Gas Pressure	Weight
	°C	mm x 10 ³	gm
1	100	1.4	2.2
2	110	1.3	1.9
3	120	1.2	2.5
4	130	1.2	2.9
5	140	1.2	3.3
6	150	1.3	3.8
7	160	1.5	4.0
8	170	1.7	3.5
9	180	1.8	3.0
10	190	2.0	2.9
11	200	1.9	3.1
12	210	1.8	3.5
13	220	1.4	3.6
14	230	1.2	4.5
15	240	1.2	5.7
16	250	1.2	7.3

Baxter, J. G., E. LeB. Gray, and A. O. Tischer:
 Preparation and Characteristics of Synthetic Constant-
 Yield Mixtures, *Ind. Eng. Chem.*, 29, 977 (1937).

temperature range between 100 and 180 degrees centigrade. It was believed that the chief weakness of this blended CYO was the lack of a large non-volatile residue. Approximately 15 per cent of the original blend was left after the removal of the 180-degree fraction.

Molecular Distillation of Fatty Acids

Molecular distillation has been applied to the investigation of fats and oils and particularly to the separation of nonglyceride lipides which are present in these substances. Although some degree of separation of the fatty acid glycerides may be effected by molecular distillation, its chief application has been in the separation of fatty acids, vitamins, and other substances from natural fats. It has not been extensively applied to the fractionation of fatty acids as such, primarily because ordinary methods of distillation generally serve to effect the desired separation more efficiently. However, there have been some notable exceptions wherein molecular distillation has made possible separations which could not be accomplished otherwise⁽⁷⁹⁾.

Farmer and van den Heuvel⁽⁴⁸⁾ used molecular distillation to fractionate the methyl esters of highly unsaturated fatty

acids from fish oils. Schuwirth⁽⁸¹⁾ also molecularly distilled methyl esters of unsaturated fatty acids obtained from brain phosphatides. Molecular distillation is particularly useful in separating monomeric and polymeric fatty acids and esters. Lambau and Dollear⁽⁶⁸⁾ were unable to prepare linoleic acid or linolenic acids of high purity except by molecular distillation to separate the monomeric acids from the small amount of polymers which invariably accompanied the otherwise pure acids.

Work of Gray and Cawley on Molecular Distillation of Fatty Acids. Gray and Cawley⁽⁵⁰⁾ appear to have been the first to have used fatty acids to study the influence of structure on the elimination maximum. Their interest was primarily to study structure influences on the molecular distillation of vitamins A and A₂. Fatty acids were used in their research because (1) they had elimination maxima in the same range as the vitamins, (2) they were easily estimated by titration in a neutral oil such as synthetic constant yield oil, and (3) sufficient numbers of the series (of fatty acids) were available or could be prepared to make the desired comparisons.

Gray and Cawley⁽⁵⁰⁾ distilled such saturated acids as lauric, myristic, palmitic, and stearic acids and unsaturated acids as oleic, linoleic, 9,11-linoleic, and α -eleostearic

acids. From their work they developed the following conclusions:

(1) A CH_2 group added to the molecular chain raised the elimination maximum by five degrees centigrade,

(2) Each non-conjugated double bond lowered the elimination maximum two degrees, and

(3) When double bonds were conjugated, each additional double bond raised the maximum three degrees.

Work of Lombardi and Tyler. Lombardi⁽⁷⁰⁾ and Tyler⁽⁸⁴⁾ molecularly distilled several fatty acids in a centrifugal still in the laboratories of the Virginia Polytechnic Institute. Lombardi determined the elimination maxima of lauric, myristic, palmitic, and stearic acids and the composite elimination curve for a mixture of lauric and stearic acids. Tyler attempted the separation of a mixture of palmitic and stearic acids using molecular distillation.

The Nomenclature and Structure of the
Fatty Acids Investigated

Table V, page 56, presents the nomenclature and structure of the long-chained fatty acids selected for investigation in this study. The various structures to be studied will be briefly discussed.

Saturated Acids. The empirical formula for all of the members of the saturated fatty acid series is $C_n H_{2n} O_2$ where "n" may be any even or odd integer⁽⁷³⁾. Three even-numbered acids (palmitic, stearic, and arachidic) and three odd-numbered acids (pentadecylic, margaric, and nonadecylic) were chosen for the study. The structure of all these acids is similar; all are straight-chained acids differing only in the number of carbon atoms in the chain (number of CH_2 groups).

Degree of Saturation. The acids exhibit varying degrees of saturation from completely saturated to triethenoid or three double bonds in the structure. Four monoethenoid, two diethenoid, and two triethenoid acids are included.

Isomerism. Both positional and geometrical isomerism⁽⁷⁵⁾ are exhibited by acids chosen for the study. Positional isomerism is represented by the variation in position of the double bond. For example, oleic has a double bond between

TABLE V

The Nomenclature and Structure of the Fatty Acids Investigated

Common Name	Systematic Name and Location of Double Bonds	Formula	Molecular Weight	Structure
Pentadecylic	n-Pentadecanoic	$C_{14}H_{29}COOH$	242.39	Saturated
Palmitic	n-Hexadecanoic	$C_{15}H_{31}COOH$	256.42	Saturated
Margaric	n-Heptadecanoic	$C_{16}H_{33}COOH$	270.44	Saturated
Stearic	n-Octadecanoic	$C_{17}H_{35}COOH$	284.47	Saturated
Nonadecylic	n-Nonadecanoic	$C_{18}H_{37}COOH$	298.49	Saturated
Arachidic	n-Eiccanoic	$C_{19}H_{39}COOH$	312.52	Saturated
Palmitoleic	9,10-Hexadecenoic	$C_{15}H_{29}COOH$	254.40	Monoethenoid
Oleic	9,10-Octadecenoic (cis)	$C_{17}H_{33}COOH$	282.45	Monoethenoid
Elaidic	9,10-Octadecenoic (trans)	$C_{17}H_{33}COOH$	282.45	Monoethenoid
Vaccenic	11,12-Octadecenoic	$C_{17}H_{33}COOH$	282.45	Monoethenoid
Linoleic	9,10,12,13-Octadecadienoic	$C_{17}H_{31}COOH$	280.44	Diethenoid
9,11-Linoleic	9,10,11,12-Octadecadienoic	$C_{17}H_{31}COOH$	280.44	Conjugated Diethenoid
Linolenic	9,10,12,13,15,16-Octadecatrienoic	$C_{17}H_{29}COOH$	278.42	Triethenoid
α -Eleostearic	9,10,11,12,13,14-Octadecatrienoic	$C_{17}H_{29}COOH$	278.42	Conjugated Triethenoid

Markley, K. S.: "Fatty Acids," pp. 20-28, 48. Interscience Publishers, Inc., New York, N. Y., 1947.

the ninth and tenth carbon atoms while vaccenic acid has its double bond in the 11-12 position. The diethenoid acids (linoleic and 9,11-linoleic) and the triethenoid acids (linolenic and α -eleostearic) used also exhibit positional isomerism.

Geometrical isomerism is dependent on spatial arrangement of the component parts of the molecule with respect to the double bond. Oleic acid and elaidic acids are geometrical or cis-trans isomers with the double bond of both acids located in the 9-10 position.

Conjugated Double Bondage. The diethenoid and triethenoid acids may be classified as conjugated or unconjugated depending on the relative position of the double bonds⁽⁷²⁾. If the double bonds are separated by one or more single-bonded carbon atoms, $-C=C-C_n-C=C-$, the acid is said to be unconjugated. Linoleic and linolenic acids are examples of unconjugated acids. When double-bonded carbon atoms are adjacent to one another, $-C=C-C=C-$, the acid is referred to as conjugated. 9,11-Linoleic and α -eleostearic are the conjugated isomers of linoleic and linolenic acids, respectively.

III. EXPERIMENTAL

The purpose of this investigation, the plan of experimentation, the materials and apparatus used, the methods of constructional and operational procedure followed, and the data and results obtained in the investigation are presented.

Purpose of Investigation

The purpose of this investigation was the determination of the effects of various molecular structures of fatty acids on their molecular distillation characteristics when distilled in a laboratory-size centrifugal molecular still. Straight-chain saturated (C_{15} , C_{16} , C_{17} , C_{18} , C_{19} , and C_{20}) and unsaturated (C_{18} with one, two, and three double bonds) fatty acids were used in the study. Such effects as the chain length, presence and location of double bonds in the molecule, and positional and cis-trans isomerism were studied.

Plan of Experimentation

The plan followed in the investigation consisted of a literature review, the redesign and construction of the centrifugal molecular still, the preliminary tests made on the equipment and the constant-yield oil, the operational tests, and the analysis of results.

Literature Review. A survey of all available literature pertaining to molecular distillation was made to gain an insight into the work of previous investigators. Particular attention was devoted to fatty acid experimentation performed at the Virginia Polytechnic Institute and other laboratories.

Redesign and Construction of Equipment. The centrifugal molecular still first built by Coli (1949) and modified by Bull and Demakis (1953) was completely remodified to improve distillation operation and decrease leak possibilities. Changes in the equipment included a magnetic drive for the evaporating rotor; modified feed system including a positive-displacement feed-return pump; water-cooled condensing surface; all-aluminum feed, distillate, and residue tanks; modified vacuum system; and use of swagelok fittings and valves throughout the flow system.

Preliminary Tests. A number of preliminary tests were made on the unit to determine its operating characteristics and familiarize the operators with the techniques to be used in the operational tests. Tests were also made to study various blends of mineral oils in the determination of the proper blending of oils to obtain a constant-yield oil.

Experimental Tests. Each of the fatty acids used in the study was molecularly distilled from solution in a blended constant-yield oil. Standardized operating conditions were employed in each test so that results could be compared directly from one test to another. If sufficient acid were available, duplicate tests were made for each acid to improve the accuracy of the determination of the elimination curve and maximum.

Analysis of Results. The data obtained and the results of the investigation were discussed to evaluate the experimental work performed. The effect of structural differences in the fatty acid molecule were considered with respect to molecular distillation of the acids. Recommendations for future studies and for further modifications in still design to improve operation were presented.

Materials

The following materials were used in this investigation:

Alcohol, Ethyl. Technical grade, 95 per cent, USP, meets ACS specifications. Obtained from U. S. Industrial Chemicals, Inc., Baltimore, Md. Used as the extracting solvent in the titration of fatty acid samples.

Benzene. Purified, code No 1444, Lot No G-100-J. Obtained from Allied Chemical and Dye Corporation, General Chemical Division, New York, N. Y. Used to clean equipment and glassware during course of investigation.

Fatty Acids. The fatty acids used in the investigation are presented in Table VI, page 62.

Grease. High vacuum, celvacene heavy. Manufactured by the Consolidated Vacuum Corporation, Rochester, N. Y. Used in testing for leaks around fittings and bell jar of molecular still system.

Oil. Cenco, hyvac, Nos 93050C and 93055C. Obtained from Central Scientific Company, Chicago, Ill. Used as lubricant and sealing fluid in Cenco hyvac and megavac pumps.

Oil. Mineral, colorless, light and heavy grades; light oil boiling range at 10 mm mercury, 330 to 360 °C; heavy oil boiling range, 360 to 390 °C. Manufacturer unknown. Obtained

TABLE VI

Source of Fatty Acids Used in Distillation Studies

Acid	Formula	Molecular Weight	Source of Acid
Arachidic	$C_{19}H_{39}COOH$	312.52	Bios Laboratories, New York, N. Y.
Elaidic	$C_{17}H_{33}COOH$	282.45	Bios Laboratories, New York, N. Y.
α -Eleostearic	$C_{17}H_{29}COOH$	278.42	Bios Laboratories, New York, N. Y.
Linoleic	$C_{17}H_{31}COOH$	280.44	Bios Laboratories, New York, N. Y.
Linoleic	$C_{17}H_{31}COOH$	280.44	Eimer and Amend, New York, N. Y.
9,11-Linoleic	$C_{17}H_{31}COOH$	280.44	Bios Laboratories, New York, N. Y.
Linolenic	$C_{17}H_{29}COOH$	278.42	Bios Laboratories, New York, N. Y.
Margaric	$C_{16}H_{33}COOH$	270.44	Bios Laboratories, New York, N. Y.
Nonadecylic	$C_{18}H_{37}COOH$	298.49	Bios Laboratories, New York, N. Y.
Oleic	$C_{17}H_{33}COOH$	282.45	General Chemical, New York, N. Y.
Oleic	$C_{17}H_{33}COOH$	282.45	Merke and Company, New York, N. Y.
Palmitic	$C_{15}H_{31}COOH$	256.42	Eimer and Amend, New York, N. Y.
Palmitoleic	$C_{15}H_{29}COOH$	254.40	Bios Laboratories, New York, N. Y.
Pentadecylic	$C_{14}H_{29}COOH$	242.39	Bios Laboratories, New York, N. Y.
Stearic	$C_{17}H_{35}COOH$	284.47	Eimer and Amend, New York, N. Y.
Vaccenic	$C_{17}H_{33}COOH$	282.45	Bios Laboratories, New York, N. Y.

from Tech Drug Store, Blacksburg, Va. Used in preparing constant-yield oil blend.

Oil. Voltesso No 36. Obtained through courtesy of Esso Standard Oil Company, Linden, N. J. Used in preparing constant-yield oil blend.

Phenolphthalein. CP, meets ACS specifications. Obtained from Palo-Myers, Inc., New York, N. Y. Used as indicator in the titration of the fatty acid samples obtained from molecular distillation.

Potassium Hydrogen Phthalate. CP, meets ACS specifications. Obtained from Eimer and Amend, New York, N. Y. Used to standardize potassium hydroxide solution used in titration of fatty acids.

Potassium Hydroxide. CP, pellets, lot No E355, meets ACS specifications. Obtained from Allied Chemical and Dye Corporation, General Chemical Division, New York, N. Y. Used to prepare alkali solution for titration of fatty acid samples.

Solder. Sil-fos, 15 per cent silver content alloy, starts to melt at 1185 °F and is completely liquid at 1300 °F. Distributed by Southern Oxygen Company, Roanoke, Virginia. Used in welding numerous connections in the construction of the still assembly.

Solder. Lead-zinc solder, No 10, 50/50 grade. Manufactured by the National Lead Company, Baltimore, Md. Used in construction of water-cooled condenser.

Water, Tap. Obtained from Virginia Polytechnic Institute water mains. Used as condenser cooling water in constant-temperature bath.

Apparatus

The following apparatus and equipment were used in the course of this investigation.

Balance. Analytical, Seeder-Kohlbusch with chain-weights and magnetic damping attachments, capacity 200 grams each pan, sensitivity 1/20 milligram. Obtained from Phipps and Bird, Inc., Richmond, Va. Used to weigh acid samples in preparation of feed mixture.

Cell. Dry, No 6, -1/2 v, two used, connected in series. Manufactured by National Carbon Company, Cleveland, Ohio. Used in conjunction with the potentiometer for temperature measurements.

Cell. Standard, Eppley, student, cadmium, unsaturated, catalog No 11-506-38. Obtained from Fisher Scientific Co., Silver Spring, Md. Used for standardizing the potentiometer.

Fittings. Swagelok, brass and aluminum, assorted tees, male connectors, and valves for use with 1/4-inch copper tubing and 1/4- and 5/16-inch aluminum tubing. Obtained from Shelby and Jones Company, Havertown, Penn. Used in connecting copper and aluminum flow lines and making connections to the base plate and various tanks of the system.

Gage. McLeod, vacuum gage, type MG-07, triple range, table model, pump operated, range 0 to 5000 microns. Manufactured by and obtained from Consolidated Vacuum Corporation, Rochester, N. Y. Used to measure the absolute pressure within the system during tests.

Galvanometer. Pointer type, dc, catalog No 11-506-27, model B with scale of 60 divisions of 1 millimeter each, sensitivity 0.20 microampere per millimeter. Obtained from Fisher Scientific Company, Silver Spring, Md. Used in conjunction with potentiometer for temperature measurements.

Glassware. Assorted pyrex glassware such as beakers of various sizes, erlenmeyer flasks, 50-milliliter burets, graduated cylinders, and funnels. Obtained from Fisher Scientific Company, Silver Spring, Md. Used in feed preparation and sample titrations.

Heater. Immersion coil type, flexible copper sheath, 115 v, 100 w. Obtained from the American Instrument Company, Silver Spring, Md. Used as the heating element in the constant temperature bath.

Heating Bands. Glas-Col, catalog No 11-463-20, 2 inches wide and 6 feet long, 115 v, 400 w, ac or dc. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to heat feed, residue, and distillate tanks.

Heating Coil. Nykelkrom wire, catalog No 114507, 115 v, 1450 w. Manufactured by H. W. Tuttle and Company, Adrian, Mich. Used as the feed preheater on the gravity feed flow line.

Hot Plate. Fisher autemp, catalog No 11-467-1, model A, 115 v, ac. Obtained from Fisher Scientific Company, Silver Spring, Md. Used to preheat the feed mixture to dissolve the fatty acid and to heat the fatty acid samples during titration.

Instrument Panel. The following items are mounted on the instrument panel of the centrifugal molecular still.

Autotransformers. Powerstat, type 116, 115 v, 60 cy, ac, 1 KVA maximum, eight used. Manufactured by the Superior Electric Company, Bristol, Conn. Six powerstats used to control the rotor heater, feed preheater, feed tank heater, residue and distillate tank heater, constant-temperature

bath heater, and rotor drive motor. Two powerstats provided as spares.

Clock. Telechron electric wall clock, plastic case, 5-inch face, sweep second hand, No 6-664, 115 v, 60 cy, ac. Obtained from the Fisher Scientific Company, Silver Spring, Md. Used in the determination of the feed rate.

Pilot Lights. No 1377 F and S flush pilot lights, 110 v, ac. Sixteen required. Obtained from General Electric Supply, Roanoke, Va. Used to indicate whether current was "on" or "off" to the powerstats and other electrical circuits.

Switches. Single-pole, single-throw, toggle. Sixteen required. Obtained from General Electric Supply, Roanoke, Va. Used to turn power to the powerstats and vacuum pump motors "on" and "off".

Switch. Double-pole, double-throw, toggle. Obtained from General Electric Supply, Roanoke, Va. Used to complete either feed or residue thermocouple circuit.

Motor. Electric, companion type SPH, single phase, 115 v, 60 cy, ac, 1/4 hp, 1750 rpm. Obtained from Sears, Roebuck and Company, Roanoke, Va. Used to drive feed pump.

Motor. Electric, type ADS, style 957656-B, serial KU, 1/4 hp, variable speed. Manufactured by Westinghouse Electric Corporation, Pittsburgh, Penn. Used as drive for rotor.

Potentiometer. Fisher, type S, catalog No 11-506-1, two ranges, 0 to 0.017 v, and 0 to 1.7 v. Obtained from Fisher Scientific Company, Silver Spring, Md. Used to measure voltage across thermocouples during operation of the molecular still.

Pump. Nitralloy rotary gear pump, size 4327-01-8557, serial No 3084, rotation either direction, maximum capacity 20 to 25 cubic inches per minute at 1750 rpm. Pump equipped with standard mounting brackets; specially fitted with oil cup No 1003 and with 1/4-inch IPT for No 1600 cast iron lantern ring. Obtained from Northern Ordnance Pump Company, Minneapolis, Minn. Used to circulate feed from residue tank to feed tank.

Pump. Centrifugal, all-rubber bantam, No AR-4360, complete with enclosed drive. Obtained from Schaar and Company, Chicago, Ill. Used to circulate cooling water to the still condenser coils.

Still Head Assembly and Magnetic Drive. Drawing 1, page 78, shows an exploded drawing of the reconstructed still head assembly and magnetic drive. The component parts of the assembly are as follows:

Base Plate. Shown as item A, brass, 15 inches in diameter, 1-1/2 inches thick; drilled to accommodate feed inlet, vacuum, distillate, and residue outlets, rotor heater leads (spark plugs), vacuum gage and residue thermocouple outlets, and water connections for the condenser; circular groove 8-7/8 inches I. D. x 9-1/2 inches O. D. x 1/16-inch deep machined into the face of the plate to accommodate the silicone gasket used to permit sealing of the bell jar to the base plate. Brass plate obtained from Smith-Courtney Company, Richmond, Va. Machining was performed by the Industrial Engineering Shops Department, Virginia Polytechnic Institute, Blacksburg, Va.

Bearings. Ball, self-aligning, SKF No 1203. Four required. Obtained from SKF Industries, Charlotte, N. C. Used in the construction of the drive shaft and rotor shaft assembly.

Bell Jar. Pyrex, high form, 14-1/2 inches long by 8-7/16 inches I. D. Obtained from Fisher Scientific Company, Silver Spring, Md. Used as vacuum chamber of molecular still.

Collecting Gutter. See item F, Drawing 2, page 81. Rolled bronze; gutter constructed to fit around the periphery of rotor with a clearance of 1/32-inch;

outside diameter of gutter is 5-3/4 inches; inside diameter is 4-1/4 inches; thickness is 3/4-inch. Soldered to the back of the gutter is a 3/4-inch copper sleeve, 4-3/4 inches in diameter with a 1/4-inch lip to catch any dripping or overflow from the gutter. There is a 5/16-inch copper tubing outlet on the outer edge of the gutter and a corresponding outlet on the sleeve extension. Both outlets enter a common header that serves as residue draw-off line. The gutter was designed by Coli⁽³³⁾ and fabricated by the Comas Cigarette Machine Company, Salem, Va. Used to collect the residue as it is thrown as a fine spray from the edge of the revolving rotor.

Coupling. Flexible, type FCR-12, 1/2-inch bore. Manufactured by the Boston Gear Works, Quincy, Mass. Used to connect the drive shaft of the rotor motor to the drive shaft of the magnetic drive assembly.

Drive Magnet Holder. Shown as item E in Drawing 1, page 78. Brass disc, 1-1/2 inches long by 5-1/4 inches O. D., machined as shown to permit attachment to drive shaft with setscrew and to accommodate 25 permanent Alnico magnets. Fabricated by the Industrial Engineering Shops Department, Virginia Polytechnic Institute, Blacksburg, Va. Used as drive magnet holder.

Drive Shaft Assembly. Shown as item F, Drawing 1, page 78. Brass, 3-5/8 inches long by 6 inches O. D., machined to accommodate 1/2-inch drive shaft, 4-1/2 inches long, set in two sets of 1/2-inch ball bearings press-fitted into the assembly. One end of shaft is connected to magnet holder, E, when unit is assembled and the other end is connected to the rotor drive motor by a flexible coupling. The entire assembly is attached to the housing and base plate assembly (D and A) by four 4-1/4 inch bolts which pass through holes drilled in the assembly. The drive shaft assembly and drive magnet holder disc form the drive half of the magnetic drive unit.

Gasket. Silastic, No 7-170, silicone rubber, 8-7/8 inches I. D. by 9-1/2 inches O. D. by 1/8-inch thick. Cut from 18 by 18-inch piece of silicone rubber obtained from the Connecticut Hard Rubber Company, New Haven, Conn. Used as the seal between the bell jar and the base plate of the molecular still.

Heater. Chromalox ring element, catalog No A-20, type A, 115 v, 60 cy, ac, 300 w, chrome steel sheath, single heat, for temperatures up to 1200 °F maximum. Obtained from Edwin L. Wiegand Company, Pittsburgh, Penn. Used as rotor heater.

Housing. Shown as item D, Drawing 1, page 78. Brass 4-7/16 inches long by 6 inches O. D. Inside of housing machined to various diameters as shown to accommodate the rotor shaft assembly and rotor magnet holder. Four inches O. D. and 3-25/32 inches I. D. end of housing machined as such to provide a thin (7/64-inch) brass section at magnetic coupling area of housing. The housing was permanently connected to the base plate, A, by brazing around the complete periphery of the housing. Machining and brazing performed by the Industrial Engineering Shops Department, Virginia Polytechnic Institute, Blacksburg, Va. The attachment of the housing to the base plate provided a leakproof vacuum changer to which the bell jar could be attached.

Magnets. Fifty used, permanent type, No 4Y21P4, style 2, rectangular U shape, sintered, ground and magnetized. Obtained from Permag Company, Brooklyn, N. Y. Used in construction of non-contacting magnetic coupling for rotor drive.

Rotor. Aluminum, 4.11 inches O. D., 2.075 inches thickness at outer edge, angle of inclination of rotor evaporating surface 52-1/2 degrees, slant height of rotor surface 2.59 inches. Designed by Coli⁽³⁴⁾ and fabricated

by the Comas Cigarette Machine Company, Salem, Va. Used as the evaporating surface of the molecular still.

Rotor Magnet Holder. Shown as item C, Drawing 1, page 78. Brass disc, 1-3/8 inches long by 3 inches O. D., machined to be attached to rotor shaft by means of a set-screw and to accommodate 25 magnets. Machining performed by the Industrial Engineering Shops Department, Virginia Polytechnic Institute, Blacksburg, Va. Used as rotor magnet holder.

Rotor Shaft Assembly. Shown as item B, Drawing 1. Brass, 1-5/8 inches long by 4 inches O. D., machined to accommodate 1/2-inch rotor shaft, 8-1/8 inches long, set in two sets of 1/2-inch ball bearings press-fitted into the assembly. One end of shaft is connected to magnet holder, C, and the other end is connected to the rotor. The entire assembly is fitted snugly into the housing, D, and held in place with two 1/4-inch oval point setscrews. The rotor shaft assembly and rotor magnet holder form the rotor half of the magnetic drive unit.

Spark Plugs. No 45, ac, side contacts removed, 1/2-inch length of a No 10 bolt was welded to the center terminals to attach heater leads. Base plate drilled and tapped to accommodate plugs, vacuum-tight seal obtained.

by tightening plugs down on 1/8-inch thick lead gaskets. Manufactured by General Motors Corporation, Detroit, Mich. Used to connect rotor heater leads to electric power source through base plate.

Tachometer. Hand tachometer, type 25A, serial No 679, 200 to 10,000 rpm. Obtained from the Metron Instrument Company, Denver, Colo. Used to measure the speed of the rotor.

Tank. Open end, stainless steel, 2-gallon capacity. Manufacturer unknown. Used as the constant-temperature bath for condenser cooling water.

Tank, Loading. See item G, Drawing 2, page 81. Copper, cylindrical, 1-1/2 inches O. D. by 2-1/4 inches high, open at one end, concave bottom with 1/4-inch copper tubing welded to center for drain. Constructed in the Chemical Engineering Department, Virginia Polytechnic Institute, Blacksburg, Va. Used as feed loading tank.

Tanks, Feed and Residue. See items J and H, Drawing 2. Aluminum, cylindrical, 6-1/2 inches O. D. by 7 inches high, closed at both ends, flat top, concaved bottom for drainage, all swagelok connections with 1/8-inch male connectors. Constructed in the Industrial Engineering Shops Department, Virginia Polytechnic Institute, Blacksburg, Va. Used as the feed and residue tanks in the still system.

Tank, Distillate. See item K, Drawing 2, page 81. Aluminum, cylindrical, 4-1/2 inches, O. D. by 5 inches high, closed both ends, flat top, concaved bottom for drainage, all swagelok connections with 1/8-inch male connectors. Constructed in the Industrial Engineering Shops Department, Virginia Polytechnic Institute, Blacksburg, Va. Used as distillate collection tank.

Thermocouples. Copper-constantan. Constructed from 3/32-inch copper tubing (serving as copper lead) and insulated Leeds and Northrup No 24 constantan wire. Wire inserted into tubing and beaded at one end forming junction; junction secured and made vacuum tight by fusing the copper and constantan together at the junction. Thermocouples inserted into the feed and vacuum lines through the run of a swagelok aluminum tubing tee and secured into place by tightening the fitting. Two required. Constructed in the Chemical Engineering Department, Virginia Polytechnic Institute, Blacksburg, Va. Used to measure the temperature of the feed and residue during operational tests.

Thermometer. Certified, catalog No 15-040, range from -10 to 300 °C in 1/10 °C increments. Obtained from Eimer and Amend, New York, N. Y. Used in calibration of the thermocouples.

Thermoregulator. Liquid-filled, expansion type thermostat, type R-1, No 4980281G16, range from 65 to 135 °F, 110/220 v,

25 amp. Manufactured by General Electric, Schenectady, N. Y.
Used to control the constant-temperature bath heating element.

Vacuum Pump. Genco, hyvac, 10 liters per minute capacity, 340 rpm, equipped with a 1/4-hp, 115 v, 60 cy, ac, 1750 rpm motor. Obtained from Central Scientific Company, Chicago, Ill. Used as the backing pump for the McLeod gage.

Vacuum Pump. Genco megavac, 31 liters per minute capacity, 325 rpm, equipped with a 1/4-hp, 115 v, 60 cy, ac, 1750 rpm motor. Four required. Three pumps used to evacuate the still system and one used to evacuate the distillate tank in preparing the tank for collection of distillate fractions.

Valve. Throttling, globe-type needle valve, No 10-F-40, forged carbon steel body, 1/8-inch. Obtained from the Dragon Engineering Company, Los Angeles, Calif. Used as the feed rate control valve.

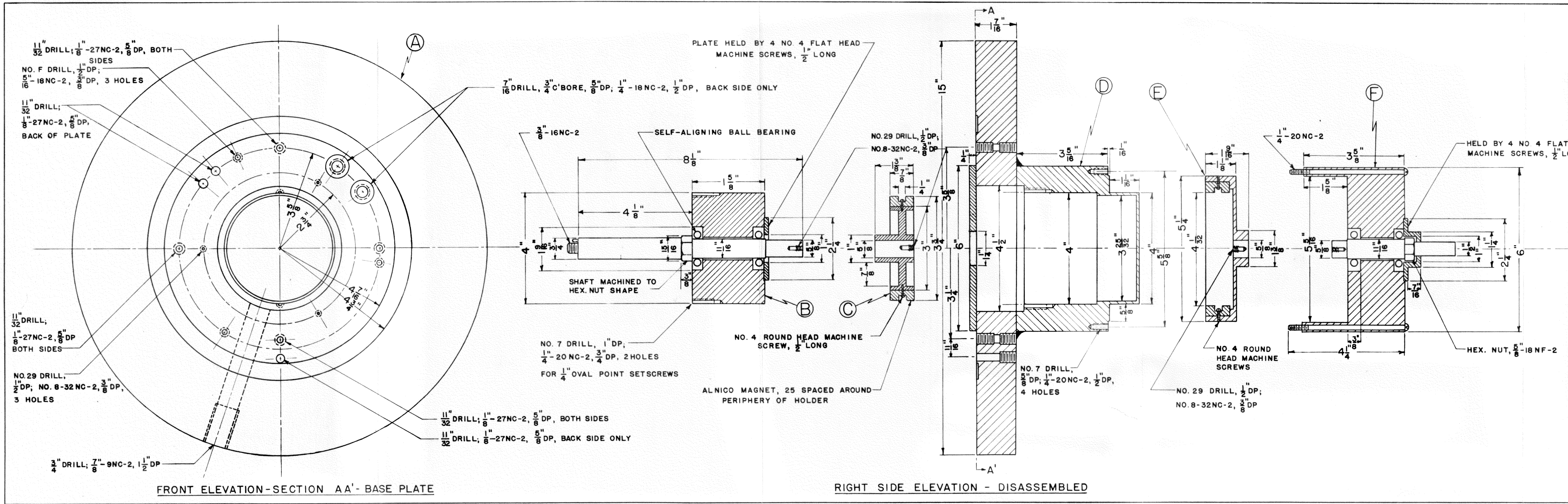
Method of Procedure

The methods of procedure followed in the performance of this study are explained under the headings of (1) redesign and construction of the centrifugal molecular still, (2) preliminary tests, (3) operational procedure, (4) distillation of fatty acids, and (5) analytical procedure.

Redesign and Construction of Centrifugal Molecular Still.

The redesign and construction of a new five-inch centrifugal molecular still was undertaken to overcome leak difficulties encountered in previous designs⁽¹⁹⁾ and to provide for smoother and easier operation. The basic modification was the design of the still head assembly with a magnetic drive to eliminate leaks which developed in driving the rotor by means of a packed shaft. The design and construction procedure is briefly outlined with consideration of the still head assembly, the frame support, the still accessories, the vacuum system, the vacuum measuring system, the control panel board, and the constant-temperature bath. A change in the original design to incorporate a gravity-feed system in place of a forced-feed system is also discussed.

Still Head Assembly. The still head assembly, shown in Drawing 1, page 78, was constructed to include the



DEPARTMENT OF CHEMICAL ENGINEERING VIRGINIA POLYTECHNIC INSTITUTE BLACKSBURG, VIRGINIA		
MAGNETIC DRIVE AND BASE PLATE		
SCALE: 1/2" = 1"	DATE: 4/12/54	CASE NO. 54
DRAWN BY: JWB	CHECKED BY: JWB	FILE NO. 799
APPROVED BY: JWB	DATE: 4/12/54	DRWG. NO. 1

magnetic drive, a brass base plate, a water-cooled condenser, and a "high-form" bell jar. The material of construction for the assembly, with the exception of the pyrex glass bell jar, was brass, which was non-magnetic and did not interfere with the operation of the magnetic drive.

Magnetic Drive. Due to the difficulties encountered by Bull⁽¹⁹⁾ in trying to prevent leaks through the packing around the rotor shaft, it was decided to eliminate any direct connection between the rotor shaft and the drive shaft of the rotor drive motor. This was accomplished by machining a 6-inch diameter, 3-1/2 inch long brass housing, item D, Drawing 1, to accommodate a 3-inch brass disc, item C, fitted with 25 permanent Alnico magnets. The disc was attached to one end of the 7/8-inch diameter rotor shaft. The drive magnets were bolted to a 5-1/4 inch diameter machined counter-sunk disc, item F, and so machined that, when assembled, the outer magnets would "engage" the inner magnets, setting up the necessary magnetic field required as the drive "connection". The parts of the assembly were machined so that a minimum of air gap and metal thickness separated the magnets; the brass housing was 7/64-inch thick, with approximately 1/64-inch air gap

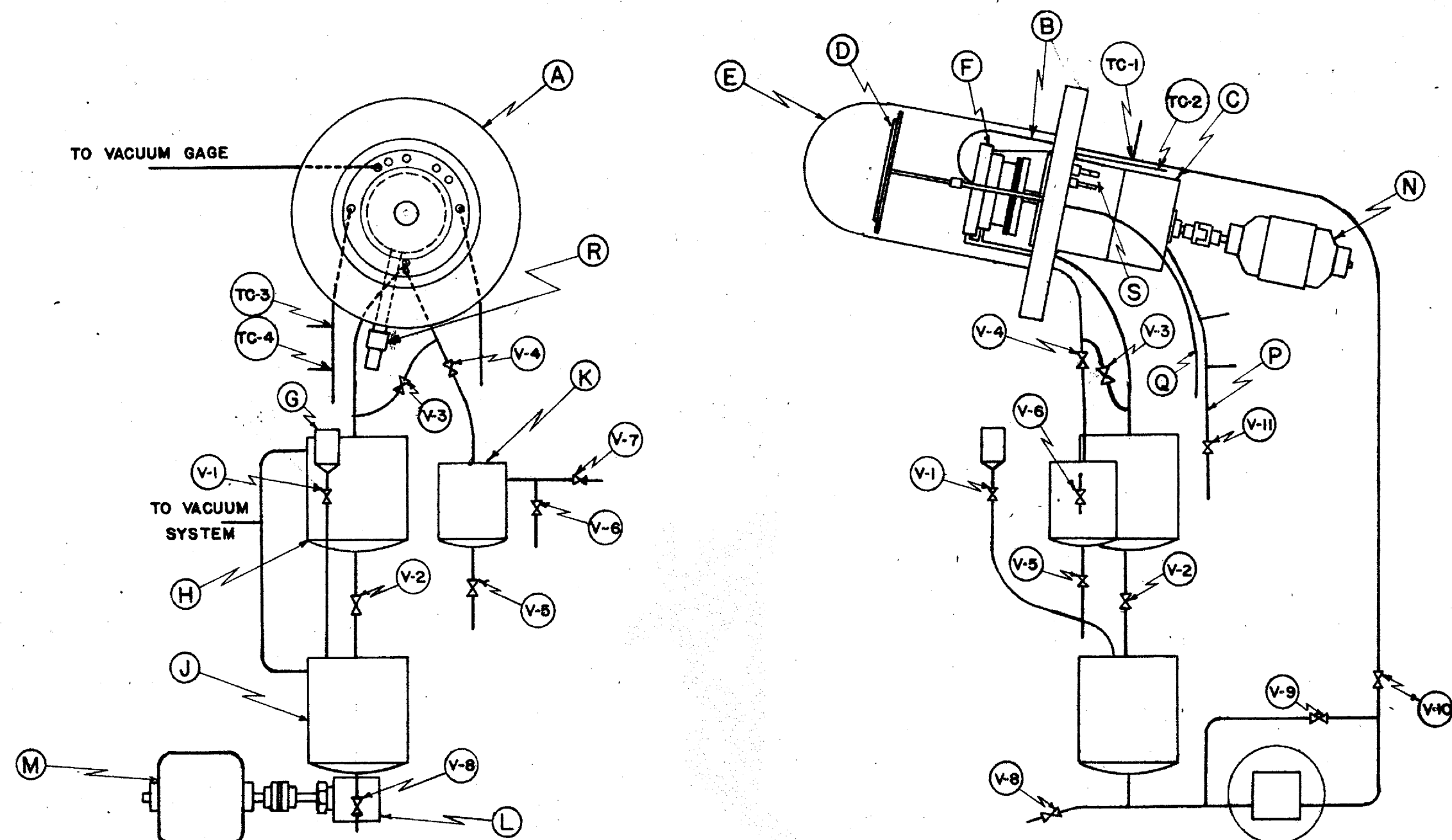
on each side. The magnets were arranged in alternating matching groups -- six, six, six, and seven, alternating N-S, S-N, N-S, and S-N, respectively -- for both the drive and rotor magnet assemblies.

For alignment purposes, the rotor shaft was machined to fit through two 1/2-inch ball bearings, which were press-fitted and locked into a 4-inch diameter, 2-5/8 inch long, machined sleeve. The rotor shaft projected through the base plate, shown as item A, far enough to accommodate the back plate, rotor heater, and rotor.

The outer magnet disc or drive disc was aligned so that it would maintain proper clearance between the housing and the magnets by connection to one end of the 7/8-inch drive shaft. The drive shaft was held in place by two sets of 1/2-inch ball bearings and connected by means of a flexible coupling to the drive motor, item N, Drawing 2, page 81.

In this manner, the rotor drive end of the magnetic drive assembly was made a completely sealed unit.

Base Plate. To accommodate the changes necessitated by the magnetic drive, a new brass



FRONT ELEVATION

RIGHT SIDE ELEVATION

KEY TO SYMBOLS

- A - BASE PLATE
- B - FEED NOZZLE
- C - MAGNETIC DRIVE
- D - CONDENSER
- E - BELL JAR
- F - GUTTER AND ROTOR HEATER ASSEMBLY
- G - LOADING TANK
- H - RESIDUE TANK
- J - FEED TANK
- K - DISTILLATE TANK
- L - FEED PUMP
- M - FEED PUMP MOTOR
- N - ROTOR MOTOR
- P - INLET WATER LINE
- Q - OUTLET WATER LINE
- R - MAIN VACUUM LINE
- S - SPARK PLUGS
- TC-1 - FEED THERMOCOUPLE
- TC-2 - RESIDUE THERMOCOUPLE
- TC-3 - FEED TC COLD JUNCTION
- TC-4 - RESIDUE TC COLD JUNCTION
- V-1 TO V-11 - VALVES

NOTE: ANGLE IRON SUPPORT FOR SYSTEM NOT SHOWN.

DEPARTMENT OF CHEMICAL ENGINEERING VIRGINIA POLYTECHNIC INSTITUTE BLACKSBURG, VIRGINIA		
CENTRIFUGAL MOLECULAR STILL WITH MAGNETIC DRIVE		
SCALE: 1/8" = 1" DRAWN BY: <i>Jwb</i> CHECKED BY: <i>Jwb</i> APPROVED BY: <i>Jwb</i>	DATE 4/7/54 4/12/54 4/12/54	CASE NO. 54 FILE NO. 799 DRWG NO. 2

plate, item A, Drawings 1 and 2, had to be constructed. The plate was machined from a brass disc, 15 inches in diameter and 1-1/2 inches thick, to accommodate taps for spark plugs for heater connections, S, vacuum outlet, R, feed inlet, distillate and residue outlets, vacuum gage connection, residue thermocouple inlet, and water connections for the condenser, P and Q. A circular groove, 8-7/8 inches I. D. by 9-1/2 inches O. D. by 1/16-inch deep was machined into the face of the base plate to accommodate the silicone rubber gasket which acted as the seal between the bell jar and the base plate.

Water-cooled Condenser. In order to provide better control of the condenser temperature, it was decided to employ a water-cooled condenser inside a "high form" bell jar, item E, Drawing 2, instead of a short bell jar and no condensing surface other than the bell jar as used by Bull⁽⁷⁾. A copper condenser, item D, Drawing 2, was built from an 1/8-inch copper plate, 8 inches diameter. To the back (away from the rotor) of the condenser plate, six concentric spirals of 1/4-inch copper tubing were soft-soldered. The inlet and outlet water lines which passed from the condenser plate through the base plate

served as the support for the condenser. The clearance between the condenser plate and the inside of the bell jar was small enough (approximately $3/32$ -inch) that a negligible amount of vapor passed the front of the condenser during distillation.

Incorporation of Previous Still Head Features.

In the redesign and construction of the new still head assembly, some features of the assembly used by Coli and Bull were retained. These included the five-inch rotor⁽³⁴⁾, the collecting gutter⁽³³⁾, and the rotor heater⁽⁸⁾. A description of these features and their design may be found in the given references.

Frame Support. The supporting frame for the still was constructed of $1-1/4$ by $1-1/4$ by $1/8$ -inch angle iron, and was 36 inches high, 21 inches wide, and 16 inches long. The construction was such that the space between the supporting members was kept at a maximum to accommodate the necessary tanks, tank supports, flow lines, and feed pump. The still assembly was mounted on top of the frame and supported by two 2 by 2 by $3/16$ -inch pieces of angle iron, $15-1/2$ inches long, welded to a 16 by $6-1/4$ by $1/2$ -inch iron plate, which in turn was welded to the frame. The mount for the drive motor was constructed from an iron

plate, 7 by 5-1/4 by 3/8 inches, bolted on one end to an 1/8-inch supporting iron brace, and welded on the other end to a 3/8 by 1 by 16 inch piece of strap iron. The strap iron and support were in turn bolted to the top of the frame. The entire frame support was bolted to the floor with 1/4-inch diameter, 1-1/2 inch long anchors to provide additional support and to prevent lateral movement of the entire unit.

Still Accessories. In the all-metal still built by Bull, the flow lines, tanks and accessory equipment were constructed of copper or copper tubing. To gain increased capacity and flexibility in the operation of the still, the following changes were made to the accessory equipment.

Distilland and Residue Tanks. The distilland (feed) and residue tanks were made larger than those constructed by Bull⁽⁶⁾ in order to handle greater quantities of liquid. The tanks, H and J, Drawing 2, page 81, constructed of aluminum pipe, were 6-1/2 inches O. D. by 7 inches high, closed at both ends with a flat top and a concave bottom for drainage. They were installed in the assembly with assorted aluminum swagelok fittings. Valves in the flow lines to and from the tanks were Hoke valves with

swagelok ends to provide a vacuum-tight unit. All flow lines, with the exception of the vacuum lines, were constructed of 1/4-inch aluminum tubing. The vacuum system connection line was constructed of 5/16-inch aluminum tubing.

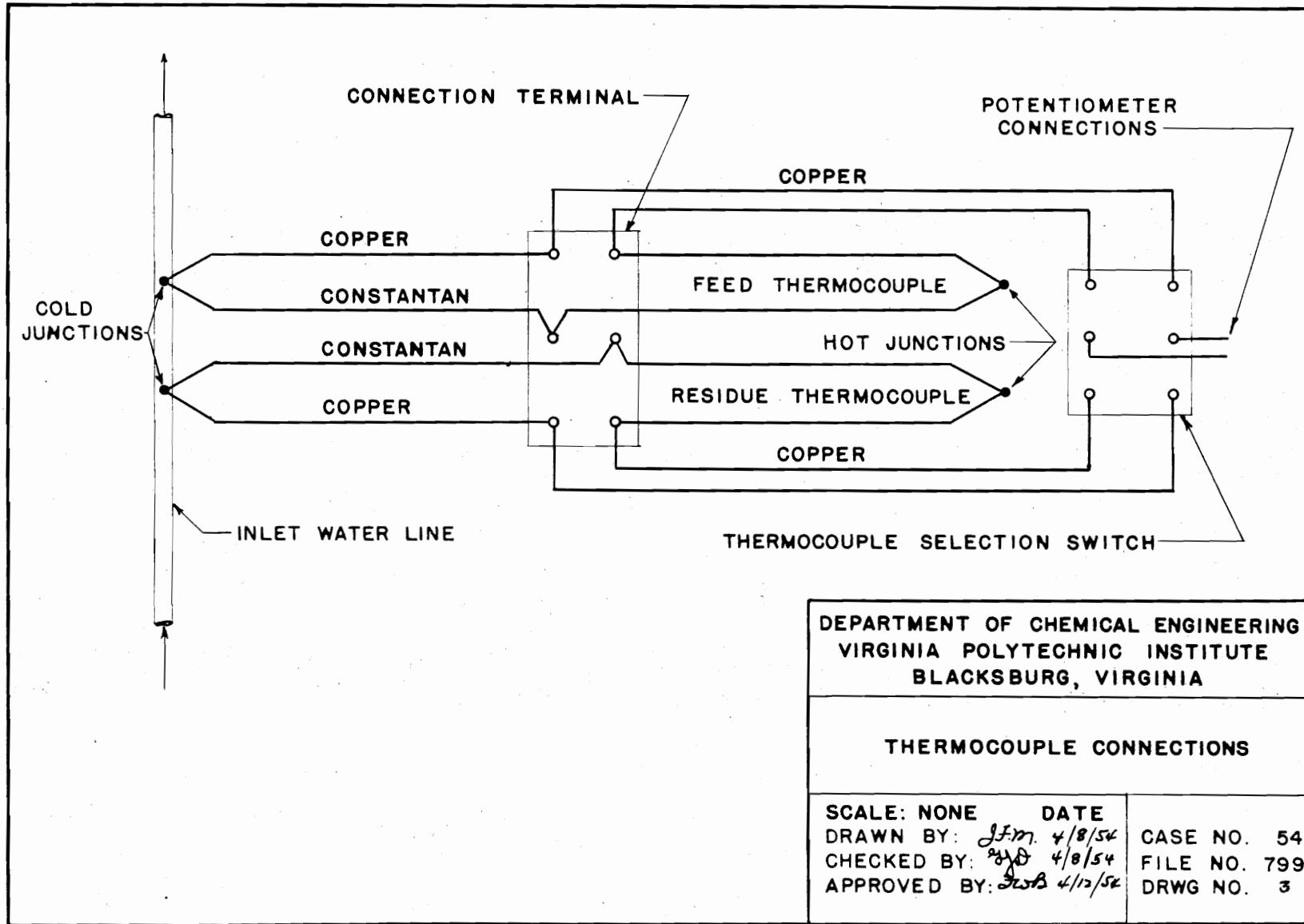
Distillate Tank. The distillate tank, K, was also constructed of aluminum. The tank was 4-1/2 inches O. D. by 5 inches high, and closed at both ends; the top was flat and the bottom concave to allow for drainage. The vacuum connection of the distillate tank to the megavac was of 1/4-inch copper tubing, all other tubing connections were 1/4-inch aluminum tubing.

Thermocouples. The feed and residue thermocouples were constructed according to the procedure described by Bull⁽¹⁰⁾. The feed and residue thermocouples were inserted into the proper locations and secured by swagelok fittings. To eliminate the use of an ice bath for the cold junction, the following change was made: two more thermocouple junctions were constructed, similar to the hot junctions. These were installed into a 1/4-inch aluminum tubing water line

by use of swagelok tees. The thermocouples could then be calibrated against cold tap water which remained at a nearly constant temperature (12 ± 1 degrees centigrade). A schematic wiring diagram for the thermocouple setup is shown in Drawing 3, page 87.

Feed Pump. At the recommendation of Bull⁽²³⁾, the magnetic feed pump was replaced by a positive displacement nitralloy rotary gear pump having a maximum capacity of 20 to 25 cubic inches per minute at 1750 revolutions per minute. The pump, as purchased, was provided with an oil cup and an oil lantern ring to act as a vacuum seal. The feed pumping system, as first designed, incorporated the use of a feed bypass for feed rate control. In the final system, the feed was gravity-fed and the feed pump was used merely to transfer the feed from the residue tank to the feed tank. The change from a forced-feed to a gravity-feed system will be further discussed.

Heaters. The heaters used in the system were similar to those used by Bull⁽⁵⁾. A ring-type heater element located around the rotor shaft and approximately 1/8-inch from the back of the rotor provided the heat for the rotor. A nichrome wire element, coiled spirally



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 VIRGINIA POLYTECHNIC INSTITUTE
 BLACKSBURG, VIRGINIA

THERMOCOUPLE CONNECTIONS

SCALE: NONE	DATE	
DRAWN BY: JFM	4/8/54	CASE NO. 54
CHECKED BY: JFD	4/8/54	FILE NO. 799
APPROVED BY: JWB	4/12/54	DRWG NO. 3

around the feed flow line (not shown in drawing) acted as the feed preheater. The tanks were heated by two glas-col heating bands, one wrapped around the feed tank and the other wrapped around both the distillate and residue tanks.

Vacuum Producing System. It was decided that the diffusion pumps used by Bull⁽¹¹⁾ would not be used in the system because a satisfactory vacuum could be produced without them and because they required at least a one-hour period for placing into operation and an additional one-hour shutdown period for cooling the diffusion pump oil under forepump vacuum. The system was evacuated by connecting three megavac pumps to a common manifold made of two-inch copper pipe. The manifold was connected to the vacuum outlet of the base plate and to the vacuum connections of the feed and residue tank. The distillate tank was individually evacuated by use of a fourth megavac so that it could be vented to the atmosphere and reevacuated as necessary for removal of distillate fractions from the still.

Vacuum Measuring System. The absolute pressure in the system was measured with a triple-scale, vacuum pump-operated McLeod gage with a range from 0 to 5000 microns of mercury. The gage was connected to the base plate by

means of 1/4-inch copper tubing. A hyvac pump was also connected to the McLeod gage with 1/4-inch copper tubing.

Control Panel Board. To facilitate ease of control and operation of the molecular still, a 30-1/2 by 46-inch panel board was constructed of 3/8-inch plywood. The following control elements were mounted on the panel board: eight powerstats for the control of the roter heater, feed preheater, rotor drive motor, feed tank heater, distillate and residue tanks heater, and constant-temperature bath heater with two provided as spares; sixteen single-pole single-throw switches for completing and breaking circuits to the powerstats and motors driving the feed pump, distillate megavac, and gage hyvac; and a double-pole double-throw switch for changing the thermocouple potentiometer circuit for determining either the feed or residue temperature. An electric clock was also mounted on the panel board to provide a method for timing the feed rate. The panel board was mounted on 1/2 by 1/2 by 1/8-inch angle iron and attached to the wall by 1/4-inch wall anchors.

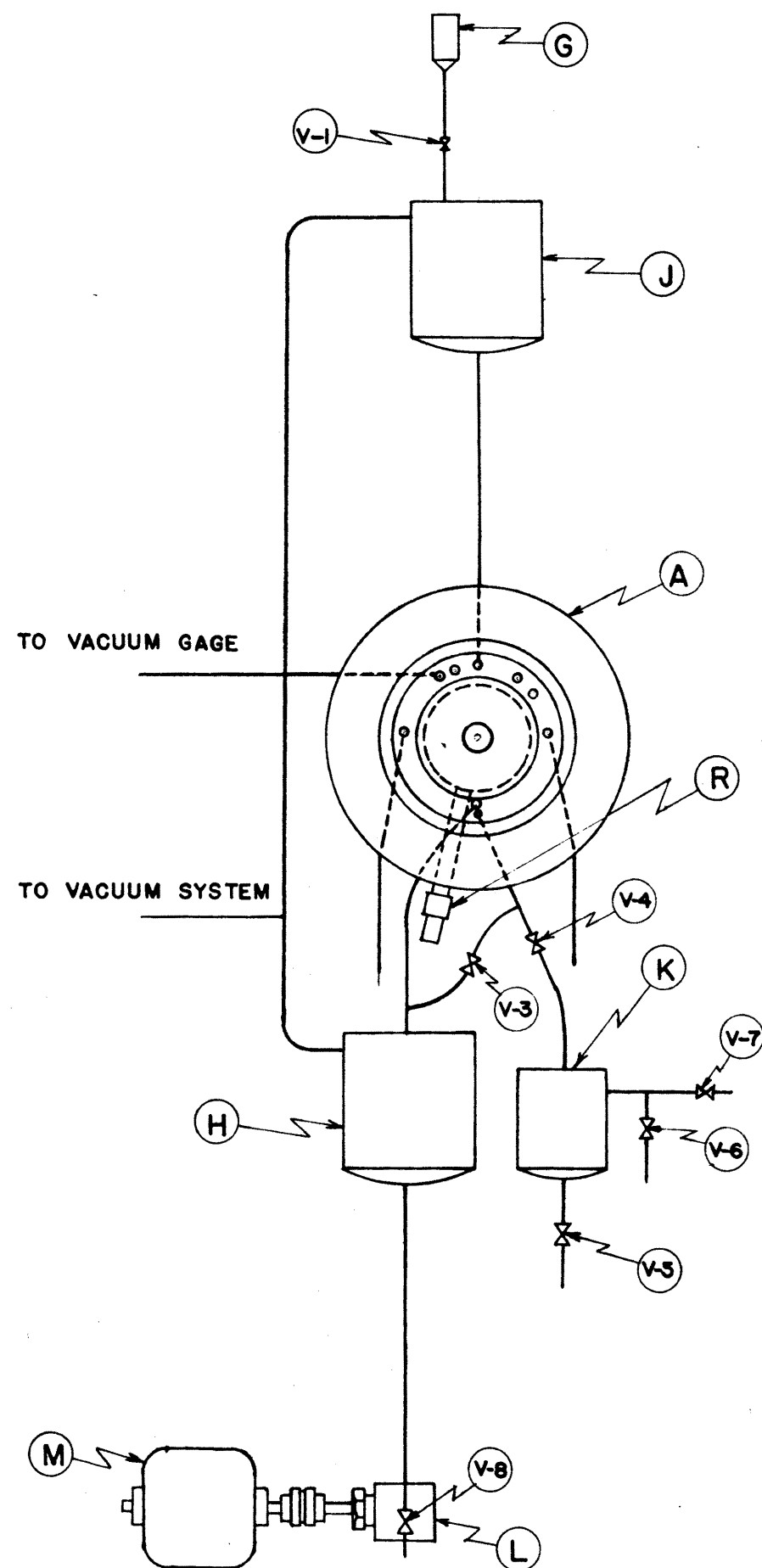
Constant-temperature Bath. The crystallization of the fatty acid on the condenser when tap water was used as the cooling medium resulted in the need for a constant-temperature

bath to supply cooling water at approximately 45 degrees centigrade. A stainless steel tank with an approximate capacity of two gallons was used as the bath. An immersion coil heating element was placed in the water of the bath and controlled with an adjustable liquid-filled bulb thermostat which "opened" or "closed" the electrical circuit to the heating element as necessary for maintenance of the desired temperature in the bath. A small centrifugal pump was used to circulate the cooling water from the bath, to the condenser located inside the bell jar, and back to the bath. The connection from the bath tank to the pump and the cooling water flow lines were made of 1/4-inch copper tubing.

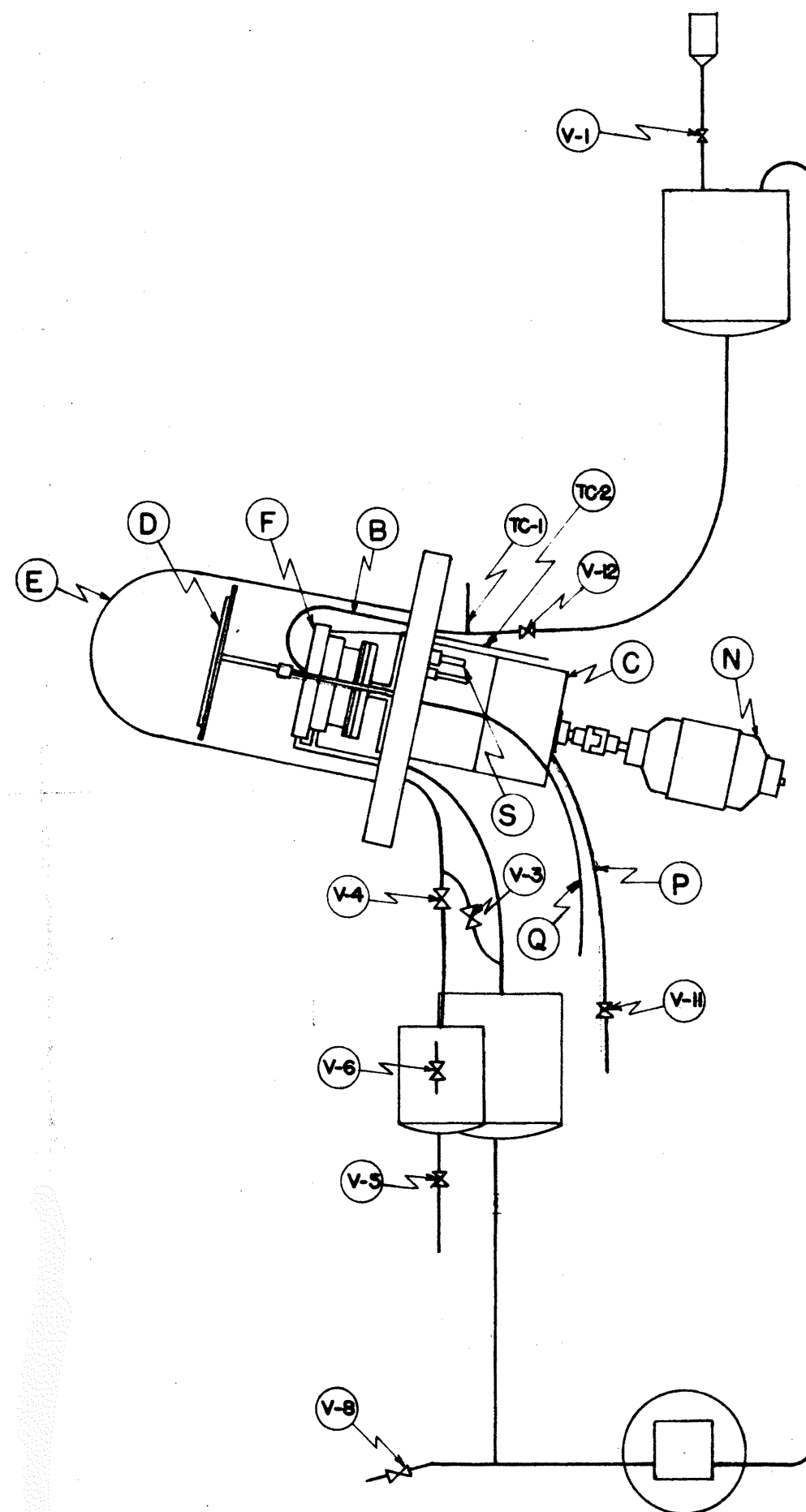
Gravity Feed System. The original redesigned still provided for a forced-feed system in which the feed rate was controlled by adjustment of the feed valve, V-10, and the feed bypass valve, V-9, Drawing 2, page 81. The control obtained by this system was found to be most unsatisfactory since the capacity of the feed pump was so large that a great majority of the feed through the pump had to be recycled through the bypass. The valve openings could not be adjusted to maintain the desired feed rates. This

necessitated a redesign of the system to use a gravity feed system. The feed tank, J, was changed from a position below the residue tank, Drawing 2, page 81, to a position approximately 18 inches above the base plate, Drawing 4, page 92. The feed pump remained in the same position, and with the removal of the bypass line, was used only to transfer the feed from the residue tank to the feed tank. The rate at which the feed was returned to the feed tank by the pump was then unimportant except that it be rapid enough that only an approximate 25-milliliter holdup remained in the lines and residue tank after 5 or 6 minutes of pumping. A control valve, V-12, replaced control valve V-10 and more adequately served to regulate the feed rate. Drawing 4, page 92, shows the molecular still system with gravity feed used in all the operational tests.

Preliminary Tests. The preliminary tests consisted of the calibration of the feed and residue thermocouples, the development of a mineral oil blend for constant-yield oil, and the preliminary operational tests made on the centrifugal still to develop an operating technique and familiarize the operators with the equipment.



FRONT ELEVATION



RIGHT SIDE ELEVATION

KEY TO SYMBOLS

- A - BASE PLATE
- B - FEED NOZZLE
- C - MAGNETIC DRIVE
- D - CONDENSER
- E - BELL JAR
- F - GUTTER AND ROTOR HEATER ASSEMBLY
- G - LOADING TANK
- H - RESIDUE TANK
- J - FEED TANK
- K - DISTILLATE TANK
- L - FEED PUMP
- M - FEED PUMP MOTOR
- N - ROTOR MOTOR
- P - INLET WATER LINE
- Q - OUTLET WATER LINE
- R - MAIN VACCUM LINE
- S - SPARK PLUGS
- TC-1 - FEED THERMOCOUPLE
- TC-2 - RESIDUE THERMOCOUPLE
- V-1 TO V-12 - VALVES

DEPARTMENT OF CHEMICAL ENGINEERING
VIRGINIA POLYTECHNIC INSTITUTE
BLACKSBURG, VIRGINIA

CENTRIFUGAL MOLECULAR STILL
WITH GRAVITY FEED

SCALE: 1/8" = 1"	DATE	
DRAWN BY: J.F.M.	3/1/55	CASE NO. 55
CHECKED BY: J.F.M.	3/1/55	FILE NO. 799
APPROVED BY: J.F.M.	3/3/55	DRWG NO. 4

NOTE: ANGLE IRON SUPPORT FOR SYSTEM NOT SHOWN

Thermocouple Calibration. The feed and residue thermocouples were calibrated by placing the hot junction of each thermocouple in an oil bath equipped with a standard thermometer and an electric stirrer. The cold junctions were located in a tap water line constructed for the purpose of calibrating the thermocouples against tap water temperature. The oil was agitated and heated at the rate of 0.5 degrees centigrade per minute. Potentiometer readings for both thermocouples were taken at various temperatures from 50 to 170 degrees centigrade both as the temperature was increased and as it was allowed to decrease. Spot checks were also made at the freezing and boiling points of water by placing the hot junction of each thermocouple in ice and in boiling water. A calibration curve was drawn for the potentiometer readings versus the temperatures for each thermocouple.

The thermocouples were calibrated for a cold junction temperature of 12 degrees centigrade. During the duration of the experimental tests, tap water temperature varied from 11 to 13 degrees centigrade. When the cold junction or tap water temperature varied from 12 degrees, proper corrections up to ± 0.04 millivolt were made to the potentiometer readings.

Development of Constant-yield Oil Blend. A satisfactory blend of mineral oils was developed by distilling various oils to determine their individual ranges of distillation and by testing various blends of the most suitable of these oils.

Light and heavy medicinal mineral oils and five various petroleum oils - Voltesso No 36, Marcol-JX, XCT White Oil, Mentor 28, and Solvent No 65 Neutral - were distilled under operating conditions similar to those to be employed in the experimental tests. From these tests it was decided that a blend of the light and heavy mineral oils and Voltesso No 36 would provide a constant-yield oil over the desired temperature range of 80 to 150 degrees centigrade.

Various blends of these three oils were then distilled again using techniques similar to those to be employed in the experimental tests. A blend of 225 milliliters of Voltesso No 36, 175 milliliters of light mineral oil, and 425 milliliters of heavy mineral oil was found to give a satisfactory constant-yield oil. Approximately half of this blend remained as residue (carrier oil) after the last distillate fraction was removed from the still. The amount of residue could be varied without loss of constancy in the yields by increasing or decreasing the amount of heavy mineral oil in the blend.

The blend mentioned was, however, used as the solvent constant-yield oil for all of the tests on fatty acids.

Preliminary Operational Tests. Numerous vacuum tests were made on the newly-constructed centrifugal still and on its component parts to eliminate minor leaks as much as possible.

A number of tests were performed to develop a technique and a set of suitable operating conditions for the experimental tests. These served as well to familiarize the operators with the operating characteristics of the redesigned still.

A number of important characteristics were determined from these preliminary tests. The feed holdup in the flow lines was found to be approximately 25 milliliters. A number of feed rates were attempted and an optimum feed rate of 60 to 65 milliliters per minute was selected as the most suitable for ease of control and smoothness of operation. Tap water was found to be unsuitable for use as the cooling medium for the condenser because crystallization of the fatty acids resulted in improper drainage from the condenser. This necessitated the construction of a constant-temperature bath to provide cooling water for the condenser at a constant and controllable temperature. A cooling water

temperature of 45 degrees centigrade was arbitrarily selected and found to be satisfactory in all tests.

Operational Procedure. Before the actual operational test procedure could be started, the feed had to be prepared and charged to the feed tank, the vacuum system had to be sealed and placed into operation, and the feed had to be heated and degassed. The distillate fractions could then be collected at the proper temperatures and feed rates. After the completion of the test, the system had to be shut down and prepared for the subsequent test. In describing the various procedures, reference is made to the schematic flow diagram, Drawing 4, page 92.

Preparation of Feed. A constant-yield oil was prepared for each test by blending 225 milliliters of Voltesso No 36, 175 milliliters of light mineral oil, and 425 milliliters of heavy mineral oil. This provided an initial feed volume of 825 milliliters, of which 25 milliliters were considered as feed holdup in the flow lines.

To this blend was added approximately 0.5 gram of the fatty acid to be tested. The acid was accurately weighed using an analytical balance since the weight of acid used was important in the calculation of yields for each temperature fraction. After the addition of the acid, the feed mixture of acid and oils was heated to approximately

60 degrees to completely dissolve the acid before the oil solution was charged to the still.

Preparation of McLeod Gage. The hvac pump used to operate the McLeod gage was turned "on" as the first step in readying the vacuum system for operation. The gage was opened to the pump to allow the mercury in the gage reservoir to be relieved of any oil vapors from a previous test and to prevent surging of mercury in the gage when the still was evacuated. This "degassing" of the mercury required at least 15 minutes before the gage would function properly.

Charging of Feed to Still. The feed mixture was charged by means of loading tank G and valve V-1. Valve V-12 was closed before charging the feed to the still to prevent feed from spilling onto the rotor. Valve V-1 was closed after the entire feed volume had drained into the feed tank J.

Start-up Procedure. In readying the still for operation, the following valves were closed: V-1, V-4, V-5, V-8, and V-12. All other valves, V-3, V-6, and V-11, were opened. The silicone gasket was placed into position in the groove of the base plate, A, Drawing 1, page 78, and the bell jar, E, Drawing 4, page 92, was then centered on the gasket. The bell jar was pressed firmly against the

gasket and the three system megavac pumps and the distillate tank megavac were turned "on". The vacuum in the system served to hold the bell jar in place once the system was evacuated. The McLeod gage was observed at all times during this start-up and the backing pressure to the gage (hyvac pump pressure) was balanced against the system pressure to prevent mercury from being drawn from the gage into the flow lines of the still.

While the system was being evacuated, the tap water for the cold junction of the thermocouples was turned "on" and the potentiometer was balanced against the standard cell. The heating element for the constant-temperature bath and the condenser water pump were also turned "on".

Heating and Degassing of Feed. The rotor motor, N, was turned "on" and the controlling powerstat adjusted for a rotor speed of approximately 1000 revolutions per minute. The feed was allowed to flow to the rotor by opening valve V-12. The feed rate was adjusted to approximately 60 milliliters per minute. The exact feed rate was unimportant at this point since this was primarily a preheating and degassing period. The feed recycle pump, L, was turned "on" to return the feed from the residue tank, H, to the feed tank, J. The various heaters in the system were turned "on"

and adjusted by powerstat controls. Initially, the voltage input to the rotor heater was adjusted to about 75 volts while that to the preheater coil was about 30 volts. The voltage to both the feed tank heater and the residue and distillate tank heater was adjusted and remained at 50 volts.

The preheating and degassing operation required at least two hours. When the absolute pressure in the system leveled off at 20 microns or below, the degassing operation was considered complete.

Collection of Distillate Fractions. When the degassing of the feed was complete, the feed rate and feed and residue temperatures were adjusted in preparation for collection of the first distillate fraction. The feed rate was adjusted by partially opening or closing valve V-12. This adjustment could only be based on the visual observation and approximation of the feed rate by the operator. The temperatures of the feed and residue were adjusted and maintained at the proper temperatures (62 and 86 degrees centigrade, respectively) for the first fraction by powerstat control of the heater voltage. The feed was permitted to recycle to the rotor, to the residue tank, and back to the feed tank. Any distillate which collected in the bell jar during the preheating, degassing, and temperature adjustment period was continuously returned to the feed mixture through bypass valve V-3.

When the proper feed and residue temperatures were reached, the collection of the first (86-degree) distillate fraction was started by closing valve V-3. The feed pump was immediately turned "off" and the time noted for exact determination of the feed rate. The total feed volume (with the exception of the feed holdup in the flow lines) was allowed to pass over the rotor. The total elapsed time for the "pass" was determined by noting when the last of the feed had left the nozzle. By dividing the feed volume by the elapsed time, the feed rate was determined.

Distillate fractions at feed rates between 60 and 65 milliliters per minute were considered "acceptable". If the feed rate was not within this range, the distillate fraction was "not acceptable". The two possibilities require different procedures.

Acceptable Feed Rate Procedure. If the feed rate were satisfactory, the distillate collected at the lowest point of the bell jar was drained into the distillate tank, K, by opening valve V-4. When drainage was complete, valve V-4 was closed, valve V-3 was opened, the feed pump was turned "on", to again recycle the feed. The distillate was removed from tank K by turning "off" the distillate-tank megavac,

venting the tank to the atmosphere by opening valve V-7, and draining the distillate by opening valve V-5. After complete drainage of the fraction, valves V-5 and V-7 were closed and the megavac pump again turned "on" to reevacuate the distillate tank for collection of the next acceptable fraction.

The distillate fraction was collected in a graduated cylinder for measurement of the oil volume which distilled over with the fatty acid. This was done in order to determine the new volume of feed in the still for feed rate calculations for the subsequent fraction.

When an acceptable fraction had been collected, feed and residue temperatures were increased in preparation for taking the next higher fraction. Minor adjustments of the feed rate were made, again on the judgment of the operator. It was important that at least 10 minutes was allowed between the end of one fraction collection and the beginning of the next to insure that all the feed mixture was returned from the residue tank to the feed tank.

Fractions were collected at residue temperatures of 86, 92, 98, 104, 110, 116, 122, 128, 134, 140, and 146 degrees centigrade with the feed temperature in each case

being 24 degrees below the residue temperature. In other words, heating of the feed on the rotor raised its temperature by 24 degrees.

Unacceptable Feed Rate Procedure. If the feed rate were unsatisfactory, the distillate was returned to the feed in preparation for recollection of the fraction. This was done by opening valve V-3 to allow the distillate to drain from the bell jar to the residue tank. The feed pump was again turned "on" to recycle the feed. The feed rate was adjusted by partially opening or closing valve V-12. After at least 10 minutes of pumping and recycling the feed, the collection of an acceptable fraction could again be attempted.

Shut-down Procedure. As soon as the final distillate fraction was collected, the power to the rotor heater, the feed preheater, the tank heaters, the feed pump, the rotor motor, the condenser water pump drive, the condenser water heater, and the vacuum pumps was turned "off". The system was opened to the atmosphere by opening valves V-7 and V-4. When the system had been vented, the hyvac pump used to operate the McLeod gage was turned "off". The tap water for the thermocouple cold junctions was also turned "off".

Preparation of the Still for Subsequent Tests. The bell jar was removed and the residue remaining in tank H was drained by opening valve V-8. As soon as drainage of the residue was complete, valve V-8 was closed and approximately 250 milliliters of light grade mineral oil (preheated to 100 degrees centigrade) was added to the feed tank through the loading tank, G, by opening valve V-1. The feed pump and rotor were briefly turned "on" and the "wash" oil was circulated through the flow lines and tanks and over the revolving rotor for several minutes. The wash oil was then drained by opening valves V-8 and V-5. The system was then considered "clean" and ready for the next test.

Distillation of Fatty Acids. Six straight-chain saturated fatty acids (pentadecylic, palmitic, margaric, stearic, nonadecylic, and arachidic), four monoethenoid fatty acids (palmitoleic, oleic, elaidic, and vaccenic), two diethenoid fatty acids (linoleic, and 9,11-linoleic) and two triethenoid fatty acids (linolenic and α -eleostearic) were distilled using the operational procedure described above. At least two tests were made using each acid to indicate the duplicability of results. The operating conditions for each test were as follows: (1) feed rate of 60 to 65 milliliters per minute, (2) operating pressure of 12 ± 2 microns of mercury, absolute, after the removal of the first and second

fractions, (3) a 24-degree centigrade temperature difference between the feed and the residue, (4) condenser cooling water temperature of 45 ± 1 degrees centigrade, (5) one pass of the feed over the rotor per fraction, and (6) a rotor speed of 1000 ± 50 revolutions per minute.

Analytical Procedure. The fatty acid fractions were analyzed by titration with standardized potassium hydroxide solution using a modification of the method presented by Snell and Biffen⁽⁸²⁾. The entire fraction of fatty acid-oil solution was poured from the graduated cylinder used for collection into a 250-milliliter erlenmeyer flask. Fifty milliliters of 95 per cent ethyl alcohol that had been neutralized to the phenolphthalein end point with 0.0254 normal alkali solution were added to extract the fatty acid from the oil. The immiscible liquids were heated to boiling and the flask swirled thoroughly to dissolve the free fatty acid as completely as possible in the alcohol layer. The mixture was titrated with 0.0254 normal potassium hydroxide solution (with continued swirling) until the pink end point was reached and persisted for at least 30 seconds. The weight of acid in each fraction was calculated directly from the volume of potassium hydroxide solution used in the titration.

Data and Results

The data and results of this investigation are presented in tabular and graphic form.

Thermocouple Calibration. The calibration data for the feed and residue thermocouples for a temperature range from 0 to 170 degrees centigrade are given in Table VII, page 107, and the calibration curve is given in Figure 9, page 108.

Constant-yield Oil. A summary of the data obtained for the distillation of constant-yield oil during the operational tests is given in Table VIII, page 109. The smallest and largest volumes obtained for each temperature fraction as well as the average volumes are presented.

Molecular Distillation of Saturated Fatty Acids. The data obtained from the molecular distillation of six saturated fatty acids - pentadecylic, palmitic, margaric, stearic, nonadecylic, and arachidic acids - are presented in Table IX, page 110. The elimination curves for these acids are shown in Figures 10 to 15, pages 111 to 116.

Molecular Distillation of Monoethenoid Fatty Acids. The data from the molecular distillation of four monoethenoid fatty acids - palmitoleic, oleic, elaidic, and vaccenic acids - are presented in Table X, page 117. The individual elimination

curves for these distillations appear in Figures 16 to 19, pages 118 to 121.

Molecular Distillation of Diethenoid and Triethenoid Fatty Acids. The data for the distillation of two diethenoid acids - linoleic and 9,11-linoleic - and two triethenoid acids - linolenic and α -eleostearic - are presented in Table XI, page 122. Figures 20 to 23, pages 123 to 126, give the individual elimination curves for these acids.

Summary of Individual Elimination Maxima. A list of the individual elimination maxima for all of the acids investigated is presented in Table XII, page 127.

TABLE VII

Calibration Data for Feed and Residue Thermocouples

Temperature °C	Potentiometer Readings	
	Feed Thermocouple mv	Residue Thermocouple mv
0	-0.60	-0.60
50	1.63	1.60
60	1.91	2.00
70	2.55	2.61
80	2.86	2.90
90	3.28	3.20
98	3.63	3.66
100	3.74	3.71
110	4.22	4.08
120	4.55	4.50
130	4.95	5.10
140	5.47	5.65
150	6.00	5.95
160	6.45	6.43
170	7.00	6.90

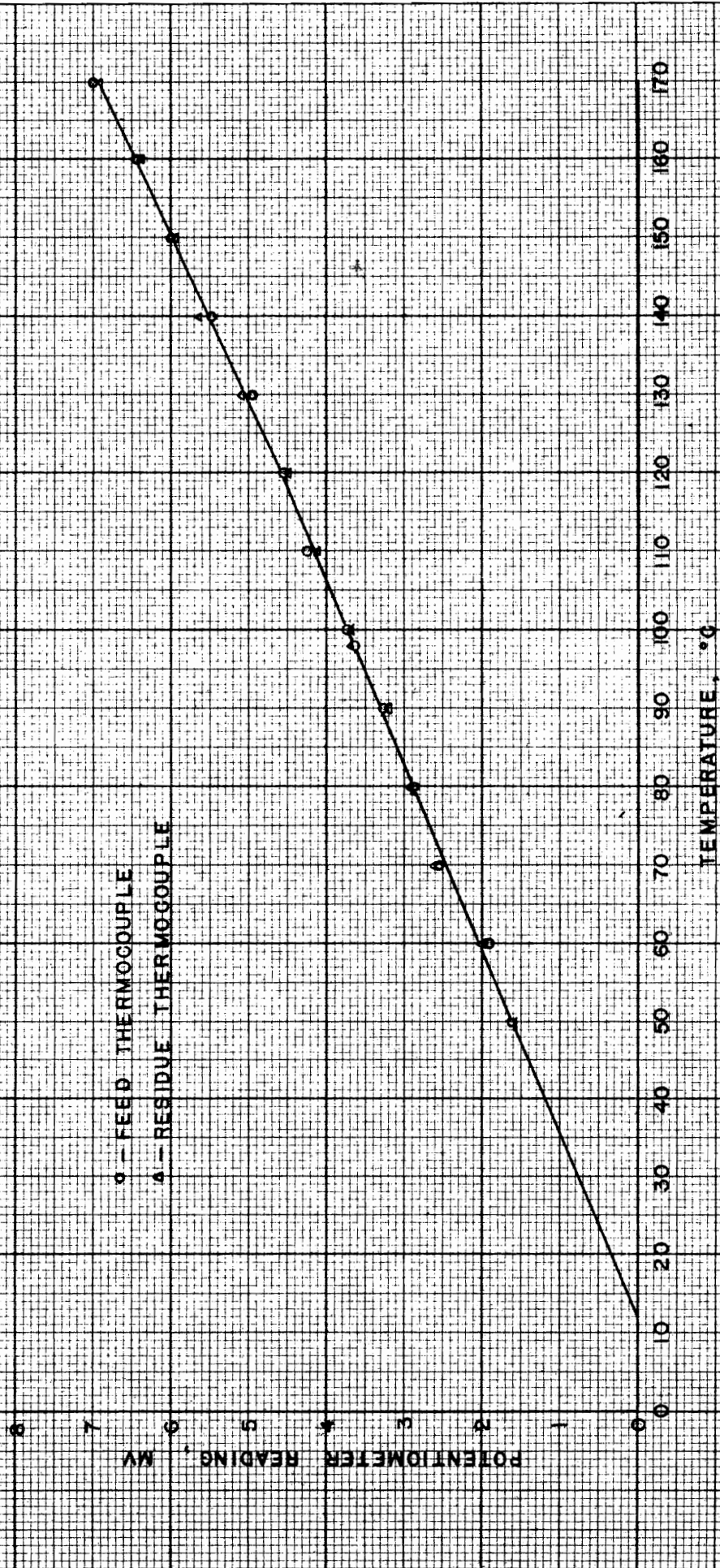


FIGURE 9. CALIBRATION CURVE FOR FEED AND RESIDUE THERMOCOUPLES

TABLE VIII

Molecular Distillation of Constant-Yield Oil

Temperature of Fraction	Volume of Fraction		Average Volume	Yield of Original Blend
°C	Smallest ml	Largest ml	ml	vol %
86	6	20	12.6	1.53
92	28	41	33.6	4.07
98	34	47	39.4	4.78
104	32	48	38.8	4.70
110	35	44	39.8	4.82
116	36	45	38.4	4.66
122	36	47	40.0	4.85
128	35	49	42.6	5.16
134	40	54	44.7	5.42
140	38	50	45.0	5.45
Residue	--	--	450.1	54.56
Total	--	--	825.0	100.00

Data obtained from 28 operational tests on fatty acids.

TABLE IX

Data and Results for the Molecular Distillation of Six SaturatedFatty Acids: Pentadecylic, Palmitic, Margaric, Stearic,
Nonadecylic, and Arachidic Acids

Reter Speed: 1000 ± 50 rpm
 Condenser Water Temperature: 45 ± 1 °C
 Feed Passes Across Reter Per Fraction: One

Acid	Temperature of Fraction		Absolute Pressure in Still	Feed Rate ml/min	Weight of Acid in Fraction gm	Yield of Acid	
	Feed °C	Residue °C				in Fraction wt %	Cumulative wt %
Pentadecylic	62	86	17	62	0.0176	3.53	3.53
	68	92	14	61	0.0754	15.12	18.65
	74	98	12	63	0.1095	21.95	40.60
	80	104	12	64	0.0921	18.46	59.06
	86	110	12	63	0.0739	14.82	73.88
	92	116	12	65	0.0526	10.55	84.43
	98	122	13	64	0.0319	6.40	90.83
	62	86	15	65	0.0132	2.64	2.64
	68	92	13	64	0.0873	17.42	20.06
	74	98	13	64	0.1138	22.78	42.84
	80	104	14	61	0.0973	19.46	62.30
	86	110	13	65	0.0744	14.89	77.19
	92	116	13	64	0.0513	10.28	87.47
	Palmitic	62	86	17	60	0.0189	3.76
68		92	14	63	0.0758	15.07	18.83
74		98	13	65	0.0930	18.49	37.32
80		104	13	64	0.0983	19.54	56.86
86		110	13	62	0.0838	16.66	73.52
92		116	12	63	0.0523	10.40	83.92
98		122	12	61	0.0346	6.88	90.80
104		128	11	63	0.0196	3.90	94.70
62		86	17	63	0.0218	4.52	4.52
68		92	14	63	0.0700	14.50	19.02
74		98	12	62	0.0958	19.85	38.87
80		104	12	63	0.0967	20.05	58.92
86		110	12	60	0.0699	14.49	73.31
92		116	12	61	0.0478	9.91	83.32
98	122	13	64	0.0246	5.10	88.42	
104	128	13	64	0.0218	4.52	92.94	
Margaric	62	86	16	61	0.0110	2.18	2.18
	68	92	13	60	0.0390	7.72	9.90
	74	98	13	62	0.0585	11.59	21.49
	80	104	12	63	0.0811	16.06	37.55
	86	110	12	65	0.0971	19.23	56.78
	92	116	12	65	0.0824	16.32	73.10
	98	122	12	64	0.0611	12.10	85.20
	104	128	12	62	0.0371	7.35	92.55
	110	134	13	65	0.0199	3.94	96.49
	62	86	15	65	0.0115	2.30	2.30
	68	92	14	64	0.0335	6.70	9.00
	74	98	13	64	0.0598	11.96	20.96
	80	104	13	65	0.0739	14.78	35.74
	86	110	13	61	0.0947	18.94	54.68
92	116	13	64	0.0776	15.52	70.20	
98	122	13	63	0.0611	12.22	82.42	
104	128	13	63	0.0433	8.66	91.08	
110	134	13	64	0.0254	5.08	96.16	
Stearic	62	86	18	65	0.0046	0.92	0.92
	68	92	13	60	0.0299	5.97	6.89
	74	98	11	65	0.0423	8.44	15.33
	80	104	11	65	0.0647	12.91	28.24
	86	110	10	63	0.0853	17.02	45.26
	92	116	10	65	0.0824	16.44	61.70
	98	122	10	65	0.0709	14.15	75.85
	104	128	10	62	0.0560	11.17	87.02
	110	134	10	63	0.0380	7.58	94.60
	116	140	10	60	0.0217	4.33	98.93
	62	86	16	62	0.0073	1.46	1.46
	68	92	14	65	0.0220	4.40	5.86
	74	98	13	64	0.0454	9.09	14.95
	80	104	12	64	0.0699	13.99	28.94
86	110	12	61	0.0863	17.37	46.31	
92	116	12	65	0.0770	15.41	61.72	
98	122	12	61	0.0722	14.45	76.17	
104	128	11	64	0.0570	11.41	87.58	
110	134	11	61	0.0362	7.25	94.83	
116	140	11	63	0.0206	4.12	98.95	
Nonadecylic	62	86	17	64	0.0016	0.32	0.32
	68	92	15	63	0.0052	1.04	1.36
	74	98	14	61	0.0146	2.92	4.28
	80	104	13	62	0.0257	5.14	9.42
	86	110	13	64	0.0421	8.43	17.85
	92	116	12	61	0.0579	11.59	29.44
	98	122	13	63	0.0698	13.97	43.41
	104	128	13	61	0.0795	15.91	59.32
	110	134	14	62	0.0688	13.77	73.09
	116	140	14	63	0.0478	9.57	82.66
	62	86	15	60	0.0023	0.46	0.46
	68	92	14	62	0.0091	1.81	2.27
	74	98	13	62	0.0182	3.63	5.90
	80	104	13	65	0.0265	5.29	11.19
86	110	14	61	0.0474	9.45	20.64	
92	116	14	61	0.0595	11.87	32.51	
98	122	14	61	0.0771	15.37	47.88	
104	128	15	61	0.0792	15.80	63.68	
110	134	13	63	0.0713	14.22	77.90	
116	140	13	63	0.0438	8.73	86.63	
Arachidic	62	86	17	62	0.0012	0.24	0.24
	68	92	14	65	0.0142	2.84	3.08
	74	98	14	64	0.0195	3.89	6.97
	80	104	13	61	0.0366	7.35	14.32
	86	110	13	62	0.0374	7.47	21.79
	92	116	13	64	0.0396	7.91	29.70
	98	122	15	60	0.0518	10.34	40.04
	104	128	15	61	0.0461	9.21	49.25
	110	134	15	64	0.0482	9.62	58.87
	116	140	15	64	0.0468	9.35	68.22
	62	86	15	64	0.0025	0.52	0.52
	68	92	15	65	0.0145	3.02	3.54
	74	98	15	65	0.0207	4.27	7.81
	80	104	14	64	0.0292	6.02	13.83
86	110	14	60	0.0405	8.35	22.18	
92	116	14	61	0.0428	8.83	31.01	
98	122	14	63	0.0453	9.34	40.35	
104	128	14	62	0.0422	8.70	49.05	
110	134	16	65	0.0451	9.30	58.35	
116	140	15	61	0.0437	9.02	67.37	

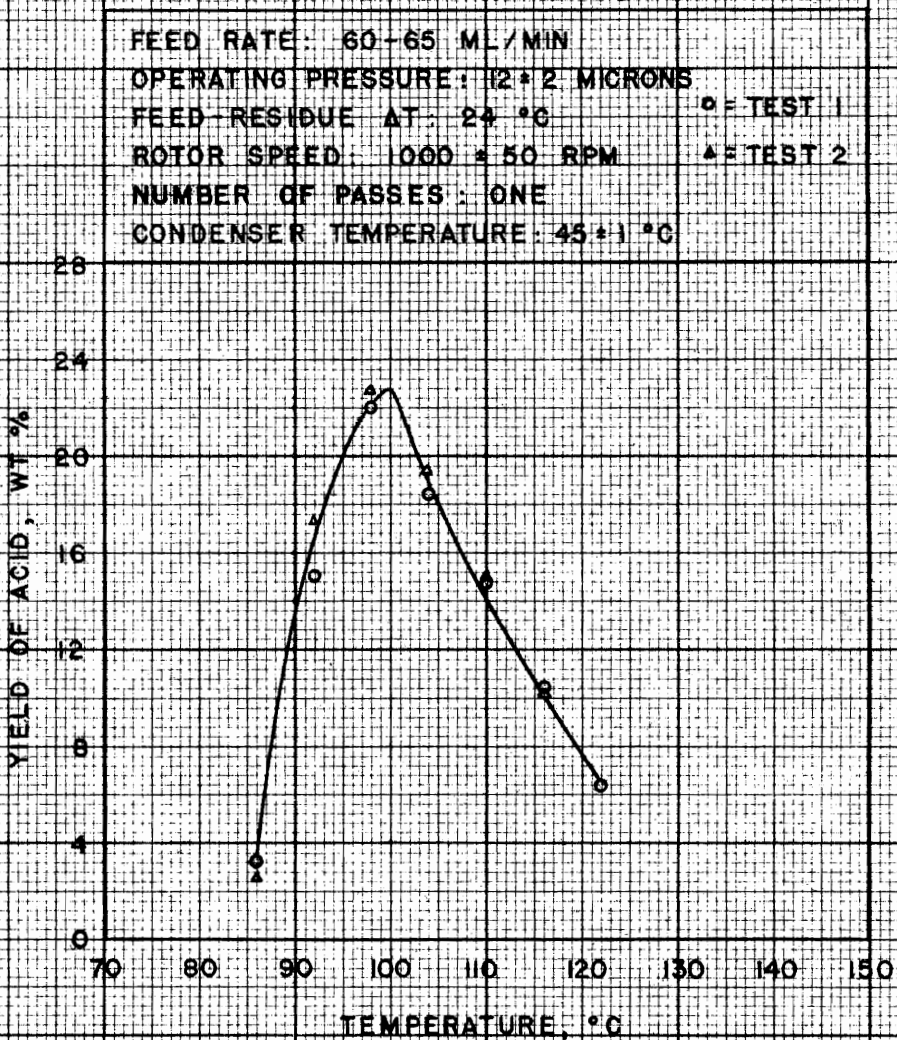


FIGURE 10. ELIMINATION CURVE FOR THE MOLECULAR DISTILLATION OF PENTADECYLIC ACID.

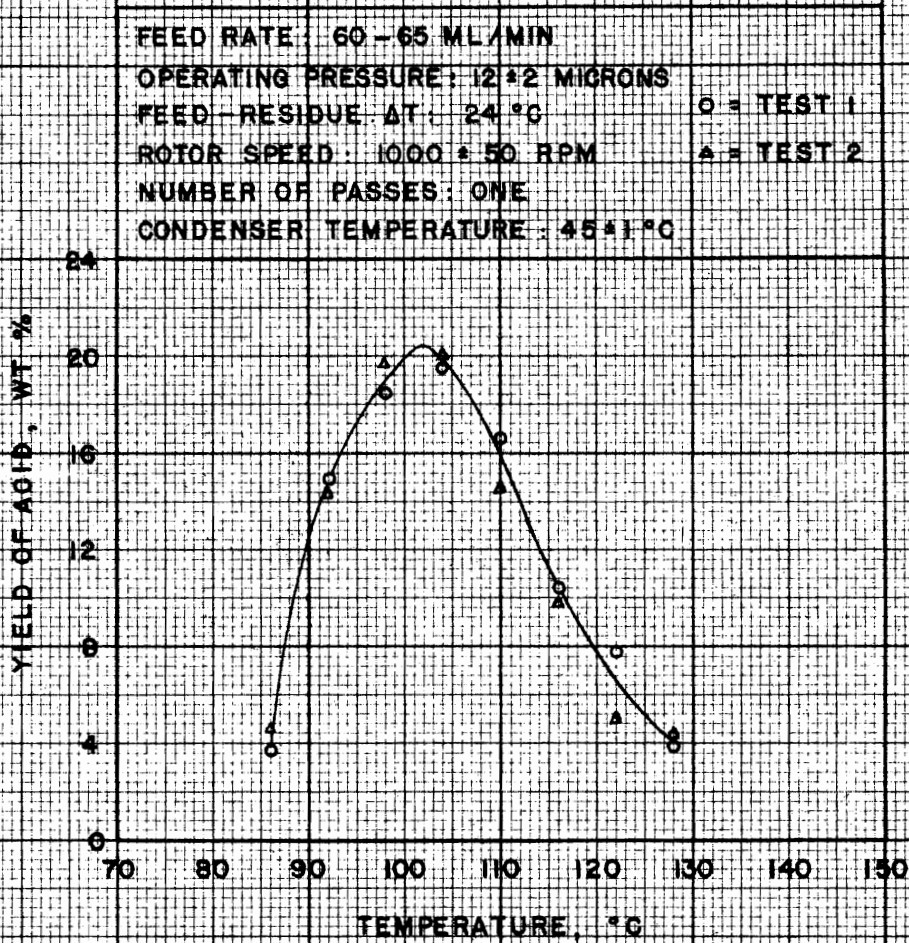


FIGURE II. ELIMINATION CURVE FOR THE MOLECULAR DISTILLATION OF PALMITIC ACID.

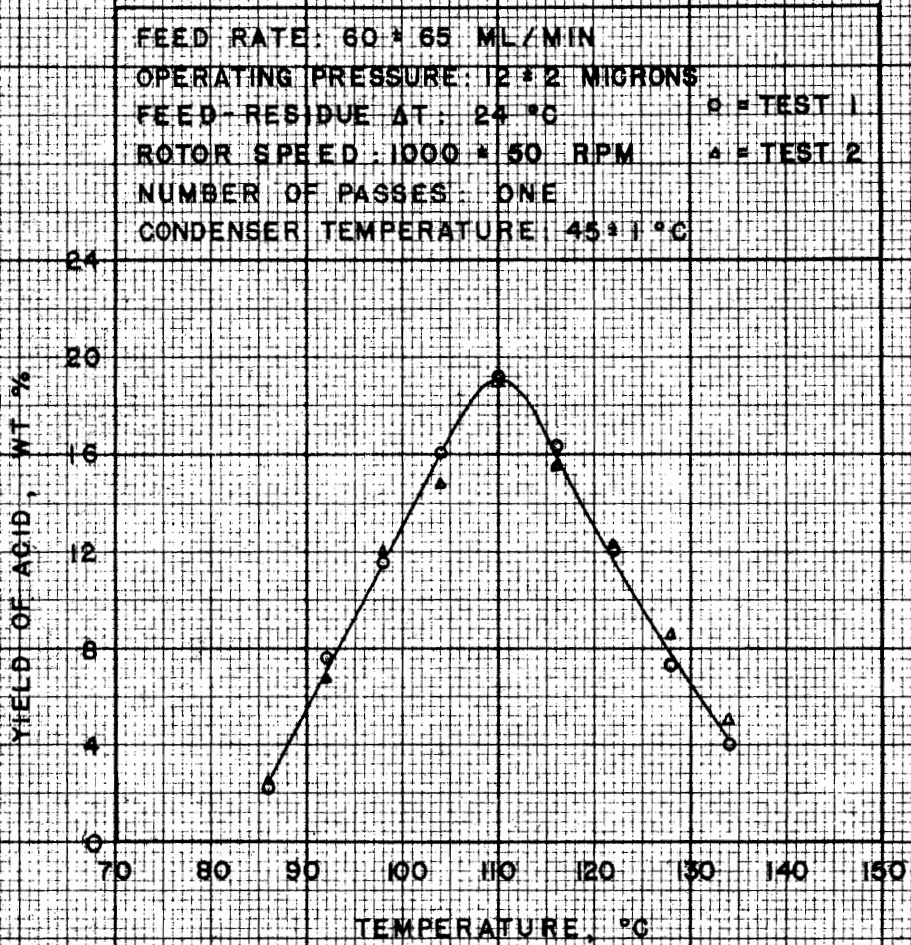


FIGURE 12. ELIMINATION CURVE FOR THE MOLECULAR DISTILLATION OF MARGARIC ACID.

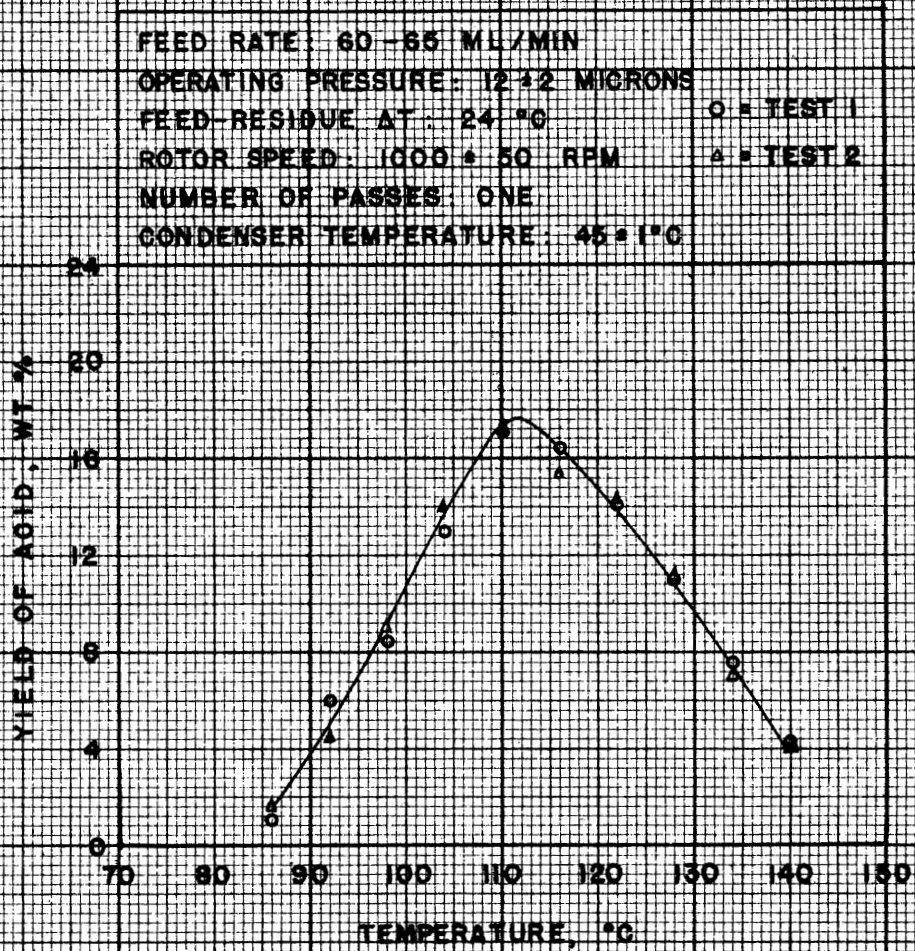


FIGURE 13. ELIMINATION CURVE FOR THE MOLECULAR DISTILLATION OF STEARIC ACID.

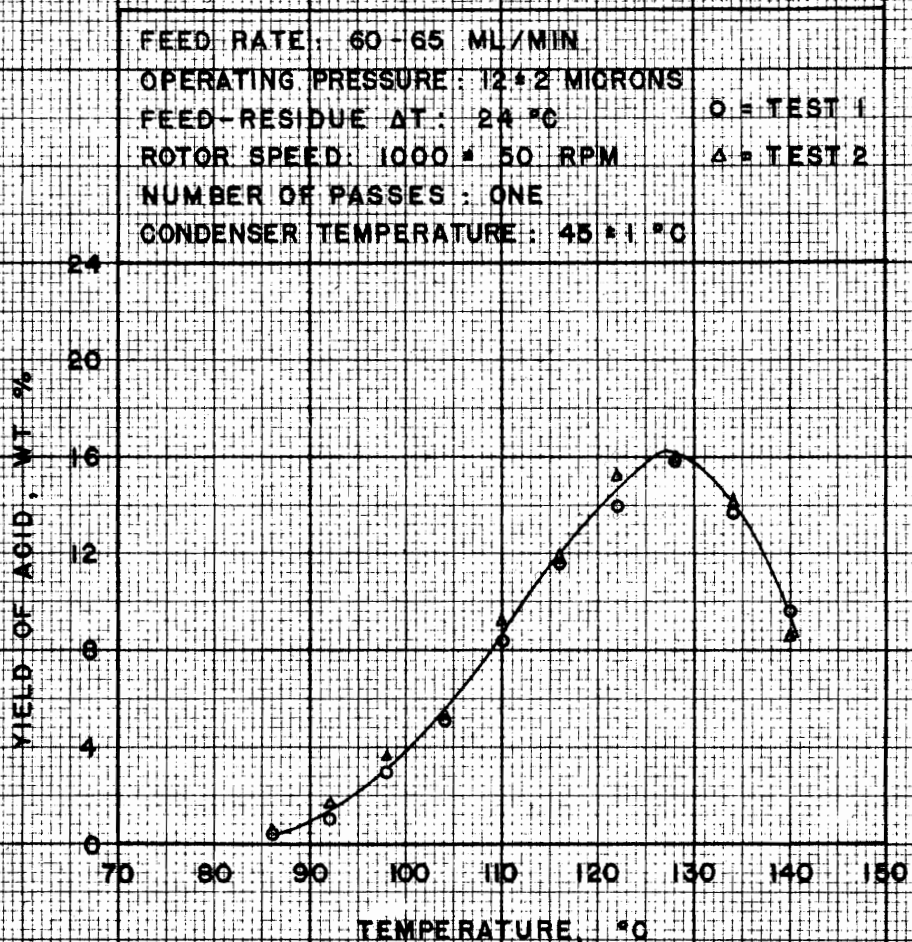


FIGURE 14. ELIMINATION CURVE FOR THE MOLECULAR DISTILLATION OF NONADECYLIC ACID.

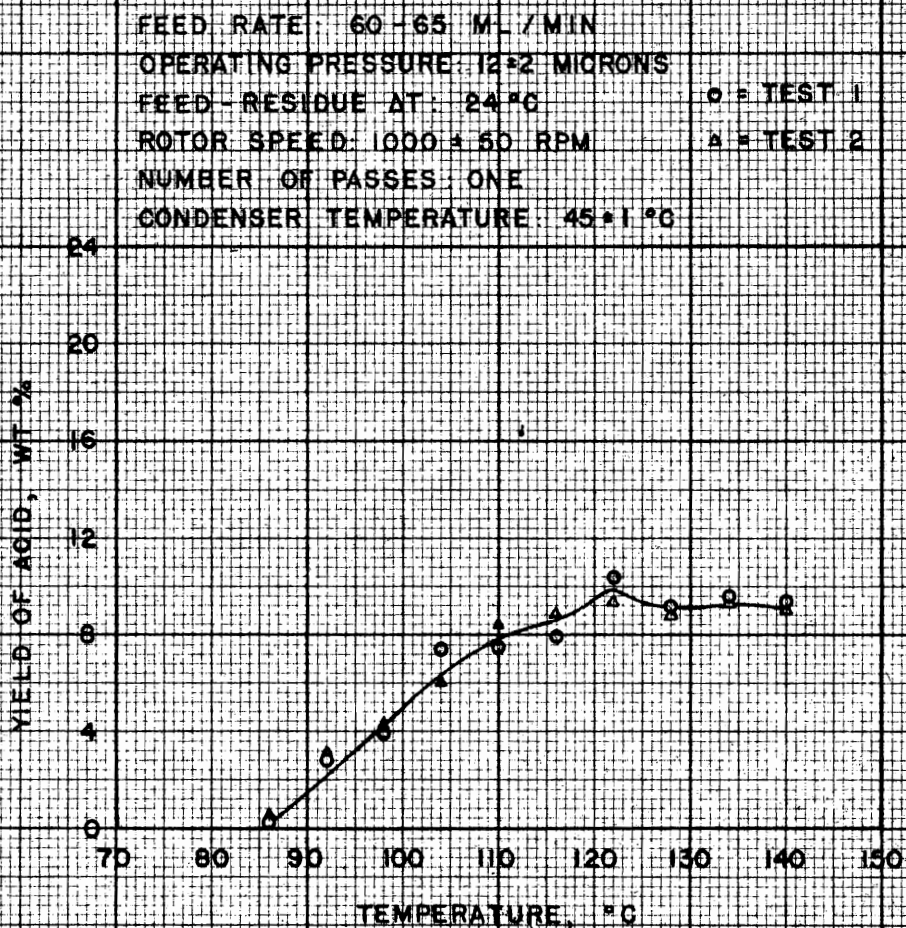


FIGURE 15. ELIMINATION CURVE FOR THE MOLECULAR DISTILLATION OF ARACHIDIC ACID.

TABLE X

Data and Results for the Molecular Distillation of Four MonoethenoicFatty Acids: Palmitoleic, Oleic, Elaidic, and Vaccenic Acids

Reter Speed: 1000 ± 50 rpm
 Condenser Water Temperature: 45 ± 1 °C
 Feed Passes Across Reter Per Fraction: One

Acid	Temperature of Fraction		Absolute Pressure in Still	Feed Rate	Weight of Acid in Fraction	Yield of Acid in Fraction	
	Feed	Residue				wt %	Cumulative
	°C	°C	microns	ml/min	gm	wt %	wt %
Palmitoleic	62	86	17	61	0.0078	7.57	7.57
	68	92	14	60	0.0129	12.52	20.09
	74	98	13	62	0.0181	17.57	37.66
	80	104	12	62	0.0142	13.79	51.45
	86	110	12	65	0.0107	10.39	61.84
	92	116	12	63	0.0094	9.13	70.94
	62	86	19	60	0.0064	6.69	6.69
	68	92	15	65	0.0124	12.97	19.66
	74	98	14	64	0.0180	18.83	38.49
	80	104	13	64	0.0136	14.23	52.73
	86	110	13	64	0.0108	11.50	64.00
	92	116	12	64	0.0090	9.41	73.44
	98	122	13	61	0.0071	7.43	80.87
	104	128	13	64	0.0048	5.02	85.89
Oleic	62	86	16	64	0.0139	2.75	2.75
	68	92	14	64	0.0390	7.72	10.47
	74	98	13	64	0.0597	11.82	22.29
	80	104	12	63	0.0717	14.20	36.49
	86	110	12	64	0.0782	15.48	51.97
	92	116	12	61	0.0796	15.76	67.73
	98	122	12	65	0.0574	11.36	79.09
	104	128	12	60	0.0505	10.00	89.09
	62	86	15	61	0.0158	3.12	3.12
	68	92	12	60	0.0386	7.63	10.75
	74	98	10	61	0.0625	12.36	23.11
	80	104	12	61	0.0725	14.33	37.44
	86	110	11	61	0.0827	16.35	53.79
	92	116	11	65	0.0612	12.10	65.89
98	122	12	61	0.0702	13.88	79.77	
104	128	12	61	0.0473	9.35	89.12	
110	134	12	65	0.0332	6.56	95.68	
Elaidic	62	86	18	61	0.0069	1.41	1.41
	68	92	16	61	0.0395	8.05	9.46
	74	98	14	60	0.0549	11.19	20.65
	80	104	14	61	0.0699	14.25	34.90
	86	110	14	64	0.0738	15.05	49.95
	92	116	14	64	0.0699	14.25	64.20
	98	122	14	63	0.0634	12.93	77.13
	104	128	15	61	0.0491	10.00	87.13
	110	134	15	62	0.0297	6.06	93.19
	62	86	17	65	0.0051	1.02	1.02
	68	92	14	65	0.0237	4.73	5.75
	74	98	12	61	0.0491	9.79	15.54
	80	104	13	63	0.0575	11.47	27.01
	86	110	13	64	0.0747	14.90	41.91
92	116	13	65	0.0875	17.45	59.36	
98	122	13	65	0.0762	15.20	74.56	
104	128	13	64	0.0657	13.10	87.66	
110	134	13	64	0.0448	8.93	96.59	
Vaccenic	62	86	20	60	0.0029	0.57	0.57
	68	92	16	64	0.0199	4.01	4.59
	74	98	14	64	0.0354	7.13	11.72
	80	104	13	63	0.0564	11.36	23.08
	86	110	12	60	0.0704	14.19	37.27
	92	116	13	60	0.0779	15.69	52.96
	98	122	13	65	0.0679	13.68	66.64
	104	128	14	60	0.0587	11.83	78.47
	110	134	14	63	0.0424	8.54	87.00
	62	86	19	65	0.0029	0.57	0.57
	68	92	17	60	0.0196	3.81	4.38
	74	98	14	60	0.0393	7.65	12.03
	80	104	14	63	0.0562	10.94	22.97
	86	110	13	60	0.0781	15.20	38.17
92	116	13	63	0.0818	15.92	54.09	
98	122	14	63	0.0712	13.86	67.95	
104	128	14	65	0.0568	11.05	79.00	
110	134	14	63	0.0448	8.72	87.72	

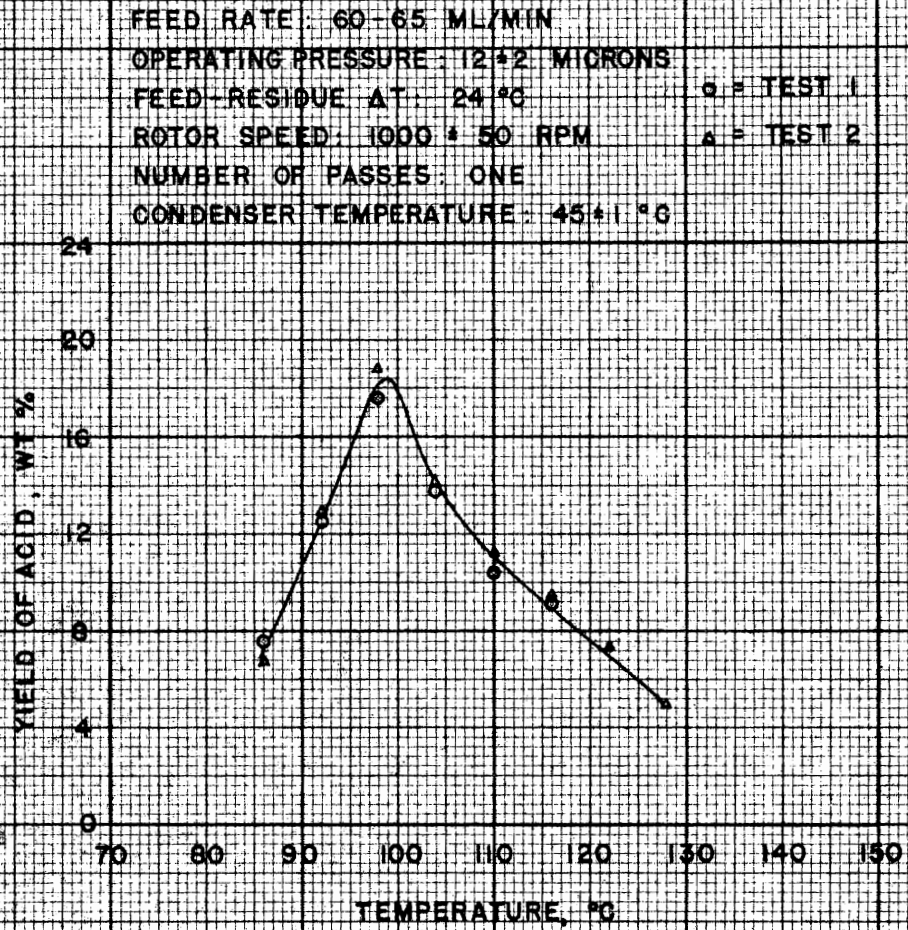


FIGURE 16. ELIMINATION CURVE FOR THE MOLECULAR DISTILLATION OF PALMITOLEIC ACID.

FEED RATE : 60-65 ML/MIN
OPERATING PRESSURE : 12 ± 2 MICRONS
FEED-RESIDUE ΔT : 24°C
ROTOR SPEED : 1000 ± 50 RPM
NUMBER OF PASSES : ONE
CONDENSER TEMPERATURE : $45 \pm 1^\circ\text{C}$

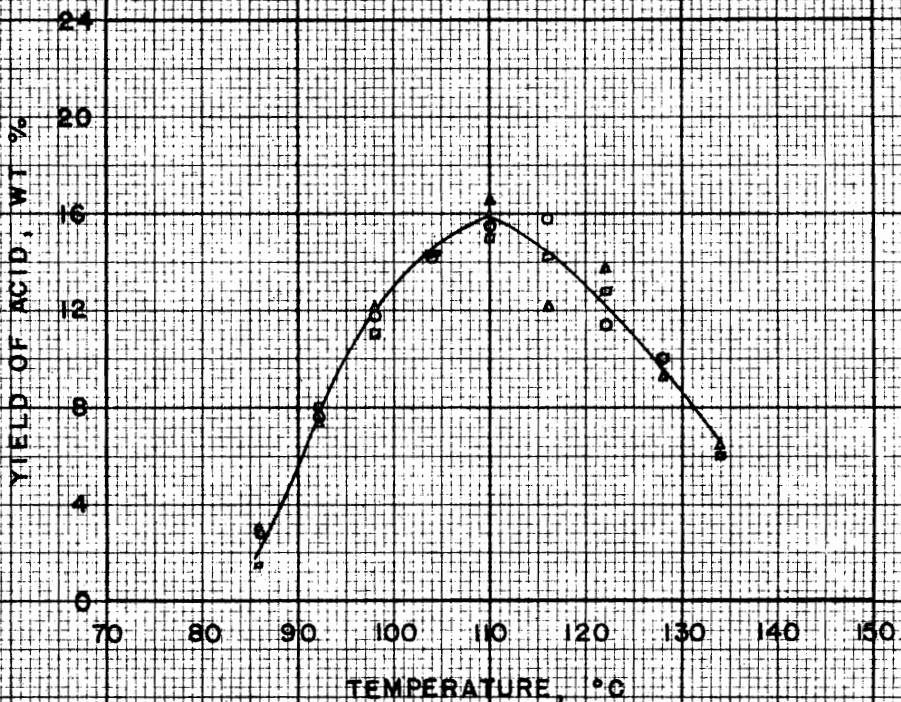


FIGURE 17. ELIMINATION CURVE FOR THE MOLECULAR DISTILLATION OF OLEIC ACID.

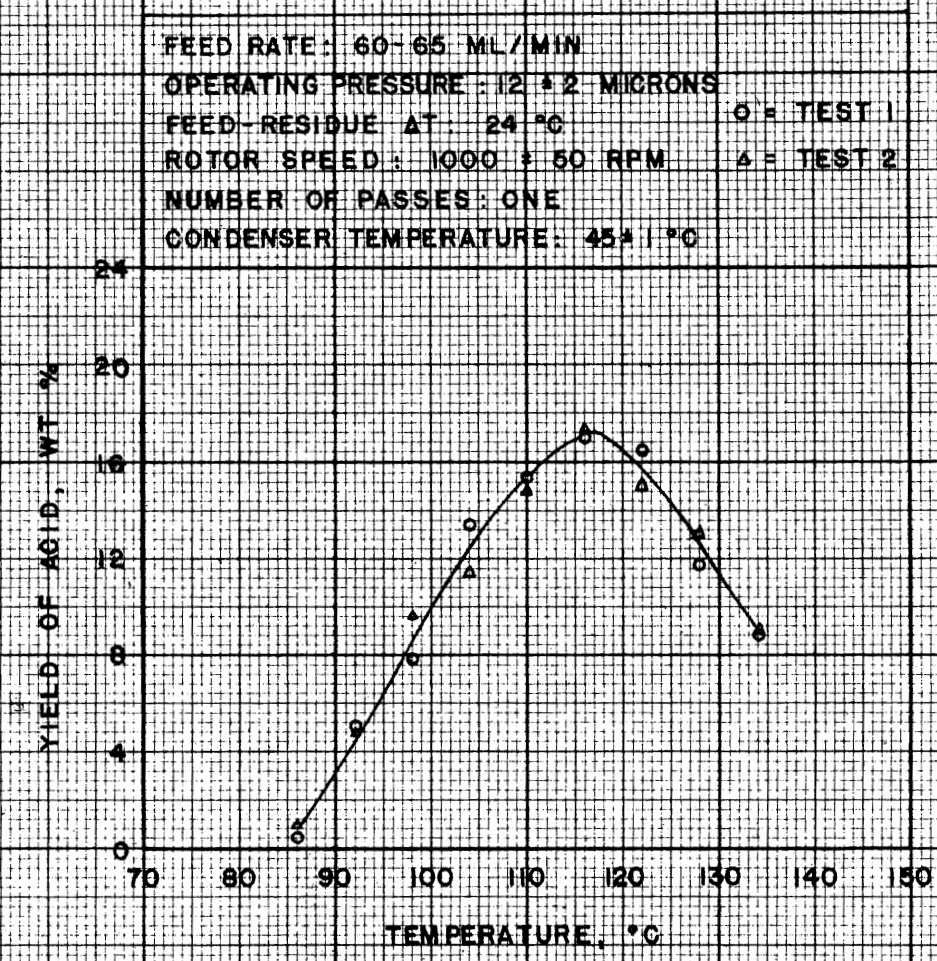


FIGURE 18. ELIMINATION CURVE FOR THE MOLECULAR DISTILLATION OF ELAIDIC ACID.

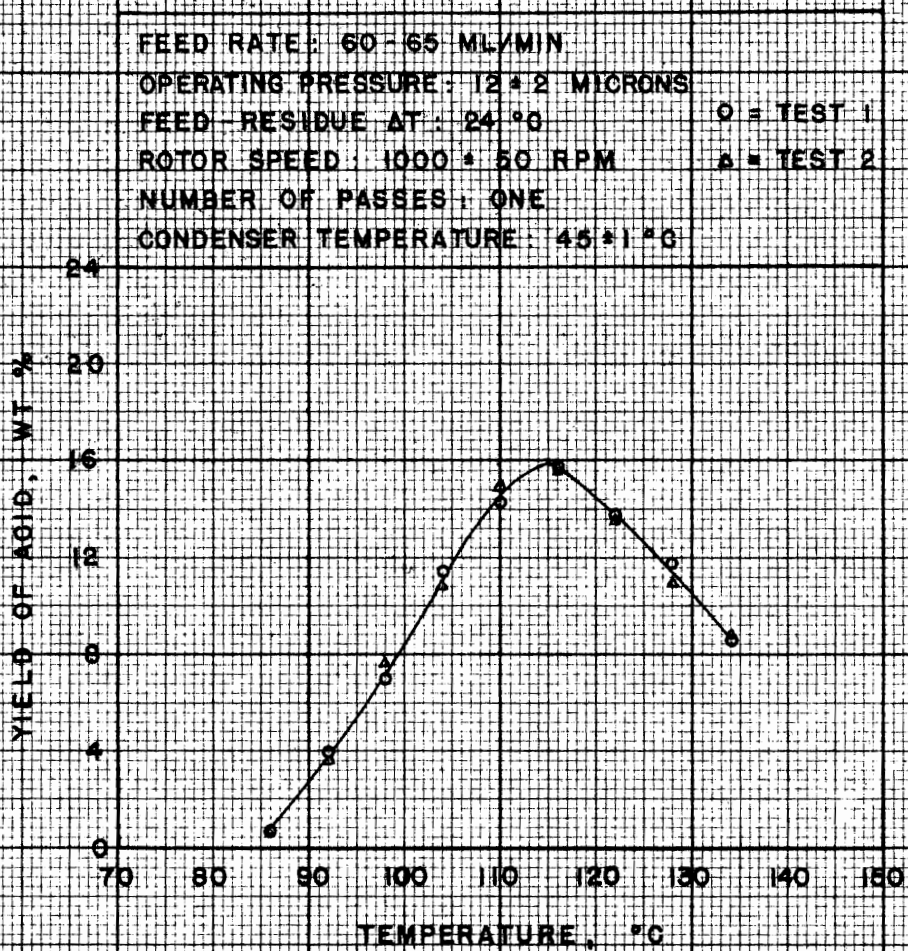


FIGURE 19. ELIMINATION CURVE FOR THE MOLECULAR DISTILLATION OF VACCENIC ACID.

TABLE XI

Data and Results for the Molecular Distillation of Two Diethenoid
and Two Triethenoid Fatty Acids: Linoleic, 9, 11-Linoleic,
Linolenic, and α -Eleostearic Acids

Reter Speed: 1000 \pm 50 rpm
Condenser Water Temperature: 45 \pm 1 $^{\circ}$ C
Feed Passes Across Reter Per Fraction: One

Acid	Temperature of Fraction		Absolute Pressure in Still	Feed Rate ml/min	Weight of Acid in Fraction gm	Yield of Acid in Fraction	
	Feed $^{\circ}$ C	Residue $^{\circ}$ C				microns	wt %
Linoleic	62	86	17	61	0.0095	2.52	2.52
	68	92	13	62	0.0297	7.90	10.42
	74	98	14	62	0.0438	11.64	22.06
	80	104	13	60	0.0562	14.94	37.00
	86	110	14	60	0.0600	15.95	52.95
	92	116	15	65	0.0541	14.38	67.33
	98	122	14	61	0.0458	18.18	79.51
	104	128	13	63	0.0346	9.20	88.71
	62	86	15	65	0.0063	1.46	1.46
	68	92	14	62	0.0285	6.62	8.08
	74	98	14	61	0.0515	11.96	20.04
	80	104	13	61	0.0614	14.26	34.30
	86	110	12	64	0.0666	15.47	49.77
	92	116	12	61	0.0598	13.89	63.66
98	122	12	65	0.0548	12.73	76.39	
104	128	13	62	0.0471	10.94	87.33	
110	134	12	64	0.0256	5.95	93.28	
9,11-Linoleic	62	86	15	64	0.0060	2.00	2.00
	68	92	12	63	0.0141	4.70	6.70
	74	98	12	63	0.0235	7.83	14.53
	80	104	12	64	0.0293	9.77	24.30
	86	110	12	65	0.0348	11.60	35.90
	92	116	14	60	0.0450	15.00	50.90
	98	122	13	64	0.0356	11.87	62.77
	104	128	12	63	0.0266	8.87	71.64
	110	134	13	65	0.0172	5.73	77.37
	116	140	13	65	0.0127	4.23	81.60
	122	146	14	65	0.0088	2.93	84.53
	62	86	17	62	0.0057	1.81	1.81
	68	92	14	60	0.0150	4.76	6.57
	74	98	13	60	0.0242	7.68	14.25
	80	104	13	62	0.0308	9.78	24.03
	86	110	13	65	0.0357	11.33	35.36
	92	116	13	61	0.0439	13.94	49.30
	98	122	13	63	0.0372	11.81	61.11
104	128	13	61	0.0305	9.68	70.79	
110	134	13	64	0.0221	7.02	77.81	
116	140	14	64	0.0158	5.02	82.83	
Linolenic	62	86	17	61	0.0071	1.60	1.60
	68	92	12	65	0.0296	6.71	8.31
	74	98	12	65	0.0525	11.90	20.21
	80	104	12	61	0.0799	18.12	38.33
	86	110	12	60	0.0833	18.89	57.22
	92	116	12	63	0.0583	13.22	70.44
	98	122	12	60	0.0481	10.91	81.35
	104	128	13	60	0.0320	7.26	88.61
	62	86	18	60	0.0058	1.30	1.30
	68	92	13	62	0.0233	5.24	6.54
	74	98	11	61	0.0629	14.15	20.69
	80	104	12	61	0.0827	18.60	39.29
	86	110	12	60	0.0813	18.29	57.58
	92	116	13	62	0.0629	14.15	71.73
98	122	12	63	0.0502	11.29	83.02	
104	128	13	63	0.0364	8.19	91.21	
α -Eleostearic	62	86	17	63	0.0022	0.92	0.92
	68	92	15	64	0.0111	4.64	5.56
	74	98	13	61	0.0175	7.32	12.88
	80	104	13	63	0.0180	7.53	20.41
	86	110	13	63	0.0265	11.08	31.49
	92	116	13	64	0.0303	12.67	44.16
	98	122	14	64	0.0357	14.93	59.09
	104	128	13	63	0.0310	12.96	72.05
	110	134	13	60	0.0279	11.67	83.72
	116	140	14	62	0.0193	8.07	91.79
	62	86	17	60	0.0053	2.91	2.91
	68	92	14	61	0.0092	5.06	7.97
	74	98	13	62	0.0152	8.36	16.33
	80	104	13	60	0.0165	9.05	25.38
	86	110	13	65	0.0195	10.71	36.09
	92	116	13	65	0.0223	12.24	48.33
	98	122	13	60	0.0286	15.70	64.03
	104	128	13	65	0.0227	12.50	76.53
110	134	15	64	0.0168	9.22	85.75	

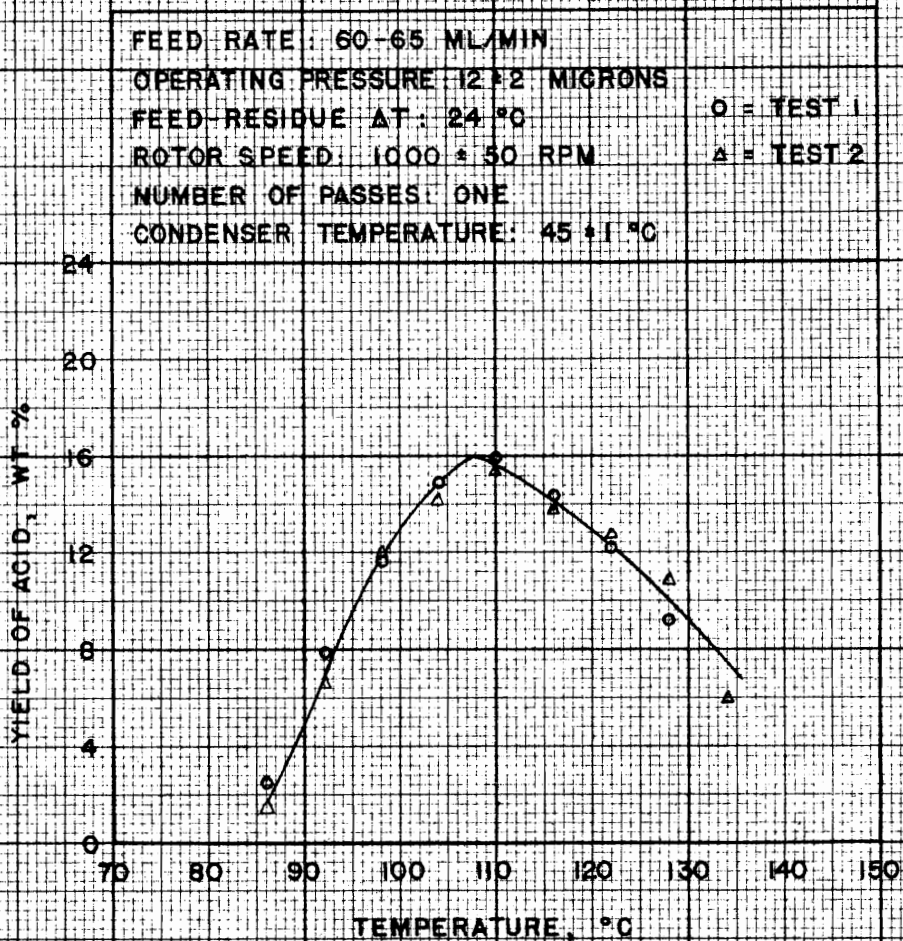


FIGURE 20. ELIMINATION CURVE FOR THE MOLECULAR DISTILLATION OF LINOLEIC ACID.

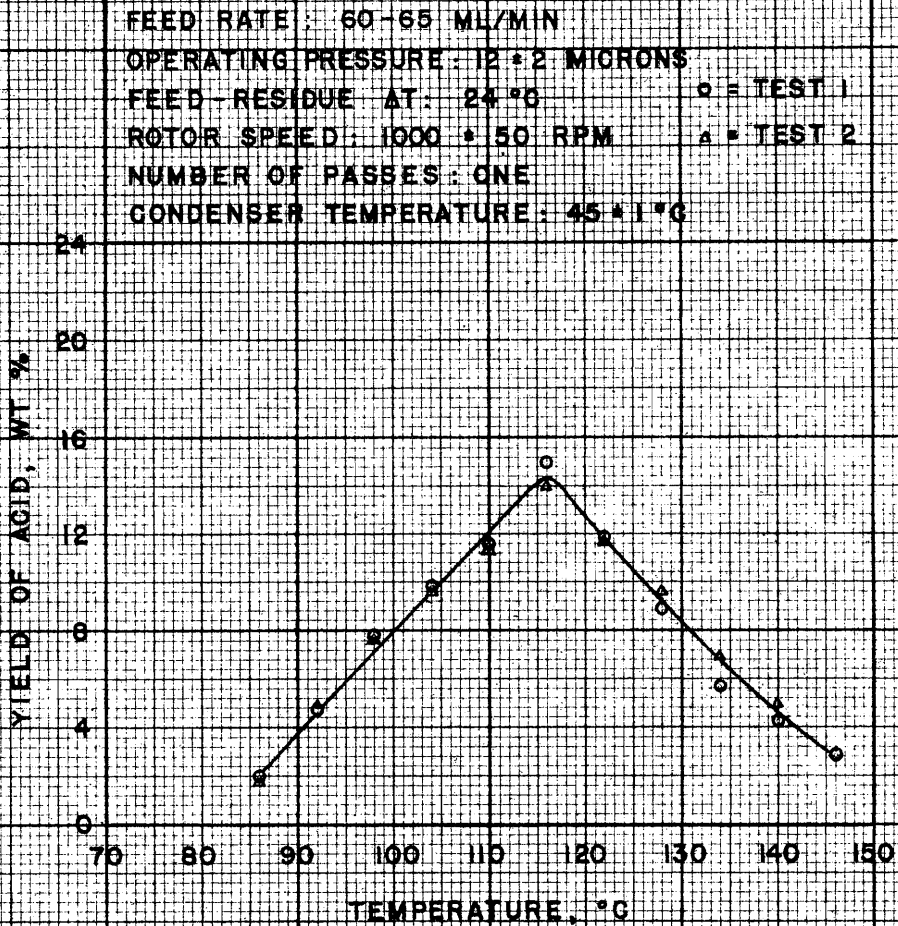


FIGURE 2. ELIMINATION CURVE FOR THE MOLECULAR DISTILLATION OF 9,11-LINOLEIC ACID.

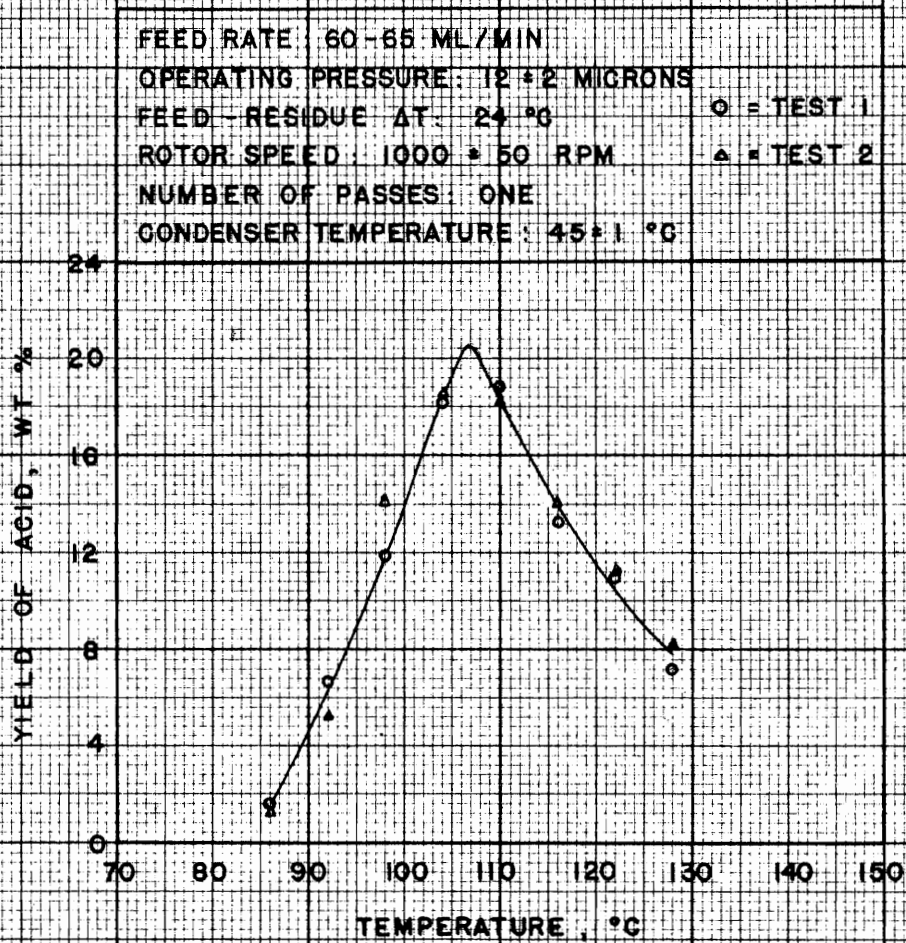


FIGURE 22. ELIMINATION CURVE FOR THE MOLECULAR DISTILLATION OF LINOLENIC ACID.

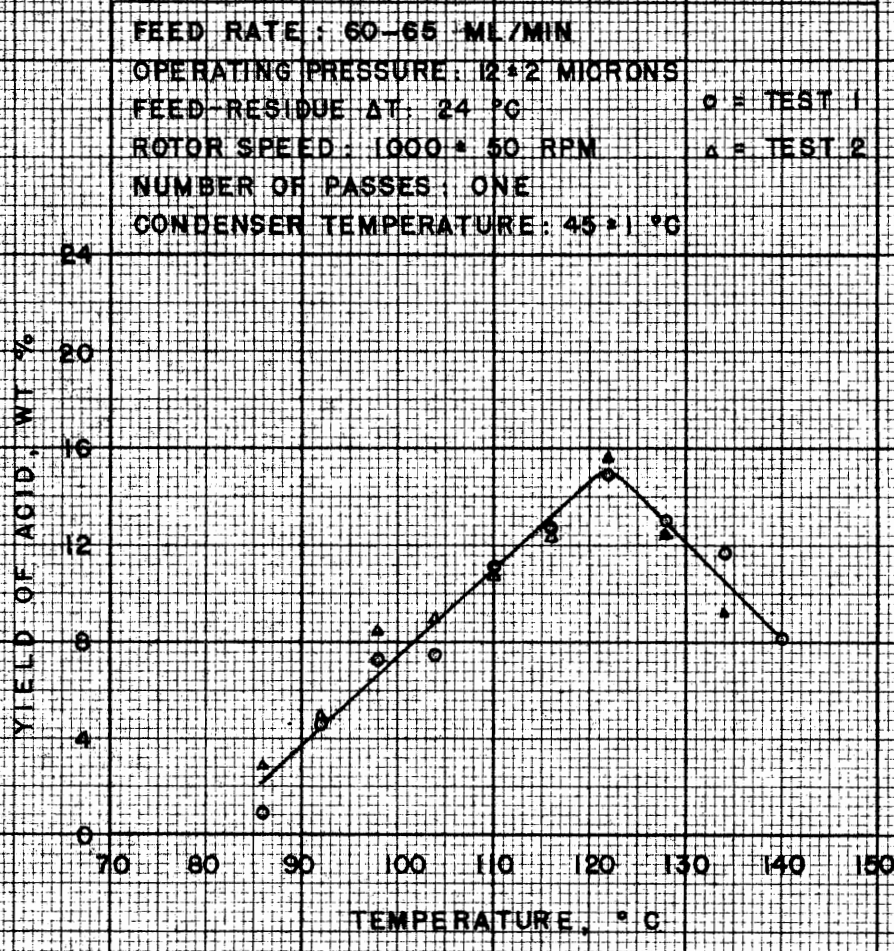


FIGURE 23. ELIMINATION CURVE FOR THE MOLECULAR DISTILLATION OF α -BLEOSTEARIC ACID.

TABLE XII

Summary of Elimination Maxima of
Fatty Acids Investigated

Acid	Maximum °C
Pentadecylic	100
Palmitic	102
Margaric	110
Stearic	112
Nonadecylic	127
Arachidic	122
Palmitoleic	99
Oleic	110
Elaidic	117
Vaccenic	115
Linoleic	108
9,11-Linoleic	116
Linolenic	107
α -Eleostearic	122

IV. DISCUSSION

In order to study the effect of molecular structure of a substance on its molecular distillation, a series of tests was made on a laboratory-sized centrifugal molecular still. The results of the investigation are discussed, recommendations are made for future studies, and the limitations of the experimentation are presented.

Discussion of Results

In the discussion of results a consideration of several of the operational features of the redesigned molecular still and the evaluation of the various results obtained during the investigation are discussed.

Redesign and Construction of Centrifugal Molecular Still.

Although satisfactory for temporary use, the final still construction employed by Bull⁽⁹⁾ and Demakis⁽³⁷⁾ incorporating an enclosed drive motor was not considered dependable enough for use in this investigation. The decision was made, therefore, to completely redesign the still to incorporate recommendations by Bull and Demakis in hopes that a system could be developed in which more complete faith could be placed. The major changes involved in the redesign and reconstruction are individually discussed to

indicate the extent to which the aims of the redesign were achieved.

Magnetic Drive. A completely-sealed magnetic drive was constructed to eliminate the use of a packed shaft (Coli⁽³²⁾ and Bull⁽¹³⁾) or a drive motor enclosed in the vacuum system (Bull⁽⁹⁾). Two major problems were faced in the design of the drive: whether the magnetic field would be strong enough to provide a drive and whether the initial torque of the rotor shaft assembly could be overcome to start the rotor disc turning. A small magnetic drive had been satisfactorily used in a falling film still by Priznar, Wilt, and Nachod⁽⁸⁰⁾. Initial tests using a plastic model indicated that the drive would function if the air gap between the drive and rotor magnets could be kept at a maximum of $1/4$ inch. Further, it was established that a brass plate between the magnets would not substantially diminish the magnetic field. On this rather scanty evidence, it was decided to attempt a design and construction of a magnetic drive. The gap between the drive and rotor magnets was made $9/64$ -inch wide with the brass shell being $7/64$ -inch thick and the clearance between the revolving magnets and the brass shell being $1/64$ -inch on each side.

The constructed drive performed excellently. The rotor could be started slowly by powerstat control of the variable speed drive motor to allow the initial torque of the motor to be overcome. Once the rotor began revolving the speed could be increased to the operating speed (1000 revolutions per minute) rapidly without resulting in a "breakaway" of the drive magnets from the rotor magnets. It should be stated here that each rotor magnet had to remain "clutched" to its mating magnet in the drive or "breakaway" resulted. It was established in preliminary tests on the assembly that at speeds over 3000 revolutions per minute, the drive magnets would "breakaway" and the rotor would stop completely. At the desired rotor speeds employed in the operational tests, however, no stoppage of the rotor occurred.

Feed Pump. In previous investigations on molecular stills at the Virginia Polytechnic Institute, small magnetic pumps of glass⁽³¹⁾ or metal⁽¹⁰⁾ construction were used as the feed pumps. Bull⁽²³⁾ describes the difficulties in control and the pulsating action inherent in the magnetic pump he employed. In order to avoid such difficulties, it was decided to employ a small gear pump especially designed for vacuum operation by the addition of an oil lantern

ring to seal the drive shaft. The gear pump was first employed in the system as a forced-feed pump with a bypass provided on the exit side of the pump, Drawing 2, page 81, to permit control of the excess pump capacity. The operation of the pump in this manner was unsatisfactory because of difficulty in controlling the feed rate in the desired range. Redesign of the feed system led to the use of a gravity-feed with the feed pump being used to return the feed to the gravity-feed tank from the residue tank. In this capacity, the gear pump served quite adequately with the major consideration, a vacuum-tight pumping system, being met. No loss of vacuum was experienced by starting or stopping the pump during fraction collection or in its continuous operation during recycling of the feed.

Gravity-feed System. The forced-feed system provided controllable feed rates between 100 and 150 milliliters per minute. At rates below 100 milliliters per minute, this system produced a pulsating feed. At higher feed rates than 150 milliliters per minute, overflow of the collecting gutter resulted in dumping of the feed into the bell jar and contamination of the distillate. In attempting operation at feed rates over 100 milliliters per minute, it was noted that considerable splashing of feed from the rotor occurred.

This, like overflow from the collecting gutter, resulted in contamination of the distillate. To eliminate splashing as much as possible, feed rates between 50 and 75 milliliters per minute were necessary. Since these rates could not be achieved using the forced-feed system without pulsation of the feed and poor control, it was decided to modify the still assembly to provide gravity-feed, Drawing 4, page 92. The gravity-feed system met the desired requirements. Much improved feed control resulted in a range estimated from 50 to 100 milliliters per minute. The feed preheating was easily controlled by wrapping a nichrome coil element around the copper tubing feed line through which the feed passed from the tank to the feed nozzle. As discussed in the procedure, the difficulty was not in controlling the feed rate but in estimating and measuring it.

Feed, Residue, and Distillate Tanks. The feed, residue, and distillate tanks were reconstructed of aluminum rather than of brass as employed by Bull⁽⁶⁾. The tanks were made at least twice as large to permit more flexibility in the experimental use of the still for both basic distillation studies and for pilot-plant size operation. The literature⁽⁸⁶⁾ indicated that aluminum would provide a less corrosive system and one which was not as likely to cause oxidation of such

substances as fatty acids. For the same purpose, the flow lines were initially constructed of aluminum tubing rather than copper tubing. It was found, however, that oxidation of the acids did not occur at low operation pressures and temperatures of the still and several of the flow lines were later changed to copper to provide increased flexibility in use of swagelok fittings.

Another important consideration in the decision to reconstruct the tankage system was to incorporate the use of swagelok fittings rather than an all-welded construction. The use of swagelok fittings provided a vacuum-tight system while making the system more flexible than a welded construction because any part of the flow system could be quickly and easily disassembled to check for clogged lines, vacuum leaks, and so forth.

Vacuum System. The diffusion pumps employed by Bull⁽¹¹⁾ were eliminated from the system because it was believed that the added reduction in pressure obtained from their use did not warrant the disadvantages inherent to their use:

- (1) increased system volume,
- (2) additional time (up to one hour) for beginning operation of the system for heating and degassing the diffusion pump oil,
- (3) additional time (of at least one hour) for cooling the pump oil under vacuum

after completion of the test, and (4) variable still pressure from test to test because of contamination of the pump oil. After consideration of these disadvantages, it was decided to employ three megavac pumps operating in parallel with a common manifold as the evacuation system for the still. This arrangement provided a dependable vacuum system which could quickly be placed into operation and which could be shut down immediately on completion of each test.

The vacuum system did not incorporate the use of a cold trap between the still and the vacuum pumps to prevent the passage of oil vapors to the pumping system. Undoubtedly, some oil was carried into the vacuum pumps as vapor during the tests. That this was the case was indicated by the slight change that occurred in the absolute pressure obtainable in the system after new pump oil had been used for several tests. The lowest pressure obtainable using new pump oil was 10 to 11 microns of mercury. After use of this oil for several tests (approximately 50 hours of operation) the minimum pressure increased to about 14 microns. When new oil was placed in the three megavac pumps, the minimum pressure decreased by 2 to 3 microns. From this phenomenon, it seemed likely that the vacuum pump oil was being contaminated with small amounts of mineral oil from

the constant-yield oil blend. The amount of mineral oil lost to the vacuum system was considerably less than five milliliters per test, however, since material balances on the oil blend indicated that no more than this amount was lost.

The distillate tank was evacuated separately from the rest of the system in order that it could be vented to the atmosphere as necessary for removal of distillate fractions and reevacuated without affecting the main system. The megavac pump used for this purpose performed satisfactorily in that it reduced the pressure in the distillate tank (within 15 minutes) so that no change in the main system pressure occurred when the tank was opened to the system for drainage of the distillate from the bell jar.

Condenser. Both Coli⁽³³⁾ and Bull⁽⁷⁾ employed the bell jar which enclosed the still head assembly as the condensing surface for the distillate obtained during operation of their molecular stills. The temperature of the bell jar varied as the test progressed because it received varying amounts of heat both from the rotor heater by conduction and radiation and from the condensing vapors. This investigator believed that, for experimental purposes, the temperature of the condensing surface should

remain nearly uniform. In order to achieve this, the plate condenser used in the system was constructed such that cooling water at any desired temperature could be used to control the condenser temperature. Some condensation continued to occur on the bell jar surfaces between the rotor and the condenser. From visual observation, it is estimated that at least 80 per cent of the condensation occurred on the plate.

The condensing surface plate was placed approximately 3-3/4 inches from the outermost edge of the rotor. A closer placement would have resulted in difficulty for the operator in observing the feed to the rotor. At the operating pressure of the still, 12 ± 2 microns of mercury, absolute, this distance was at least several multiples of the mean free path of the distilling molecules. Theoretically, therefore, true molecular distillation was not occurring since the requirement that the evaporating surface-condensing surface distance be in the range of the mean free path was not met. Recent literature⁽⁵¹⁾ has indicated, however, that this consideration is not of nearly as great importance as previously supposed possibly because large molecules such as nonspherical oil molecules have "undeflected mean free paths" several times larger than calculated by classical theory.

Thermocouples. The feed and residue thermocouples were similar in construction to those used by Bull⁽¹⁰⁾ except that swagelok rather than compression-type fittings were used for a more vacuum-tight seal. The calibration of the two thermocouples resulted in data for each, Table VII, page 107, which indicated that one calibration curve would suffice for both thermocouples. The potentiometer readings for both thermocouples were plotted against the corresponding temperatures as shown in Figure 9, page 108, and a single curve drawn through the points. The thermocouples provided very adequate temperature measurements on the two streams with temperature lag being essentially negligible since fraction collection was performed only after the temperatures of the feed and residue had steadied at the desired levels.

Still Operating Conditions. The choice of operating conditions was a most important one since the results obtained hold only for the prescribed conditions of operation. Numerous investigations have pointed out the decided effect of the many variables involved in molecular distillation. Bull⁽²¹⁾ and Coli⁽³⁵⁾ in their individual studies of variables affecting distillation in similar stills to the one used in this investigation describe the effect of such variables as operating pressure, rotor speed, feed

rate, number of passes of feed over the rotor per fraction, and temperature differential between feed and residue.

For the purpose of this study the choice of conditions was one of selecting those which would provide the smoothest still operation and ease of control. Once the conditions had been chosen and specified, the operational tests could be compared because the conditions were kept constant in all tests. It is important to remember that individual results such as elimination maxima cannot be directly compared with those obtained from other investigations in which different operating conditions were used. Hickman⁽⁵⁶⁾ states with regard to comparison of elimination maxima from several studies, however, that the elimination maximum will occur for each substance in a fixed relative order with definite temperature intervals between the maxima. Changing the conditions will then shift all the maxima up or down the temperature scale but will not seriously alter the separation or relative order. If a base substance is distilled in two studies, other substances distilled in the studies can be compared by comparison of each substance to the base substance of each study.

The operating conditions used in this investigation are individually considered to indicate the reasoning behind the choice and the variance of the condition during the tests.

Feed Rate. A feed rate of 60 to 65 milliliters per minute was chosen as the optimum for smoothness of operation and ease of control. Within this range, splashing of the feed from the rotor was negligible. While some slight splashing occurred in a few tests at the higher temperatures it was believed that this was due to flashing of a small amount of superheated feed which vaporized as it left the feed nozzle.

It should again be pointed out that the feed rate had to be approximated by visual observation on the part of the still operator at the beginning of each fraction collection and that exact measurement of the rate was made by timing the passage of feed over the rotor during fraction collection. Since fractions were not collected unless the feed rate was in the range between 60 and 65 milliliters per minute, the only difficulty which arose from the approximation of the feed rate was the necessity of recycling the distillate and recollecting the fraction. Many tests were made in which only one or two fractions had to be recycled after the operators had gained experience in estimating the feed rate.

Operating Pressure. The operating pressure, which was the minimum to which the system could be exhausted, was

12 \pm 2 microns of mercury, absolute. This pressure was maintained through each test with the exception of the period of the first fraction collection. Even after 2 to 3 hours of preheating and degassing the feed, the pressure during collection of the first fraction could not be lowered below 15 microns and was usually about 17 microns. It is believed that this was due to a slight amount of oil in the constant-yield blend having a higher vapor pressure than the rest of the oil. At any rate, when the first fraction of approximately 10 to 12 milliliters of oil (and fatty acid) was removed as distillate, the pressure decreased to 12 to 14 microns and remained in the selected operating range for the rest of the test.

Condenser Water Temperature. Initially, it had been planned to use tap water as the condenser cooling water. Since tap water temperature does not normally vary by more than one degree centigrade for long periods of time, this would have provided constant-temperature cooling water at about 12 degrees centigrade without necessitating the construction of a constant-temperature bath. When a test was made to distill an oil solution of stearic acid, however, crystallization of the acid occurred on the condenser plate and drainage of the complete distillate was impossible. Of

course, many of the acids employed in the study which had melting points below 12 degrees centigrade would not have crystallized. In order to make the tests completely comparable, however, it was decided that the condenser temperature should be the same for each test. Consequently, a cooling water temperature of 45 degrees centigrade was arbitrarily selected since it was believed that no crystallization of any of the acids would occur at this temperature. This proved to be true; no crystallization was noted at any time during the operational tests. Cooling water at 45 degrees centigrade was obtained by the construction of a constant-temperature bath from which water could be circulated to the condenser. The water in the bath varied by plus or minus one degree. The water rate through the condenser coils was fast enough in comparison to the small amount of heat transferred to the water that the temperature of the cooling water was increased by less than one degree in passing through the coils.

Fraction Collection Temperatures. In most previous investigations on molecular distillation, the fraction collection temperatures have been either 5 or 10 degrees centigrade apart. Bull⁽²⁴⁾ collected distillate fractions at 10-degree increments from 90 to 180 degrees centigrade and described this temperature increment as satisfactory for

basic distillation studies. He suggests the use of smaller increments if possible for more accuracy in the determination of elimination maxima. With this in mind, this investigator attempted the use of five-degree increments beginning with a first fraction collection at a residue temperature of 90 degrees centigrade. The resulting elimination curves were found to be "shorter" or "flatter" than those obtained by Bull. This was to be expected since lower yields resulted from the smaller temperature increases. It was believed that "flatter" elimination curves would provide no more accuracy than the ones obtained using 10-degree increments. To benefit from the use of smaller temperature increments and yet to provide fairly "sharp" elimination curves, six-degree increments were selected beginning with a first fraction collection at a residue temperature of 86 degrees centigrade. As many as eleven fractions up to 146 degrees centigrade were collected in the operational tests although only fractions up to 134 degrees centigrade were generally needed for establishing the elimination maximum of most of the acids studied.

Feed-residue Temperature Differential. It was decided that as wide a temperature differential as possible between the feed and residue would be used. This meant that as much heating as possible would be performed on the rotor in order

to hold the feed temperature to a minimum and thereby reduce thermal decomposition hazards. A further consideration in this decision was the possibility of feed flashing as it left the rotor if high feed temperatures were used. Flashing of the feed was highly undesirable because it would have resulted in feed being carried to the distillate as liquid. Demakis⁽³⁹⁾ states that in the still used by Bull and himself, temperature differentials of less than seven degrees between the feed and residue resulted in flashing. Bull⁽¹⁷⁾ studied the effect of the temperature differential and found that no difference was evident in the distillation using either 10 or 20-degree differentials. He suggested that a 20-degree differential was more difficult to control and maintain. During the course of this investigation, it was developed that approximately a 25-degree differential could be maintained with relative ease. Since fractions were collected every six degrees, a multiple of this temperature increment, 24 degrees centigrade, was arbitrarily selected as the feed-residue temperature differential. Little difficulty was met in holding this temperature difference during the operational tests. Control of both temperatures was generally to plus or minus 1/2 degree when the operator took numerous temperature readings during each fraction collection

period and made compensating adjustments to the heater-controlling powerstats.

Rotor Speed. Bull⁽²²⁾ found that between 1000 and 5000 revolutions per minute, the rotor speed had no effect on either the elimination curve or the elimination maximum of the substance being distilled. It was decided, however, in the interests of uniformity, to perform all tests at one rotor speed. A speed of 1000 revolutions per minute was selected as providing the smoothest flow of feed over the rotor surface and, therefore, the least likelihood of splashing. Variations of the rotor speed by as much as 50 revolutions per minute from this speed were considered unimportant.

Feed Passes Across the Rotor. A consideration of the number of passes of the feed across the rotor per fraction is important both as a standardized operating condition and in comparison to the techniques used by other investigators. In the experimental tests, the entire feed was allowed to pass completely over the rotor once for each fraction. This technique differed considerably from that employed by Bull⁽¹⁵⁾ who used what he described as two "nominal" passes per fraction and in which the residue was continually recycled to the feed tank while distillate collection was

timed for a predetermined two-pass period. Most techniques described in the literature also employed a different procedure from that used in this investigation. Hickman⁽⁵⁷⁾, for example, describes a one-pass technique in which the feed rate was varied from fraction to fraction to make the total distillation time for each fraction the same. In other words, as the initial constant-yield oil diminished, the feed rate was decreased so that the pass of the feed over the rotor required the same time for each fraction. It seemed to this investigator that Hickman's method served to introduce additional variables to the technique such as the inherent change in feed thickness on the rotor with change of the feed rate. For this investigation, therefore, feed rates were kept essentially constant and the time required for succeeding fractions diminished directly with the volume of constant-yield oil.

Constant-yield Oil. A discussion of the constant-yield oil considers the initial preparation of the mineral oil blend and the results obtained in the operational tests using the blend.

Preparation of Constant-yield Oil. Previous investigators have generally employed constant-yield oils which were prepared by molecular distillation of a mixture of triglycerides or mineral oils and reblending equal volumes of

each fraction from the distillation. This technique required many distillations to prepare a sufficient amount of constant-yield oil before the experimental tests could be performed. Bull⁽²⁰⁾ developed a blend of mineral oils which provided a satisfactory constant-yield oil without preliminary distillations and blending of distillate fractions. He suggested that in most tests, satisfactory drainage could be obtained even though the volumes of oil in succeeding fractions varied to some extent. Bull also found that, in numerous instances, reblended fractions provided an oil mixture which was not as satisfactory as his initial oil blends. The main difficulty which he encountered was in providing a non-distilling residue to add bulk to his constant-yield oil.

For the purposes of this investigation, it was believed that a blend of oils could be developed which would provide nearly constant yields of oil during distillation. Since temperatures as high as those encountered by Bull were not necessary in the distillation of the fatty acids, it was further believed that the heavy mineral oil used by Bull could be used to advantage as the non-distilling portion of the blend. Light mineral oil, distilling in the range from 110 to 140 degrees centigrade under the conditions established for still operation, provided fractions within this range.

The major problem was then to locate a mineral oil which would distill in the range between 80 and 100 degrees centigrade. It was also desirable that this oil be essentially colorless so that difficulty would not arise in noting the end point during titration of the fatty acid which would be dissolved in each oil fraction. Five mineral oils were distilled in preliminary tests and Voltesso No 36 was found to be most satisfactory. Various blends of this oil with light and heavy mineral oils were then distilled using the technique to be employed in the experimental tests. A blend of 225 milliliters of Voltesso No 36, 175 milliliters of light mineral oil, and 430 milliliters of heavy mineral oil was found to give an adequate constant-yield oil of the desired volume for use in the tests. It should be stated further that very little of the heavy mineral oil distilled below 140 degrees centigrade and that the volume of non-distilling residue could therefore be varied almost at will by varying the amount of this oil in the blend.

Distillation of Blended Constant-yield Oil. Although several individual tests were made on the oil blend to study the fraction volumes obtained, it was believed that data from the experimental tests would more adequately typify the distillation characteristics of the blend. These data appear

in Table VIII, page 109, and show the range of volumes and the average volumes of the fractions for 28 experimental tests.

Although the difference between the smallest and largest volumes for one particular fraction is often large, 13 to 16 milliliters, it should be remembered that these data represent the extremes of operation, when one or more of the conditions of operation were at the ends of their allowable range or when experimental error on the part of the operator (such as incomplete drainage of the distillate) occurred.

The average volumes present a more nearly fair indication of the constancy of the blend. With the exception of the very small first (12.6 milliliters) and small second (33.6 milliliters) fractions, variance in the average volumes of the fraction was by only 6.6 milliliters, from 38.4 to 45.0 milliliters. Further, average volumes for the six middle fractions from 98 to 128 degrees centigrade varied only from 38.4 to 42.6 milliliters. The small first fraction was not considered as particularly harmful to the accuracy of the tests since very little acid distilled at the temperature of this fraction in most of the tests. Certainly, it can safely be said that any drainage error which might have resulted in the first fraction did not affect the determination of the elimination maximum. It should be pointed out, however, that fatty acids,

such as lauric and myristic acids, which distill in large quantities below 90 degrees could not be handled using this constant-yield oil blend without further consideration of the possible error introduced by improper drainage.

The data for the molecular distillation of the constant-yield oil indicate that the blend provided a large non-distilling residue. After 10 fractions were removed, an average residue volume of 450.1 milliliters remained, 54.56 volume per cent of the original volume of 825 milliliters.

Molecular Distillation of Fatty Acids. Fourteen fatty acids illustrating various molecular structures were distilled to study the effect of molecular structure on the elimination maximum. The data and results for the distillation tests are presented in Tables IX, X, and XI, pages 110, 117, and 122. An elimination curve for each acid follows the table in which the data for that acid appear. Before the effects of the various molecular structures are considered, several points of interest should be briefly discussed. These are the duplicate tests performed for each acid, the general shape of the elimination curves obtained and the results of the distillation test on arachidic acid.

Duplicate Tests. Since at least two distillations were performed for each acid, an indication was gained of the duplicability of results. Most of the duplicate tests were

made with one operator making the first test and a second operator making the second test. Further, in each test, the titration of the fatty acid fractions was performed by the two alternating operators with the first operator making the titrations when the second had performed the operation of the still and the collection of the distillate fractions. The data obtained from duplicate tests should therefore provide some indication of the agreement of results which can be expected from two or more individual operators each trained in use of the technique developed during the investigation. In general, it can be stated that agreement between tests was very good. Yields for the same fraction in duplicate tests usually agreed to closer than one per cent with only a few rare instances occurring when more than a difference of two per cent in yields occurred. In plotting the data for determination of the elimination curve and elimination maximum, it will be noted that a single curve was drawn for points from both distillations. In most cases, two curves would not have varied enough in the general shape and elimination maximum to have warranted the use of individual curves for each test.

It should be pointed out that three distillations were made and reported for oleic acid, Table X, page 117. A third distillation was performed for this acid because of considerable

variance (3.66 and 2.52 per cent, respectively) in the yields for the 116- and 122-degree centigrade fractions. The third test provided values for these two yields which fell between the previous values. An elimination curve was then plotted with regard to average values for the two fractions.

General Shape of the Elimination Curve. The elimination curves were generally "shorter" and "broader" than those normally obtained by other investigators^(43,53). It was believed that this was due to the use of smaller temperature increments, 6 degrees, than those normally employed, 10 degrees, and to the fact that acid distillation increased rapidly from the first fraction to a maximum usually within four or five fractions. If distillation could have been and had been started with a fraction at 74 degrees centigrade rather than at 86 degrees centigrade and 10-degree temperature increments between fractions had been used, the elimination curves would probably have been similar in shape to those established by classical theory⁽⁴³⁾. Distillation would have begun more slowly; risen, slowly at first, and then rapidly to a maximum; and fallen off rapidly after the maximum had been reached.

Some mention should be made here of a factor involved in the selection of the operating conditions since these conditions were of the utmost importance in establishing

the shape of the elimination curves. Since it appeared that stearic acid would be used as the best basis for comparison of the other acid distillations, several operating conditions (primarily the feed rate and 6-degree temperature increment) were selected to provide a normally sharp elimination curve for this acid, Figure 13, page 114. Once the operating conditions were established, they were employed for all of the other tests as well as for stearic acid. Since the other acids differ from stearic acid in volatility and other characteristics, the shape of the elimination curves could be expected to vary. Acids which distilled at lower temperatures than stearic acid, such as pentadecylic acid, Figure 10, page 111, had taller and narrower elimination curves and those which distilled at higher temperatures, such as nonadecylic acid, Figure 14, page 115, had shorter and broader curves.

Molecular Distillation Test of Arachidic Acid. The distillation tests performed on arachidic acid indicated that the acid samples used were impure. This conclusion was reached from a study of the elimination curve, Figure 15, page 116, obtained for this acid. No sharp elimination maximum was evident although there appeared to be a slight maximum at 122 degrees centigrade. Markley⁽⁷⁴⁾ suggests a possible

explanation of the impurity present in a statement that arachidic and lignoceric (C_{24} saturated) acids are often found together in many fats and are extremely difficult to separate analytically. Further, it seemed evident from the fact that only 68 per cent of the original acid was recovered up to a temperature of 140 degrees centigrade that the impurity acid was less volatile than arachidic acid. Lignoceric acids meets this requirement. If the acid samples distilled were a mixture of approximately 50 per cent of each of arachidic and lignoceric acids, a composite elimination curve similar to the one in Figure 15, page 116, might be obtained. Two elimination maxima might then be evident in the composite curve, but neither would be distinct. It is believed that this is the phenomenon exhibited by the elimination curve for the impure arachidic acid. It is probable that the slight maximum obtained in the curve is that for arachidic acid and that the maximum for the impurity (if lignoceric acid) is not evident or was above a temperature of 140 degrees centigrade, the last fraction taken during the distillations.

To further establish whether the acid samples were pure, a melting point determination was made on the acid. The melting point was found to be 62.5 degrees centigrade compared to a literature value⁽⁷⁷⁾ of 75.4 degrees centigrade for pure

arachidic acid. A lowering of the melting point would be expected if the acid were contaminated by the presence of a second acid.

If a sufficient amount of arachidic acid had been available, successive molecular distillations could have been performed to separate the arachidic acid in the samples from the higher distilling acid. Portions of the fractions up to 122 degrees centigrade could have been reblended and redistilled a number of times until a sharp elimination curve could be established for arachidic acid.

Effect of Molecular Structure on the Elimination Maximum. The elimination maxima of the fatty acids are summarized in Table XII, page 127. The effect of molecular structure on the elimination maximum will be considered for the various structures studied such as chain length, effect of unconjugated and conjugated double bonds in the chain, and positional and cis-trans isomerism.

Effect of Chain Length. To study the effect of chain length, six long-chained saturated fatty acids were distilled. The carbon chain varied from 15 carbon atoms in pentadecylic acid to 20 in arachidic acid. The elimination maxima obtained were at 100, 102, 110, 112, 127, and 122 degrees for the C_{15} , C_{16} , C_{17} , C_{18} , C_{19} , and C_{20} acids, respectively. Since the length of the chain is increased in the series by the addition

of one CH_2 group at a time, the effect of this group should be the difference between adjacent members of the series. The differences varied as follows: +2, +8, +2, +15, and -5 degrees. No definite effect can be established, therefore, from the consideration of the series as a whole. If the odd-numbered and even-numbered acids are considered separately, however, a more systematic pattern emerges. Reasons for the validity of this consideration will be further advanced after a discussion of each group of three acids.

Even-numbered Acids. The even-numbered acids, palmitic, stearic, and arachidic acids, show a difference of 10 degrees centigrade in their elimination maxima, 102, 112, and 122 degrees centigrade, respectively. It would then seem that the addition of two CH_2 groups at one time raises the elimination maximum by 10 degrees centigrade. This is the same conclusion drawn by Gray and Cawley⁽⁵⁰⁾ in their study of the even-numbered acids from C_{12} to C_{18} . They found elimination maxima for lauric, myristic, palmitic, and stearic acids as 88.5, 98.0, 108.0, and 118.0 degrees centigrade, respectively. Hickman⁽⁵⁸⁾ found the same effect, a 10-degree rise in the elimination maximum, in a study of a homologous series of anthraquinone dyes where two CH_2 groups were

added to the molecule. In Hickman's study the length of the chain of two amino radicals on the anthraquinone molecule were increased by one CH_2 group being added to each; that is, the series went from 1,4-dimethyldiaminoanthraquinone to 1,4-diethyldiaminoanthraquinone to 1,4-dipropyldiaminoanthraquinone, etc. Both investigations concluded that one CH_2 group raises the elimination maximum by five degrees. It is the opinion of this investigator that such a conclusion is valid only when the series is a truly homologous one. The addition of one CH_2 group to the saturated fatty acids did not raise the maximum five degrees. This would indicate that the even-numbered and odd-numbered saturated fatty acids should not be considered in the same homologous series. Further reasons for this consideration follows a discussion of the results of the distillation of the odd-numbered acids.

Odd-numbered Acids. The elimination maxima for the C_{15} , C_{17} , and C_{19} acids were found to be 100, 110, and 127 degrees centigrade, respectively. Again, as in the even-numbered acids, the addition of two CH_2 groups to the C_{15} molecule raised the elimination maximum by 10 degrees. However, an additional two CH_2 groups raised the maximum by 17 degrees centigrade. No characteristics of

nonadecylic acid could be found in the literature which would account for this variation. The possibility of an impurity in this acid was checked by determination of the melting point which was found to be the same as given in the literature ⁽⁷⁸⁾, 68.6 degrees centigrade.

Structural Variations Between the Odd- and Even-numbered Acids. Many studies reported in the literature indicate structural differences between the odd- and even-numbered acids that would account for the zigzag pattern of the elimination maxima. Markley ⁽⁷⁶⁾ describes organic crystals, such as the fatty acids, as being "molecular in structure rather than atomic as in the case in elemental and inorganic substances. The points on the crystal lattice are occupied by molecules and, consequently, the unit cells of organic crystals are large". By unit cell, Markley means the smallest element which contains a representation of the lattice, the repetition of which unit builds up the cell. It is the smallest parallelopiped, which, when repeated, gives the macroscopic crystal. Stearic acid as well as the other acids used in this study, have been found to have a unit cell which is an elongated monoclinic prism containing four molecules. Within the molecules of the

unit cell, the carbon atoms are arranged in a zigzag pattern having an angle corresponding to the tetrahedral carbon angle, namely $109^{\circ}28'$ (76). In even-numbered carbon chains, therefore, the end groups (C-C) are parallel while in the odd-numbered chains, they lie at an angle to each other. According to Malkin (71), this zigzag arrangement of the carbon atoms accounts for the alternation of properties of long-chain aliphatic compounds having odd- and even-numbered carbon atoms. The difference in orientation of the end groups necessitates a difference in the inclination of the chains in the crystal layers which in turn influence the physical properties of the crystal. In the case of the long-chain aliphatic compounds of an odd- or even-numbered homologous series, the addition of a pair of CH_2 groups affects the crystal lattice in only one direction without affecting the inclination of the chains.

Effect of Unconjugated Double Bonds. A comparison of the elimination maxima of the monoethenoid palmitoleic and oleic acids with the saturated acids, palmitic and stearic acids, having the same number of carbon atoms will indicate the effect of one double bond in the fatty acid molecule. Palmitoleic acid had an elimination maximum of 99 degrees

centigrade compared to 102 degrees centigrade for palmitic acid; oleic acid had a maximum of 110 degrees centigrade compared to 112 degrees centigrade for stearic acid. These results indicate that the effect of one double bond is a decrease in the elimination maximum from 2 to 3 degrees centigrade.

With a second double bond added to the C_{18} molecule in an unconjugated position, the elimination maximum was lowered an additional two degrees, the maximum of linoleic acid being 108 degrees centigrade. A third double bond in an unconjugated position lowered the maximum one degree to 107 degrees centigrade for linolenic acid. Within the accuracy of the distillation tests, it would probably be safe to conclude that each double bond in the fatty acid molecule lowers the elimination maximum by $2 + 1$ degrees. This is essentially the same conclusion drawn by Gray and Cawley⁽⁵⁰⁾.

It should be noted that particular attention was made to the addition of each double bond to an unconjugated position. Oleic acid has a double bond in the 9-10 position, linoleic acid has double bonds in the 9-10 and 12-13 positions, and linolenic acid has bonds in the 9-10, 12-13, and 15-16 positions. The effect of conjugated double bonds varies considerably from that of unconjugated double bonds.

Effect of Conjugated Double Bonds. When the second double bond in the fatty acid molecule occurred in the conjugated position as in 9,11-linoleic acid (9-10 and 11-12) positions rather than 9-10 and 12-13 as in linoleic acid), the elimination maximum was increased instead of being decreased. The elimination maximum of 9,11-linoleic acid was found to be 116 degrees centigrade, an increase of six degrees from the monoethenoid oleic acid. The difference in elimination maxima between the two diethenoid acids, the unconjugated linoleic and the conjugated 9,11-linoleic, was therefore eight degrees.

The addition of a third double bond into a conjugated system as in α -eleostearic acid (9-10, 11-12, 13-14) raised the elimination maximum an additional six degrees to 122 degrees centigrade. The difference between the maxima of the unconjugated and conjugated triethenoids was 15 degrees (between linolenic and α -eleostearic acids).

Some variance between the elimination maxima of unconjugated and conjugated fatty acids was to be expected since, in general, the arrangement of the double bonds in conjugated positions, as contrasted to the unconjugated or isolated arrangement, results in marked differences in most chemical and physical properties of the two types of acids.

Effect of Positional and Cis-trans Isomerism. Two examples of positional isomerism have already been considered in discussing the effect of conjugation of the double bonds in the molecule. Positional as well as cis-trans isomerism was also studied with regard to monoethenoid C₁₈ acids. Three C₁₈ acids were distilled: oleic and elaidic acids, which are cis-trans isomers with the double bond of each located in the 9-10 position, and vaccenic acid which is a positional isomer of both the other acids with the double bond in the 11-12 position. A decided difference in the elimination maxima was noted. The cis isomer (oleic) had an elimination maximum of 110 degrees centigrade compared to the maximum of 117 degrees centigrade for the trans isomer (elaidic). The elimination maximum of the positional isomer was 115 degrees centigrade.

As in the case of isomerism between conjugated and unconjugated acids, the changes in the properties of the acids due to changes in the structure forewarn of expected differences in the elimination maxima.

Summary of the Effects of Molecular Weight and Structure on the Molecular Distillation of Fatty Acids. In a summary of the effects of molecular weight and structure on molecular distillation, this investigator believes that two general statements should be made.

First, molecular weight alone should not be considered in theorizing which of two or more substances will distill first or if two substances can be separated by molecular distillation, unless the differences in molecular weights are considerable. This study indicated that many substances of different molecular weights varied less in elimination maxima than did isomers with the same molecular weights.

Second, certain structures appear to have a definite effect in lowering or raising the elimination maximum if a homologous series or a series of substances with similar or nearly similar properties is under consideration. It would seem safe, therefore, to predict the distillation characteristics or possibilities of separation in these cases.

Recommendations

The following recommendations are made for future molecular distillation studies and for modification of the equipment of the centrifugal molecular still for improved operation.

Recommendations for Future Studies. Several additional studies are recommended for future work to enlarge the scope of research using the centrifugal molecular still.

Molecular Structure. A continuation of this investigation should be made to study the effects of numerous structures not considered by this investigation. Such studies might include the effect of triple bonds, halogens, nitrates, and sulfates in the fatty acid molecule, and the distillation of such substances as the methyl and ethyl esters of the fatty acids. The ultimate objective of such studies would, of course, be to gather more data toward a correlation which would permit the prediction of the distillation characteristics of any substance from its molecular weight and structure. It is believed that along with such studies, there must be a concurrent investigation of the vapor pressures of the substances undergoing distillation. Little or no data are available in the literature for the vapor pressures of substances at the temperature conditions encountered in the still. These data

will probably have to be determined before any important correlations can be developed.

Condenser Studies. A study should be made to determine the effect of both the placement of the condenser plate and the temperature of the condenser on the distillation characteristics of the molecular still. The condenser plate could be spaced at distances varying from 1/2-inch to 6 inches from the rotor by varying the length of the copper-tubing connections to the inlet and outlet water lines. A number of distillations of the same substance, such as stearic acid, using different plate-to-rotor spacings could then be made to determine the effect of the evaporating-to-condensing surface distance.

In the same manner, a series of tests could be made to determine the effect of condenser temperature. The cooling water temperature could be varied from test to test and the average temperature of the condenser plate could be determined by placing the hot junctions of several thermocouples at various points on the plate surface. It is recommended that the acid used for these tests be one that will not crystallize on the condenser plate when low cooling water temperatures are studied. Such acids as oleic or linoleic acids would be satisfactory.

A further study might be made to determine the amount of condensation on the condenser plate as opposed to that on the bell jar surface between the rotor and the condenser. This could be accomplished by collecting the distillate from the condenser separately from that condensing on the bell jar. It is entirely feasible that additional fractionation might result from the difference in temperatures on the two condensing surfaces.

Pilot-plant Size Studies. The reconstructed molecular still can handle a capacity of feed that would permit pilot plant size distillations of such substances as peanut and cottonseed oils. With only minor modification such as increased heating capacity and insulation of the flow lines, the still could be used to distill batch quantities up to one-half gallon. If separation of particular components of such substances as peanut oil is desired or if only a general molecular distillation is to be attempted, the use of the still is recommended.

Recommendations for Equipment Modifications. Two equipment modifications are recommended to improve the ease of operation of the molecular still.

Measurement of Feed Rate. A rotameter should be incorporated in the system to measure the feed rate and eliminate

the need for estimating this important variable. This direct measurement method would prevent the distillate recycling and recollection necessitated by improper feed rates. It is believed that a suitable rotameter could be obtained which would be or could be made vacuum-tight. The rotameter would require calibration at each fraction temperature for each blend of constant-yield oil used in the distillations since the viscosity of the oil changes radically with increased temperature and removal of portions of the original feed volume by distillation.

Vacuum Measuring System. It is recommended that the McLeod gage used for measuring the absolute pressure be replaced with a thermocouple gage for use in routine operation of the still. This type of gage would permit faster pressure determinations while providing nearly as accurate readings as the McLeod gage. Further, the thermocouple gage would not be contaminated by oil vapors or require the long copper tubing connection (approximately six feet) to the system necessitated by use of the McLeod gage. The McLeod gage should be connected to the system for occasional recalibration of the thermocouple gage.

Limitations

A centrifugal molecular still with a five-inch rotor and provided with a vacuum-tight magnetic drive was used to study the effect of molecular structure on the elimination maxima of fatty acids. The limitations imposed on this investigation include those of the acids used, operating pressures, feed rates, rotor speed, temperature differential between feed and residue, condenser water temperature, number of passes of the feed over the rotor per fraction, mineral constant-yield oil, and analysis of distillate samples.

Acids Used. Fourteen fatty acids were used in the study. Six of these were long-chained saturated acids - pentadecylic, palmitic, margaric, stearic, nonadecylic, and arachidic - illustrating straight carbon chains from 15 to 20 carbons. The eight unsaturated acids included four monoethenoids, palmitoleic, oleic, elaidic, and vaccenic acids; two diethenoids, linoleic and 9,11-linoleic acids; and two triethenoids, linolenic and α -eleosteraric acids. The weights of acid employed in each test varied from 0.950 to 0.5139 grams.

Operating Pressure. The tests were conducted at an operating pressure varying from 10 to 14 microns. This pressure was achieved

after two to three hours of degassing the fatty acid-constant-yield oil mixture.

Feed Rate. The feed was passed over the rotor for distillation at a feed rate varying between 60 and 65 milliliters per minute. The feed rate was approximated by the operator before distillate collection and timed during passage of the feed volume over the rotor. If the feed rate were found to be between 60 and 65 milliliters per minute, the distillate fraction collected was considered acceptable and drained from the system for analysis.

Rotor Speed. Although the rotor speed was found to have no effect on the distillation, a rotor speed of 1000 ± 50 revolutions per minute was used in all the operational tests. The rotor speed was controlled by powerstat control of the variable speed drive motor.

Feed-residue Temperature Differential. The temperature differential between the feed temperature and the residue temperature was maintained at 24 degrees centigrade for all fractions collected during the tests. Control of both temperatures was to $1/2$ degree of the desired temperature.

Condenser Water Temperature. The cooling water flowing through the condenser coils was maintained at 45 ± 1 degrees centigrade by a constant-temperature bath. In passing through the coils the temperature was not raised more than one degree.

Number of Feed Passes. The feed was allowed to pass over the rotor once per distillate fraction collection. This was accomplished by pumping all the feed to the feed tank and allowing it to flow by gravity through the preheating feed line onto the revolving rotor. The time required for one pass of the feed over the rotor varied from 13.3 minutes for the 86-degree centigrade fraction to 7.6 minutes for the 140-degree centigrade fraction.

Constant-yield Oil Blend. The constant-yield oil employed in the tests was a mixture of three colorless mineral oils. The initial feed volume of 825 milliliters was made up from 225 milliliters of Voltesso No 36, 175 milliliters of light-grade mineral oil, and 425 milliliters of heavy-grade mineral oil. The heavy mineral oil acted as a non-distilling carrier oil which remained as residue after the 140-degree centigrade fraction was removed from the still.

Analysis of Acid Samples. The distillate fractions were analyzed by extracting the fatty acid with ethyl alcohol and titrating with 0.0251 normal potassium hydroxide solution to the phenolphthalein end point.

V. CONCLUSIONS

The effect of molecular structure on the elimination maxima of fatty acids was studied using a magnetically-driven centrifugal molecular still with a five-inch rotor. A standardized technique was developed and the operating conditions were maintained constant for all tests as follows: operating pressure, 12 ± 2 microns of mercury, absolute; feed rate, 60 to 65 milliliters per minute; rotor speed, 1000 ± 50 revolutions per minute; feed-residue temperature differential, 24 ± 1 degrees centigrade; condenser water temperature, 45 ± 1 degrees centigrade; and number of passes of the feed over the rotor per fraction, one. From the investigation, the following conclusions may be drawn:

1. The addition of two CH_2 groups in the carbon chain raises the elimination maximum of the even-numbered saturated fatty acids by 10 degrees centigrade. The elimination maxima of palmitic, stearic, and arachidic acids were found to be 102, 112, and 122 degrees centigrade, respectively.

2. The addition of two CH_2 groups in the carbon chain of the odd-numbered saturated fatty acids does not necessarily raise the elimination maximum by 10 degrees. The addition of two CH_2 groups to the pentadecylic molecule raised the maximum from 100 degrees to 110 degrees centigrade for margaric acid. An additional two CH_2

groups resulted in a maximum of 127 degrees centigrade for non-adeylic acid, however, an increase of 17 degrees centigrade.

3. The effect of an addition of a double bond in unconjugated position in a fatty acid is a lowering of the elimination from 1 to 3 degrees. Palmitoleic and oleic acids had elimination maxima 3 and 2 degrees, respectively, from the saturated acids, palmitic and oleic. The diethenoid acid, linoleic, had an elimination maximum of 108 degrees centigrade, 2 degrees lower than the monoethenoid, oleic acid. An additional double bond as in the triethenoid, linolenic acid, lowered the maximum an additional 1 degree to 107 degrees centigrade.

4. The addition of a double bond into the conjugated position in the fatty acid molecule raises the elimination maximum by 6 degrees. Oleic acid had an elimination maximum of 110 degrees centigrade; the conjugated diethenoid, 9,11-linoleic acid, had a maximum of 116 degrees centigrade; and the conjugated triethenoid, α -eleostearic acid, had a maximum of 122 degrees centigrade.

5. Positional isomerism has a decided effect on the elimination maximum. The 9,10-octadecenoic acid (oleic) had an elimination maximum of 110 degrees centigrade while the 11,12-octadecenoic acid (vaccenic) had a maximum of 115 degrees centigrade.

6. Cis-trans isomerism also has a pronounced effect on the elimination maximum. Two cis-trans isomers of 9,10-octadecenoic acid had elimination maxima of 110 (oleic) and 117 (elaidic) degrees centigrade.

VI. SUMMARY

Molecular distillation presents a method of separation for substances of high molecular weights which would suffer thermal decomposition at the higher temperatures that would be required for conventional distillation. In general, the separatory power of molecular stills is poor and in order to obtain relatively pure substances from mixtures, a series of redistillations may have to be performed.

The distillation of individual substances under molecular distillation conditions is best characterized by an elimination curve which is a plot of the yield of the substance undergoing distillation against the temperature of distillation. This elimination curve exhibits a definite maximum which is characteristic of the substance being distilled if standardized techniques and operating conditions are employed.

It was the purpose of this investigation to study the effects of molecular structure on the elimination maximum of fatty acids. Such molecular structural variances as chain length, presence and position of double bonds, conjugation and unconjugation of the double bonds, and positional and cis-trans isomerism were studied.

The centrifugal molecular still with a five-inch rotor and a bell-jar condensing surface available at the beginning of this investigation was almost completely reconstructed to improve ease of operation and maintenance of a vacuum-tight system. Final design included a magnetic drive to replace the vacuum-enclosed drive and packed shaft drives used in previous investigations. Other modifications included the aluminum feed, residue, and distillate tanks, a water-cooled condensing plate within a high-form bell jar, a gear pump feed recycle system, a gravity-feed system, an evacuation system employing three megavac pumps operating in parallel, a modified and reconstructed still head assembly to accommodate the magnetic drive, and the removal of all electrical controls from mounting on the still assembly to a panel board.

Initial tests were made to obtain a constant-yield oil and to standardize an operating technique. A mixture of light and heavy mineral oils and Voltesso No 36 was found to give a satisfactory constant-yield oil. The conditions of operation under the standardized technique were as follows: operating pressure, 12 ± 2 microns of mercury, absolute; feed rate, 60 to 65 milliliters per minute; feed-residue temperature differential, 24 ± 1 degrees centigrade; condenser water temperature, 45 ± 1 degrees centigrade; rotor speed, 1000 ± 50 revolutions per minute; and

number of passes of the feed volume over the rotor per distillate fraction, one. The first fraction was collected at a residue or fraction temperature of 86 degrees centigrade and fractions were taken thereafter at six-degree increments up to 140 degrees centigrade or as high as necessary for establishment of an elimination curve.

Fourteen fatty acids were distilled in duplicate tests in the study. Six of these were long-chained saturated fatty acids; pentadecylic, palmitic, margaric, stearic, nonadecylic, and arachidic acids, which varied in the length of the carbon chain from 15 to 20 carbons. The elimination maxima determined for these acids were 100, 102, 110, 112, 127, and 122 degrees centigrade, respectively. Four fatty acids containing one double bond in the molecule were studied and the maxima were found to be as follows: palmitoleic, 90; oleic, 110; elaidic, 117; and vaccenic, 115 degrees centigrade. The elimination maxima of the diethenoids studied, linoleic and 9,11-linoleic acids, were found to be 108 and 116 degrees centigrade, respectively; and those of the triethenoids studied, linolenic and α -eleostearic acids, were found to be 107 and 122 degrees centigrade, respectively.

It was concluded from the investigation that the addition of two CH_2 groups in the carbon chain raises the elimination maximum of even-numbered saturated fatty acids by 10 degrees centigrade, and that a similar addition did not necessarily raise the elimination maximum

of the odd-numbered acids by the same amount. Further, it was found that each double bond in an unconjugated position in the fatty acid molecule lowered the elimination maximum from 1 to 3 degrees. Each double bond added to the molecule in a conjugated position raised the elimination maximum by 6 degrees. Both positional and cis-trans isomerism were found to have a pronounced effect on the elimination maximum.

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VIII. ACKNOWLEDGMENTS

The author is deeply indebted to his advisor, Dr. Fred W. Bull, without whose patience, guidance, and encouragement this work could not have been successfully completed.

The author is also indebted to his fellow co-worker, Mr. Julian F. Mote, for his invaluable assistance in the still construction and the experimentation.

Special appreciation is due Mr. M. B. Smith and the members of the Industrial Engineering Shops for their work in the construction of the still head assembly.

The author is grateful also to the numerous individuals and groups who have in various ways been helpful in the progress of the work and especially to the following for their contributions:

Dr. Dudley Thompson and Mr. Hugh Woodle, Department of Chemical Engineering, for making slides used by the author in presentation of this work.

Mr. Charles C. Swoope, Esso Standard Oil Company, for supplying the mineral oils used in the preparation of a constant-yield oil.

Mr. M. A. Price, for his assistance in the construction of the molecular still assembly.

And, to all the members of the Chemical Engineering Department, for advice given during the progress of this investigation.

IX. VITA



Mr. George J. Demakis was born in Manchester, New Hampshire, on May 8, 1931, of Greek immigrant parents. At the age of four, his parents moved to Quantico, Virginia, his home at the present date. His elementary education was obtained at Quantico and Dumfries (Virginia) grammar schools and he received his high school training at Occoquan District High School. After graduation from high school in June, 1948, he applied and was accepted for admission to the Virginia Polytechnic Institute. In June,

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