TABLE 2

Heat Capacity, c_p, of Highly Hydrogenated Cottonseed Oil in Solid and Liquid States at Various Temperatures.

Solid oil, tempered			Solid oil, quickly chilled			Liquid oil		
Temp. °K.	Observed c_p	Deviation of obs. from calc. value	Temp. °K.	Observed c_p	Deviation of obs. from calc. value	Temp. °K.	Observed c_p	Deviation of obs. from calc. value
	cal./g.	*cal./g.*		*cal./g.*	*cal./g.*		*cal./g.*	*cal./g.*
203.3	0.270	0	196.2	0.275	0	340.1	0.524	0.001
210.9	0.281	0.001	203.4	0.284	0.001	344.1	0.526	—0.001
218.4	0.291	0.001	211.3	0.296	0	347.6	0.530	0
226.5	0.300	—0.001	218.6	0.306	0	351.5	0.535	0.001
233.8	0.310	—0.001	225.4	0.315	—0.001	355.1	0.537	—0.001
241.6	0.321	0	232.3	0.326	0.001	....	....	....
248.4	0.332	0.001	240.8	0.338	0.001	....	....	....
255.6	0.342	0.002	....	....	....	....	....	....

was first detected in the tempered sample at 258° K., ±1° (—15° C.) and in the quickly chilled sample at 247° K., ±1° (—26° C.).

Previously reported heat of fusion values for highly hydrogenated cottonseed oil (3) are slightly higher than the present value for the tempered sample.

The difference in the heat of fusion of the two samples, amounting to 2.4 calories per gram, cannot be considered a true heat of transition, in view of the probable heterogeneity of the rapidly solidified sample. The heat of fusion of commercially prepared lots of hydrogenated oil of this approximate iodine value should generally lie between the two experimentally determined values.

Summary

1. The heat content of a quickly chilled sample, and that of a slowly chilled and tempered sample, of almost completely hydrogenated cottonseed oil, has been measured over a temperature range within which there is in each case complete transformation of the oil from a solid to a liquid form.

2. Heat capacity data have been calculated for the liquid oil and for the quickly chilled and the tempered solid oil. Equations expressing the changes in heat capacity with temperature have been derived. A correlation of the heat capacity data on highly hydrogenated cottonseed oil and similar data previously obtained on unhydrogenated cottonseed oil, and on partially hydrogenated oil, in both liquid and solid states, is presented.

3. The heat of fusion calculated for the quickly chilled and for the tempered solid oil is given.

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Precise Laboratory Fractional Distillation of Fatty Acid Esters

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SINCE the first attempts, over 65 years ago, to utilize fractional distillation to separate individual fatty acids, the art has gradually improved until today this process is a common commercial operation. On a laboratory scale Professor Hilditch and his coworkers have been the foremost proponents of this technique, which has been extended and amplified by Dr. H. E. Longenecker in this country. The latter has recently reviewed this field (1).

The more widespread use of fractional distillation in the fatty acid field, however, has been hampered by an incomplete understanding of basic principles on the part of many investigators. Frequently this has resulted in the use of inefficient fractionating equipment and consequent unsatisfactory results. It is the purpose of this paper to review, in the light of our experience, the more important features of fractional distillation technique as applied to fatty acid esters.

Fractional distillation may be looked upon as a process in which vapors leaving the liquid in the still pot are allowed to pass upwards through a column at the top of which they are condensed. A portion of the condensate is returned as "reflux" downwards through the column where it is brought into more or less intimate contact with the ascending vapors. Here a heat interchange takes place between the relatively cooler liquid and the warmer vapors so that the more volatile part of the liquid is vaporized while the more easily condensible part of the vapors is condensed. Under ideal conditions the heat lost by the rising vapors is gained by the descending liquid, there being no loss or gain of heat from the outside. The net result is a concentration of the more volatile material in the top of the column with increasing concentration of less volatile material as the bottom of the column is approached.

A pictorial representation of the process is seen in Fig. 1 which shows a so-called vapor-liquid equilibrium curve. As a hypothetical case, a liquid of x_1 mole % of B at t_1 will give rise to vapor which when

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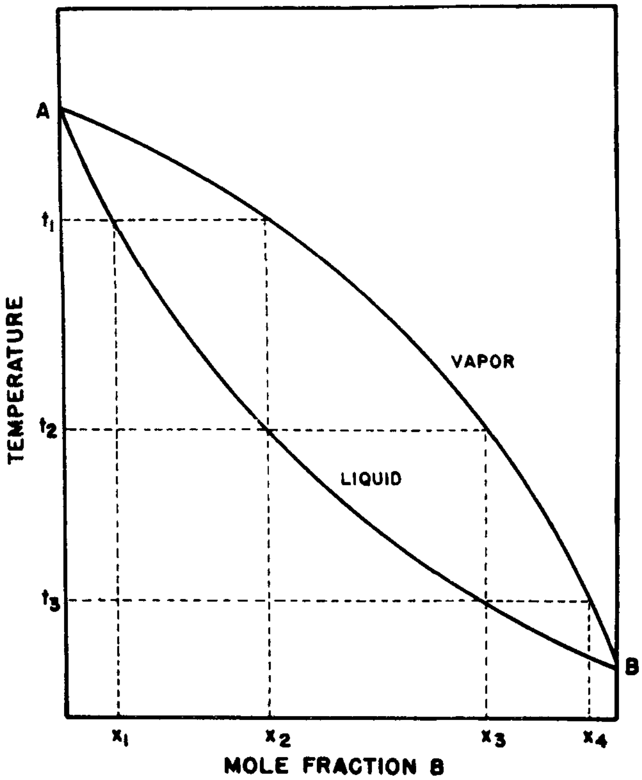

FIG. 1. Boiling-point diagram.

cooled to t_2 will give liquid containing x_2 mole % of B. Vaporization of this liquid at t_2 will give vapor which when cooled to t_3 will give liquid containing x_3 mole % B.

Figure 2 is a diagrammatic representation of such a multiple distillation or process. Thus, if liquid x_1 is heated to the boiling point it will give vapor of composition x_2 at temperature t_1. If vapor x_2 is now admitted into a liquid of the same composition at temperature t_2 so that the only heat exchange that can occur is between liquid and vapor, heat will be added to the liquid and a thermally equivalent amount of vapor x_3 will be formed at temperature t_2. This, on being passed into liquid of the same composition, will cause vapor at temperature t_3 to be produced. A fractionating column may be looked upon as an apparatus in which a succession of such steps occurs giving rise to a final vapor which when condensed is very rich in the most volatile component.

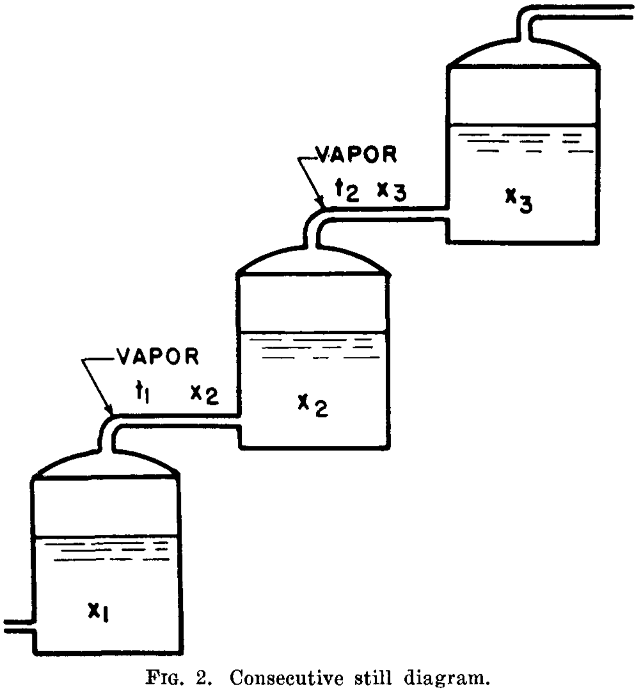

FIG. 2. Consecutive still diagram.

It follows from this that unless partial condensation occurs along the sides of the column, no fractionating column has any utility if it is not provided with a device to return reflux. On the other hand, if partial condensation along the sides of the column is relied upon, the fractionation will vary with the rate of distillation, approaching zero when the column vapors attain sufficient velocity to permit all of them to go through the column uncondensed, that is, to have the column act merely as a hot tube.

WITH this brief review of fractional distillation theory we may now consider certain individual features:

1. *Still pot*—Besides being of suitable size the still pot should possess a side arm which can be utilized in measuring pressure drop between the pot and the head of the column. The importance of constant pressure drop will be seen later.

2. *Column diameter*—In selecting the proper column diameter it must be remembered that increased diameter increases column capacity, capacity being roughly proportional to the square of the diameter as shown by the data of Podbielniak (2) (Table 1).

TABLE 1

Effect of Column Diameter on Capacity and Hold-up
[Heli-Grid Packing of Podbielniak(2)]

Packing dia. (mm.)	Max. cap. cc./hr.	Ratio cap. to dia. (2)	Hold-up *	Ratio hold-up to dia. (2)
8.0	240	3.8	4.0	0.063
11.0	360	3.0	7.2	0.059
13.0	560	3.3	11.2	0.066
22.0	1,500	3.1	30.0	0.062

* Cubic centimeter's hold-up at 50% maximum capacity for 36-inch column.

The table also shows that hold-up is likewise proportional to the square of the diameter. Hence, large diameter columns require correspondingly large samples for sharp cuts.

3. *Column insulation*—A rectifying column is most efficient when it is adiabatic throughout its length, that is, when there is no lateral heat flow either into or out of the column. According to Marshall and Sutherland (3) a lagged column is 2.4 to 41.5 times as efficient as an unlagged column operated at the same distillation rate. Insulation is ordinarily accomplished with asbestos, magnesia, an air jacket, or a vacuum jacket. However, at the relatively high temperatures necessary in methyl ester distillations all but the vacuum jacket are ordinarily supplemented with heat supplied by resistance wire or hot vapors. For example, Tongberg, Quiggle and Fenske (4) wrapped resistance wire in sections, each of which was independently controlled, in the insulation. The heat was so regulated that a thermocouple on the exterior column surface registered the same temperature as did another between the heating element and the column. Such an arrangement is satisfactory, but serious constructional difficulties

arise when, for example, an air jacket is desired instead of lagging for insulation.

The present authors favor a vacuum jacket containing metallic reflectors, now commercially available. With such equipment it was found unnecessary to add any heat to the column during distillation of material boiling up to 200° C., and the outside of the column was essentially at room temperature. Hence, there was no need for multiple thermocouples and variacs, and the consequent increased mechanical manipulations during distillation. The principal disadvantage of vacuum jackets is their relatively high cost.

4. *Column packing*—Numerous types of column packing can now be fabricated in the laboratory or purchased commercially. These vary widely in their fractionating effectiveness, some being more than 50 times as efficient as others (Table 2). Ordinarily one selects the most efficient types, i.e., those with the lowest H.E.T.P. (height equivalent to a theoretical plate), keeping in mind, however, such other important factors as corrosion-resistance, low hold-up, high through-put, and low pressure drop. Unfortunately, the most efficient packings are not easily fabricated in the laboratory and are fairly expensive to purchase, but, nevertheless, it must be remembered that the use of inefficient types necessitates the use of longer column for a given degree of fractionation, causing a higher pressure drop through the column and resultant higher temperatures in the still pot. This is undesirable because of the increased conjugation and polymerization of unsaturated fatty acids in the pot (5,6).

TABLE 2

H.E.T.P.'s of Column Packing Material

Packing	H.E.T.P. (cms.)
Heli-Grid (16)	0.5- 1.5
Stedman (13)	1.3
Multiple concentric glass tubes (18)	1.8
Spinning band (15)	2.2
Concentric tubes (17)	1.9- 5.6
Spiral screen (19)	1.7
Glass helices (7)	2.5- 6.3
Vigreux (indentations only) (15)	6.0
Widmer (spiraled glass rod) (15)	8.2
No. 16 single link iron jack chain (14)	10.7
0.25 in. Al single turn helices (14)	12.7-27.2
0.25 x 0.25 in. carbon Rashig rings (14)	11.9-15.3
Open tower (7)	64.7-74.2

5. *Pressure drop through packing*—The pressure at the bottom of a packed column is always greater than that at the top by an amount which is a function of the packing, vapor velocity, and reflux. Obviously, this pressure drop should be kept as low as possible to avoid excessive pot temperatures. For example, in a column of 26 mm. pressure drop, if the head temperature is 141° (measured pressure 1.2 mm.), the pot contents will be at 220°.

Pressure drop should be kept constant to insure a constant boil-up. In many types of columns a given reflux setting does not mean a constant reflux ratio because the boil-up varies and, for example, a constant take-off with increased liquid descending in the column gives increased reflux. For accurate and precise work, the pressure drop should be measured and maintained constant at the most favorable level.

6. *Fractionating efficiency of packing*—Columns are commonly tested to determine their so-called number of "theoretical plates"* by distilling certain brinary mixtures at atmosphere pressure and under total reflux. Not infrequently columns are used without any such determination and thus without any quantitative measurement of their efficiency. Even if plates are determined, however, investigators may be misled by assuming that the efficiency determined under conditions of total reflux obtains for, say, a reflux ratio of 20:1. Experimentally a column of 25 plates and a reflux ratio of 20:1 may be necessary to give the same fractionation as a 15-plate column under total reflux. Also, it is not always recognized that the H.E.T.P. varies with molecular weight, tending to become higher as molecular weight increases. This has been discussed in Morton's text (7) where it is suggested that, since vapor volume at the boiling point of a unit weight of substance is indirectly proportional to molecular weight and directly proportional to the absolute temperature, in the case of high molecular weight material an equal volume of vapor comes into contact with a reduced quantity of backflow. It follows that H.E.T.P.'s as ordinarily determined are minimum values for methyl ester distillations, or stated in another way, columns exhibit less than their rated number of theoretical plates when operating on high molecular weight substances.

7. *Reflux regulation*—It is obvious from theoretical considerations that reflux is essential. However, it is not uncommon to find columns being used with apparatus in which there is no provision for return of condensate as reflux, thus nullifying the possibilities in the column used. Also, reflux regulating devices are often so designed that an exact reflux ratio

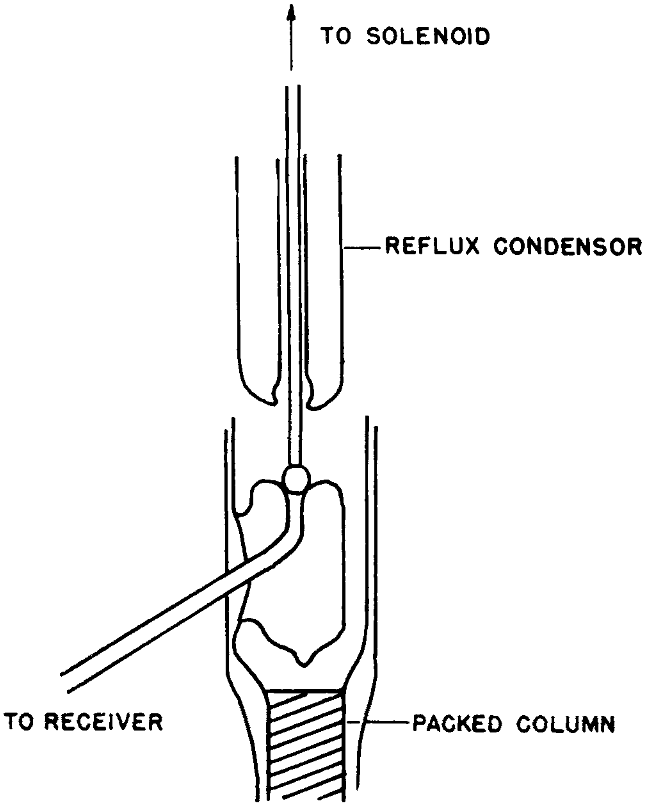

FIG. 3. Podbielniak intermittent take-off device.

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*A column section that will affect equilibrium between vapor and liquid is called a theoretical plate.

cannot be determined or maintained. For precise results one should maintain a constant rate of distillation and a controllable reflux setting; then a desired reflux ratio can be employed at any time. Of the many reflux regulating devices described in the literature one of the best is an intermittent take-off controlled by an electric timing device, as shown in Figure 3.

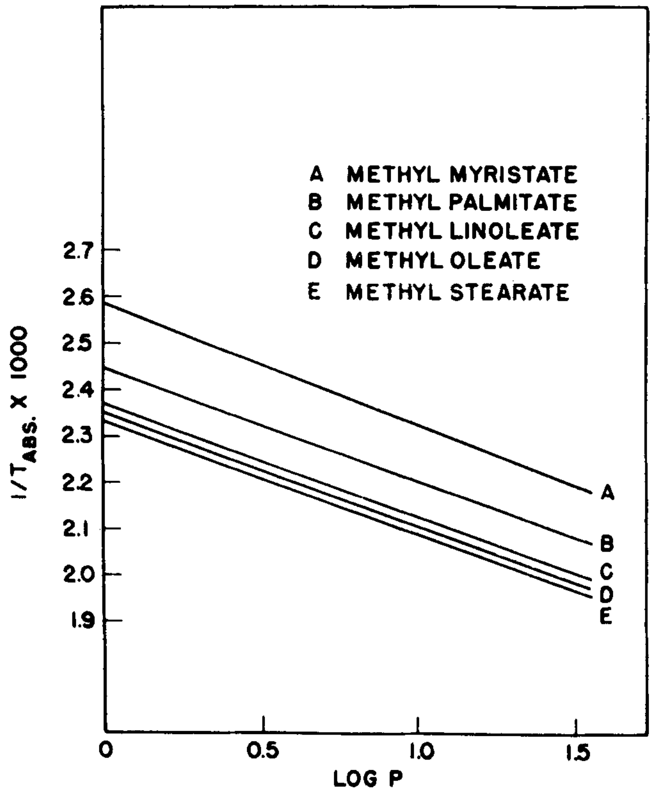

FIG. 4. Pressure-boiling point relationships of methyl esters of fatty acids. A, methyl myristate; B, methyl palmitate; C, methyl linoleate; D, methyl oleate; E, methyl stearate.

8. *Operating pressure — range and constancy*—There is no advantage in distilling at very low pressures when packed columns are used since the pressure drop in the column ordinarily takes the boiling points out of the range where they decrease appreciably when pressure is further reduced. For example, methyl palmitate may be distilled at a head temperature of 136° at 1 mm. or 149° at 2 mm., but the pot temperature will vary less than 1° if a 26-mm. pressure drop is used. In such a column an increase in pressure from 1.2 to 10.0 mm. at the head will increase the pot temperature only 7°. On the other hand, it is unwise to work at very low head pressures since small pressure variations will have a large effect on the boiling point of the material distilled. Thus, in a methyl palmitate distillation a decrease in head pressure from 1.0 to 0.5 mm. will lower the boiling point about 12.5°, whereas, a 0.5 mm. pressure decrease at the 10 mm. level will lower the boiling point only about 1°. Since distillation "cuts" are ordinarily made on the basis of temperature changes, it is obvious that pressure variations must be reduced to the limit and an operating pressure selected so that any unavoidable pressure changes will not seriously affect the boiling point of the distillate.

9. *Measurement of distillation pressure*—It is now widely recognized that boiling points of low vapor pressure substances have frequently been reported erroneously because of incorrect pressure measurement. Probably most of the old literature values for boiling points below 10 mm. are in error for this reason. An extreme case is the following. A sample of methyl linoleate was found to boil at 170° in a Claisen flask or at 140° in an alembic flask (where pressure drop was avoided) although the pressure at the vacuum pump was less than 1 mm. in both cases.

In order to obtain reliable boiling point data for fatty acid esters the present authors measured the true boiling points for methyl myristate, palmitate, stearate, oleate, and linoleate under pressures of 1 to 20 mm.* The determinations were carried out in a specially constructed flask similar to that used by Ralston *et al.* (8) for determining the boiling points of fatty acids. A constant pressure device including a sulfuric acid manostat was substituted for the surge tank system used by Ralston *et al.* Maximum variations from the desired pressure were ±0.1 mm. The results obtained are shown in Table 3. Purity of the esters was established by standard methods, and all temperatures were corrected.

In Figure 4 the reciprocals of the boiling points (in absolute degrees) are plotted against the logs of the pressures. The straight line plots obtained are indicative of correct pressure measurements since

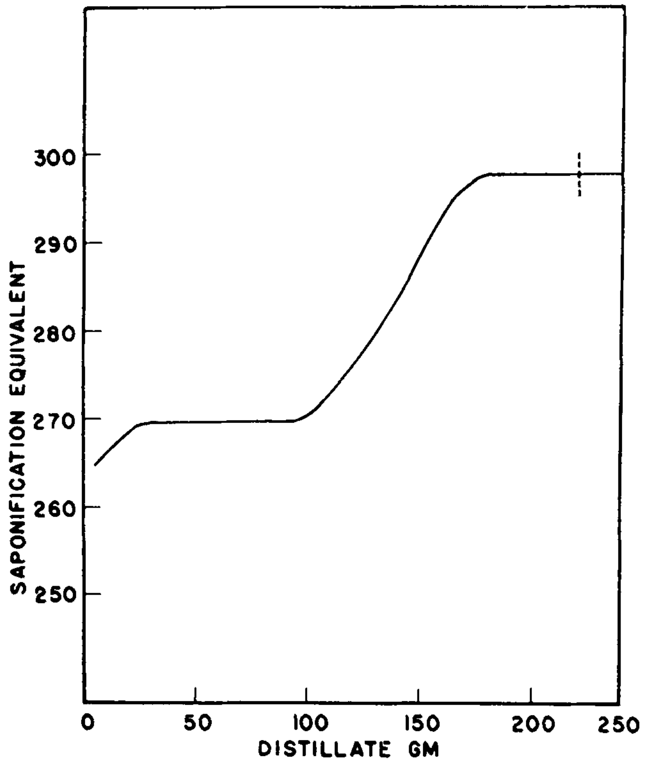

FIG. 5. Fractional distillation of methyl esters of U.S.P. stearic acid using a Whitmore column.

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* Since this paper was written Althouse and Triebold [Ind. Eng. Chem. (Anal. Ed.) *16*, 605 (1944)] have reported boiling point data on fatty acid methyl esters, and in many cases their data are in serious disagreement with those reported here. However, several obvious inaccuracies appear in Althouse and Triebold's work. For example, methyl linoleate is reported to boil higher than methyl oleate which in turn is reported to boil higher than methyl stearate. This is contrary to practical distillation experience. Thus, we have obtained 95% methyl oleate in the first fractions from the distillation of a methyl oleate-methyl stearate mixture, and we have also obtained some concentration of methyl linoleate in the first fractions from the distillation of a methyl linoleate-methyl oleate mixture.

TABLE 3

Effect of Pressure on Boiling Points of Fatty Acid Methyl Esters

Ester	Pressure in millimeters of mercury				
	1	2	5	10	20
Methyl myristate	114	125	143.5	157.5	172.5
Methyl palmitate	136	149	166.5	180.5	196.5
Methyl stearate	155.5	170	189.5	204.5	222
Methyl oleate	152.5	166.5	186	201	218.5
Methyl linoleate	149.5	163	182.5	198	215

breaks in the slope of the curves are found only where pressure drop occurs as has been shown by Hickman (cited by Morton).

From these boiling point data it is also possible to calculate the latent heats of vaporization of the methyl esters by means of the Clausius-Clapeyron equation. In the 1-20 mm. pressure range, the molal heats of vaporization are shown in Table 4.

TABLE 4

Heats of Vaporization (Calories per Mole)*

Methyl myristate	17,550	Myristic acid	20,800
Methyl palmitate	18,900	Palmitic acid	22,100
Methyl stearate	19,000	Stearic acid	22,800
Methyl oleate	18,900		
Methyl linoleate	18,750		

* Values for the free fatty acids were calculated from the data of Pool and Ralston (9).

Having considered in some detail the general aspects of fractional distillation it is of interest to compare two columns representing older and newer ideas in column design. Figure 5 shows a typical fractionation obtained with the so-called Penn. State column [Whitmore and Lux (10)] using a reflux ratio of about 12 to 1. From 250 grams of methyl esters prepared from U.S.P. stearic acid there were obtained approximately 75 g. (30.0%) C_{16} methyl esters, 60 g. (24.0%) C_{18} methyl esters, and 80 g. (32.0%) of a mixture of C_{16} and C_{18} esters. This column tested at about 8 theoretical plates with the CCl_4-benzene test mixture.

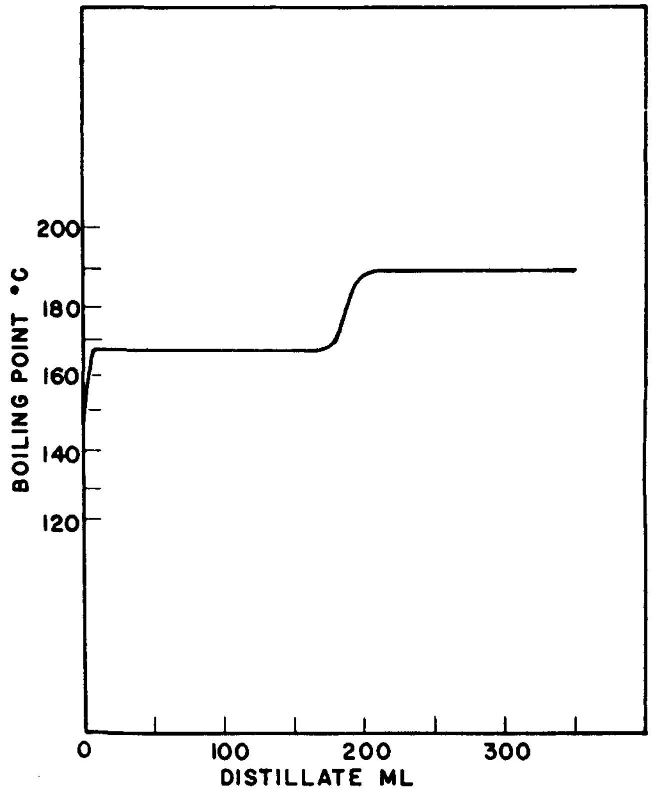

Fig. 6. Fractional distillation of methyl esters of U.S.P. stearic acid using a Podbielniak column.

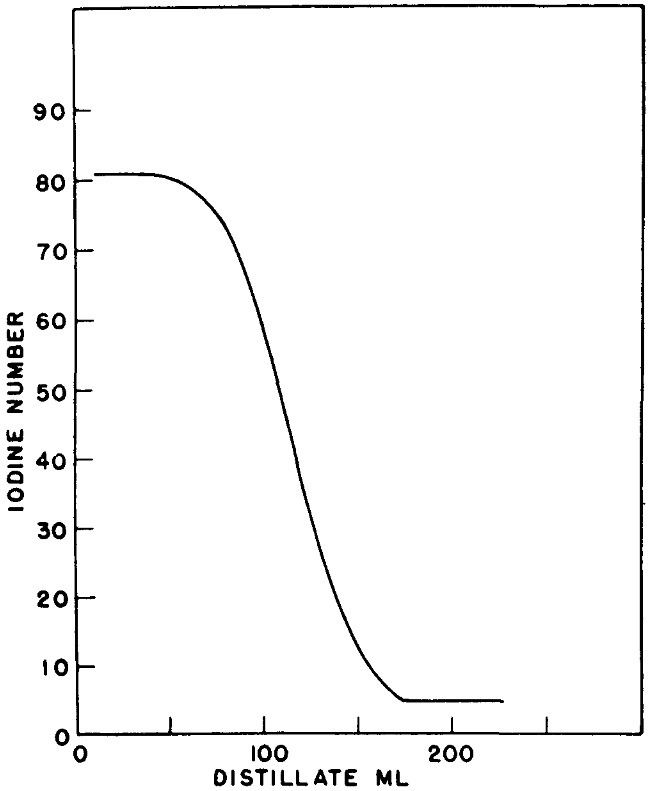

Fig. 7. Fractional distillation of a methyl oleate-methyl stearate mixture.

Figure 6 shows the separation possible when the same material is distilled in a Podbielniak column at a reflux ratio of about 6:1. In this case there were obtained 48.2% C_{16} methyl esters, 42.8% C_{18} esters, and 5.7% mixture of C_{16} and C_{18} esters, which is a considerable improvement over the Whitmore type column. It should be noted that in a continuous system such a column would make it possible to obtain 100% methyl palmitate in one pass, using the same reflux ratio. The column used in these experiments tested at 55 theoretical plates using a n-heptane-methylcyclohexane test mixture.

When an equal mixture of methyl stearate and methyl oleate (Figure 7) was distilled through the Podbielniak column using a reflux ratio of about 11:1, the first fractions contained about 95% methyl oleate. Thus, it is seen that in a continuous distillation, despite the boiling point difference of only about 3°, 95% methyl oleate could be obtained in one pass. The higher boiling point of C_{18} saturated methyl esters has been pointed out previously by Longenecker (11), Klem (12), and by Weitkamp and Brunstrum (13), who were able to obtain 77% methyl oleate by distillation of a 50-50 mixture of oleate and stearate through a Stedman column.

When an equal mixture of methyl oleate-linoleate was distilled (Figure 8) no appreciable fractionation was obtained, despite the fact that the boiling point difference in this case is again 3°. Evidently, methyl oleate and linoleate associate extensively. Thus, it is unlikely that unsaturated acid esters of the same

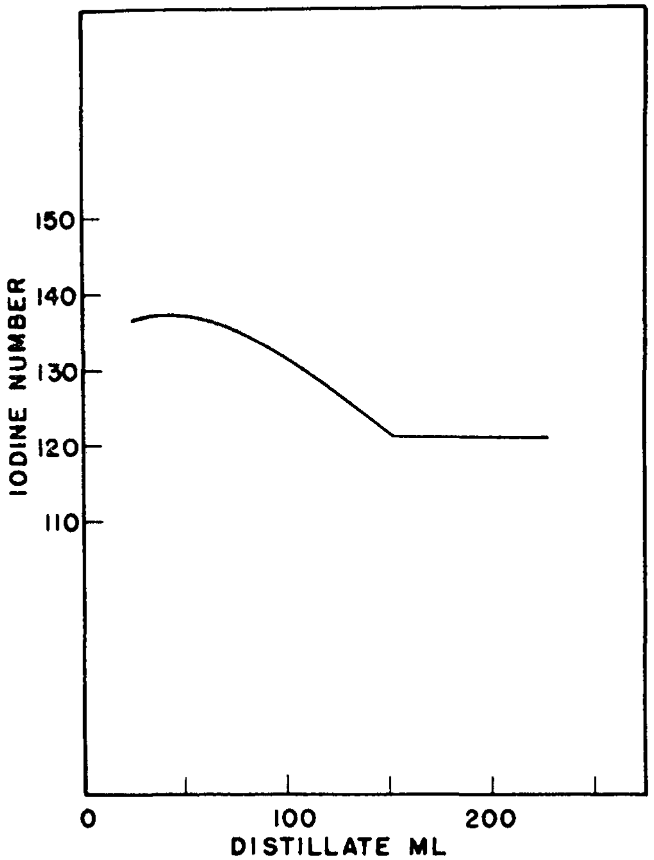

FIG. 8. Fractional distillation of a methyl linoleate-methyl oleate mixture.

chain length will ever be fractionated by a straight distillation. However, as commercial columns are improved we may look forward to unvarying chain length in commercial fatty acids wherever this is desired.

Summary

Important factors in the construction and operation of laboratory fractionating columns are discussed. These include column diameter and insulation, packing, pressure drop, effect of reflux and molecular weight on fractionating efficiency, reflux regulation, choice of operating pressure, constant pressure maintenance, and accurate measurement of pressure. Accurate boiling points in the 1-20 mm. range are reported for the first time for methyl esters of myristic, palmitic, stearic, oleic, and linoleic acids. Heats of vaporization are given.

Two types of columns, representing two stages of development in column design, are compared with respect to fractionating efficiency, and experimental results are given for the distillation of 50-50 mixtures of palmitic and stearic, stearic and oleic, and oleic and linoleic methyl esters through a Podbielniak column.

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The Fatty Oil Industry in Canada[1]

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THE function of the Oils and Fats Administration in Canada is to organize, control, and be responsible for supply, distribution, and price control of all fatty oils and products manufactured therefrom including soaps, detergents, protective coatings, fatty food products, and a variety of finished goods and materials too numerous to mention. It is, therefore, analogous to a combination of the functions of the sections of the WFA, OPA, and the WPB dealing with fats and their products.

Before I attempt to deal in detail with my subject, I should remind this audience that in order intelligently to convert the Canadian statistics to the like United States position, you must multiply our returns by 12 in order to arrive at a comparable figure.

When it is considered that Canada is the fourth largest producer of war supplies and equipment among the United Nations and that the energies of half of the working population are absorbed by the war effort, the implications of the tremendous change which has taken place in the Canadian economy due to the impact of war can be better appreciated. This gathering will understand that this enormous industrialization program must inevitably be paralleled by an increase in fatty oil consumption both in industry and in the dietary. Industrial demands of fats for non-food purposes are estimated to have increased at least 60% above the pre-war level (1935-1939) and while the dietary requirements are strictly controlled, there is a constant pressure induced by increased purchasing power, longer working hours, and greater employment.

Under normal circumstances Canada imported over 50% of her oils and fats requirements, exclusive of butter. This is a considerable import requirement, and in a global conflict it is a serious threat to a balanced economy and to the war effort. Unlike our enemies, Canada and the United States were not pre-

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[1] This paper was presented at the fall meeting in Chicago, October 25-27, 1944.