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The Amplified Distillation of Methyl Esters of Fatty Acids*

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Introduction

ACCORDING to the theory of distillation the components of a volatile mixture may be separated from each other in any desired approach to purity. It is only necessary to provide sufficient theoretical plates.

In the application of fractional distillation to analytical work certain practical limitations must be considered. If a large number of theoretical plates is required for a given separation, it follows that a correspondingly large amount of a given component must be present before any is available for separation at the desired purity. The reason for this is that as a cut point is approached and passed, there is a gradual change in the composition of the distillate from lower boiling component to higher boiling component. The amount of this inseparable mixture is a function of the column hold-up per theoretical plate.

Amplified distillation is a technique by which the interjacent mixtures inevitably encountered in ordinary fractional distillation may be eliminated in certain specific instances. This permits a more nearly complete separation of the components in the desired purity and is especially useful in case certain components occur in small proportions or in case the sample is of limited availability. Amplified distillation does not alter the efficiency of a given still but merely allows the full efficiency of the still to be developed with respect to the separation of each component, regardless of the amount or proportion present in a given mixture.

In amplified distillation an additional component is introduced. This component is so selected that it distills between the components of the mixture and is easily distinguishable and separable from them. For the amplified distillation of methyl esters a hydrocarbon mixture of petroleum origin meets these requirements and has the added advantages of a smooth true boiling point curve and ready availability. It is only necessary to select a commercial product having the appropriate distillation range.

Amplified distillation should not be confused with azeotropic distillation in which the desired effect of the added component is to alter the partial vapor pressures of the components of the mixture differently. Azeotropic distillation is usually employed for the separation of dissimilar substances having similar boiling points. Amplified distillation is useful in the separation of similar substances such as adjacent members of homologous series or structural isomers.

The idea of amplified distillation is not new. Bratton, Felsing, and Barley (1) used kerosene to enhance the separation of certain petroleum bases. In this case, in addition to the advantage of dilution, the spread between the boiling points of the bases was increased fortuitously due to azeotrope formation. Later Axe and Bratton (2) extended the method to the separation of binary mixtures of homologous fatty acids such as propionic and butyric. They reported a maximum recovery of pure acid in only 73% yield, due to limited efficiency of their distillation equipment. In this case the formation of azeotropes with the hydrocarbon diluent probably hindered the separation.

Apparatus and Materials

The laboratory vacuum distillation apparatus used in this investigation was identical with that described in an earlier paper (3) except for the substitution of a more efficient, spiral-conical-pattern, wire gauze packing (4). The packed section was 44 inches in length by one inch inside diameter. The overall efficiency was approximately 100 theoretical plates. Distillations were carried out at a head pressure of 2 mm.

Two commercially available mineral oils were used as diluents: Eureka White Oil (55 Seconds Saybolt Universal Viscosity at 100° F.) and Mineral Seal Oil (42 Seconds Saybolt Universal Viscosity at 100° F.).

Amplified distillations were carried out on palmitic acid, "double distilled cottonseed fatty acid" and the methyl esters of the cottonseed fatty acids. Palmitic acid was obtained by hydrolysis of a heart cut of methyl palmitate and was recrystallized to a constant melting point of 62.6° C. The "double distilled cottonseed fatty acid" was a commercial material. The methyl esters were prepared by refluxing the acid with anhydrous methanol saturated with hydrogen

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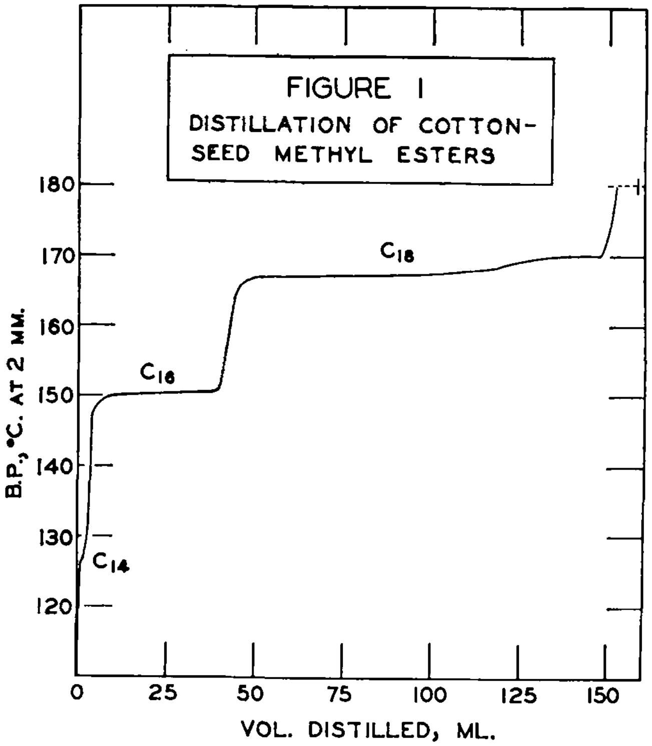
FIGURE I
DISTILLATION OF COTTONSEED METHYL ESTERS

chloride. Composition of the cottonseed acids as determined by amplified distillation of the methyl esters was as follows:

Acid	Mol. %
C_{12}	0.9
C_{14}	1.4
C_{16}	25.9
C_{18}	69.1
C_{20}	0.5
Miscellaneous	2.2

A typical distillation curve for the cottonseed esters is shown in Figure 1. The C_{14}–C_{16} and C_{16}–C_{18} interjacent mixtures each amounted to 5-6 ml. or about 3-4% of the charge. Consequently, the C_{12}, C_{14}, C_{20} and miscellaneous esters could not be estimated accurately or in some cases even detected by ordinary fractional distillation.

Amplified Distillation of Fatty Acids

Fatty acids form azeotropes with hydrocarbons. This may be attributed to the polar carboxyl group. When a given fatty acid is distilled with an appropriate mineral oil, a characteristic azeotropic elimination curve is obtained. Such a curve, shown in Figure 2, represents the distillation of four grams of palmitic acid with 150 grams of Eureka White Oil. Five ml. (4 gram) fractions were taken and the acid contents, determined by titration with standard alkali, were plotted as ordinates to give the elimination curve. It will be noted that the acid began to be distilled about 35° C. below its normal boiling point of 179° C. at 2 mm. pressure (5) and was completely eliminated about 7° C. below the boiling point. The distillation temperature rose sharply as soon as the acid was depleted showing that the acid-oil mixture formed a minimum boiling azeotrope. The shape of the elimination curve is suggestive of a logarithmic function and if the logarithum of the concentration of fatty acid in the distillate is plotted against the distillation temperature, a straight line (within the limits of experimental error) is obtained. A point corresponding to 100% concentration will be on this line at the normal boiling point of the acid. A family of such curves, one for each homologue is useful for the identification of fatty acids in the presence of other fatty acids but not for quantitative analysis since adjacent curves overlap.

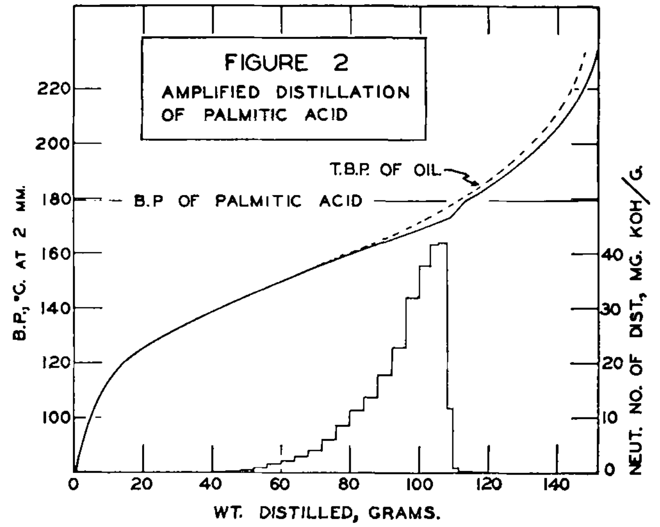
FIGURE 2
AMPLIFIED DISTILLATION OF PALMITIC ACID

The amplified distillation of 10 grams of cottonseed fatty acid with 140 grams of Eureka White Oil is shown in Figure 3. It will be noted that the elimination curve for the C_{16} acid overlaps the curve for the C_{18} acid and the curve for the C_{20} acid is completely obscured. Thus a limitation on the usefulness of amplified distillation for qualitative analysis of fatty acid mixtures is that minor components will be detected only if they are lower boiling than the major components.

The Amplified Distillation of Fatty Acid Esters

In Figure 4 is shown the amplified distillation of 10 grams of methyl esters of cottonseed fatty acids with 140 grams of Eureka White Oil. The methyl

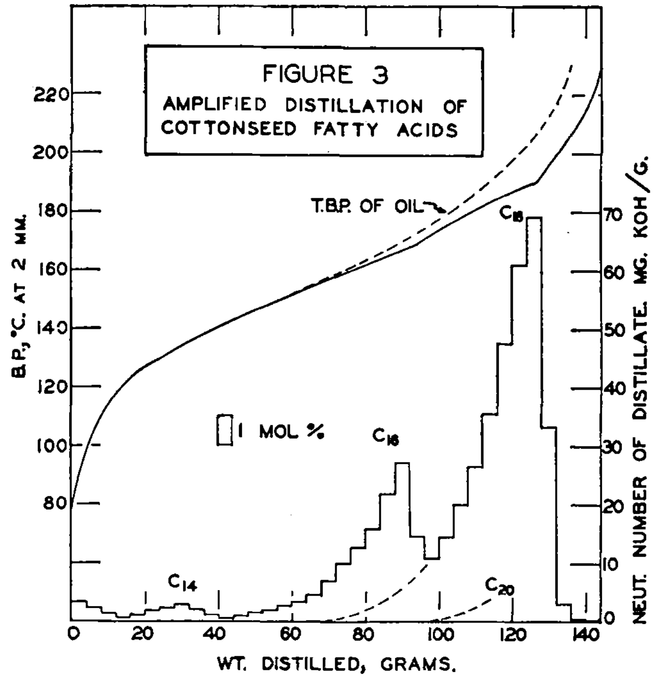
FIGURE 3
AMPLIFIED DISTILLATION OF COTTONSEED FATTY ACIDS

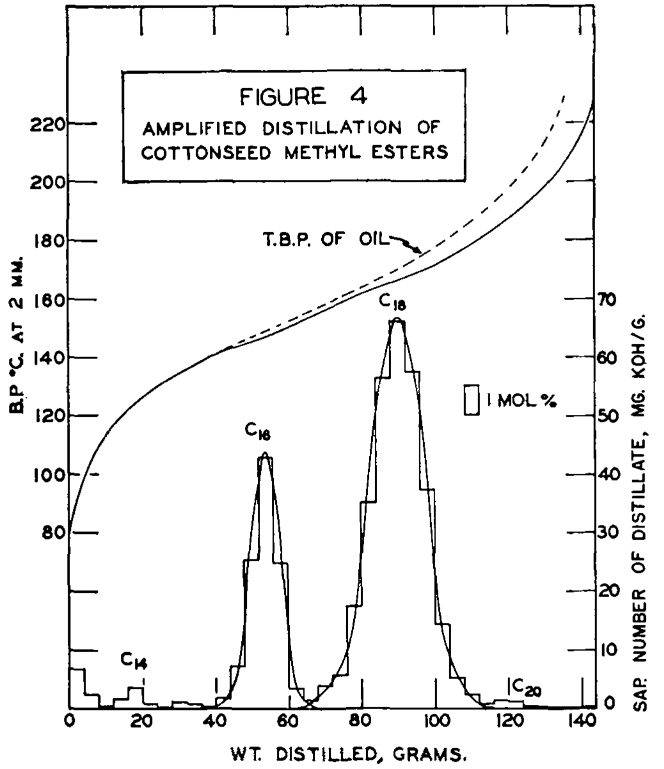

FIGURE 4
AMPLIFIED DISTILLATION OF COTTONSEED METHYL ESTERS

esters of fatty acids are relatively non-polar and exhibit little if any tendency to form azeotropes with mineral oil. Unlike the fatty acids, the esters distill at their normal boiling points in the presence of the mineral oil diluent, i.e. the peak of the elimination curve coincides with the normal boiling point of the ester. The shape of the elimination curve is suggestive of Maxwell's distribution curve and the data approximate the probability equation very well. Theoretical curves calculated from the probability equation

$$y = be^{-\left(\frac{x}{a}\right)^2}$$

are shown superimposed on the C_{16} and C_{18} elimination curves. In the above equation the constant *b* is the maximum height of the curve. It is related to the constant *a* and the area under the curve by the equation:

$$\text{Area} = ab\sqrt{\pi}.$$

The base of Maxwell's distribution curve extends indefinitely in both directions. Similarly the bases of the elimination curves extend indefinitely and necessarily overlap. It has been estimated that the elimination curves for the C_{16} and C_{18} esters in Figure 4 overlap less than 1% so that acids of better than 99% purity could be recovered from these fractions.

In the routine application of the method of amplified distillation to fatty acid esters a single fraction is taken for each ester. Cut points are midway between the boiling points of adjacent esters. The acid equivalent of each fraction is determined by saponification with standard alkali. The free acid may be recovered by the usual procedures and subjected to the tests for iodine absorption, ultraviolet absorption and so on. Excellent analyses can be obtained on samples as small as a fraction of a gram.

In order to illustrate the application of amplified distillation to the detection of minor components a "light end" cut from 400 grams of "double distilled cottonseed fatty acids" esters was distilled with 140 grams of Mineral Seal Oil (42 Seconds Saybolt Universal Viscosity at 100° F.). The curves are shown in Figure 5. For best results an oil with a somewhat lower distillation range should have been used. The two largest peaks in the elimination curve are due to C_{12} (0.9 mol. %) and C_{14} (1.4 mol. %) esters. The peak between C_{12} and C_{14} is due to the dimethyl ester of sebacic acid (0.15 mol. %). After two recrystallizations from distilled water the free acid melted at 133° C. cor. and was identical with authentic sebacic acid. The small peak between C_{14} and C_{16} is probably due to the homologous C_{12} dibasic acid. The unresolved portion distilling below C_{12} may contain lower homologues of both the monobasic and dibasic series. No claim is made that dibasic acids are original constituents of cottonseed oil since the origin of the sample does not preclude the possibility of contamination.

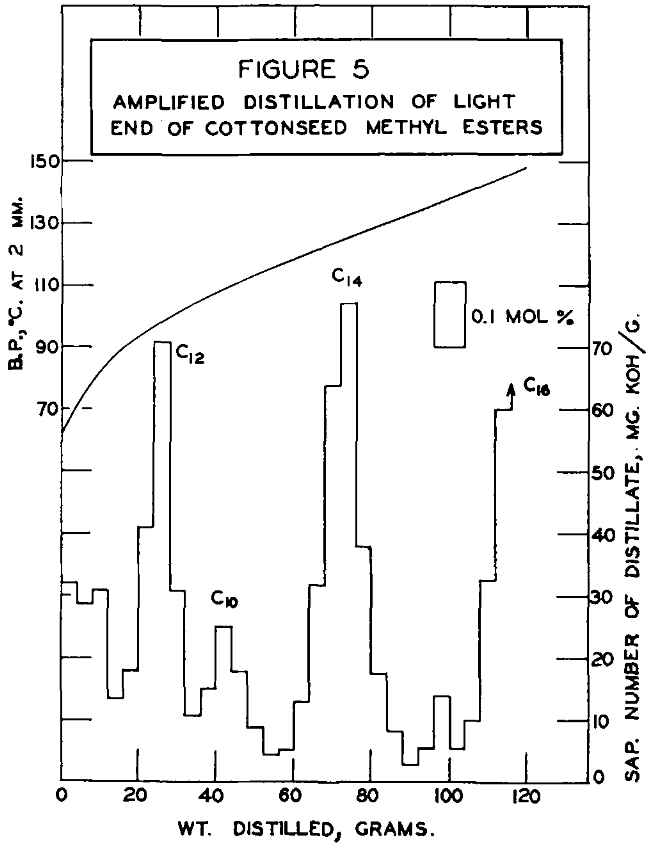

FIGURE 5
AMPLIFIED DISTILLATION OF LIGHT END OF COTTONSEED METHYL ESTERS

Summary

Amplified distillation is a useful technique for the quantitative analysis of mixtures of fatty acid esters, especially for the detection and estimation of minor components and for the analysis of small samples. The amplified distillation of free fatty acids is largely limited to qualitative work on account of the formation of azeotropes with mineral oils.

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