Solubilities of Cottonseed Oil and the Phase Distribution of Fatty Acids in Methyl Alcohol at Elevated Temperature and Pressure[1]

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Abstract

A study was made to determine whether methyl alcohol could be used for the selective extraction of fatty acids from crude cottonseed oil under high temperature and high pressure conditions. Equilibrium data and phase relationships were obtained at several temperatures, and corresponding triangular phase diagrams were prepared. From these, it was concluded that the proposed process would not be commercially attractive inasmuch as excessive amounts of solvent would be needed.

Introduction

THE USE OF SOLVENTS for extracting and refining vegetable oils has been studied for years. Although solvent extraction is now well established in the cottonseed industry, solvent refining has met with little success. This is most likely due to the fact that present alkali refining techniques are highly perfected and also that the removal of color bodies from the oil during caustic soda refining is far superior to any other procedures which have been developed.

A selective solvent extraction should have several advantages. Since there is no chemical reaction, there would be no saponification of neutral oil and the refining losses would be lower. Purer products would be obtained by this process and valuable constituents such as tocopherols, sterols, phosphatides, and fatty acids could be isolated.

A number of solvents have been investigated and their solvent properties for cottonseed oil and its constituents recorded. Furfural (1) and propane (2) have each found commercial use, limited, however, to processes designed for the separation of saturated and unsaturated components. Harris (3) and coworkers developed a method for treatment of cottonseed oil-isopropyl alcohol miscella by liquid-liquid extraction with hexane to separate a fatty acid fraction. Holbrook (4) studied the effect on caustic refining loss of pre-refining by means of liquid-liquid extraction. Of the solvents tested, methanol gave better reduction of caustic refining loss than acetone or isopropyl alcohol, reducing the loss from 11.2 to 5.0%. Ayers (5) proposed the use of a caustic soda-methanol solution, and a German patent (961,380) covers the use of caustic dissolved in isopropyl alcohol as a refining agent.

A number of factors must be considered in the search for a solvent or solvent combination for separation of impurities from vegetable oils. Some of these are: selectivity and adequate solubility for the substances to be extracted, little or no miscibility with the oil, stability against chemical reaction or decomposition, low viscosity, sufficient interfacial tension to avoid emulsions, and proper boiling point to permit solvent recovery by distillation. Certain other factors are desirable, such as: low fire and explosion hazard, low toxicity, low latent heat or vaporization, and noncorrosiveness.

Methanol meets many of the above criteria. Holbrook's (4) study showed that methanol dissolved fatty acids much more readily than the glyceride portions of the oil (i.e., it was a highly selective solvent). This very desirable quality was offset by the fact that the fatty acids were still only slightly soluble. In practice this meant that large quantities of solvent would be needed. The large ratio of solvent to fatty acid would make recovery of the solvent expensive.

The solubilities of both fatty acids and glycerides in methanol were found by Patel (6) to increase with an increase in temperature. The maximum temperature studied was limited by the low boiling point of methanol. It is obvious that higher temperatures could be employed with a pressurized system.

It was felt that high temperature operation might lessen the two major difficulties previously mentioned. The solubility would be increased and perhaps less solvent would be needed. Separation of much of the solvent might be possible by cooling the extract. Energy requirements would then be low as no phase change would be involved. This article concerns the investigation of such a high temperature-high pressure methanol extraction process.

Phase diagrams were prepared for the refined cottonseed oil-oleic acid-98% methanol system at several fixed temperatures. The phase boundaries were determined by sealing known compositions in glass tubes and gradually cooling them in an oil bath from above their critical solution temperature. When the critical solution temperature was reached (change from one-phase to two-phase system) a readily observed turbidity would develop. The 98% methanol was used as a solvent instead of anhydrous alcohol because the results were not reproducible when anhydrous alcohol was used. This was due to an alcoholysis reaction favored by the elevated temperature. The addition of 2% water served to inhibit this reaction.

The results are given as a triangular phase diagram in Figure 1.

A laboratory device was fabricated in order to measure the equilibrium composition of the conjugate phases. Essentially it consisted of an electrically heated, well insulated, high pressure vessel equipped with sampling taps and a stirring mechanism. When conditions had reached equilibrium, small samples were withdrawn from each layer for analysis. Care was taken that no vaporization losses occurred.

The equilibrium data are presented as a selectivity diagram, Figure 2, and as an equilibrium diagram, Figure 3. Figure 2 shows that 98% methanol remains a highly selective solvent at elevated temperatures. Figure 3 shows that the equilibrium distribution ratio

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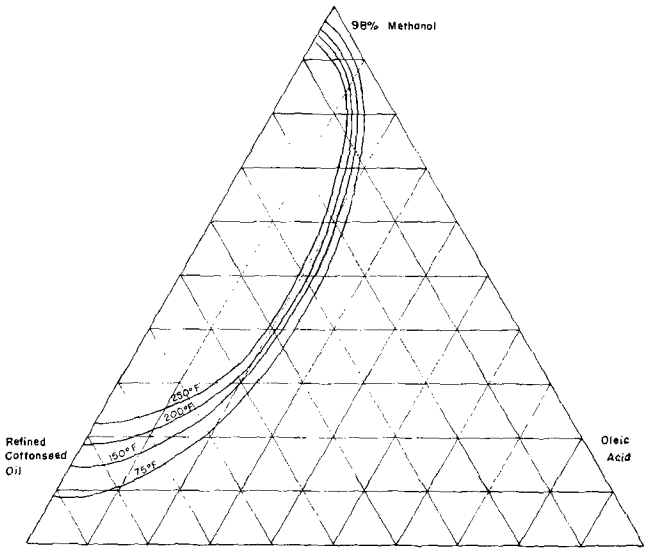

FIG. 1. Phase diagram for an oleic acid, cottonseed oil, 98% methanol system.

remains low, changing from 0.75 at 86F to 1.0 at 260F.

When the above information was available, it became apparent that the proposed process was not commercially attractive. Although the selectivity was excellent, the distribution ratio never exceeded 1.0. Systems where this ratio is 1.0 or less usually require excessive amounts of solvent. This is definitely true for the methanol system studied.

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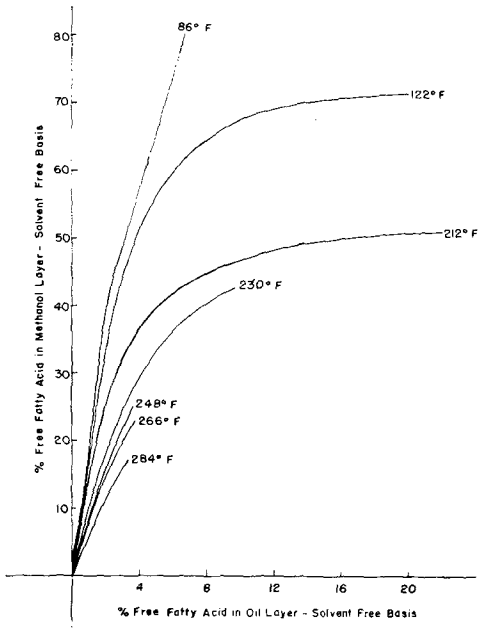

FIG. 2. Selectivity diagram for extraction of fatty acids in cottonseed oil using 98% methanol.

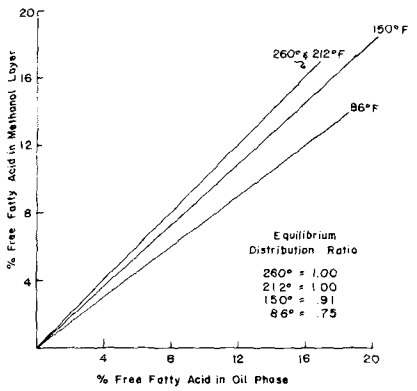

FIG. 3. Equilibrium distribution of fatty acids in 98% methanol-fatty acid-cottonseed oil system.

The Influence of Temperature, Heating Time, and Aeration upon the Nutritive Value of Fats

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Abstract

In order to determine the biological significance of the changes which occur when fats are heated to high temperatures in air, cottonseed oils were heated and aerated under several controlled conditions. In general, the data indicate that the changes induced are proportional to the severity of the conditions and that treatments more severe than those usually encountered in processing or cooking are necessary to produce detectable damage.

Oils which had been subjected to prolonged aeration at 60C (16 days or more) or exposed to air in thin layers maintained at 180–220C supplied less available energy and caused development of larger livers than untreated samples when compared in rat feeding tests. Heating in deep layers caused less damage than heating to the same temperatures in thin films, indicating that exposure to oxygen accelerates nutritional impairment.

The cooking of food in fats changes condition so greatly that direct extrapolation of data obtained in tests using fat alone is not justified. Fat extracted from foods has not been found to contain harmful substances by the tests used.

Introduction

NUMEROUS INVESTIGATORS have indicated that excessive laboratory heating and/or oxidation impairs the nutritive value of fats and may result in the formation of substances which give adverse physiological reactions when fed (1–14). While this type of research is of utmost importance in demonstrating the tendencies of fats to undergo changes under various conditions, most of it has not been designed to