

Segregation of Fish Oils with Liquid Propane and Butane

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FISH OIL REFINING has been studied for a long time because of the characteristics of the raw material which limit its utilization. The oil consists of a complex mixture of triglycerides with a variety of saturated and unsaturated compounds. The high iodine value (170–200) suggests the possibility of obtaining an appropriate drying oil that could compete with those of vegetable origin. Compared with the latter, fish oils contain higher percentages of saturated (25–35%) and monounsaturated (23–30%) fatty acids. It is thus important to eliminate all or part of these components which will not allow an appropriate drying of the coating. In addition, fatty acids are present with more than 22 carbons and up to six double bonds which oxidize easily, impairing the odor and color of the product.

Fractional crystallization, remodelling, and extraction with solvents can be used for modifying the oil composition. Solvent extraction is widely applied in the petroleum industry for segregating and purifying lubricants. Among the solvents used for selective fractionation are liquid hydrocarbons, furfural, and methyl ethyl ketone.

With liquid propane, the solubility of triglycerides decreases with temperature. A lower critical solubility temperature (CST) exists, above which there are two phases in equilibrium. The solubility of the components is determined by the degree of unsaturation and chain length. Hixson and others (1,2) have studied the solubility of pure triglycerides and fatty acids in liquid propane by using vegetable oils. They determined CST for different components and studied the separation of such systems as propane-abietic acid-sunflower oil. Commercial separation of fish oils with liquid propane has been applied in South Africa to obtain Vitamin A concentrates (3).

This study reports on the possibility of using liquid propane near its critical temperature for separating fish oils in two fractions of different iodine value.

Fractionation studies were performed in a Magne-

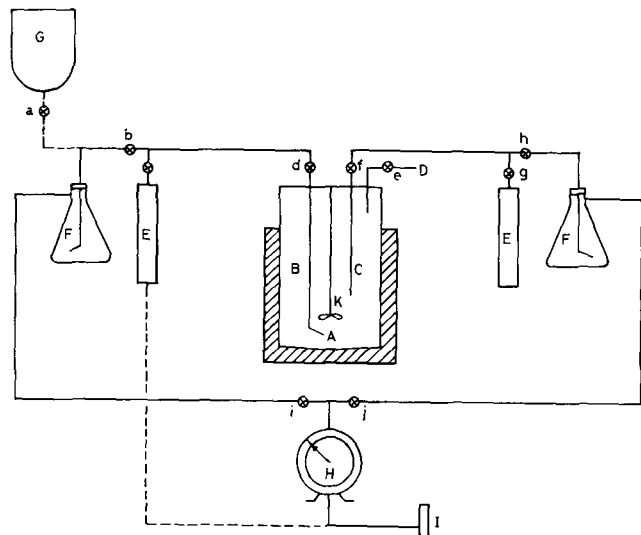


FIG. 1. Equipment layout: A, autoclave; B, sampling line, lower phase; C, sampling line, upper phase; D, drain; E, sampling tubes; F, traps; G, LPG bottle; H, gas meter; I, burner.

TABLE I
Characteristics of Raw Material

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Anchovy oil			
Acid number	0.4	Iodine value	186
Saponification number	188.8	Color (Hellige)	11
Fatty Acid Composition, %, in Order of Elution			
Lauric	Traces	Stearic	5.4
Myristic	5.5	Oleic	23.1
Myristoleic	Traces	Linoleic	4.4
Pentadecylic	0.5	Unknown B	4.2
Palmitic	21.4	Unknown C	3.0
Palmitoleic	11.5	Unknown D	19.0
Unknown A	2.1		
Propane			
Propane	92.6%		
Butane, isobutane			
pentane	4.6		
Odorizer	2.8		
Butane			
Butane	90.8		
Propane, isobutane			
pentane	9.2		

dash high-pressure autoclave, provided with agitation and temperature control (Fig. 1). The oil and the hydrocarbon were charged and maintained at a fixed temperature until equilibrium in fatty acid composition was attained, as indicated by repeated sampling of the two phases. Sample separators of 150 cm³ capacity, manufactured from 1-in. steel tubing, were used as collectors. The gas released by the samples was measured with a wet meter calibrated to 0.03 liter. The residual oil was then heated under vacuum to eliminate the last traces of solvent. Iodine values were determined by the Wijs method. Table I indicates the characteristics of the raw material which was employed.

Separations performed at 65.6, 77.1, and 94.6C are indicated in Fig. 2 for liquid propane. The equilibrium curves were left open because otherwise it would have meant extracting an oil fraction obtained from the upper phase (with an iodine value lower than that of the original oil). This procedure is not recommended (4) because it has been found that the equilibrium composition of the phases varies with the degree of extraction, depending particularly on the carbon chain-length and saturation of the fatty acids which are present in the oil.

Extraction efficiency is sometimes measured in terms of the separation range, defined as the difference in iodine values of both phases. Table II indicates the results which are obtained in this work.

It can be observed that, for different curves, the range decreases with temperature and that, for the same curve, it decreases with decreased solvent-to-oil ratios.

No segregation was observed when using liquid butane. Two phases were formed, but the oils which were dissolved presented iodine value variations within the experimental error of the analytical method.

TABLE II
Extraction Range (Iodine Value Units)

Temperature, °C	Higher than starting material	Lower than starting material
94.6	15.0	9.0
77.1	12.0	9.5
65.6	10.0	5.0

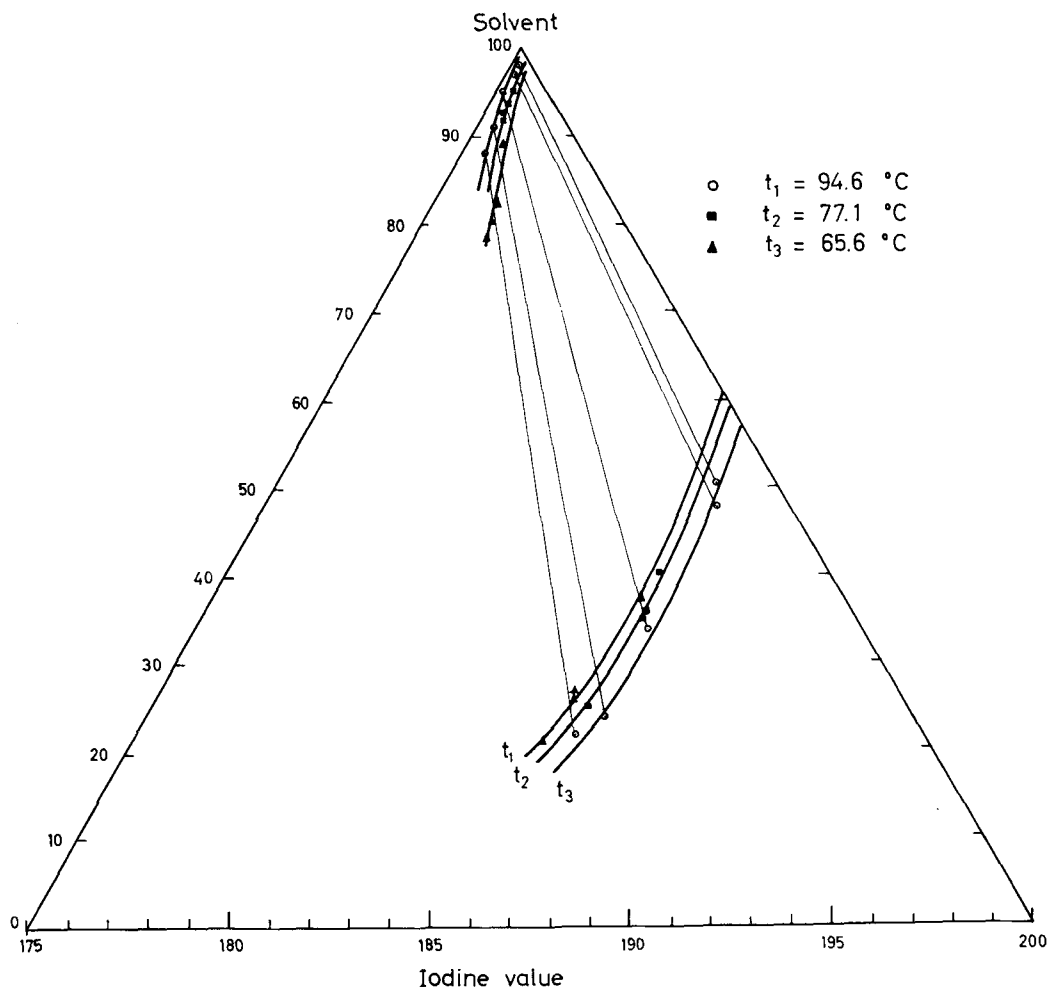


FIG. 2. Triangular extraction diagram.

The decrease of the extraction range with temperature can be explained on the basis of the decrease of triglycerides solubility with temperature. Thus, if the temperature is increased to near the critical temperature of propane (96.8C), only the low molecular weight low iodine value components will stay in solution. It can also be observed that the extraction range is rather small, with steep slopes for the tie lines. This indicates the need of a large number of stages for performing the separation.

The abnormal behavior of butane can be explained by using the results of Hixson (2) relative to the variation of CST with the molecular weight of the triglycerides. With propane it was found that, for each 100-g increase in molecular weight, CST decreased by about 8.3C. There must exist at least a 5C difference in CST in order to effectively separate the two triglyceride phases. Lack of separation attained

with butane could be caused by a low variation in CST; two separate phases could be formed but of similar composition and iodine value.

Mention must also be made of the fact that liquid propane contained methyl mercaptan as an odorizer. The polarity of this solute may have produced a change in the solubility of the different fatty acids.

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REFERENCES

1. Hixson, A. W., and J. V. Bockelmann, *Trans. Am. Institute of Chem. Engineers* 40, 675-694 (1944).
2. Drew, D. A., and A. W. Hixson, *Ibid.* 38, 891-930 (1942).
3. Stubbs, A. L., *The South African Industrial Chemist* 5(1), 8-12 (1951).
4. Treybal, R. E., "Liquid Extraction," McGraw-Hill Book Company, New York, 1951.

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