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Extraction Rate of Fish Oil from Tuna Flesh

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Abstract

Extraction rates of fish oil in tuna flesh with dichloroethane, isopropyl alcohol, ethyl alcohol, methlethylketone, hydroxyethylmethylether and their respective azeotropes with water were studied. The apparent diffusivities were all in the order of 10^{-7}cm²/sec except hydroxyethylmethylether, which gave a value of 10^{-6} cm²/sec. The theoretical and practical meanings are discussed.

Introduction

The fish meal process now widely used consists of cooking, compression in a hydraulic press to extract part of the oil, centrifugation drying in rotary drum dryers, grinding and packing. The resultant product contains about 65% protein, 5–8% oil, 15% ash and the rest is moisture. The highly unsaturated fish oil is partly oxidized in the drying and some antioxidant added to prevent further peroxide formation. However, the fish can still oxidize, to give a strong, disagreeable flavor to the meal so it is not recommended for final feeding of chickens or pigs, as it would impart flavor to the meat. An alternative process which costs somewhat more but completely eliminates the fish flavor, uses solvent extraction instead of compression, and, as expected, the product of the process is better and could be suitable for human food[1]. We have investigated the extraction rates of fish oil from tuna flesh with dichloroethane (DEC) and determined the extraction rate, and dependencies on fiber direction and temperature. We observed that the R-t curve has a break point, and speculated on the mechanism[2][3][4]. Further studies are in progress.

Realstic order-of-magnitude extraction rates with various solvents and different species are necessary for practical plant design. We used the solvents, DCE, isopropyl alcohol (IPA), ethyl alcohol (EA), methylethylketone (MEK), hydroxyethylmethylether (HEME), their respective azeotropes with water. All the solvents mentioned except HEME have boiling points between 73° and 83°C, and were chosen for the ease of solvent removal and the prevention of evaporation loss, which counteract each other.

Theoretical

Fish flesh is not a single chemical entity and its properties, which include diffusivity, depend upon fish, part of the body, sex, age, season of capture, time

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after death, and treatment after capture. These characteristics are probabilistic rather than deterministic and any measured value is a sample or at best a mean of samples. 'Apparent' is used to distinguish practical and probabilistic from theoretical and deterministic. In the practical application, however, these sample values work effectively, and at least some order-of-magnitude value of the apparent diffusivity is indispensable for designing a plant.

If linear relationships exist between mass flux and concentration gradient, the well known Fick's law can represent the extraction rate of cubic solid in 3-dimensional space as follows.

$$\frac{\partial C}{\partial t} = \left(D_x \frac{\partial^2 C}{\partial x^2} + D_y \frac{\partial^2 C}{\partial y^2} + D_z \frac{\partial^2 C}{\partial z^2} \right) \tag{1}$$

Since fish flesh is nearly isotropic[2], (1) is reduced to

$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2} \right) \tag{2}$$

Integration of (2) under the initial condition of $t=0$, $C=C_0$, and the boundary conditions of $L=0$ and $L=L_0$, $C=0$ yields

$$R = \left[\frac{8}{\pi^2} \cdot \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} \exp \left\{ -(2m+1)^2 \cdot \pi^2 \cdot F_i \right\} \right]^3 \tag{3}$$

where $F_i = Dt/L_0^2$.

If $F_i > 0.05$, (3) is reduced to

$$\log C = -0.2736 - 12.86 F_i \tag{4}$$

The relation between R and F_i is as shown in Fig. 1 and the apparent diffusivity D can be obtained from F_i by introducing the respective values of t and L_0.

Experimental

Blocks of dorsal flesh of tuna (8 mm × 8 mm × 8 mm) with an oil content of ca. 1% were used for experiments. Two cubes were put into an Erlenmeyer flask containing 70 ml of each solvent. The flask was kept at 40°C in a shaking waterbath for a predetermined period of time. The flask was removed from the bath and the solvent evaporated, first on a sandbath and then on a waterbath. Fish oil is determined by gravimetry and the oil remaining with the residue after 20 hours was assumed to be null. The R-value was calculated from data at each instant of time, and each D value obtained from Fig. 1. The mean value of ten to twelve D's of different duration was taken as the final value.

Results and Discussion

The estimated values of the apparent diffusivity with various solvents are given in Table 1. The values can deviate from 50 to 200% of the most probable ones. For the sake of safety and economy, the solvents used in an experiment was confined to 70 ml, the fish flesh, around 1 g, and the extracted oil, about 10 mg in total. The measurement errors can be up to ten percent due to the sensitivity
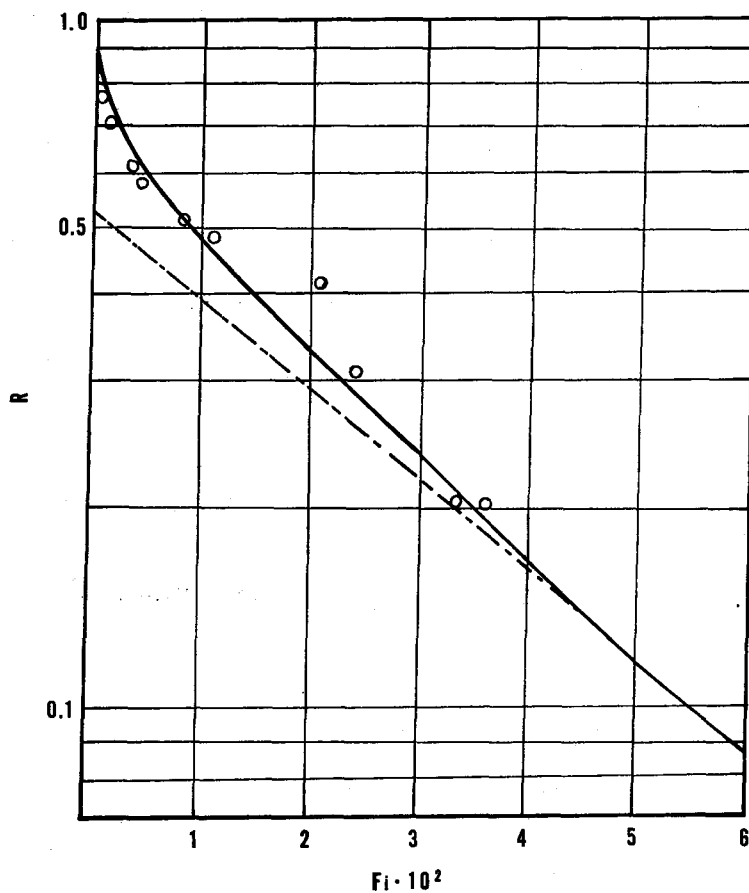
Fig. 1. Relation between F_i and R.

Table 1. *Diffusivities with various solvents.*

Solvent	Composition wt. basis	B.p. C^o	Diffusivity $cm^2/sec \cdot 10^7$
DCE	100	82.4	7
IPA	100	82.4	10
IPA+W*	68:32	80.1	6
EA	100	78.3	9
EA+W*	96:4	78.2	7
MEK	100	79.6	4
MEK+W*	64:36	73.6	13
HEME	100	124.3	8
HEME+W*	20:80	99.5	32

* The + sign denotes the azeotrope.

of the chemical balance. Since the experimental errors were rather large, datum points with larger R values were assumed to be more correct and weighted more heavily than smaller ones. The edge of the cubic samples varied randomly from block to block by several percent. The samples were tissue composites and did not have unique physical properties.

Notwithstanding these sources of error, the data reveal the following important facts:

The magnitude of the apparent diffusivity of fish oil from the dorsal flesh of tuna is 10^{-7}cm²/sec, halfway from liquid diffusivity which is 10^{-5} cm²/sec, to solid diffusivity, 10^{-9}cm²/sec.

No fundamental differences were observed in the apparent diffusivity among the solvents examined, except the HEME-water azeotrope where the apparent diffusivity was 3.2×10^{-6} cm²/sec. This rather high value can be attributed to the existence of the hydrophilic hydroxyl group and oleophilic methoxyl group.

In general, water containing solvents leached water-soluble protein. The amounts of the protein differed from experiment to experiment and made the measurements ambiguous. In commercial application, the washed out protein could cause a reduction in yield and create unfavorable problems in fish oil refining.

The residue of the MEK was harder and more brownish than others, which suggests possible chemical changes.

One of the recommended commercial extraction processes is a countercurrent mixer-settler type which consists of 3 to 4 stages where fish are ground to pieces smaller than 1 mm and the solvents regenerated by distillation[1]. In this form of application, the apparent diffusivities show that the extraction comes to an end within 30 min. If a 3-stage process is used, the necessary duration is less than 10 min/stage, which is less than the manipulation time. Therefore, no care need be taken for the extraction time.

From the point of product yield and process simplicity, the first processing stage should use DCE as the solvent to recover more protein. Chlorohydrocarbons are known to be poisonous to the liver and the kidney but the solvent can be removed in the succeeding stages and, at least in U.S. regulations, DCE is permitted in food processing[5].

Nomenclature

D=Apparent diffusivity, cm²/sec.
t=Time, hr or sec.
x, y, z=Length along the axis, respectively.
L_0=Edge length of the cube.
R=Fraction of the fish oil remaining with the residue. Dimensionless.
F_i=Fick number, Dt/L_0^2. Dimensionless.

Acknowledgement

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