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Oxidation Stability Model of Fish Oil

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Abstract

High content of polyunsaturated fatty acid in fish oil makes it very susceptible to oxidation, which prevent fish oil from successful application to food processing or functional foods. To resolve this problem, oxidation stability model of fish oil was developed using the following differential equation : $dp/dt = k \cdot p(t) \cdot [P_{max} - p(t)]$. This differential equation can be integrated using analytical techniques to give : $p(t) = P_{max}/[1 + \{(P_{max}/P_{(0)}) - 1\} \cdot EXP(-K_p \cdot t)]$. At 50, 60, 70 and 80° C, K_p were 0.00535, 0.01345, 0.02516 and 0.04675, respectively. The proposed model was well agreed with the measured data except for some minor deviations. In addition, K_p was expressed as a function of temperature : $K_p = (1/P_{max})\ EXP\ [1 - (8148/T) + 20.1]$. Where T is absolute temperature (°K)

Key words : polyunsaturated fatty acid, oxidation stability model, functional foods

INTRODUCTION

High content of polyunsaturated fatty acid (PUFA) in fish oil makes it very susceptible to oxidation (1,2). To utlilize fish oil commercially, oxidation stability of fish oil is first and fore most of vital importance. Stability of fats and oils during storage can be produced by a procedure called stability tests. Standard tests are based on storage of fats under normal conditions and changes in odor, peroxide contents, ultraviolet absorption or carbonyl contents can be determined (3). The basic disadvantages of such tests are their very long duration. Due to this fact, accelerated tests were introduced. They are based on reduction of the induction period by elevation of temperature, UV irradiation, intensive oxygenation, etc. Among the most commonly used methods are the classic Active Oxygen method (4) with some modification, oxidation of fish oil upon forced aeration was undertaken.

Various studies on this matter have been carried out but prediction study of oxidation stability have been neglected. Most researches have been focused on the induction period of fat and oil oxidation upon addition of various antioxidants (1,2,5-7); in contrast, basic engineering data were insufficient. Especially the accurate prediction of oxidation stability are prerequisite to utilize fish oil commercially due to its high content in PUFA. Therefore, the basic model to predict oxidation stability was derived and verified. The proposed model can be used for the investigation of the kinetics of oxidation of fats and for evaluation of their oxidation stability. It can be applied for both fundamental research and routine industrial analyses.

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MATERIALS AND METHODS

Materials

Refined fish oil from sardine was donated by Dr. K. Hada of Japan Fisheries Co., Ltd. Before the experiment, fish oil was flushed with moisture-free nitrogen gas, closed with airtight cap, and stored at 5° C until use.

Chemical analysis

Peroxide value and iodine value were determined by AOAC methods (8).

Oxidation of fish oil with forced aeration

Fish oil of 60ml was placed in the reaction vessel (250ml) equipped with thermometer and air sparger. To prevent fish oil from evaporating during oxidation

process, condenser was installed in the vent of the vessel. Reaction vessel was placed in the water bath of a given temperature. Aeration rate was 70ml/min using air pump equipped with moisture trap. At the predetermined time, an aliquot of sample was withdrawn to determine the changes in peroxide value.

THEORETICAL

Details of how oxidation of fats and oils takes place indicate that essentially it is a degradation process which occurs at the double-bond sites in glyceride molecules (9). Heat energy puts the electrons in an excited state. When enough energy has been absorbed so that the electron reaches a critical excitation level, the excess energy is dissipated by the electron breaking away from the rest of the molecule and taking a proton with it. This leaves a fatty acid molecule with a carbon atom containing an unpaired electron, which consists of extremely unstable chemical structure. This structure is called free radical. Free radicals are extremely unstable substances and will seek another electron to complete the stable paired electron structure. Thus fat and oil oxidation takes place in a series of steps, which is described as follows :

$$RH \xrightarrow[\text{I}]{-H\cdot} R\cdot \xrightarrow[\text{II}]{+O_2} ROO\cdot \xrightarrow[\text{III}]{+H\cdot} ROOH \quad (1)$$

Step I corresponds to the induction period; oxidation stability of fats and oils increases as the reaction rate of step I decreases. The formation of peroxides will be proportional to the concentrations of R· and O_2 in step II. If oxygen is saturated during the reaction, reaction rate will be the function of the R· concentration. Considering the instability of free radicals (ROO·), the reaction rate of step III should be much faster: thereby equation (1) may be simplified as equation (2).

$$RH \xrightarrow{-H\cdot} R\cdot \xrightarrow[+H\cdot]{+O_2} ROOH \quad (2)$$

After an induction period, a rapid increase in the peroxide value increases rapidly and after passing a maximum, the peroxide value decreases. Fat and oil oxidation model incorporate the assumption that the rate of peroxide formation (p) is proportional to the existing peroxide at any time (t). In addition, when the rate of peroxide breakdown becomes higher than that of peroxide formation, the concentration of peroxide will decrease. In this case the rate equation will be as follows:

$$\frac{dp}{dt} = k \cdot p(t) \cdot [P_{max} - p(t)] \quad (3)$$

where k, p(t), and P_{max} are rate constant, peroxide value at any time (t), and theoretical maximum peroxide value, respectively. This differential equation can be integrated using analytical techniques to give:

$$p(t) = \frac{P_{max}}{1 + [\frac{P_{max}}{p(0)} - 1] \cdot EXP(-K_p \cdot t)} \quad (4)$$

To simplify the equation (4), Pmax was calculated from the iodine value of the fish oil (6945meq/kg oil). $k \cdot P_{max}$ was designated as K_p, lump sum constant. To determine K_p, equation (4) was transformed as follows:

$$\frac{1}{p(t)} = \frac{1}{P_{max}} + [\frac{1}{p(0)} - \frac{1}{P_{max}}] \cdot EXP(-K_p \cdot t) \quad (5)$$

Assume $\frac{1}{P_{max}} \cong 0$, then the equation (5) will become:

$$\frac{1}{p(t)} = \frac{1}{p(0)} \cdot EXP(-K_p \cdot t) \quad (6)$$

Further the equation (6) will be transformed as follows:

$$\ln \frac{1}{p(t)} = \ln \frac{1}{p(0)} - K_p \cdot t \quad (7)$$

By plotting $\ln \frac{1}{p(t)}$ vs t, K_p can be estimated by linear regression.

RESULTS AND DISCUSSION

Estimation of K_p at various temperatures

Fatty acid composition of fish oil consisted 14.3% saturated fatty acids and 81.50% unsaturated fatty

acids ; unsaturated fatty acids with two or more double bonds, in particular, were composed of 35.29% of total fatty acids (data not shown). In addition, the ratio of saturated fatty acid to unsaturated ones was 0.18, indicating the high degree of unsaturation. The possible application of fish oil as functional foods was promising seeing that the content of eicosapentaenoic acid in fish oil was remarkably high. However, the high degree of unsaturation will make fish oil very susceptible to oxidtation. Therefore, the prediction of oxidation stability of fish oil should be made to develop fish oil as functional foods.

The changes in peroxide value were monitored as the oxidation process of fish oil was carried out at various temperatures. Based upon the proposed model, the measured values were compared to the theoretical values. Sherwin (6) proposed the end point for the activated oxygen test to be the peroxide levels of 20 meq/kg oil for lard and 70meq/kg oil for cotton seed oil. Since the fish oil contained more unsaturated fatty acids than cottonseed oil, 100meq/kg oil was arbitrarily selected as the end point. The changes in peroxide values around the end point are of great concern in the model of this study.

At the oxidation temperature of 50° C, K_p was estimated as 0.00535 (r=0.9868) and the measured peroxide values were well agreed with theoretical ones (Fig. 1). However, over 800min, theoretical values were significantly lower than measured ones. This discrepancy resulted from the fact that, in reality, actual peroxide value cannot reach the theoretical maximum peroxide value. This drawback may be insignificant because the purpose of this study was to determine the oxidation stability of fish oil, not to demonstrate the progress of the entire oxidation process. In addition, up to peroxide level of 300meq/kg oil, the proposed model exhibited the good agreement with the measured data.

Oxidation rates at 60° C became about two times faster than that at 50° C (Fig. 2) and K_p was 0.01345 (r=0.9931). Throughout the oxidation process, most measured peroxide values were well agreed with the model. K_p at 70° C and 80° C were 0.02516 (r=0.99 18) and 0.04 675 (r=0.9686), respectively (Fig. 3 and 4). Most measured peroxide values fitted well with the model with minor deviations.

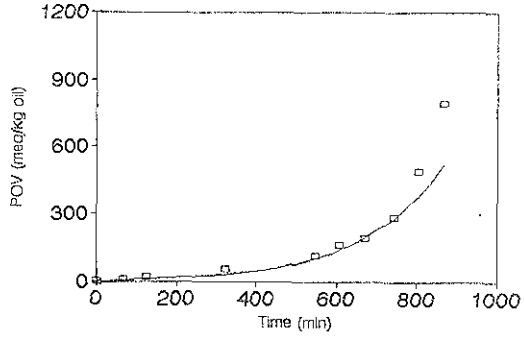

Fig. 1. Changes in peroxide value of fish oil at 50° C with forced aeration (72ml/min).
Experimental (□), predicted (--)

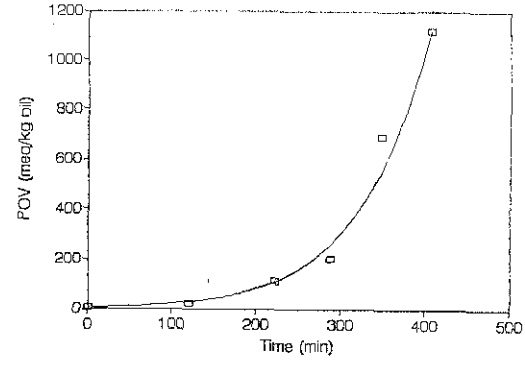

Fig. 2. Changes in peroxide value of fish oil at 60° C with forced aeration (72ml/min).
Experimental (□), predicted (—)

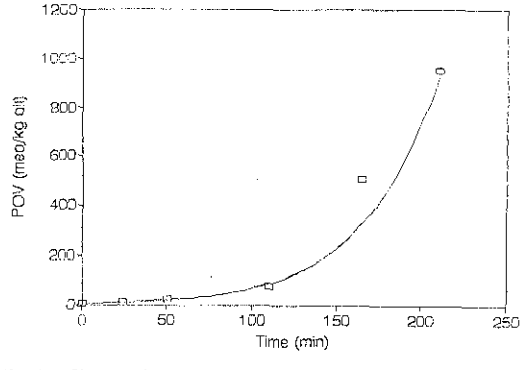

Fig. 3. Changes in peroxide value of fish oil at 70° C with forced aeration (72ml/min).
Experimental (□), predicted (--)

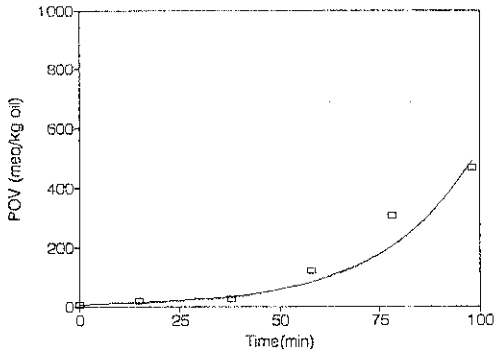

Fig. 4. Changes in peroxide value of fish oil at 80° C with forced aeration (72ml / min).
Experimental (□), predicted (—)

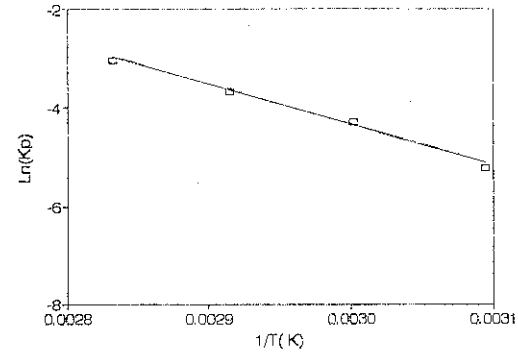

Fig. 5. ln (K) as a function of 1 / T.

K_p as a function of temperature

Lump sum constant, K_p might be able to be expressed as a function of the oxidation temperature. If possible, the proposed model should be applicable to the different oxidation temperatures. Thus, as shown in Fig. 5, Arrehnius equation was employed to predict K_p at different temperatures. At any given temperature, K_p can be determined as follows :

$$K_p = \frac{1}{P_{max}} \text{EXP}\left[1 - \frac{8148}{T} + 20.1\right]$$

where T is absolute temperature (° K).

To apply the proposed model to predict oxidation stability of fish oil under various storage conditions, appropriate correcton must be made by comparing the oxidation data under the forced aeration with those under storage conditions. If proper correction factors for the model were estimated, the accurate prediction can be successfully made for the oxidation stabiliy of fish oil.

In this model, P_{max} was considered to be independent upon temperatures ; however, P_{max} was likely to be the function of temperatures. Therefore, it is necessary for the proposed model to be improved. Further research is in progress to determine P_{max} and K_p by numerical methods.

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어유의 산화안정성 예측

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요 약

어유는 고도불포화지방산 함량이 높아 산화가 쉽게 되므로 식품가공용이나 기능성식품으로 응용되기에는 많은 제약이 따른다. 이러한 문제를 해결하기 위하여 어유의 산화안정성을 예측할 수 있는 기본 모델을 다음과 같은 식을 이용하여 제시하였다. $dp/dt = k \cdot p(t) \cdot [P_{max} - p(t)]$. 상기식을 적분하면, $p(t) = P_{max}/[1 + \{(P_{max}/P_{(0)}) - 1\} \cdot EXP(-K_p \cdot t)]$. 여기서 산화온도가 50, 60와 70 및 80°C일 때, K_p는 각각 0.00535, 0.01345와 0.02516 및 0.04675였다. 상기식은 대부분 측정치와 잘 일치하였다. 또한 K_p를 아래와 같이 온도의 함수로 표현할 수 있었다. $K_p = (1/P_{max})\ EXP\ [1 - (8148/T) + 20.1]$, 여기서 T 절대온도(°K)이다.