Kinetics of Fish Meal Oxidation

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ABSTRACT

A mathematical model has been developed for the oxidation kinetics of fish meal, based on assumptions of the theory of gas liquid reactions and the kinetics of homogeneous oxidation reactions. This foresees that if diffusional control exists for the oxygen, the observed reaction will be of the first order with respect to this component. The specific rate constant for the reaction will be a function of the interfacial area. The performance of the model was tested experimentally.

INTRODUCTION

Normally the extent of the oxidation of the unsaturated lipids in products such as fish meal is deduced from the results obtained by the classic treatment of the oxidation kinetics of pure lipids (1-6).

Nevertheless, certain results which have appeared in the literature (3,6-8) lead to suppose that under special circumstances physical effects are observed in the apparent rate of oxidation in the case of fish meal.

This situation is at odds with the classical treatment which does not include the aforementioned influences.

Since oxidation reactions are considered to be chain reactions, they are divided in two parts for the purpose of study: one corresponding to the period of induction and the other to that of plain oxidation. The kinetic expressions which appear in the literature usually refer to the second part (9).

REACTION MECHANISM IN THE OXIDATION OF PURE UNSATURATED LIPIDS

It has been studied and demonstrated that the reaction of oxidation of pure lipids occurs through a mechanism of the chain type by free radicals (9,10).

The initial assumptions in the developing of this model are: (a) the first reaction is the formation of free radicals which is catalyzed by light or else by trace metals; (b) the propagation stage is due to the reaction of the radicals with oxygen or with the organic molecule; (c) the finishing stage is that of the reaction between chain carriers.

According to this, a typical scheme for this sequence is:

$$\text{Initiation} \left\{ \begin{array}{l} R \longrightarrow R\cdot \\ R + O_2 \longrightarrow RO_2\cdot \end{array} \right\}$$

$$\text{Propagation} \left\{ \begin{array}{l} R\cdot + O_2 \xrightarrow{k_2} RO_2\cdot \\ RO_2\cdot + RH \xrightarrow{k_3} R\cdot + RO_2H \end{array} \right\}$$

$$\text{Finishing} \left\{ \begin{array}{l} 2R\cdot \xrightarrow{k_4} R - R \\ R\cdot + RO_2\cdot \xrightarrow{k_5} \\ 2RO_2\cdot \xrightarrow{k_6} \end{array} \right\} \begin{array}{l} \text{Stable products} \\ \text{that do not take} \\ \text{part in the chain.} \end{array}$$

The reaction rate for the above reactions are:

$$\text{Initiation} \left\{ -r_1 = f(R, O_2) \right.$$

$$\text{Propagation} \left\{ \begin{array}{l} -r_2 = k_2 [R\cdot] [O_2] \\ -r_3 = k_3 [RO_2\cdot] [RH] \end{array} \right. \qquad \text{(I)}$$

$$\text{Finishing} \left\{ \begin{array}{l} -r_4 = k_4 [R\cdot]^2 \\ -r_5 = k_5 [R\cdot] [RO_2\cdot] \\ -r_6 = k_6 [RO_2\cdot]^2 \end{array} \right.$$

If the length of the chain is large, it is acceptable to consider that the number of radicals produced in the initiation stage is negligible compared to that of the propagation stage; according to this it can be supposed $r_2 = r_3$.

If the quasistationary state hypothesis is accepted, the rate of radicals formation is equal to that of the consumption.

After the above suppositions, an expression to show the concentration of free radicals can be obtained.

As the reaction rate is usually studied by keeping track of the oxygen pressure, equation (I) can be used. In it the $[R\cdot]$ value must be replaced by the expression found in the way it was discussed in the above paragraph, to obtain the following general expression:

$$r_2 = \frac{d[O_2]}{dt} = -r_1^{0,5} [RH] [O_2] / \left\{ k_2^{-2} k_4 [RH]^2 + \right.$$
$$\left. + 2 k_2^{-1} k_3^{-1} k_5 [O_2] [RH] + k_3^{-2} k_6 [O_2]^2 \right\}^{0,5} \qquad \text{(II)}$$

This equation has been checked by a series of investigations with pure reactives (11-14).

When considering both extreme cases of high and low oxygen concentration, this equation is greatly simplified. The resulting expressions are:

High oxygen concentration

$$r(I) = \frac{d[O_2]}{dt} = -k_3 r_1^{0,5} [RH] / k_6^{0,5} \qquad \text{(III)}$$

This expression is applied under normal conditions (atmospheric autooxidation) allowing for the concept that the rate of absorption of O_2 in unsaturated compounds is of zero order with respect to O_2 (15,16).

Low concentration of O_2

$$r(II) = \frac{d[O_2]}{dt} = -k_2 r_1^{0,5} [O_2] / k_4^{0,5} \qquad \text{(IV)}$$

This is to say that at very low concentration of O_2, the reaction rate is first order with respect to the concentration of it.

This result has led to the industrial practice of storing the fish meal in containers of low O_2 permeability (17-20).

ANALYSIS OF THE CLASSICAL TREATMENT WITH REFERENCE TO ITS APPLICABILITY TO THE OXIDATION OF FISH MEAL

The following observations may be made on the classical treatment of the oxidation of fish meal.

(a) The entire development is carried out assuming a homogeneous reaction, when the process is actually heterogeneous from the point of view of the phases.

(b) Although in the case of the kinetic studies mentioned, agitation makes the elimination of the diffusional resistance feasible, experimental evidences have shown that the mentioned resistances are appreciable in the case of fish meal (3,6,7).

(c) Under normal conditions, the concentration of oxygen in the liquid phase (oil) is low, of the order of 0,3 ppm (21). For this reason the existence of an external resistance to the diffusion results in a relatively important depletion of the concentration of oxygen in the oil.

(d) The mechanism of oxidation of lipids in fish meal is not as simple as that described by the classical treatment, if it is considered that in the meal there exist other reactions which consume up to 10 times more oxygen than necessary (22).

In accordance with this analysis, we believe that it is more convenient to talk of an apparent oxidation kinetics in all the fish meal without including the part corresponding to the induction period in the model which would complicate it without adding greatly to its advantages. This is more germane to the industrial requirements than the elucidation of an oxidation mechanism for a given substance.

The equation representative of this overall adjustment is:

$$O_2 + z\,RH \longrightarrow \text{Products} \qquad \text{(V)}$$

THEORY OF GAS LIQUID REACTIONS

The theory of gas liquid reactions has been applied largely to industrial processes with mass transfer with simultaneous chemical reaction (23,24).

The applications cover the problem of two fluids alone, and also the existence of a third stationary nonreactive phase.

In the fish meal oxidation problem two fluids, oxygen and oil, and a solid phase are found. The solid phase constitutes the oil support, and the oxygen must diffuse through its macro and micropores system before it reacts with the unsaturated lipids. Although a homogeneous chemical reaction will take place, the diffusion can affect the overall reaction rate.

Thus, the homogeneous kinetics expressions found (III) (IV) may be used to develop heterogeneous ones by using the expressions that describe the mass transfer with chemical reaction in binary systems.

In this situation it is feasible to formulate two systems of equations which represent the phenomena.

The first system would be the one corresponding to the situation established by expression (III) for which we have:

$$\begin{cases} D_{O_2} \dfrac{\partial^2 C_{O_2}}{\partial X^2} = z\,k\,C_{RH} & \text{(VI)} \\[2ex] D_{RH} \dfrac{\partial^2 C_{RH}}{\partial X^2} = k\,C_{RH} & \text{(VII)} \end{cases}$$

with the following boundary conditions:

$$\text{for } X = 0 \; C_{O_2} = C_{O_2,i} \quad \left.\frac{\partial C_{RH}}{\partial X}\right|_{x=0} = 0$$

$$\text{for } X = L \; C_{RH} = C_{RH}(L) \; C_{O_2} = 0$$

It is an assumption in the model that L would keep constant during the whole process.

For the case established by the expression, (IV) we could write:

$$\begin{cases} D_{O_2} \dfrac{\partial^2 C_{O_2}}{\partial X^2} = z\,k\,C_{O_2} & \text{(VIII)} \\[2ex] D_{RH} \dfrac{\partial^2 C_{RH}}{\partial X^2} = k\,C_{O_2} & \text{(IX)} \end{cases}$$

where the boundary conditions would be the same as those in the previous case.

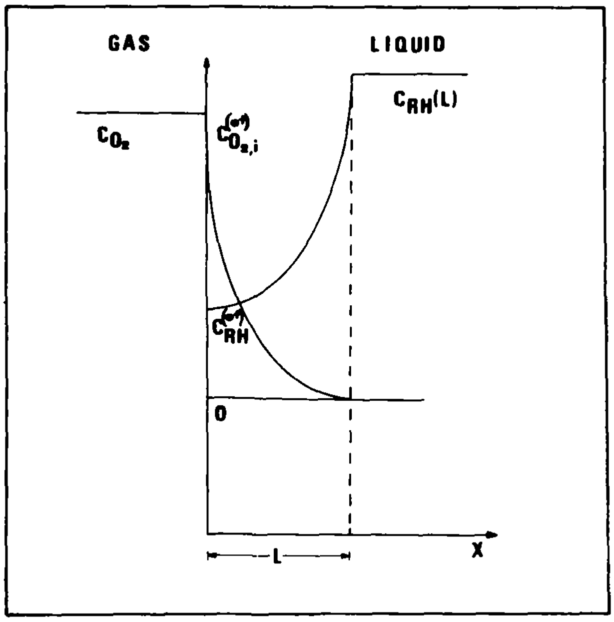

FIG. 1. Concentration profiles at the gas (O_2) liquid (fish oil) interface.

In this case the mass transfer limitation is mainly associated with the unsaturated reactive lipids. We can imagine a situation in which the reactive lipids react so quickly with oxygen (e.g., at the surface or in the liquid film) that the limitation comes from the diffusion rate of such reactive lipids from the oil body. This may be the case in the spontaneous fish meal autooxidation.

In spite of the homogeneous chemical reaction, which can be of zero order with reference to oxygen, the mass transfer will affect the reactive lipid concentration in the reaction zone.

Figure 1 is a picture of the proposed model.

The solution of systems (VI) (VII) with the specified boundary conditions, determined by Hikita and Asai (25) gives the following results:

(a) The C_{O_2} profile in the liquid film

$$C_{O_2}(X) = C_{O_2}(O+) - \frac{C_{O_2,i}}{L} X + \frac{Z\; C_{RH}\;(L)}{\dfrac{D_{O_2}}{D_{RH}} \cosh\left|\sqrt{\dfrac{k}{D_{RH}}}\;L\right|} \qquad \text{(X)}$$

$$\left(\frac{X}{L} - 1\right)\left(\cosh\left|\sqrt{\frac{k}{D_{RH}}}\;L\right| - 1\right)$$

The C_{RH} profile inside the film will be:

$$C_{RH}(X) = C_{RH}(L)\,\frac{\cosh\left|\sqrt{\dfrac{k}{D_{RH}}}\;X\right|}{\cosh\left|\sqrt{\dfrac{k}{D_{RH}}}\;L\right|} \qquad \text{(XI)}$$

(b) The oxygen average mass transfer rate

$$N_{O_2}(I) = \left|\frac{D_{O_2}}{L}\right| C_{O_2,i} + Z\,C_{RH}(L)\left|\frac{D_{RH}}{L}\right|\left[\cosh^{-1}\left|\sqrt{\frac{k}{D_{RH}}}\;L\right| - 1\right] \qquad \text{(XII)}$$

From the average mass transfer rate, an apparent kinetic expression can be obtained:

$$r\,(I) = \frac{d(O_2)}{d\,t} = -\,N_{O_2}\,(I)\,A_v \qquad \text{(XIII)}$$

According to it the reaction rate expression is:

$$r\,(I) = -K_I\,P_{O_2} - K'_I\,C_{RH}\,(L) \tag{XIV}$$

where:

$$K_I = A_v\,H\left(\frac{D_{O_2}}{L}\right) \tag{XV}$$

$$K'_I = Z\,A_v\left|\frac{D_{RH}}{L}\right|\left[\cosh^{-1}\left|\sqrt{\frac{k}{D_{RH}}}\;L\right| -1\right] \tag{XVI}$$

The solution of systems (VIII) (IX) is obtained by using the expression of Hatta (26) which allows us to reach the following expression:

(a) The O_2 profile in the liquid film

$$C_{O_2}\,(X) = \frac{1}{\sinh\left|L/\sqrt{\frac{D_{O_2}}{k}}\right|}\left\{C_{O_{2,i}}\sinh\left|\frac{L-X}{\sqrt{\frac{D_{O_2}}{k}}}\right| + \right. \tag{XVII}$$

$$\left. + C_{O_2}\,(L)\sinh\left|\frac{X}{\sqrt{\frac{D_{O_2}}{k}}}\right|\right\}$$

(b) The oxygen average mass transfer rate when

$$L\sqrt{\frac{k}{D_{O_2}}} >>> 1$$

$$N_{O_2}\,(II) = \sqrt{k\,D_{O_2}}\quad C_{O_{2,i}} \tag{XVIII}$$

In the same way, as previously shown:

$$r\,(II) = \frac{d\,[O_2]}{d\,t} = -N_{O_2}\,(II)\,A_v \tag{XIX}$$

Therefore,

$$r(II) = -K_{II}\,P_{O_2} \tag{XX}$$

where:

$$K_{II} = A_v\,H\,\sqrt{k\,D_{O_2}} \tag{XXI}$$

In the expression (XIV) it is possible to relate $C_{RH}\ (L)$ and P_{O_2} in the following way:

$$z\,(C_{RH}^{\circ} - \overline{C_{RH}})\;V_2 = (P_{O_2}^{\circ} - P_{O_2})\,\frac{V_1}{RT} \tag{XXII}$$

From which the relation between $\overline{C_{RH}}$ and P_{O_2} may be obtained.

On the other hand,

$$\overline{C_{RH}} = \overline{C_{RHp}}\;\frac{V_L}{V_2} + C_{RH}\,(L)\;\frac{V_2 - V_L}{V_2} \tag{XXIII}$$

By integrating expression (XI) in the film the $\overline{C_{RH_p}}$ value is obtained, resulting

$$\overline{C_{RH_p}} = C_{RH}\,(L)\;\tanh\left|\sqrt{\frac{k}{D_{RH}}}\;L\right| / \left|\sqrt{\frac{k}{D_{RH}}}\;L\right| \tag{XXIV}$$

In replacing these values in equation (XIV) and grouping the constants, the following is obtained:

$$r\,(I) = -\,K_1 P_{O_2} - K'_1 \tag{XXV}$$

where:

$$K_1 = A_v\,H\left(\frac{D_{O_2}}{L}\right) \tag{XXVI}$$

$$+\frac{\sqrt{k\,D_{RH}}\;A_v\left[\cosh^{-1}\left|\sqrt{\frac{k}{D_{RH}}}\;L\right| - 1\right]\;V_1}{RT\left[\tanh\left|\sqrt{\frac{k}{D_{RH}}}\;L\right|\;V_L + (V_2 - V_L)\left(\sqrt{\frac{k}{D_{RH}}}\;L\right)\right]}$$

and $K'_1 =$

$$\frac{A_v\,\sqrt{D_{RH}\,k}\left[\cosh^{-1}\left|\sqrt{\frac{k}{D_{RH}}}\;L\right| -1\right]\left(C_{RH}^{\circ}\,z\,V_2\,RT - P_{O_2}^{\circ}\,V_1\right)}{\left[\tanh\left|\sqrt{\frac{k}{D_{RH}}}\;L\right|\;V_L + \left(V_2 - V_L\right)\left(\sqrt{\frac{k}{D_{RH}}}\;L\right)\right]\;(R\,T)} \tag{XXVII}$$

From the analysis of the expressions (XX) (XXV) it is possible to forecast the following experimental behavior.

(a) The pseudo-homogeneous reaction rate expression, or the observed macroscopic kinetics, should be of the first order with respect to oxygen, provided diffusional control exists, regardless of the order with respect to oxygen that the microscopic reaction rate may have.

(b) The apparent reaction rate constant should increase with the specific area.

(c) The variation with temperature is hard to assess from the parameters involved in expressions (XXVI) and (XXVII) alone. A lack of data exists to predict an average k, D_{RH} or H parameter from the individual values of the compounds in the mixture. However, if diffusional control exists, only small variations with temperature in the overall constants K_1 and K'_1 should be expected, according to the usual knowledge on gas liquid reactions (23,24).

DEVELOPMENT OF INVESTIGATION

The experiments were performed with fish meal from anchovies and hake frames (provided by local fish meal factories), using the modified pump method (7).

The apparent specific reaction rate constant and its variation with the initial pressure of oxygen, with the interfacial area, and with temperature, was determined.

For the determination of the apparent specific reaction rate constant, the integral method of Mangelsdorf and Swinbourne was used (27,28) applied to the analysis of the variation of concentration of oxygen with time (29). The accuracy of the model is verified by the observance of a straight line, from which the value of the apparent reaction rate constant can be calculated.

The computation of the slope is carried out using the technique of least squares, analyzing the incidence of the dispersion of results by experimental error through the coefficient of correlation and the limits of confidence. The latter have been calculated using the procedure proposed by Mandel (30) and Jaech (31) in case of estimates when the errors in the measurements are not independent.

The experimental results which were obtained are shown in Figure 2, suggesting first order behavior. Nevertheless, we cannot assert that the first order behavior found corresponds to oxygen or to the unsaturated lipids, as in both cases the measured variation would be the same.

If the reaction with respect to unsaturated lipids were of the first order, varying the initial pressure of oxygen the initial reaction rate should not vary. If it is of first order with respect to oxygen, it should increase with the initial concentration of oxygen. Experiments were performed to answer this question, the results being shown in Figure 3. From their analysis the existence of a real first order behavior with respect to oxygen appears clearly.

To study the effect of the variation of the interfacial area on the apparent reaction rate constant, experiments were made with fish meal from anchovies and the cuts of filletted hake at a temperature of 100 C, under a pressure of O_2 of 4 kg/cm2 and with pellets of different densities.

The results are shown in Figure 4, from which the theoretical prevision that a smaller interfacial area gives a smaller apparent reaction rate constant is verified.

The effect of the variation of temperature on the reaction rate working at a pressure of 4 kg/cm2 within the

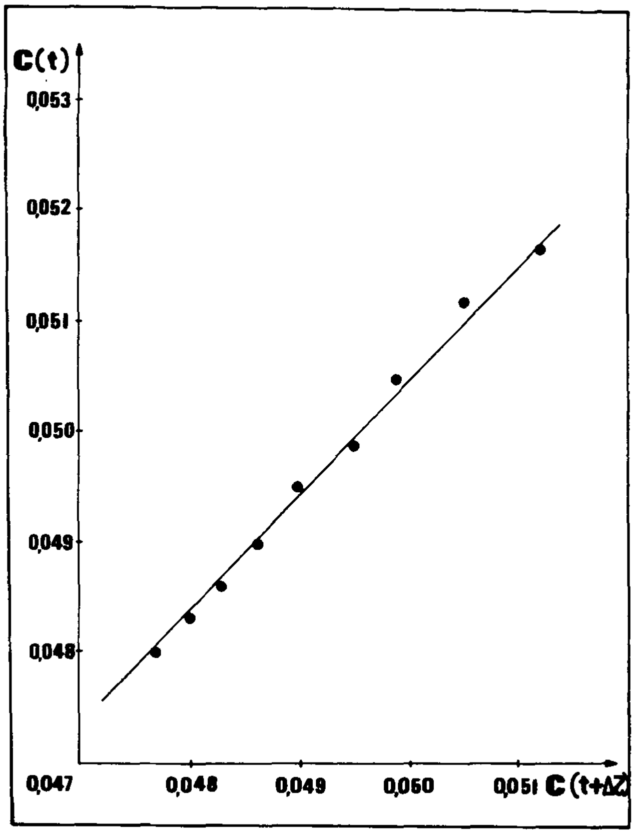

FIG. 2. Typical experimental plot of O_2 consumption,, showing the first order model correspondence.

temperature range of 70-110 C was studied. The results are shown in Figure 5. It is shown that the variation of K detected in the range of working temperatures is very small; this is in accordance with what can be expected in the case of diffusional control.

ANALYSIS OF THE RESULTS

In accordance with the results shown in Figures 2 and 3, the real first order behavior with respect to oxygen of the apparent reaction rate is verified.

The results given in Figure 4 satisfy the prevision of the model that the apparent reaction rate constant diminishes with the increase of the apparent density.

From the variation of K with temperature shown in Figure 5, a small temperature dependence is found.

NOTATION

A_v	Surface area per unit volume.
$C_{O_{2,i}}$	Concentration of O_2 in the interface.
$C_{O_{2,i}}^{(O+)}$	Concentration of O_2 in the interface on the side of the liquid.
$C_{RH}(L)$	Concentration of RH in the body of the liquid.
C_{RH}^{o}	Initial concentration of RH.
$C_{RH}(O+)$	Concentration of RH in the interface on the side of the liquid.
$\overline{C_{RH}}$	Mean concentration of RH in the liquid.
$\overline{C_{RH_p}}$	Mean concentration of RH in the film.
D_{O_2}	Molecular diffusivity of O_2.
D_{RH}	Molecular diffusivitiy of RH.
H	Henry's law constant.
k	Specific reaction rate constant.
K	Apparent specific reaction rate.

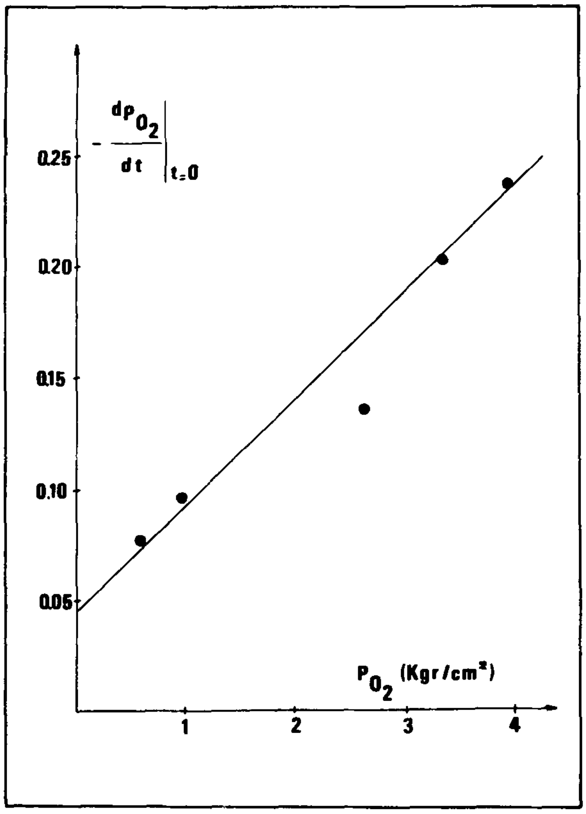

FIG. 3. Initial rate of O_2 consumption vs. oxygen pressure in the pump.

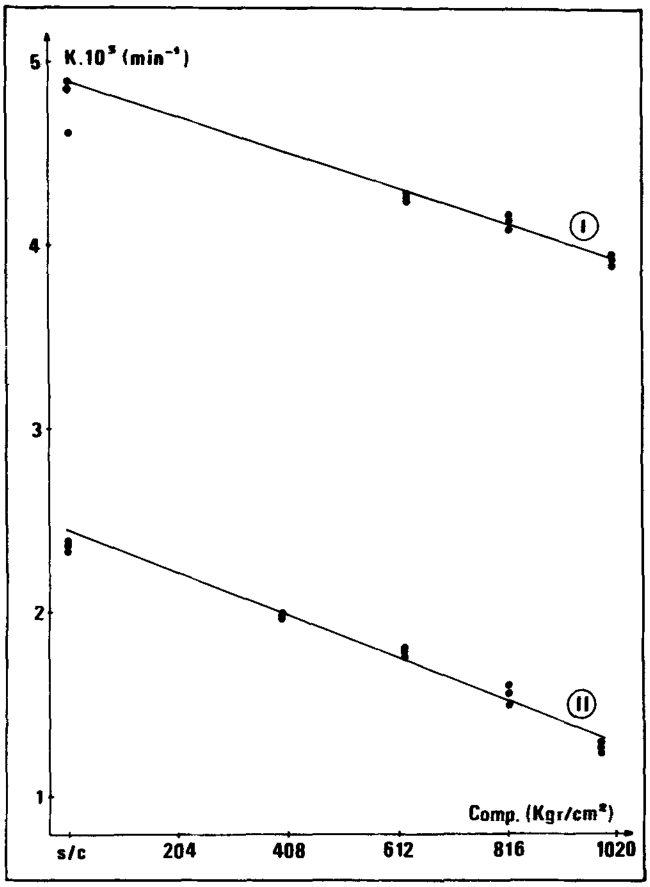

FIG. 4. Specific apparent rate constant of oxidation vs. degree of pellet pressure compactation. (I) Anchovies meal, (II) Hake meal.

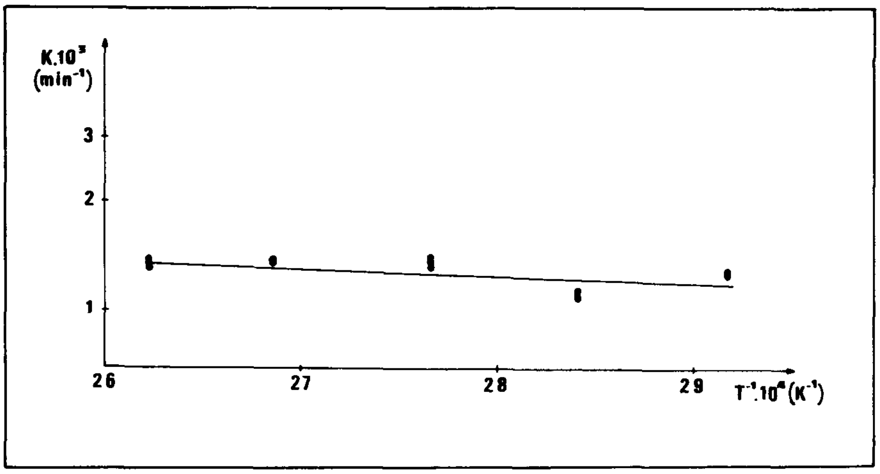

FIG. 5. Specific apparent rate constant of oxidation vs. temperature at constant apparent density.

k_2	Specific reaction rate constant for the formation of peroxide radicals
k_3	Specific reaction rate constant for the formation of hydroperoxide radicals.
k_4	Specific reaction rate constant for the disappearance of alkyl radicals.
k_6	Specific reaction rate constant for the disappearance of peroxide radicals.
L	Thickness of diffusion film.
N_{O_2} (I)	Oxygen average mass transfer rate for high oxygen concentration.
N_{O_2} (II)	Oxygen average mass transfer rate for low oxygen concentration.
P_{O_2}	Pressure of O_2.
$P^{\circ}_{O_2}$	Initial pressure of oxygen.
R	Gas constant.
RH	Unsaturated lipids.
r_1	Rate of formation of free radicals.
r (I)	Reaction rate for high concentrations of O_2.
r (II)	Reaction rate for low concentrations of O_2.
T	Absolute temperature.
V	Volume of unsaturated lipids.
V_1	Volume of O_2.
V_2	Total volume of oil.
V_L	Volume of oil in the film.
z	Stoichiometric coeficient.

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