Effect of Oil-Droplet Diameter on Lipid Oxidation in O/W Emulsions

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Abstract: The effect of oil-droplet diameter on lipid oxidation in O/W emulsions is unclear, and conflicting results have been reported. These conflicts may be due to different experimental conditions being used, such as the type of oil, the type of emulsifier, temperature, and the range of oil-droplet diameters tested. The method used to evaluate the oxidation could also have varied among studies. In O/W emulsions, oxygen dissolved in the aqueous phase is transferred to the oil phase through the oil-water interface and is consumed in the oil phase by oxidation. Therefore, the effect of the oil-droplet diameter on the lipid oxidation rate was evaluated by simultaneously solving the mass balance equations of oxygen and oil in the oil phase. The simulation showed that the oil-droplet diameter does not affect the lipid oxidation rate in O/W emulsions with oil-droplet diameters on the order of micrometers or less because the oxidation reaction itself is rate-limiting.

Key words: lipid oxidation, O/W emulsion, oil-droplet diameter, oxidation kinetics, mass transfer

1 Introduction

Lipids are one of three major nutrients and are an important energy source for humans. Polyunsaturated fatty acids (PUFAs), such as eicosapentaenoic acid and docosahexaenoic acid (DHA), are examples of lipids with physiological functions that can reduce the risk of cardiovascular disease and prevent cancer. Such functions are called the tertiary functions of foods. Therefore, PUFAs are attracting attention as food ingredients due to these desirable functions^{1,2)}. However, they are easily oxidized, which subsequently reduces the flavor of foods they are present in and negatively affects the food safety^{3,4)}. Therefore, to maintain food quality it is important to rationally suppress their oxidation.

Lipid oxidation in bulk systems has been extensively studied, and it is known that many factors, such as lipid type, temperature, and oxygen concentration, affect the oxidation⁵⁻⁷⁾. Lipid oxidation in O/W emulsions has also been studied, where the oil-droplet diameter also affects lipid oxidation. Oxygen required for oxidation is supplied from the aqueous phase to the oil phase through the oil-water interface. Sometimes, when the oil-droplet diameter is large, the oxidation is suppressed or delayed due to the resultant small specific surface area of the oil phase. On the other hand, reducing the oil-droplet diameter promotes lipid oxidation because it provides a sufficient supply of

oxygen. That is, the mass transfer of oxygen through the oil-water interface is rate-limiting for lipid oxidation when the oil droplets are large, while the oxidation itself is the rate-limiting step when the droplets are small. However, the oil-droplet diameter that determines the rate-limiting step for the oxidation is unclear.

The effect of oil-droplet diameter on lipid oxidation has been experimentally investigated, but conflicting results have been reported. Some studies report that reducing the droplet diameter promotes oxidation⁸⁻¹¹⁾, while others state that it delays it¹²⁻¹⁵⁾. Furthermore, there are reports stating that this parameter has no effect on lipid oxidation¹⁶⁻²¹⁾. These conflicting results may be due to the difficulty of the experiment, where typically only the oil-droplet size is changed while the other reaction conditions remain unchanged. The method employed for evaluating the oxidation also varies among these studies, which could also contribute to the discrepancies.

In this context, we propose a model to estimate the effect of oil-droplet diameter on lipid oxidation in an O/W emulsion. By using the parameters related to lipid oxidation and the mass transfer of oxygen through the oil-water interface, we discuss the oil-droplet diameter at which the effect of oxygen mass transfer through the oil-water interface becomes apparent.

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2 Model

The entire oxidation process of n-6 PUFAs and the first half of the oxidation process of n-3 PUFAs can be expressed by an autocatalytic equation (Eq. (1)) that depends on the concentrations of unoxidized and oxidized lipids^{5, 22}.

$$\frac{dC_F}{dt} = -k'C_F(C_{Ft} - C_F) \quad (1)$$

where C_F is the concentration of unoxidized lipids in the oil droplet, t is the time, k' is the oxidation rate constant, and the subscript t indicates the total of unoxidized and oxidized lipids. The oxidation rate constant k' depends on the oxygen concentration in the lipid and its dependence is expressed by a Langmuir–Hinshelwood-type equation (Eq. (2))^{5, 7}.

$$k' = \frac{kC_X}{K_X + C_X} \quad (2)$$

where k is the rate constant, C_X is the oxygen concentration in the oil droplet, and K_X is the saturation constant of oxygen. From Eqs. (1) and (2), the lipid oxidation rate can then be expressed by Eq. (3).

$$\frac{dC_F}{dt} = -\frac{kC_X}{K_X + C_X} C_F(C_{Ft} - C_F) \quad (3)$$

The C_{Ft} value can be calculated by Eq. (4) using the density ρ and the molar mass M of the lipid.

$$C_{Ft} = \rho/M \quad (4)$$

Under the following four assumptions, the increasing rate of oxygen concentration in an oil droplet can be expressed by Eq. (5): (a) oxygen is transferred from the aqueous phase into the oil droplet through an oil-water interface with a mass transfer coefficient of k_i ; (b) oxygen diffuses quickly in the oil droplet, and the oxygen concentration in oil droplets with a radius of r_p is homogeneous; (c) the oil-droplet diameter does not change during the oxidation^{13, 21}; and (d) the stoichiometric coefficient between lipid and oxygen is unity²³.

$$\frac{dC_X}{dt} = -\frac{kC_X}{K_X + C_X} C_F(C_{Ft} - C_F) + k_i \frac{3}{r_p} (C_X^* - C_X) \quad (5)$$

where C_X^* is the oxygen concentration in the oil droplet that would be in equilibrium with the oxygen concentration in the aqueous phase. Assuming that the oxygen concentration C_{Xa} of the aqueous phase is constant due to the sufficiently large volume of the aqueous phase, C_X^* is expressed by Eq. (6).

$$C_X^* = K_d C_{Xa} \quad (6)$$

$$K_d = \frac{H_w}{H_L} \quad (7)$$

where H_w and H_L are the Henry constants of oxygen to water and lipid, respectively. The concentration of unoxidized lipids C_F is divided by the total concentration of unoxidized and oxidized lipids C_{Ft} , and the oxygen concentration C_X in the oil droplet is divided by the oxygen concentration in the oil droplet that would be in equilibri-

um with the aqueous phase C_X^* . This allows Eqs. (3) and (5) to be rewritten as Eqs. (8) and (9), respectively.

$$\frac{dY}{d\theta} = -\frac{X}{\kappa_X + X} Y(1 - Y) \quad (8)$$

$$\frac{dX}{d\theta} = -\alpha \frac{X}{\kappa_X + X} Y(1 - Y) + \frac{1}{\phi} (1 - X) \quad (9)$$

where

$$Y = C_F/C_{Ft} \quad (10)$$

$$X = C_X/C_X^* \quad (11)$$

$$\theta = kC_{Ft}t \quad (12)$$

$$\alpha = C_{Ft}/C_X^* \quad (13)$$

$$\kappa_X = K_X/C_X^* \quad (14)$$

and

$$\phi = \frac{kC_{Ft}}{3k_i/r_p} \quad (15)$$

In these equations, Y is the fraction of unoxidized lipid, X is the oxygen saturation in the oil droplet, and θ is the dimensionless time. ϕ is a parameter representing the ratio of the oxidation rate to the oxygen transfer rate, and has the same meaning as the Theile modulus for solid catalysts²⁴. The changes in Y and X with time were calculated by solving Eqs. (8) and (9) using the classical 4th-order Runge-Kutta method and the implicit Euler method at appropriate increments of dimensionless time under the conditions listed in **Table 1**. Both methods gave practically the same values. The emulsion was assumed to be placed in atmospheric air. The density of DHA methyl ester at 25°C was used as the value of DHA ethyl ester, which was unavailable²⁵. The density of DHA ethyl ester at 65°C was estimated by extrapolating the temperature dependence of the density of DHA methyl ester²⁵. The H_L values at 25°C were estimated from the evaporation enthalpy at 25°C²⁶ using Eq. (16)²⁷.

$$H_L \times 10^{-4} = 7.536 \times 10^{-6} \cdot \Delta H_{\text{vap}} + 1.0782 \quad (16)$$

The H_L values at 65°C were estimated from the temperature dependence of H_L using Eq. (17)²⁷.

$$\frac{d \ln H_L}{d(1/T)} = \frac{\Delta H_{\text{sol}}}{R} \quad (17)$$

where ΔH_{sol} is the dissolution enthalpy of oxygen at 25°C²⁷. Dividing the reported value of oxygen partial pressure^{5, 7} by H_L gave K_X , and dividing the value obtained from the temperature dependence of the concentration-based rate constant⁵ by C_{Ft} gave k .

Table 1 Conditions used for the estimations performed with Eqs. (8) and (9).

		Methyl linoleate		DHA ethyl ester	
		294.47		356.54	
M	[g/mol]	294.47		356.54	
T	[°C]	25	65	25	65
$\rho \times 10^{-3}$	[g/m ³]	0.8820 ^[25]	0.8534 ^[25]	0.9162 ^[25]	0.8865
C_{Ft}	[mol/m ³]	2995	2898	2569	2486
$\Delta H_{\text{vap}} \times 10^{-3}$	[J/mol]	107.8	—	131.8	—
$\Delta H_{\text{sol}} \times 10^{-3}$	[J/mol]	—1	—1	—1	—1
$H_{\text{L}} \times 10^{-4}$	[m ³ ·Pa/mol]	1.89	1.98	2.07	2.17
$H_{\text{W}} \times 10^{-4}$	[m ³ ·Pa/mol]	7.98	12.0	7.98	12.0
K_{d}	[—]	4.22	6.05	3.86	5.53
C_{Xa}	[mol/m ³]	0.267	0.177	0.267	0.177
C_{X}^*	[mol/m ³]	1.13	1.07	1.03	0.98
$K_{\text{X}} \times 10^2$	[mol/m ³]	6.51	6.20	5.31	5.07
$k \times 10^8$	[m ³ /(mol·s)]	0.182	3.31	0.721	12.9
$k_{\text{f}} \times 10^{6[27]}$	[m/s]	1.0	1.0	1.0	1.0
$\alpha \times 10^{-3}$	[—]	2.66	2.70	2.50	2.54
$\kappa_{\text{X}} \times 10^2$	[—]	5.78	5.78	5.17	5.17

Fig. 1 Changes in (a) the fraction of unoxidized lipid Y and (b) the oxygen saturation X during the oxidation of methyl linoleate at $\phi = 1 \times 10^{-5}$ (—), $\phi = 1 \times 10^{-4}$ (---), $\phi = 1 \times 10^{-3}$ (— · —), $\phi = 2 \times 10^{-3}$ (····), and $\phi = 4 \times 10^{-3}$ (— · · ·).

3 Results and Discussion

3.1 Lipid oxidation under various conditions

The fraction of unoxidized lipid Y_0 and the oxygen saturation in the oil droplet X_0 at the dimensionless time of $\theta = 0$ were assumed to be 0.999 and 1.0, respectively. The effect of oil-droplet diameter on the oxidation of methyl linoleate in O/W emulsions at 25°C was estimated. **Figure 1** shows the changes in the fraction of unoxidized lipid Y and the oxygen saturation X for various ϕ values over dimensionless time.

The curves for the fraction of unoxidized lipid Y overlapped when $\phi \leq 1 \times 10^{-4}$, but as ϕ increased the curves gradually decreased. Oxygen saturation X decreased with

dimensionless time except when $\phi = 1 \times 10^{-5}$. No significant decrease in oxygen saturation was recognized when $\phi = 1 \times 10^{-5}$. Additionally, the X value increased again when the lipid was almost oxidized. An increase in X at the end of oxidation such as this indicates that oxygen consumption decreased. These results indicate that an increase in ϕ , that is, an increase in the oil-droplet radius r_p , restricts the mass transfer of oxygen through the oil-water interface to delay lipid oxidation. The dimensionless time required for the fraction of unoxidized lipid Y to reach 0.5, ($\theta_{0.5}$) was used to reflect the degree of delay in lipid oxidation.

The changes in Y and X for the oil droplets in the emulsions were determined using methyl linoleate with different

Fig. 2 Changes in (a) the fraction of unoxidized lipid Y and (b) the oxygen saturation X during the oxidation of methyl linoleate with initial fractions of unoxidized lipid (Y_0) of 0.999 (—), 0.995 (·····), and 0.950 (---).

Y_0 values as the oil phase at the initial oxygen saturation (X_0) of 1 (Fig. 2). As Y_0 decreased $\theta_{0.5}$ decreased as well, indicating that higher Y_0 values cause more delay in the oxidation. Moreover, the curves representing the changes in Y almost overlap when translated. This suggests that the initial fraction of unoxidized lipid Y_0 scarcely affects the oxidation rate, but does only the induction period for the oxidation. The extent of the decrease in oxygen saturation X did not depend on the Y_0 value, but lower Y_0 caused X to begin decreasing more rapidly and was linked to the lipid oxidation.

3.2 Diagram to evaluate factors affecting lipid oxidation

The effect of the mass transfer rate of oxygen through the oil-water interface on lipid oxidation was assessed by the ratio of $\theta_{0.5}$ at any ϕ to that for $\phi \rightarrow 0$ ($\theta_{0.5}(\phi \rightarrow 0)/\theta_{0.5}$), which means that the effect of oxygen mass transfer on the oxidation is negligible for infinitely small oil droplets. This index has the same meaning as the effectiveness coefficient for solid catalysts²⁴), and the ratio is equal to 1 when the mass transfer rate of oxygen is sufficiently faster than the lipid oxidation rate. When the oxygen transfer rate limits the oxidation rate, the denominator of the ratio increases. The longer the oxidation is delayed, the smaller the ratio becomes. We then calculated the $\theta_{0.5}(\phi \rightarrow 0)/\theta_{0.5}$ ratio for various ϕ values to determine the oil-droplet diameter that affects lipid oxidation. The time at which lipid oxidation was delayed was set to be $\theta_{0.5}(\phi \rightarrow 0)/\theta_{0.5} = 0.9$, and the ϕ value at that time was estimated.

The relationship between the $\theta_{0.5}(\phi \rightarrow 0)/\theta_{0.5}$ ratio and the ϕ values for methyl linoleate and DHA ethyl ester oxidation in the O/W emulsion was evaluated under conditions of 25°C, $Y_0 = 0.999$, and $X_0 = 1$ (Fig. 3). The ϕ for $\theta_{0.5}(\phi \rightarrow 0)/\theta_{0.5} = 0.9$ was 2.33×10^{-3} for methyl linoleate. Therefore, from Eq. (15), when the oil-droplet diameter is ≥ 2.56 mm, the effect of the oxygen transfer rate at the oil-water interface becomes apparent. The oil-droplet diameter at which

Fig. 3 Relationships between $\theta_{0.5}(\phi \rightarrow 0)/\theta_{0.5}$ and ϕ for the oxidation of methyl linoleate (—) and DHA ethyl ester (---) at 25°C in an O/W emulsion (ϕ represents the ratio of the oxidation rate to the oxygen-transfer rate, as defined by Eq. (15); $\theta_{0.5}(\phi \rightarrow 0)/\theta_{0.5}$ is the ratio of $\theta_{0.5}$ at any ϕ to $\theta_{0.5}$ for $\phi \rightarrow 0$).

the oxygen transfer rate at the interface began to affect methyl linoleate oxidation (at 65°C) was estimated to be 149 μm . A similar estimate was made for DHA ethyl ester, which is much easier to oxidize than methyl linoleate, and the oil-droplet diameters were determined to be 807 μm and 47 μm at 25°C and 65°C, respectively. In every case, the oil-droplet diameters were larger than those found in common food O/W emulsions.

The effect of the mass transfer rate of oxygen through the oil-water interface on the DHA ethyl ester oxidation rate at 65°C with various Y_0 values was then investigated

Ratio of oxidation rate to oxygen transfer rate, ϕ

Fig. 4 Relationships between $\theta_{0.5}(\phi \rightarrow 0)/\theta_{0.5}$ and ϕ for the oxidation of DHA ethyl esters with different Y_0 values at 65°C in an O/W emulsion (the definitions of ϕ and $\theta_{0.5}(\phi \rightarrow 0)/\theta_{0.5}$ are the same as those stated in Fig. 3). The initial fractions of unoxidized lipid (Y_0) used are 0.999 (—), 0.995 (-----), and 0.950 (---).

(Fig. 4). The ϕ values for $\theta_{0.5}(\phi \rightarrow 0)/\theta_{0.5} = 0.9$ were estimated to be 2.54×10^{-3} , 2.29×10^{-3} , and 1.78×10^{-3} for DHA ethyl esters with $Y_0 = 0.999$, 0.990 and 0.950, respectively. These ϕ values corresponded to oil-droplet diameters of 47 μm , 43 μm , and 33 μm , respectively. These estimates suggest that the mass transfer rate of oxygen through the oil-water interface does not significantly affect the lipid oxidation rate in O/W emulsions.

4 Conclusion

A model was proposed to evaluate how the mass transfer rate of oxygen through the oil-water interface impacted the lipid oxidation rate in O/W emulsions. Using the values reported for the partition coefficient of oxygen in oil, the mass transfer coefficient of oxygen moving through the oil-water interface, and the kinetic parameters for lipid oxidation, we estimated the oil-droplet diameter at which the mass transfer of oxygen through the oil-water interface began to affect the lipid oxidation. The effects of the oil type, temperature, and the initial fraction of unoxidized oil on the diameters were estimated. In every case, the oil-droplet diameter was larger than those seen in common O/W emulsions. Therefore, it can be concluded that the specific surface area of oil droplets does not affect the oil oxidation rate in common O/W emulsions.

Conflict of Interest

The authors declare that there are no conflicts of interest.

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