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Fundamental Studies on the Thawing of Frozen Fish—II

Kinetics and Prediction on Skipjack-meat Discolouration

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Abstract

The discolouration-rates in skipjack-meat were determined as function of storage temperatures. The discolouration of skipjack-meat under various storage conditions was confirmed to appear as a first-order reaction which depends upon the amount of remaining oxymyoglobin (MbO_2). The effect of storage temperature on the discolouration -rate was accounted for by Arrhenius equation. The prediction of discolouration of skipjack-meat was in good agreement with the results obtained from the thawing tests.

In the previous report[1], we reported on physical problems about thawing temperature, thawing rate and temperature distribution after thawing, which are the main factors affecting quality deterioration of frozen skipjack-meat during thawing.

Many investigators have studied the discolouration in tuna and skipjack meat during storage[2-7], but there is limited literature dealing with kinetics of discolouration of skipjack-meat during thawing.

The specific objects of this study were (1) to investigate the discolouration-rate in skipjack-meat as affected by storage temperature; (2) to predict the skipjack-meat discolouration after thawing, basing on kinetic results obtained; (3) to discuss the thawing condition suitable to the retention of the desired skipjack-meat colour after thawing.

Experimental

Materials

Cubes (ca. 1×1×1 cm) and fillets of skipjack-meat were used for storage tests. Cubes were prepared from a skipjack (1.5–2.0 kg) landed at Kagoshima port. Fillets were prepared from a skipjack (1.3–2.4 kg) landed at Makurazaki port, which was frozen at −40°C before preparation for experimental convenience. As a thawing sample the infinite slab (thermal center: 5 cm) of skipjack-meat was used, as described in the previous report[1].

Storage test

Each set of 5 cubes was put in the petri dish (dia. 9 cm) and stored at −25°, −20°,

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−15°, −10°, −5°, 0°, 10°, 20°, and 30°C respectively. Fillets were packaged individually in the sealed polyethylene bags and stored at −20°, −15°, −10°, 0°, 5°, and 10°C. A portion of cubes and that of fillets were taken out at some intervals and were submitted to meat-colour-measurment. Storage conditions were controlled at the range of ±1°C in the stocker.

Thawing test

The infinite slab of frozen skipjack meat was placed in a controlled stocker made for air thawing and in vacuum vessel made for vacuum thawing, as were described previously[1]. Air velocity in the stocker was set at 0 and 1 m/sec. Water-thawing was carried out in a small water box equipped with circulator. Water velocity was set at 0 and 2.5 m/min. Temperature of thawing mediums was controlled at 10°, 15°, 20°, and 25°C±1 in these systems. Thawing samples were frozen at −25°C. Thawing time was defined as the time for the thermal center (5 cm depth from surface) of the thawed sample getting to −2°C.

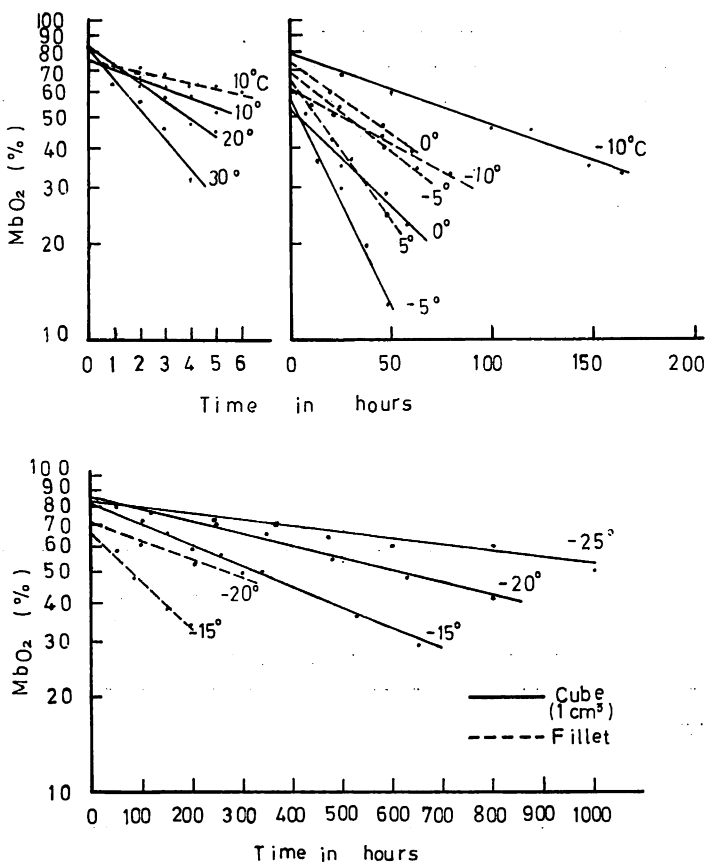

Fig. 1. Effect of temperature and time on decrease of MbO_2% in skipjack meat during storage.

Measurment of meat colour

Metmyoglobin formation (metMb%) was made by BITO's method[5]. The amount of remaining oxymyoglobin (MbO_2%) was determined from metMb% and was applied to analyses for the rate of discolouration.

Results

Order of reaction

The plot of the logarithm of MbO_2% in skipjack meat versus storage-time yieled straight line (Fig. 1), this indicated the first-order reaction. MATSUURA et al.[7] reported that autoxidation of myoglobin isolated from fish followed the first-order reaction. The results obtained in this study were in good agreement with their report.

Effect of storage temperature

The Arrhenius equation is often used to account for temperature effctive on the reaction rate. Basing on the rate constants, Arrhenius plot was prepared (Fig. 2).

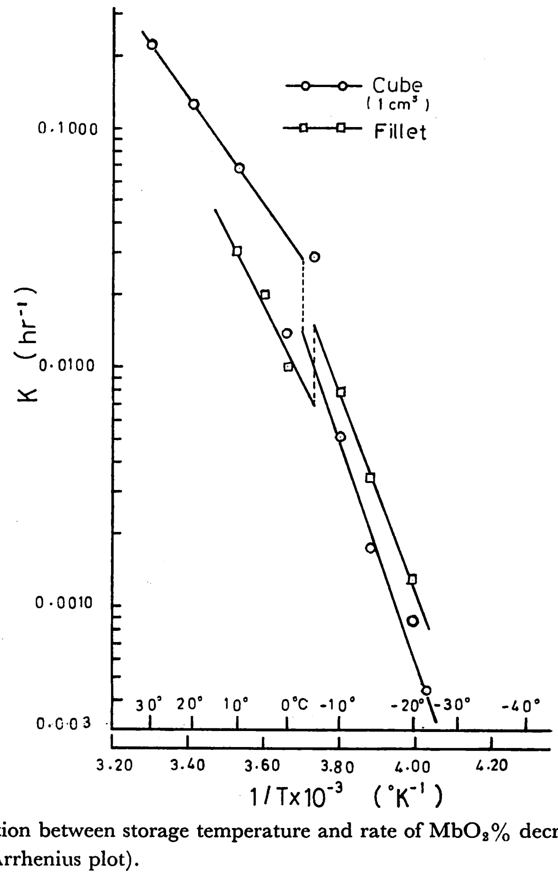

Fig. 2. Relation between storage temperature and rate of MbO_2% decrease in skipjack meat (Arrhenius plot).

The activation energy (*Ea*) and frequency factor (*A*) for the discolouration of skipjack-meat (cube & fillet) were presented in Table 1. These results indicate that *Ea* in fillet was greater than that in cube when storage temperature was above -2.7°C, and that smaller than that of cube when below -4.9°C. From Fig. 2 it appears that a change in kinetics of discolouration occurred within the range of 3° and 5°C. This is evident from the break in curve in this region. This result might be due to the phase change of water in skipjack meat.

Table 1. Activation energy (*Ea*) and frequency factor (*A*) of skipjack meat.

Sample	Temp.	*Ea* (Kcal/mol)	*A* (−)
Cube	above −2.7°C	10.181	4.954×10^{6}
(1 cm^3)	below −2.7°C	21.110	1.637×10^{15}
Fillet	above −4.9°C	14.040	1.995×10^{9}
	below −4.9°C	18.796	3.251×10^{18}

Prediction of MbO$_2$% after thawing

Provided that there is a fluctuating temperature in storage, it is possible to determine the change for a first-order reaction from the following equation[8)]

$$2.303\log\left(\frac{a}{a-x}\right)=A\int_0^t e^{-Ea/RT}dt \qquad \cdots\cdots(1)$$

Where, a=initial amount, $(a-x)$=amount remaining at passed time t, A=frequency factor, R=gas constant, Ea=energy of activation, T=absolute temperature.

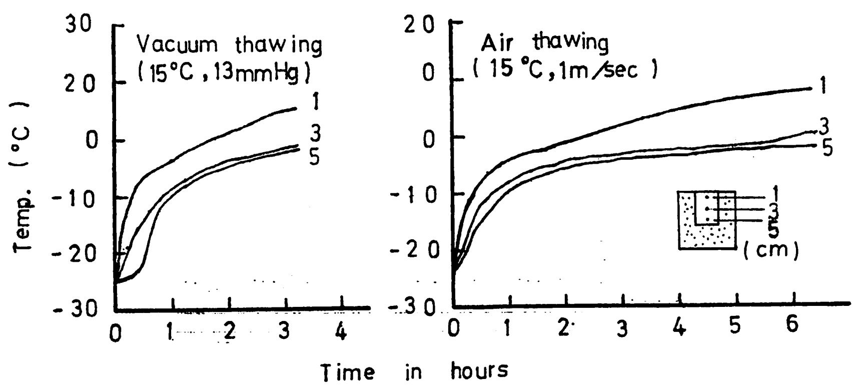

Fig. 3. Temperature changes at different portions of skipjack meat during thawing in vacuum and in air (1 m/sec) at 15°C.

Accordingly, equation (1) was applied to predict the discolouration of skipjack-meat after thawing. The $A\int_0^t e^{-Ea/RT}dt$ may be found graphically by plotting $Ae^{-Ea/RT}$ versus t and by determining the area, in certain units, below the resulted curve. For example, $Ae^{-Ea/RT}$ was shown in Table 2.

Table 2. $Ae^{-Ea/RT}$ determined for variation of temperature during thawing.

t (hrs)	θ* (°C)	A* (−)	$Ea/R \times 10^3$* (°K)	$Ae^{-Ea/RT}$ (−)
0	−25.0	3.251×10^{13}	9.469	8.696×10^{-4}
0.4	−8.5	〃	〃	9.277×10^{-3}
0.8	−5.0	〃	〃	1.489×10^{-2}
1.2	−3.0	1.995×10^{9}	7.073	9.823×10^{-3}
1.6	−1.0	〃	〃	9.905×10^{-3}
2.0	1.0	〃	〃	1.225×10^{-2}
2.4	2.5	〃	〃	1.411×10^{-2}
2.8	4.0	〃	〃	1.625×10^{-2}
3.2	5.0	〃	〃	1.744×10^{-2}

* Temperature at 1 cm depth during vacuum thawing (Shown in Fig. 3)

** Shown in Table 1., R=1.985 cal/°K mol (gas constant)

The area below the curve was 0.0346. The change occurring after thawing may be determined from $2.303 \log \frac{a}{a-x} = 1.0346$, or $\frac{a}{a-x} = 1.035$. Basing on kinetic results obtained with fillet. The discolouration in skipjack meat after thawing was predicted in good agreement with the experimental results. But, the prediction in case of cube didn't agree with experimental results.

Table 3. Experimental and calculated results of MbO_2% decrease in skipjack meat after thawing.

Thawing method	Measurement point	MbO_2%			
		Experimental		Calculated**	
		Initial	After thawing	Cube	Fillet
Vacuum thawing* (15°C, 13 mmHg)	1 cm depth	53.7 (±0)	52.3 (±0.3)	49.4	51.3
	3 cm depth	53.5 (±0.3)	52.5 (±0.3)	51.6	52.1
Air thawing* (15°C, 1 m/sec)	1 cm depth	53.7 (±0)	49.5 (±3.7)	42.6	49.2
	3 cm depth	53.5 (±0.3)	52.1 (±1.8)	47.3	50.1

* Thawing curves were shown in Fig. 3.

** Based on kinetic results obtained with cube (1 cm^3) and fillet of skipjack meat.

Discussion

Attempts were made to predict the discolouration in skipjack meat occurring after and during its thawing. Accordingly, the prediction was in good agreement with experimental results. This procedure was applied to discuss the thawing condition suitable for the desired skipjack-meat quality (colour) after thawing.

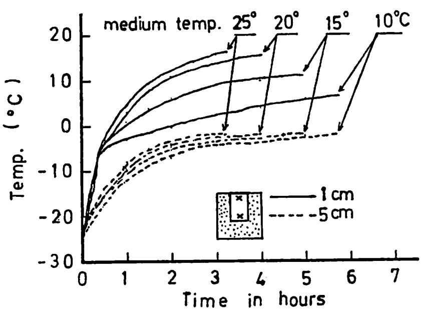

Fig. 4. Temperature changes at 1 cm depth from surface of skipjack meat during thawing in running water (2.5 m/min).

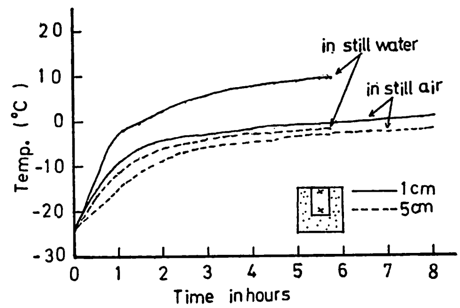

Fig. 5. Temperature changes at 1 cm depth from surface of skipjack meat during thawing in still water and still air.

The ratio of MbO_2% to the initial amount was calculated from both the thawing curves shown in Fig. 4 and 5, and the kinetic results of fillet, and it was shown in Table 4. These results indicated that skipjack-meat colour thawed in the still air and in vacuum was superior to those in water and blowing air. KOZIMA et al.[9] and BITO[10] have reported the same experimental results as the results predicted in this study.

Table 4. Ratio of MbO_2% after thawing to initial MbO_2% on water-, air- and vacuum-thawing.

Thawing method		Ratio of MbO_2% $\left(\frac{a}{a-x}\right)^*$ 10°C	15°C	20°C	25°C
Water	0 m/min	—	1.104	—	—
thawing**	2.5 m/min	1.082	1.104	1.117	1.091
Air	0 m/sec	—	1.072	—	—
thawing**	1.0 m/sec	—	1.112	—	—
Vacuum thawing***		1.046	1.036	1.032	1.034

* Calculated from temperature changes at 1 cm depth of skipjack meat by basing on kinetic results of fillet.

** Thawing curves were shown in Figs. 4 and 5.

*** Thawing curves were shown in Fig. 7 of previous report.[1]

It may be concluded that provided the thawing curve and initial amount of metMb% are given, it is possible to apply this procedure to predicting the skipjack-meat discolouration during thawing under various conditions. Further studies are needed along those lines.

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