Research Article

Thermal oxidative stability analysis of hoki and tuna oils by Differential Scanning Calorimetry and Thermogravimetry

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In this study, oxidative stability of hoki and tuna oils were measured at 80°C by Differential Scanning Calorimetry (DSC) and thermogravimetric analysis (TGA) under an air atmosphere. The onset time for oxidation (t_o) of hoki oil occurred earlier in the TGA (222.50 min) compared to DSC (640.83 min) as the sample gained weight prior to decomposition. Conversely, the t_o of tuna oil could not be recorded since tuna oil was rapidly oxidized. The predicted shelf life of hoki oil for onset of oxygen uptake and subsequent decomposition at 4°C, by Arrhenius extrapolation of TGA and DSC under different isothermal treatments were 0.56 and 1.39 years, respectively. Temperature programmed decomposition of hoki and tuna oils by TGA occurred in three thermal stages, suggesting a progressive degradation of polyunsaturated fatty acids (PUFA), monounsaturated fatty acids (MUFA), and saturated fatty acids (SFA), followed by volatilization of polymerization and pyrolysis products.

Practical applications: Fish oil has been marketed as dietary supplements and as an ingredient for food products. However, these products are susceptible to oxidation due to the high-PUFA content in fish oil. Oxidative and thermal stability of fish oil are important parameters in the processing and production of fish oil and fish oil fortified food products. These data can be used by fish oil and food manufacturers to optimize processing conditions for fish oil and food products fortified with fish oil. The oxidative stability of fish oils over temperature ranges and storage times can be measured by both isothermal and non-isothermal DSC and TGA analyses. These techniques are more rapid and provide continuous data compared to conventional shelf life studies and alternative instrumental methods. Shelf life of the fish oils can be predicted by an Arrhenius extrapolation from elevated isothermal DSC and TGA analyses.

Keywords: DSC / Fish oil / Lipids / Lipid oxidation / Oxidative stability / Shelf life / Thermal stability / TGA

Received: June 16, 2015 / Revised: September 2, 2015 / Accepted: September 8, 2015

DOI: 10.1002/ejlt.201500310

1 Introduction

The positive relationship between fish oil and human health has increased the consumption of fish oil and its market demand. Food manufacturers have incorporated fish oil into food products and marketed them as functional foods and supplementation products. Unfortunately, these products are very prone to oxidation since fish oil contains a high amount of polyunsaturated fatty acids (PUFA). Lipid oxidation of PUFA produces undesirable off-flavors, which in turn, gives a negative impact on sensory and customer acceptance of fish oil and fish oil fortified food products [1, 2]. Hence, oxidative and thermal stability of fish oil are important parameters in the processing and production of fish oil and fish oil-fortified food products.

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Abbreviations: AOM, active oxygen method; **DHA,** docosahexaenoic acid; **DSC,** differential scanning calorimetry; E_a, activation energy; **EPA,** eicosapentaenoic acid; **FFA,** free fatty acid(s); **MUFA,** monounsaturated fatty acid(s); **PUFA,** polyunsaturated fatty acid(s); **TG,** triglyceride(s); **TGA,** thermogravimetric analysis; R_{WG}, maximum rate of weight gain; **SFA,** saturated fatty acid(s); t_{mdr}, time of maximum rate of thermal decomposition (DSC) or rate of weight gain (TGA); t_{max}, time for maximum thermal decomposition (DSC) or weight gain (TGA); t_o, onset time for oxidation; T_{OD}, onset temperature for thermal decomposition; W_{max}, maximum weight gain

Differential Scanning Calorimetry (DSC) and thermogravimetric analysis (TGA) can be used to measure the quality of fish oil [3, 4]. Both instruments require small sample sizes and simple operation protocols, do not require any chemicals or solvents, can provide reproducible data, and have a good correlation with other oxidative stability methods. TGA can be used to measure the lipid oxidation process through weight gain or weight loss of a sample due to oxygen uptake or thermal decomposition [5]. The onset time or induction period measured by TGA and DSC indicates the beginning of lipid oxidation and change in quality of the oil, respectively [6].

Hoki (*Macruronus novaezelandiae*) is a hake species in the family of Merlucciidae and is reported as the largest fishery in New Zealand [7]. It is estimated that the total catch of hoki in 2011–2012 was 130 000 metric tonnes [8]. Hoki oil is sold in liquid and fish oil capsule form as dietary supplementation products. It contains 12.70% of docosahexaenoic acid (DHA) and 8.19% eicosapentaenoic acid (EPA) [9]. Tuna is a highly migratory pelagic fish under the family of Scombridae and has been marketed as fresh, cooked, or canned products. Tuna oil has been incorporated in infant formula and food products [10] and contains 26.86% DHA and 6.35% EPA [9]. The objectives of the present study are to investigate the thermal oxidative stability of hoki and tuna oils and to predict the shelf life of hoki oil using accelerated temperatures.

2 Materials and methods

2.1 Materials

Hoki (*M. novaezelandiae*) and tuna oils were supplied by SeaDragon Marine Oils, Nelson, New Zealand. The oils had been extracted from the skin, bones, and offals of hoki and tuna fish. The oils, previously kept at −20°C, were thawed at room temperature prior to thermal analysis.

2.2 Oxidative stability of hoki and tuna oils at 80°C by DSC and TGA (isothermal)

The sample (5–8 mg) was weighed into a pre-weighed Tzero (TA Instruments Ltd., New Castle, USA) open aluminum pan. A blank open aluminum pan was used as a reference pan. Calibration was carried out according to the DSC instrument manual (TA Instruments Ltd.) using indium. The sample and reference pans were placed in the DSC (Q2000; TA Instruments Ltd.) cell and isothermally heated at 80°C under an air atmosphere. An onset time (t_o) of the DSC oxidation reaction was measured from the intersection of the extrapolated baseline and tangent line (leading edge) of the exotherm as reported by Tan et al. [11]. The time for maximum reaction (heat flow) was recorded as t_{max}. The time for maximum rate of thermal decomposition (t_{mdr}) was recorded from the derivative of the heat flow curve.

The oxidative stability of the oils was also determined by TGA (Q50, TA Instruments Ltd.). A sample (10–25 mg) was placed into a platinum pan (TA Instruments Ltd.) and heated at 80°C under an air atmosphere. Calibration was conducted according to the TGA instrument manual (TA Instruments Ltd.). The onset time (t_o) or induction period was measured from the extrapolation of the baseline and upward portion of the curve as reported by Mikula and Khayat [12]. A maximum weight gained (W_{max}) and time for maximum weight gained (t_{max}) were recorded. The time for maximum rate of weight gain (t_{mdr}) was recorded from the derivative of the weight gain.

Data of DSC and TGA analyses were analyzed and plotted using TA Universal Analysis 2000 software (TA Instruments Ltd.). The data were normalized based on the sample weight.

2.3 Effects of temperature on oxidative stability of hoki oil by DSC and TGA (isothermal)

Analysis of oxidative stability of hoki oil was repeated at 60 and 70°C using DSC and at 50, 60, and 70°C using TGA. The t_o, t_{max}, and t_{mdr} for thermal decomposition (DSC) and weight gained (TGA) were recorded. The maximum rate of weight gain (R_{WG}) of the TGA was determined from the slope of an upward portion of the curve according to Mikula and Khayat [12].

Arrhenius plots were plotted using the onset time (t_o) data of the DSC and TGA analyses. The shelf life and activation energy (E_a) of the sample were predicted using the following Arrhenius equations according to SETARAM [13].

$$\text{Ln Onset} = A(1/T) + B$$

$$E_a = A \times R$$

where T = temperature (°K), A = slope of an Arrhenius plot, B = intercept on the Y axis, E_a = activation energy, and R = gas constant (8.314 J/mol/°K)

2.4 Thermal decomposition of hoki and tuna oil by TGA (non-isothermal)

Approximately, 10–25 mg of sample was placed into the TGA platinum pan and the sample was heated from 25 to 700°C at 2°C/min in an air atmosphere. Data on the percentage of weight changes were obtained from the TA Universal Analysis 2000 software as mentioned above and further analyzed using a Microsoft Excel spread sheet. The onset temperature for thermal decomposition (T_{OD}) was extrapolated from the thermal decomposition curve according to Dweck and Sampaio [14].

2.5 Statistical analysis

All measurements were carried out in triplicate and data were reported as mean ± standard deviation (SD). Statistical data

analyses were carried out using IBM SPSS Statistics version 20 software. A univariate, multivariate, one way ANOVA, and Tukey test were carried out for significant difference determination between samples at $p < 0.05$.

3 Results and Discussion

3.1 Oxidative stability of hoki and tuna oils at 80°C (isothermal)

Figure 1a and b shows the DSC and TGA oxidative stability curves of hoki and tuna oils at 80°C. Oxidation of hoki oil occurred earlier in the TGA than DSC as the sample gained weight prior to thermal decomposition. Onset times for oxidation (t_o) of tuna oil could not be recorded as it was rapidly oxidized (Fig. 1b). The primary oxidation products (hydroperoxides) of tuna oil were rapidly decomposed, where their decomposition rate was faster than the formation rate. Rapid decomposition was previously reported for menhaden, bonito and sardine oils [15], crude herring oil [16], unrefined pollock oil [17], and fish oil supplements [1]. In these studies, the decomposition rates of hydroperoxides of fish oils were also faster than their formation rates.

The trend for time (t_{max}) for maximum thermal decomposition (DSC) and weight gained (TGA) of hoki oil was similar to that of its onset time (t_o), where the t_{max} for TGA was earlier than the t_{max} for DSC (Table 1). Contrastingly, the t_{max} of tuna oil for thermal decomposition (DSC) was earlier than the maximum weight gained (TGA). Both t_{max} (TGA and DSC) of tuna oil were significantly earlier than hoki oil ($p < 0.05$). The t_{max} can also be used as an indicator to compare oil stability, especially when the t_o could not be recorded or detected. The time for maximum rate of thermal decomposition (t_{mdr}) of tuna oil (DSC) was earlier than the maximum rate for weight gained (TGA). A maximum weight gained (W_{max}) of tuna oil was significantly higher than hoki oil ($p < 0.05$). Hence, weight gain was not seen prior to decomposition commencing (Fig. 1b) but was

Table 1. Oxidative stability of hoki and tuna oils

Instrument	Parameter	Hoki	Tuna
DSC	t_o (min)	640.83 ± 32.63[a]	nr
	t_{max} (min)	825.00 ± 21.65[a]	121.41 ± 7.21[b]
	t_{mdr} (min)	721.51 ± 20.91[a]	8.17 ± 1.78[b]
TGA	t_o (min)	222.50 ± 19.84[a]	nr
	t_{max} (min)	649.56 ± 43.90[a]	417.37 ± 33.57[b]
	t_{mdr} (min)	310.80 ± 29.3[a]	14.94 ± 1.33[b]
	W_{max} (%)	2.87 ± 0.16[b]	3.78 ± 0.30[a]

Mean ± SD, $n = 3$.
nr, could not be recorded; t_o, onset time for oxidation; t_{max}, time for maximum thermal decomposition (DSC) or weight gain (TGA); t_{mdr}, time for maximum rate of thermal decomposition (DSC) or rate of weight gain (TGA) obtained from the respective derivative curve; and W_{max}, maximum weight gain.
[a,b]Values with different superscripts within a row are significantly different at $p < 0.05$.

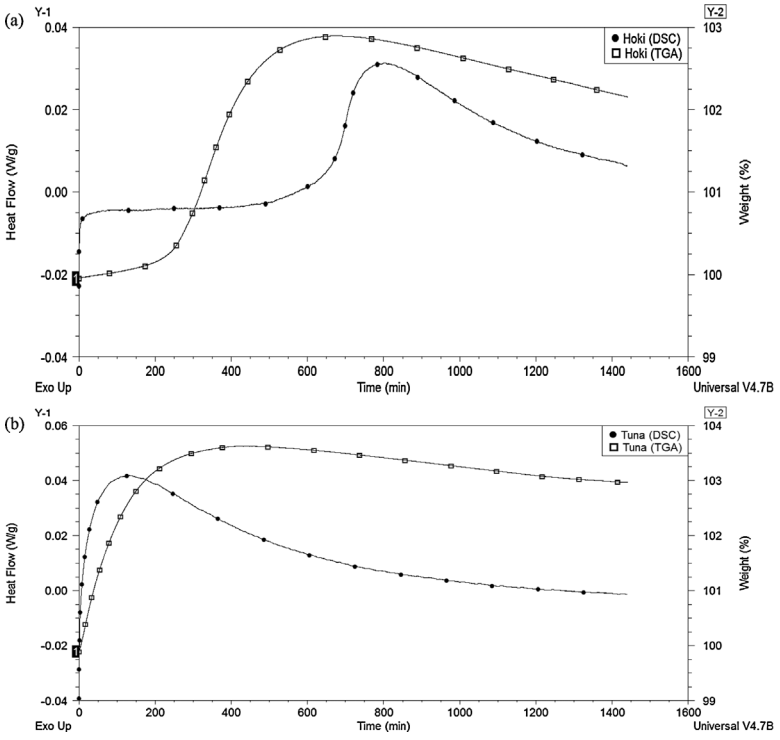

Figure 1. Oxidative stability of hoki and tuna oils by DSC and TGA at 80°C.

reached later in the TGA curve (Table 1) when more stable triglycerides (TG) were being oxidized.

The results at 80°C showed that tuna oil is more susceptible to thermal oxidation and rapidly oxidized probably since it contains a high percentage of PUFA, mainly DHA. Furthermore, our earlier study [9] found a higher value of free fatty acids (FFA) in tuna oil (3.67%) compared to the hoki oil (1.23%). Tuna oil contains TG with multiple PUFA [18–20] that make it more susceptible to oxidation due to more PUFA occupying *sn*-1,3 positions. Hoshina et al. [21] heated the oils with TG structures of PPL, PPP/PPL/PLL (1:1:1), PPP/PPL (1:1), and PPP/LLL (2:1), containing palmitic acid (16:0) and linoleic acid (18:2n6) at 150 and 180°C. They found FFA and carbonyl compounds in the oils increased with heating time and the values of these compounds were higher in the PPP/LLL than in other oils after 12 h heating.

Tan et al. [11] reported that the onset times measured by isothermal DSC for vegetable oils with a higher unsaturated fatty acid content were lower compared to the oils with more saturated fatty acids (SFA). Other studies on oxidative stability of vegetable oils showed similar results [22, 23]. Tuna oil with a high percentage of FFA is more susceptible to oxidation and in agreement with Tan et al. [22] who suggested that unbound fatty acids are less stable to oxidation than fatty acids bound to glycerol molecules.

3.2 Effects of changing the isothermal temperature on oxidative stability of hoki oil

3.2.1 DSC

The effect of heating temperature on oxidative stability of hoki oil by DSC is illustrated in Fig. 2. The t_o, t_{max}, and t_{mdr} of hoki oil were inversely correlated with heating temperature (Table 2). The results of the present study are in accordance with previous studies on vegetable oils by DSC [11, 22, 23]. Cross [24] reported a good correlation coefficient ($r = 0.974$) between a conventional Active Oxygen Method (AOM) and DSC, indicating that DSC is a rapid method to measure oils stability, where DSC can carry out a determination of oil stability that would require 14 days via AOM, in less than 4 h.

Table 2. Effects of temperature on oxidative stability of hoki oil by DSC

Time (min)	60°C	70°C	80°C
t_o	2990.00	1350.00	680.00
t_{max}	3458.45	1650.02	870.33
t_{mdr}	3128.25	1483.65	745.88

$n = 1$.
t_o, onset time for oxidation; t_{max}, time for maximum thermal decomposition (DSC); t_{mdr}, time for maximum rate of thermal decomposition (DSC) obtained from the derivative curve.

Arain et al. [25] also reported a good correlation ($r > 0.99$) on the oxidative stability of plant oils measured by DSC and Rancimat.

3.2.2 TGA

Figure 3 illustrates the effect of temperature on the oxidative stability of hoki oil via TGA. The times recorded for t_o, t_{max}, t_{mdr}, and W_{max} of hoki oil were inversely correlated with heating temperature (Table 3), and in accordance with Frankel [26] suggests that the oxidation rate of lipid is exponentially associated with temperature.

At 80°C, hydroperoxides were extensively produced but they are rapidly decomposed since they are not stable at high temperatures [1, 16]. This finding shows that the hydroperoxide formation and the decomposition of hoki oil reached an equilibrium level faster as the temperature increased as illustrated in Fig. 3 and in accordance with a PV plot against time at different heating temperatures for linseed oil [27]. On the other hand, the maximum rate of weight gained (R_{WG}) increased with increasing temperature. The results of the effect of temperature on oxidative stability of hoki oil in the present study are in accordance with Mikula and Khayat [12] findings on soybean oil.

The maximum weight gained (W_{max}) for hoki oil decreased with heating temperature since hydroperoxides do not accumulate but rapidly decompose at high temperatures. This finding is supported by an earlier t_{max} of hoki oil at a higher heating temperature compared to the lower

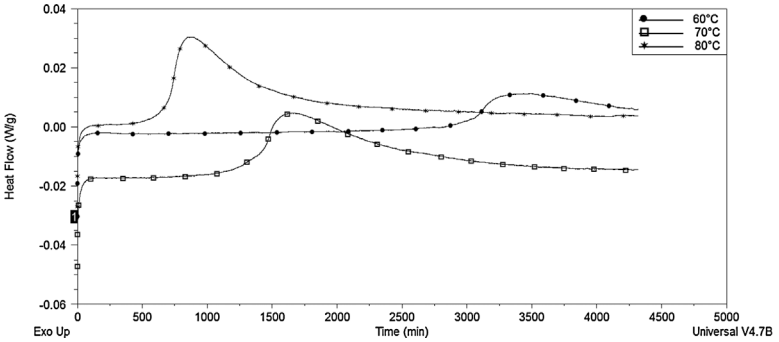

Figure 2. Oxidative stability of hoki oil at 60°C, 70°C and 80°C by DSC.

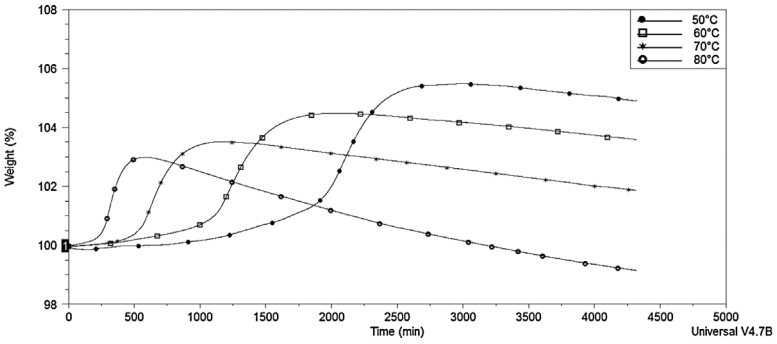

Figure 3. Oxidative stability of hoki oil at 50°C, 60°C, 70°C and 80°C by TGA.

temperature. The hydroperoxides started to decompose after they reached the t_{max} and the secondary oxidation products, such as aldehydes, ketones, and alcohol were produced.

Both DSC (Table 2) and TGA (Table 3) data on the effects of temperature on oxidative stability of hoki oil follow the Q_{10} law on the relationship between temperature and rate of chemical reaction. The t_o, t_{max}, and t_{mdr} of hoki oil were reduced by approximately half with an increase of 10°C. A similar finding on reduction of onset time for oxidation (t_o) of vegetable oils measured by DSC was reported in previous studies [11, 23, 25].

3.2.3 Shelf life prediction

Data for onset time for oxidation (t_o) via DSC and TGA at 60, 70, and 80°C (Tables 2 and 3) were used to construct Arrhenius plots for hoki oil. By using the Arrhenius plots, the shelf life of hoki oil at a lower temperature can be predicted. The predicted times (Fig. 4) for safe storage of hoki oil prior to oxygen uptake (TGA) and resulting rancidity (DSC) at 4°C are 0.56 and 1.39 years, respectively. The predicted shelf life of hoki oil via TGA was earlier than DSC as the oil gained weight due to oxygen uptake and formation of primary oxidation products prior to decomposition of primary oxidation products. Afterwards, the formation of secondary products, which cause rancidity of oils, occurs and reduces the sensory acceptance.

Activation energies (E_a) of hoki oil obtained from DSC and TGA were 73.46 and 67.75 kJ/mol, respectively. The E_a values of hoki oil obtained from TGA were lower than DSC since the oil gained weight prior to thermal decomposition at all experimental temperatures. This observation is illustrated by an earlier t_o of hoki oil via TGA than DSC (Table 1). Adhvaryu et al. [28] suggested E_a is related to the degree of PUFA in oils, and lower E_a values were observed for oils with higher PUFA contents since less energy is required to initiate oxidation.

The results of the present study show that the prediction of shelf life of the fish oil can be successfully carried out by an accelerated heating technique at an elevated temperature using DSC and TGA. DSC and TGA can be used to replace conventional shelf life prediction methods. Previous studies showed the onset times for oxidation of oils measured by the DSC technique correlated well with AOM [24] and Rancimat [23, 25, 29] methods.

3.3 Thermal decomposition of hoki and tuna oils by TGA (non-isothermal)

Figure 5a and b shows the thermal decomposition process for hoki and tuna oils. The figures show the weight loss and the

Table 3. Effects of temperature on the oxidative stability of hoki oil by TGA

Parameter	50°C	60°C	70°C	80°C
t_o (min)	1790.00	1010.00	485.00	210.00
$R_{WG} \times 10^{-3}$ (%/min)	7.51	7.99	9.72	14.71
t_{max} (min)	2996.42	1996.54	1137.45	570.73
t_{mdr} (min)	2079.24	1218.52	634.45	315.52
W_{max} (%)	5.50	4.50	3.55	3.01

$n = 1$.

t_o, onset time for oxidation; R_{WG}, maximum rate of weight gain; t_{max}, time for maximum weight gain (TGA); t_{mdr}, time for maximum rate of weight gain obtained from the derivative curve; W_{max}, maximum weight gain.

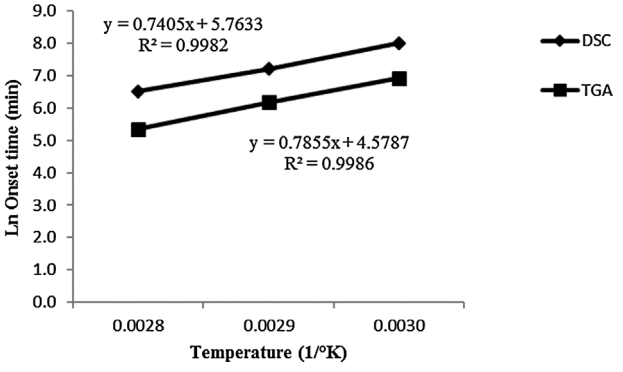

Figure 4. The Arrhenius plot for oxidation and decomposition onset times of hoki oil by DSC and TGA.

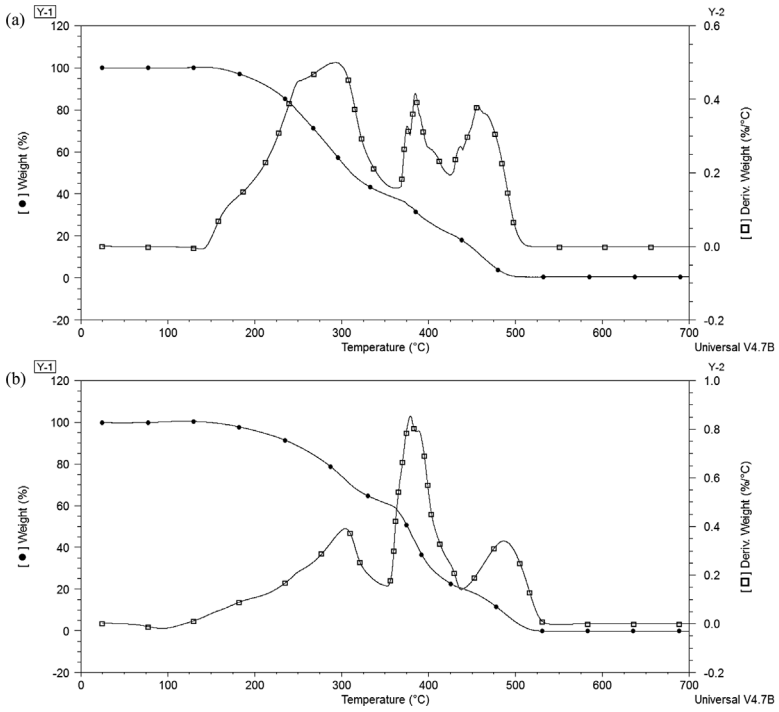

Figure 5. Thermal decomposition of (a) hoki and (b) tuna oils by TGA.

rate of weight loss during thermal decomposition of these fish oils from 25 to 700°C by TGA. The onset temperature for thermal decomposition (T_{OD}), recorded from the thermograms ($n = 3$) of hoki (172.67 ± 2.31°C) was not significantly different from tuna oil (168.33 ± 2.89°C; $p > 0.05$). The T_{OD} of the fish oils in the present study were earlier than olive (287.99°C) and corn (305.95°C) oils in Dweck and Sampaio [14].

A comparison of change in weight as a function of temperature is illustrated in Fig. 6 where the TGA thermograms of hoki and tuna oils are presented in an overlay. At a temperature range of 75–125°C, there was a slight increase in weight (0.6%) in tuna oil due to oxygen uptake or absorption. A slight increase (0.1%) in the initial sample weight was observed slightly later in hoki oil (between 100 and 150°C). Tuna oil has more PUFA (42.57 ± 0.04%) than hoki oil (28.79 ± 1.25%; [9]) that may decompose earlier. An increase in the sample weight occurred at the beginning of oxidation as the oil gained weight due to oxygen uptake, and formation of hydroperoxides.

The overall weight of tuna oil was significantly different from hoki oil in the temperature ranges from 275 to 375°C and 475 to 500°C (Fig. 6) possibly due to the high-SFA content (32.34%) in tuna compared to hoki (24.05%; [9]), being more resistant to heat and formation or build up of polymers, which are stable at this temperature range. Sathivel et al. [3] reported that the length and degree of unsaturation, and the intermolecular dispersion forces influenced heat decomposition of fatty acids. Fatty acids with a longer carbon chain are more stable toward thermal decomposition than a short chain fatty acid due to an increase of intermolecular dispersion forces [30].

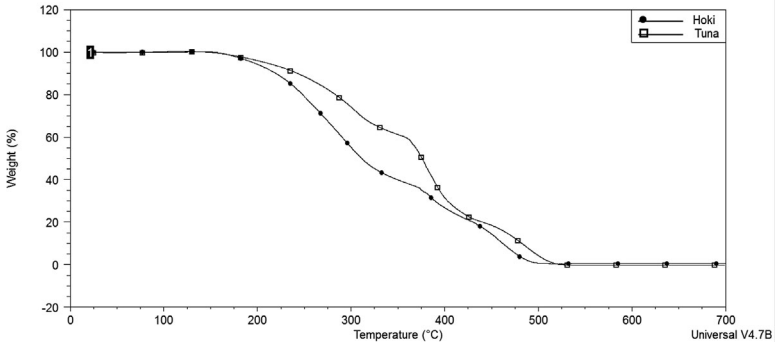

Figure 6. Comparison of weight loss of hoki and tuna oils as a function of temperature.

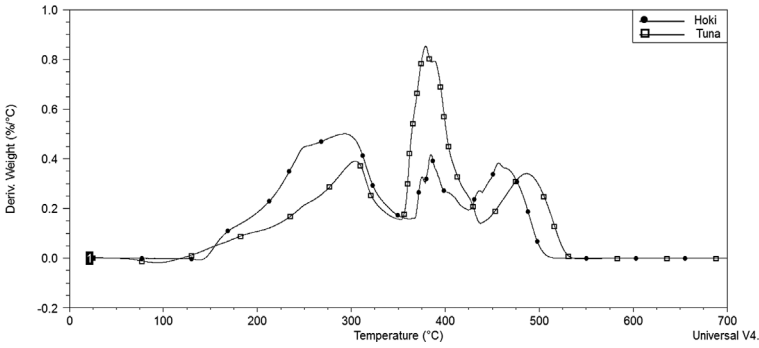

Figure 7. Rate of weight loss of hoki and tuna oils measured by TGA.

The findings of the present study on the increasing weight loss due to temperature increases are in accordance with previous works on pink and red salmon oils (200 to 450°C; [4]), unrefined salmon oil (250 to 550°C; [31]), and unrefined pollock oil (200 to 535°C; [17]).

In the present study, thermal decomposition of the fish oils occurred in three temperature ranges, illustrated in Fig. 7 as an overlay of the derivative curves from Fig. 5a and b. These findings are in accordance with previous studies on vegetable [32, 33] and fish [34] oils.

The temperature range of each stage of the thermal decomposition is shown in Table 4. The T_{OD} of the fish oils occurred later than the initial onset temperature of stage 1 (Table 4) as calculated from the respective derivative curve (Fig. 5a and b) since the oils gained weight due to peroxide formation prior to decomposition. The first, second, and third stages in the present study may represent a progressive degradation of PUFA, MUFA, and SFA, followed by volatilization of polymerization and pyrolysis products. This supports the delay in weight loss for tuna oil in the temperature range of 275 to 375°C (Fig. 6) due to higher SFA content compared with the hoki oils.

Thermal decomposition of PUFA (stage 1) of tuna oil started at a lower temperature (94.24°C) compared to the hoki oil in the present study. This correlates with high-PUFA content, mainly DHA and also PUFA positional distribution in tuna oil TG structures where the lower temperature range for thermal decomposition of PUFA of tuna oil correlates with the rapid thermal decomposition of PUFA and hydroperoxide formation as measured by isothermal DSC reported in Section 3.1. Tuna oil may have two or three moles of DHA per TG as reported in previous studies on TG molecular analysis of tuna oil [19, 20]. Wijesundera et al. [35] reported the superior oxidative stability of DHA at the *sn*-2 positional distribution evidenced by a faster degradation of DHA in PPD compared to PDP (where P is palmitic acid and D is DHA). Here a relatively more rapid decomposition for tuna oil may be partially explained by our previous finding where the percentage ratio of DHA at *sn*-2 to *sn*-1,3 position was lower than for hoki oil [36]. Tuna oil also has a larger area under the peaks of stage 2 compared to hoki oil, probably due to an increase of SFA content, although decomposition in this region begins marginally earlier (Table 4).

Table 4. Temperature range of thermal decomposition stages of hoki and tuna oils

Fish oil	Stage 1[a] (°C)	Stage 2[a] (°C)	Stage 3[a] (°C)
Hoki	139.91–360.48[b]	360.48–425.91[b]	425.91–522.19[c]
Tuna	94.24–349.65[c]	349.65–436.51[b]	436.51–537.97[b]

[a]Average temperature taken from three replicates ($n = 3$).
[b,c]Values with different superscripts within a column are significantly different at $p < 0.05$ for the initial temperature of each stage.

4 Conclusion

The fish oils in the present study are susceptible to thermal oxidation due to their high-unsaturated fatty acid content. The t_o of hoki oil occurred earlier in the TGA than DSC as samples gained weight prior to thermal decomposition. On the other hand, the t_o for tuna oil could not be recorded as it was rapidly decomposed at the beginning of oxidation at 80°C and then became more stable after it reached the equilibrium between formation and decomposition of hydroperoxides, possibly initially due to its high-PUFA content followed by a higher SFA content, respectively.

DSC and TGA can be used as rapid methods to assess oxidative stability of oils. The times for onset of oxidation (t_o), time for maximum thermal decomposition or weight gained (t_{max}), maximum rate of thermal decomposition or rate of weight gained (t_{mdr}), and maximum weight gained (W_{max}) were inversely correlated with heating temperature. Both measurement of oxidative stability of fish oils by DSC and TGA follow the Q_{10} law on the relationship between temperature and rate of chemical reaction. Prediction of shelf life of the fish oils is possible by an Arrhenius extrapolation from elevated isothermal DSC and TGA analyses. The thermal decomposition process of the fish oils over a

temperature range of 25 to 700°C occurred in three stages or temperature ranges, possibly related to degradation of PUFA, MUFA, and SFA and polymerization and volatilization of the products. Differences between the thermal behavior of the fish oils were consistent with major fatty acid compositional differences. For example, tuna oil commenced decomposition earlier than the hoki oil due to higher PUFA but was more stable at high temperature as it contains more SFA.

We would like to thank SeaDragon Marine Oils Ltd., New Zealand, for the fish oil samples, Assoc. Prof. Stephen Moratti and Mr. Ian Stewart for their technical advice and assistance in the DSC and TGA analyses.

The authors have declared no conflict of interest.

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