J Am Oil Chem Soc (2011) 88:1641–1648
DOI 10.1007/s11746-011-1824-x

ORIGINAL PAPER

Effects of Oil Extraction Methods on Physical and Chemical Properties of Red Salmon Oils (*Oncorhynchus nerka*)

Huaixia Yin · Kevin Mis Solval · Jiaqi Huang · Peter J. Bechtel · Subramaniam Sathivel

Received: 19 October 2010 / Revised: 7 March 2011 / Accepted: 4 April 2011 / Published online: 28 April 2011

Abstract The following four methods were used to extract salmon oil from red salmon heads: RS1 involved a mixture of ground red salmon heads and water, no heat treatment, and centrifugation; RS2 involved ground red salmon heads (no water added), heat treatment, and centrifugation; RS3 involved a mixture of ground red salmon heads and water, heat treatment, and centrifugation; and RS4 involved ground red salmon heads, enzymatic hydrolysis, enzyme inactivation by heat and centrifugation. The four extracted oil samples were evaluated for chemical, thermal, and rheological physical properties. The RS4 process recovered significantly higher amounts of crude oil from red salmon heads than the other three extraction methods, while containing a higher % of free fatty acids and higher peroxide values than RS1, RS2, and RS3 oils. Oleic acid, eicosenoic acid, EPA, and DHA were the predominant fatty acids accounting for about 60% of all unsaturated fatty acids. The RS1, RS2, RS3, and RS4 extractions contained 9.3, 9.05, 9.35, and 9.45% of EPA and 8.8, 8.55, 9.0, and 9.1% of DHA in the oil, respectively. Weight losses of the oils increased with increasing temperatures between 200 and 500 °C. The % weight losses at 500 °C were 94.50, 94.58, 94.94, and 95.47% for RS2, RS1, RS3, and RS4, respectively. The apparent viscosities of all the oil samples decreased with the increases in the temperature. The RS1 extract was more viscous ($P < 0.05$) than those of RS2, RS3, and RS4 between 0 and 25 °C.

Keywords Red salmon oil · Extraction methods · Rheological properties · Thermal properties

H. Yin · K. M. Solval
Department of Food Science, Louisiana State University Agricultural Center, Baton Rouge, LA 70803-4300, USA

J. Huang
Fishery Industrial Technology Center, University of Alaska Fairbanks, School of Fisheries & Ocean Sciences, Kodiak, AK 99615, USA

P. J. Bechtel
USDA/ARS Subarctic Research Unit, University of Alaska Fairbanks, Kodiak, AK 99615, USA

S. Sathivel (✉)
Department of Food Science and Department of Biological and Agricultural Engineering, Louisiana State University Agricultural Center, Baton Rouge, LA 70803-4300, USA
e-mail: ssathivel@agcenter.lsu.edu

Introduction

People are becoming more aware of the health benefits of dietary marine omega-3 fatty acids. Fish oils have been claimed to help maintain human health and maintain heart and vascular health in humans [1, 2]. In 2004, sales of fish oil supplements were valued at $310 million, which was about a tenfold increase compared to the previous decade [3]. In 2006, 99,000 metric tons of salmon byproducts were generated from 331,798 metric tons of salmon harvested in Alaska [4]. Much of the oil in the red salmon is found in the heads (15–18% lipids). The quality of the oil can be increased by processing to remove undesirable components, such as free fatty acids, off-odors, and peroxides.

Producing and purifying oil from red salmon heads for the growing fish oil market can benefit the salmon industry. Extracting oil from red salmon heads can add value to red salmon byproducts, which are often underutilized. Small fish oil processors and entrepreneurs are interested in establishing small scale, cost effective oil extraction, clarification, and stabilization methods for salmon oils.

A number of methods including rendering, enzymatic hydrolysis, chemical extraction, mechanical pressing, and use of centrifugal force can be used for the extraction of fish oil. Unpurified fish oil contains a variety of impurities such as free fatty acids, primary oxidation products, minerals, pigments, moisture, phospholipids, and insoluble impurities that reduce the oil quality. The amounts of these impurities present in the oil depend on the fish oil extraction method. A series of refining processes are normally used to remove these impurities, and for degumming, deodorization, bleaching, and neutralization. Operating costs associated with these refining steps are loss of oil during processing and the generation of soap stock waste streams from the free fatty acids removed during the neutralization processing step [5–8]. By altering the initial extracting procedures it may be possible to produce oils that contain fewer impurities and thus reduce the need for further processing of the oil. However, there is little literature on the effects of different extraction methods on salmon oil quality.

The amounts of impurities present in the red salmon oil influence the rheological and thermal properties of the oils [9, 10]. Knowledge of the rheological properties at different temperatures can be used to solve problems related to the transfer or movement of bulk quantities of liquids, i.e., at low temperatures and flow rates, impurities in the oils can precipitate on the pipe walls causing pressure and other problems in the delivery system. Thermogravimetric analysis (TG) can be used to measure the thermal stability of red salmon oil and is capable of depicting the mass changes of red salmon oils as a function of temperature during thermal processes. The objective of this study was to compare the effects of different extraction methods on the chemical, nutritional, thermal, and rheological properties of red salmon oil extracted from red salmon heads.

Experimental Procedures

Red Salmon Oil Production

Red salmon heads were obtained in three separated batches from a commercial fish processing plant in Kodiak, AK, USA. The heads were frozen at −40 °C until shipped overnight to Louisiana and kept at −40 °C until thawed for processing. Thawed salmon heads were finely ground in a Butcher–Boy grinder. Four methods were used to extract the red salmon oil: (1) water was added to the red salmon heads (water: minced head, 1:1 v/w) and the mixture was centrifuged for 30 min at 7,520×*g*; (2) minced red salmon heads were cooked for 30 min at 75 °C (no water) and then centrifuged for 30 min at 7,520×*g*; (3) Water was added to the red salmon heads (water: minced head, 1:1 v/w) and the mixture was cooked for 30 min at 75 °C, centrifuged for 30 min at 7,520×*g*; and (4) 0.1% (w/w) of Alcalase (Novozyme Corp., >0.24 U/g) (no water) was added to the ground red salmon heads, which were then heated for 75 min at 50 °C. When the time was up, samples were placed in an 85 °C water bath for 15 min, and then they were centrifuged for 30 min at 7,520×*g*. The resulting crude oil was collected and stored at −23 °C until used. Three experimental crude oil extractions by each method were conducted.

Analysis of PV, FFA, Water Activity (a_w), Yield, and Color of Red Salmon Oil

The peroxide values (PV) of the red salmon oil samples were measured by titration according to an AOAC method [11]. The results were expressed in terms of milliequivalent of peroxide per kilogram of oil. FFA content was determined using titration according to an AOAC method [12]. The percentage of FFA was expressed as oleic acid equivalents. A calibrated Rotronic water activity meter (AwQUICK, Rotronic Instrument Corp., Huntington, New York, USA) was used to measure the water activity of the salmon oils at 25 °C. Color of the red salmon oils was determined using the chroma meter LABSCAN XE (Hunterlab, VA, USA). Color data were reported in CIELAB color scales (L^* value is degree of lightness to darkness, a^* value is degree of redness to greenness, and b^* value is degree of yellowness to blueness).

Analysis of the Fatty Acid Composition of Red Salmon Oil

The fatty acid composition of red salmon oils was determined at the POS Pilot Plant Corp Laboratory, Saskatchewan, Canada. The fatty acid methyl esters (FAME) were prepared according to the AOAC procedure 969.33 [11] and fatty acid in the red salmon oil samples was determined according to AOAC procedure 996.06 [11]. Triplicate determinations were performed.

Analysis of Tocopherols, Mineral, Moisture, and Insoluble Impurity Contents of Red Salmon Oils

Tocopherols, mineral, moisture, and insoluble impurity contents of oil samples were determined at the POS Pilot Plant Corp Laboratory, Saskatchewan, Canada. Levels of tocopherols in the oil samples (alpha, beta, gamma, and delta) were determined according to AOCS Ce8-89 [12] and reported as mg/g of oil. Mineral content of red salmon oil samples was determined according to AOCS Ca17-01 and AOCS Ca 20-99 [12] and reported as ppm. The moisture content of red salmon oil samples was measured

using the Karl Fisher Titration Method (AOAC Method 984.20 [11]. Insoluble impurities in red salmon oil samples were measured according to AOCS Ca-46 [12]. Moisture and volatile matters were removed from the oil sample according to AOCS Ca 2b-38 [12]. The oil residue was dissolved in kerosene and filtered through a Gooch crucible. The remaining kerosene in the crucible was removed by washing with petroleum. The crucible was dried at 101 °C until constant weight was obtained. Insoluble impurities value in the oil was calculated as: insoluble impurities (%) = [gain in mass of crucible/mass of the residue] × 100.

Thermal Properties of Red Salmon Oils

Thermal stability of the unpurified red salmon oil was analyzed using a Thermogravimetric Analyzer (Model Q50, TA Instruments, New Castle, DE, USA). Approximately 1–1.2 mg of the oil sample was added to an aluminum pan, the pan was placed in a furnace and the exact sample weight was determined. The sample was heated to 700 °C under an air atmosphere at an increasing rate of 5 °C/min. Sample weight differences were automatically recorded every 0.5 s. Collected data were analyzed and plotted using the TA Universal Analyzer Software. The graph was normalized based on the sample weight basis.

Rheological Properties of Red Salmon Oils

An Advanced Rheometer (Model AR2000; TA Instruments Ltd., New Castle, DE, USA) fitted with a cone plate geometry (acrylic plates with a 20-mm diameter, having a 100-μm gap between the two plates) was used to study the rheological properties of the oil samples at −10, −5, 0, 5, 10, 15, 20, and 25 °C. The viscosities of the red salmon oils were measured at a shear rate of 200/s. The mean values of triplicate samples were reported.

The effect of temperature on apparent viscosity can be described through the Arrhenius relationship as described in Eq. 1 [13].

$$k = Ae^{(-E_a/RT)} \quad (1)$$

where k is the reaction rate constant, A is the frequency factor, E_a is the activation energy (kJ/mol), R is the gas constant (8.314 J/mol/K), and T is the temperature (K).

Statistical Analysis

Means and standard deviations of the data were reported. Analysis of variance (ANOVA) comparison was performed at the significant level of $P < 0.05$ using SAS version 8.2 [14]. Tukey's studentized range tests were performed to locate differences among the different treatments.

Results and Discussion

PV, FFA, Water Activity (a_W), Yield, and Color of Red Salmon Oil

The values of PV, FFA, water activity (a_W), yield, and color of red salmon oil opbtained by the different extraction treatments are shown in Table 1. The PV value is a good indicator of primary oxidation products produced during the oil extraction. It was reported [15] that oil with a PV less than 5 mequiv/kg can be considered as fresh oil, while an oil with a PV of 7.5 mequiv/kg is unacceptable for human consumption [16, 17]. The enzymatic extraction process (RS4) recovered the highest amount (8.46%) of crude oil from red salmon heads compared to other extraction methods but the oil had a higher PV (8.78 mequiv/kg of oil) (Table 1). The RS3 process recovered a lower amount (4.07%) of crude oil from red

Table 1 PV, FFA, water activity, yield, and color of red salmon oil from different oil extraction methods

Sample	RS1	RS2	RS3	RS4
PV (mequiv/kg)	6.05 ± 0.60^{bc}	6.56 ± 0.71^{b}	4.72 ± 0.31^{c}	8.78 ± 0.85^{a}
FFA (%)	0.43 ± 0.04^{b}	0.44 ± 0.03^{b}	0.45 ± 0.01^{b}	0.57 ± 0.02^{a}
a_W	0.85 ± 0.11^{ab}	0.82 ± 0.03^{ab}	0.94 ± 0.02^{a}	0.70 ± 0.02^{b}
Yield (%)	1.56 ± 0.02^{d}	7.09 ± 0.08^{b}	4.07 ± 0.23^{c}	8.46 ± 0.18^{a}
Color L^*	39.45 ± 0.40^{b}	39.60 ± 2.27^{b}	48.07 ± 2.17^{a}	44.81 ± 0.33^{a}
Color a^*	9.92 ± 0.09^{a}	10.02 ± 0.86^{a}	7.38 ± 0.35^{b}	10.94 ± 0.20^{a}
Color b^*	23.78 ± 0.67^{b}	27.50 ± 3.30^{b}	27.36 ± 0.20^{a}	33.41 ± 1.04^{a}

Each value is an average of three determinations with its SD

Values with the same superscript letters in each row are not significantly different ($p > 0.05$)

RS1, process involved a mixture of ground red salmon heads and water, no heat treatment, and centrifugation; RS2, process involved ground red salmon heads (no added water), heat treatment, and centrifugation; RS3, process involved a mixture of ground red salmon heads and water, heat treatment, and centrifugation; RS4, process involved ground red salmon heads, enzymatic hydrolysis, and centrifugation

salmon heads while the peroxide value (4.72 mequiv/kg of oil) was lower than the other oils. The RS4 process involved two heat treatments: a heat treatment to provide optimum alcalase enzyme activity and a second heat treatment to inactivate the enzyme at 85 °C for 15 min. The heat treatments might have increased the primary oxidation reaction more than other salmon extraction methods. During primary lipid oxidation, hydroperoxides form and these hydroperoxides were detected by the PV analyses.

An acceptable level of FFA in purified fish oil has been reported to be 0.15% [18]. Among all the oils, the RS4 oil contained the highest %FFA (0.57 ± 0.02%). All red salmon oils had a higher amount of %FFA than is acceptable [18], which indicates that further purification processing is needed. Young [18] reported that appropriate fish oil processing conditions may reduce FFA up to 50%. The FFA content can also be used to estimate the amount of oil that will be lost during refining processes designed to remove free fatty acids. RS3 had higher water activity (0.94) than did the other oils, and this may be caused by the cooking process of the red salmon head with water. The color of salmon oil is associated with fat soluble pigments and the RS4 process had more pigments with $a^* = 10.94$ and $b^* = 33.41$ than the other oils. These data clearly demonstrated that the extraction methods affected recovery of the crude oil from red salmon heads, peroxide value, %FFA, and the amount of pigments in the oil.

Fatty Acid Methyl Ester Composition of Red Salmon Oil

The FAME compositions of RS1, RS2, RS3, and RS4 oils are given in Table 2. Saturated fatty acids values for RS1, RS2, RS3, and RS4 oils were 20.6, 20.8, 21.3, and 21.8%, respectively. Oleic acid was the predominant fatty acid in red salmon oil accounting for about 16–17% of the total fatty acids. The total of polyunsaturated fatty acids present in red salmon oil was higher than the total saturated fatty acids and amounted to 29.4, 28.75, 29.6, and 29.9% for RS1, RS2, RS3, and RS4, respectively. Among unsaturated fatty acids, oleic acid, eicosenoic acid (C20:1n9), EPA (C20:5n3), and DHA (C22:6n3) were the predominant fatty acids accounting for about 60% of all the unsaturated fatty acids.

EPA and DHA are important long chain omega-3 polyunsaturated fatty acids, with many reported heath benefits including prevention and treatment of cardiovascular

Table 2 Fatty acid methyl ester composition of red salmon oil from different extraction methods (% of oil)

	RS1	RS2	RS3	RS4
C14 (Myristic)	4.2 ± 0.0^{b}	4.1 ± 0.0^{c}	4.2 ± 0.0^{b}	4.3 ± 0.0^{a}
C16 (Palmitic)	13.0 ± 0.0^{b}	13.2 ± 0.0^{b}	13.5 ± 0.07^{a}	13.7 ± 0.07^{a}
C16:1n7 (Palmitoleic)	5.4 ± 0.0^{a}	5.3 ± 0.0^{b}	5.4 ± 0.0^{a}	5.4 ± 0.0^{a}
C18 (Stearic)	2.4 ± 0.0^{b}	2.4 ± 0.0^{b}	2.6 ± 0.0^{a}	2.6 ± 0.0^{a}
C18:1n9 (Oleic)	16.4 ± 0.0^{c}	15.9 ± 0.0^{d}	17.0 ± 0.07^{b}	17.2 ± 0.0^{a}
C18:1 (Octadecenoic)	3.1 ± 0.0^{a}	3.1 ± 0.0^{a}	3.1 ± 0.07^{a}	3.0 ± 0.0^{a}
C18:2n6 (Linoleic)	2.0 ± 0.0^{a}	2.0 ± 0.0^{a}	2.0 ± 0.0^{a}	2.0 ± 0.0^{a}
C18:3n3 (alpha-Linolenic)	1.2 ± 0.0^{a}	1.1 ± 0.0^{b}	1.2 ± 0.0^{a}	1.2 ± 0.0^{a}
C18:4n3 (Octadecatetraenoic)	2.4 ± 0.0^{a}	2.3 ± 0.0^{b}	2.3 ± 0.0^{b}	2.4 ± 0.0^{a}
C20:1n9 (Eicosenoic)	10.8 ± 0.0^{a}	11.1 ± 0.0^{a}	9.95 ± 0.07^{b}	9.8 ± 0.35^{b}
C20:4n3 (Eicosatetraenoic)	1.5 ± 0.0^{a}	1.6 ± 0.07^{a}	1.6 ± 0.07^{a}	1.6 ± 0.0^{a}
C20:5n3 (Eicosapentaenoic)	9.3 ± 0.0^{a}	9.05 ± 0.07^{b}	9.35 ± 0.07^{a}	9.45 ± 0.07^{a}
C22:1n11(Cetoleic)	7.1 ± 0.0^{b}	7.4 ± 0.0^{a}	6.35 ± 0.07^{c}	6.0 ± 0.0^{d}
C22:5n3 (Docosapentaenoic)	2.05 ± 0.07^{a}	2.05 ± 0.07^{a}	2.15 ± 0.07^{a}	2.15 ± 0.07^{a}
C22:6n3 (Docosahexaenoic)	8.8 ± 0.0^{b}	8.55 ± 0.07^{c}	9.0 ± 0.0^{ab}	9.1 ± 0.07^{a}
Saturates	20.6 ± 0.0^{d}	20.8 ± 0.0^{c}	21.3 ± 0.0^{b}	21.8 ± 0.0^{a}
Monounsaturates	44.6 ± 0.0^{a}	44.75 ± 0.07^{a}	43.5 ± 0.0^{b}	43.2 ± 0.2^{b}
Polyunsaturates	29.4 ± 0.0^{b}	28.75 ± 0.07^{c}	29.6 ± 0.14^{ab}	29.9 ± 0.07^{a}
Omega 3	25.8 ± 0.0^{c}	25.15 ± 0.07^{d}	26.1 ± 0.07^{b}	26.4 ± 0.0^{a}
Omega 6	3.3 ± 0.0^{a}	3.3 ± 0.0^{a}	3.3 ± 0.07^{a}	3.2 ± 0.0^{a}
Omega 9	29.0 ± 0.0^{a}	28.8 ± 0.0^{b}	28.6 ± 0.0^{c}	28.55 ± 0.07^{c}

Fatty acid methyl esters with values less than 1.0% are not included. Each value is an average of three determinations with its SD

Values with the same superscript letters in each row are not significantly different ($p > 0.05$)

See Table 1 for brief description of RS1, RS2, RS3 and RS4

disease, mental illness and immune dysfunction. The intake of EPA and DHA in the United States was reported to be 0.1–0.2 g/day [19], which is lower than the typical recommendations of 0.3–0.5 g/day [20]. The RS1, RS2, RS3, and RS4 oils contained similar amount of EPA (9.3, 9.05, 9.35, and 9.45%, respectively) and DHA (8.8, 8.55, 9.0, and 9.1%, respectively). At least 3.5 g of the red salmon oil taken per day would meet the recommendations for the EPA and DHA intake. Total omega-3 fatty acids in the RS1, RS2, RS3, and RS4 oils were 25.8, 25.15, 26.1, and 26.4%, respectively. All the oil samples had only minor differences in fatty acids composition, which demonstrated that extraction procedures did not greatly affect fatty acid composition.

Tocopherols, Mineral, moisture, and Insoluble Impurity Contents of Red Salmon Oils

The effects of the extraction methods on mineral, moisture, and insoluble impurities of red salmon oils are shown in Table 3. Tocopherols play a role as a vitamin and natural antioxidant. The most biologically active component of tocopherol is α-tocopherol, which is capable of capturing free radicals and breaking lipid peroxidation chain reactions [21]. Total α-tocopherol contents in the RS1 and RS2 oils were 0.17 mg/g, while RS3 and RS4 oils had less than 0.01 mg/g of α-tocopherol (not listed in the table). Both RS3 and RS4 production processes involved heating, which might have contributed to the low α-tocopherol values. It has been reported that at high temperatures, some quantity of α-tocopherol degrades over time [21].

Ca, Fe, K, Mg, P, and Na were the most abundant minerals found in the extracted red salmon oil samples (Table 3). Different extraction procedures resulted in different amounts of minerals in the oils. Phosphorus levels ranged from 10.04 ppm in RS1 to 44.90 ppm in RS4. The phosphorus present in red salmon oil samples may be attributed to the phospholipids and calcium–phosphate complexes [18]. The oil extracted by the RS2 process had a higher level of potassium than the other extraction processes, while RS3 oil contained a higher amount of magnesium. Our study indicated that levels of minerals in the oil depended on the extraction methods. RS4 had higher levels of both P and Ca possibly an indication of a higher level of calcium–phosphate complexes. All oil samples had copper contents below the acceptable maximum level for copper of 0.23 ppm and iron below the maximum level of 8 ppm [18, 22]. Metal, such as copper and iron in the oils catalyzes oxidation [23]. Lunde [24] reported that unpurified edible oils are expected to contain a certain amount of minerals because phospholipids have been reported to bind minerals in the oil. Minerals such as phosphorous, iron, magnesium, sodium, and calcium in the oil can be reduced to trace levels by neutralization [25]. Neutralization may also remove phospholipids during the washing step. All oil samples had only trace levels of cadmium, mercury, lead, silicon, and selenium contents (Table 3).

Table 3 Minerals, moisture, and insoluble impurity contents of red salmon oils extracted using different methods

	RS1	RS2	RS3	RS4
Aluminum (ppm)	<0.20	<0.20	<0.20	<0.20
Calcium (ppm)	4.30 ± 0.03^{c}	4.21 ± 0.08^{c}	9.80 ± 0.07^{b}	11.10 ± 0.00^{a}
Copper (ppm)	<0.05	0.06 ± 0.00^{a}	0.08 ± 0.01^{a}	0.07 ± 0.00^{a}
Iron (ppm)	0.60 ± 0.01^{d}	1.33 ± 0.03^{c}	2.36 ± 0.03^{b}	2.49 ± 0.02^{a}
Potassium (ppm)	0.81 ± 0.03^{d}	5.96 ± 0.04^{a}	2.70 ± 0.00^{b}	1.58 ± 0.03^{c}
Magnesium (ppm)	0.68 ± 0.01^{d}	1.18 ± 0.07^{c}	3.42 ± 0.08^{a}	3.18 ± 0.01^{b}
Phosphorus (ppm)	10.04 ± 0.57^{d}	16.8 ± 0.35^{c}	40.25 ± 0.78^{b}	44.90 ± 0.28^{a}
Sodium (ppm)	1.69 ± 0.03^{d}	7.04 ± 0.19^{a}	4.52 ± 0.09^{c}	6.59 ± 0.05^{b}
Zinc (ppm)	0.08 ± 0.00^{c}	0.09 ± 0.00^{c}	0.16 ± 0.01^{b}	0.22 ± 0.00^{a}
Cadmium (ppm)	<0.03	<0.03	<0.03	0.07
Mercury (ppm)	<0.02	<0.02	<0.02	<0.02
Lead (ppm)	<0.02	<0.02	<0.02	<0.02
Silicon (ppm)	<0.05	<0.05	<0.05	<0.05
Selenium (ppm)	<0.05	<0.05	<0.05	<0.05
Moisture (%)	0.23 ± 0.00^{c}	0.81 ± 0.01^{b}	0.98 ± 0.01^{a}	0.22 ± 0.00^{c}
Insoluble Impurities (% wt)	<0.01	0.07 ± 0.01	0.0	<0.01

Each value is an average of three determinations

See Table 1 for brief description of RS1, RS2, RS3 and RS4

The moisture contents (%) were 0.23, 0.81, 0.98, and 0.22% for RS1, RS2, RS3, and RS4 oils, respectively. RS2 and RS3 samples which were obtained from red salmon heads heated at higher temperatures contained more moisture compared with samples RS1 and RS4 with no heating or lower temperature heating. This indicates that extraction temperature might be a factor affecting moisture content. The contents of insoluble impurities were low with the highest value of 0.1% for RS2. This study demonstrated that the extraction process affected the amount of impurities, mineral, and moisture contents in the oil samples.

Thermal Properties

The TG behaviors of the red salmon oil extracted with different methods are shown in Fig. 1. Samples were heated from room temperature to 700 °C and regardless of the extraction methods, the weight loss of oils drastically increased with increasing heating temperature between 200 and 500 °C. In the initial stage, the oxidation of the oil samples can lead to formation of oxidation products, which results in an increase in sample mass [26]. In this study, no weight gain was observed in the TG curves for the salmon oil samples extracted using different methods, indicating that thermal decomposition of red salmon oils was not related to oxygen absorption. Based on the TG curves (Fig. 1), the thermal stabilities of the oil samples are as follows: RS2 > RS1 > RS3 > RS4. The weight losses at 500 °C were similar for RS2, RS1, RS3, and RS4 at 94.50, 94.58, 94.94, and 95.47%, respectively. Sathivel et al. [27] reported that the weight loss of fish oils due to thermal decomposition was higher in refined oils than crude oils. The interaction in the unrefined oils of impurities such as phospholipids, complex metals, free fatty acids, and peroxides and their breakdown products can reduce the effectiveness of heat transfer in the samples, which can result in a decrease in energy available to evaporate the volatiles [28, 29]. This study also demonstrated that extraction procedures had an effect on the % of thermal degradation of the red salmon oil from heads. Almost all (>99.96%) of the unrefined red salmon oil samples were decomposed at 550 °C.

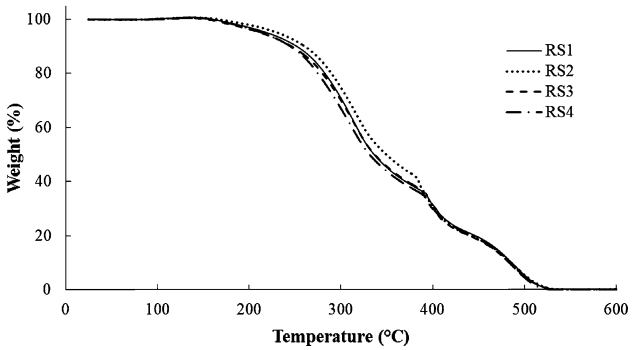

Fig. 1 Thermal degradation of red salmon oils from different extraction methods using TG from 20 to 700 °C. See Table 1 for brief description of RS1, RS2, RS3 and RS4

Rheological Properties

Apparent viscosity for all four of the red salmon oil samples decreased significantly ($P < 0.05$) with increasing temperature between −10 and 25 °C (Table 4). RS4 oil exhibited the highest viscosity at −10 °C. From 0 to 25 °C, RS1 oil was more ($P < 0.05$) viscous than the other samples. Oil impurities in the unrefined red salmon oil samples may result in an aggregated colloidal dispersion system, which may be the reason for the different apparent viscosities exhibited in the oil samples [30]. It has been reported that free fatty acids in the oil may increase the

Table 4 Apparent viscosity ($\times 10^{-3}$ Pa s) of red salmon oils extracted using different methods

Temperature (°C)	RS1	RS2	RS3	RS4
−10	353.43 ± 11.42^{aB}	403.77 ± 12.38^{aA}	301.03 ± 8.62^{aC}	422.40 ± 16.86^{aA}
−5	196.67 ± 0.49^{bAB}	198.53 ± 2.15^{bA}	192.27 ± 0.32^{bBC}	188.37 ± 2.59^{bC}
0	152.70 ± 0.26^{cA}	150.60 ± 0.20^{cB}	147.37 ± 0.25^{cC}	144.03 ± 0.06^{cD}
5	121.53 ± 2.40^{dA}	119.80 ± 0.26^{dAB}	117.50 ± 0.30^{dB}	113.20 ± 0.26^{dC}
10	98.84 ± 0.12^{eA}	97.38 ± 0.14^{eB}	95.89 ± 0.55^{eC}	92.35 ± 0.24^{eD}
15	81.60 ± 0.24^{fA}	81.21 ± 0.17^{fA}	80.06 ± 0.08^{fB}	77.29 ± 0.01^{efC}
20	69.29 ± 0.13^{gA}	68.76 ± 0.14^{fgB}	67.96 ± 0.20^{gC}	65.70 ± 0.24^{fgD}
25	59.83 ± 0.42^{gA}	58.74 ± 0.18^{gB}	59.13 ± 0.34^{hAB}	56.93 ± 0.15^{gC}

Each value is an average of three determinations with its SD

Values with the same uppercase letters in each row are not significantly different ($p > 0.05$)

Values with the same lowercase letters in each column are not significantly different ($p > 0.05$)

See Table 1 for brief description of RS1, RS2, RS3 and RS4

Table 5 Activation energy (E_a) and frequency factor (μ_∞) for different red salmon oil extraction methods

Sample	μ_∞	Ea (J/mol)
RS1	1.37E-06 ± 1.82E-7[b]	26381.98 ± 132.51[b]
RS2	1.19E-06 ± 7.45E-8[d]	26682.12 ± 341.80[a]
RS3	1.56E-06 ± 1.92E-7[a]	26013.67 ± 276.01[c]
RS4	1.30E-06 ± 7.21E-8[c]	26363.69 ± 193.39[b]

Each value is an average of three determinations with its SD

The same letters in each column are not significantly different ($p > 0.05$)

See Table 1 for a brief description of RS1, RS2, RS3, and RS4

viscosity because more shear force is required for flow [31]. In our study, RS4 oil had the highest FFA concentration (Table 1), and exhibited the highest apparent viscosity at −10 °C (Table 4). However at other temperatures from −5 to 25 °C, the apparent viscosity of RS4 was not greater than oils from the other processing treatments. This may due to the low FFA of the oils. Purification processes can remove impurities resulting in a reduction in the apparent viscosity [32].

The Arrhenius equation was employed to calculate the average magnitude of activation energy (E_a) of the red salmon oils (Table 5). E_a indicates the energy barrier that must be overcome before the elementary flow process can occur [13]. RS2 had a higher magnitude ($P < 0.05$) of E_a than that of RS1, RS3, and RS4. The results indicated that the extraction methods affected the apparent viscosity and flow behavior properties of the red salmon oils from heads. The frequency factors were different for all extraction methods and values ranged from 1.30E-06 to 1.56E-06.

This study demonstrated the effect of the extraction methods on chemical, thermal, and rheological properties of red salmon oil, which is useful for designing the purification process of the oil. The RS4 oil which was produced by enzymatic extraction process recovered more oil but had a higher %FFA and PV value than other oil samples. All oil samples had similar FAME profiles and EPA and DHA contents. The oil samples contained different amounts of minerals. The thermal stability of the oil samples is as follows: RS2 > RS1 > RS3 > RS4. The apparent viscosity of all oil samples was significantly decreased with increased temperature. Information on chemical, thermal and rheological properties from this study can be used for the design of a purification process to produce red salmon oil suitable for human consumption.

References

1. Haglund O, Wallin R, Wretling S, Hultberg B, Saldeen T (1998) Effects of fish oil alone and combined with long chain (n-6) fatty acids on some coronary risk factors in male subjects. J Nutr Biochem 9:629–635
2. Kronhout D, Bosschieter EB, Coulander C (1985) The inverse relation between fish consumption and 20-year mortality from coronary heart disease. N Engl J Med 312:1205–1209
3. ADFG Alaska commercial salmon harvests and exvessel values 2006. http://www.cf.adfg.state.ak.us/geninfo/finfish/salmon/catchval/blusheet/06exvesl.php (accessed October 2007)
4. Fiorillo J (2005) Are fish oil supplements in threat? Intrafish 3:18–20
5. De BK, Bhattacharyya DK (1998) Physical refining of rice bran oil in relation to degumming and dewaxing. J Am Oil Chem Soc 75:1683–1686
6. Tandy DC, McPherson WJ (1984) Physical refining of edible oil. J Am Oil Chem Soc 61:1253–1258
7. Van Hoed V, Depaemelaere G, Vila Ayala J, Santiwattana P, Verhe′ R, De Greyt W (2006) Influence of chemical refining on the major and minor components of rice bran oil. J Am Oil Chem Soc 83:315–321
8. Seetharamaiah GS, Prabhakar JV (1986) Oryzanol content of Indian rice bran oil and its extraction from soapstock. J Food Sci Technol 23:270–273
9. Sathivel S, Huang J, Prinyawiwatkul W (2008) Thermal properties and applications of the Arrhenius equation for evaluating viscosity and oxidation rates of unrefined pollock oil. J Food Eng 84:187–193
10. Sathivel S, Prinyawiwatkul W, Negulescu II, King JM (2008) Determination of melting points, specific heat capacity and enthalpy of red salmon oil during different purification steps. J Am Oil Chem Soc 85:291–296
11. Association of Official Analytical Chemists (AOAC) (1999) Official methods of analysis, 16th edn. AOAC International, Arlington
12. American Oil Chemists' Society (1998) Official methods and recommended practices of the American Oil Chemists' Society (AOCS), 5th edn. American Oil Chemists' Society, Champaign
13. Rao MA (1999) Floe and functional models for rheological properties of fluid foods. In: Rao MA (ed) Rheological of fluids and semisolids. Principal and applications. Aspen Publishers, Gaithersburg, p 27
14. SAS (2002) SAS/STAT User's Guide, version 8.2. SAS Institute, Cary
15. Gracey J, Collims DS, Huey R (1999) Food poisoning and meat microbiology. In: Gracey J, Collims DS, Huey R (eds) Meat hygiene, 10th edn. Saunders, Philadelphia, p 407
16. Robards K, Kerr AF, Patsalides E (1988) Rancidity and its measurement in edible oils and snack foods: a review. Analyst 113:213–224
17. Schnepf M, Spencer G, Carlat J (1991) Chemical and sensory characteristics of stored menhaden oil/soybean oil blends. J Am Oil Chem Soc 68:281–284
18. Young FVK (1986) The Chemical and physical properties of crude fish oils for refiners and hydrogenators. Fish Oil Bulletin No. 18. International Fishmeal and Fish Oil Organisation, Hertfordshire
19. Kris-Etherton PM, William SH, Lawrence JA (2002) Fish consumption, fish oil, omega-3 fatty acids, and cardiovascular disease. Circulation 106:2047–2057
20. Kris-Etherton PM, Taylor DS, Yu-Poth S, Huth P, Moriarty K, Fishell V, Hargrove RL, Zhao G, Etherton TD (2000) Polyunsaturated fatty acids in the food chain in the United States. Am J Clin Nutr 71:179S–188S
21. Ricciarelli R, Zingg JM, Azzi A (2002) The 80th Anniversary of Vitamin E: beyond its antioxidant properties. Biol Chem 383:457–465
22. Bimbo AP (1998) Guidelines for characterizing food-grade fish oil. Int News Fats Oils Relat Matter 9:473–483

23. Young FVK (1986) The refining and hydrogenation of fish oil. Fish Oil Bulletin No. 17. International Fishmeal and Fish Oil Organisation, Hertfordshire, pp 1–27
24. Lunde G (1971) Activation analysis of trace elements in lipids with emphasis on marine oils. J Am Oil Chem Soc 48:517–522
25. Hvolby A (1989) Removal of nonhydratable phospholipids from soybean oil. J Am Oil Chem Soc 48:503–509
26. Hassel RL (1976) Thermal analysis: an alternative method of measuring oil stability. J Am Oil Chem Soc 53:179–181
27. Sathivel S, Prinyawiwatkul W, Negulescu II, King JM, Basnayake BFA (2003) Thermal degradation of fatty acids and catfish and menhaden oils at different purification steps. J Am Oil Chem Soc 80:1131–1134
28. Wiedermann LH (1981) Degumming, refining and beaching soybean oil. J Am Oil Chem Soc 58:159–166
29. Wesolowski M, Erecinska J (1998) Thermal analysis in quality assessment of rapeseed oils. Thermochim Acta 323:137–143
30. Sathivel S, Yin H, Bechtel PJ, King JM (2009) Physical and nutritional properties of catfish roe spray dried protein powder and its application in an emulsion system. J Food Eng 95:76–81
31. Teeter HM, Cowan JC (1956) Viscometric properties of higher fatty acids and their derivatives. J Am Oil Chem Soc 33:163–168
32. Sathivel S, Prinyawiwatkul W, Negulescu II, King JM, Basnayake BFA (2003) Effects of purification process on the rheological properties of red salmon oil. J Am Oil Chem Soc 80:829–832