Thermal and Flow Properties of Fish Oils

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Introduction

Alaska fishmeal operators produce over 30,000 mt of unrefined fish oil annually. Marine fish oil contains a high quantity of omega-3 fatty acids, which play an important role in human health. Information on thermal stability, melting point, specific heat capacity, enthalpy, and rheological properties of cold-water marine fish oils is not available. Thermal and rheological analyses are used as indicators of fish oils quality and provide useful information for the design of purification steps for unrefined fish oils.

The food industry uses thermal analysis, thermogravimetry analyzer (TG) and differential scanning calorimetry (DSC) for oil and fat characterization. These methods require less time and provide precise stability data (Wesolowski and Erecinska, 1998). DSC has been used to investigate the thermal conductivity and specific heat (Buhri and Singh, 1994)), melting and crystallization (Kaisersberger, 1989). The influence of composition of fat, content of water, production materials, aging and heat treatment on oil and fat quality can be demonstrated on the basis of DSC investigation.

TG analysis could be used to determine the quality of fish oils at different refining steps (Sathivel, 2003). Wesolowski and Erecinska (1998) reported that TG analysis was very useful in defining the quality of rapeseed oils compared with chemical analysis.

Knowledge of rheological properties helps solve problems related to the movement and utilization fish oil (Sherman, 1970). At low temperatures, impurities of a crude oil tend to precipitate on the walls of pipes and solid particles in the oil increase the viscosity of the oil. The fish oil refining process involves degumming, neutralizing, bleaching, and deodorizing
(Young, 1978). Impurities, such as free fatty acids, proteins, moisture, pigments, and volatile flavors, are sequentially removed from the oil, which changes the flow properties of the oil (Wiedermann, 1981). The objective of this study was to evaluate thermal stability, melting point, specific heat capacity, enthalpy, and rheological properties of unrefined salmon and pollock oils.

Materials and Methods

Fresh unrefined salmon and pollock oils were prepared at Fishery Industrial Technology Center, Kodiak, Alaska and stored at 4 ^{o}C until analyzed. Thermal stability of the unrefined oils was analyzed using the Thermogravimetric Analyzer. The DSC experiments were conducted using a Differential Scanning Calorimetry. The thermogram peak was used to provide an estimate of enthalpy and the thermogram peak points were

used to determine the melting points. The TA Instrument Software was used to calculate the specific heat capacity from the DSC transition curve.

Rheological properties of salmon and pollock oils samples were measured using an AR 2000 Rheometer. Each oil sample was placed in the temperature-controlled parallel plate and allowed to equilibrate to –4, 0, or 24^{o}C. Shear stress was measured at –4, 0, and 24 ^{o}C at varying shear rates from 0 to 500s^{-1}. The power law was used to analyze the flow behavior index of the oil samples. The effect of temperature on viscosity was described using the Arrhenius relationship [$\mu_a = \mu_{\infty A} \exp(E_a/RT)$]. Viscosity ($\mu_a$) of the oil samples was measured at –4, 0, 4, 8, 12, 16, 20, and 24^{o}C at a shear rate of 500 s^{-1} by using the AR 2000 Rheometer. A plot of In μ_a (viscosity) versus $1/T$ (1/absolute temperature) was constructed for each oil sample. The slope of the straight line, the intercept and the regression coefficient were calculated using the trend line of the plot. The magnitude of activation energy (Ea) was calculated as the slope of the plot multiplied by the gas constant (R), and the frequency factor ($\mu_{\infty A}$) was an exponential of the intercept. Viscosities of salmon and pollock oils samples were predicted at 3, 6, 9, 12, 15, 18, and 21^{o}C using $\mu_a = \mu_{\infty A} \exp(E_a/RT)$ with calculated values of Ea/R *and* $\mu_{\infty A}$. Viscosity (μ_a) of the salmon and pollock oils samples was measured at 3, 6, 9, 12, 15, 18, and 21^{o}C at a shear rate of 500s^{-1} by using the AR 2000 Rheometer, and values were compared with predicted viscosity values of salmon and pollock oil samples.

Results and Discussion

The thermal degradation of oils occurred in 3 step, which probably corresponded to polyunsaturated fatty acids from 200 to 390^{o}C, monounsaturated fatty acids from 390 to 480^{o}C, and saturated fatty acids from 490 to 600^{o}C. The phase transition of oils occurred over a wide range of temperatures.

Melting points of -70 to 13.5^{o}C for salmon oil and –35 to 15^{o}C for pollock oil were observed. The low temperature onset melting points of the oils were attributed to polyunsaturated fatty acids. Enthalpy was 40 j/g for salmon oil and 35 j/g for pollock oil. Specific heat capacity ranged from 0.8 to 2.3 and 0.6 to 3.5 (j/g/°C) for salmon and pollock oils, respectively.

The flow behavior index (n) of the oil samples was equal to 1.0 for both oil samples, which indicated that they were Newtonian fluids. Viscosity of salmon and pollock oils was temperature-dependent, and could be predicted by the Arrhenius equation.

Conclusion

Knowledge of thermal and rheological properties of fish oils is important for oil purification, handling and utilization operations, and in the quality evaluation of oils.

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