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ORIGINAL PAPER

Determination of Melting Points, Specific Heat Capacity and Enthalpy of Catfish Visceral Oil During the Purification Process

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Abstract Changes in melting points, enthalpy, and specific heat capacity of catfish visceral oil at each step of the purification process were studied. Melting points of −46.2 to 21.2 °C for crude oil, −45.9 to 11.5 °C for degummed oil, −44.3 to 11.4 °C for neutralized oil, −47.1 to 9.9 °C for bleached oil and −52.3 to 8.0 °C for deodorized oil were observed. Enthalpy (kJ/kg) was 74.1 for crude oil, 74.7 for degummed oil, 75.1 for neutralized oil, 79.3 for bleached oil, and 84.3 for deodorized oil. The specific heat capacities at 20 °C for crude, degummed, neutralized, bleached, and deodorized oils were 1.69, 1.96, 1.97, 1.91, and 1.83 kJ/kg °C, respectively.

Keywords Catfish · Enthalpy · Fish oil purification · Melting point · Specific heat capacity

Introduction

Channel catfish (*Ictalurus punctatus*) fillet is one of the most popular fish products consumed in the United States [1]. By-products of catfish processing consist of heads, frames, skin, and viscera, which often end up in landfills or rendering plants. The average weight of viscera is about 265 g, about 10% of the weight of a live whole catfish, with a fat content of 33.6% [2]. Therefore, the viscera could be used to recover catfish oil that could be purified into edible oil.

During the extraction and purification process, catfish oil is subjected to temperature changes. Changes in the physical state of oil caused by temperature are known as phase transitions, the most common of which are melting (solid to liquid) and crystallization (liquid to solid). Due to phase transitions, the overall physical and chemical properties of oil may drastically alter the final oil quality [3]. Phase transition is associated with enthalpy [4], which explains whether an oil changes from one physical state to another by absorbing (endothermic) or releasing (exothermic) heat. Specific heat capacity is an important measure which provides information about the amount of energy that must be supplied or withdrawn to change temperature by a given amount.

Differential Scanning Calorimetry (DSC) offers a simple method of investigating characteristics of melting and freezing points of fats. The influence on composition of fat, water content, production materials, aging and heat treatment can be studied by DSC analysis. DSC has been used to investigate the thermal conductivity and specific heat [5], melting and crystallization [6, 7], oil content [8], and phase transition [9] of foods. Dollimore [10] thoroughly reviewed the overall application of DSC for several thermal analysis materials.

Information on melting point, specific heat capacity, and enthalpy of catfish visceral oil important for designing and optimizing the purification process for catfish oil is not available. Therefore, the objective of this study was to determine the melting points, enthalpy and specific heat

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capacity of catfish visceral oil at different purification steps.

Experimental Procedures

Fatty Acids

Myristic acid (C14:0), palmitic acid (C16:0), stearic acid (18:1), arachidic acid (20:0), palmitoleic acid (16:1), oleic acid (18:1), linoleic acid (18:2), linolenic acid (C18:3), cis-11,14-eicosadienoic acid (C20:2), arachidonic acid (20:4), and cis-4,7,10,13,16,19-docosahexaenoic acid (C22:6) were bought from Sigma company, St Louis, MO. Purity of all fatty acids was 99%, except 98% for C20:2 and 90% for C20:4.

Crude Catfish Visceral Oil Preparation

Catfish viscera were obtained from a local seafood store in Baton Rouge, LA. The viscera were frozen at −20 °C until used. The thawed viscera were finely ground in a 1-HP Model 84181D Hobart Chopper Bowl (Hobart Corporation, Troy, OH, USA) at 3,450 rpm for 10 min. Water (water/ground viscera, 5:1 v/w) was added and the mixture heated to 70 °C for 15 min. The solid particles were separated from the liquid phase by filtering through cheesecloth, and the solid particles were pressed to remove most of the liquid. The crude oil was separated from the water phase and remaining viscera particles by centrifuging at 5,000 rpm (2,560×g) for 30 min. The resulting crude oil was collected and stored at −20 °C until used. Three crude oil extractions were conducted.

Oil Refining

Crude catfish visceral oils were refined as follows. The term "neutralized" oil refers to the oil that has been degummed and neutralized; "bleached" oil refers to the oil that has been degummed, neutralized and bleached; and "deodorized" oil refers to the oil that has been degummed, neutralized, bleached and deodorized.

The modified method of Dijkstra and Opstal [11] was used for degumming; 100 g crude catfish oil was removed from frozen storage, placed in a 600-mL beaker, and heated to 70 °C in a temperature-controlled water bath; 3 mL 3% aqueous citric acid solution was added to the oil, and the mixture was thoroughly mixed at 70 °C for 1 min. The oil was then cooled to room temperature and centrifuged at 2,560×g for 10 min to remove precipitated gum.

The degummed oil was neutralized according to the AOCS Official Method Ca 9b-52 [12]. Sodium hydroxide (12.6 g of 9.5% NaOH solution) was added to the degummed oil (100 g) and the mixture was heated to 65 °C for 30 min with constant stirring with a magnetic stirrer. The sample was then cooled to room temperature and kept undisturbed for 6 h. After centrifuging at 2,560×g for 10 min, the oil was decanted from the precipitated soap. Demineralized water (50 mL) was added to wash out any remaining soap; this was repeated three times. Water and impurities were removed by centrifuging at 2,560×g for 10 min.

The neutralized oil was bleached according to the method of Scott and Latshaw [13]. The neutralized oil was heated in a water bath and bleached with 4% (w/w) activated earth (CS Z1077, American Oil Chemists' Society, Champaign, IL, USA) at 70 °C for 10 min with constant stirring using a magnetic stirrer. The activated earth with absorbed impurities was removed from the oil by centrifuging at 2,560×g for 30 min.

The bleached oil was deodorized using a laboratory distillation unit according to the method of Bitner et al. [14]. The distillation unit consisted of a 500-mL round–bottom boiling flask with three outlets. One outlet was connected to a vacuum pump, another outlet was connected to a glass distillation column, and the remaining outlet was sealed with a thermometer. The flask was placed on a heating system. The oil (100 mL) was added to the flask and heated to 100 °C for 30 min under vacuum (5 mm Hg). The temperature was manually controlled. The volatile products were condensed in a cooling system installed on the vacuum line and the distillate was collected.

Differential Scanning Calorimetry (DSC)

A Model DSC 2920 Differential Scanning Calorimetry (TA Instruments, New Castle, DE, USA) was used to determine the melting point, enthalpy, and specific heat capacity of catfish oil at each purification step, and the melting points and enthalpies for individual fatty acids were determined. All experiments were conducted in triplicate, and representative DSC thermograms of catfish visceral oil were presented.

Melting Point and Enthalpy

About 0.5–1 mg of oil sample was placed in a small aluminum sample pan. The pan was then placed on the sample platform of the DSC. An empty aluminum pan was placed on the reference platform. For determination of the melting point a linear heating rate of 5 °C/min over a temperature

range of −75 to 125 °C was used. Liquid nitrogen was used to chill the samples to a lower temperature.

Specific Heat Capacity

For specific heat capacity determination, approximately 0.9 mg of sample was weighed and placed in a small aluminum sample pan. The pan was placed on the DSC sample platform. Then an empty aluminum pan of a similar weight was placed on the DSC reference platform. The sample was equilibrated at −75 °C and then heated to 80 °C at a rate of 2 °C/min. The temperature was modulated to ±0.5 °C every 40 s. All data were normalized on a sample weight basis (1 mg) before the enthalpy, melting points, and specific heat capacity were calculated using TA Universal Analyzer Software (TA Instruments, New Castle, DE, USA).

Statistical Analysis

Means and standard deviations of the data collected were reported. Analysis of Variance (ANOVA) and Tukey's studentized range test were performed to detect significant differences among the different treatments at the significant level of $P < 0.05$ using SAS version 8.2 (SAS Institute Inc.).

Results and Discussion

Melting Points of Individual Fatty Acids

Observed melting points of individual fatty acids (Table 1) were similar to those reported elsewhere [15] and showed an obvious relationship between chemical structure and melting points of fatty acids. The melting point of saturated fatty acids increased with increasing chain length; this may be due to the intermolecular dispersion force which increases with the increased number of carbons in chains [3, 16]. In the case of unsaturated fatty acids, the increased number of double bonds decreased the melting point. For example, comparing C18:0 with C18:1, C18:2, and C18:3, there was a decrease in the melting point of 73.3, 80.6, and 88.6 °C for an addition of one, two and three double bonds, respectively. The lowest melting point (−47.4 °C) was observed for C22:6, the fatty acid with more double bonds found in this study. Fatty acids are in the crystalline solid state at temperatures below their melting points, and the *cis*-double bonds in the chain prevent them from packing closely in the crystal lattice, thus decreasing the stability of the crystals [3].

Table 1 Melting points and enthalpies of individual fatty acids

Samples[a]	Onset temperature (melting point °C)	Maximum temperature (°C)	Enthalpy (kJ/kg)
C14:0	53.5	55.5	198.3
C16:0	59.8	63.9	212.8
C18:0	67.6	70.0	226.3
C20:0	70.6	75.8	236.9
C16:1	−0.90	1.64	125.8
C18:1	−5.7	15.2	152.2
C18:2	− 13.0	−4.1	119.1
C18:3	−21.0	−10.4	115.0
C20:2	−8.3	0.9	103.1
C20:4	−43.4	−38.4	113.3
C22:6	−47.4	−42.2	82.1

[a] Commercial samples with 99% purity, except 98% for C20:2 and 90% for C20:4

Melting Points of Catfish Oil

Table 2 and Figure 1a–e show typical melting curves of crude, degummed, neutralized, bleached, and deodorized

Table 2 Melting points, enthalpies, and specific heat capacities of catfish visceral oils at each purification step

	Melting point peak (°C)						Enthalpy (kJ/kg)	Specific heat capacity (kJ/(kg °C)) at 20 °C
	A	B	C	D	E	F		
Crude	21.2 ± 0.5[a]	−0.2 ± 1.1	−6.1 ± 2.3[a]	−14.5 ± 2.7[a]	−22.5 ± 3.2[a]	−46.2 ± 0.3[a]	74.1 ± 0.3[a]	1.69 ± 0.01[d]
Degummed	11.5 ± 0.7[b]	n/d	−6.0 ± 1.7[a]	−14.6 ± 2.4[a]	−25.0 ± 1.5[a]	−45.9 ± 1.4[a]	74.7 ± 7.9[a]	1.96 ± 0.01[a]
Neutralized	11.4 ± 0.5[b]	n/d	−5.0 ± 1.6[a]	−15.9 ± 1.0[a]	−25.0 ± 0.5[a]	−44.3 ± 1.2[a]	75.1 ± 5.0[a]	1.97 ± 0.01[a]
Bleached	9.9 ± 0.3[c]	n/d	−5.4 ± 0.9[a]	−17.1 ± 0.9[a]	−25.6 ± 0.8[a]	−47.1 ± 2.1[a]	79.3 ± 0.8[a]	1.91 ± 0.01[b]
Deodorized	8.0 ± 0.3[d]	n/d	−5.8 ± 0.7[a]	−13.9 ± 0.6[a]	−25.9 ± 0.5[a]	−52.3 ± 2.4[b]	84.3 ± 3.5[a]	1.83 ± 0.01[c]

Values are means ± SD of three determinations

n/d not detected

[a–d] Means with the same superscript letter in each column are not significantly different ($P > 0.05$)

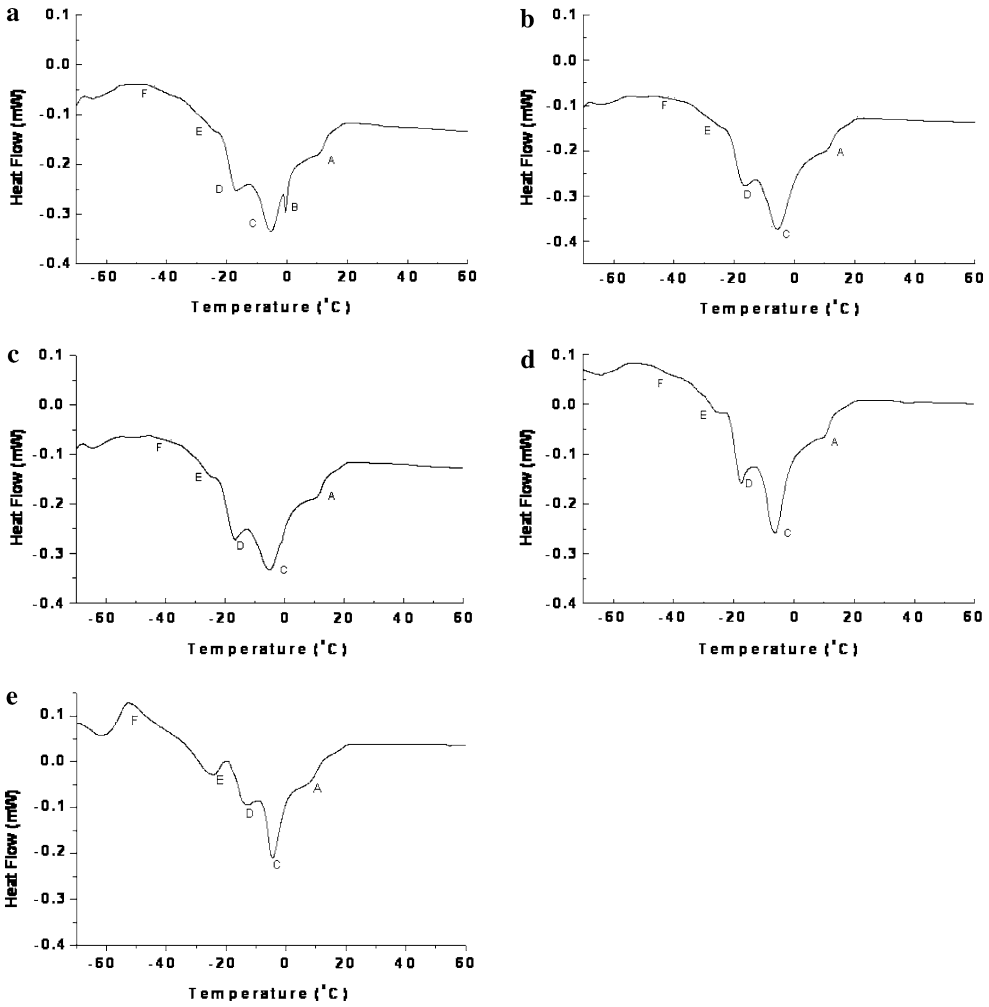

Fig. 1 Typical DSC thermograms of catfish visceral oil. **a** Crude oil, **b** degummed oil, **c** neutralized oil, **d** bleached oil, and **e** deodorized oil. Letters *A–F* indicated exothermic peaks and corresponding numerical values are meeting points in °C

catfish visceral oil. The melting points of catfish oil ranged from −46.2 to 21.2 °C for crude oil, −45.9 to 11.5 °C for degummed oil, −44.3 to 11.4 °C for neutralized oil, −47.1 to 9.9 °C for bleached oil and −52.3 to 8.0 °C for deodorized oil. Six (A, B, C, D, E, and F) distinct endothermic peaks, considered as melting points, were observed in the DSC thermogram for crude catfish visceral oil (Fig. 1a). Peak B showed a small sharp peak that might be a melting point of freezable water, part of the water that was added during extraction of oil from catfish viscera and remained in the crude oil. Water melts close to 0 °C and gives a very sharp peak [17, 18]. Peaks E and F were not sharp, indicating impurities.

The DSC thermogram (Fig. 1b) for degummed catfish visceral oil shows five peaks. The absence of Peak B, attributed to melting of freezable water (Fig. 1a), indicates that water present in crude oil was removed during the degumming process. Other melting points of the degummed oil showed similar values to those observed in crude oil, except for the melting point A, which decreased from 21.2 to 11.5 °C. The DSC thermogram (Fig. 1c) of neutralized oil showed a similar pattern to that of degummed oil; however, a very small peak B was observed. This peak may be due to the remaining water used during neutralization to remove soaps. The bleached oil showed sharper peaks and the peak B for freezable water was not observed (Fig. 1d). The melting point *A* of bleached oil was lower than that of crude oil. The DSC thermogram of deodorized oil (Fig. 1e) shows peaks that were sharper and narrower than those observed for oils from other purification steps. The melting point of peak A was reduced to 8 °C compared with that of the bleached oil (9.9 °C).

The DSC thermograms (Fig. 1a–e) showed that there were changes in melting points of catfish oils during purification. Sharp melting points were observed in purified deodorized oil. Crude catfish oil contains impurities such as phospholipids, free fatty acids, aldehydes, ketones, water, and pigments. Those impurity components have different

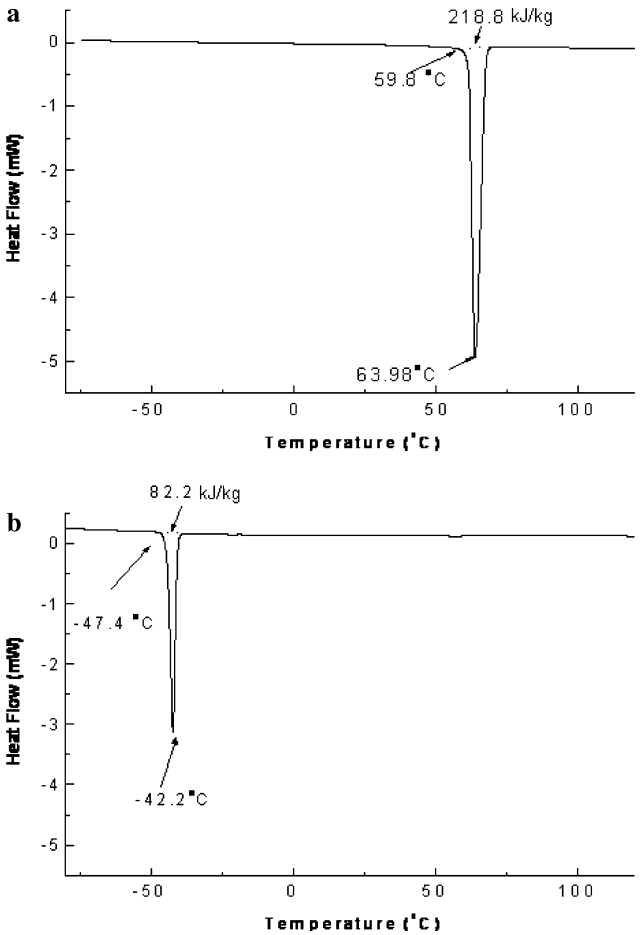

Fig. 2 Typical DSC thermograms of (**a**) palmitic acid and (**b**) DHA. Numerical values at the peaks are melting points (°C); values above the DSC trace are enthalpies

melting points; therefore, sharp peaks were not observed as compared to pure fatty acids (Fig. 2). During degumming, phospholipids and water are removed [19, 20]. Free fatty acids are removed during neutralization, and pigments, minerals, free fatty acids, aldehyde, and ketones are removed during bleaching [20, 21]. Melting point peaks of catfish oils (Fig. 1a–e) were sharper after each purification step that removed impurities from the oil. Catfish oil melting point range was relatively smaller than the melting points of −69.6 to −0.36 °C and −64.7 to 20.8 °C, respectively, for red and pink salmon oils reported by Sathivel [22]. The melting point of the fatty acids may define the properties of triglycerides, of which they are a part. Triglycerides contain three fatty acid groups, so their physical properties are more complex than those of the individual fatty acids. In this study, we did not analyze the triglyceride composition of the catfish oil. However, the trends in melting points observed for catfish oils would likely reflect its fatty acid composition. Fatty acids found in catfish visceral oil were C14:0, C16:0, C16:1, C18:0, C18:1, C18:2, C18:3, C20:0, C20:1, C20:2, C20:4 and C22:6, and the catfish visceral oil contained more than 68% of total unsaturated fatty acids [2]. The negative melting points of catfish oil may be attributed to these unsaturated fatty acids.

Enthalpy

Figure 2a and b represent the peaks of the thermograms obtained from C16:0 and C22:6 during heating from −75 to 120 °C. The "onset" temperature is a typical parameter, which represents the beginning of the melting process defined as the intersection of the tangent at the first leg of the main peak with the base line [4]. Integration of the total peak area is used to determine enthalpy. Enthalpy of saturated fatty acids increased with increasing chain length and the enthalpy of unsaturated fatty acids generally decreased with increasing numbers of double bonds (Table 1). Comparing C16:1 with C16:0, a decreased enthalpy of 87.0 kJ/kg was observed for one double bond added. Comparing C18:0, with C18:1, C18:2, and C18:3, the enthalpy progressively decreased for each double bond added. The lowest enthalpy was observed for C22:6. However, C20:4 showed a higher enthalpy than C20:2. The enthalpy of catfish oil did not significantly change after each purification step that removed impurities from the oils (Table 2). The enthalpy of catfish oil was higher than those reported for red and pink salmon oils [22] of 40 and 39 kJ/kg, respectively.

Specific Heat Capacity

Specific heat capacity is an important measure that provides information about the amount of energy that must be supplied or withdrawn to change temperature by a given amount. For DSC, the specific heat capacity is determined from the equation: $Q = m\mathrm{Cp}\ (\mathrm{d}T/\mathrm{d}t)$, where Q is the heat flow per unit time, m is the sample mass, Cp is specific heat capacity of material and $\mathrm{d}T/\mathrm{d}t$ is the rate of change of the external temperature. The temperature-dependent specific heat capacities of crude, degummed, neutralized, bleached and deodorized catfish oils ranged from 1.69 to 1.97 kJ/(kg °C) at 20 °C (Table 2). The specific heat capacity of 0.8–1.6 kJ/(kg °C) was reported for red salmon oil while 1.3–2.3 kJ/(kg °C) for pink salmon oil [22].

Purification processes are necessary to recover the oil from catfish viscera and convert the crude oil into edible oil. Information reported here on thermal degradation, melting point, specific heat capacity, and enthalpy of catfish oils will be useful for designing the process and optimizing unit operations for catfish oil purification steps. This information may be applicable to other edible fish oil processing.

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