Thermal Degradation of FA and Catfish and Menhaden Oils at Different Refining Steps

Subramaniam Sathivel[a,*], Witoon Prinyawiwatkul[b], Ioan I. Negulescu[c], Joan M. King[b], and B.F.A. Basnayake[d]

[a]Fishery Industrial Technology Center, University of Alaska Fairbanks, Kodiak, Alaska 99615, [b]Department of Food Science, Louisiana State University Agricultural Center, Baton Rouge, Louisiana 70803, [c]School of Human Ecology and Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803, and [d]Department of Agricultural Engineering, Faculty of Agriculture, University of Peradeniya, Sri Lanka

ABSTRACT: The thermal degradation (weight loss) of individual FA and of catfish and menhaden oils collected from different refining steps was investigated by thermogravimetric analysis. The heat resistance of FA was partially dependent on chain length and degree of unsaturation. The weight loss of catfish and menhaden oils increased with increased heating temperatures, regardless of the oil refining process. All oil samples (except crude catfish oil) were decomposed after the heating temperature reached 550°C. Based on the thermogravimetric curves, the following thermal stability sequence at different refining steps for both catfish and menhaden oils was proposed: crude > degummed > neutralized > bleached > deodorized oils.

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KEY WORDS: Catfish oil, fatty acids, fish oil stability, menhaden oil, thermogravimetric analysis.

There is growing world demand for high-quality fish oil, and the production of fish oil can be quite profitable if suitable processing methods are adopted. FA composition and resistance to oxidation determine the quality of fish oil. Thermal analysis measures physical or chemical changes such as sample weight and specific heat in a material as a function of temperature. Use of a thermogravimetric (TG) analyzer and a differential scanning calorimeter for quality characterization of fats and oils has been of great interest in the food industries. These methods require less time (1) and provide precise stability data.

A thorough knowledge of the thermal decomposition of fish oils may lead to new technologies to improve their stability. A TG analyzer is a balance that measures changes in weight as a function of temperature while the sample is subjected to a controlled temperature program. Wesolowski and Erecinska (1) found that, compared with a chemical analysis, a TG analysis was useful in defining the quality of rapeseed oils. Hassel (2) reported that the TG analysis was an alternative method for measuring the stability of vegetable oil. The technique was used to study the effect of biophenols on olive oil stability (3). Compared to previous techniques such as the active oxygen method or the oxygen bomb method (4), the TG analysis offers such advantages as a smaller sample size, good precision, and the ability to evaluate a continuous oxidation process.

Fish oil refining steps include extracting crude oil, degumming, neutralizing, bleaching, and deodorizing. It is important to know the stability of fish oil at different refining steps in order to obtain high-quality purified oil. The objectives of this study were to understand the effects of increasing the heating temperature on the weight loss of catfish and menhaden oils collected from different refining steps as well as to study the effects of heating temperature on the weight loss of individual FA by a TG analysis.

EXPERIMENTAL PROCEDURE

Sample preparation. FA samples were purchased from the Sigma Company (St. Louis, MO). Catfish viscera were obtained in three separate batches from a local seafood store in Baton Rouge, Louisiana. The viscera were frozen at −20°C until used. The thawed viscera were finely ground in a 1-hp Hobart chopper bowl (Model 84181D; Hobart Corporation, Troy, OH) at 3,450 rpm for 10 min. Water (water/oil, 5:1 vol/wt) was added, and the mixture was heated at 70°C for 15 min. The solid particles were separated from the liquid phase by filtering through cheesecloth, and the particles were pressed to remove most of the liquid. The crude oil was separated from the water phase and the remaining viscera particles by centrifuging at 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. Crude menhaden oil was supplied by Omegaprotein Inc. (Reedville, VA).

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

A method modified from Dijkstra and Opstal (5) was used for degumming. A sample of crude oil (100 g) was removed from storage and placed in a 600-mL beaker and then heated to 70°C in a temperature-controlled water bath. Three milliliters of 3% aqueous citric acid solution was added to the oil, and the mixture was thoroughly mixed at 70°C for 1.0 min. The oil was then cooled to room temperature and centrifuged at 2,560 × *g* for 10 min.

*To whom correspondence should be addressed at Fishery Industrial Technology Center, University of Alaska Fairbanks, 118 Trident Way, Kodiak, AK 99615. E-mail: sathivel@sfos.uaf.edu

The degummed oil was neutralized according to AOCS Official Method Ca 9b-52 (6). NaOH (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. The oil was washed 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 (7). 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) at 70°C for 10 min with constant stirring with 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 in a laboratory distillation unit according to the method of Bitner *et al.* (8). The distillation unit consisted of a 500-mL round-bottomed 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 then added to the flask and heated to 100°C for 30 min under vacuum (5 mm Hg); the temperature was controlled manually. The volatile products were condensed in a cooling system installed on the vacuum line, and the distillate was collected.

Thermal analysis. Thermal stabilities of individual FA and catfish and menhaden oils were analyzed using a TG analyzer (Hi-Res Modulated TGA 2950; TA Instruments, New Castle, DE). Approximately 0.5–1 mg of each sample was added to an aluminum pan, the pan was placed in the furnace, and the exact sample weight was determined. The sample was heated from 100 to 600°C in an inert nitrogen atmosphere at a rate of 5°C/min. Differences in sample weights were automatically recorded every 0.5 s. Data were analyzed and plotted using TA Universal Analyzer Software. The graphs were normalized based on sample weights.

RESULTS AND DISCUSSION

Effects of heating temperatures on the weight loss of individual FA are provided in Table 1. All unsaturated FA, except 22:6, were completely decomposed after reaching 400°C, whereas all saturated FA were decomposed after reaching 450°C. For unsaturated C_{18} FA, those with more double bonds were less heat resistant. Compared with 18:1, 18:2 and 18:3 had more weight loss between 100 to 350°C. Saturated FA with longer carbon chain lengths were more resistant to thermal decomposition at 100–200°C; however, 14:0 was slightly more resistant to thermal decomposition at 250, 300, and 350°C than were 16:0, 18:0, and 20:0 (Table 1). The heat decomposition of FA was partially dependent on chain length and degree of unsaturation. The intermolecular dispersion forces increased with an increased number of carbons in the chains (9); therefore, FA with longer carbon chains were more resistant to thermal decomposition than short-chain FA.

TABLE 1
Remaining Weight (%) of FA During Heating[a]

	Heating temperature (°C)							
FA	100	150	200	250	300	350	400	450
14:0	99.95	97.19	45.81	7.96	5.77	0.45	0.03	D
16:0	99.84	99.11	79.42	4.16	2.55	0.38	0.07	D
18:0	99.91	99.51	89.65	4.90	2.62	0.36	0.09	D
20:0	99.91	99.69	91.78	4.93	2.92	0.40	0.1	D
16:1	99.83	98.27	74.45	1.19	0.83	0.16	D	D
18:1	99.98	99.65	93.17	37.30	1.13	0.35	D	D
18:2	99.95	99.27	86.76	3.97	1.05	0.23	D	D
18:3	99.90	99.21	80.21	1.20	0.95	0.15	D	D
22:6	99.83	99.18	91.12	5.22	2.19	1.64	1.12	D

[a]D, decomposed.

The TG curves (Figs. 1 and 2) show the thermal behavior of catfish and menhaden oils collected from various refining steps. Between 200 and 500°C, the weight loss of oils increased with increasing heating temperature, regardless of the refining step. A dramatic reduction in weight occurred between 300 to 450°C for both catfish and menhaden oils. At 550°C, all oil samples (except the crude catfish oil) were decomposed. In an oxygen atmosphere the onset of oxidation in the oils is characterized by oxygen absorption by the FA chain, leading to the formation of oxidation products known as peroxides. This behavior is usually identified by an increase in the initial sample mass (2). No weight gain was observed in the TG curve for either catfish or menhaden oil analyzed under a nitrogen atmosphere, indicating that thermal decomposition of the oils was not related to oxygen absorption.

Based on the TG curves (Figs. 1 and 2), the proposed thermal stability of both catfish and menhaden oils is as follows: crude oil > degummed oil > neutralized oil > bleached oil > deodorized oil. A slightly higher loss of mass was observed in deodorized catfish and menhaden oils than in the crude oils. Weight losses between 350 and 450°C were 67.99 and 64.79% for deodorized catfish and menhaden oils, respectively, whereas they were 58.81 and 52.73% for crude catfish and menhaden oils, respectively. This may be due to the presence of impurities in the crude oils. Unrefined oils contain soluble impurities, such as phospholipids, complex metals and minerals (notably iron, calcium, and magnesium), FFA, and peroxides and their breakdown products, that are highly interactive with the oil (10). Sathivel *et al.* (11) reported that the mineral content, FFA, and water activity of the catfish oil decreased in deodorized oil compared with crude oil. According to previous investigations, soluble impurities are removed through the edible oil refining steps (5,7,8,11).

The presence of impurities reduces the effectiveness of heat transfer to unrefined oils, resulting in less energy available to evaporate the volatiles. The weight loss of edible oils due to thermal decomposition is higher in refined oils than in crude or unrefined oils. The higher value at the initial temper-

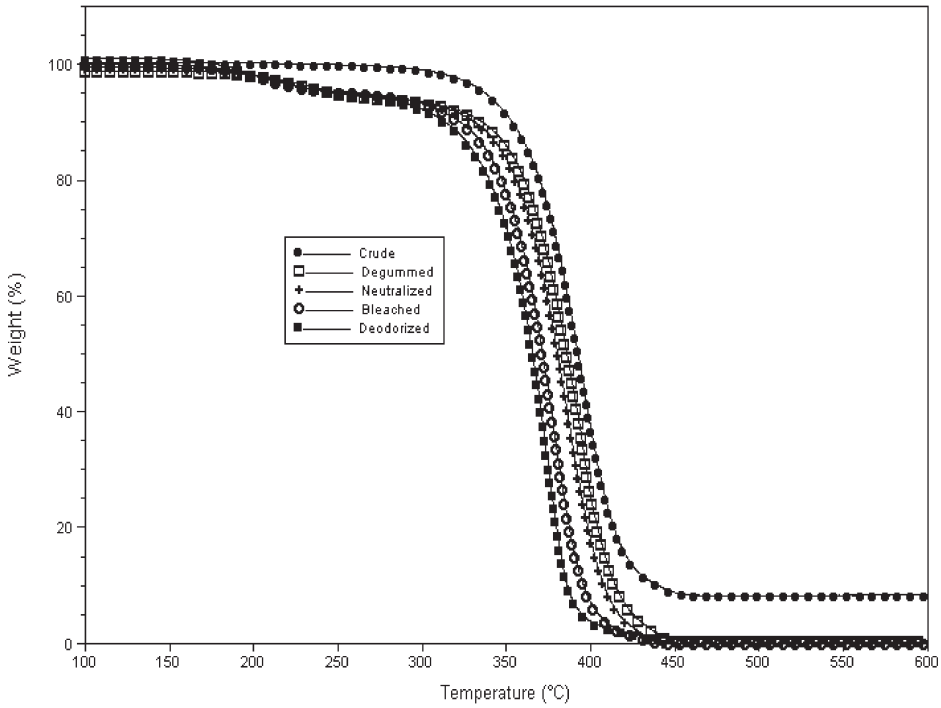

FIG. 1. Thermogravimetric curves indicating remaining weight (%) of catfish oils at 100–600°C.

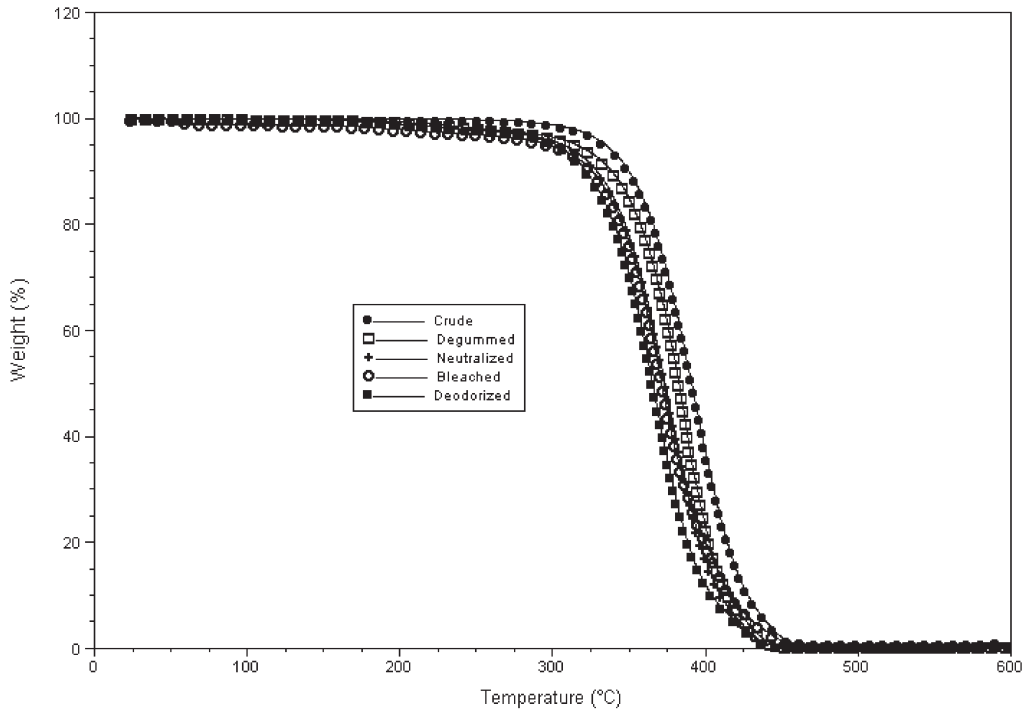

FIG. 2. Thermogravimetric curves indicating remaining weight (%) of menhaden oils at 100–600°C.

ature of decomposition implies a higher quality of oil (1). In this study, refining catfish and menhaden oils tended to reduce their relative resistance to thermal decomposition; however, the results in Figures 1 and 2 suggest that in some temperature ranges, some stages of refining did not appear to significantly degrade the performance of the oils. This study indicates that a TG analysis can be used to determine the quality of fish oils at different refining steps.

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