Effects of Purification Process on Rheological Properties of Catfish Oil

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ABSTRACT: Effects of oil refining steps (degumming, neutralizing, bleaching, and deodorizing) on rheological properties of catfish oil were investigated. Four rheological models (Newtonian, Bingham, Herschel–Bulkley, and Casson) were used to fit the experimental data. Refined catfish oil behaves like a Newtonian fluid. Based on the Casson model, the yield stress values of oils gradually decreased after each refining step. The highest shear rate index (0.904) was observed in the deodorized oil. The Casson model was used to predict rheological properties because it works well at both lower and higher shear rates.

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Rheology is one of the most important properties of foods and food ingredients determining their suitabilities for particular applications. Knowledge of rheological properties helps solve problems related to the transfer or movement of bulk quantities of a liquid (1). At low temperatures, impurities in a crude oil tend to precipitate on the walls of pipes. Some solid particles in the bulk flow increase the viscosity of the oil, causing an increased pressure drop in the pipeline. As a result of increased viscosity, oil flow properties exhibit non-Newtonian behavior.

The fish oil refining process involves degumming, neutralizing, bleaching, and deodorizing. Impurities, such as FFA, proteins, moisture, pigments, and volatile flavors, are sequentially removed from the oil (2). Removing impurities may change the flow properties of the oil.

Crude oil may be considered a structured disperse system because the complex mixture of liquid hydrocarbon derivatives acts as a dispersion medium and the aggregated impurities make up the dispersed phase. The impurities of crude oils influence flow characteristics and determine their non-Newtonian properties (3). The power law model has been used to describe flow properties of liquid-based food products.

There is no satisfactory model for predicting viscosities of edible oils, which are shear-rate dependent and affected by different processing steps. Prediction and mathematical representation of flow characterization of oils from each purification step are very important for the optimal design of unit operations and for improved control of final product quality. Catfish oil is a new product and has not yet been produced on a commercial scale, so it is important to characterize the rheological properties at different refining steps. Therefore, the objectives of this work were to investigate the effects of refining on rheological properties of catfish oil and to determine the suitability of different models for describing rheological behavior of catfish oil.

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EXPERIMENTAL PROCEDURES

Samples and sample preparation. Catfish viscera were obtained in three separated 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 Corp., Troy, OH) at 3450 rpm for 10 min. Water was added (water/ground viscera, 5:1, vol/wt), 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 phase was separated from the water phase and viscera particles by centrifuging at 5000 rpm ($2560 \times g$) for 30 min. The resulting crude oil was collected and stored at −20°C until used. Three experimental crude oil extractions were conducted.

Crude catfish oil was refined as follows. The term "neutralized" oil refers to catfish oil that has been sequentially degummed and neutralized; "bleached" oil refers to oil that has been sequentially degummed, neutralized, and bleached; and "deodorized" oil refers to oil that has been sequentially degummed, neutralized, bleached, and deodorized.

Degumming. The method of Dijkstra and Opstal (4) was used for degumming. Crude oil (100 g) was taken from frozen storage, placed in a 600-mL beaker, and then heated to 70°C in a temperature-controlled water bath. Aqueous citric acid (3 mL) solution (3%) 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 $2560 \times g$ for 10 min.

Neutralization. Degummed oil was neutralized according to AOCS Official Method Ca 9b-52 (5). Sodium hydroxide (12.6

g of 9.5% NaOH solution) was added to 100 g of degummed oil, and the mixture was heated to 65°C for 30 min with constant stirring using a magnetic stirrer. The sample was then cooled to room temperature and kept undisturbed for 6 h. After centrifuging at 2560 × *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 washing step was repeated three times. Water and impurities were removed from the oil by centrifuging at 2560 × *g* for 10 min.

Bleaching. The neutralized oil was bleached according to the method of Scott and Latshaw (6). The neutralized oil was heated in a temperature-controlled water bath and bleached with 4% (w/w) activated earth (CS Z1077, AOCS, Champaign, IL) at 70°C for 10 min using a magnetic stirrer. The activated earth with absorbed impurities was removed from the oil by centrifuging at 2560 × *g* for 30 min.

Deodorization. The bleached oil was deodorized using the method of Bitner *et al.* (7). 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 inserted. 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 from the column.

*Rheological measurements***.** The rheological properties of catfish oils were measured using a dynamic shear rheometer with a concentric cylinder measurement cell (Constant Stress Rheometer, Model CS-10; Bohlin Instruments, Cranbury, NJ). The diameter of the inner cylinder was 2.5 cm, and the diameter of the outer cylinder was 2.75 cm. Each sample was placed in the temperature-controlled vessel and allowed to equilibrate to the required temperature (25 ± 0.1°C) for 5 min prior to taking measurements. Shear stress was measured at various shear rates from 0 to 1200 s^{-1}. The mean values of triplicate samples were reported. The CV for rheological measurements (data not shown) was less than 10%.

Rheological models. For a Newtonian fluid, the shear stress (τ_{xy}) (Eq. 1) is directly proportional to shear rate, (dV_x/dY), where η is the apparent viscosity.

$$\tau_{xy} = \eta\left(\frac{dV_x}{dY}\right) \qquad [1]$$

The viscosity of a Newtonian fluid is independent of shear rate and apparent viscosity, and is determined as the ratio of shear stress to shear rate. The viscosity of a pseudoplastic fluid decreases with increased shear rates, whereas the opposite is observed for a dilatant fluid. A pseudoplastic fluid without a yield stress (τ_o) is most often described by a simple two-parameter power function model.

The Herschel–Bulkley model (Eq. 2) is a generalized power law equation with a yield stress. The Herschel–Bulkley model is one of the most extensively used equations to describe the flow characteristics of shear-thinning fluids over a wide range of shear rates.

$$\tau_{xy} = \tau_o + K\left(\frac{dV_x}{dY}\right)^n \qquad [2]$$

where τ_{xy} = shear stress, τ_o = yield stress (Pa), n = shear rate index, K = consistency coefficient (Pa·s^n), and dV_x/dY = shear rate.

The Bingham plastic fluid is similar to a Newtonian fluid because there is a linear relationship between shear stress and shear rate after the application of the threshold shear stress. This threshold shear stress is called the yield stress of the fluid. The behavior of Bingham plastic fluid can be mathematically expressed by Equation 3:

$$\tau_{xy} = \tau_o + \eta_p\left(\frac{dV_x}{dY}\right) \qquad [3]$$

where τ_o = the Bingham yield stress (Pa) and η_p = the Bingham plastic consistency coefficient (Pa·s).

The Casson model (Eq. 4) is another common rheological fluid model, taking into account both the nonlinearity of the flow curve and the existence of a yield stress. The Casson model has been used to describe the flow behavior of a liquid with suspended particles (i.e., suspension), and it was initially developed for describing pigment suspension:

$$\tau_{xy}^{\,0.5} = \tau_0^{\,0.5} + \eta_c^{\,0.5}\left(\frac{dV_x}{dY}\right)^{0.5} \qquad [4]$$

where τ_o = yield stress (Pa) and $\eta_c^{0.5}$ = higher shear limiting viscosity (Pa·s).

Fitting models. The shear rates were gradually increased to 1200 s^{-1}, while the shear stress progressively increased accordingly (up to 53.3 Pa). The rheological equations describing the Newtonian, Herschel–Bulkley, Bingham plastic, and Casson models were used to fit the shear rate and shear stress data. Model-fitting to the experimental data was carried out using a curve fit program (CurveExpert 1.3, © Daniel Hyams). The best-fit model was based on the prediction coefficient (R^2).

Apparent viscosity. The Casson equation was used to predict the apparent viscosity at different shear rates for crude oil, which was then compared with the experimental viscosity.

RESULTS AND DISCUSSION

Flow parameters. Tables 1–4 present the flow parameters of the Newtonian, Herschel–Bulkley, Bingham plastic, and Casson models, respectively, for catfish oils. The yield stresses for catfish oils at different refining steps determined by the Bingham plastic model (Table 3) were higher than those given by other models (Tables 2, 4). The yield stress and the consistency coefficient (K) of deodorized oil were less than those of the crude catfish oil (Table 2).

The shear rate index, n, obtained from the Herschel–Bulkley equation, varied between 0.758 and 0.904. The highest shear rate index (0.904) was observed for the deodorized catfish oil (Table 2). The catfish oil showed a gradual decrease in consistency coefficient (K) values after the degumming step (Table 2). The regression coefficients (R^2) for the four fitted models were greater than 0.95 for all purification steps (Tables

TABLE 1
Flow Parameters for Catfish Oils Using the Newtonian Model (Eq. 1)[a]

Oils	η (Pa·s)	R^2
Crude	0.049	0.951
Degummed	0.036	0.978
Neutralized	0.034	0.979
Bleached	0.029	0.978
Deodorized	0.026	0.985

[a] η, apparent viscosity (Pa·s); R^2, prediction coefficient.

TABLE 2
Flow Parameters for Catfish Oils Using the Herschel–Bulkley Model (Eq. 2)[a]

Oils	τ_o (Pa)	n	K (Pa·s^n)	R^2
Crude	2.73	0.794	0.179	0.995
Degummed	0.365	0.758	0.184	0.999
Neutralized	0.946	0.819	0.109	0.998
Bleached	0.816	0.819	0.093	0.997
Deodorized	1.063	0.904	0.047	0.997

[a] τ_o, yield stress; *n*, shear rate index; *K*, consistency coefficient. See Table 1 for other abbreviation.

1–4). For example, prediction coefficients of the Herschel–Bulkley, Bingham plastic, Casson, and Newtonian models for crude catfish oil were 0.995, 0.991, 0.998, and 0.951, respectively. The discrepancy in the prediction coefficients by different models appeared to be minor, and the prediction of each model was nearly superimposed (figures not shown).

The plot of log shear stress vs. log shear rate for catfish oils in each refining step is shown in Figure 1, and the results indicate that catfish oil behaves like a Newtonian fluid. Because the Casson model works well at both lower and higher shear rates, it was more appropriate for predicting the viscosity of the crude catfish oils (8). To determine the viscosity of the crude catfish oil, the Casson model may be rewritten as follows:

$$\eta = A + \frac{B}{\sqrt{\dfrac{dV_x}{dY}}} + \frac{C}{\dfrac{dV_x}{dY}} \qquad [5]$$

where $A = \eta_c$, $B = 2\tau_o\eta_c^{0.5}$, and $C = \tau_o$.

Figure 2 illustrates model-fitting using the data from the predicted apparent viscosity (Eq. 5) and the experimental viscosity for crude catfish oil. The predicted apparent viscosity by the rewritten Casson model agreed satisfactorily with the experimental apparent viscosity. The degree of fit as shown by the distribution along the 45° line is acceptable. The prediction coefficient (R^2) was 0.969.

TABLE 3
Flow Parameters for Catfish Oils Using the Bingham Plastic Model (Eq. 3)[a]

Oils	τ_o (Pa)	η_p (Pa·s)	R^2
Crude	4.79	0.042	0.991
Degummed	2.41	0.033	0.992
Neutralized	2.42	0.030	0.995
Bleached	2.08	0.026	0.993
Deodorized	1.40	0.024	0.995

[a] η_p, Bingham consistency coefficient. See Tables 1 and 2 for other abbreviations.

TABLE 4
Flow Parameters for Catfish Oils Using the Casson Model (Eq. 4)[a]

Oils	τ_o (Pa)	η_c (Pa·s)	R^2
Crude	2.27	0.028	0.998
Degummed	0.952	0.025	0.998
Neutralized	0.776	0.023	0.998
Bleached	0.670	0.020	0.996
Deodorized	0.658	0.014	0.996

[a] η_c, Casson higher shear limiting viscosity. See Tables 1 and 2 for other abbreviations.

Crude oils contain soluble impurities, such as phospholipids, complexed metals (notably iron, calcium, and magnesium minerals), FFA, and peroxides and their breakdown products, that are highly interactive with the oil (2). The interaction between oil and impurities depends on the size and shape of the impurities, the nature of intermolecular forces, the chain length, the presence or absence of side chains, the nature of polar groups, and the hydrogen bonding of molecules present in impurities.

The interaction between oil and impurities may be attributed to the formation of an aggregated colloidal dispersion system, which often shows strong shear-thinning characteristics when shear force is applied to the system. The oil that contains larger amounts of FFA may require more shear forces in order to flow (9). The structural integrity of crude oil is disrupted when shear force is applied. FFA and mineral content of the crude catfish oil were gradually reduced in subsequent refining steps as reported by Sathivel *et al.* (10). Degumming, neutralizing, bleaching, and deodorizing remove impurities. Minerals that are complexed by phospholipids should be removed by degumming and alkali refining steps (11). Degumming and neutralizing normally reduce the phosphorus, iron, magnesium,

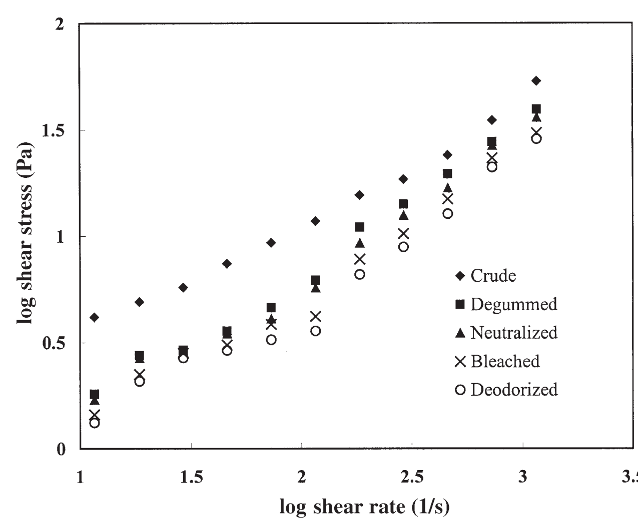

FIG. 1. Rheological properties of catfish oil at each refining step at 25°C.

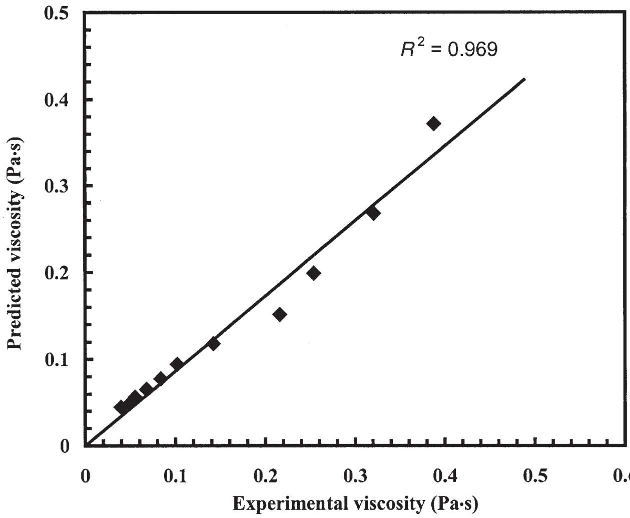

FIG. 2. Predicted apparent viscosity from the rewritten Casson model (Eq. 5) compared with the experimental apparent viscosity of crude catfish oil.

and calcium in the oil to trace levels (12). FFA are removed by neutralizing, and oxidation products are removed by bleaching (2).

This study shows that rheological properties of catfish oils are affected by refining. The consistency coefficient of the oils decreased after each subsequent refining step due to removal of impurities. Although the difference in the prediction coefficient among the four models investigated is small, the Casson model appeared to be appropriate for predicting catfish oil viscosity because it works well at various shear rates. The information from this study will be useful for practical operations, such as the transfer of bulk catfish oil, if it is to be commercialized.

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