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Properties and Stability of Catfish Oil-in-water Emulsions as Affected by Oil and Emulsifier Concentrations

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Abstract. This study was conducted to investigate the effect of oil and emulsifier concentrations on the properties and stability of catfish oil-in-water emulsions. Beverage-type emulsions were prepared with 5 and 10% catfish oil as dispersed phases and the emulsions were stabilized by sodium caseinate (emulsifier) at 0.10, 0.25 and 0.5% concentrations. Almost all emulsions exhibited a monomodal type of droplet size distribution with average sizes of 9 – 17 and 16 – 33 μm for surface-weighted ($d_{3,2}$) and volume-weighted ($d_{4,3}$) mean diameters, respectively. All emulsions demonstrated a thixotropic flow behavior with apparent viscosities ranging from 87 – 166 mPa.s. The interaction of oil and emulsifier concentrations was found to give significant ($p < 0.05$) effects on the droplet size distribution and viscosity of the emulsions. The physical stability of the emulsions was found to be significantly ($p < 0.05$) affected by the oil concentration alone whereby the phase separation was high in the emulsion containing 5% oil. Inversely, the peroxide value was significantly ($p < 0.05$) affected by the emulsifier concentration alone in which the highest concentration (0.5%) exhibited a high lipid oxidation.

Keywords: Catfish oil, emulsion, oil-emulsifier interaction, droplet size, viscosity, stability.

1. Introduction

African catfish (*Clarias gariepinus*) is a main species used for aquaculture industry mainly in Africa, and has also been introduced in Europe and southern Asia. The fish contains the highest amount of oil (10.9%) compared to the other types of catfish such as *Clarias batrachus* (9.73%) and *Clarias macrocephalus* (8.99%). Fish oil is one of major fishery products with pharmaceutically importance. Fish oil is known to have docosahexanoic acid (DHA) and ecosapentanoic acid (EPA) or omega-3 fatty acids in various amounts depends on the type of fish itself and other factors. EPA and DHA are crucial for growth and development especially for the infants [1] and also for preventing treatment of coronary artery disease (arteriosclerosis), hypertension, arthritis and autoimmune disorders [2]. African catfish oil contains about 25% polyunsaturated fatty acid (PUFA) with a significant amount of EPA and DHA [3].

Recently, consumption of fish oil in the form of emulsion seems to become increasingly popular. Moreover, a number of scientific studies on fish oil emulsions are available such as on salmon, tuna and menhaden oil-in-water emulsions [4, 5]. In short, these studies found that properties and stability of fish oil emulsions are much affected by the level of oil itself as well as other minor ingredients especially emulsifier. However, being a complex system, interaction effect between oil and emulsifier at an interfacial phase of the emulsion should also be of concern. Despite catfish oil is known to have important health benefits due to its omega-3 fatty acid content, yet no research has been done on its potential as functional foods like fish oil emulsion. Therefore, the objective of the present study was to investigate the interaction effects between catfish oil and sodium caseinate at different concentrations and the interaction effect between both factors on the stability and properties of catfish oil-in-water emulsion.

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2. Methodology

2.1. Emulsion preparation

Beverage-type emulsions were prepared by homogenizing mixture of African catfish oil (5 and 10%), sodium caseinate (0.1, 0.25 and 0.5%), deionized water and carboxymethyl cellulose using a high speed homogenizer at 10000 rpm under room temperature [6].

2.2. Physical properties and stability analyses

The droplet size was measured by a laser diffraction method in terms of surface-weighted ($d_{3,2}$) and volume-weighted ($d_{4,3}$) mean diameters. Emulsion were diluted in distilled water to a droplet concentration of less than about 0.5 wt% and gently stirred using vortex before the measurement. The drops of emulsion were introduced into the sample preparation unit until the concentration reached the optimum one, indicated by the instrument. The viscosity was measured by using a viscometer at a shear rate of 600 s^{-1}. The emulsion stability towards phase separation was evaluated under centrifugation force (3500 rpm for 30 min). Centrifugation produced layers of an aqueous phase at the bottom, an emulsion phase in the middle and oil phase on top. The height of the separated layers was measured and converted to relative percentage as follows: % layers = (height of the separated layer/the total height of the emulsion) x 100% [6]. The emulsion stability towards lipid oxidation was evaluated in terms of peroxide value which was determined by the standard iodometric AOAC Method 965.33 (AOAC, 1990), directly on emulsion sample without any oil pre-extraction [7]. Measurement on emulsion stability was also involved emulsions that have been stored for 30 days at 25°C.

2.3. Experimental design and statistical analysis

A 3 x 2 full factorial design with a completely randomized design was applied. Data (at least duplicate) were firstly subjected to a two-way ANOVA to determine a significant ($p < 0.05$) interaction effect between two different factors (i.e. oil and emulsifier with different levels). A one-way ANOVA with Tukey's Multiple Comparisons was further carried out to determine significant differences between means by using a Minitab 14 statistical package.

3. Results and Discussion

The droplet size distribution (DSD) of all emulsions was found to be monomodal which clearly showed one maximum peak (Fig. 1). In average, the DSD of the emulsion containing 5% oil ranged from 0.96 to 104.71 µm meanwhile the range of droplet size of the emulsion containing 10% oil was 1.10 -104.71 µm which was slightly larger than that of the emulsion containing 5% oil. Results also showed that there was a significant ($p < 0.05$) interaction effect between oil and emulsifier concentrations on the emulsion DSD. This reflects that the effect of oil concentration on the emulsion DSD was significantly depended on sodium caseinate concentration since higher concentration of oil needed higher concentration of emulsifier in order to enhance the adsorption of sodium caseinate and surface coverage of oil droplets which eventually inhibited the droplet aggregation or coalescence effectively [5].

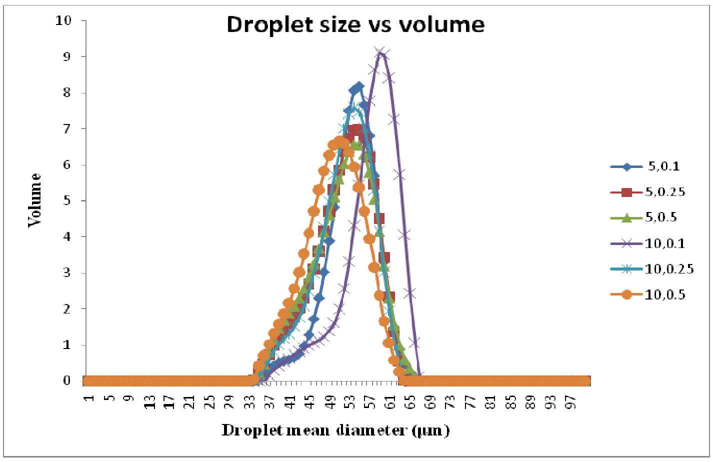

Fig. 1: Droplet size distribution of the freshly prepared emulsions

The surface-weighted mean diameter seemed to be decreased with increases in emulsifier concentration at both oil concentrations. This result was generally in agreement with the result obtained by Day and co-workers [4] who found that the mean droplet size was significantly increased when the protein concentration (sodium caseinate) was decreased from 0.5 to 0.1%**.** There are several possible reasons to explain the decrease in mean droplet size with an increase in protein concentration. When the concentration of protein in the emulsion increased, the rate at which the droplet surface covered with protein will increase and thus the frequency of droplet collisions will decrease due to an increase in aqueous viscosity. Consequently, the mean droplet size of the prepared emulsion will decrease. The smallest droplet size can be obtained with 10% oil and 5% sodium caseinate. However, the droplet size of this emulsion was only significantly different ($p < 0.05$) from that of emulsion with 10% oil and 0.1% sodium caseinate concentrations compared to the other formulations as shown in Table 1. This could be due to the fact that, 0.1% of sodium caseinate was not enough to cover the droplet surface of emulsion, hence lead to the aggregation and flocculation of the oil droplets which eventually resulted in larger droplet size [5].

TABLE 1: Mean droplet size of the freshly prepared emulsions

Oil (%)	Emulsifier (%)	Surface weighted mean	Volume weighted mean
5	0.10	$10.55^{b} \pm 1.86$	$20.35^{b} \pm 0.09$
5	0.25	$9.51^{b} \pm 0.02$	$18.66^{b} \pm 0.26$
5	0.50	$9.30^{b} \pm 0.31$	$19.03^{b} \pm 0.19$
10	0.10	$17.35^{a} \pm 2.63$	$33.59^{a} \pm 3.29$
10	0.25	$10.02^{b} \pm 0.09$	$18.45^{b} \pm 0.35$
10	0.50	$8.15^{b} \pm 0.79$	$16.18^{b} \pm 2.76$

a-b Means with different letter within the same column are significantly different ($p < 0.05$) ($n = 2$).

The viscosity of the catfish oil-in-water emulsions exhibited a thixotropic behaviour as the viscosity of the emulsions seemed to be decreased with time when the emulsions were subjected to the constant shear rate (Fig. 2). Typically, emulsions that exhibit this behaviour contain droplets that are aggregated by weak forces. The aggregated droplets are gradually disrupted and collapsed because of the shearing of the materials, hence decreased the resistance to flow and consequently cause the reduction of the apparent viscosity over time [8]. There was a significant interaction effect ($p < 0.05$) on apparent viscosity (at 1 min) of the emulsions indicating that both effects of catfish oil and emulsifier on the emulsion viscosity were found to be interdependent to each other (Table 2). The highest viscosity of the emulsion was at 10% oil concentration and 0.10% emulsifier concentration. However, the viscosity of the emulsion was only significantly different ($p < 0.05$) from that of emulsion at 5% catfish oil and 0.5% emulsifier but about the same as the remaining emulsions. It is also found that low concentration of emulsifier (0.25%) in the emulsion was not sufficient to adsorb at the interface, hence caused the oil droplets to coalesce, and thus increased the viscosity [9]. This explains the significant difference between catfish oil emulsion containing 5% oil at 0.5% sodium caseinate with the emulsions containing 10% and 5% catfish oil at 0.10% and 0.5% of sodium caseinate, respectively.

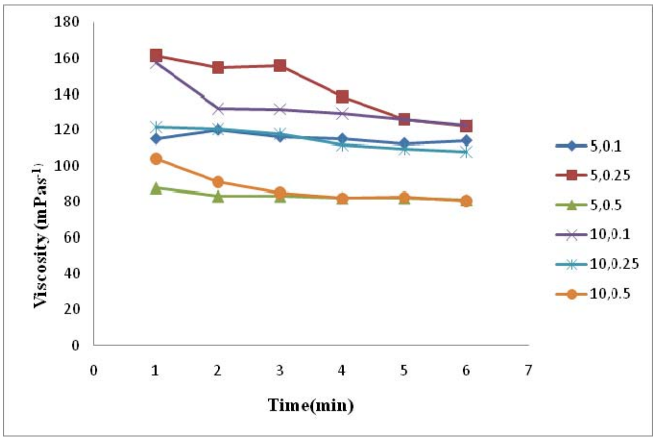

Fig. 2: The viscosity of the freshly prepared emulsions.

TABLE 2: Apparent viscosity (at 1 min) of the freshly prepared emulsions.

Oil (%)	Emulsifier (%)	Viscosity (mPa.s)
5	0.10	$115.00^{ab} \pm 14.14$
5	0.25	$161.50^{a} \pm 33.23$
5	0.50	$87.50^{b} \pm 4.95$
10	0.10	$157.50^{a} \pm 2.12$
10	0.25	$121.50^{ab} \pm 14.85$
10	0.50	$104.00^{ab} \pm 16.97$

$^{a-b}$Means with different letter within the same column are significantly different ($p < 0.05$) (n = 2)

Table 3 shows the phase separation stability of the freshly prepared and 30-days stored catfish oil-in-water emulsions. There was no significant interaction effect between oil and emulsifier concentrations on the emulsion stability. However, the oil concentration alone did affect the emulsion stability of the fresh emulsions. The emulsion phase was significantly ($p < 0.05$) higher at 10% oil concentration compared to 5% oil concentration. The emulsion containing 10% oil seemed to be more stable because at higher oil concentration, the packing fraction of oil droplets will increase which in turn will enhance the emulsion viscosity by reducing the creaming rate [9]. Previous study on menhaden oil-in-water emulsion similarly found that the oil concentration played important role in determining the emulsion stability [5]. It has been observed that at low oil-phase volume fraction (5%), creaming was rapidly occurred due to the weak flocculated network resulting from a low emulsion viscosity.

TABLE 3: Emulsion phase of freshly prepared and stored emulsions

Oil (%)	Emulsion phase (%)	
	Fresh	Stored (30 days)
5	$4.92^{b} \pm 1.99$	$7.24^{a} \pm 6.39$
10	$9.22^{a} \pm 3.7$	$10.54^{a} \pm 8.33$

$^{a-b}$Means with different letter within the same column are significantly different ($p < 0.05$) (n = 3)

Oxidation is a major cause of oil deterioration and hydroperoxides formed by the reaction between oxygen and unsaturated fatty acid are the primary product of this reaction. Hydroperoxides have no flavour or odour but they can breakdown rapidly to form aldehydes which contribute to very strong, disagreeable flavour and odour. Peroxide value (PV) is a measure of oxidation or rancidity at early oxidation stage. From Table 4, the highest PV obtained from the freshly prepared emulsions was at the highest concentration of emulsifier (0.5%) regardless of oil concentration. The emulsion was found to be significantly different ($p < 0.05$) from the emulsion containing 0.1% emulsifier. This might be related to the droplet size of the emulsion itself whereby the smallest droplet size was found to be in the emulsion at 0.5% emulsifier concentration. Small droplet size will contribute to the larger surface area which eventually will provide a high potential of contact among oxygen, water soluble free radicals as well as antioxidants at the emulsion interface.

TABLE 4: Peroxide value of freshly prepared and stored emulsions

Emulsifier (%)	Peroxide value (mEq/kg)	
	Fresh	Stored (30 days)
0.10	$1.38^{b} \pm 0.28$	$4.53^{a} \pm 0.57$
0.25	$1.99^{ab} \pm 0.31$	$3.44^{a} \pm 0.54$
0.50	$2.17^{a} \pm 0.36$	$3.58^{a} \pm 0.62$

$^{a-b}$Means with different letter within the same column are significantly different ($p < 0.05$) (n = 3)

The PV results in the present study was found to be parallel to the previous study by Nakaya et al. [10] who found that a decrease in the droplet size of cod liver oil-in-water emulsions could cause an increase in oxidative stability of the emulsions. Besides, the emulsions showed an increase in their PV after 30 days of storage. However, the emulsions were considered to undergo a mild oxidation process (PV < 5 mEq/kg) throughout the storage although the values were quite higher than that of fresh emulsions.

The present study found that the effects of oil concentration on DSD and viscosity of the prepared emulsions were significantly depended on the emulsifier concentration and *vice versa*. Both physical properties of DSD and viscosity also influenced the stability of the emulsions towards lipid oxidation and phase separation, respectively. Thus, it is possible to produce a stable beverage-type emulsion based on catfish oil by manipulating suitable concentration of oil and emulsifier in the system.

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