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Kinetics of Oil-in-Water Emulsion Stabilization using Lecithin and Biosilica

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Oil-in-water (O/W) emulsion has been widely used in food emulsions such as mayonnaise, dressings, and sauces. However, O/W emulsion is inherently thermodynamically unstable and easily destabilizes with time. Synthetic polymeric emulsifiers have been commonly used to stabilize these emulsions. However, those synthetic emulsifiers may induce obesity and other unexpected side-effects. In this experiment, bio-emulsifier mixtures consisting of soy lecithin and bio-silica were combined to stabilize the o/w emulsion in order to obtain more healthful food emulsions with acceptable quality. Lecithin concentrations were varied from 0.05-1.5% and concentrations of pure bio-silica particles derived from rice husks were in the range of 0.5-3%. The effects of the concentrations of these emulsifier mixtures on the O/W emulsions stability were studied. Additionally, the effects of storage temperatures on the O/W emulsions stability in the presence of both lecithin and bio-silica were investigated. The kinetics parameters of resulting O/W emulsions were analyzed using zero and first order kinetic models. In general, emulsions destabilized with time and followed the first order kinetic model. The destabilization rates of emulsions in the presence of emulsifier mixture would decrease by approximately 25-50% as compared to the destabilization rates of emulsions in the presence of lecithin or bio-silica as their sole emulsifier. Variations of lecithin and bio-silica concentrations in the emulsifier mixtures were not significant to the O/W emulsions stabilization. Furthermore, destabilization rate constants of O/W emulsions stored at the refrigerated temperature were ~2 times lower than those stored at room temperature.

Keywords: oil-in-water emulsion; biosilica; lecithin; emulsifier; kinetics; first order

INTRODUCTION

Oil-in-water emulsion (O/W) is an emulsion system consisting of oil phase as the dispersed medium and aqueous phase as the dispersion medium. Many

processed food products such as mayonnaise, ice cream, and other dairy products are some examples of O/W emulsions. In order to obtain a stable O/W emulsion, a food additive namely emulsifier is needed. Synthetic emulsifiers

are currently predominated over the natural emulsifiers due to their practical uses. However, synthetic emulsifiers may cause obesity in the long-term (Simmons *et al.* 2014), thus their uses should be limited. Natural emulsifiers are very potential to be more intensively used in food product formulations since they show low toxicities and are highly biodegradable (Koglin *et al.* 2010). Natural polymeric emulsifiers such as lecithin, sodium caseinate, soy protein (Pichot *et al.* 2010 and Wang *et al.* 2011) are mainly used in food industries. Some solid particles such as clay, bentonite, silica, and solid lipid nanoparticles (Abend *et al.* 1998, Binks *et al.* 2005, Binks and Lumsdon 2000, Chevalier and Bolzinger 2013) have been also widely used in stabilizing food emulsions.

According to previous investigation, it turned out that emulsions which were stabilized only using polymeric emulsifier or solid particles did not have a long-term stability. The emulsion stability were significantly enhance when the amphiphilic emulsifier was combined with solid particles as emulsifiers mixtures (Pichot *et al.* 2010, Pichot *et al.* 2009, Eskandar *et al.* 2011). The polymeric emulsifier would easily attached to the interfaces between oil and water reducing the surface tension between 2 phases, whereas the solid particles would act as a rigid barrier at the interfaces preventing coalescences between the droplets. Therefore, the resulting emulsion is more stable and has long-term stability (Pichot *et al.* 2009).

The emulsifier mixture tends to reduce the destabilization rate of the emulsion.

Emulsion starts to destabilize mainly due to *coalescence*, whereas droplets merge with other droplets resulting in bigger droplets formation which trigger creaming and finally phase separation. Coalescence occurred is generally following the first order kinetics model (Wanli *et al.* 2000, Tempel 1953). Besides that, the destabilization process of emulsion is also indicated by the reduction of emulsion turbidity. The rate of turbidity reduction also followed the first order kinetics model (Mirhosseini *et al.* 2008). The effects of ingredient formulations, process parameters, and storage temperatures on the emulsion shelf-life could be simply predicted from these kinetics studies.

Many researchers have been investigated the stabilities of O/W emulsions using mixed amphiphilic and particles emulsifiers (Pichot *et al.* 2010, Pichot *et al.* 2009, Eskandar *et al.* 2011), however, there are still very few studies on the kinetics of emulsion stability. The aim of this experiment is to study the kinetics of oil-in-water emulsion stabilization using lecithin and biosilica. Both lecithin and biosilica derived from rice husk are *food-grade* and thus suitable to be incorporated into food products formulation. This research could be used as the model or references for food formulators in food industry, specifically in their attempt to develop more healthful O/W food products.

EXPERIMENT

Materials

Lecithin (PT. BRATACO, Surabaya, Indonesia), 200 mesh rice husk derived

biosilica, soybean oil (Happy Soya Oil, Indofood, Indonesia), and demineralized water.

Preparation of O/W Emulsions using Mixed Emulsifiers of Lecithin and Biosilica

All O/W emulsions were prepared by dispersing 20% b/b oil phase into aqueous phase. Lecithin with varying concentrations of 0.05 – 1.5% b/b were added in the oil phase, whereas biosilica with varying concentrations of 0.5 - 3% b/b were dispersed in the demineralized water. Both phases were heated to 45°C for 1 hour and continuously stirred using a magnetic stirrer on a hotplate. Afterwards, oil phase was poured into the aqueous phase and homogenized using a rotor-stator homogenizer (IKA T25 digital ULTRA TURRAX, Germany) at 20,000 rpm for 5 minutes. O/W emulsion prepared without emulsifiers was prepared as the control. The O/W emulsions were transferred into transparent 40 ml glass vials (ID= 25 mm, height= 95 mm) until reaching the height of ~ 8 cm from the bottom and then stored at room (~ 28°C) or refrigerated (~ 8°C) temperatures for stability tests.

Determination of O/W Emulsion Stability

O/W emulsion stability was determined by measuring the emulsion height within certain time intervals. Emulsion was defined as liquid with milky appearance, whereas oil layer and milky cream were formed on the upper part of the emulsion and biosilica was sedimented at the bottom. Emulsion stability (% S) was calculated according to equation

$$\%S = \frac{h_t}{h_0} \times 100\% \quad (1)$$

whereas h_t is emulsion height at a certain time and h_0 is initial emulsion height.

Determination of Destabilization of O/W Emulsion Kinetics Order

The data used for the determination of destabilization of O/W emulsion kinetics order were selected within the first 20 to 40 minutes prior to the initial occurrence of phase separation.

The emulsion destabilization rate could be represented by the Eq. 2 (Levenspiel 1999). The experimental data were evaluated using zero order and first order kinetics models as represented by Eq. 3 and Eq. 4, respectively. The most appropriate model was selected based on the best obtained correlation coefficient (R^2) calculated using the least square procedure.

$$-r_A = -\frac{dS}{dt} = k S^a \quad (2)$$

$$S = S_0 - k_0 t \quad (3)$$

$$\ln(S) = \ln(S_0) - k_1 t \quad (4)$$

with $-\frac{dS}{dt}$ the rate of emulsion destabilization, a the order of emulsion destabilization rate, k_0 and k_1 the emulsion destabilization rate constant for the zero order (% stability/ minute) and for the first order (per minute), respectively, t the storage time (minute), the percentage of emulsion stability after time t and S_0

the initial emulsion stability percentage.

RESULTS AND DISCUSSIONS

O/W emulsions are not thermodynamically stable thus destabilizing with time. However, their kinetic stabilities could be improved by the addition of appropriate emulsifiers. Emulsifiers helped reduce the surface tension between oil and water thus enhancing the dispersion of oil droplets and improving the emulsion stability in overall. In this experiment, the decreases of emulsions stabilities for the first 20 to 40 minutes were studied using zero order and first order kinetics models. This instability was mainly due to oil layer formation on the top and the sedimentation of silica particles at the

bottom. Bigger oil droplets were creaming due to their light densities, whereas the silica particles which were not well absorbed in the interfaces were sedimented due to their heavy densities. The constants of emulsion destabilization rates according to zero and first kinetics order could be seen in **Table 1**.

It was obvious from **Table 1** that R^2 obtained from first order was better in comparison to R^2 of the corresponding zero order. This convinced that emulsion instability occurred according to the first order kinetics. This confirmed the previous investigation (Wanli *et al.* 2000, Tempel 1953, Mirhosseini *et al.* 2008). The lowest destabilization constant was obtained when silica 2% was combined with 1.5% silica. The fittings of the experimental data of this sample using zero order and first

Table 1. Kinetic emulsion destabilizing rates constants and R^2 values according to zero-order and first order kinetic models fitted to the experimental data of stability of emulsions.

Emulsifiers	Zero order		First order	
	k_0 (% stability/min)	R^2	$k_1 \times 10^3$ (min^{-1})	R^2
Room Temperature (~28 °C)				
Without emulsifier	0.2398	0.9252	2.5	0.928
1.5%L+ 0.5%S ^a	0.2756	0.7830	2.9	0.7920
1.5%L+ 2%S	0.2185	0.8723	2.3	0.8789
1.5%L+ 3%S	0.2359	0.7766	2.5	0.7844
Room Temperature (~28 °C)				
2%S+0.05%L	0.3833	0.9443	4.0	0.9484
2%S+0.6%L	0.2320	0.8864	2.4	0.8930
2%S+1.5%L	0.2185	0.8723	2.3	0.8789
Refrigerated Temperature (~8 °C)				
2%S+1.5%L	0.1869	0.8954	1.9	0.9001

^a L and S denoted as Lecithin and Silica, respectively

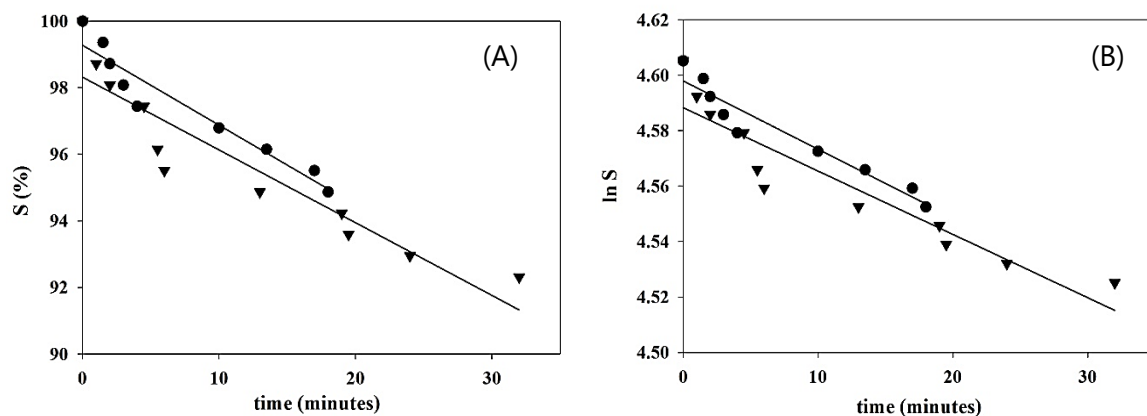


Fig. 1: Oil-in-water emulsion stability with time stored at room temperature ($\sim 28^{\circ}\text{C}$). The full lines represent the fitted kinetic models A) Zero order and B) First order. (●) without emulsifiers; (▼) with 2% silica and 1.5% lecithin.

Table 2. Measured O/W emulsions stabilities upon the addition of silica and lecithin of varying concentrations after 30 minutes and 3 days at room temperatures ($\sim 28^{\circ}\text{C}$)

Emulsion stability without emulsifier (30 minutes) = 75%					
Emulsion stability without emulsifier (3 days) = 58.974%					
2% Silica			1.5% Lecithin		
[Lecithin] (%)	Emulsion stability (%)		[Silica] (%)	Emulsion stability (%)	
	30 minutes	3 days		30 minutes	3 days
0.05	92.308	60.897	0.5	91.667	60.256
0.6	92.308	60.256	2	92.949	62.821
1.5	92.308	62.821	3	92.308	60.256

order kinetics models were depicted on **Fig. 1**.

Furthermore, the destabilization constants were tended to decrease with the increase of lecithin concentrations. On the other hand, it was decreasing with the silica addition up to 2% and then increasing when silica concentration added was 3%. This suggested an optimum silica concentration of 2% were the most suitable within those systems. Silica molecules consisted of silanol group (Si-OH) and siloxane group (Si-O-Si). Silica tended to attract the other silica particles due to their interactions via hydrogen bonding amongst the silanol groups. The

increased silica concentration might increase the silica present in the continuous phase which could consequently accelerate the leaching out of silica particles previously adsorbed at the interface.

Both short-term and long-term stabilities of O/W emulsions prepared using mixed emulsifiers of varying concentrations of lecithin and silica were increased compared to the emulsion without emulsifiers at all as could be seen in **Table 2**. However, there was no significant effect of concentrations of lecithin and silica on the overall emulsion stability. The emulsion stabilized using 2%

silica and 1.5% lecithin showed the highest long-term stability. This indicated the potential uses of biosilica and lecithin as natural emulsifier mixtures for stabilizing O/W food emulsions.

Finally, storage of O/W emulsion at refrigerated temperatures could decrease the destabilization rate by approximately 20% (**Table 1**). This could be understood since at lower temperatures, the viscosities of both oil phase and aqueous phase were increased so that the kinetic movements of lecithin molecules silica particles out of the interfaces were slowed down as well as the coalescence rate of oil droplets. Storage at low temperatures could retard the emulsion destabilization and improve the shelf-life of O/W emulsion products.

CONCLUSIONS

In this experiment, O/W emulsions were kinetically destabilized following the first order kinetics models. The destabilization rate of emulsions stabilized by combination biosilica and lecithin were approximately 10% lower compared to the emulsion without emulsifiers addition. Furthermore, the concentrations variations of both lecithin and silica in the mixed emulsifiers did not significantly influence the instability rates of O/W emulsions. The emulsion destabilization rate of emulsion stored at refrigerated temperatures is about 20% lower compared to that stored at room temperature. This research showed a potential application of mixed natural emulsifiers such as lecithin and silica as the substitutes of synthetic emulsifiers for stabilizing O/W food emulsion both for

short-term and long-term periods. Many trials on O/W emulsion formulations, other natural emulsifiers' selections, and process optimization are still needed to be further investigated. It is not impossible that there would have been some innovation breakthroughs for the development of more healthful food emulsion products for the better future.

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