A kinetic study of oil-in-water emulsion formation stabilized by rice husk ash and lecithin

L Sapei, S W Kurniawan and A P Siantoro

Department of Chemical Engineering, Faculty of Engineering, University of Surabaya, Raya Kalirungkut, Surabaya 60293 East Java, Indonesia

Email: lanny.sapei@staff.ubaya.ac.id

Abstract. Many food products are in the forms of emulsions whereby at least one phase is dispersed in other phases. Since emulsions consist of different immiscible phases, they tend to be unstable with time despite the incorporation of emulsifiers. In this study, the stabilities of oil-in-water (O/W) emulsions prepared using emulsifier mixtures of rice husk ash (RHA) and lecithin were monitored with time and destabilization kinetics of emulsion were studied. Rice husk ash of 2% was combined with various lecithin concentrations ranged from 0.5% to 3%, and they were added into the oil phase. The emulsification was carried out using a rotor stator homogenizer. The results showed that the rate of emulsion destabilization followed the first order kinetic model. The lowest value $k_1$ of $0.4 \times 10^{-3}$ minute$^{-1}$ was obtained from the combination of 2% RHA and 2% lecithin. This implied the synergism action of RHA with lecithin in stabilizing the emulsion. The mixtures of lecithin and RHA seemed to be quite promising in stabilizing the O/W emulsion system for designing healthy O/W emulsion food-based products.

1. Introduction

Food is an essential basic need of human being. Therefore, the overall quality of food products such as appearance, texture, flavour, nutrient, and stability has to be considered. Stabilizers are usually added into food formulations in order to improve the texture and appearance of food products. Emulsifiers are amongst the stabilizers which are commonly added into food formulations containing oil and water phases. Emulsifiers generally consist of one or more hydrophobic groups and one or more hydrophilic groups. Due to its amphiphilic nature, emulsifiers are adsorbed on the oil-water interfaces while reducing the surface tension arising between them and help dispersion of the dispersed phased in the continuous phase. There are increasing attempts to reduce the use of polymeric emulsifiers since they may cause some adverse effects, such as air entrapment, foaming, irritancy, and detrimental interaction with living matter [1] and also obesity [2].

Emulsion stabilized by particles which is so called Pickering emulsion has recently been gaining a great interest since it may impart an extreme stability to emulsion by hindering droplets coalescence, may reduce toxicity thus safer to use in vivo, and may bestow other preferred traits such as porosity, responsiveness, etc [3]. Solid particles such as carbon, silica, clays, iron oxides, hydroxides, metal sulfates, and alumina have been used as stabilizers of either O/W or W/O emulsions [4-7]. Recently, some other solids such as hydroxyapatite, magnetic nanoparticles, chitosan, cyclodextrin, nanotube,
and some food-grade stabilizers and organic particles, including Janus colloidal particles, microsphere, and microcapsule can effectively serve as Pickering emulsifiers [3, 8-9]. Therefore, the applications of Pickering emulsions have become widespread for examples as catalysts, delivery vehicles, porous scaffolds, stimuli-responsive materials, and so on [3].

Silica as an abundant material found in the earth crust has also been richly accumulated in several parts of plants such as horsetail outer epidermal layer [10-12] and rice husk. Silica accumulated in the living tissues is generally known as biosilica [10-11], which is considered safe, and there is No Observed Adverse Effects Level (NOAEL) of 50,000 ppm (mg/L) for dietary silica [13]. Silica is also amongst the additive for foods (E 551) and is typically used as an anti-caking agent. There have been many evidences supporting the potential health benefits of silica such as its contribution to collagen formation and bone health, as well as prevention of toxicity to the brain and maintenance of blood vessel integrity [13]. Therefore, biosilica has a great potential to be incorporated in food systems not only due to its function as emulsifier but also due to its inherent health benefit.

There have been few investigations on the use of biosilica as emulsifiers. Sapei et al. investigated the use rice husk biosilica combined with lecithin [14] and Tween 20 [15] for the stabilization of O/W emulsion and the use of rice husk silica/ Tween-20 for stabilizing the double W/O/W emulsion [16]. It turned out that the incorporation of biosilica together with emulsifiers enhanced the emulsion stability. The destabilization of emulsion with time followed the first kinetic model implying the predominant coalescence phenomena during the emulsion instability process. The lowest destabilization constants obtained were about 2.3x10^{-3} min^{-1} and 1.5x10^{-3} min^{-1} for the O/W emulsions stabilized with rice husk silica combined with lecithin and Tween-20, respectively. Some other researchers used colloidal hydrophilic silica particles (Aerosil) combined with other emulsifiers such as monoolein, lecithin, Tween-60, sodium caseinate) in order to develop “food grade” O/W emulsions [17-19]. It has been observed that use of mixed silica particles and emulsifiers produced O/W emulsions with higher stability due to the formation of smaller droplet sizes compared to those stabilized by either emulsifiers or silica particles. There has been no investigation on the use of rice husk ash for stabilizing O/W emulsion yet. In fact, rice husk ash consists of about ~ 94% silica and other compounds containing metals such as K, Mg, Ca, Fe, etc [20]. This research aimed to investigate the potential use of rice husk ash combined with lecithin to enhance the stability of O/W emulsion based on the emulsion destabilization kinetic study.

2. Materials and Methods

2.1 Materials

Lecithin (PT. Brataco, Surabaya, Indonesia); rice husk was obtained from paddy milling in Mojokerto, East Java, Indonesia; palm cooking oil (Sunco, PT. Milkie Oleo Nabati Industri, Bekasi, Indonesia); demineralized water.

2.2 Preparation of rice husk ash

Rice husks were separated from the dust and debris and then washed with water and finally rinsed with demineralized water prior to drying in an oven (Memmert, Germany) at 105°C for 2 hours. Dried rice husks were burnt in the furnace (Ney VULCAN D-550, Dentsply Ceramco, USA) to remove the organic compounds at 750°C for 5 hours. Rice husk ash (RHA) which was gray in color consisted of silica of about 94% [20]. The rice husk ash was subjected to milling followed by screening with 200 mesh screen prior to further use as the emulsifier.

2.3 Preparation of O/W emulsion stabilized with RHA and lecithin mixtures

Oil phase with the fraction of 0.3 was heated up to 50°C followed by the gradual addition of varying lecithin concentrations of 0.5 – 3% under stirring with a magnetic stirrer. RHA of 2% was subsequently added little by little into the oil. Mixing was continued to 15 minutes until lecithin was well solubilised in the oil. Aqueous phase consisting of demineralized water was heated to 50°C prior
to mixing with the oil phase. The emulsification was carried out using a rotor-stator homogenizer (IKA T25 digital ULTRA TURRAX, Germany) at 20,000 rpm for 5 minutes after aqueous phase was poured into the oil phase. The emulsion was kept in a transparent 40 ml glass vial (ID= 25 mm, height= 95 mm) until the height of ~ 5.65 cm from the bottom was attained and then stored at a room temperature of ~ 28°C. The percentages used belonged to weight %.

2.4 Determination of emulsion stability

The emulsion stability was simply determined using equation (1). The height of emulsion was measured at a certain time interval, i.e. every 1 minute for the first 30 minutes, followed by the measurement in every 5 minutes until 60 minutes, and then the measurement was taken in every 10 minutes until 120 minutes and each day up to 7 days. The stable emulsion layer was indicated by a milky appearance with the formation of neither cream nor silica particles sediment.

\[
\% S = \frac{h_t}{h_0} \times 100\% \tag{1}
\]

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

2.5 Determination of kinetic models of destabilization rate of o/w emulsion.

The data used for the kinetic models determination was within 0-120 minutes since the emulsion stability remained more or less constant after 120 minutes. The destabilization rate of o/w emulsion was fitted using the zero order and first order kinetic models. The most appropriate kinetic order would be chosen based on the best obtained correlation coefficient \((R^2)\) calculated using the least square procedure. The emulsion destabilization rate could be written in an equation as follows [21]:

\[
- \frac{dS}{dt} = k S^a \tag{2}
\]

\[
S = S_0 - k_0 t \tag{3}
\]

\[
\ln(S) = \ln(S_0) - k_1 t \tag{4}
\]

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

3. Results and Discussion

An emulsion is a mixture of at least two immiscible liquids whereas one phase is dispersed in another phase. An emulsifier is required to stabilize the dispersion of the dispersed phase in the continuous phase by lowering the interfacial tension between the two phases thus droplets coalescences or flocculation could be hindered. However, O/W emulsion will definitely undergo instability with time indicated by creaming due to the inherent thermodynamic instability of the emulsion. The macroscopic observation of O/W emulsion stabilized by 2% RHA and 2% lecithin could be seen in Figure 1. It turned out that the emulsion was not stable right after the emulsification (t= 1 min). Creaming and oil layer formation was seen as the results of oil droplets coalescences. RHA seemed to be suspended in the cream layer rather than being adsorbed on the oil-water interfaces. Some RHA was deposited at the bottom of the vials due to sedimentation. Possibly, RHA which was mainly composed of hydrophilic silica did not well intermixed with lecithin in the oil phase, thus lowering its emulsifying capacity on the interfacial layer. It could have been dispersed in the aqueous phase to improve its adsorption in the oil-water interfaces. Previous investigation used oil phase as the loading phase of hydrophilic silica, however sonication was applied to improve the silica dispersity [22]. The stability
of the emulsions was slightly decreasing with time within the range of 50-60% as depicted in Table 1 which was hardly seen in Figure 1. After 7 days, the cream layer seemed thinner since the oil was out from the cream leading to the increase of oil layer. The RHA tended to be sedimented which was not clearly seen in Figure 1. The emulsion instability was mainly due to the coalescences of oil droplets leading to the enlargement of dispersed oil droplets as could be seen in Figure 2.

Figure 1. Stability of O/W emulsions stabilized with 2% RHA and 2% lecithin after being stored at a certain time. A) 1 min; B) 120 min; C) 7 days.

Table 1. O/W emulsion stability stabilized using RHA/lecithin.

| Emulsifiers                  | Emulsion Stability, S (%) |
|------------------------------|---------------------------|
|                              | t = 1 min | t = 60 min | t = 120 min |
| 2% RHA                       | 60.18     | 56.64      | 54.87       |
| 1.5% lecithin                | 61.95     | 53.10      | 53.10       |
| 0.5% lecithin + 2% RHA       | 61.95     | 53.10      | 51.33       |
| 1% lecithin + 2% RHA         | 61.95     | 56.64      | 53.10       |
| 1.5% lecithin + 2% RHA       | 60.18     | 58.41      | 56.64       |
| 2% lecithin + 2% RHA         | 61.95     | 60.18      | 58.41       |
| 2.5% lecithin + 2% RHA       | 60.18     | 58.41      | 56.64       |
| 3% lecithin + 2% RHA         | 60.18     | 58.41      | 56.64       |

Figure 2. The microscopic images of O/W emulsion stabilized with 2% RHA and 2% lecithin after being stored at a certain time. A) 1 min; B) 120 min; C) 7 days.

It was obvious from table 1 and figure 3 that the emulsion stability after 60 or 120 min was improved when lecithin concentration was increased up to 2% and then decreased. Furthermore, the emulsion stability was much improved when combined RHA/lecithin was used instead of single
emulsifier of RHA or lecithin only. The kinetics study was conducted to confirm the effect of lecithin addition on RHA stabilized O/W emulsions as depicted in Table 2. The calculated $k$ constant represented the rate of emulsion stability reduction as time elapsed.

The destabilization process of emulsion followed the first order rather than zero order kinetic models based on the best obtained correlation coefficient ($R^2$). This was in line with the previous study [14-15] implying the predominant coalescences of dispersed oil droplets as the main factor of emulsion instability. The lowest destabilizing rate constant $k_1$ of $0.4 \times 10^{-3}$ min$^{-1}$ was obtained for the emulsion stabilized with 2% RHA combined with 2% lecithin. Higher lecithin concentration reduced the emulsion stability indicated by the higher $k_1$. Lecithin was effective in stabilizing W/O emulsion due to its hydrophobicity therefore the excess of lecithin could lower O/W emulsion stability. Lecithin concentration seemed to influence the stability of emulsion stabilized with RHA in contrast to emulsions stabilized with rice husk silica/ lecithin [14]. Furthermore, the obtained $k_1$ was much lower with the order of 1 in comparison to those obtained from rice husk silica/ lecithin [14] and rice husk silica/ Tween-20 [15]. This may indicate a higher emulsifying capacity of RHA compared to rice husk silica. Probably this was due to the presence of salts containing metals such as Na, K, Ca, Mg retained in RHA which helped reduce the interfacial tension between oil and water.

Table 2. Kinetic emulsion destabilizing rates constants and $R^2$ values according to zero-order and first order kinetic models of O/W emulsions stabilized using 2% RHA and various lecithin concentrations.

| Emulsifiers          | Orde 0          | Orde 1          |
|----------------------|-----------------|-----------------|
|                      | $k_0$ (% stability/min) | $R^2$ | $k_1 \times 10^3$ (min$^{-1}$) | $R^2$ |
| 2% RHA               | 0.0438          | 0.8768          | 0.8            | 0.8556 |
| 2% lecithin          | 0.0943          | 0.8420          | 1.6            | 0.8532 |
| 0.5% lecithin + 2% RHA | 0.0894          | 0.8085          | 1.6            | 0.8275 |
| 1% lecithin + 2% RHA | 0.0812          | 0.8982          | 1.4            | 0.9104 |
| 1.5% lecithin + 2% RHA | 0.0445          | 0.9936          | 0.8            | 0.9949 |
| 2% lecithin + 2% RHA | 0.0266          | 0.8182          | 0.4            | 0.8247 |
| 2.5% lecithin + 2% RHA | 0.0264          | 0.8885          | 0.5            | 0.8940 |
| 3% lecithin + 2% RHA | 0.0374          | 0.9398          | 0.6            | 0.9439 |

The synergism between silica particles with emulsifiers has been reported in many publications [14-15, 17-18, 22]. The presence of emulsifiers modified the wettability of solid particles and most likely enhanced the inter-particle interactions [23]. The adsorption of small amount of lecithin in the

Figure 3. Emulsion stability vs time. A) Comparison of stability of emulsions prepared using 2% RHA with varying lecithin concentrations; B) Comparison of stability of emulsions prepared using combination RHA/lecithin and single emulsifier.
interfacial layer helped reduce the interfacial tension between the two liquid phases followed by the adsorption of RHA which provided a steric hindrance surrounds the oil droplet. A rigid interfacial film consisting of RHA particles and lecithin could also contribute to the improved emulsion stability.

4. Conclusions
The use of mixed rice husk ash (RHA) with lecithin for stabilizing O/W emulsions was studied and supported by the investigation of emulsion destabilization kinetics. Both RHA and lecithin were loaded into the oil phase prior to mixing with the aqueous phase. It turned out that the increase of lecithin concentrations up to 2% improved the stability of RHA stabilized emulsions. The excess of lecithin concentration decreased the emulsion stability. Lecithin adsorbed on the interfacial layer could help decrease the interfacial tension and together with adsorbed RHA particles could form a rigid film which provided a steric hindrance against droplet-droplet coalescence. The emulsion destabilization kinetics followed the first order model. The combination of 2% RHA and 2% lecithin resulted in the lowest k1 value of 0.4 x 10^-3 min^-1, which was 4 times smaller and 2 times smaller than k1 obtained from lecithin only and RHA only, respectively. RHA/lecithin stabilizing emulsions seemed promising for developing healthier food emulsion products.

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