Characterisation of crude palm oil O/W emulsion produced with Tween 80 and potential in residual oil recovery of palm pressed mesocarp fibre

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Abstract. Surfactant-assisted aqueous extraction has been proposed as a “green” alternative to hexane extraction for the recovery of oil from plant matters. An efficient aqueous surfactant extraction system usually use an extended type of ionic surfactant with the ability to produce Winsor type III microemulsion, reducing the interfacial tension (IFT) between plant oil and surfactant solution to an ultralow level (10⁻³ mN/m). However, the safe used of this surfactant in food processing is uncertain leading to non-food application of the recovered oil. In the present study, the potential of Tween 80, a commercial food-grade non-ionic surfactant, was evaluated in the recovery of residual oil from palm-pressed mesocarp. The emulsion produced between Tween 80 and crude palm oil (CPO) was characterised in terms of IFT, droplet size, viscosity and phase inversion temperature (PIT). The effect of surfactant concentration, electrolyte (NaCl) and temperature were studied to determine whether a Winsor Type III microemulsion can be produced. Results shows that although these parameters were able to reduce the IFT to very low values, Winsor type III microemulsion was not produced with this single surfactant. Emulsion of CPO and Tween 80 solution did not produce a PIT even after heating to 100°C indicating that middle phase emulsion was not able to be formed with increasing temperature. The highest percentage of oil extraction (38.84%) was obtained at the concentration above the critical micelle concentration (CMC) of Tween 80 and CPO, which was at 0.5 wt% Tween 80 with 6% NaCl, and temperature of 60°C. At this concentration, the IFT value is 0.253 mN/m with a droplet size of 4183.8 nm, and a viscosity of 7.38 cp.

1. Introduction
Crude palm oil (CPO) is usually obtained by mechanical screw press. After this mechanical pressing, there is still 5-11% residual oil per dry weight retained in the palm-pressed fibre (PPF). Subramaniam et. al. (2013) reported that the residual oil from PPF contains higher vitamin E which is 1700-2600 ppm as well as higher carotenes of 1400-1600 ppm compared to common CPO which are 600-1000 ppm and 500-700 ppm respectively. This precious substances left in residual oil from PPF make it significant to be extracted [1].

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Surfactant-assisted aqueous extraction process (SAAEP) has been proposed as an environmentally friendly alternative to hexane extraction for the recovery of oil from plant materials such as corn germ and canola seeds [2]. The surfactant reduces the high interfacial tension (IFT), the surface energy exerted by intermolecular interactions, between two immiscible phases of oil and water [2]. An efficient aqueous surfactant extraction system usually has the ability to reduce the IFT value to an ultralow level ($10^{-3}$ mN/m) [3]. Previous researches have shown that ultralow value of IFT contributed to significantly high extraction efficiency and free oil recovery [2,3]. Formulating microemulsion between surfactant and vegetable oils in the form of triglycerides is quite challenging compared to hydrocarbons. The complexity of the large triglyceride molecules as well as its sensitivity to air, light and temperature render the emulsification process difficult compared to hydrocarbon oils. Other than that, when triglycerides undergo decomposition, the products formed i.e. mono-and-di-acylglycerol are also amphiphiles and will change the surface activities such as the critical micelle concentration (CMC) of the formulation [4].

Proper structure and system of surfactant will contribute to the condition whereby hydrophilic-lipophilic balance can be achieved. This is called the middle phase microemulsion. This transition phase can be achieved by electrolyte addition at optimum salinity for anionic surfactants as well as increasing temperature to the phase inversion temperature (PIT) for non-ionic surfactants [5]. Previously, conventional surfactants was not able to reduce the IFT between oil and water to an ultralow level. Extended surfactant, a special surfactant with unique structure of having groups of intermediate polarity in between hydrophilic and lipophilic group of the surfactant, acts like a linker or a bridge that will provide stronger interaction between the hydrophobic group of the surfactant and the hydrophobic oil as well as between hydrophilic group of surfactant and water. This strong interaction will contribute to IFT reduction to the ultralow level [2,3]. However, the health and safety aspects of extended surfactant in food processing application is uncertain.

Tween 80 is a commercial food-grade non-ionic surfactant that has relatively low toxicity, low irritation potential and is widely used in pharmaceutical microemulsion preparation [6]. The structure of Tween 80 comprised of polyoxyethylene (20) and sorbitan monooleate. Compared to Tween 20 and Tween 40, Tween 80 is less viscous and possess a lower CMC, which means that the system will use less surfactant to achieve minimum IFT [7]. In this study, the potential of Tween 80 in the recovery of residual oil from palm-pressed mesocarp was evaluated. The effect of surfactant concentration, electrolyte (NaCl), and temperature was studied to determine whether a Winsor Type III microemulsion can be produced by using this single commercial surfactant. The IFT, droplet size and viscosity was then correlated to the oil extraction efficiency.

2. Materials and Methods

2.1 Materials

Tween 80 (R&M), Sodium Chloride (R&M), and n-hexane were purchased from Evergreen Sdn Bhd. Crude palm oil and palm pressed fibre (PPF) was kindly provided by Palm Oil Mill Sg Tengi under Felda Plantation Sdn. Bhd.

2.2. Determination of Phase Inversion Temperature (PIT)

0.1g of CPO was mixed with Tween 80 based on specified ratios. This CPO-Tween 80 mixture was homogenised using a magnetic stirrer at room temperature. Next, water was added to make 100 % (w/w) mixtures. The mixtures were heated from room temperature until 100°C at an interval of ~1.0°C/min while stirring at ~500 rpm on hot plate stirrer. The physical appearance of CPO/Tween 80 emulsion was observed throughout the heating process. The clear temperature and temperature when emulsion turns back to cloudy were reported to determine the presence of PIT and the type of emulsion formed [8].
2.3. Measurement of Interfacial Tension (IFT)
The IFT between CPO and the aqueous Tween 80 solution was measured using a spinning drop tensiometer (SVT 20N). Tween 80 solutions were prepared at specified concentrations and injected into a 10 ml glass capillary tube. Then, one drop of CPO was injected into the capillary. The capillary was rotated until an elongated cylindrical drop was obtained and measurement of IFT was taken at equilibrium. From preliminary observation, the IFT reached equilibrium within 30 minutes to an hour. Therefore, the measurements were taken within this period [3]. All measurements for IFTs involving CPO were maintained at 60°C to prevent crystallisation [9].

2.4. Measurement of Droplet Size
0.1 g of CPO was weighed and mixed with specified concentrations of Tween 80 and stirred using a magnetic stirrer until homogenized. Then, distilled water was mixed and homogenized again at 60°C for 10 minutes to form emulsion. After that, 2 ml of emulsion was injected into a glass cuvette and droplet size was measured using Nanoplus. The reading was taken at the region of optimum intensity [10].

2.5. Viscosity Analysis of Extraction Medium
Different concentrations of Tween 80 solution were mixed with 6% NaCl solution. These mixtures were shaken in a water bath shaker at 60°C at 185 rpm for 30 minutes. This condition was considered based on the extraction condition. Next, the viscosity of the solutions was measured using the Brookfield Programmable DV-II Viscometer using spindle no 2.

2.6. Oil Extraction Efficiency using SAAEP
PPF was dried until the moisture content was less than 5 wt%. The residual oil content of this PPF after pressing was analysed by Soxhlet extraction and used as the reference total oil to calculate the oil extraction efficiency of SAAEP. The reference total oil of PPF used was 16.94% per dry weight. 8 g of PPF was mixed with 200 g Tween 80 solution in a 500 ml bottle. Then, the mixture was shaken using a horizontal thermo shaker at 60°C at 185 rpm for 30 minutes. The slurry was then centrifuged using a swing bucket rotor at 3500rpm for 1 hour. Then, the centrifuge bottle was placed in a freezer for 1 hour and the free oil was scrapped. The middle and solid layers were left to cool at room temperature and the middle layer was pipetted out. The solid was dried and the residual oil after SAAEP was extracted using hexane via Soxhlet apparatus. The residual oil was weighed and subtracted from the reference total oil of PPF to obtain the oil extraction efficiency [2].

3. Results And Discussion

3.1. Effect of Tween 80 concentration on IFT reduction

![Figure 1](image_url)

*Figure 1.* Effect of concentration of Tween 80 on IFT between CPO and Tween 80 solution (60°C, 1 hour).
Referring to Figure 1, Tween 80 concentration was varied in order to observe its effect on the reduction of IFT. The measurements were conducted at 60°C to prevent crystallisation since CPO exists as a semi solid at room temperature [5]. IFT value between pure water and CPO was 4.908 mN/m (data not shown). IFT value between water and oil depends on the types and composition of oil. For example, previous literature has reported that the IFT value between soybean oil and water was 5.3 mN/m [11]. Different types of CPO also give different IFT which was in the range of 6.0-9.6mN/m from the different study [9]. As seen in Figure 1, when very low concentration of Tween 80 was introduced into the system, starting at a concentration of 0.001wt%, the IFT value dropped to 2.518 mN/m. This reduction proves that there was an adsorption of surfactant at the oil-water interfaces due to the interaction between the hydrophobic oil and the hydrophobic molecule of the surfactant and between water molecules and the hydrophilic part of the surfactant [7]. At a concentration of 0.05 wt%, an equilibrium IFT of 0.51 mN/m was obtained and after this concentration, the IFT value reaches equilibrium and cannot be reduced further. The CMC of Tween 80/CPO solution can then be considered as 0.05 wt%. Different surfactant has their own effectiveness level which represents its ability and limit to reduce the IFT to a minimum level [5]. Previous study using different type of surfactant also showed that the IFT between triglycerides and the surfactant solution cannot achieve an ultralow value. IFT of the surfactant with triolein can only reach 2.6 X 10^{-1} mN/m, whereas IFT with n-octane can reach 4.9X10^{-3} mN/m [4]. If a microemulsion can be produced between the surfactant solution and CPO, a second drop in IFT should be seen when the concentration is increased after the CMC, but this was not the case for Tween 80/CPO emulsion even though the concentration of Tween 80 was increased up to 30 wt%. A very high concentration of Tween 80 however is considered impractical for extraction purposes.

3.2. Effect of temperature on CPO solubilisation
The importance of increasing temperature in non-ionic surfactant is similar to the addition of electrolyte in anionic surfactant which has been proven to cause significant reduction in IFT between some vegetable oils and water in previous literatures [2,3]. Observation of the phase behaviour of CPO/Tween 80 solution at increasing temperature and different concentration of Tween 80 was conducted to investigate the existence of a phase inversion temperature (PIT). PIT occurs between the solubilisation temperature and the cloud point temperature where clear emulsion turns back to a cloudy solutions [8]. From our preliminary experiments, it was found that pure Tween 80 solution in water did not exhibit a cloud point since the solution maintained as a clear phase up to a temperature of 100°C [4]. The cloud point temperature can be considered as pseudo-phase inversion, in which the inversion from non-ionic detergent-in-water phase (D/W) to water-in-detergent phase (W/D) occurs. Phase inversion temperature (PIT) of emulsion is expected to be near the cloud point of the solution used. The presence of oil in emulsion may lower or raise the cloud point of the surfactant [12].

| Table 1. Solubilisation Temperature CPO/Tween 80 at different concentrations |
|---------------------------------|-------------------------------|-----------------|-----------------|
| Concentration Of Tween 80 | Ratio Of CPO:Tween 80 | Composition | Solubilization Temperature |
|---------------------------------|-------------------------------|-----------------|-----------------|
| 1% | 0.1:1 | 0.1g CPO 1g Tween 80 98.9g Water | No Clear Emulsion |
| 5% | 0.1:5 | 0.1g CPO 5g Tween 80 94.9g Water | 78°C |
| 10% | 0.1:10 | 0.1g CPO 10g Tween 80 89.9g Water | 75°C |
| 50% | 0.1:50 | 0.1g CPO 50g Tween 80 49.9g Water | 80°C |
Emulsions of CPO/Tween 80 at room temperature for all concentration of Tween 80 shows a milky appearance until the temperature reached the solubilisation temperature as shown in Table 1. After this temperature the milky solution turn to clear emulsions. This occurs at about 75 to 80 °C for Tween 80 concentration of 5 % and higher. However, until boiling occurs, there was no transition seen from the clear phase back to a cloudy phase. Therefore, there were no cloud points present for emulsions of CPO/Tween 80. It can be deduced that Tween 80/ CPO solution did not exhibit the inversion from Winsor Type I to Winsor Type II microemulsion. As the transition did not occur, the temperature where the middle phase Winsor Type III microemulsion occur also cannot be determined from the phase inversion technique. Nevertheless, it can be inferred that middle phase microemulsion of Tween80/CPO might be produced only at a higher temperature than 75 °C. Temperature close to the water boiling point however was not economically practical for extraction purposes.

3.3. Effect of NaCl on IFT reduction

As seen in Figure 2, the addition of NaCl reduces the IFT to a small degree. With up to 6 wt% NaCl, the IFT can be reduced to 0.253 mN/m from 0.449 mN/m with no NaCl. Although the effect of electrolyte was not significant in non-ionic surfactant compared to anionic surfactant, electrolyte still contributes to the mechanism of ‘salting out’ of the hydrophobic groups in non-ionic surfactant. This process resulted in the hydrophobic groups become more dehydrated and adsorption increases. Increase in adsorption at the interface of oil and water causes the IFT to decrease. In contrast, for anionic surfactant, the repulsion of ionic charges between the hydrophilic/hydrophobic group of ionic surfactant and the electrolyte assists in the IFT reduction of the system. However, in non-ionic surfactant system, as the electrolyte only effects the hydrophobic group, the ‘salting out’ will occur only when the surfactant molecules are in the monomeric form [5].

3.4 Droplet Size Measurements

| Concentration Of Tween 80 (w/v %) | Interfacial Tension With CPO (mN/m) | Emulsion Droplet Size (nm) |
|----------------------------------|-------------------------------------|---------------------------|
| 0% (distilled water only)        | 4.908                               | -                         |
| 0.5 % ( without NaCl)            | 0.449                               | 1395.8                    |
| 0.5 % (with 6% NaCl)             | 0.253                               | 4183.8                    |
| 30 % (without NaCl)              | 0.623                               | 13.5                      |
| 30% (with NaCl)                  | 0.238                               | 19.8                      |
As the concentration of Tween 80 increases, the size of the emulsion droplet decreases (Table 2). At 30 w/v% Tween 80 concentration, the droplet size became less than 100 nm. This shows that the emulsion size was in microemulsion range although the interfacial tension did not reach an ultralow value. Similarly, previous literature involving the emulsion of palm oil and Tween 40 also showed that increasing concentration of surfactant reduces the size of emulsion droplet to microemulsion range but yet the IFT was not able to reach an ultralow value [13]. The addition of an electrolyte (NaCl) reduces the IFT but did not cause the size of the droplets to reduce.

3.5 Oil Extraction efficiency

Referring to Figure 3(a), the percentage of oil extraction from PPF using pure water only is about 21%. When Tween 80 was added at 0.001% and 0.005%, the extraction efficiency was almost in the same range although the IFT decreases. These low Tween 80 concentrations may not be enough to reduce the IFT until a value that can detach the oil from mesocarp fibre. However, when the concentration was increases to 0.5%, the oil extraction efficiency increases to about 37%. The highest extraction efficiency correlates with the CMC of Tween 80 in CPO as seen previously in Table 2. At this CMC, the IFT is the lowest, and it is the onset of micelle formation. This contributes to the maximum increase in extraction efficiency. Similarly, previous literature involving extraction of
soybean oil from soybean seeds shows that the reduction of IFT increase the extraction efficiency of aqueous extraction process. When the IFT of water/sodium dodecyl sulphate (SDS)/oil reduces from 5.3 mN/m (without surfactant) to 2.1 mN/m with the addition of 3 %( w/w) SDS, soybean oil the extraction efficiency increases from 71.7% to 84.8%. However, further increase in Tween 80 concentration to 10% and 30 % causes the oil extraction efficiency to become much lower than extraction using pure water. Hence, although at 30% concentrations the droplet size is in the microemulsion range which is desirable for extraction, the efficiency is the lowest. Correlation between Tween 80 concentration and viscosity (Figure 3b) shows that the viscosity of 10 and 30 % solution is very high compared to 0.5 wt %. Hence the high viscosity of the solution may reduce the flowability of CPO into the extraction medium. Although high concentration of Tween 80 was able to break up the oil droplets into microemulsion size, the oil is not able to diffuse from the surface of solid mesocarp into the bulk surfactant solution due to the viscous medium. Diffusion of oil is a very important mechanism in extraction [11]. Furthermore, different extraction mechanisms take place at different surfactant concentrations. Usually below and near the CMC, synergism between roll-up and snap-off mechanism resulted in the liberation of free oil phase while at a much higher surfactant concentration than the CMC, solubilisation mechanism takes place which require complicated demulsification process. Therefore, microemulsion system must be optimized at low surfactant concentration to increase the extraction via rollup and snap-off mechanism and to avoid solubilisation mechanism [14].

4. Conclusion
The work shows that the IFT between CPO and Tween 80 solution is greatly affected by Tween 80 concentration up to the critical micelle concentration. The equilibrium IFT achieved is 0.51 at 0.05 wt % Tween 80. The addition NaCl however only has slight effect on the IFT and was not able to reduce the IFT to an ultra-low level. CPO can be solubilised in the Tween 80 solution at a temperature of 75 °C and higher. However, the phase inversion temperature of CPO/Tween 80 emulsion was not observed up to 100 °C temperature limit. Therefore it can be deduced that microemulsion of CPO/Tween 80 solution cannot be achieved at 75 °C or lower. In terms of droplet size, microemulsion size can be achieved using a high concentration of Tween 80 (30% w/v), although the IFT did not drop to an ultra-low range. The highest percentage of oil extraction (38.84%) was obtained at the critical micelle concentration (CMC) of Tween 80 and CPO, which was at 0.5 wt% Tween 80 with 6% NaCl, and temperature of 60°C. At the CMC, the IFT value is 0.253mN/m with a droplet size of 4183.8 nm, and a viscosity of 7.38 cp. As the Winsor Type III microemulsion and ultralow IFT can greatly enhance aqueous extraction process, further works are ongoing to identify method to create the middle phase microemulsion for Tween80/CPO emulsion particularly using a mixed surfactants formulation.

5. References
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