Optimization of palm oil extraction from Decanter cake of small crude palm oil mill by aqueous surfactant solution using RSM

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Abstract. The use of hexane to extract vegetable oil from oilseeds or seed cake is of growing concern due to its environmental impact such as its smelling and toxicity. In our method, used Response Surface Methodology (RSM) was applied to study the optimum condition of decanter cake obtained from small crude palm oil with aqueous surfactant solution. For the first time, we provide an optimum condition of preliminary study with decanter cake extraction to obtain the maximum of oil yield. The result from preliminary was further used in RSM study by using Central Composite Design (CCD) that consisted of thirty experiments. The effect of four independent variables: the concentration of Sodium Dodecyl Sulfate (SDS) as surfactant, temperature, the ratio by weight to volume of cake to surfactant solution and the amount of sodium chloride (NaCl) on dependent variables are studied. Data were analyzed using Design-Expert 8 software. The results showed that the optimum condition of decanter cake extraction were 0.016M of SDS solution concentration, 73° C of extraction temperature, 1:10 (g:ml) of the ratio of decanter cake to SDS solution and 2% (w/w) of NaCl amount. This condition gave 77.05% (w/w) oil yield. The chemical properties of the extracted palm oil from this aqueous surfactant extraction are further investigated compared with the hexane extraction. The obtained result showed that all properties of both extractions were nearly the same.

1. Introduction
One small crude palm oil mill located in the southern part of Thailand name Sangarun Palm Oil Co.,Ltd. (Thailand) produced crude palm oil around three tons per day. This mill not only produced palm oil but also by-products such as decanter cake, cake before filtration and cake after filtration were also produced too. All by-products had around 900-1,200 kilograms per day. The mill owner tried to make value added from the by-products by extraction the residue oil that left in all by-products. One popular technique is to use hexane as solvent for oil extraction. Hexane has been broadly used in the vegetable oil industry due to its high oil extraction efficiency, over 99%. Vegetable oils are typically produced from oilseeds by either hexane extraction or a combination of mechanical processing and hexane extraction. However, there are growing health concerns and increased environmental regulations regarding the use of hexane in vegetable oil extraction. Exposure to hexane at 15 ppm/day for three months has been shown to cause peripheral nerve damage, and hexane is also a potential hazardous explosive material. Thus, extraction systems must fully contain hexane and provide for a leak detection. Future laws may be even more stringent; therefore, hexane-free extraction approaches are needed [1]. So, a new oil extraction technique is needed to replace hexane solvent. It is found that aqueous surfactant solution combined with sodium chloride technique is promising technique to replace hexane technique.
An aqueous extraction process, used water as a solvent, is one of the methods to extract vegetable oil. Currently, this method can achieve >70% of oil extraction efficiency [2]. However, to accomplish this yield, the extractor must execute at 50°C and a large amount of chemical reagent applied to adjust a pH to 12 [3].

A surfactant is an amphiphilic compound comprised of polar and non-polar parts, thus enabling the surfactant to reduce interfacial tension (IFT) of the system. By definition, IFT is the repulsive energy between two different species of molecules [4]. In other words, it is minimum energy required to separate one phase into another phase, increasing the surface area among the two phase. A high IFT value implies that the two species of molecules are very different in polarity [1]. The IFT value between water and vegetable oil is very high, between 20 and 30 mN/m [6]. Moreover, reduced IFT aids disruption of the oil trapped inside the oilseed matrix; the oil droplets are then readily transported to the aqueous phase [7]. Several reports showed that the IFT should be reduced to 0.01 mN/m (ultralow level) by incorporation of surfactant with co-solvent or use of an extended surfactant [5, 8-10].

Response surface methodology (RSM) is a useful statistical technique which has been applied in research into complex variable processes. It employs multiple regression and correlation analyses as tools to assess the effects of two or more independent factors on the dependent variables. Its principal advantage is the reduced number of experimental runs required to generate sufficient information for a statistically acceptable result. Response surface methodology has been successfully applied in the study and optimization of biodiesel production with rapeseed oil, soybean oil, etc. [11]. Hence, the objectives of this work are: (1) maximize the oil recovery by the effect of temperature, surfactant concentration, ratio of cake to SDS solution and %NaCl (w/w) in decanter cake by using aqueous surfactant solution combined with sodium chloride; (2) determine the above optimum condition in decanter cake extracted using aqueous surfactant solution combined with sodium chloride by response surface methodology (RSM); (3) compare the properties of the crude palm oil obtained from hexane and SDS surfactant extraction.

2. Materials and Methods

Sodium dodecyl sulfate (SDS, biotechnology grade), Methanol (≥99.9% purity), hexane (99% purity). Only decanter cake was used in this research that obtain from small crude palm oil mill named Sangarun Palm Oil Co., Ltd. (Thailand).

Crude palm (4 g) was mixed with 40 mL of 0.02 M SDS solution. The mixture was mixed for 30 min, 70°C for temperature at 1,500 rpm (IKA, C-MAG HS7, Germany) on a digital hot plate/stirred and then centrifuged for 30 min at 8,000 rpm (CEN-D Nanasiam Intertrade, LDJ-5C). After centrifugation, two layers were obtained: liquid layer and solid layer. The liquid layer occurred on the top was separated and further heated. After that hexane was added into the liquid for oil recovery. The extracted oil was evaporated under vacuum evaporator to obtain crude palm oil. The palm oil extraction yield was calculated followed the Equation 1.

\[
\text{Oil yield (\%) = } \left( \frac{\text{weight of oil}}{\text{weight of sample}} \right) \times 100
\]

Method

2.1 Preliminary study of oil extraction

Decanter cake was extracted by aqueous surfactant solution. There are four variable effects for study on oil extraction. These are concentration of sodium dodecyl sulfate (SDS) (0.01 M, 0.02M, 0.03M, 0.04M and 0.05M), temperature (50°C, 60°C, 70°C, 80°C and 90°C), ratio of amount of cake to SDS (1g:5mL, 1g:10mL, 1g:15mL and 1g:20mL) and amount of sodium chloride (NaCl) (1%, 2%, 3%, 4% and 5% (w/w)) with keeping the constant of stirring at 1500 rpm and 30 min of contact time. The preliminary study is conducted for preliminary optimum condition that they will applied on RSM study.
2.2 RSM study of oil extraction

The obtained preliminary optimum condition was used to design the experiment for RSM and central composite design (CCD) using 5-level-4-factors. At five levels of independent variables from -2 to +2, 30 experiments were required. Surfactant concentration (A), temperature (B), the ratio of cake to SDS solution (C) and %NaCl (w/w) (D). The central values (zero level) chosen from preliminary studied for experimental design. The level and independent variable used for reaction were shown in Table 1. The experimental data were analyzed using a second order polynomial equation (Eq.2) to find the interaction between %oil yield and the independent variables.

\[ Y = \beta_0 + \sum_{i=1}^{2} \beta_i X_i + \sum_{i=1}^{2} \sum_{j=i+1}^{2} \beta_{ij} X_i X_j \]  

(2)

where, \( Y \) is the respond (%oil yield), \( \beta_0 \) is the intercept, \( \beta_i \), \( \beta_{ii} \) and \( \beta_{ij} \) are the linear, quadratic and interactive coefficients, respectively and \( X_i \) and \( X_j \) are the independent variables. Statistical analysis of equation was employed to evaluate the analysis of variance (ANOVA) and Design Expert 8 software (State Ease Inc., Minneapolis, Mn, USA) was used to design the experiments and carry out the regression analysis and plotting graphical of data. The independent variable and level used for reaction experiment parameter were designed as shown in table 1.

| Table 1. Independent variables and levels for CCD of RSM |
|-----------------------------------------------|
| Variables | Symbol | Coded | Levels |
|----------|--------|-------|-------|
| Surfactant concentration (M) | A | 0.005 | 0.01 | 0.015 | 0.02 | 0.025 |
| Temperature (°C) | B | 50 | 60 | 70 | 80 | 90 |
| Cake to SDS solution ratio (g:mL) | C | 1:6 | 1:8 | 1:10 | 1:12 | 1:14 |
| NaCl (%w/w) | D | 1 | 1.5 | 2 | 2.5 | 3 |

2.3 Analysis of crude palm oil

Both crude palm oils obtained from hexane extraction using soxhlet extractor and SDS solution extraction were analyzed their properties for comparison. These properties were free fatty acid (FFA), iodine value (IV), deterioration of bleachability index (DOBI), saponification value (SV), Moisture content (MC) and Insoluble impurities.

3. Results and Discussion

3.1 The result from preliminary study of oil extraction

3.1.1 Effect of surfactant concentration

Increasing the SDS concentration from 0.01 M to 0.02 M resulted in increasing oil yield after that the oil yield decreased from the SDS concentration from 0.02 M to 0.05 M. At the critical micelle concentration (CMC) of each surfactant system, where the first micelle is formed, the IFT of the system is dramatically reduced [4]. In water, the CMC of SDS was 0.008 M at 25°C [12]. This reduces the IFT among the oil and water phases leading to degradation of oil into the surfactant solution [8, 9]. It can be that the CMC of SDS in the process of extraction should be higher than 0.008 M at 25°C. So, in this effect, the concentration of SDS at 0.02 M was selected for optimum condition.

3.1.2 Effect of Temperature

Increasing temperature from 50°C to 70°C resulted in increased oil yield after that the oil yield decreased from 70°C to 90°C. There was no increase in oil yield after 70°C (figure 2). One of explanation may be a reduction of IFT during the extraction temperature. The highest oil yield achieved at 70°C. This result could be explained by the IFT of the process. The IFT between palm oil and SDS solution on this work was small. Therefore, SDS solution reduced the heat energy required to disperse palm oil into the extraction medium. These results suggest to use of 0.02 M SDS at 70°C.
3.1.3 Effect of Cake to SDS solution ratio
Experiments were conducted with 4 g of decanter cake at different amounts of cake to SDS solution. The ratio of cake to SDS solution from 1g:5mL to 1g:20mL had impact on the oil yield (figure 3). However, increasing the cake to SDS solution ratio to higher than 1g:10mL, oil yield was decreased. This may be similar to the “Effect of Temperature” that an increase in SDS concentration from 0.02 M to 0.03M resulted was dissimilarity. As explain above, increased SDS concentration in the system may increase emulsion formation.

3.1.4 Effect of %NaCl (w/w)
In recent studies, surfactants have been used for the extraction of oil from cruciferous [13] and palm kernel oil seeds by selecting optimum surfactant and salt concentrations based on interfacial tension (IFT) and phase behavior data [9]. The optimum salinity of the system denotes the electrolyte concentration where the surfactant system attained minimum IFT. Increasing the amount of NaCl from 1% to 2% resulted oil yield increase, after that the oil yield decrease from the amount of NaCl 2% to 5%. The result was shown in figure 4. The obtained highest oil yield with NaCl is at 2% (w/w).

The summary results from preliminary study of oil extraction from figure 1 to figure 4 were 0.02 M of SDS concentration, 70°C, 1g:10mL of cake to SDS ratio and 2% of NaCl amount. These conditions were used in CCD of RSM study.
3.2 The results from RSM study of oil extraction

The conditions for aqueous extraction of oil from decanter cake were optimized by RSM using CCD in Table 2 shows the experimental design with code variable observed and predicted values of % oil yield. A Design-Expert 8 software was employed to determine and evaluate the coefficients of the full regression model equation and their statistical significance. The second polynomial model for the % oil yield is regressed as shown in Equation 3

\[ Y = 76.39 + 3.25A + 4.38B + 3.94C + 2.66D - 3.69AB - 0.26AC - 1.63AD \\
- 0.2BC + 0.75BD + 1.08CD - 1.43A^2 - 3.53B^2 - 3.97C^2 - 4.64D^2 \]  

(3)

Where \( A, B, C \) and \( D \) correspond to the coded values of the four variables (surfactant concentration, temperature, ratio of cake to surfactant and %NaCl). The oil yield was in the range of 42.91-73.93% (w/w). The \( p \) value of the model was less than 0.0001 indicating that the model was significant. In addition, the suitability of model was also tested by using the regression equation determination coefficient (\( R^2 \)). Regression analysis showed the coefficient of determination (\( R^2 = 0.9002 \)) was satisfactory for validating the significant of the model. All the independent variables (\( A, B, C \) and \( D \)), four quadratic terms (\( A^2, B^2, C^2 \) and \( D^2 \)) and three interaction terms (\( AB, BC \) and \( BD \)) had significant effect on \( Y (p<0.05) \). In figure 5 and figure 6 shows the results express the interactions between the two independent variables while the another two variables were maintained at the central point.

| Run | Surfactant concentration (M) | Temperature (°C) | Cake to surfactant ratio (g/mL) | NaCl (%w/w) | Observed Oil (%) | Predicted Oil (%) |
|-----|-----------------------------|------------------|-------------------------------|-------------|-----------------|------------------|
| 1   | -1                          | -1               | -1                            | -1          | 42.91           | 45.74            |
| 2   | -1                          | -1               | -1                            | +1          | 44.53           | 41.73            |
| 3   | -1                          | -1               | +1                            | -1          | 58.56           | 56.73            |
| 4   | -1                          | -1               | +1                            | +1          | 65.11           | 63.95            |
| 5   | -1                          | +1               | -1                            | -1          | 48.82           | 50.43            |
| 6   | -1                          | +1               | +1                            | -1          | 55.53           | 52.88            |
| 7   | -1                          | +1               | +1                            | +1          | 63.61           | 60.94            |
| 8   | -1                          | +1               | +1                            | +1          | 72.02           | 73.49            |
| 9   | +1                          | -1               | -1                            | -1          | 61.92           | 60.43            |
| 10  | +1                          | -1               | -1                            | +1          | 58.70           | 56.78            |
| 11  | +1                          | +1               | +1                            | +1          | 63.78           | 62.45            |
| 12  | +1                          | -1               | +1                            | -1          | 64.06           | 65.43            |
| 13  | +1                          | +1               | -1                            | -1          | 66.56           | 67.80            |
| 14  | +1                          | +1               | +1                            | -1          | 67.32           | 65.42            |
| 15  | +1                          | +1               | +1                            | +1          | 67.98           | 66.97            |
| 16  | +1                          | +1               | +1                            | +1          | 70.91           | 67.43            |
| 17  | -2                          | 0                | 0                             | 0           | 45.73           | 43.56            |
| 18  | +2                          | 0                | 0                             | 0           | 66.82           | 65.03            |
| 19  | 0                           | -2               | 0                             | 0           | 53.72           | 52.45            |
| 20  | 0                           | +2               | 0                             | 0           | 67.13           | 66.03            |
| 21  | 0                           | 0                | +2                            | 0           | 49.08           | 51.45            |
| 22  | 0                           | 0                | 0                             | -2          | 68.35           | 70.34            |
| 23  | 0                           | 0                | +2                            | 0           | 68.19           | 70.94            |
| 24  | 0                           | 0                | 0                             | +2          | 71.56           | 70.34            |
| 25  | 0                           | 0                | 0                             | 0           | 73.65           | 75.76            |
| 26  | 0                           | 0                | 0                             | 0           | 72.86           | 75.76            |
| 27  | 0                           | 0                | 0                             | 0           | 72.94           | 75.76            |
| 28  | 0                           | 0                | 0                             | 0           | 73.11           | 75.76            |
| 29  | 0                           | 0                | 0                             | 0           | 73.93           | 75.76            |
| 30  | 0                           | 0                | 0                             | 0           | 73.46           | 75.76            |
Figure 5. The 3-D response surface plot for the effect of (a) %NaCl/SDS concentration, (b) %NaCl/temperature, (c) %NaCl/ cake to SDS solution ratio, (d) temperature/cake to SDS solution ratio, (e) temperature/SDS concentration and (f) cake to SDS solution ratio/SDS concentration on oil yield.

The response surface plot of %oil yield from reaction with independent variables was shown in figure 5. The response surface plot showed the optimal condition between the various variables. Figure 5a, 5b and 5c showed the interaction between %NaCl (D) with SDS concentration (A), temperature (B) and cake to SDS solution ratio (C) respectively. It revealed the increased %oil conversion with increasing the variables. In addition, the figure 5d and 5e showed the interaction between temperature (B) with SDS concentration (A) and cake to SDS solution ratio (C). The figure 5f showed the interaction between cake to SDS solution ratio (C) with SDS concentration (A). The %oil yield increased with increasing of variables.

The optimum condition of this process was predicted by applying numerical optimization of Design-Expert 8 software using RSM. The oil production was produced with high oil yield (77.05 %) at 0.016 M of SDS at 73°C of temperature, 1g:10mL of cake to SDS solution ratio and 2% of NaCl (w/w) amount by constant keeping 1,500 rpm of stirring rate and 30 min of extraction time.

3.3 The result of oil analysis

The quality of the difference extraction crude palm oil was tested by following the standards of AOCS. The results were shown in Table 3.

| Parameter                  | Test Method                        | Extracted by SDS | Extracted by hexane | Limit crude palm oil |
|----------------------------|------------------------------------|------------------|---------------------|---------------------|
| Free Fatty acid (%w)       | AOCS official method Ca 5a-40      | 7.92             | 7.75                | ≤ 5.00              |
| Iodine value (g I/100 g)   | AOCS official method Cd 1-25       | 47.71            | 48.28               | ≥ 50.00             |
| DOBI                       | Developed by Dr. P.A.T. Swoboda     | 0.95             | 0.97                | ≥ 2.00              |
| Saponification (mg KOH/g)  | -                                  | 180.76           | 182.27              | -                   |
| Moisture content (%w)      | -                                  | 0.71             | 0.69                | ≤ 0.50              |
| Insoluble impurities (%w)  | -                                  | 0.0055           | 0.0037              | ≤ 0.50              |
| Oil yield (%w/w)           | -                                  | 77.05            | 78.36               | -                   |
4. Conclusion
The aqueous surfactant extraction offered several advantages when compared with hexane extraction. The aqueous surfactant extraction method can be operated at ambient temperature using non-toxic and nonflammable solvents. Surfactant concentration, temperature, ratio of cake to SDS solution and \%NaCl (w/w) were impacted on oil yield. The highest yield oil extraction after using RSM was 77.05\% respectively, using SDS 0.016 M at 73°C with cake to SDS solution ratio 1g:10mL, stirring at 1,500 rpm for 30 min and 2\% NaCl (w/w). The properties of decanter cake were compare with extracted by aqueous surfactant and Soxhlet hexane extraction, the results shown that all properties of both extractions were nearly the same.

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