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Microemulsion-Based Palm Kernel and Peanut Oil Extraction using Nonionic Surfactant Brij 30 Solution

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Abstract : Soxhlet extraction method using hexane is widely used for vegetable oil extraction. This method is very efficient but the presence of hexane residue in the extract is not favorable. However, the difficulty in complete removal of this residue in the extract is a problem. Thus, this study introduces microemulsion-based extraction of palm kernel oil and peanut oil using polyoxyethylene (4) lauryl ether nonionic surfactant or the commercial name Brij 30 as an alternative method to replace solvent extraction. Parameters that were studied to find the optimum oil extraction conditions are weight of sample, surfactant concentration, and contact time. Once the optimum conditions were obtained, solvent extraction was done for comparison. The oil collected from both extractions was compared based on their extraction efficiencies and Fourier Transform Infrared Spectroscopy (FTIR) characterization. Dried and ground palm kernel and peanut (0.2-0.5 mm) were shaken with surfactant on rotary shaker at 150 rpm for every parameter. This enables the oil to be collected because it is liberated from the samples as a separate phase from the aqueous phase. Optimum oil extraction of 59.2 % and 87.15 % was achieved at weight of sample of 1.0 g, 30 minutes extraction time at 150 rpm and 0.015 M surfactant concentration for palm kernel and peanut respectively. Percentage of palm kernel and peanut oil extraction using microemulsion-based extraction are 59.2 % and 87.157 % respectively which are lower compared to solvent extraction; 88.5 % and 91.37 % respectively. FTIR characterization on both methods shows not much difference due to the same source of origin. The formation of oil was proven by ester formation that was detected at 1743 cm^{-1}. Although microemulsion-based extraction efficiency is lower than extraction using solvent, the process requires shorter time than solvent-based extraction method. Furthermore, the usage of surfactant especially the polyoxyethylene-based group is environmentally friendly compared to solvent such as hexane.

Keywords: microemulsion-based extraction, palm kernel, peanut, Brij 30, solvent extraction.

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Introduction

Vegetable oil can be extracted through several methods and processes. Methods that are used for vegetable oil extraction are solvent-based extraction, microemulsion-based extraction, aqueous-based extraction, mechanical extraction and supercritical fluids. The most cost-effective oil recovery method for oilseed processing is hexane extraction that gives a production of residual oil content below 1 %. However, hexane is considered as highly flammable material, hence the extraction process demand an expensive plant that is fully equipped in order to handle the solvent. In addition to that, the usage of residual hexane in the commercial oil will eventually affect the consumer health [1].

Since hexane is considered as hazardous and highly volatile solvent, therefore, microemulsion-based extraction is used as an alternative method to replace hexane in vegetable oil extraction [2]. Microemulsion-based extraction was used in this study because this method is considered as a clean technology since the surfactant used is environmental friendly and biodegradable. According to [2], the quality of oil extracted using surfactant microemulsion-based technique is of similar or better quality with oil extracted using hexane solvent based on the water content, fatty acids composition and surfactant partitioning into oil phase.

Microemulsion-based extraction is a method where the unique properties of surfactant were used to extract oil from oil-yielding crops by forming microemulsion or micelle at the critical micelle concentration (CMC). Surfactants are defined as amphiphilic molecules that have a hydrophilic 'head' and a hydrophobic 'tail'. Microemulsion is a thermodynamically stable homogeneous mixture of oil and water that were stabilized by surfactants and sometimes co-surfactants [3]. Critical micelle concentration (CMC) is the concentration of surfactant which monomers forming colloidal aggregates [4]. In a micelle structure, the hydrophobic parts of the surfactant lies in the center of the aggregate while the hydrophilic parts is directed outward towards the aqueous medium [3].

Microemulsion-based extraction conducted by [2] from palm kernel oil found that grain size of 0.212 and 0.425 mm gives optimum oil extraction efficiency of 93.99 and 94.13 % respectively at 30 minutes contact time and 1.0 g seeds loading with mixed anionic extended surfactants 3 wt% Comperlan KD and 0.1 wt% Alfoterral 145-5PO. Another study by [5] on peanut oil and canola oil extractions using anionic surfactants alkyl-propoxylate-ethoxylate-sulfate (APES) and alkyl-propoxylate-sulfate (APS) found out best surfactant concentration to extract oil is in the range of 0.15 wt% - 0.35 wt%. Both peanut and canola seeds produced 93-95 % oil extraction efficiency at optimum conditions where seed to liquid ratio at 1-5, as well as the extraction process occurred for 30 minutes at 150 shakes/minute.

The significance of this study was to use a more environmental friendly approach in extracting oil from palm kernel seeds and peanuts where biodegradable surfactant Brij 30 was used. Polyoxyethylene (4) lauryl ether or the commercial name Brij 30 is a type of linear alcohol ethoxylate belongs to the polyoxyethylene-based nonionic surfactant. The molecular formula for Brij 30 is $OH(CH_2CH_2O)_4(CH_2)_{15}CH_3$. The molecular weight of Brij 30 is 362 g mol^{-1} [6]. Batch studies were carried out to find optimum oil extraction conditions. The parameters studied were weight of sample, surfactant concentration, and contact time. Once the optimum conditions were obtained, solvent extraction using hexane was done for comparison. The oil collected from both extractions was compared based on their extraction efficiencies and Fourier Transform Infrared Spectroscopy (FTIR) characterizations.

Materials and Methods

The nonionic surfactant Brij 30 is obtained from Sigma and used as received. The peanut was purchased at the local market while palm kernel was obtained from a local oil palm plantation in Serian, Sarawak. Deionized water was used in order to prepare the surfactant solutions.

Palm kernel seeds and peanuts were ground using mortar and pestle into granules with particle size 0.2-0.5 mm mesh size. The samples were then kept in desiccators which maintain the atmosphere of low humidity. The samples were divided into different weight ranging from 0.03 g to 5 g. Contact time was varied from 15 minutes to 180 minutes on a rotary shaker at 150 rpm with surfactant concentration ranging from 0.005 - 0.030 M (from below till above the CMC). The aqueous and oil layer was separated by using separatory funnel. The oil collected was left in the desiccator for moisture removal before subjected to FTIR characterization.

Hexane extraction is conducted by using Soxhlet extraction method. The ground samples were inserted into thimble according to optimum weight identified from microemulsion-based extraction. Then, round bottom flask was filled with hexane and heated to evaporate the hexane. The temperature was controlled in order to get an evenly drops of condensed hexane and the samples were left for eight hours. Rotary evaporator was used to obtain solvent free oil [7].

Fourier transform infrared spectroscopy (FTIR) was used to observe changes in chemical bonding of molecules after the extraction process. The FTIR spectra were recorded in range of 4000-370 cm^{-1} in the transmittance mode. The infrared spectroscopies of extracted oils were recorded as thin film (NaCl) disc.

The amount of absorption percentage for surfactant extraction was calculated using the following formula (Equation 1);

$$\text{Extraction Efficiency}(\%) = \frac{\text{initial mass of raw material(g)} - \text{final mass after extraction(g)}}{\text{initial mass of raw material (g)}} \times 100\%$$

The total mass loss was considered as the weight of oil extracted. The amount of absorption percentage for solvent extraction based on three replicates was calculated according to the following equation (Equation 2);

$$\text{Extraction Efficiency (\%)} = \frac{\text{Average weight of oil (g)}}{\text{Mass sample (g)}} \times 100\ \%$$

Results and Discussion

Contact time

Palm kernel oil extraction based on time was varied from 10 to 180 minutes. The surfactant concentration used was chosen randomly to observe the contact time taken by the oil to be extracted using Brij 30 surfactant.

A graph (Figure 1) was plotted based on the percentage extraction efficiency of the oil at different contact time. According to Figure 1, contact time up to 30 minute shows very high extraction efficiency of 50.6 %. Contact time after 30 minute shows decreasing in extraction efficiency. Decrease in extraction efficiency at longer contact time is due to solubilization of free oil into micelles which lead to less oil production [8]. Thus contact time at 30 minutes is considered the optimum time used for oil extraction.

Similar pattern was observed in peanut oil extraction by Brij 30 (Figure 2). The extraction was done with 0.01 M Brij 30, 1.0 g of peanut samples and shaking speed of 150 rpm. The results showed that contact time up to 30 minutes has the maximum extraction efficiency which is 93.99 %.

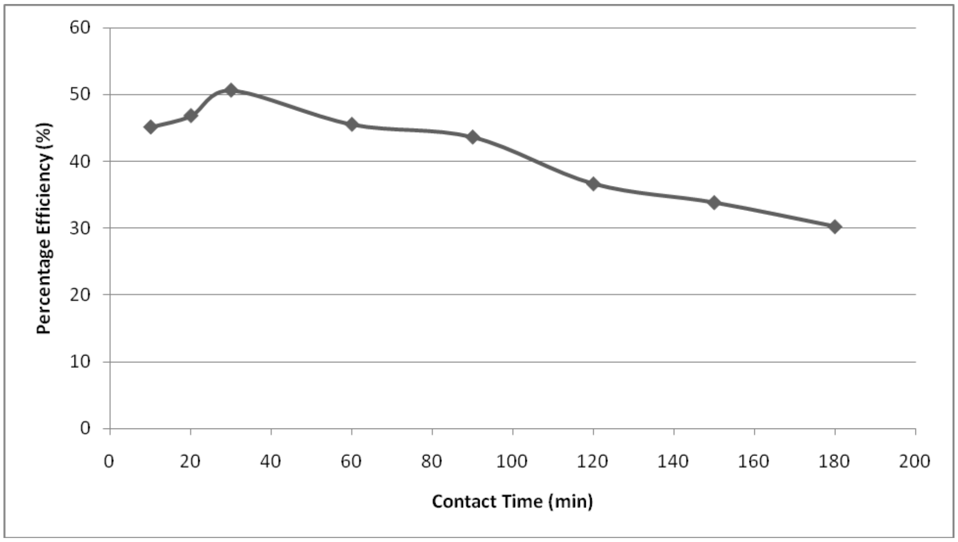

Figure 1 : Palm kernel oil extraction efficiency based on contact time

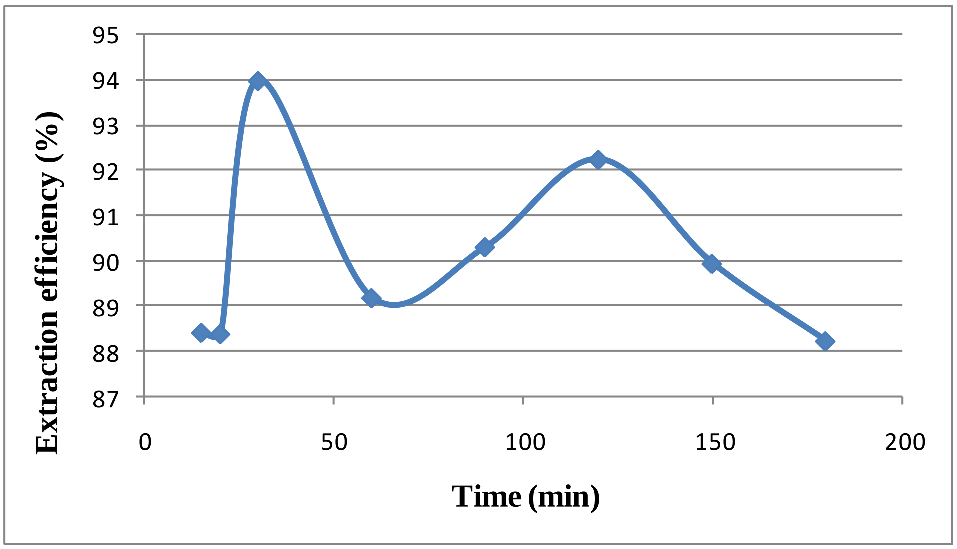

Figure 2: Peanut oil extraction efficiency based on contact time

Brij 30 Concentration

The second parameter tested is surfactant concentration. Brij 30 concentrations were varied from below to above the CMC value of Brij 30; 0.005 M to 0.030 M. The extraction was done at optimum contact time of 30 minutes, 1.0 g of palm kernel samples and rotated at a constant speed of rotary shaker (150 rpm).

Graph on Brij 30 surfactant efficiency to extract palm kernel oil is also plotted (Figure 3). According to Figure 3, concentration of 0.015 M shows highest extraction efficiency of 50.5 % where it is in range of CMC value. Based on the graph, when surfactant concentration used is higher than the CMC value, oil extraction efficiency would decrease. This might due to the aggregation of surfactant monomers and increase in micelles formation at above the CMC values of surfactant concentration [5].

Similar pattern was observed in peanut oil extraction by Brij 30 (Figure 4). The extraction was done at optimum contact time of 30 minutes, 1.0 g of peanut samples and rotated at a constant speed of rotary shaker (150 rpm). Based on the results there were a steady decrease in the extraction efficiency above the CMC values of Brij 30 surfactant. The highest extraction efficiency value was at 0.015 M of surfactant concentration which is 94.45 %.

Figure 4 shows the extraction efficiency values increased slightly at 0.015 M concentration and decrease steadily at higher surfactant concentration. This proven that the optimum surfactant concentration obtained (0.015 M) was still in the range of CMC values of Brij 30 that is 7-15.00 mg/L [9]. Furthermore, the detachment of oil from peanut seeds was suitable in the range of CMC values of the surfactant. This might due to the aggregation of surfactant monomers and increase in micelles formation at above the CMC values of surfactant concentration [5].

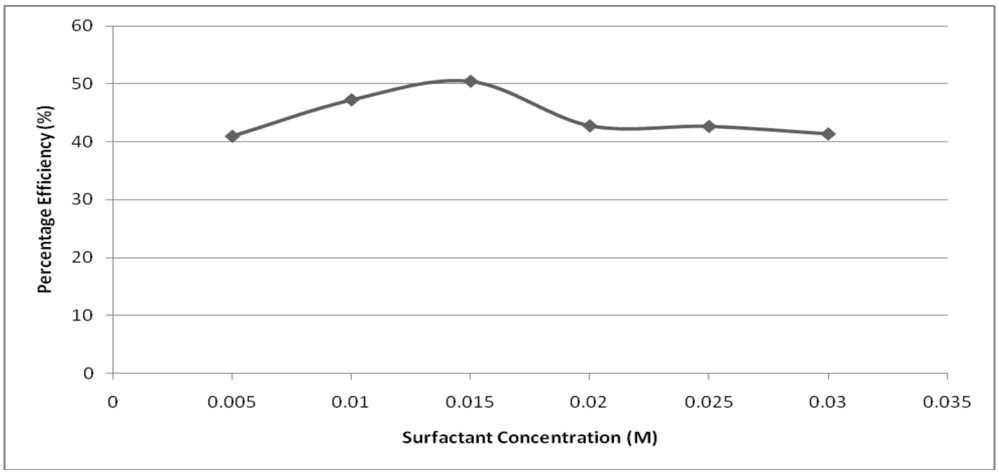

Figure 3: Brij 30 surfactant concentration effect on palm kernel oil extraction efficiency

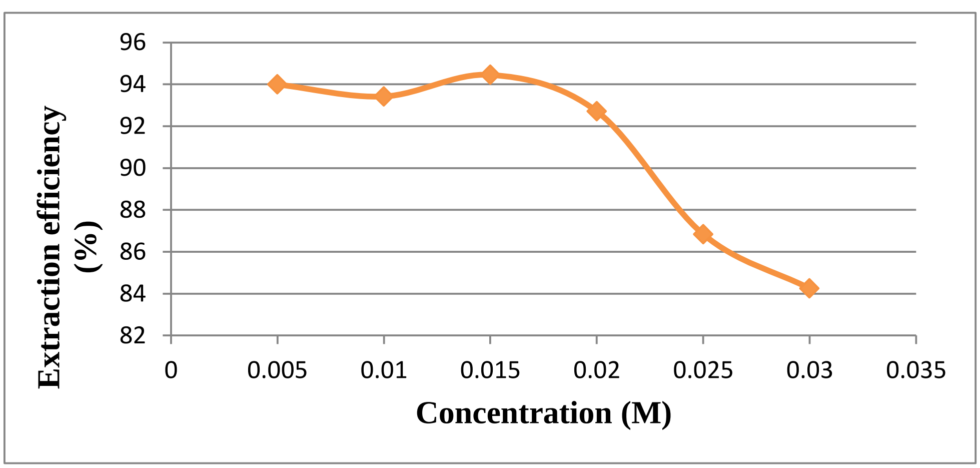

Figure 4: Brij 30 surfactant concentration effect on peanut oil extraction efficiency

Sample weight

According to Figure 5, weight of 1g palm kernel shows gives the highest extraction efficiency of 50.5 %. This is because, as the weight of the sample increases, the extraction efficiency decreases since higher mass of sample leads to less penetration between the surfactant monomer within the samples and thus, decreasing the extraction of oil [2]. Figure 5 also shows the fluctuation of percentage efficiency based on weight of palm kernel as it increases. Hence, it can be concluded that the optimum sample weight is 1.0 g. enhanced the capability of the surfactant monomer to interact with the surface and reduced the interfacial tension (IFT) which allows oil to be liberated from the seeds [2]. The weight of samples was varied from 0.5 g to 5 g because different load of samples could affect the extraction efficiency values. At Brij 30 optimum concentration of 0.015 M and contact time of 30 minutes, peanut samples were agitated on rotary shaker at 150 shakes/minute. Peanut samples of 1.0 g produced the highest extraction efficiency of 87.90 %. The extraction efficiency values decreased steadily at

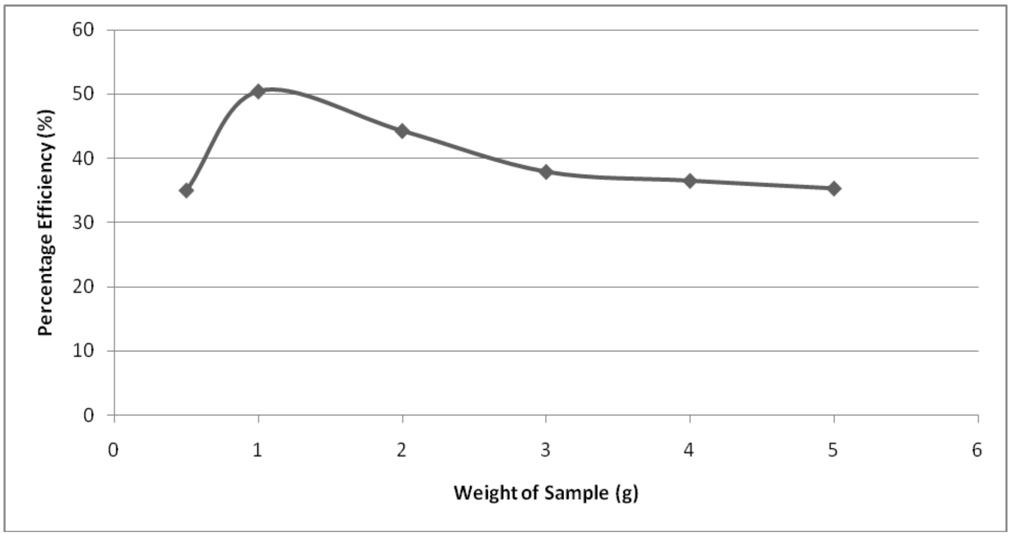

Figure 5 : Effect of sample weight on palm kernel oil extraction efficiency

Similar pattern was also observed in peanut oil extraction by Brij 30 (Figure 6). The peanut samples were sieved at a particle size of 0.2-0.5 mm because it provides larger surface area that higher weight of samples. As the weight of samples increases, the extraction efficiency decreases. This is due to less surfactant penetration at higher samples mass and less coalesces between surfactant monomers and oil [2].

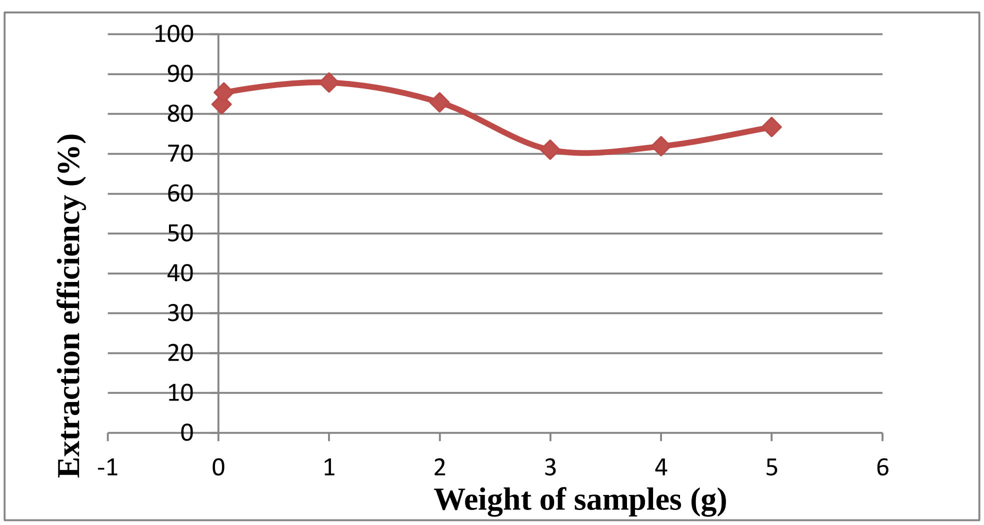

Figure 6 : Effect of sample weight on peanut oil extraction efficiency

Solvent based extraction

Solvent-based extraction method using hexane was done once optimum conditions were obtained by extraction using surfactant. The mass of sample used is 1.0 g according to optimum weight based on surfactant extraction method. Hexane is used in this extraction since hexane is favorable in extracting oil.

Palm kernel oil extraction efficiency was calculated using equation 2. The average extraction efficiency from three replicates using hexane is 88.5 % while average extraction efficiency using surfactant is 59.2 %. Although hexane is hazardous and required up to eight hours in completing the process, higher percentage of oil was extracted due to the binding capacity and solubility of vegetable oil in the solvent used [10]. The oil is easily liberated from the seed because of the loose packing of seed inside the thimble.

Extraction using hexane on peanut also yields higher extraction efficiency compared to surfactant extraction. The average extraction efficiency from three replicates using hexane is 91.37 % while the average extraction efficiency using surfactant is 87.15 %. Although the fraction of oil extracted by hexane is higher compared to surfactant, the crude oil produced may have less quality in terms of low free fatty acid presents [5].

Fourier Transform Infrared Spectroscopy (FTIR) characterization

Figure 7 and figure 8 shows spectra of palm kernel and peanut oil extracted from microemulsion-based surfactant and soxhlet methods respectively. Both spectra of extracted oil from microemulsion-based method and solvent extraction method are similar where broad O-H band at 3584-3476 cm-1 and slopes into asymmetric -C-H band at 2924-2856 cm-1 were observed. The intense peak of C=O stretch in oil for both extraction methods is at 1743-1747 cm-1. However, slight difference can be observed in the absorbance spectrum of symmetric -C-H bending. Microemulsion-based method shows broader peak due to the interaction between the oil and the surfactant and as for soxhlet method, it shows intense peak due to usage of hexane as solvent for oil extraction.

Conclusion

Optimum oil extraction of 59.2 % and 87.15 % was achieved at weight of sample of 1.0 g, 30 minutes extraction time at 150 rpm and 0.015M surfactant concentration for palm kernel and peanut respectively. Percentage of palm kernel and peanut oil extraction using microemulsion-based extraction are lower compared to solvent extraction; 88.5 % and 91.37 % respectively. FTIR characterization on

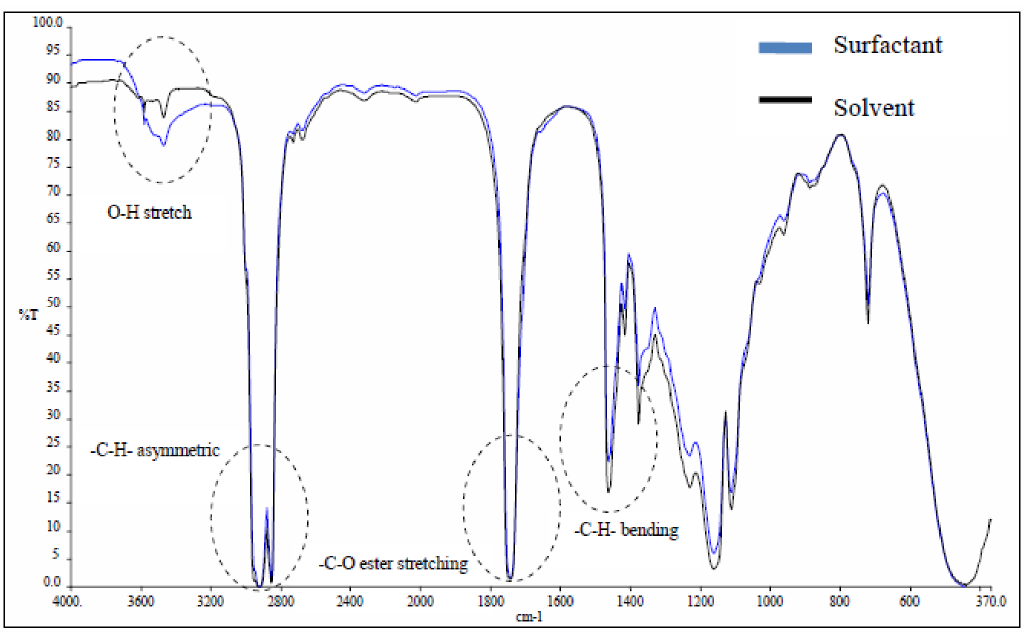

Figure 7 : FTIR Spectra of palm kernel oil from surfactant-based and solvent method

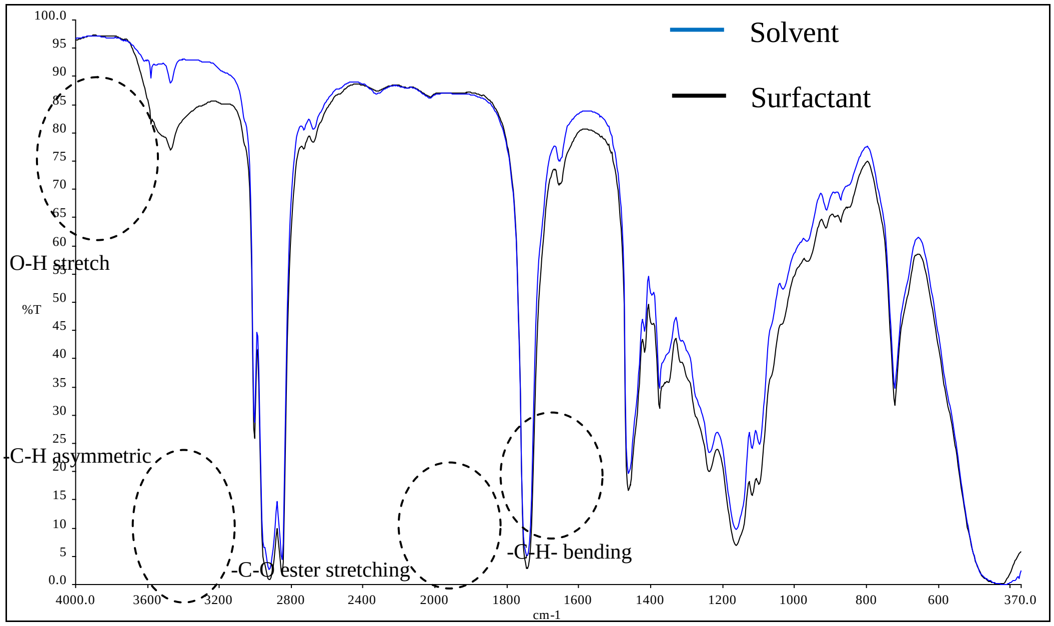

Figure 8 : FTIR Spectra of peanut oil from surfactant-based and solvent method

both methods shows not much difference due to the same source of origin. The formation of oil was proven by ester formation that was detected at 1743-1747cm^{-1}.

Extraction using surfactant can reduce the toxic substances such as hexane exposed to the environment since the usage of polyoxyethylene (POE) group is environmentally friendly and low energy is needed since this method can be done at room temperature. Although the extraction efficiency is much lower than extraction using solvent, the process requires shorter time than solvent-based extraction method. The process also does not require removal of surfactant since the surfactant usage is very small. In addition based on visual observation, the color of extracted oil from both solvent extraction and surfactant microemulsion-based are similar.

References

1. Wu, H., Jiang, L., Zhu, X., Wu, H. and Li, Y. (2011) Microemulsion Fermentation Simultaneous Extraction Processing of Oil and Protein from Soybean. *Journal of Advanced Materials Research*, **156-157**, 1059-1068.
2. Naksuk, A., Sabatini, D.A. and Tongcumpou, C. (2009) Microemulsion-Based Palm Kernel Oil Extraction Using Mixed Surfactant Solutions. *Journal of Industrial Crops and Products*, **30**, 194-198.
3. Myers, D. (2006) *Surfactant Science*. 3rd ed. Hoboken, N. J.: John Wiley & Sons, Inc.
4. Edwards, D. A., Luthy, R. G. and Liu, Z. (1991) Solubilization of Polycyclic Aromatic Hydrocarbons in Micellar Nonionic Surfactant Solutions. *Environmental Science & Technology*, **25** (1), 127-133.
5. Do, L.D. and Sabatini, D.A. (2010) Aqueous Extended-Surfactant Based Method for Vegetable Oil Extraction: Proof of Concept. *Journal American Oil Chemist`s Society*, **87**, 1211 - 1220.
6. Hait, S. K. and Moulik, S. P. (2001) Determination of Critical Micelle Concentration (CMC) of Nonionic Surfactants by Donor-Acceptor Interaction with Iodine and Correlation of CMC with Hydrophile-Lipophile Balance and Other Parameters of the Surfactants. *Journal of Surfactants and Detergents*, **4 (3)**, 303-309.
7. Ixtaina, V. Y., Martínez, M. L., Spotorno, V., Mateo, C. M., Maestri, D. M., Diehl, B. W. K., Nolasco, S. M. and Tomás, M. C. (2011) Characterization of Chia Seed Oils Obtained by Pressing and Solvent Extraction. *Journal of Food Composition and Analysis*, **24**, 166–174.
8. Nguyen, T., Do, L. and Sabatini, D.A. (2010) Biodiesel Production Via Peanut Oil Extraction Using Diesel-Based Reverse Micellar Microemulsions. *Elsevier Journal*, **89**, 2285-2291.
9. Yeh, D.H., Pennel, K.D. and Pavlostathis, S.G. (1998) Toxicity and Biodegradability Screening of Nonionic Surfactants using Sediment-Derived Methanologenic Consortia. *Water Science Technology*, **38**, 55-62.
10. Saxena, D.K., Sharma, S.K. and Sambi, S.S. (2011) Comparative Extraction of Cottonseed Oil by N-hexane and Ethanol. *ARPN Journal of Engineering and Applied Science*, **6**, 84-89.