CHAPTER IV

RESULTS AND DISCUSSIONS

4.1 Phase behavior study and preliminary extraction

4.1.1 Systems of nonionic surfactant aqueous solution

Phase behavior study aimed to determine the suitable surfactant system for Jatropha seeds extraction based on microemulsion phenomena. This experimental section was first set up with the fatty alcohol C 12-14 ethoxylate nonionic surfactants obtained from PTT Chemical Public Company Limited with 5 different series. The different numbers of ethoxylate group in each surfactant was expected to result in different behavior of these surfactant solutions with Jatropha oil. The nonionic surfactant solution at 3%wt from each surfactants were prepared and gently mixed with the oil at unity volume ratio. The results of phase for each surfactant solution are described in Table 4.1.

Table 4.1 Phase behavior of nonionic surfactant at 3% wt with Jatropha oil from visual observation.

Code	Chemical name of nonionic surfactants	Description of phase behavior
LS1	Fatty alcohol C 12-14 (1) ethoxylate	Incomplete separation, the system was turbid
LS2	Fatty alcohol C 12-14 (2) ethoxylate	Partially separation, the phases were transparent
LS3	Fatty alcohol C 12-14 (3) ethoxylate	Incomplete separation, the upper layer was clear and the lower part became turbid
LS7	Fatty alcohol C 12-14 (7) ethoxylate	Incomplete separation, the system was very turbid

Code	Chemical name of nonionic surfactants	Description of phase behavior
LS9	Fatty alcohol C 12-14 (9) ethoxylate	Incomplete separation, the system was very turbid

Note * Number in blanklet refers to ethoxylate (EO) group in the surfactant molecule

From results as described in Table 4.1, the system of LS2 was the only nonionic surfactant that was found most transparent while other systems turned turbid after mixed the surfactant solutions with the Jatropha oil. If compared each system of this surfactant series, LS1 containing only one EO group is the most hydrophobic surfactant and LS9 containing 9 EO group is the most hydrophilic surfactant in this series. The highest composition of fatty acids in Jatropha oil are C-18 fatty acids consisting of Stearic (18:0), Oleic (18:1) and linoleic (18:2) as explained in Chapter 2. From number of C-18, these fatty acids are rather hydrophobic, however, containing acid functional group as well as double bonds making these compounds also slightly polar. With this combination of characteristics, properties of the oil are more complicated than HC oil. Thus, to select surfactant system that can be able to form microemulsion with was difficult and needed to investigate the optimum solution. Even though LS2 system exhibited the transparent solution in phase study, it may not be able to conclude that microemulsion is already formed.

Nonetheless, since this experiment was carried out to select the surfactant, preliminary test for seed extraction was also conducted to observe the performance of these surfactant series mixing 1 g of seed per 10 mL of solution, shaking in an orbital shaker at 130 rpm for 1 min and centrifuged at 2500x for 20 min. The results of this observation are described in Table 4.2 and illustrated in Figure 4.1.

Table 4.2 Characteristic of surfactant solutions system before and after extraction from visually observation

System (3%wt)	Appearance of solutions before extraction	Appearance of system after extraction
LS1	Soluble; separated in stable condition	Complete separation, the system was clear

System (3%wt)	Appearance of solutions before extraction	Appearance of system after extraction
LS2	Soluble; separated in stable condition	Complete separation, the system was clear
LS3	Soluble; turbid solution	Incomplete separation, the system was turbid.
LS7	Soluble; homogenous solution	Incomplete separation, the system was turbid.
LS9	Soluble; homogenous solution	Incomplete separation, the system was turbid.

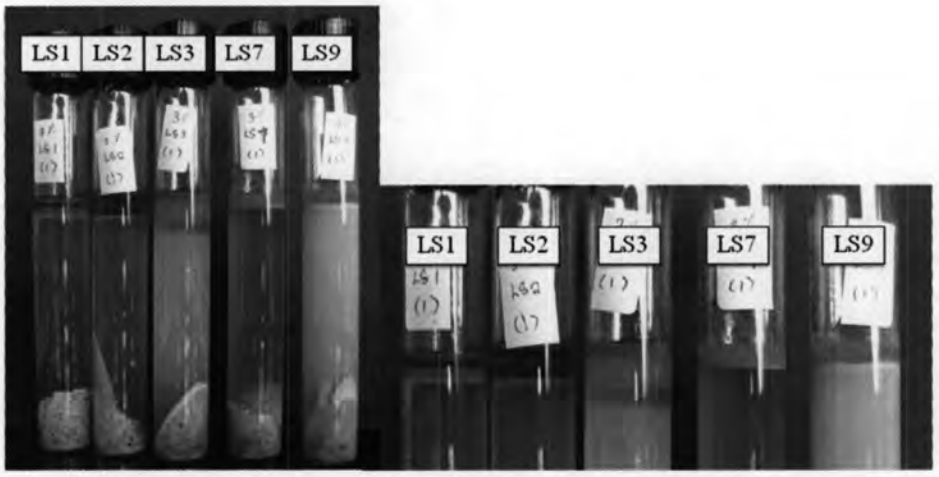


Figure 4.1 Photos of extraction results by surfactant systems of LS series

As seen in Figure 4.1, it was likely that oil was able to be extracted from all experimented nonionic surfactant at concentration of 3%wt, nevertheless, the efficiency of the extraction was resulted from different microemulsion formations (the results of extraction yield is shown in Table 1, of the Appendix). The systems of LS1 and LS2 were completely separated into 3 phases and yielded comparatively clearer and higher amount of oil. While the systems of LS3, LS7 and LS9 were found turbid for all phases which resulted in incomplete separation. This indicated the partition of oil into all phases. As a consequence, they are considered not a desirable system for extraction. When compared the systems of LS1 and LS2, LS2 gave

higher oil yield and more transparent oil than LS1; therefore, LS2 may be considered to be the most appropriate nonionic surfactant for Jatropha oil extraction.

4.1.2 Systems of mixed nonionic and anionic surfactants aqueous-based solution

As Rosen (2004) stated that nonionic surfactant is generally sensitive to temperature ; therefore, it was introduced to mix with anionic surfactant to make a system become temperature insensitive. Alfoterra 145-4PO was selected for this study since it is an extended surfactant which has been reported to be able to enhance microemulsion promotion for vegetable oil due to its special formula (Witthayapanyanon, 2008). Alfoterra 145-4PO was mixed with the solution of LS2 at different concentration of both surfactants. The results of each solution are described in Table 4.3.

Table 4.3 The systems of mixed surfactants solution for phase behavior observation

System			System appearance
LS2	**Alfoterra 145-4PO**	**NaCl**	
1%	0.02%	0.2% - 1.0%	- Lower and turbid excess oil phase - Incomplete separation - Higher % of Alfoterra 145-4PO and NaCl, lower aqueous phase - Microemulsion did not occur
	0.04%	0.2% - 1.0%	
	0.06%	0.2% - 1.0%	
	0.08%	0.2% - 1.0%	
	0.10%	0.2% - 1.0%	
3%	0.02%	0.2% - 1.0%	- Clear system the separated phases could be observed - Microemulsion is suspected to be occured - Higher % of Alfoterra 145-4PO and NaCl, lower aqueous phase
	0.04%	0.2% - 1.0%	
	0.06%	0.2% - 1.0%	
	0.08%	0.2% - 1.0%	
	0.10%	0.2% - 1.0%	
5%	0.02%	0.2% - 1.0%	- Turbid system - Microemulsion did not occur - Higher excess oil phase - Higher % of Alfoterra 145-4PO and NaCl, lower aqueous phase
	0.04%	0.2% - 1.0%	
	0.06%	0.2% - 1.0%	
	0.08%	0.2% - 1.0%	
	0.10%	0.2% - 1.0%	

From the observation, the effects from different percent weight of LS2 were firstly determined. The 1% LS2 caused higher aqueous phase, lower free oil phase and the system was turbid and incomplete separation. This could be the implied that the low interaction among the phases due to the small aggregation number of the surfactant. When the concentration increased to be 3%, the free oil phase was also increased and system appearance was clearer, therefore, the concentration of LS2 at 3% might be considered as the optimum concentration for microemulsion formation from this experiment. Lastly, the 5% LS2 caused high turbidity as the system initiate to be more hydrophobic which was not facilitated for the aqueous. The surfactant tends to be in the oil phase and caused turbid oil phase which was suspected to be macroemulsion formation instead.

Secondly, the systems were overall observed that the higher concentration of Alfoterra 145-4PO cause lower aqueous phase. At the concentration of Alfoterra 145-4PO higher than 0.06%, the free oil phase was significantly increased. This could be explained that the higher concentration of Alfoterra 145-4PO facilitated the higher partition of the hydrophilic head and hydrophobic tail of the molecule into the interface and resulted in an increase of solubilization and reduce interfacial tension. However, the concentration shall be optimum to minimize solubilization of the system.

Lastly, the observation was found that at the same percent weight of LS2 and Alfoterra 145-4PO, the higher concentration of sodium chloride tended to result in the higher oil phase due to the increase of solubilization.

. Conclusively, the concentration of LS2 including the concentration of extended anionic surfactant and sodium chloride all have impacts toward the phase behavior in terms of solubilization and interfacial tension. This could be implied theoritically that an increase of anionic sulfonates and electrolyte can cause the phase behavior transition. Moreover, Naksuk (2007) revealed that the extended anionic surfactants may play important role as it can enhance microemulsion formation as well as reducing interfacial tension down to ultralow values. To obtain an appropriate microemulsion formation system, the concentration of extended anionic surfactant and sodium chloride shall be optimum for minimize solubilization as well as maximize interfacial tension. However, the visual observation of phase behavior has

done in broad concentrations which could be seen only in overall estimation. The concentration of LS2 would be expanded to be more detailed in order to investigate the extraction in the next section.

4.2 Determination of the Optimum Condition for Extraction

From the result in previous parts, various parameters of chemical and physical conditions were evaluated for determination of the suitable conditions for oil extraction from Jatropha seeds including, concentration of surfactant, salt concentration, pretreatment, contact time, and solid liquid ratio.

4.2.1 Effect of fatty alcohol C 12-14 (2) ethoxylate concentration on extraction efficiency

As aforementioned, the previous section of 4.1.2 has done with broad range of LS2 for basic observation. The overall image of microemulsion formation system was found with the estimation range of appropriate LS2 concentration, however, the intensively percent weight of LS2 have been expanded in order to confirm the previous section. The percent weight of LS2 were expanded from 1%, 3%, and 5% to be more detailed as 1%, 1.5% , 2%, 2.5%, 3%, 3.5%, 4%, 4.5% and 5%, respectively.

The oil yield measurement was done by suction of excess oil phase using pasture pipette and weighted. The extraction efficiency was calculated based on weigh of total seeds used. The results of oil extraction efficiency of LS2 in different percentages are shown in Appendix (Table 2) and illustrated in Figure 4.2.

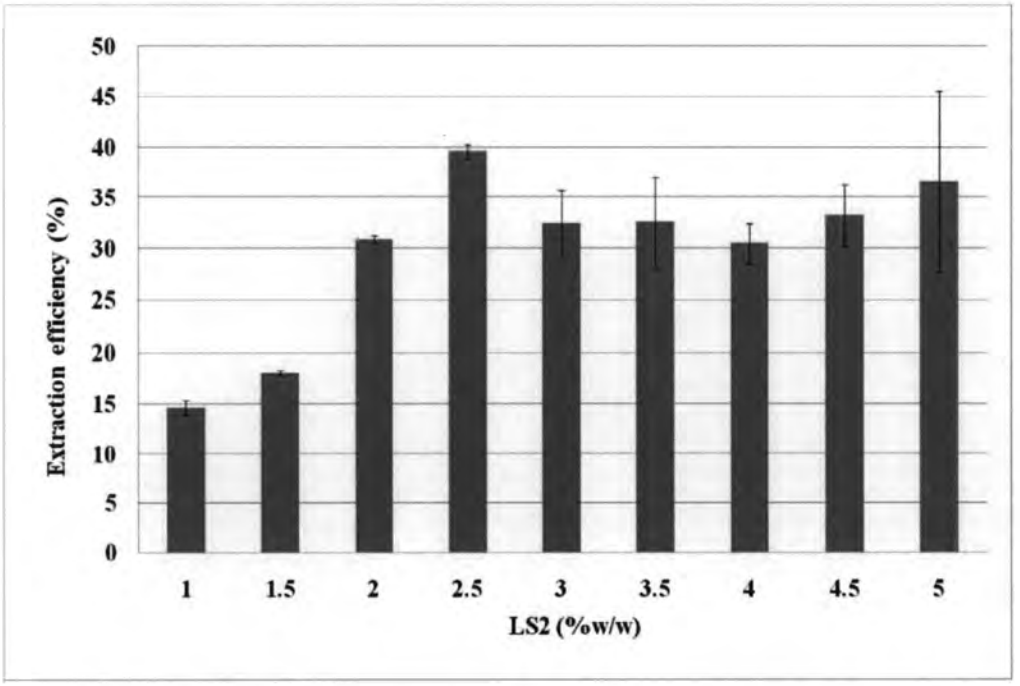


Figure 4.2 The extraction efficiency of LS2 at various concentrations

Figure 4.2 shows that for the surfactant solutions containing LS2 from 2%wt and higher were able to extract the Jatropha oil higher than 30%. The system of LS 2.5%wt was exhibit the highest efficiency at 39.59%. The result may indicate that at 2.5%wt of surfactant was enough to adsorb on ground seeds to reduce interfacial tension of oil and seeds surface and allowed the oil to be mobilized. However, for further experiment to determine for the optimum surfactant systems, the concentrations of LS2 from 2.0% to 5.0% were selected to mix with anionic surfactant as described in next section.

4.2.2 Jatropha oil extraction by mixed surfactants

Anionic surfactant was introduced to mix with nonionic surfactant in order to promote microemulsion formation as mentioned. In addition, mixture of nonionic and anionic surfactant system is generally making a surfactant system insensitive to temperature which is more suitable for application. From the previous study by Naksuk (2007), palm kernel oil was also extracted by the mixture of nonionic

surfactant and anionic surfactant. Her work revealed that by mixing an extended anionic surfactant with nonionic, Comperlan KD, microemulsion formation with long chain fatty acid from palm kernel oil was occurred due to the extended surfactant was reported to enhance microemulsion formation of vegetable oil as well as reducing interfacial tension down to ultra low values (Withayapanyanon et al, 2006).

The extended surfactants are surfactants naturally in which groups of intermediate polarity, such as polypropyleneoxides or copolymers of propyleneoxides and ethylenoxide, are inserted between the hydrocarbon tail and hydrophilic head group. According to the unique structure of this class of surfactant, the surfactant is stretched out further into both oil and water phases of the interface which provides more suitable for solubilizing hydrophilic and hydrophobic regions of the interface which provide more suitable for solubilizing hydrophilic and hydrophobic molecules (Naksuk, 2007). In addition, several papers have demonstrated the benefit of using extended surfactants to enhance oil solubilization of microemulsion with highly hydophobic oils, as well as triglyceride and vegetable oil (Do et at., 2008).Therefore in this present study, an extended surfactant- Alfoterra145-4PO--was introduced to mixed with the LS2.

As mentioned in the previous section that the system of LS2 at seven concentrations (2%, 2.5%, 3%, 3.5%, 4%, and 5%) selected for mixing with Alfoterra 145-4PO. The preliminary experimental result indicated that the higher concentration of Alfoterra 145-4PO, the higher of the middle layer. However, the high solubilization is not a desired system due to the higher possibility of free oil to be trapped within microemulsion; therefore, the concentration of Alfoterra145-4PO was needed to be evaluated for the optimum concentration. The appropriate concentrations of Alfoterra 145-4PO selected for mixing with LS2 were 0.02%, 0.04%, and 0.06% (the system without Alfoterra 145-4PO was also displayed). Sodium chloride (0.6 %wt) was also added to the systems for promoting microemulsion formation. So, there were totally 28 systems set up for the mixed surfactant solution at different concentrations of both LS2 and Alfoterra 145-4PO (Table 4.4). The extraction results are shown in the Appendix (Table 3).

Table 4.4 Mixed surfactants solutions selected for the Jatropha oil extraction efficiency evaluation

Systems	Compositions*	
	LS2 (%wt)	Alfoterra 145-4PO (%wt)
1	2.0	0.00
2	2.0	0.02
3	2.0	0.04
4	2.0	0.06
5	2.5	0.00
6	2.5	0.02
7	2.5	0.04
8	2.5	0.06
9	3.0	0.00
10	3.0	0.02
11	3.0	0.04
12	3.0	0.06
13	3.5	0.00
14	3.5	0.02
15	3.5	0.04
16	3.5	0.06
17	4.0	0.00
18	4.0	0.02
19	4.0	0.04
20	4.0	0.06
21	4.5	0.00
22	4.5	0.02
23	4.5	0.04
24	4.5	0.06
25	5.0	0.00
26	5.0	0.02
27	5.0	0.04
28	5.0	0.06

Note * At all systems 0.6%wt of NaCl was added.

A total of 28 systems prepared in matrix dimension as described in Table 4.4 in order to observe all of the various concentrations of LS2, Alfoterra 145-4PO and sodium chloride for the most suitable systems to be obtained. However, the systems that contain LS2 at 4.0 percent weight and above (system 17 – 28) resulted in separation of oil phase and microemulsion Type II may be suspected to be formed. The occurrence may due to an increase of LS2 concentration. However, the free oil

yield was not found high for those systems. Therefore, only systems 1-16 were selected to be illustrated as in Figure 4.3.

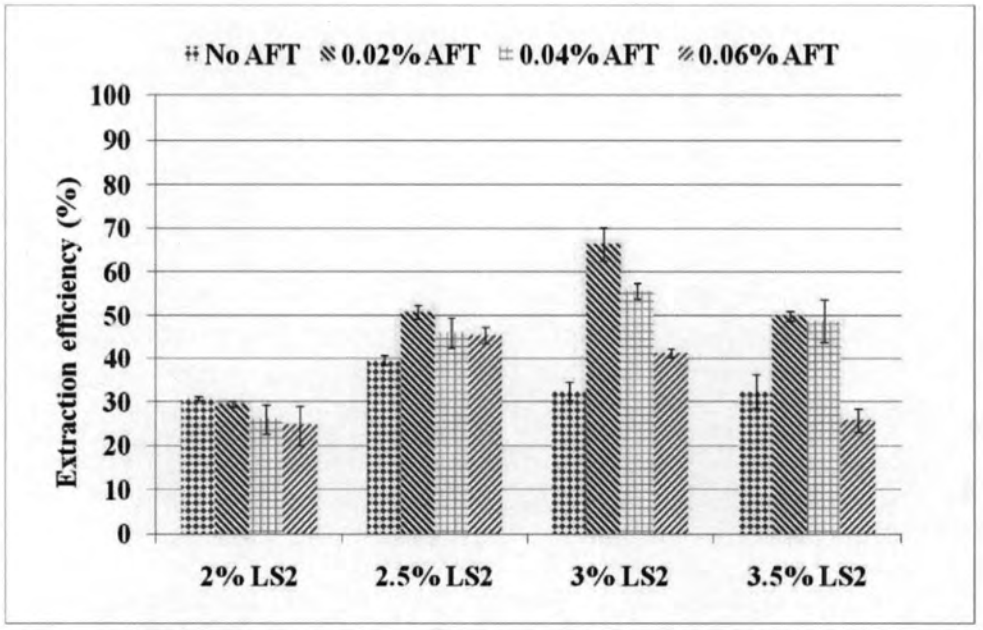


Figure 4.3 Extraction efficiency of mixed surfactants aqueous-based solution (0.6% NaCl)

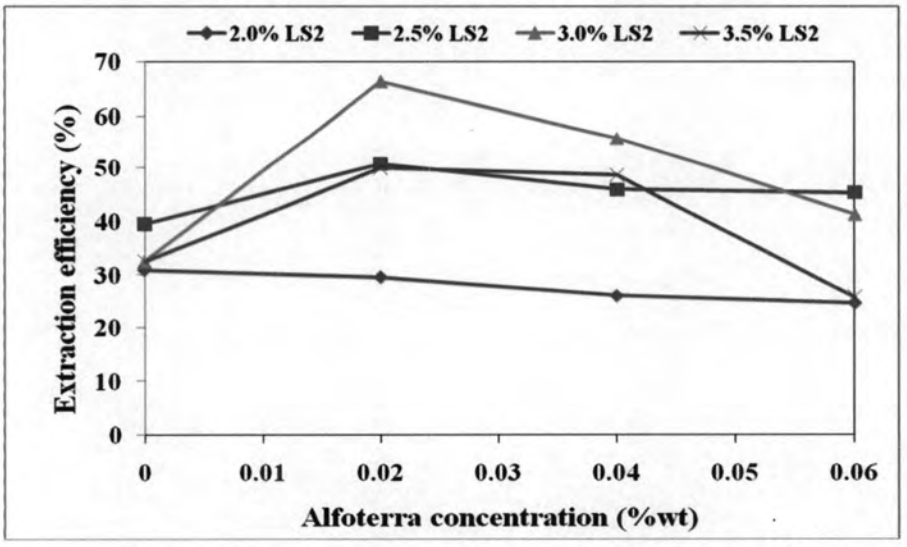


Figure 4.4 Extraction efficiency by variation of Alfoterra 145-4P0

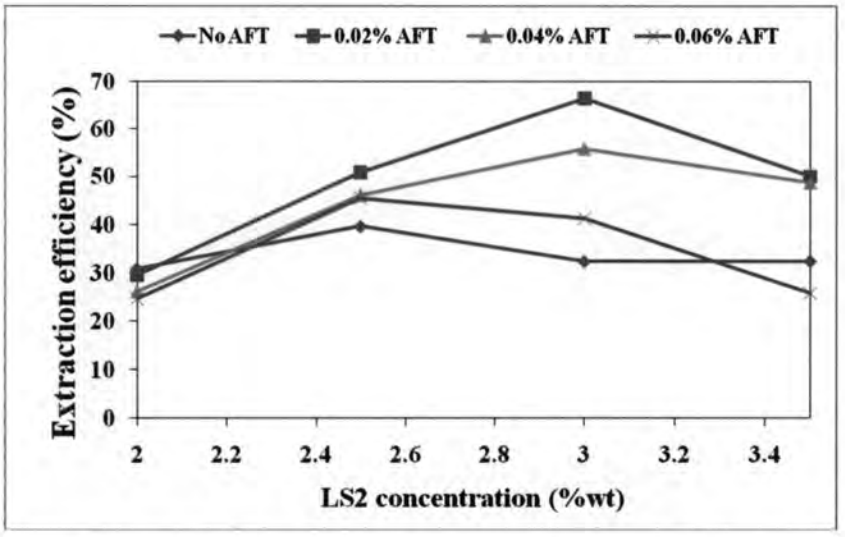


Figure 4.5 Extraction efficiency by varition of LS2

From Figures 4.4 and 4.5, the remarkable result to be pointed here is the change in concentration of Alfoterra 145-4PO resulted in high magnitude change in the extraction efficiency. This indicates that the change of Alfoterra 145-4PO concentration contribute a larger impact toward the extraction efficiency than the change of LS2 concentration.

In conclusion, the system no. 10 (3% LS2 mixed with 0.02%Alfoterra 145-4PO) and the system no. 11 (3% LS2 mixed with 0.04%Alfoterra 145-4PO) which yield the two highest extraction efficiency were chosen for further experiment.

4.2.3 Jatropha oil extraction efficiency with salinity scan

The objective of this part was to evaluate the effect of neutral electrolyte, served as sodium chloride, for enhancing a better oil yield. There was expected that addition of neutral electrolyte to the solution of ionic surfactant would increase the extent of solubilization of nonpolar solubilizate due to closer packing of surfactant head group but decrease the solubilization of the polar solubilizate (Rosen,1989). Even though high solubilization was not a desire for this work, salt adding was expected to reduce interfacial tension and hence microemulsion formation. Therefore, optimum salinity concentration is what this study needed. Salinity scan ranging from 0.2% to 1.0% NaCl were conducted with the two selected systems from

the previous section (3% LS2 mixed with 0.02%Alfoterra 145-4PO and 3% LS2 mixed with 0.04%Alfoterra 145-4PO). This range of NaCl was selected for the experiment since the preliminary experimental result indicated that the concentration of NaCl at higher than 1% caused the kernels floated up to the upper phase of the system. The experiment was carried out by adding 10 mL of the mixed surfactants aqueous-based solution into the vial and homogenous mixed with 1 g of ground Jatropha kernels then the vials were brought to shake by an orbital shaker at 130 rpm for one min and simultaneously separates each phases by gravity centrifuge at 2500 x for 20 min. The free oil was suctioned out by pasture pipette and weighed for the extracted amount. The extraction efficiency results of the two systems are shown in Figure 4.6 and in the Appendix (Table 4).

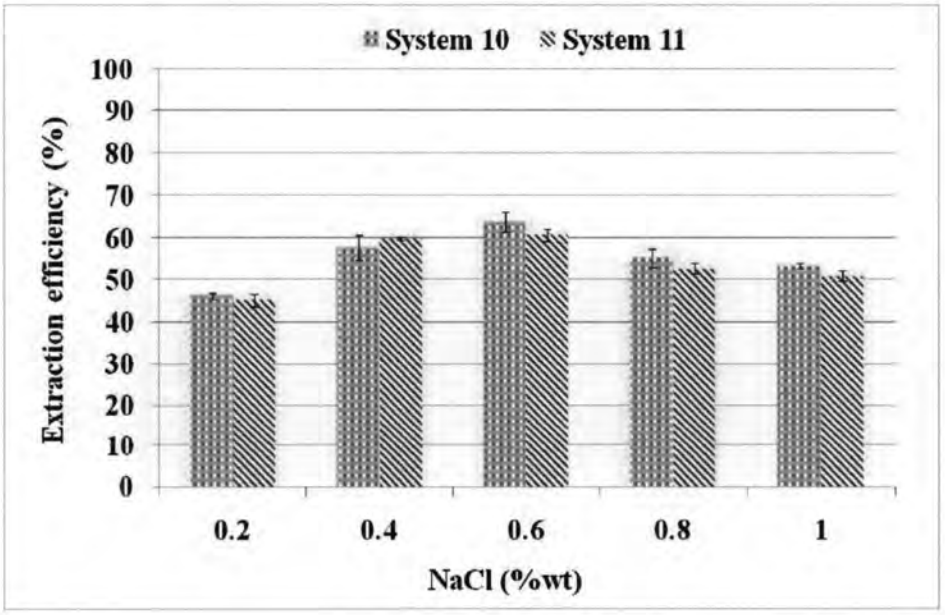


Figure 4.6 Extraction efficiency of the two systems with salinity scan;
(System 10: 3% LS2 mixed with 0.02% Alfoterra 145-4PO and
System 11: 3% LS2 mixed with 0.04% Alfoterra 145-4PO)

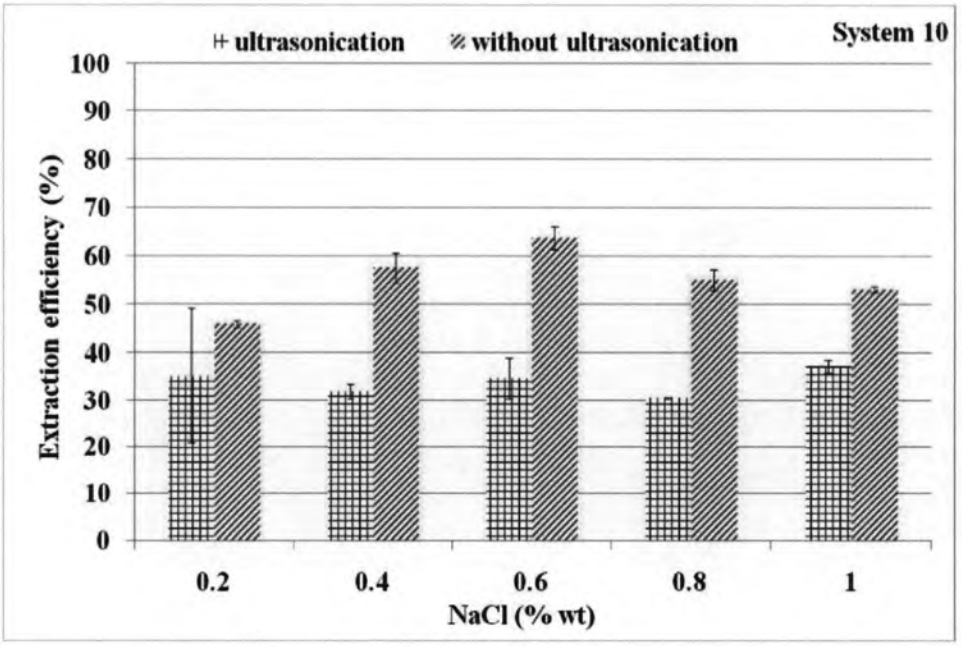
The results from both system 10 and system 11 in the Figure 4.6 show the same trend in extraction efficiency that the extraction efficiency slightly increased up to the level of 0.6% NaCl and gradually decreased at 0.8% and 1.0% of NaCl. This phenomena could be explained that in the beginning the extraction efficiency could be

increased as a result of decrease hydrophlic of the system, the oil can move up to be free oil phase until it reaches an optimum point then the extraction efficiency started to gradually decrease as the increase of sodium chloride because the higher solubilization could let the oil solubilize in microemulsion phase instead of moving up to the free oil phase, higher sodium chloride concentration could let the microemulsion system transition to Type II.

4.2.4 Jatropha oil extraction efficiency with ultrasonication as a pretreatment

Shah et al. (2005) revealed in their study that the extraction of oil from Jatropha seeds using combination of ultrasonication and aqueous enzymatic oil extraction enhanced oil extraction efficiency. Thus the study in this part aimed to improve the extraction from previous experimental sections by pre-treatment of ultrasonication. Therefore, the ultrasonication for 5 min prior being centrifuged was conducted in this section.

Since this experiment was done in pallarel with the section 4.2.3, there were both system 10 and systems 11 at five concentrations of NaCl evaluated. The numerically results of this experiment is written in Table 5 of the Appendix and the comparison results between with and without ultra-sonification pretreament is shown Figure 4.7. The Jatropha oil extraction efficiency was clearly seen that the systems with the ultrasonication yielded much lower extraction efficiency for all salt concentrations. This might be because the energy inserted into the system broken down the kernel cell or possibly effect the microemulsion system formation. In conclusion, the ultrasonication as a pretreatment did not enhance the oil yield for the chemical extraction using mixed surfactants aqueous-based solution.



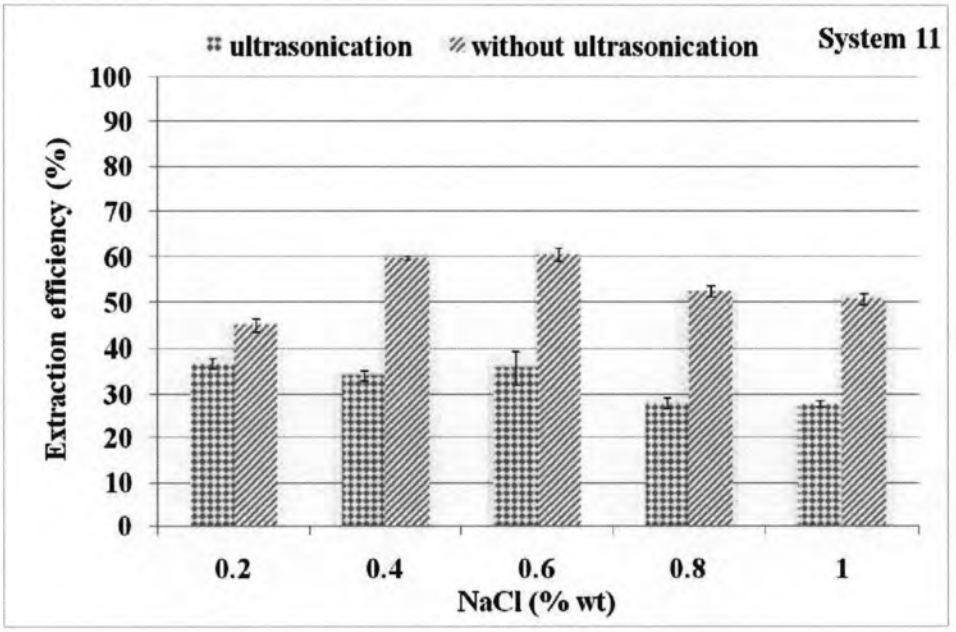


Figure 4.7 Comparison of the Extraction efficiency by
System 10: 3% LS2 mixed with 0.02% Alfoterra 145-4PO and
System 11: 3% LS2 mixed with 0.02% Alfoterra 145-4PO with and without ultrasonification pretreatment

4.2.5 Jatropha oil extraction efficiency at various contact time

The first physical parameter to be evaluated for the optimum condition for the extracton efficiency was contact time between mixed surfactants solutions and ground Jatropha kernels. The system 10 and system 11 at 0.4 and 0.6 %wt of NaCl obtained from the section 4.2.5 were selected for this experiment. Table 6 of the Appendix and Figure 4.8 illustrates the efficiency results for Jatropha oil extraction for those systems. The graphs show similar trend for both systems at both NaCl concentrations that the contact time of 1 min yielded the maximum efficiency. The extraction efficiency longer than 1 min tended decrease slightly. This results may be explained by the fact that too longer contact time increase solubilization of mobilized oil into micelle and hence reducing free excess oil phase. These results agreed with those reported by Naksuk (2007).

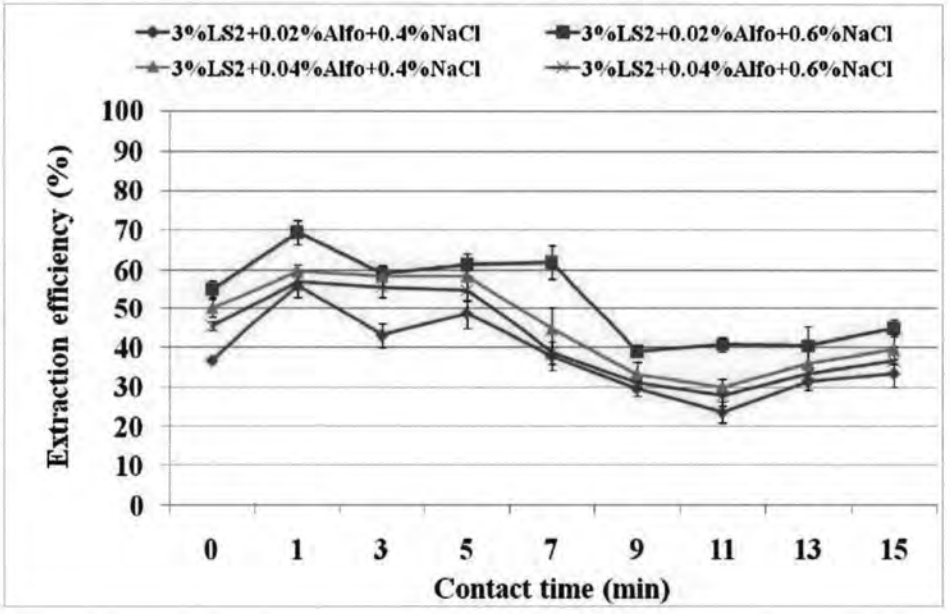


Figure 4.8 Jatropha oil extraction efficiency at various contact time of
System 1: 3% LS2 mixed with 0.02% Alfoterra 145-4PO and 0.4% NaCl;
System 2: 3% LS2 mixed with 0.02% Alfoterra 145-4PO and 0.6% NaCl;
System 3: 3% LS2 mixed with 0.04% Alfoterra 145-4PO and 0.4% NaCl;
System 4: 3% LS2 mixed with 0.04% Alfoterra 145-4PO and 0.6% NaCl

4.2.6 Jatropha oil extraction efficiency at various solid liquid ratios

The purpose of this experiment was to find the optimum condition for high extraction efficiency of mixed surfactants aqueous-based solution extracted with 1 g of Jatropha kernels. The experiment started with weighing 1 g of Jatropha extracted with various loading of the mixed surfactants aqueous-based solution from 4 mL, 6 mL, 8 mL, 10 mL, and 12 mL, respectively. The extraction condition were controlled to be the same by shaking at 130 rpm for 1 min and centrifuge at 2500 x for 20 min. Table 7 in the Appendix shows the extraction efficiency and Figure 4.9 shows the relation between extraction efficiency with various mixed surfactants aqueous-based solution loading.

From Figure 4.9, the trend shows the increase of extraction efficiency when the loading of mixed surfactants aqueous-based solution increase due to higher penetration of surfactant monomers into the kernels and more coalesce between surfactant monomers and oil. Conclusively, the optimum conditions of extraction selected from these evaluations were at 10 ml of mixed surfactants-aqueous based solution loading with 1 g of Jatropha kernels.

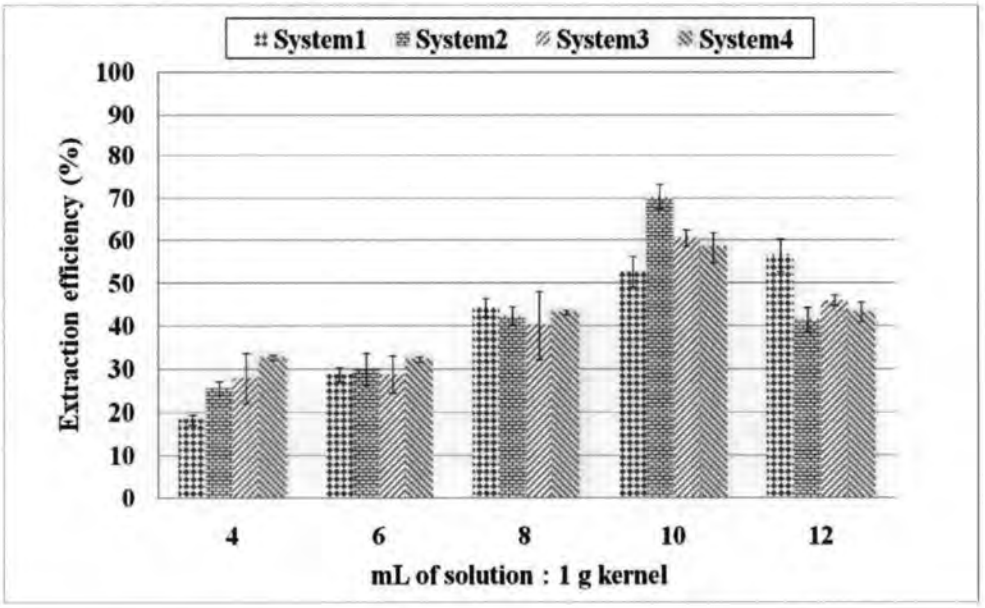


Figure 4.9 Jatropha oil extraction efficiency at various solid liquid ratio (System 1: 3% LS2 mixed with 0.02% Alfoterra 145-4PO and 0.4% NaCl;

System 2: 3% LS2 mixed with 0.02% Alfoterra 145-4PO and 0.6% NaCl;
System 3: 3% LS2 mixed with 0.04% Alfoterra 145-4PO and 0.4% NaCl;
System 4: 3% LS2 mixed with 0.04% Alfoterra 145-4PO and 0.6% NaCl)

4.3 Jatropha oil extraction efficiency of re-extraction

This experimental set was conducted in order to evaluate the feasibility of total oil extraction. For economical reason, this experiment tested for twice extraction of the same kernels and mixed surfactants aqueous-based solution. It was expected that the oil remaining in residual seeds would be extracted by the fresh solution. The extraction efficiencies of first and second extraction for all 4 systems were shown in Figure 4.10 (The data of this result is in Table 8 of the Appendix). The graph shows the additional oil yield obtained from the second extraction procedure raised up the total efficiency more than 20% for all formulation of surfactant solutions. However, the oil quality from the second batch should be further investigated due to it was not as clear as those obtained from the first extraction. In addition, extractions could be done only twice because the third time of extraction process, the kernels was swollen and floated up to the upper layer. As a result, the oil yield from the third extraction, which is significantly less than the second time, could not be measured. To conclude the result of this section, the double extraction is possible to carry out in order to enhance oil yield as much as possible; however, it should be noted here that more surfactant solution as total was also used compared to only one extraction. In addition, the oil quality from the second extraction should be examined.

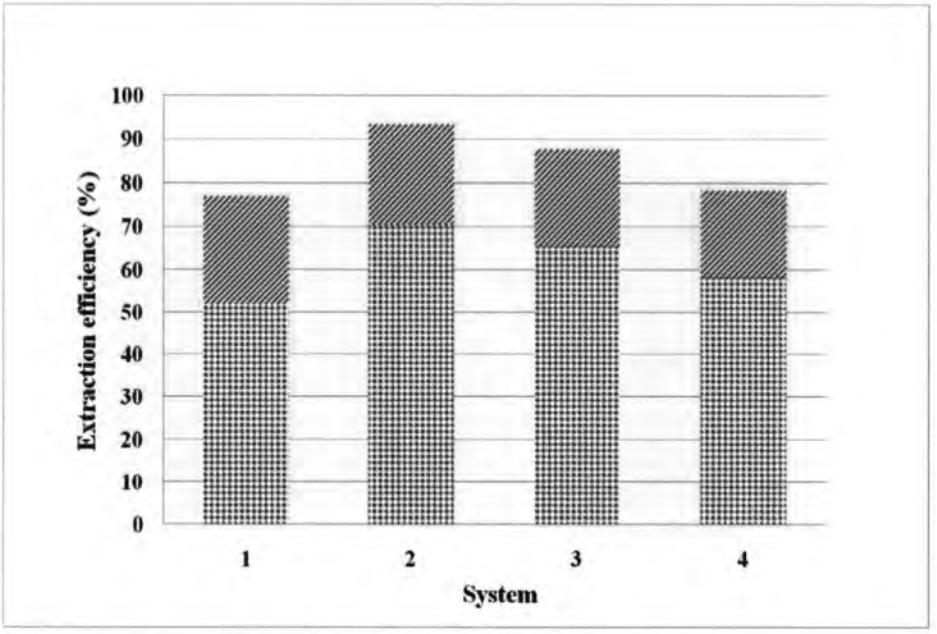


Figure 4.10 Extraction efficiency of re-extraction

(System 1: 3% LS2 mixed with 0.02% Alfoterra 145-4PO and 0.4% NaCl;
System 2: 3% LS2 mixed with 0.02% Alfoterra 145-4PO and 0.6% NaCl;
System 3: 3% LS2 mixed with 0.04% Alfoterra 145-4PO and 0.4% NaCl;
System 4: 3% LS2 mixed with 0.04% Alfoterra 145-4PO and 0.6% NaCl)

4.4 Re-use of aqueous-based mixing surfactant solution

Another way round from the previous experiment, instead of using new surfactant solution to re-extract the residue meal, the used surfactant solution was evaluated for its performance to reuse with fresh ground seed. The objective of this experiment was also to confirm that only small amount of nonionic surfactant partition into the oil phase and anionic surfactant does not adsorb on seed surface. On the other words, most surfactant remained in aqueous surfactant solution. However the concentration of LS2 in the oil phase was determined and report in the next session. The new Jatropha kernels were treated as the same condition as the previous batch; ground Jatropha kernels grain size 8 – 35 mesh, cooked at 105 °C for 90 min, loading of 1 g kernel in 10 ml of re-use mixed surfactants aqueous-based solution, contact time of 1 min at 130 rpm and centrifuged at 2500x for 20 min. The extraction

efficiency of the selected systems was shown in Figure 4.11. (Table 9 in the Appendix shows data for this experiment).

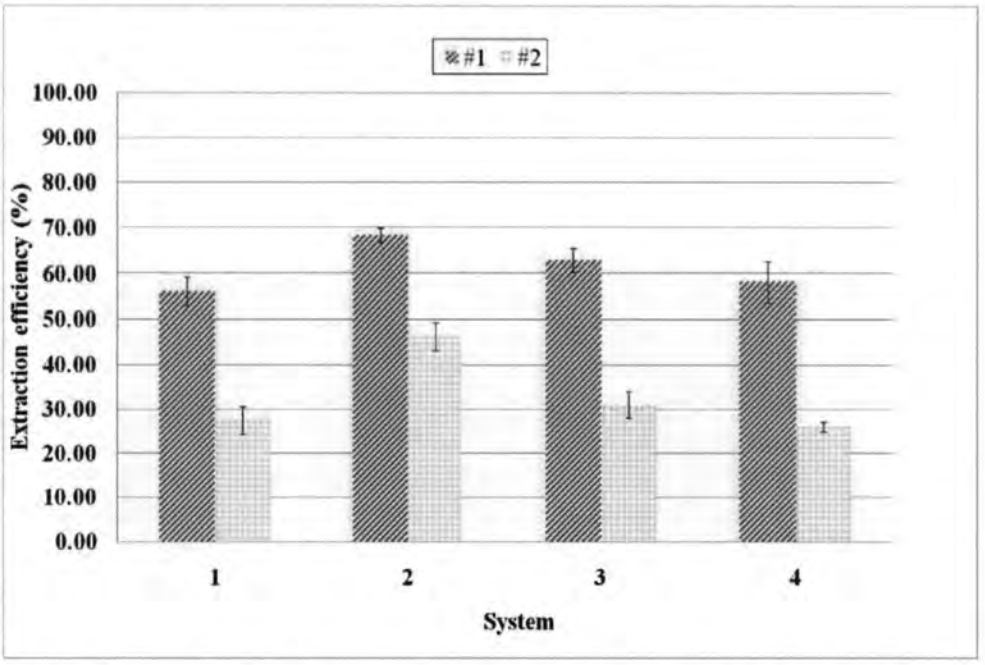


Figure 4.11 Comparison of the extraction efficiency between first batch and second batch (System 1: 3% LS2 mixed with 0.02% Alfoterra 145-4PO and 0.4% NaCl; System 2: 3% LS2 mixed with 0.02% Alfoterra 145-4PO and 0.6% NaCl; System 3: 3% LS2 mixed with 0.04% Alfoterra 145-4PO and 0.4% NaCl; System 4: 3% LS2 mixed with 0.04% Alfoterra 145-4PO and 0.6% NaCl)

Figure 4.11 shows that the efficiency of extraction by re-use surfactant lower than the extraction by newly fresh surfactant systems. The results indicate that the decrease of extraction efficiency was due to the lower concentration of either nonionic or anionic surfactant. But to consider the low solubility characteristic of LS2, it possibly tends to partition into the upper oil phase rather than in aqueous. So the re-use of aqueous-based surfactants solution possibly due to the exists Alfoterra 145-4PO in the aqueous phase. However, the further experiment of remaining surfactants in the aqueous phase has done in the section 4.6

4.5 Jatropha oil extraction efficiency by different methods

Jatropha oil extraction using hexane as a solvent was carried out using the same Jatropha kernels utilized in section 4.2. The extraction procedure followed US EPA 3540C by loading 10 g of jatropha kernels extracted with 100 mL of hexane using reflux Soxhlet method. After the extraction procedure was done, hexane was brought to be evaporated using evaporator in closed system. Then, the Jatropha oil yield was measured using weighing scale in order to be a reference for oil yield extraction efficiency by mixed surfactants aqueous-based solution technique. The extraction efficiency from hexane Soxhlet was used as a total oil or initial oil content in the Jatropha kernels. This is because the previous study indicated the extraction efficiency using hexane to be nearly 100% (Gübitz et al., 1999; Heller, 1996; Forson, 2004; Shah et al., 2005; Winkler et al., 1997 and Shah et al., 2004). This experiment was conducted in triplication as illustrated in Figure 4.12 and the data is shown in Table 12 of the Appendix.

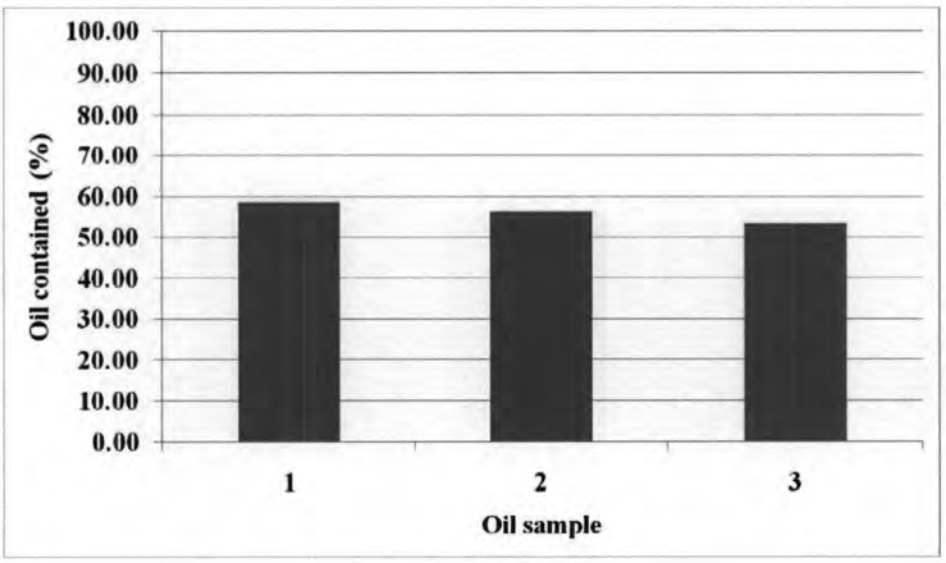


Figure 4.12 Total oil contained in Jatropha oil by hexane extraction

To compare the extraction from different methods including using mixed surfactant solution from this study, their efficiency were illustrated in Figure 4.13. The result shows that the double extraction by mixed surfactant aqueous-based solution gave the efficiency up to 93% which is comparable to the one obtained by hexane extraction. Even the single extraction also gave relatively high extraction efficiency up to 73% which is still higher than hand power small scale pressing method. These could be evidence that the Jatropha oil extraction using mixed surfactants aqueous-based solution is promising and applicable into both small scale to commercial scale production. For the extraction process used only DI water and no chemical reagent involved the extraction efficiency of 0.02% could be obtained by mechanical force and interaction.

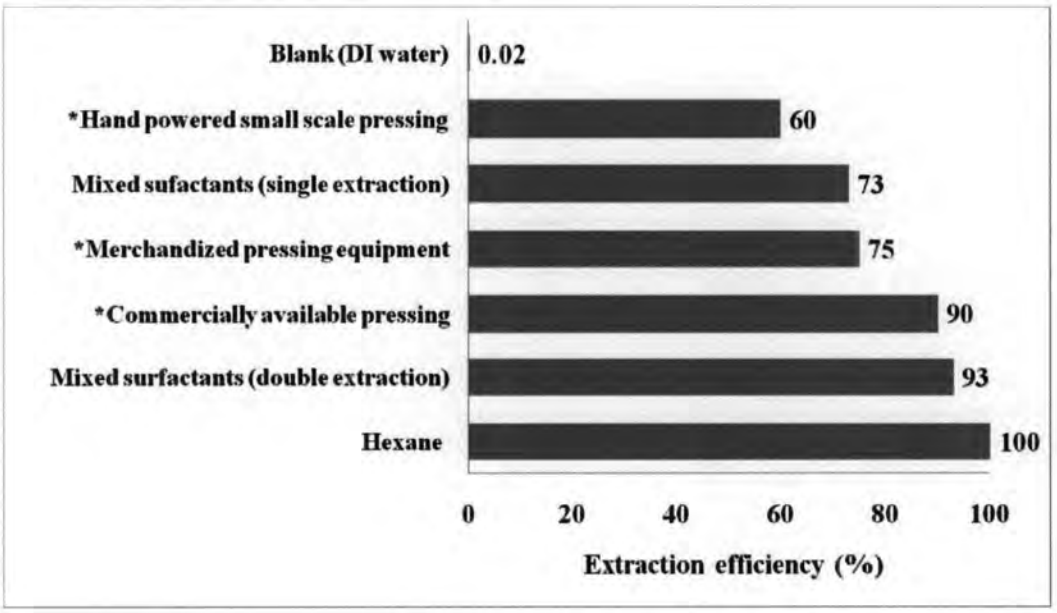


Figure 4.13 Extraction efficiency comparisons by various methods
Source: * From Jongschaap et al. (2007)

Nevertheless, to promote the method of using mixed surfactants aqueous-based solution for hexane extraction replacement, the quality of Jatropha oil shall be determined in order to prove that the oil quality from mixed surfactants aqueous-

based solution extraction is equal or even better than the one from hexane extraction. The oil quality determination is described in the next section.

4.6 Oil quality

As the insufficiency of oil yield per one batch of experiment, the only best system of mixed surfactants aqueous-based solution for highest yield of Jatropha oil extraction was selected for oil quality determination. The system contains 3% LS2, 0.02% Alfoterra 145-4PO and 0.6% NaCl was selected for the further study of oil quality in order to compare with compress method and Soxhlet extraction method using hexane as a solvent. The parameters of concerned were remaining surfactants, moisture and main fatty acid compositions in the oil. The methods for determination are already described in Chapter III. Besides quantitative parameters as mentioned, the general appearance of oil i.e., color was also visually inspected. The colors of Jatropha oil from different extraction method were shown in Figure 4.14 indicate cleary that the color of Jatropha oil obatined from mixed surfactants aqueous-based solution is not different from the one obtained from hexane extraction method. Inaddition, oil obtained from all three extraction methods was clear. For other parameters to define their properties are illustrated in Table 4.5.

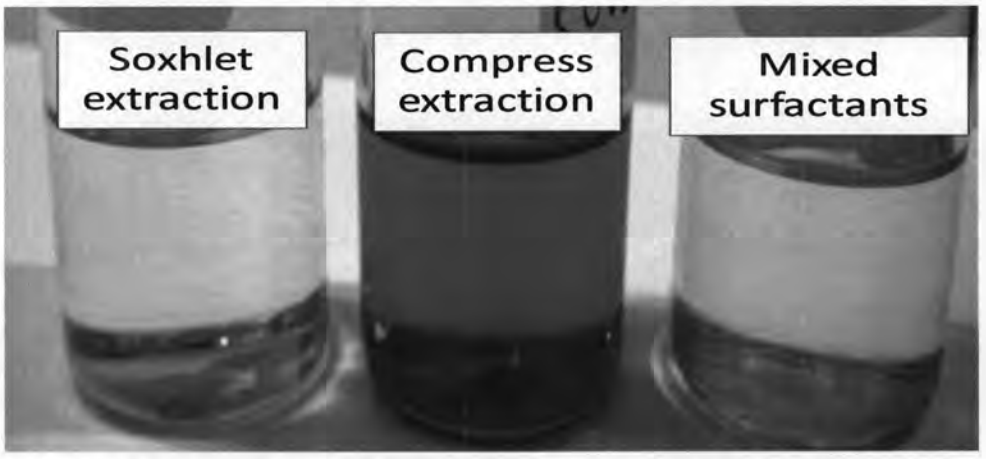


Figure 4.14 The colors of Jatropha oil obtained from various extraction methods

Table 4.5 Comparison of the qualities of Jatropha oil extracted by hexane Soxhlet, mechanical compress and mixed surfactants aqueous-based solution techniques.

Parameters	Commercial Standard	Extraction Methods		
		Compress	Hexane	Surfactant Solution
Color	Clear yellow	Clear yellow	Clear yellow	Clear yellow
Water in oil (%wt)	< 0.5	0.1829	0.0932	0.011
Surfactants remaining in aqueous phase (%wt)				
LS2	-	-	-	0.0250
Alfoterra 145-4PO	-	-	-	0.0182
Fatty acid (Norm%)				
Palmitic	-	0.24	0.49	0.53
Stearic	-	0.13	0.26	0.27
Oleic	-	0.79	1.54	1.62
Linoleic	-	0.61	1.13	1.20

Note: Norm % = Normalize percent

Table 4.5 illustrates the other oil quality comparison between hexane extraction, mechanical compress and mixed surfactants aqueous-based solution extraction. For water content, it was found that the water in Jatropha oil obtained from mixed surfactants aqueous-based solution was less than hexane extraction and mechanical compress and meets the standard. Secondly, for surfactants partition, only the remains in aqueous-phase were analyzed of LS2 and Alfoterra 145-4PO due to limitation of technique and equipment. However, the result can indicate that for Alfoterra 145-4PO, most of the surfactant was still in aqueous phase. For LS2, more than 90% loss from aqueous solution which is reasonably explained because the LS2 has very small solubility, therefore, it is a high opportunity for LS2 to be in the oil phase which is considered not to be trouble as the LS2 cause harmless to the human health and the environment. In contrast, the leftover Alfoterra 145-4PO in aqueous phase is almost the same as initial concentration. This could be implied that the proportion of surfactants in the solution have been changed, which could be confirmed by the less extraction efficiency results in section 4.4.

4.7 Phorbol esters determination

The other crucial benefit of mixed surfactant aqueous solution extraction technique is eliminating phorbol esters in the oil phase. Therefore, phobol esters concentration in oil phase from three extraction methods; compress, Soxhlet using hexane as solvent, and mixed surfactants aqueous-based solution were determined and compared as shown in Figure 4.15.

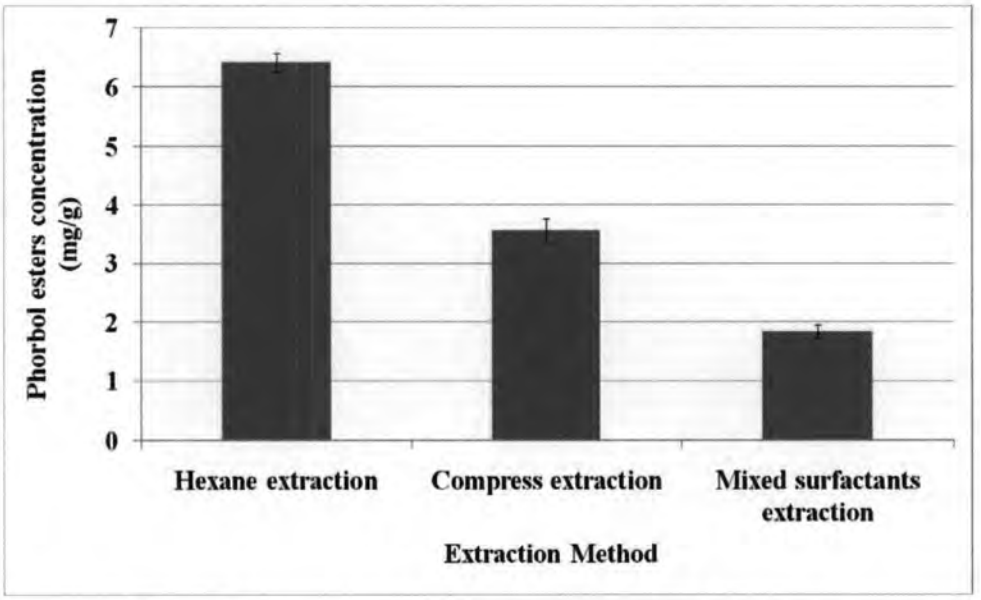


Figure 4.15 Phorbol esters concentration in Jatropha oil from various extraction methods

From Figure 4.15, it apparently shows that the concentration of phorbol esters-- the main toxic compound in Jatropha oil-- found lowest content in the oil obtained from the mixed surfactants aqueous-based solution extraction method. This method can reduce the phorbol esters down to 1.84 mg/g which significantly less than the one obtained from compress method and soxhlet extraction method.

To focus on the oil obtained from mixed surfactants aqueous-based solution extraction itself, the pie graph in Figure 4.16 shows the proportion of the phorbol esters existing in the different phases of the system. It could be noticed that the phorbol esters were trapped in microemulsion phase which occupied 53% while the

remaining in the oil occupied 29% and remaining in the mean 17%. Since phorbol esters are mostly insoluble in water, it was occupied in aqueous phase only 1%.

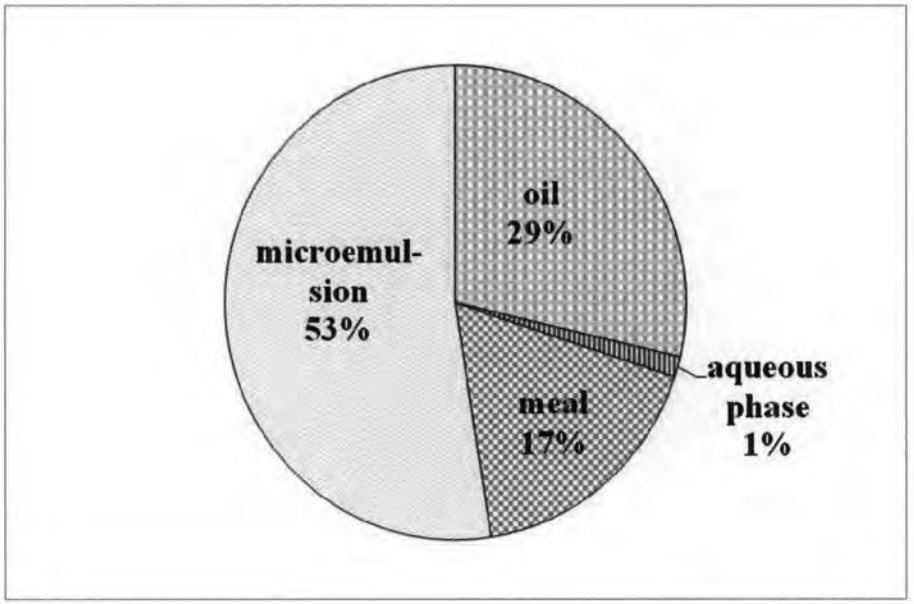


Figure 4.16 Proportion of phorbol esters in each phase of the system

As mentioned eariler, the safe level of phorbol esters should be 0.27 mg/g or lower as referred from the edible Jatropha variety (Mexican variety) reported by Goel et al., (2007). Therefore, the further detoxification may be needed for further uses either for oil or meal if for use as a consumer product. However, the extraction method using mixed surfactants aqueous-based solution is the promising method for Jatropha oil extraction because it can enhance oil yield as well as eliminate the phorbol esters in one batch process besides being nontoxic solvent as compared to hexane. Therefore, it is high potential for further development on using this extraction technique toward the environmental and economical aspects. The mixed surfactants aqueous-based which consisting of Alfoterra 145-4PO, fatty alcohol C 12-14 (2) ethoxylate nonionic surfactant and sodium chloride are all edible, biodegradable and inexpensive. The concentration of the surfactant and electrolyte used in the process was relatively low, therefore, the process may be considered applicable in small scale to commercial scale. Although there was LS2 remained in

the extracted Jatropha oil but it does not cause harmful effects in case of utilization as biodiesel or the oleochemical products because LS2 itself is nontoxic surfactant. This process is considered as inexpensive compare to the Soxhlet extraction method using hexane as solvent because it used less heat and energy input, take significantly less time (the mixed surfactants aqueous-based solution extraction take 30 min while hexane extraction take 24 hr) and safe to the environment and human health.