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PALM BASED SULPHONATED METHYL ESTERS AND SOAP

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Malaysia currently has the capacity to produce about 20% of the world's production of basic oleochemicals such as fatty acids, fatty methyl esters, other fatty alkyl esters, fatty alcohols and glycerol. Besides basic oleochemicals, there are also capacities to produce other derivatives such as mono and diglycerides, soap noodles, metallic soaps and ethylene bisstearamide.

Alpha-sulphonated methyl ester (α-SME) is an anionic surfactant that has frequently been mentioned. Due to its good detergency and less sensitive to water hardness, it could be used as a soap additive. However, α-SME received commercial significance only in Japan. Due to the availability of fatty methyl esters, which is the raw material for the production of α-SME and can be the raw material for the production of soap, it is worthwhile to consider utilizing these (fatty methyl ester and soap) to the best for Malaysia.

This paper reports on the washing behavior of α-SME based on palm fatty acid distillates, palm stearin and pure fatty acids produced on a pilot plant scale. The detergency of α-SME from palm stearin and palm fatty acid distillates were found to be similar and comparable to LAS and FAS. α-SME was also found to be mild towards the enzyme Savinase. As expected, the detergency of soap is increased via the addition of α-SME, and, at room temperature, the combination of (C12 soap:C14 α-SME) was better than (C14 soap:C14 α-SME) and which was, in turn, better than (C14 soap:C12 α-SME).

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SURFACTANTS

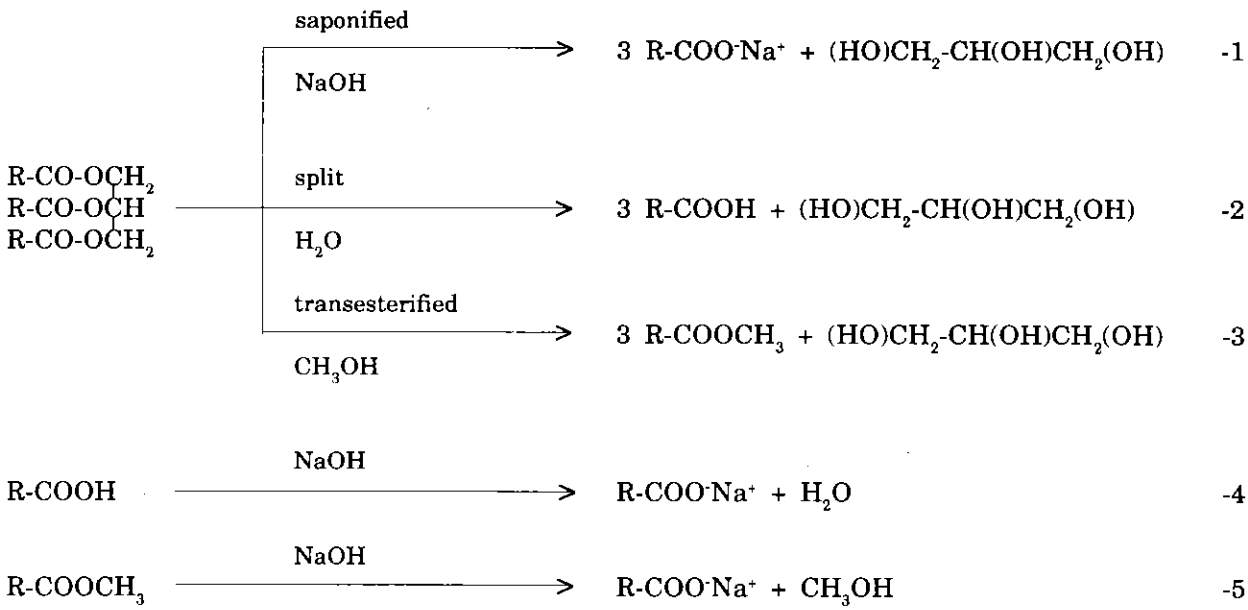
Surface active agents or surfactants represent a large family of products of diverse nature and composition. The most important application of surfactants is in the washing and cleaning area. The two important sources of raw materials for the production of surfactants for washing and cleaning are oils/fats (oleochemicals) and petroleum (petrochemicals). Linear alkyl benzene sulphonate (LAS) is an important anionic surfactant derived from petrochemicals. Next in importance are the alcohol sulphates (AS), alcohol ether sulphates (AES), and alcohol ethoxylates (AE). The starting alcohol used to produce these can either be linear or branched depending on the source *i.e* either oleochemicals or petrochemicals. Due to consumer preference, surfactants derived from oleochemicals are expected to grow in importance. This is not only because they are perceived to be more environment friendly but also because they are derived from renewable resources. Surfactants derived from vegetable oils/fats have the additional advantage of being acceptable to all religions.

SURFACTANTS FROM OLEOCHEMICALS

Oils/fats are normally saponified, split or transesterified to produce soap, fatty acids or methyl esters respectively *(Equations 1* to *3)*. Soap can also be produced from fatty acids *(Equation 4)* or methyl esters *(Equation 5)*. The use of the latter will result in the liberation of methanol and due to its toxicity, needs to be removed before the soap can be used.

Fatty methyl esters are converted to fatty alcohols via high temperature and pressure hydrogenation. From fatty alcohols, various surfactants such as fatty alcohol sulphates (FAS), fatty alcohol ethoxylates (FAE) and fatty alcohol ether sulphates (FAES) can be obtained *(Equations 6* to *9)*.

Fatty methyl esters can be used to produce another surfactant, alpha-sulphonated methyl ester (α-SME) or methyl ester sulphonate (MES) *(Equation 10)*. α-SME is prepared by reacting saturated (iodine value < 0.5) methyl ester with sulphur trioxide gas to produce a dark product which upon bleaching and neutralization yields a white colour α-SME. During sulphonation, bleaching and neutralization, the ester group



$$R\text{-}COOCH_3 \xrightarrow{H_2} RCH_2\text{-}OH \quad \text{Fatty alcohol} \qquad -6$$

$$RCH_2\text{-}OH \xrightarrow[2)\ NaOH]{1)\ SO_3} R\text{-}CH_2\text{-}SO^-_4Na^+ \quad \text{Fatty alcohol sulphate} \qquad -7$$

$$RCH_2\text{-}OH \xrightarrow{n\ \overset{O}{\diagup\diagdown}\ CH_2\text{-}CH_2} R\text{-}CH_2\text{-}(OCH_2CH_2)_n\text{-}OH \quad \text{Fatty alcohol ethoxylate} \qquad -8$$

$$R\text{-}CH_2\text{-}(OCH_2CH_2)_n\text{-}OH \xrightarrow[2)\ NaOH]{1)\ SO_3} R\text{-}CH_2\text{-}(OCH_2CH_2)_n\text{-}SO^-_4Na^+ \quad \text{Fatty alcohol ether sulphate} \qquad -9$$

in the molecule could be hydrolyzed to form a by-product called disalt *(Equation 11)*.

Disalt has a lower surface activity compared to α-SME *(Figure 1)* [Ismail, 1994]. Necessary precautions such as controlling the mole ratio of methyl ester to sulphur trioxide and pH during neutralization, are taken to minimize its formation during the preparation of α-SME. The formation of disalt can be further reduced by reesterification with methanol during neutralization *(Equation 12)* [Inagaki, 1990].

AVAILABILITY OF METHYL ESTERS IN MALAYSIA

Methyl Ester from Recovery of Minor Components

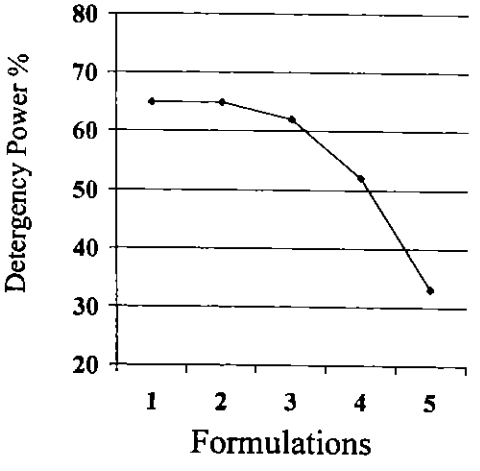
Crude palm oil (CPO) is semi-solid at room temperature and contains contaminants (free fatty acids and phospholipids) and minor components (carotenes and vitamin E). It is normally treated with phosphoric acid and bleaching earth and deodorized to remove the

$$R\text{-}CH_2COOCH_3 \xrightarrow{SO_3} R\text{-}\underset{SO_3H}{CH}\ CO_2SO_3CH_3$$

$$R\text{-}CH_2COOCH_3 \xrightarrow[NaOH]{} R\text{-}\underset{SO^-_3Na^+}{CH}\ COOCH_3 \quad \alpha\text{-SME} \qquad -10$$

$$\xrightarrow{NaOH} R\text{-}\underset{SO^-_3Na^+}{CH}\ COO^-Na^+ \quad \text{Disalt} \qquad -11$$

$$\xrightarrow[NaOH]{CH_3OH} R\text{-}\underset{SO^-_3Na^+}{CH}\ COOCH_3 \quad \alpha\text{-SME} \qquad -12$$



Ingredient	Formulations 1	2	3	4	5	Amount Used
SME	20	15	10	5	0	167 ppm
Disalt	0	5	10	15	20	
Sodium Carbonate	30	30	30	30	30	250 ppm
Zeolite	20	20	20	20	20	167 ppm
Sodium Carbonate	30	30	30	30	30	250 ppm

Figure 1. Effect of disalt on detergency of alpha-SME

Source: Zahariah Ismail (1993). Evalution of detergency, Fabric Care Research Lab., Lion Corporation, Japan.

phospholipids, free fatty acids and other minor components, resulting in the production of refined, bleached and deodorized palm oil (RBDPO). The product removed during deodorization is known as palm fatty acids distillate (PFAD) and besides the free fatty acids, contains significant amounts of triglycerides and vitamin E (Kifli, 1983).

CPO can be converted to methyl ester and, when the ester is removed, minor components such as carotenes and vitamin E can be recovered. Due to their good nutritional values, these minor components fetch high prices. The ester, a by-product from the process, can therefore be sold at a competitive price. Similarly, PFAD can be converted to methyl ester, the vitamin E recovered and the by-product ester, be sold at competitive price. In Malaysia, recovery of carotenes and vitamin E from CPO is already a commercial reality while the PFAD process is at a pre-commercialization stage. Fatty methyl ester is therefore readily available.

Methyl Ester from Palm Stearin

CPO or RBDPO can be fractionated to liquid and solid fractions to yield palm olein and palm stearin respectively. Palm olein has many edible applications and fetches a higher price than palm oil or palm stearin. Just like any other oils/fats, palm stearin can be converted to methyl ester by transesterification with methanol *(Equation 3)*.

Methyl Ester from the Oleochemical Companies

In Malaysia, the oleochemical industry was developed in the early eighties. This development was mainly due to the availability of raw materials, in particular, palm oil and palm kernel oil, good infrastructure and government support. With the implementation of Malaysia's Industrial Master Plan 1 (IMP-1), the industry has achieved remarkable growth. Currently there are fifteen companies *(Table 1)* in operation producing oleochemicals such as fatty acids, fatty methyl esters, fatty alkyl esters, fatty alcohols, soap noodles, metallic soaps, partial glycerides and glycerol. The production capacity for these products is estimated to be 1.4 million tonnes by the year 2000, about 230 000 tonnes for the production of soap noodles (Ahmad and Kang, 1997a).

Due to the availability of various palm based fatty methyl esters in Malaysia, the possibility of using them to produce α-SME and soap was investigated. The synergy between α-SME and soap was also investigated.

EQUIPMENT

EQUIPMENT	SOURCE
Eirich soap pilot plant	Purchased from Eirich, Germany
Falling film sulphonation reactor (600g/hour)	Donated by Henkel, Germany
Terg-o-tometer	Donated by Japan International Corporation Agency
Buchi Reactor	Purchased from Buchi, Germany.

MATERIALS

SYMBOL USED	EXPLANATION/SOURCE/TREATMENT
Me-PS	Palm stearin methyl ester donated by Henkel, Malaysia. It was hydrogenated, then sulphonated using the falling film sulphonation reactor (FFSR).
Me-PFAD	Methyl ester derived from PFAD obtained from PORIM's vitamin E pilot plant. It was hydrogenated and sulphonated using FFSR.
Oleum – 20%	20% sulphur trioxide in sulphuric acid, donated by Malaya Acids
SME-PFAD	α-SME obtained by sulphonating saturated Me-PFAD using the FFSR.
SME-PS	α-SME obtained by sulphonating saturated Me-PS using the FFSR
C12 SME and C14 SME	α-SME's obtained by sulphonating pure C12 and C14 methyl esters using the FFSR.
C12 Soap and C14 Soap	Soaps prepared from pure C12 and C14 fatty acids or methyl esters using the Eirich pilot plant.
Soap or soap noodles	Purchased from Unichema (now ICI), Malaysia
LAS	Linear alkyl benzene sulphonic acid donated by Lion corporation, Japan. It was neutralized with 30% sodium hydroxide to pH 7 as and when needed. The exact composition of the sulphonic acid varies from batch to batch but do not differ significantly from the following:-
Savinase	A proteolytic enzyme purchased from Novo Nordisk. The activity was determined manually using method B 280 provided by NOVO. The activity was found to be the same. In the study, the amount used was actually based on weight.
FAS	Fatty alcohol sulphates purchased from Henkel, Malaysia
Na carbonate	Sodium carbonate purchased from Fluka, 99.0% purity.
Na silicate	Sodium silicate donated by Colgate Palmolive (M) sdn.Bhd. Sodium silicate (45%), SG 1.48 to 1.5.

Active ingredient	94.8%
Acid value	186.0
Moisture	0.7%
Unsulphonated oil	4.5%
C10	10.5%
C11	34.0%
C12	31.0%
C13	25.0%

Na sulphate	Sodium sulphate purchased from Fluka, 99.0% pure.
STPP	Sodium tripolyphosphates purchased from Albright & Wilson (Code-Ampiphos STP/D)
AS 9	Cotton soiled with pigment, oil and carbon black purchased from Westlairds, UK. The soiled cloth was cut into 2cm x 3cm and the reflectance (whiteness) of the pieces measured using Macbeth Colour-Eye 3000 Spectrophotometer.
AS 10	Cotton soiled with pigment, oil and milk (high content), purchased from Westlairds, UK. The soiled cloth was cut into 2cm x 3cm and the reflectance (whiteness) of the pieces measured using Macbeth Colour-Eye 3000 Spectrophotometer.
AS 12	Cotton soiled with pigment, oil and milk, purchased from Westlairds, UK. The soiled cloth was cut into 2cm x 3cm and the reflectance (whiteness) of the pieces measured using Macbeth Color-Eye 3000 Spectrophotometer.
Ni-cat.	Nickel Catalyst – (G 95D – 26%), donated by United Catalyst Inc. USA.
CMC	Sodium salt of carboxymethylcellulose, purchased from Fluka.
C12-Me	98% Pure methyl laurate, purchased from Henkel (M).
C14-Me	98% Pure methyl myristate, purchased from Henkel (M).

TABLE 1. MALAYSIAN OLEOCHEMICAL PRODUCTION CAPACITITES IN 1995 ('000 tonnes/annum)

Company	Fatty Acid	Methyl Ester	Fatty Alcohol	Glycerine	Metallic Soaps	Food Esters	Soap Noodles	Total
CO-1	200			20	10	12	70	312
CO-2	70			10			15	95
CO-3	70			10			25	105
CO-4	120			15		5	90	230
CO-5	40			5			30	75
CO-6	40			5				45
CO-7	70			10				80
CO-8			85	10				95
CO-9		150	60	25				235
CO-10	40	25	30	10				105
CO-11						5		5
CO-12						10		10
CO-13					6			6
CO-14					6			6
CO-15						15		15
Sub-Total	650	175	175	120	22	47	230	
Total			1120			299		1419

EXPERIMENTAL PROCEDURES

1. Hydrogenation of Methyl Esters

Methyl esters from palm stearin (Me-PS) and PFAD (Me-PFAD) were hydrogenated to iodine values (IV) of less than 0.5 using a two litre Buchi reactor. Nickel catalyst (G 95D-26%) was used in all experiments. The hydrogenation conditions were:-

Parameter	Me-PS	Me-PFAD
% Nickel used	0.25	0.35-0.5
Temperature of heating oil (°C)	210	210-223
Temperature inside the reactor (°C)	195	164-199
Hydrogen pressure (bar)	5.5	5.5
Stirring rate (rpm)	500	500

2. α-SME: Falling Film Sulphonation Reactor

Saturated Me-PS and Me-PFAD were sulphonated with sulphur trioxide using the falling film sulphonation reactor (FFSR). Oleum was used as the source for sulphur trioxide gas. The oleum was passed through an evaporator heated at 150°C. The sulphur trioxide gas released was diluted with nitrogen gas and allowed to react with the methyl ester as both cascaded down the tube of the reactor. The temperature of the reactor was maintained at 85°C-90°C. The mole ratio of methyl ester to sulphur trioxide was always maintained close to 1:1.2. The dark coloured sulphonic acids formed were bleached with 4% hydrogen peroxide of 30% concentration at 60°C and then neutralized. For this study, the sulphonated esters formed after the neutralization were not reesterified with methanol. The resulting α-SME (SME-PS and SME-PFAD) therefore contained a high level of the co-product disalt.

3. Washing Active Substance (WAS)

The concentration of surfactant or active ingredient present in a sample (WAS) was determined using a two-phase titration technique (Milwidsky and Gabriel, 1982) with Hyamine 1622 (diisobutylphenoxyethoxydimethyl-benzyl ammonium chloride) as the titrant and methylene blue as the indicator.

4. Disalt

The % disalt (based on 100% WAS) in α-SME was determined by titrating with sodium hydroxide (NaOH) or tetrabutyl ammonium hydroxide (TBAH) solution. W g of α-SME sample was dissolved in hot water and a little iso-propyl alcohol. The pH of the solution was adjusted to 2.5 with 0.1N HCl and titrated immediately with NaOH or TBAH. A graph of pH *vs.* ml titrant was plotted in order to detect the end-point for the conversion of $R\text{-}COO^-$ to $R\text{-}COO^-\ Na^+$. To enhance the detection of the end-point, the first derivative (pH change/ml change) was used. Since:-

Mole of titrant = Mole of fatty acid + Mole of dibasic acid or disalt

Mole of disalt = Mole of titrant − Mole of fatty acid

Therefore:-

$$\%\ \text{disalt based on WAS} = \frac{MW}{WAS}\left(\frac{(V2\text{-}V1)\ (\text{Normality of titrant})\ (10)}{W} - \frac{(AV)(US)}{56.1 \times 10}\right)$$

Where MW = Molecular weight of disalt

V2-V1 = Volume of titrant used to convert $RCOO^-$ to $RCOO^-Na^+$

WAS = Washing active substance

AV = Acid value

US = Unsulphonated matter

5. Degree of sulphonation

$$\text{Degree of sulphonation is} = \frac{\%\ \text{Sulphonated ester} \times 100}{\%\ \text{Sulphonated ester} + \%\ \text{Unsulphonated ester} + \%\ \text{Fatty acid}}$$

$$= \frac{\text{WAS} - \text{Acid Value}}{\text{WAS} + \text{Unsulphonated matter}} \times 100$$

6. Acid Value (AV)

The acid value of the unsulphonated matter was determined using the AOCS Official Method Da 14-48.

7. Unsulphonated Matter (US)

Unsulphonated matter contained in α-SME was determined using Henkel's KGaA method outlined below:-

30g of α-SME paste was dissolved in 50ml water with slight heating. The solution was further diluted with 100ml water and the pH of the solution adjusted to below three with 10% sulphuric acid. The solution was extracted with 100ml petroleum ether (boiling point 40°C-50°C). The extraction was repeated twice. All petroleum ether extracts were combined, washed with 100ml 25% ethanol in water, dried with anhydrous sodium sulphate, filtered and the petroleum ether distilled. The residue obtained was dried under vacuum and weighed.

$$\%\ \text{Unsulphonated matter} = \frac{\text{Weight of petroleum extract} \times 100}{\text{Weight of α-SME used}}$$

8. Unsaponifiable Matter

Unsaponifiable matter was determined using PORIM's Test Method p2.7 (1995).

9. Detergent Formulae: α-SME *vs.* LAS

Ingredient	α-SME* with PO_4	α-SME * without PO_4	LAS with PO_4	LAS without PO_4
Active ingredient	26%	26%	26%	26%
STPP	24%	0%	24%	0%
Na sulphates	37.7%	61.7%	37.7%	61.7%
Na silicates	7%	7%	7%	7%
Na carbonate	5%	5%	5%	5%
CMC	0.3%	0.3%	0.3%	0.3%

* *α-SME = SME-PS and SME-PFAD*

10. Detergent Formulae: Effect of α-SME *vs.* LAS on Savinase

Ingredients	α-SME* without PO_4	LAS without PO_4
Active ingredient	26%	26%
Na sulphates	61.7%	61.7%
Na silicates	7%	7%
Na carbonates	5%	5%
Savinase**	0.8%-1.8%	0.8%-1.8%

Total % formulation = 100% + Savinase

* *α-SME = SME-PS*

** Although the range 0.8% to 1.8% were studied, only the result for 0.8% is reported.

11. Detergent Formulae: α-SME *vs.* FAS

α-SME was mixed with FAS in the ratio of 100:0, 70:30, 50:50, 30:70 and 0:100 based on WAS. Detergent formula containing 26% active ingredients were formulated using these mixtures and other ingredients as indicated in Experimental Procedure No.9.

12. Detergent Formulae: α-SME *vs.* Soap

Palm based soap noodles from Unichema were blended with SME-PS in the ratio of 0:100, 30:70, 50:50, 70:30 and 100:0 based on WAS of α-SME and total fatty matter of soap. Detergents containing 26% active consisting of mixtures of soap:α-SME were formulated with other ingredients mentioned in Experimental Procedure No.9.

13. Preparation of Soap from C12- and C14- Methyl Esters and Fatty Acids

C12 methyl ester was fed into the Eirich mixer and the required amount of caustic soda (46% concentration) added with slow stirring (590 rpm). The stirring rate was increased (1180 rpm) as the reaction proceeded to completion. During this time the temperature of the Eirich mixer increased from about 60°C to 85°C. After about 75 minutes of reaction time, a vacuum was applied and maintained for five minutes. The vacuum was then released and the soap collected. A similar process was used for C14 but with vacuum applied for 10 minutes. This Eirich pilot plant can also be used to produce soaps from fatty acids using similar processing parameters.

14. Preparation of C12 and C14 α-SME's

C12 and C14 methyl esters of 98% purity purchased from Henkel (M) were sulphonated using a similar procedure described in Experimental Procedure No.2. The bleached sulphonic acids were, however, neutralized in the presence of methanol.

15. Water Hardness

A stock solution of hard water of 5000 ppm as $CaCO_3$ hardness was prepared by dissolving 3000 ppm $CaCl_2.2H_2O$ and 2000 ppm $MgSO_4.7H_2O$ in doubled distilled water. To prepare water of various hardness, appropriate aliquots of the stock solution were diluted to one litre with double distilled water.

16. Detergency Tests

Before washing, the reflectances of the soiled swatches were measured using Macbeth Colour-Eye 3000. One litre water of appropriate hardness was poured into each stainless steel container of the Terg-o-Tometer (there are altogether four containers) and allowed to reach the desired temperature of washing. The detergents were then added into the containers and the mixture stirred for 30 minutes to ensure complete solution. Four pieces of the soiled swatches were placed, one by one, into each container, making sure that the pieces were well spread out in the detergent solution. The washings were then stirred for 10 minutes at 120 rpm. The liquors were poured out, the swatches squeezed and returned to the containers. One litre water of appropriate hardness was poured into each container, stirred for three minutes and the liquor poured out. This rinsing was repeated twice. The swatches were dried by spinning for one minute and ironed. The reflectances of these washed-swatches were measured. The detergency or % soil removal was calculated using the formula:-

% Soil Removal = [AW-BW] / [OC-BW] x 100

where AW is the reflectance of the swatches after washing, BW is the reflectance of the swatches before washing and OC is the reflectance of original cloth before soiling.

RESULTS AND DISCUSSIONS

Hydrogenation of Me-PFAD and Me-PS

In this experiment, the main purpose of carrying out the hydrogenation was to reduce the unsaturation to an IV of less than 0.5. This was an essential step before sulphonation as the presence of high unsaturation will result in the formation of internal sulphonates (sulphonation at the double bond).

Keeping the other reaction conditions constant, the minimum amount of nickel catalyst required to give an IV of less than 0.5 was investigated. The results obtained and the characteristics of the esters are given in *Table 2.*

The results indicated that about 0.45%-0.5% Ni catalyst was required to hydrogenate Me-PFAD to an IV of less than 0.5. This is approximately double the amount required to hydrogenate Me-PS. Despite the greater amount used, the IV obtained was still higher than that of Me-PS. This could be due to the higher unsaponifiable matter contained in Me-PFAD compared to Me-PS.

Sulphonation of Methyl Esters

The saturated esters obtained after hydrogenation were sulphonated using FFSR. The use of this reactor allowed us to have a first hand experience on the production of α-SME and appreciative of the difficulties frequently associated with the production of α-SME (Inagaki, 1990; Yoneyama, 1996 and Sobic, 1996) and among them are:-

1) Effect of unsaturation (if iodine value is greater than 0.5) on the quality of α-SME, where high degree of unsaturation adversely affects the colour of α-SME.
2) The high temperature, high methyl ester to sulphur trioxide ratio (1:1.2) and the post reaction time required to obtain a good

TABLE 2. HYDROGENATION OF METHYL ESTERS

HYDROGENATION CONDITIONS FOR ME-PS AND ME-PFAD

Catalyst (%)	Heating Temp (°C)	Reactor Temp (°C)	Pressure (bar)	Iodine Value**		Sample
				After 1hr	After 2hr	
0.25	210	195	5.5	0.34	-	ME-PS
0.35	210	164	5.5	-	1.34	ME-PFAD
0.40	210	164	5.5	-	0.50	ME-PFAD
0.45	223	199	5.5	-	0.44	ME-PFAD
0.50	210	180	5.5	0.48	-	ME-PFAD

CHARACTERISTICS OF HYDROGENATED ME-PS AND ME-PFAD

Parameter	ME-PFAD	ME-PS
C12:0	0.3	0.6
C14:0	1.3	1.2
C16:0	49.5	62.3
C18:0	48.5	35.5
Other	0.5	0.4
Unsap. matter*	0.7	0.3

* Unsaponifiable matter = PORIM Test Method P2.7 (1995)

** Iodine value = AOCS Official Method Tg 1-64

degree of sulphonation.

3) The darkening of α-SME which dictates the necessity to bleach.
4) The formation of disalt which adversely affects the detergency performance of α-SME.
5) The reesterification process to reduce disalt and
6) The high viscosity and the drying required to get a high solid content.

The characteristics of SME-PS and SME-PFAD obtained are as indicated in *Table 3*. The α-SME's prepared had about 40% WAS and a paste-like consistency. Their characteristics were found to be very similar and comparable to α-SME from palm stearin produced by two foreign companies.

By reesterifying with methanol during neutralization, a product of slightly higher WAS and lower disalt could be obtained. For C12-Me the WAS and disalt contents were 68.4% and 3.7% respectively while for C14-Me, the α-SME obtained has 61.4% WAS and 4.12% disalt.

Detergency of α-SME from Palm Stearin and PFAD

The detergency performances of SME-PS and SME-PFAD were studied using Terg-o-tometer, with various soiled clothes, at various temperatures, water hardness, with or without phosphates, with or without enzymes, and compared to LAS and FAS.

In general, it was found that the performances of these α-SME's were better than LAS at low temperature in the absence of phosphates (see *Figures 2* to *5)*. Under all conditions tested, α-SME's were comparable to FAS *(Figures 6* and *7)*. Since α-SME can be produced at a cheaper cost compared to LAS and FAS, these findings are of significance as they indicate the possibility of reducing the cost of a finished product if α-SME were to be used instead of, or in combination with LAS or FAS.

Detergency of Savinase in the Presence of α-SME and LAS

The results obtained are plotted in *Figure 8*. As mentioned in the experimental procedure, the concentrations of enzyme used were in the range of 0.8% to 1.8%. Since the results were very similar (only a slight increase with increased amount used), only the results of 0.8% enzyme are reported.

In general, the removal of soils from AS 10 (cotton soiled with pigment, oil and milk) was greatly increased by Savinase at room temperature and 40°C, either in the presence of LAS or α-SME. At 60°C washing temperature, the detergency of LAS with Savinase was only slightly better than LAS without Savinase and inferior to α-SME with Savinase. This was unexpected and the tests were repeated at 50°C. The results clearly indicated that Savinase is effective in the temperature range of ambient

TABLE 3. CHARACTERISTICS OF α-SME

Parameter	SME-PS	SME-PFAD	SME Company 1	SME Company 2
WAS	38	36	35	39
Disalt (based on 100% WAS)	24	22	23	NA
Colour (CCDM)*	81	81	83	84
Degree of sulphonation	94	94	94	NA

NA = Not available

CCDM = Colour and Colour Difference Metre

WAS = Washing Active Substance

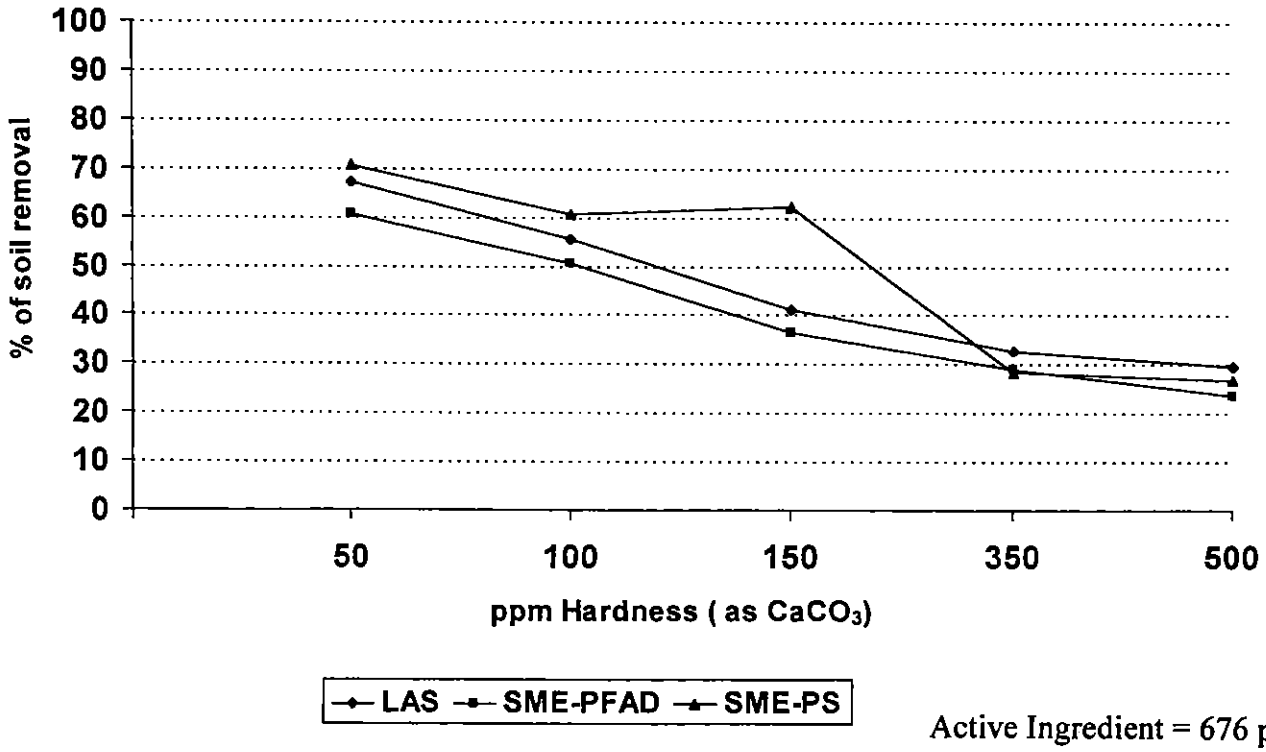


Figure 2. Detergency of α-SME vs LAS at RT and without PO_4

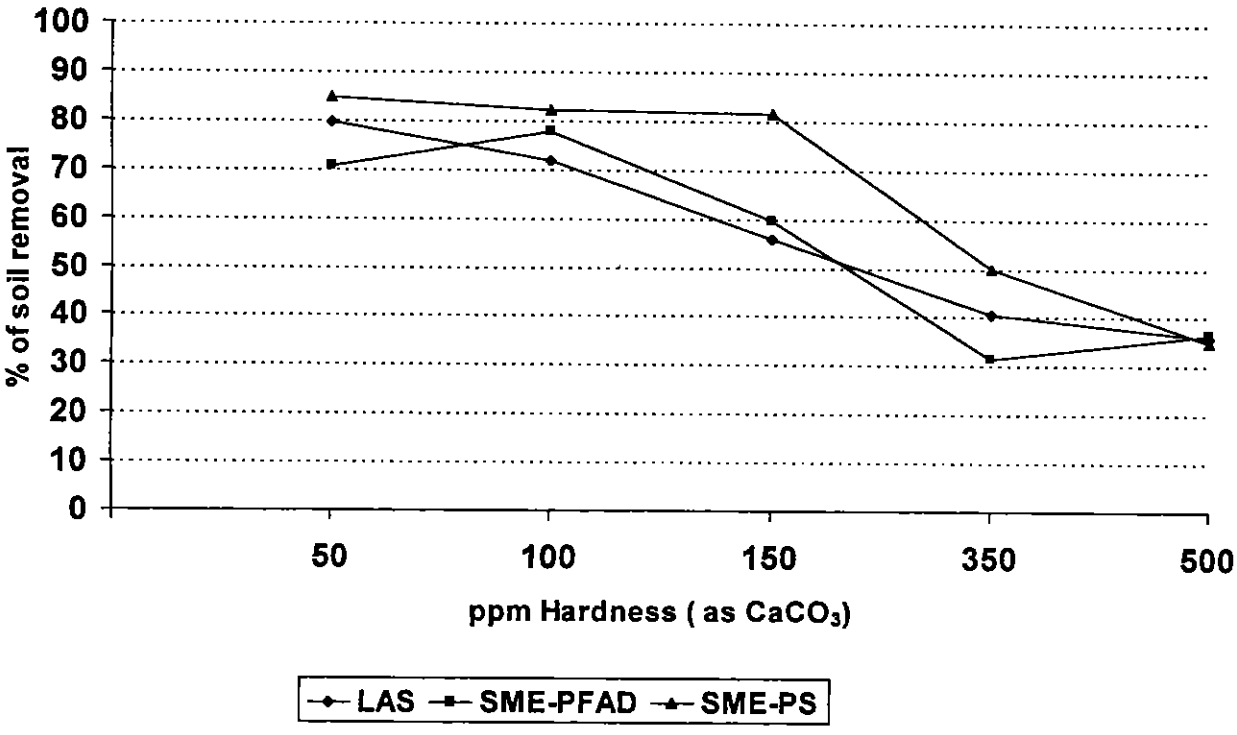
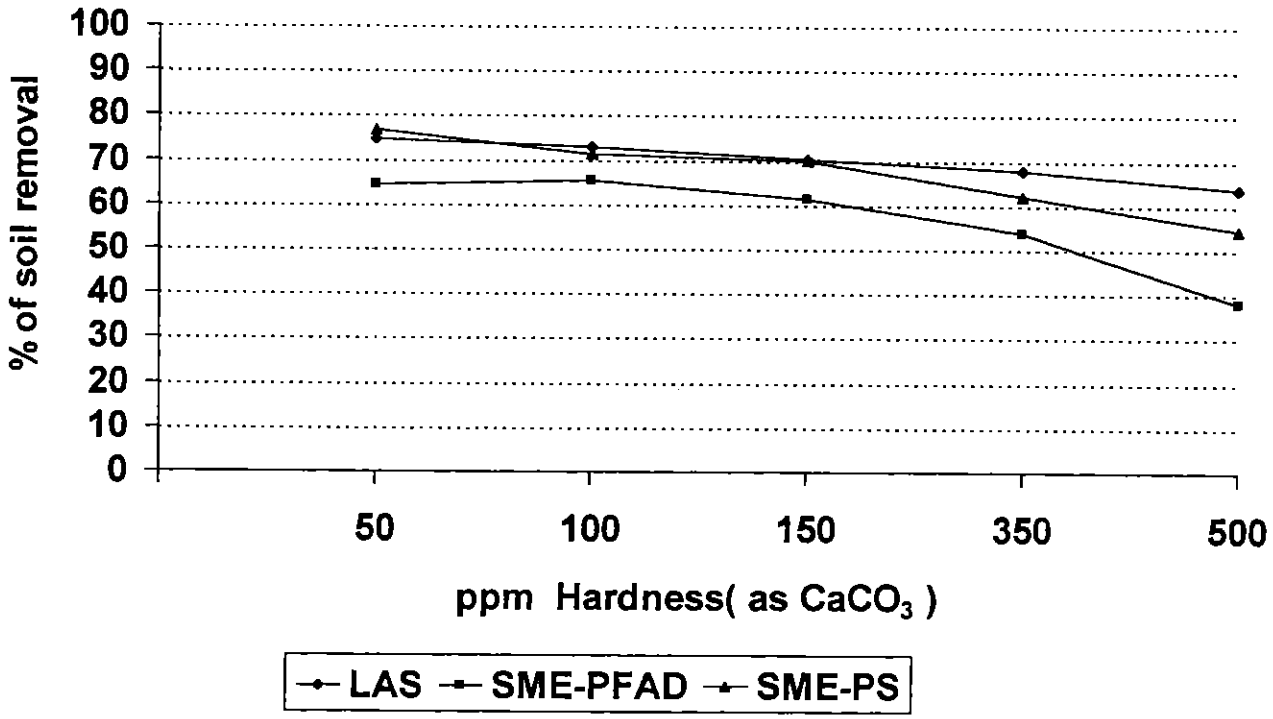
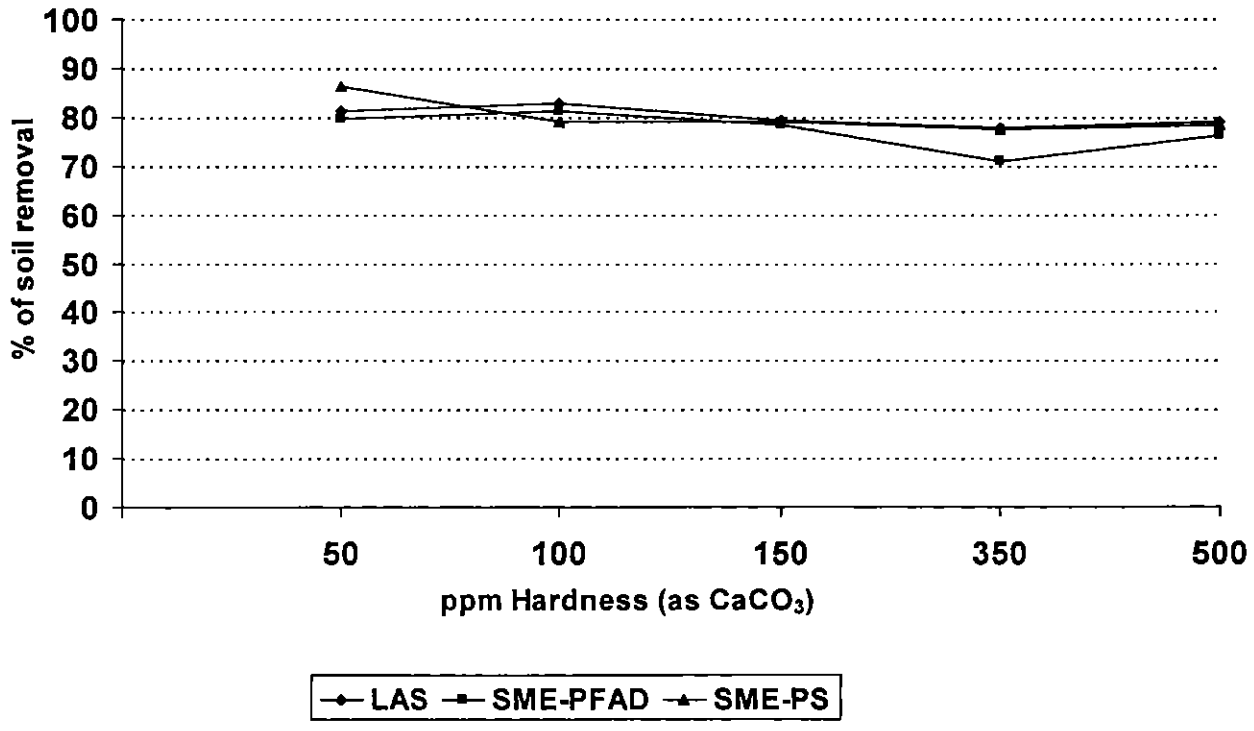


Figure 3. Detergency of α-SME vs LAS at 60°C and without PO_4



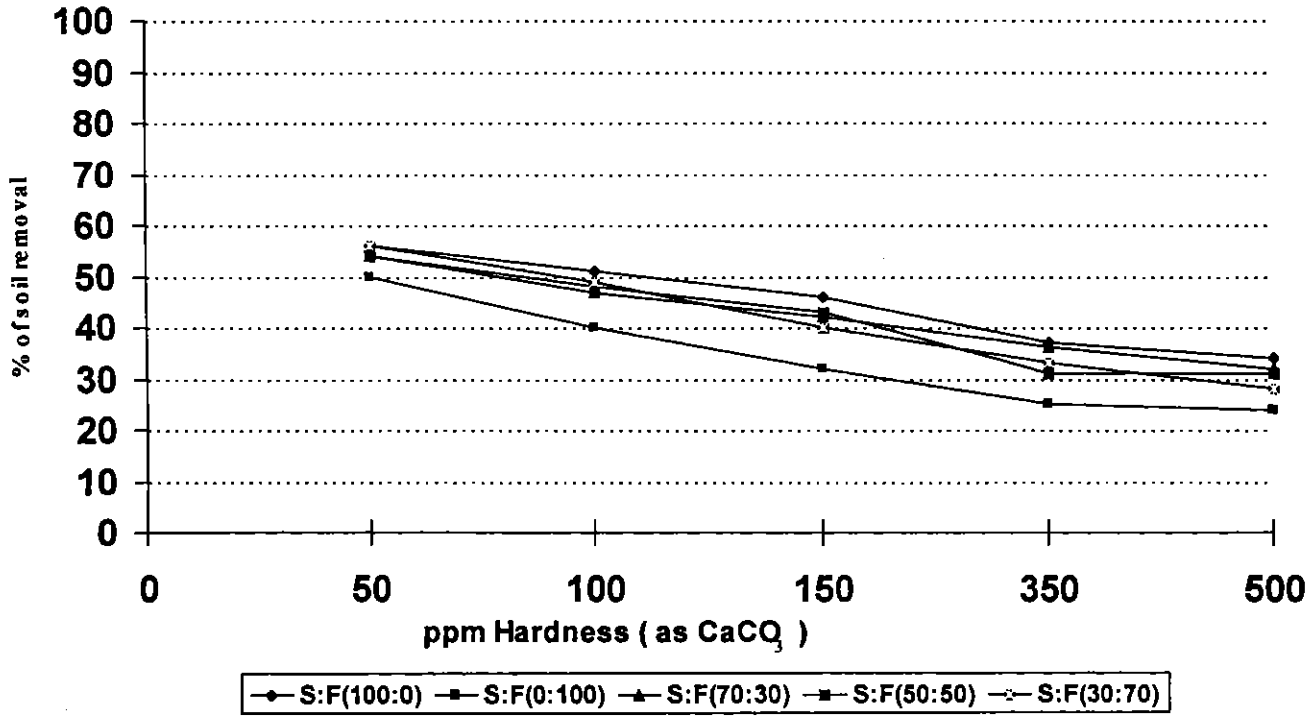
Active Ingredient = 676 ppm
Soiled Cloth AS9

Figure 4. Detergency of α-SME vs LAS at RT and with PO_4



Active Ingredient = 676 ppm
Soiled Cloth AS9

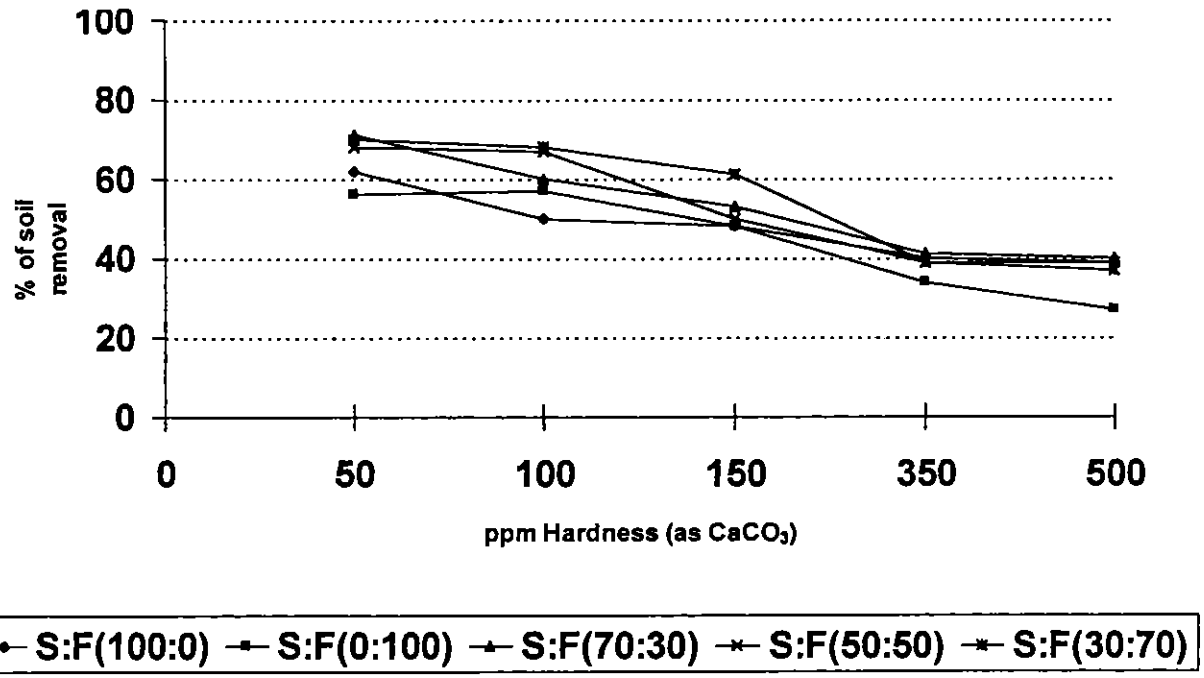
Figure 5. Detergency of α-SME vs LAS at 60°C and with PO_4



Active Ingredient = 676 ppm

Soiled Cloth AS9

Figure 6. Detergency of α-SME:FAS at RT



Active Ingredient = 676 ppm

Soiled Cloth AS9

Figure 7. Detergency of α-SME:FAS at 60°C

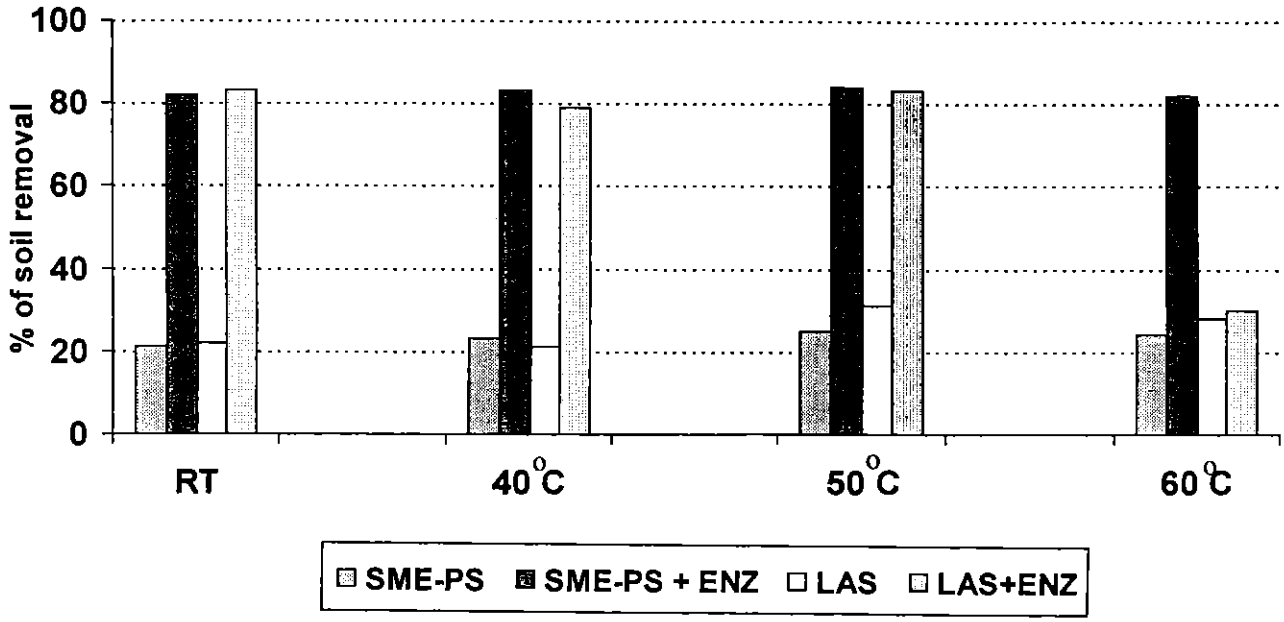


Figure 8. Detergency of SME-PS and LAS with 0.8% Savinase at 50 ppm hardness (as $CaCO_3$)

to 60°C in the presence of α-SME. In the presence of LAS, however, Savinase is deactivated at 60°C.

It is important to note that AS 10 is specifically designed to evaluate the effect of proteolytic enzymes. The soils contained a relatively high concentration of milk powder, hence an exaggerated enzyme effect was obtained which could be used to detect small variations in enzyme activity [Westlairds, UK]. AS 10 was not designed to detect differences in the performances of active ingredients. In this test, it is suspected that it was the enzyme that was deactivated, the LAS was still performing but its effect was not detected.

Detergency of Soap Noodles and α-SME

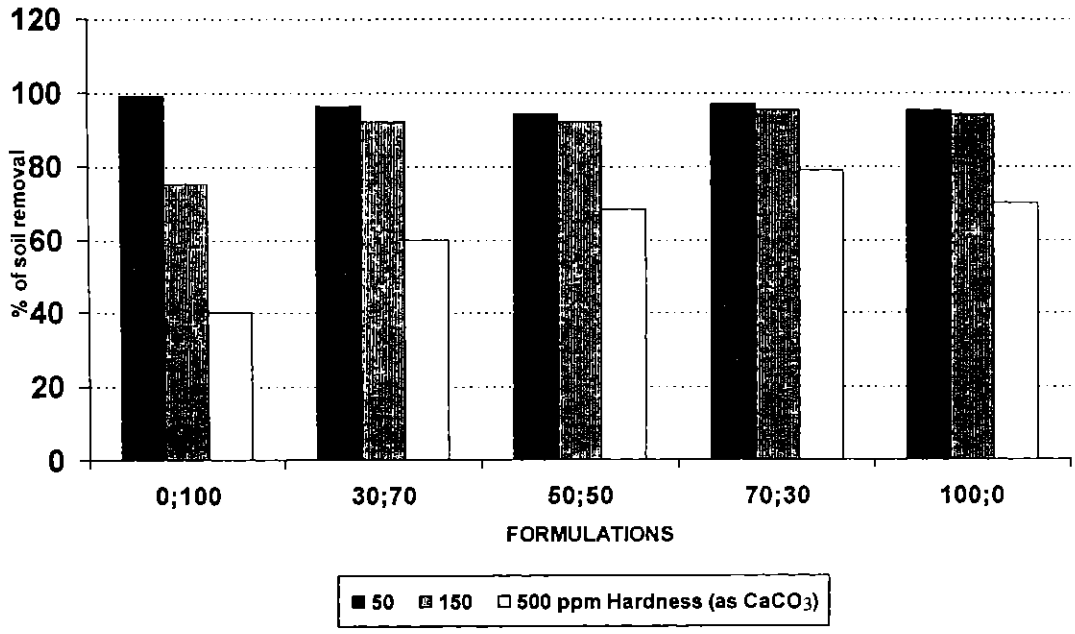
Soap noodles and SME-PS were found to exhibit good detergency performances mainly due to the combined performance of α-SME and soap *(Figure 9)*. A slight synergistic effect was observed at room temperature, in the absence of phosphates, where the detergency performances of SME-PS:soap combinations were found to be better than soap or SME-PS alone *(Figure 10)*.

The synergistic effect between soap:SME-PS expected was therefore not clearly observed. This was thought to be due to the mixture of fatty acids chain lengths used in the study. Since the detergency performances of surfactants depend on the chain lengths, the use of mixtures of fatty acid chain lengths might camouflage the synergistic effect.

Detergency of Soap and α-SME from Pure Fatty Esters

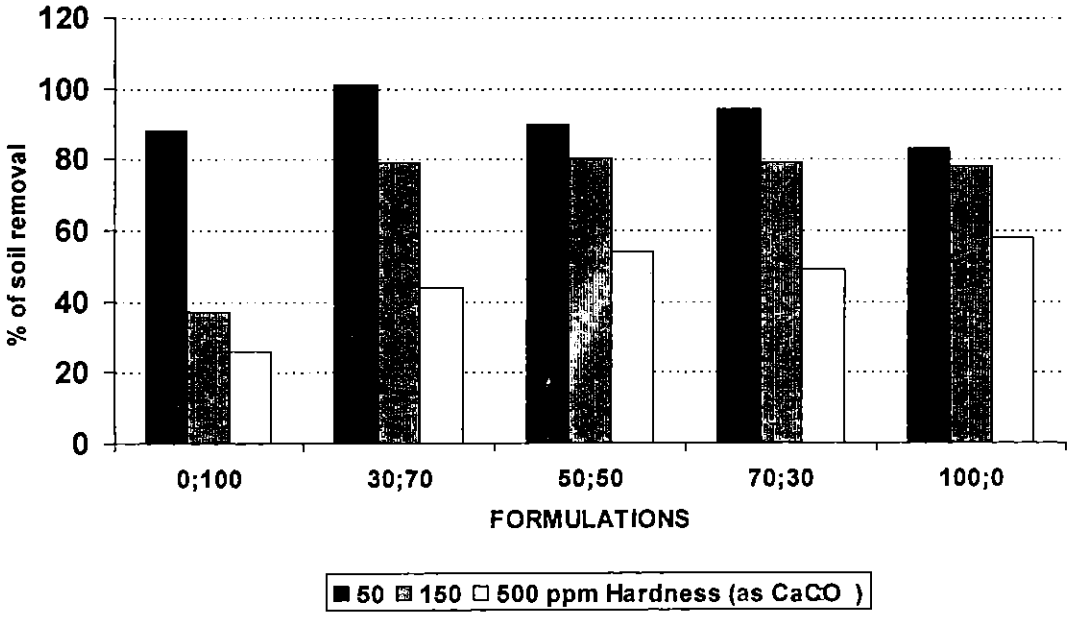
Soaps derived from pure fatty acids or fatty methyl esters were prepared using Eirich soap pilot plant. This pilot plant allows easy saponification or neutralization and removal of water or methanol generated during the reaction. The Total Fatty Matter (TFM) of the soap obtained ranged from 80% to 87%. In this study, the TFM of C12 soap and C14 soap derived from their corresponding esters were 85.0% and 80.8% respectively.

The C12 soap and C14 soap obtained from the Eirich pilot plant and C12 α-SME and C14 α-SME from the FFSR were combined in the ratios 70:30, 50:50 and 30:70 based on WAS and TFM. Their cleaning abilities were evaluated



Active Ingredient = 676 ppm
Soiled Cloth; AS12

Figure 9. Detergency of α-SME:SOAP at RT and with PO_4



Active Ingredient = 676 ppm
Soiled Cloth; AS12

Figure 10. Detergency of α-SME:SOAP at RT and without PO_4

using Terg-o-tometer, cotton soiled with pigment, milk and carbon black (AS9), at room temperature and using water of different hardness (50 ppm, 150 ppm and 350 ppm as $CaCO_3$). The results plotted in *Figures 11* to *13* clearly indicate that the combination (C12 soap: C14 α-SME) is better than (C14 soap: C14 α-SME) and is, in turn, better than (C14 soap: C12 α-SME), at all the combinations (30:70, 50:50 and 70:30) and different water hardness studied. This is believed to be due to the combined effect of foaming power, cleaning power and solubility. C12 soap has good foaming power while C14 α-SME has good cleaning power, better than C12 or C13.6 α-SME [Drozd, 1990]. Thus the combination of C12 soap and C14 α-SME had good cleaning power due to the good foaming characteristic of C12 soap and good cleaning ability of C14 α-SME. A combination of C12 soap and C14 α-SME clearly indicated the synergy between α-SME and soap, while the other two combinations only exhibited detergency due to the combined effect of α-SME and soap. In this study the authors concentrated on cleaning power at room temperature while cleaning power at higher temperature and cleaning ability of C16 and C18 soaps and α-SME's shall be the subject of our next paper.

A special study was conducted to determine the detergency performances of C12 and C14 soaps and α-SME's at 10 ppm and 100 ppm in comparison to 1000 ppm. The results are plotted in *Figure 14* and indicate that while 10 ppm concentration was too low to distinguish between the various surfactants, the detergency trend obtained using the 100 ppm concentration was similar to that obtained using 1000 ppm concentration. (A 1000 ppm concentration was used in this study only because of convenience). A similar trend of results is therefore expected if the study had been conducted using concentrations in the range of 100 to 1000 ppm. In *Figure 14*, it is also interesting to note that C12 α-SME has better detergency at increased

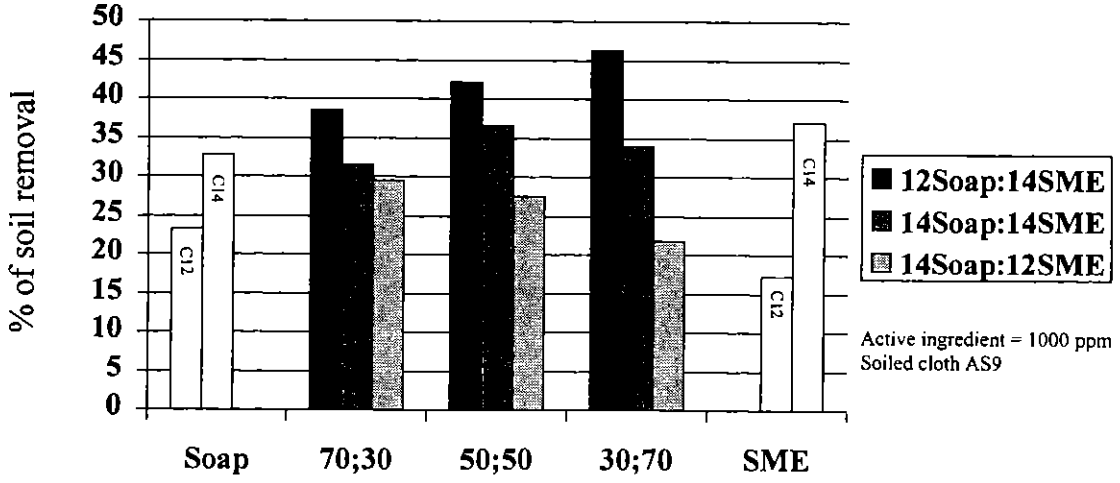


Figure 11. Detergency of C12-14 Soap:C12-14 SME at RT and 50 ppm hardness (as $CaCO_3$)

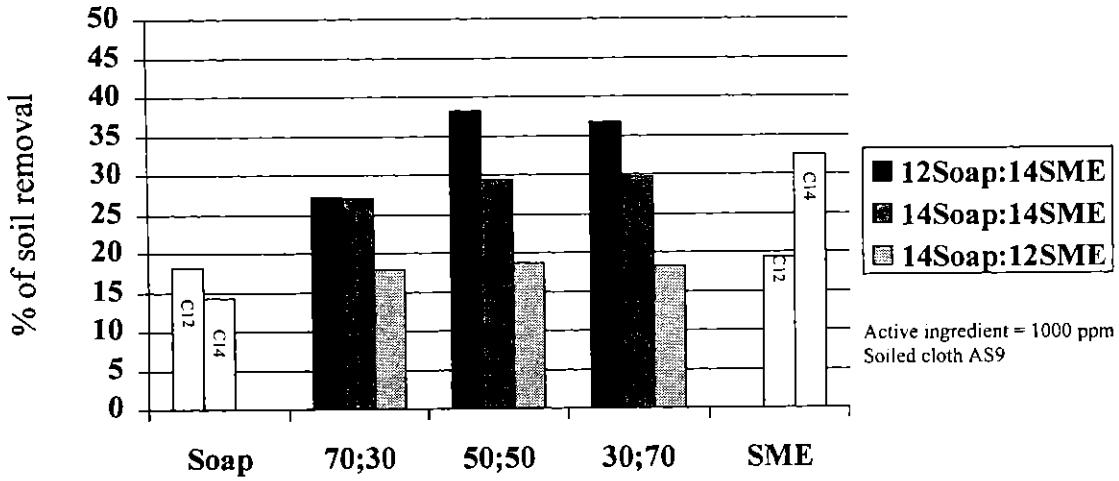


Figure 12. Detergency of C12-14 Soap:C12-14 SME at RT and 150 ppm hardness (as $CaCO_3$)

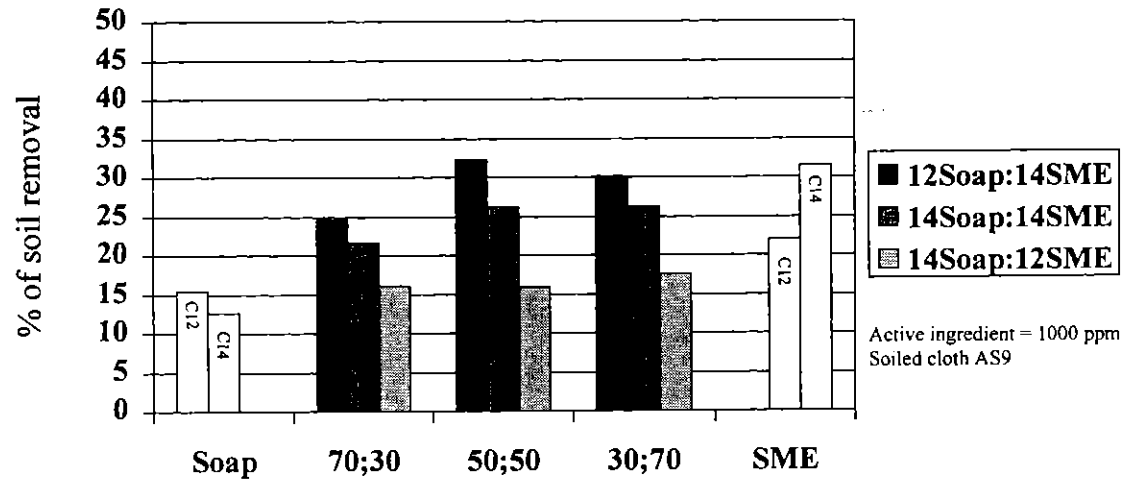


Figure 13. Detergency of C12-14 Soap:C12-14 SME at RT and 350 ppm hardness (as $CaCo_3$)

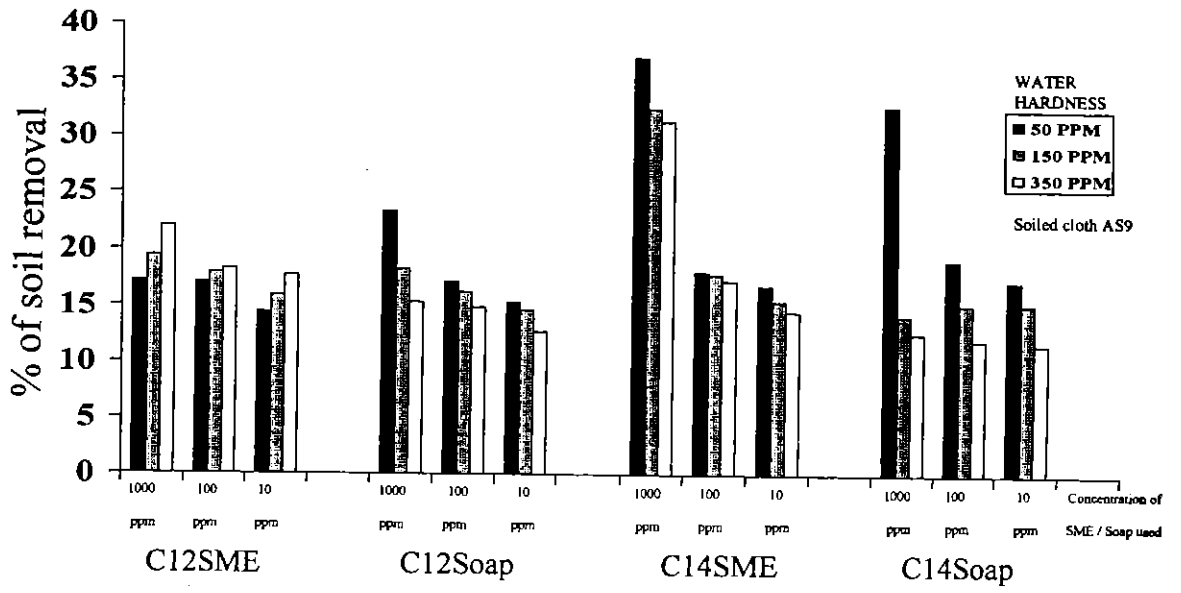


Figure 14. Effect of concentration of surfactant and water hardness on detergency

water hardness, while the sensitivity of soap towards water hardness is clearly demonstrated.

CONCLUSION

This paper discusses some of the R&D findings on work carried out in order to support the further development of oleochemical industry in Malaysia and, in particular, to enhance the utilization of fatty methyl esters. The performances of anionic surfactants, α-SME and soap, were investigated.

The detergency performances of α-SME from palm stearin and PFAD methyl esters were comparable to LAS and FAS. α-SME was also found to be mild towards a protease enzyme, Savinase. Together they exhibited excellent detergency even at 60°C. This was despite the fact that Savinase was expected to be thermostable only up to 55°C.

With a production capacity that can reach 230 000 tonnes by the year 2000, Malaysia is beginning to be recognized as the major producer of soap noodle. α-SME can enhance the performance of soap. This study indicates that formulation based on (C12 soap: C14 α-SME) is better than (C14 soap: C14 α-SME) which is, in turn, better than (C14 soap: C12 α-SME). This observation is believed to be due to a synergy between the foaming characteristic of C12 soap and the cleaning ability of C14 α-SME.

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REFERENCES

AHMAD, S and KANG, Y B (1997a). Oleochemicals and other nonfood applications of palm oil and other palm oil products, *Lipidex 1997,* Belgium.

AHMAD, S; ISMAIL, Z; CHOO, M Y and WIESE, D (1997b). Palm based anionic surfactants. *PORIM Transfer of Technology No.48.*

DROZD, J (1990). Use of sulphonated methyl ester as household cleaning products. *The Proceedings of World Conference on Oleochemicals: into 21st Century*. Edited by T.Applewhite, AOCS, Champaign, Illinois, p. 256.

INAGAKI, T (1990). Development of alpha sulfo fatty acids esters. *The Proceedings of World Conference on Oleochemicals: into 21st Century*. Edited by T. Applewhite, AOCS, Champaign, Illinois, p. 269.

ISMAIL, Z (1994). Evaluation of SME's detergency and other properties. *PORIM Report G(214)94.*

KIFLI, H (1983). Survey on characteristics of Malaysian palm fatty acids distillates and palm acid oils. *PORIM Report PO(59)83, General.*

SOBIC, P (1996). Prospects for the use of palm oil based surfactants in detergents - the current Unilever's perspective. *The Proceedings of the 1996 PORIM International Palm Oil Congress: Soap and Detergent Industry Conference.* PORIM, p. 525.

YONEYAMA, Y (1996). Palm oleochemical for use in detergents - Lion's perspective in the applications of methyl ester sulphonates. *The Proceedings of the 1996 PORIM International Palm Oil Congress: Soap and Detergent Industry Conference.*PORIM, p. 515.

Westlairds Ltd. North Green, Datchet, Slough SL3 9JH, UK. General description on the AS and PC series.