CHAPTER IV

RESULTS AND DISCUSSION

The goal of this research was to synthesize the product as a potential surfactant from soybean oil fatty acids (SOFA) by the following three steps : esterification, epoxidation, and sulfonation.

The properties of Soybean oil fatty acids (SOFA)

Physical and chemical properties of the raw material were determined. The results were shown in Table 4.1.

Table 4.1 The physical and chemical properties of SOFA

Color (ASTM D1500)	>8
Iodine Value (IUPAC II.D.7)	116.0
Viscosity at 40 °C, cSt	24.39
100 °C, cSt (ASTM D445)	7.22
Viscosity Index (ASTM D2270)	287.5
Pour Point, °C (ASTM D97)	+13
Flash Point, °C (ASTM D92)	214
Density at 20 °C, g/cm^3	0.890

The ^{13}C-NMR spectrum of soybean oil fatty acids was shown in Figure A1. It indicated the signals of paraffinic carbons (CH_2, CH_3) at 14.1-34.7 ppm, olefinic carbons (C=C) at 127.9-130.1 ppm, carbonyl (C=O) of triglyceride

residue at 173.3 ppm, and carbonyl(C=O) of carboxylic acid at 179.9 ppm.

The infrared spectrum of SOFA was shown in Figure A2, and the characteristic was shown in Table 4.2.

Table 4.2 The characteristic group absorptions of SOFA

Wave number (cm^{-1})	Functional group	Type of signals
3010	=C-H	stretching
2933, 2855	C-H	stretching
2500-3500	O-H of carboxylic	stretching
1711	C=O	stretching
1378, 1463	C-H	bending
1173-1281	C-O	stretching

Esterification of the Soybean oil fatty acids

The esterification was obtained by excess methanol in the presence of concentrated sulfuric acid at 50 °C, for 2 hours (95.5 % yield). Characteristics of methyl ester product were determined by ^{13}C-NMR, IR , and GC-MS.

The ^{13}C-NMR spectrum in Figure A3, it indicated the signals of paraffinic carbons (CH_2, CH_3) at 14.0-37.2 ppm, methyl ester (O-CH_3) at 51.2 ppm, olefinic carbons (C=C) at 125.2-130.0 ppm, carbonyl (C=O) of methyl ester at 173.9 ppm.

From the infrared spectrum was shown in Figure A4, and the characteristic absorption bands were shown in Table 4.3.

Table 4.3 The characteristic group absorptions of SOME

Wave number (cm^{-1})	Functional group	Type of signals
3010	=C-H	stretching
2926, 2855	C-H	stretching
1743	C=O	stretching
1364, 1463	C-H	bending
1119-1245	C-O	stretching

From gas chromatogram in Figure A5, it was shown that the signals of four main fatty acid methyl esters were at the retention time (min.) of 12.996, 15.462, 15.532, and 15.733. The mass spectra of all components were shown in Figure A6-A9. Comparing to the mass spectrum patterns of library, it could be concluded that they were methyl hexadecanoate, methyl 9,12-octadecadienoate, methyl octadecenoate, and methyl octadecanoate, respectively.

The peak area ratio of the GC chromatogram was determined into the percent compositions of all components, which containing methyl hexadecanoate 19.5 %, methyl 9,12-octadecadienoate and methyl octadecenoate 75.1 % and methyl octadecanoate 5.4 %.

Epoxidation of Soybean oil methyl ester (SOME)

In the second step, the epoxidation of SOME was obtained by reacting with peracetic acid solution. The optimum condition was obtained by varying the mole ratio of acetic acid and hydrogen peroxide, peracetic acid generating temperature, and the ratio of peracetic acid solution and SOME.

1. The effect of acetic acid and hydrogen peroxide mole ratio

In this study, the mole ratios of acetic acid and hydrogen peroxide were varied from 1:1, 2:1, 4:1, 5:1, 6:1, 8:1, and 10:1. The % conversion, iodine value, and epoxy content of the epoxidized soybean oil methyl ester (ESME) comparing with the mole ratio were shown in Table 4.4 and Figures 4.1-4.3.

Table 4.4 The % Conversion, Iodine Value and Epoxy Content of the ESMEs which were synthesized with various mole ratios of AcOH:H_2O_2

Mole Ratio	% Conversion*	Iodine Value	Epoxy Content
1:1	36.8	81.4	1.33
2:1	53.8	56.6	2.21
4:1	74.2	35.9	3.01
5:1	81.6	30.7	3.21
6:1	54.9	51.7	2.39
8:1	69.5	41.0	2.82
10:1	51.5	71.5	1.74

* The % conversion were calculated from Figures A3 and A10-A16.

From Figure 4.1, it was found that % conversion was increased when the mole ratio was changed increasingly. But when the mole ratio was more than 5:1, % conversion was decreased.

From Figure 4.2, the iodine value was decreased till the mole ratio was equal to 5:1. Later, it was changed increasingly.

From Figure 4.3, it could be seen that the epoxy content would be

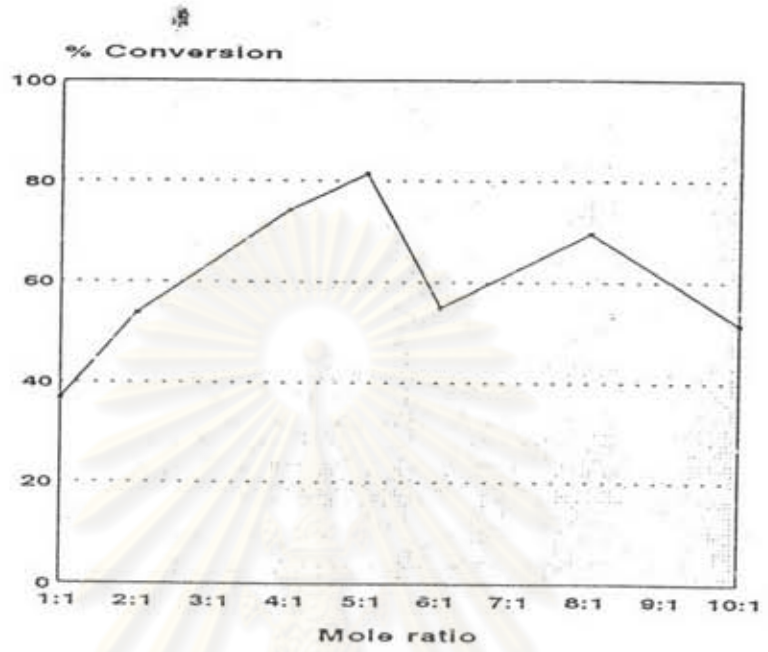

Figure 4.1 The curve of % conversion versus mole ratio of acetic acid and hydrogen peroxide

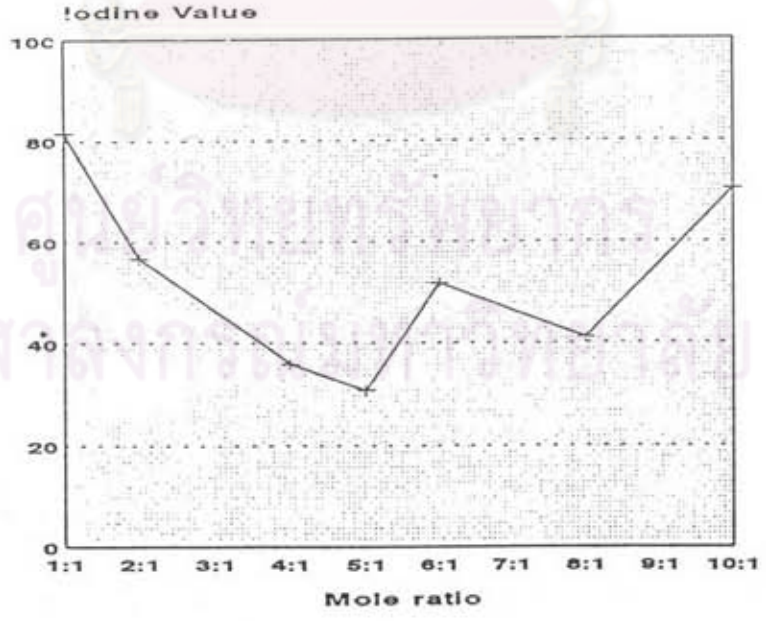

Figure 4.2 The curve of iodine value versus mole ratio of acetic acid and hydrogen peroxide

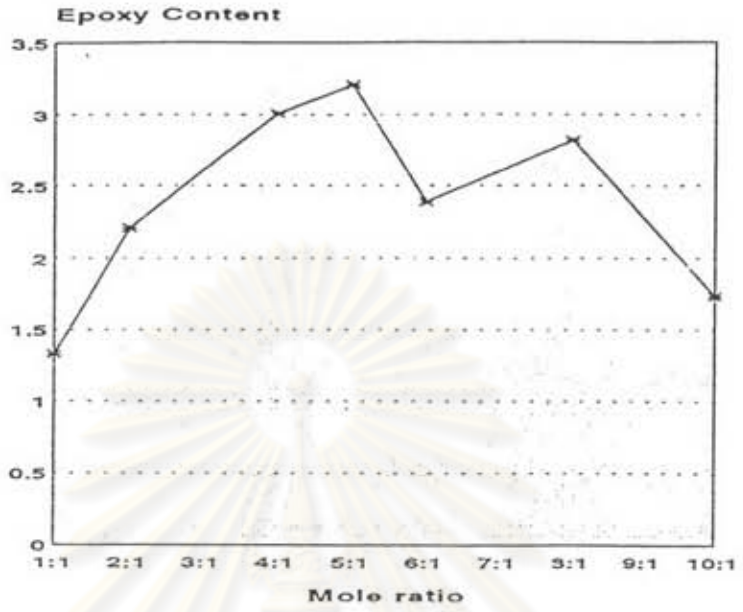

Figure 4.3 The curve of epoxy content versus mole ratio of acetic acid and hydrogen peroxide

maximized when the mole ratio had been equal to 5:1.

From the above data, it could be concluded that the appropriate mole ratio was 5:1.

2. The effect of temperature for generating peracetic acid

The effect of peracetic acid generating temperature was shown conspicuously in Table 4.5 and Figures 4.4-4.6.

From Figure 4.4, the % conversion was risen up with increasing temperature in the first stage. When the temperature was over 60 °C, the % conversion was decreased.

From Figure 4.5, the iodine value was decreased until the temperature was 60 °C. Then, it was increased continuously.

Table 4.5 The % Conversion, Iodine Value and Epoxy Content of the ESMEs which were synthesized with temperature variation for generating peracetic acid.

Temp , °C	% Conversion*	Iodine Value	Epoxy Content
30	49.0	53.6	2.36
40	55.5	48.9	2.53
50	60.1	38.2	2.93
60	81.6	30.7	3.21
80	64.7	45.3	2.66
100	16.7	89.4	1.08

* The % conversion were calculated from Figures A3 and A17-A21.

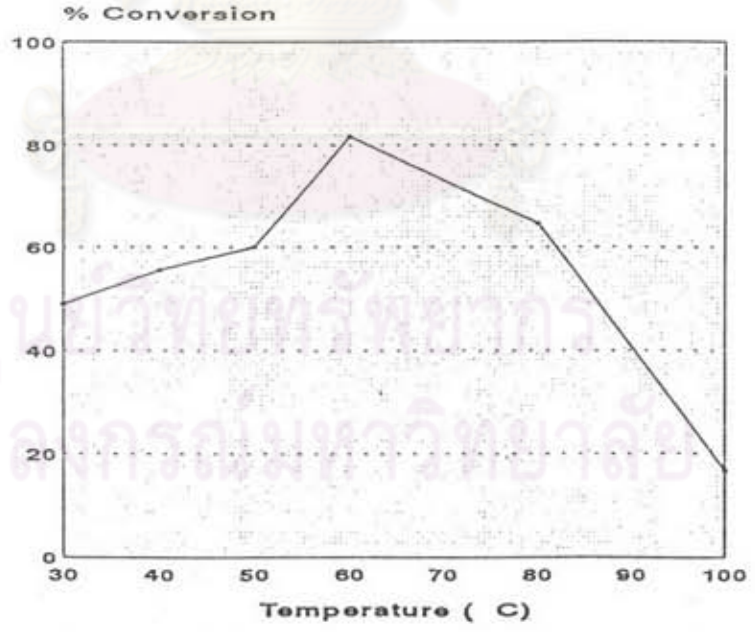

Figure 4.4 The curve of % conversion versus the temperature for generating peracetic acid

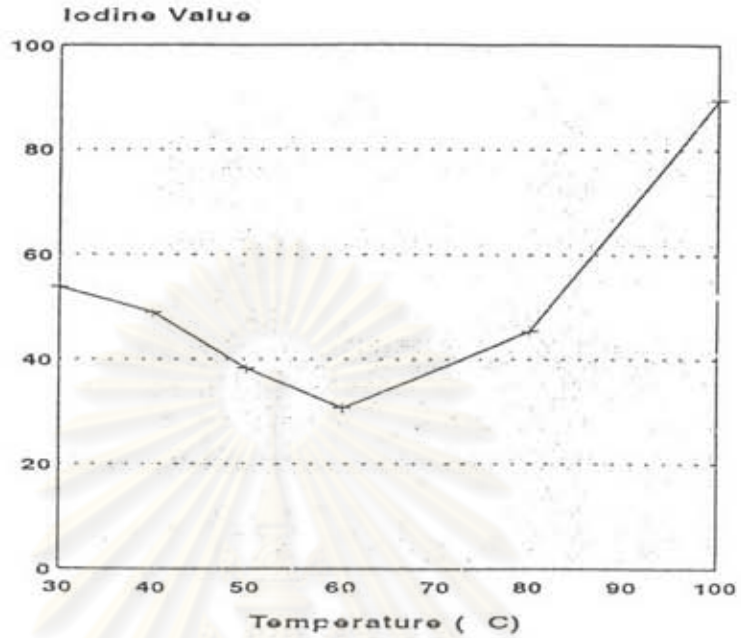

Figure 4.5 The curve of iodine value versus the temperature for generating peracetic acid

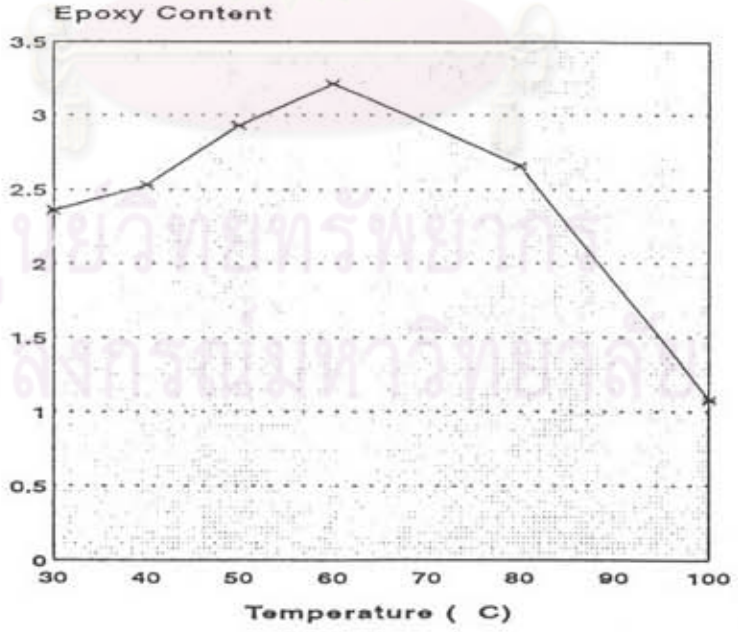

Figure 4.6 The curve of epoxy content versus the temperature for generating peracetic acid

From Figure 4.6, the epoxy content was increased, while increasing temperature. When the temperature was equal to 60 °C, the epoxy content was increased to the maximum value. Then, it was decreased abruptly.

From the above results, it could be concluded that the appropriate temperature for generating peracetic acid was 60 °C.

3. The effect of amount of peracetic acid solution

The effect of the amount of peracetic acid solution per 20 g of SOME was shown in Table 4.6 and Figures 4.7-4.9.

Table 4.6 The % Conversion, Iodine Value and Epoxy Content of the ESMEs which were synthesized with various amount of peracetic acid solution per 20 g of SOME

Amount of Peracetic acid (ml)	% Conversion*	Iodine Value	Epoxy Content
50	49.0	59.5	2.63
75	73.4	35.6	3.10
100	81.6	30.7	3.21
125	-	17.9	3.13
150	-	19.7	2.76

* The % conversions were calculated from Figures A3 and A22-A25.

From Figure 4.7, the % conversion of SOME was increased continuously, while increasing the amount of peracetic acid solution. The % conversion of SOME could not be calculated when the amount of peracetic acid

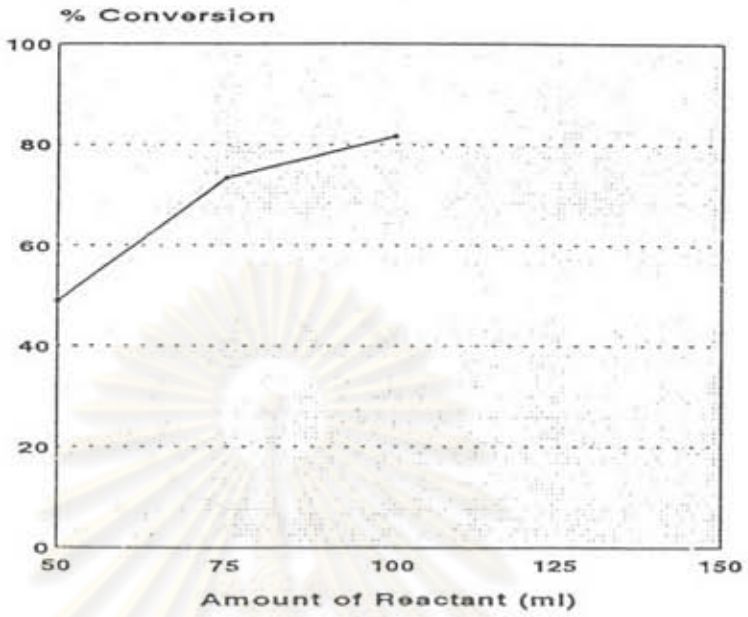

Figure 4.7 The curve of % conversion versus the amount of peracetic acid solution for reacted with 20 g of SOME

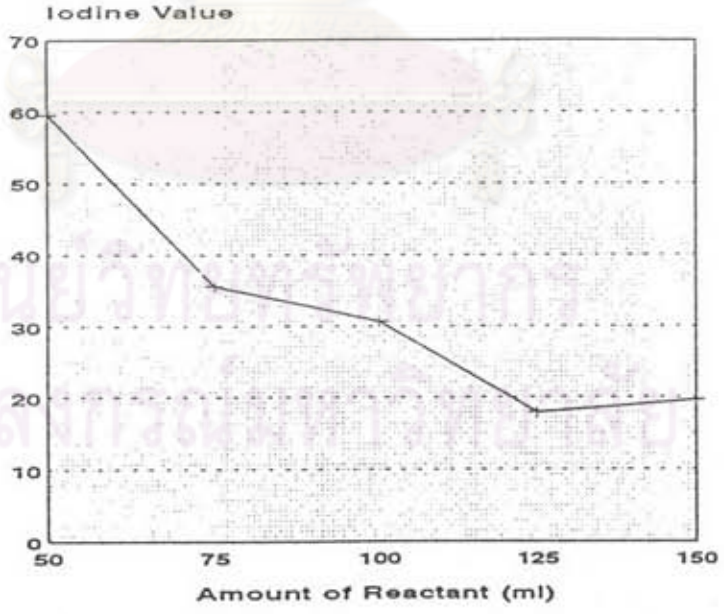

Figure 4.8 The curve of iodine value versus the amount of peracetic acid solution for reacted with 20 g of SOME

solution used was more than 100 ml. However, it was presumed that the % conversion would be increased while increasing the amount of peracetic acid solution.

From Figure 4.8, it could be seen that the iodine value was decreased while increasing the amount of the peracetic acid solution.

From Figure 4.9, the epoxy content was increased when the amount of peracetic acid solution was increased at the interval 50 to 100 ml. After the amount of peracid solution was varied over 100 ml, the epoxy content was decreased. However, the epoxy content was not differed enormously at the interval 75-125 ml. Thus, the appropriate amount was 75 ml.

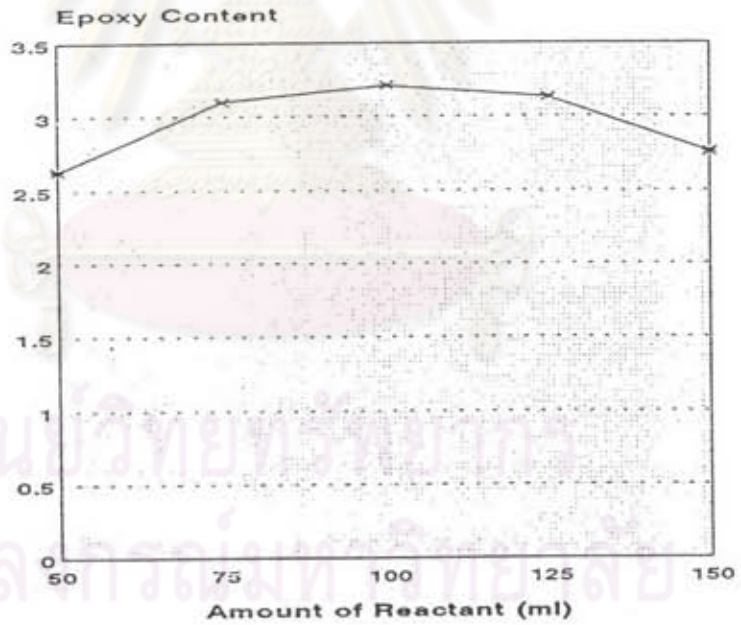

Figure 4.9 The curve of epoxy content versus the amount of peracetic acid solution for reacting with 20 g SOME

The ESME which was synthesized by using the appropriate condition was characterized by ^{13}C-NMR, IR, and GC-MS.

From the ^{13}C-NMR spectrum in Figure A26, it indicated the signals of paraffinic carbons (CH_2, CH_3) at 13.9-39.2 ppm, methyl ester (O-CH_3) at 51.0 ppm, epoxidic carbons at 53.8-56.7 ppm [27], olefinic carbons (C=C) at 123.8-132.3 ppm, and carbonyl (C=O) of methyl ester at 172.6-173.5 ppm.

The infrared spectrum was shown in Figure A27, and the characteristic absorption bands were tabulated in Table 4.7.

Table 4.7 The characteristic group absorptions of ESME

Wave number (cm^{-1})	Functional group	Type of signals
2924, 2856	C-H	stretching
1742	C=O	stretching
1464, 1377	C-H	bending
1020-1245	C-O	stretching

The gas chromatogram in Figure A28 indicated at least 12 components that might be concluded in Table 4.8.

The mass spectra of all components were shown in Figures A29-A32. From library search, it was found that the signals of GC-retention at 7.427, 10 580, 10.782, and 11.570 min. were belong to methyl hexadecanoate, methyl 9,12-octadecedienoate, methyl 9-octadecenoate, and methyl octadecanoate, respectively. Other chromatographic peaks could not be identified.

Table 4.8 The retention time of all components of ESME

Component	Retention time (min.)
1	3.925
2	5.649
3	7.427
4	10.580
5	10.782
6	11.570
7	16.484
8	16.741
9	17.657
10	25.193
11	25.944
12	27.099

Preparation of Sulfonated soybean oil methyl ester (SSME) and hydrolyzed ESME

Eventually, the ESME was sulfonated by saturated solution of sodium bisulfite. The product (SSME) could be emulsified with water at room temperature. The characteristics of SSME by IR and ^{13}C-NMR were shown in Figure A33, A34 and A35(expanded portion of A34).

From the infrared spectrum in Figure A33, it could be summerized in Table 4.9.

Table 4.9 The characteristic group absorptions of SSME

Wave number (cm^{-1})	Functional group	Type of signals
3,300-3,600	O-H	stretching
2924, 2856	C-H	stretching
1742	C=O	stretching
1464, 1377	C-H	bending
1020-1245	C-O	stretching

From Figure A34, it could be seen that the signals of epoxidic carbons at 53.8-56.7 ppm were disappeared and the signals at 71.1-82.7 ppm were presented. The signals might be the signals of C-OH of hydrolyzation products or $C\text{-}SO_3H$ of sulfonation products. Thus, the comparison of the spectra of SSME and hydrolyzed ESME was carried out to prove this appearance.

The ESME was changed to diol of soybean oil fatty acids by hydrolyzation with basic solution and followed by neutralization. The epoxide positions (C-9, C-10 for oleic acid and C-9, C-10, C-12, and C-13 for linoleic acid) were far from carboxyi position, so the carboxylic group could not be influenced the chemical shift of them. Hence, the chemical shift of SSME and hydrolyzed ESME could indicate that the sulfonation was occurred or not.

The ^{13}C-NMR spectrum of hydrolyzed ESME was shown in Figures A36 and A37 (expanded portion of A36). The comparison of chemical shift and intensity of SSME and hydrolyzed ESME was shown in Table 4.10.

From Figures A35 (expanded portion of A34), A37 and Table 4.10, they were found that the chemical shift and intensity of signals were not almost corresponded. The signals of hydrolyzed ESME were coupled at 73.50-73.81 and 74.10-74.38 ppm which belonged to C-OH of diol. Unlike hydrolyzed ESME, the prominent signals of SSME were presented at 73.45, 73.90, 74.18

and 80.14 ppm and they were not coupled. Moreover, SSME could be emulsified in water but hydrolyzed ESME could not, so the fatty chain of SSME must contain the polar moieties other than C-OH bond. From the above evidence, it could be concluded that the sulfonation was occurred. The products had to have several components, so it was very difficult to characterize the structure of them in this study.

Table 4.10 The comparison of chemical shift and intensity of SSME and hydrolyzed ESME.

Hydrolyzed ESME		SSME	
Chemical shift	Intensity	Chemical shift	Intensity
84.10	1.870	82.67	3.154
82.85	1.589	80.14	4.610
74.38	6.149	79.13	2.365
74.10	6.493	74.17	15.407
73.81	12.889	73.90	14.467
73.50	12.989	73.45	12.756
72.90	6.556	72.58	2.714
72.57	2.299	71.90	2.730
71.20	2.384	71.46	2.225
68.40	3.347	71.15	2.252
67.23	6.776	68.76	3.225
		67.40	1.952

Commercial sulfonated oil (CSO)

The ^{13}C-NMR spectrum of commercial sulfonated oil (CSO) was shown in Figure A38. It was seen that the signals of the different carbon atoms were shown as the following : paraffinic carbons (CH_2, CH_3) at 14.0-34.0 ppm, C-O of glyceride at 61.9 and 68.8 ppm, olefinic carbon (C=C) at 126.9-131.8 ppm, and carbonyl of ester (C=O) at 172.4-172.8 ppm. The other signals were the signals of tergitol NP-9 nonionic surfactant which was added into the product. The ^{13}C-NMR spectrum of pure tergitol NP-9 was shown in Figure A40.

The ^{13}C-NMR spectrum of fish oil using as raw material and oxidized fish oil were shown in Figures A41 and A42.

The ^{13}C-NMR characteristic of sulfonated soybean oil methyl ester (SSME*), preparing by commercial procedure, was shown in Figure A40. It indicated the signals of paraffinic carbons (CH_2, CH_3) at 14.0-39.3 ppm, C-O of methyl ester at 51.1 ppm, olefinic carbon (C=C) at 127.6-129.9 ppm, carbonyl of ester (C=O) at 172.7-173.7 ppm, and the residual signals of tergitol NP-9. From the above evidences, it could be seen that the signals of C-SO_3H was not found from the spectrum of both CSO and SSME*.

The ^{13}C-NMR spectrum of oxidized soybean oil methyl ester was shown in Figure A43.

Sulfonated oils used in fatliquoring process

The sulfonated oils which were synthesized in this study and received from leather industry were used in fatliquoring process. The physical appearances were shown that the wet blue tanned leathers which were fatliquored with SSME, SSME+5 % NP-9, SSME* were darker than CSO owing to the darker color of them.

The physical properties of cow leather that was fatliquored by different types were compared to unfatliquored leather in the table 4.11. It could be concluded that the strength of every type of faliquored cow leather was higher than unfatliquored cow leather because the fiber of them was coated with a film of oil which acted as lubricant. The oil reduced the internal friction and increased the durability of the leather. CSO and SSME+5 % NP-9 were produced soft and flexible leather better than SSME and SSME*. The strength of the leather that was fatliquored with SSME was higher than the others. It was the result of CSO, SSME+5 % NP-9, and SSME* produced fine emulsions in water owing to the nonionic surfactant which was added in the oil. Such fine emulsions was very stable and tended to penetrate deeply into the leather, therefore, the fibers would be loosely tighted. The leather that was fatliquored with SSME had the greatest strength because the suitable lubrication of the fibers were made by the appropriate penetration of the oil droplet.

Table 4.11 Physical strength characteristics of cow leather

Type of fatliquor	Tensile strength, N/mm^2	Elongation at break, %
none	10.94	77.5
SSME	16.75	60.0
SSME+5 % NP-9	12.78	65.2
SSME*	12.93	63.1
CSO	11.05	66.4

The scanning electron micrograph of tanned leather in Figure 4.10, was shown that the fibers were sticked together. When the leather was treated with SSME, the fibers were commenced to separate owing to suitable lubrication of the oils (Figure 4.11). The fibers were loosely tighted when the leather were

treated with SSME+5 % NP-9 or CSO because of deep penetration of oil into the leather (Figures 4.12-4.13).

Figure 4.10 Scanning electron micrograph of tanned cow leather which was not treated with fatliquor (x 240)

Figure 4.11 Scanning electron micrograph of tanned cow leather which was treated with SSME fatliquor (x 240)

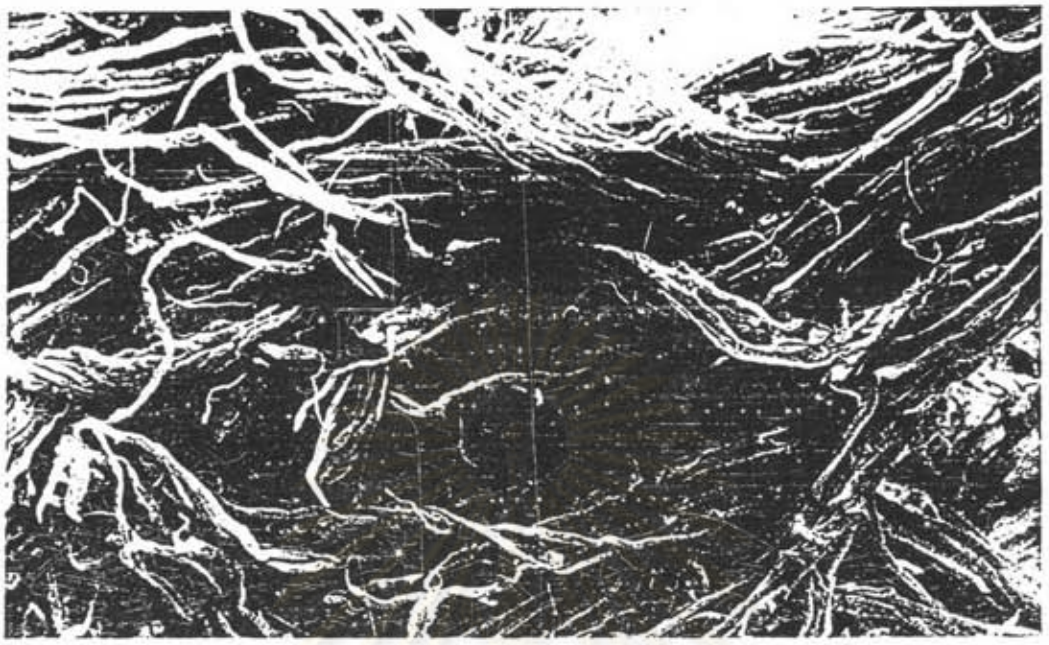

Figure 4.12 Scanning electron micrograph of tanned cow leather which was treated with SSME+5 % NP-9 fatliquor (x 240)

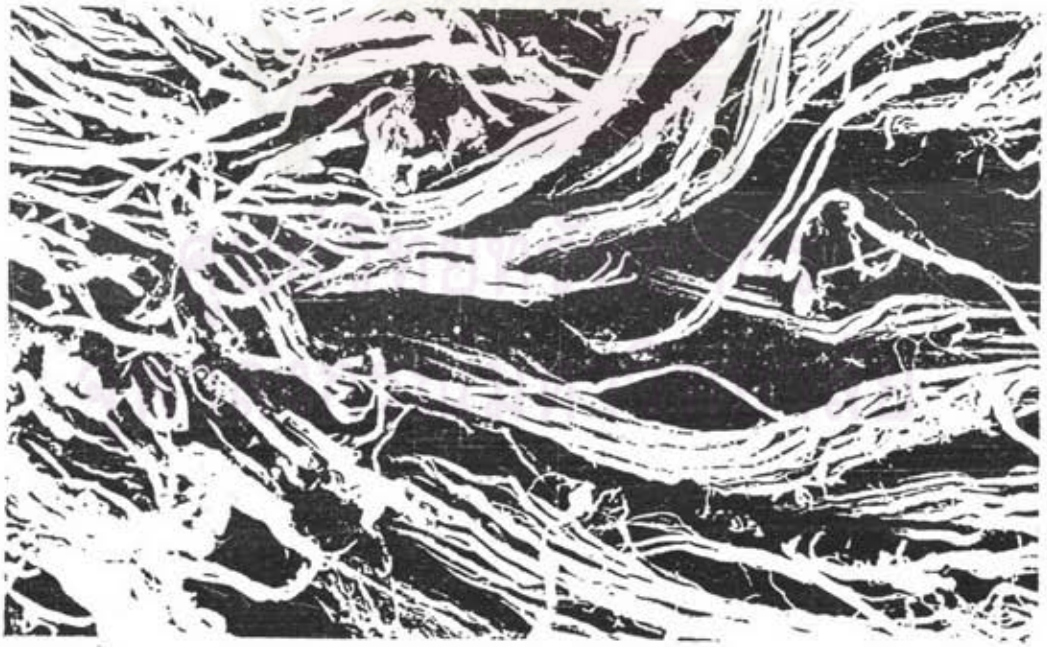

Figure 4.13 Scanning electron micrograph of tanned cow leather which was treated with CSO fatliquor (x 240)