CHAPTER IV

RESULTS AND DISCUSSION

4.1 Synthesis of sulfonated methyl ester from vegetable oil soapstocks.

Methyl ester of vegetable oil soapstocks could be prepared with methanol using sulfuric acid as a catalyst. Then sulfonated compound could be prepared from the sulfonation of unsaturated compound with oleum. The conditions of sulfonation reaction were varied and determined the concentration of sulfur content by using x-ray fluorescence. The calibration curve of sulfur were shown in Figure 4.1, 4.2, and 4.3, and the results of sulfur content from palm oil sulfonated methyl ester and rice bran oil sulfonated methyl ester were shown in figure 4.4 and 4.5, respectively.

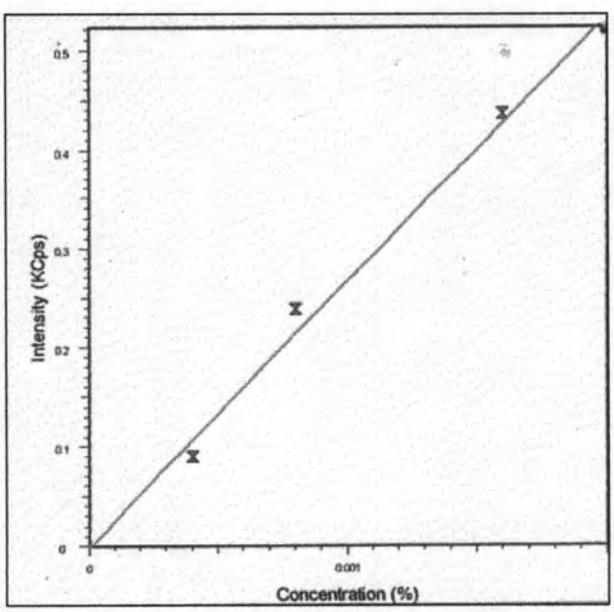


Figure 4.1 Calibration curve of sulfur content in concentration range of 0.0004-0.0020 % by volume

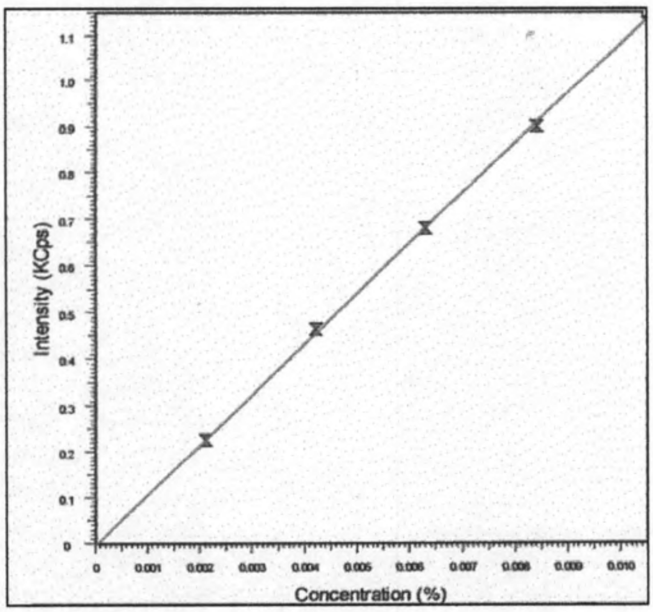


Figure 4.2 Calibration curve of sulfur content in concentration range of 0.0021-0.0105 % by volume

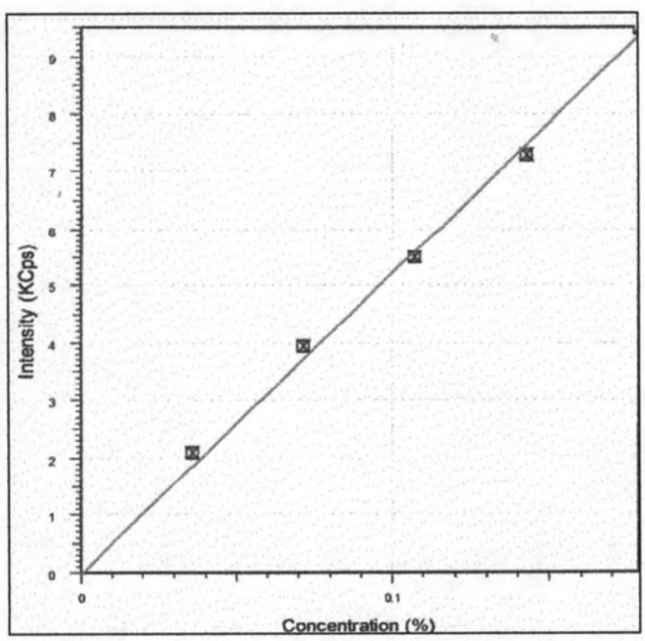


Figure 4.3 Calibration curve of sulfur content in concentration range of 0.0357-0.1783 % by volume

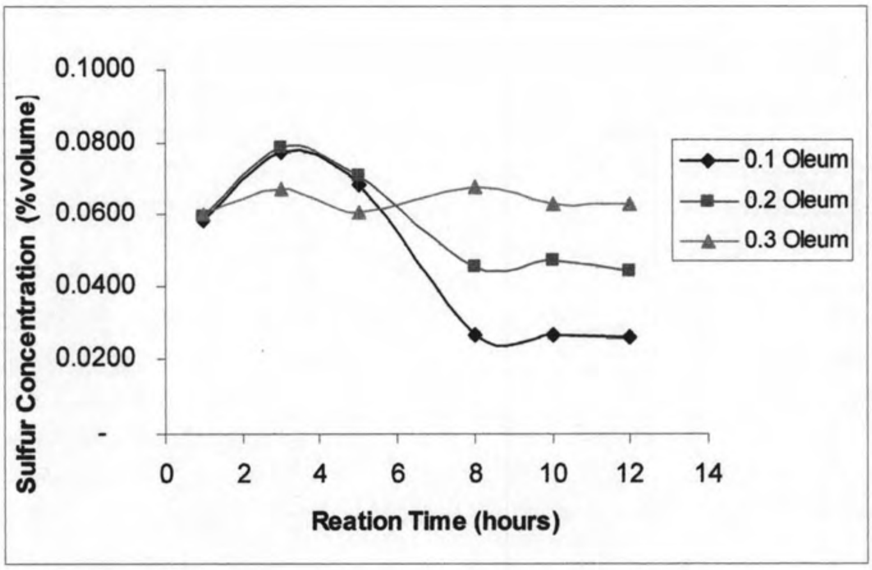


Figure 4.4 Sulfur content of sulfonation reaction from palm oil soapstock methyl ester.

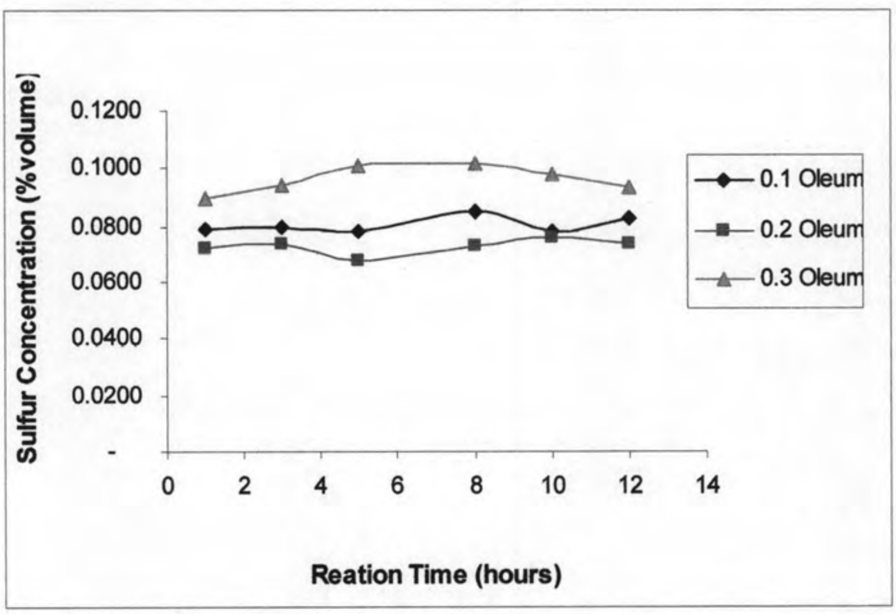


Figure 4.5 Sulfur content of sulfonation reaction from rice bran oil soapstock methyl ester.

Note: 0.1 oleum is the weight ratio of oil : oleum = 1 :0.1
0.2 oleum is the weight ratio of oil : oleum = 1 :0.2
0.3 oleum is the weight ratio of oil : oleum = 1 :0.3

From Figure 4.4 and 4.5, the optimum condition of sulfonation reaction was performed at mole ratio 1:0.2 and reaction time 3 hours, due to the reaction was completed. From Figure 4.5, both of the weight ratio and reaction time has less effect with the sulfur concentration. Therefore, the sulfonation condition of rice bran oil methyl ester was chosen at the same weight ratio of the palm oil methyl ester.

4.2 Characterization of synthesized compound

4.2.1 Palm oil methyl ester

The IR spectra of palm oil soapstock and palm oil soapstock methyl ester were shown in Figure A1 and A2, respectively. The important absoption bands of palm oil soapstock and palm oil methyl ester listed in Table 4.1.

Table 4.1 The absorption assignments of palm oil soapstock and palm oil methyl ester

Wave number (cm^{-1})		Assignments
Palm oil soapstock	**Palm oil methyl ester**	
3002	3011	= C-H Stretching
2846	2844	C-H Stretching, Aliphatic
1709	1738	C=O Stretching
1468	1466	C-H Bending, Aliphatic

The IR spectra of palm oil methyl ester (Figure A2) and the palm oil soapstock spectrum (Figure A1) could not be distinguished. The result was confirmed by using ^{1}H-NMR and ^{13}C-NMR spectra.

The ^{1}H-NMR spectra of palm oil soapstock and palm oil methyl ester were shown in Figures A3 and A4, respectively. The important signals of palm oil soapstock and palm oil methyl ester were shown in Table 4.2.

Table 4.2 The assignments of ^{1}H-NMR spectra of palm oil soapstock and palm oil methyl ester.

Position of Proton	Multiplicity	Chemical Shift (δ,ppm)	
		Palm oil soapstock	Palm oil methyl ester
a	m	0.77-0.83	0.73-0.82
b,c,d,e,f,g,h,l,m,n,o,p	m	1.15-1.95	1.13-1.94
q	t	2.19-2.26	2.14-2.21
s	s	-	3.63
t,u,v	m	4.01-4.27	-
i,j	m	5.19-5.28	5.23-5.24

From the ^{1}H-NMR spectrum of palm oil methyl ester (Figure 4) as comparing with palm oil soapstock (Figure 3), it could be observed that the signal at δ_H 3.63ppm was belonged to the protons of methoxy group of methyl ester.

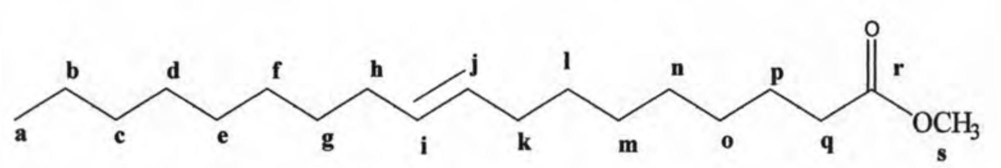
The ^{13}C-NMR spectra of palm oil soapstock and palm oil methyl ester were shown in Figure A5 and A6, respectively. The important signals of palm oil soapstock and palm oil methyl ester were shown in Table 4.3.

Table 4.3 The assignments of ^{13}C-NMR spectra of palm oil soapstock and palm oil methyl ester

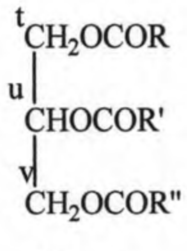
Position of Carbon	Chemical Shift (δ,ppm)	
	Palm oil soapstock	Palm oil methyl ester
a	14.05	13.96
b,c,d,e,f,g,h,l,m,n,o,p	22.05-33.94	22.60-33.86
q	34.09	33.91
s	-	51.11
t,u	62	-
v	68.86	-
i,j	127.83-130.01	127.79-129.80
r	172.60-173.01	173.915

From the ^{13}C-NMR spectrum of palm oil methyl ester (Figure A6) as comparing with palm oil soapstock (Figure A5), it was clearly seen that the signals at δ_C 62 ppm and δ_C 68.86 ppm belonged to the carbon of glycerol moiety of triglyceride were absent, and the signal at δ_C 51.11 ppm belonged to the carbon of methoxy group of methyl ester were shown instead.

From the results of spectra data, it could be concluded that the product was palm oil methyl ester and its structure was as follows:



Palm oil methyl ester



Palm oil

4.2.2 Palm oil sulfonated methyl ester

The IR spectrum of palm oil sulfonated methyl ester was shown in Figure A12. The important absorption bands of palm oil methyl ester and palm oil sulfonated methyl ester were listed in Table 4.4

Table 4.4 The absorption assignments of palm oil methyl ester and palm oil sulfonated methyl ester

Wave number (cm^{-1})		**Assignments**
Palm oil methyl ester	**Palm oil sulfonated methyl ester**	
3011	-	=CH Stretching
2844	2851	C-H Stretching, Aliphatic
1738	1738	C=O Stretching
1466	1466	C-H Bending, Aliphatic
-	1170	$-SO_3H$

From the IR spectra of palm oil sulfonated methyl ester (Figure A12) and palm oil methyl ester (Figure A5), it could be seen that the absorption bands of sulfonic acid group were shown at 1170 cm^{-1}. The result was confirmed by ^{1}H-NMR and ^{13}C-NMR spectra.

The ^{1}H-NMR spectrum of palm oil sulfonated methyl ester was shown in Figures A13. The important signals of palm oil sulfonated methyl ester were listed in Table 4.5

Table 4.5 The assignments of ^{1}H-NMR spectra of palm oil sulfonated methyl ester.

Position of Proton	Multiplicity	Chemical Shift (δ,ppm)
		Palm oil sulfonated methyl ester
a	m	0.79-0.87
b,c,d,e,f,g,h,l,m,n,o,p	m	1.18-1.97
q	t	2.19-2.28
s	s	3.62
i,j	m	5.22-5.23

From the ^{1}H-NMR spectrum of palm oil sulfonated methyl ester (Figure A13) as comparing with palm oil methyl ester (Figure A4), it could not be distinguished and $-SO_3H$ peak could not be specified.

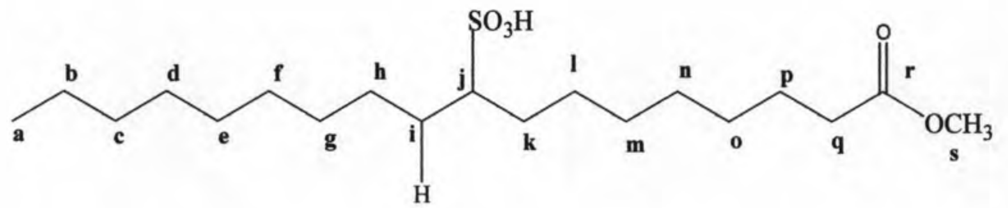
The ^{13}C-NMR spectrum of palm oil sulfonated methyl ester was shown in Figure A14. The important signals of palm oil sulfonated methyl ester were listed in Table 4.6.

Table 4.6 The assignments of ^{13}C-NMR spectra of palm oil sulfonated methyl ester

Position of Carbon	Chemical Shift (δ,ppm)
a	14.08
b,c,d,e,f,g,h,I,m,n,o,p	22.67-31.91
q	32.579
s	51.42
i,j	-
r	179.703

From the ^{13}C-NMR spectrum of palm oil sulfonated methyl ester (Figure A14) as comparing with palm oil methyl ester (Figure A6), it could not be distinguished as same as ^{1}H-NMR spectrum and $-SO_3H$ peak could not be specified.

From the results of spectra data, it could be seen that the sulfonating reaction was incompleted and the structure of palm oil sulfonated methyl ester was assigned as follows:



Palm oil sulfonated methyl ester

4.2.3 Rice bran oil methyl ester

The IR spectra of rice bran oil soapstock and rice bran oil methyl ester were shown in Figure A15 and A16, respectively. The important absoption bands of rice bran oil soapstock and rice bran oil methyl ester listed in Table 4.7.

Table 4.7 The absorption assignments of rice bran oil soapstock and rice bran oil methyl ester

Wave number (cm^{-1})		Assignments
Rice bran oil soapstock	**Rice bran oil methyl ester**	
3002	3006	=CH Stretching
2854	2850	C-H Stretching, Aliphatic
1744	1744	C=O Stretching
1452	1460	C-H Bending, Aliphatic

The IR spectrum of rice bran oil methyl ester (Figure A16) and the rice bran oil soapstock spectrum (Figure A15) could not be distinguished. The result was confirmed by using ^{1}H-NMR and ^{13}C-NMR spectra.

The ^{1}H-NMR spectra of rice bran oil soapstock and rice bran oil methyl ester were shown in Figures A17 and A18, respectively. The important signals of rice bran oil soapstock and rice bran oil methyl ester were shown in Table 4.8.

Table 4.8 The assignments of ^{1}H-NMR spectra of rice bran oil soapstock and rice bran oil methyl ester.

Position of Proton	Multiplicity	Chemical Shift (δ,ppm)	
		Rice bran oil soapstock	**Rice bran oil methyl ester**
a	m	0.77-0.83	0.75-0.82
b,c,d,e,f,g,h,l,m,n,o,p	m	1.15-1.95	1.13-1.93
q	t	2.19-2.26	2.14-2.21
s	s	-	3.62
t,u,v	m	4.01-4.27	-
i,j	m	5.19-5.28	5.22-5.27

From the ^{1}H-NMR spectrum of rice bran oil methyl ester (Figure A18) as comparing with rice bran oil soapstock (Figure 17), it could be observed that the signal at δ_H 3.62 ppm was belonged to the protons of methoxy group of methyl ester.

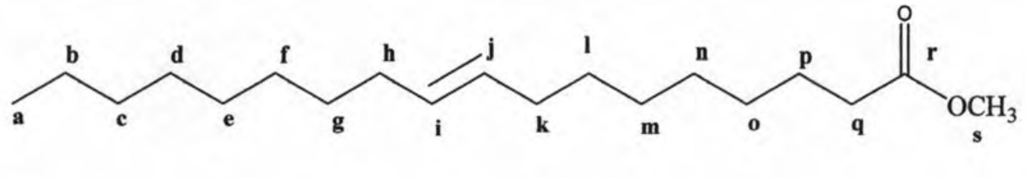
The ^{13}C-NMR spectra of rice bran oil soapstock and rice bran oil methyl ester were shown in Figure A19 and A20, respectively. The important signals of rice bran oil soapstock and rice bran oil methyl ester were shown in Table 4.9.

Table 4.9 The assignments of ^{13}C-NMR spectra of rice bran oil soapstock and rice bran oil methyl ester

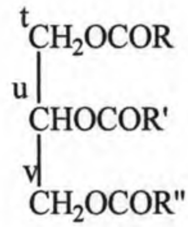
Position of Carbon	Chemical Shift (δ,ppm)	
	Rice bran oil soapstock	Rice bran oil methyl ester
a	14.05	14.02
b,c,d,e,f,g,h,l,m,n,o,p	22.55-33.94	22.52-31.87
q	34.09	33.99
s	-	51.27
t,u	62.02	-
v	68.87	-
i,j	127.83-130.01	127.84-130.05
r	172.60.173.01	174.11

From the ^{13}C-NMR spectra of rice bran oil methyl ester (Figure A20) as comparing with rice bran oil soapstock (Figure A19), it was clearly seen that the signals at δ_C 62.06 ppm and δ_C 68.87 ppm belonged to the carbon of glycerol moiety of triglyceride were absent, and the signal at δ_C 51.27 ppm belonged to the carbon of methoxy group of methyl ester were shown instead.

From the results of spectra data, it could be concluded that the product was palm oil methyl ester and its structure was as follows:



Rice bran oil methyl ester



Rice bran oil

4.2.4 Rice bran oil sulfonated methyl ester

The IR spectra of rice bran oil sulfonated methyl ester was shown in Figure A28. The important absoption bands of rice bran oil sulfonated methyl ester were listed in Table 4.10.

Table 4.10 The absorption assignments of rice bran oil methyl ester and rice bran oil sulfonated methyl ester

Wave number (cm^{-1})		Assignments
Rice bran oil methyl ester	**Rice bran oil sulfonated methyl ester**	
3006	-	=CH Stretching
2850	2851	C-H Stretching, Aliphatic
1744	1742	C=O Stretching
1460	1458	C-H Bending, Aliphatic
-	1172	$-SO_3H$

From the IR spectrum of rice bran oil sulfonated methyl ester (Figure A28) and the rice bran oil methyl ester (Figure A16), it could be seen that the absorption bands of sulfonic acid group were shown at 1172 cm^{-1}. The result was confirmed by using ^1H-NMR and ^{13}C-NMR spectra.

The ^1H-NMR spectrum of rice bran oil sulfonated methyl ester was shown in Figures A29. The important signals of rice bran oil sulfonated methyl ester were listed in Table 4.11.

Table 4.11 The assignments of ^{1}H-NMR spectra of rice bran oil sulfonated methyl ester.

Position of Proton	Multiplicity	Chemical Shift (δ,ppm)
a	m	0.78-0.81
b,c,d,e,f,g,h,l,m,n,o,p	m	1.17-1.95
q	t	2.18-2.26
s	s	3.63
i,j	m	5.23-5.29

From the ^{1}H-NMR spectrum of rice bran oil methyl ester (Figure A18) as comparing with rice bran oil sulfonated methyl ester (Figure A29),it could not be distinguished and $-SO_3H$ peak could not be specified.

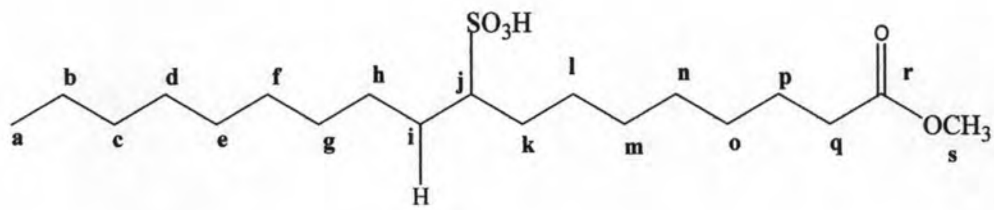
The ^{13}C-NMR spectrum of rice bran oil sulfonated methyl ester were shown in Figure A30. The important signals of rice bran oil sulfonated methyl ester were listed in Table 4.12.

Table 4.12 The assignments of ^{13}C-NMR spectra of rice bran oil sulfonated methyl ester

Position of Carbon	Chemical Shift (δ,ppm)
a	14.09
b,c,d,e,f,g,h,l,m,n,o,p	22.67-31.91
q	34.04
s	51.42
i,j	127.97-130.16

From the [13]C-NMR spectrum of rice bran oil sulfonated methyl ester (Figure A30) as comparing with rice bran oil methyl ester (Figure A20), it could not be distinguished as same as [1]H-NMR spectrum and $-SO_3H$ peak could not be specified.

From the results of spectra data, it could be seen that the sulfonating reaction was incompleted and the structure of rice bran oil sulfonated methyl ester was assigned as follows:



Rice bran oil sulfonated methyl ester

4.3 Compositions of fatty acid methyl ester products and the assignments.

The compositions of palm oil methyl ester and rice bran oil methyl ester were shown in Table 4.13 and 4.14.

Table 4.13 The assignments of fragmentation ion peak of palm oil methyl ester

Fragmentation ion peak				
t_R	**m/z**	**% Area**	**Products**	**Figure**
10.29	284	0.74	Myristic acid methyl ester	A7
14.50	270	43.34	Palmitic acid methyl ester	A8
18.71	298	4.24	Stearic acid methyl ester	A9
19.10	281	41.56	Oleic acid methyl ester	A10
20.05	294	10.67	Linoleic acid methyl ester	A11

Table 4.14 The assignments of fragmentation ion peak of rice bran oil methyl ester

Fragmentation ion peak				
t_R	**m/z**	**% Area**	**Products**	**Figure**
10.29	284	0.48	Myristi acid methyl ester	A21
14.49	270	29.77	Palmitic acid methyl ester	A22
18.71	298	2.59	Stearic acid methyl ester	A23
19.10	281	41.89	Oleic acid methyl ester	A24
20.05	294	23.86	Linoleic acid methyl ester	A25
21.37	292	0.76	Linolenic acid methyl ester	A26
22.76	326	0.65	Arachidic acid methyl ester	A27

From the Table 4.13 and 4.14, it could be seen that the composition of palm oil methyl ester and rice bran oil methyl ester are almost the same, excepted Linolenic acid methyl ester and Arachidic acid methyl ester were seen in rice bran oil methyl ester.

4.4 The components of methyl ester and sulfonated methyl ester products.

The components of methyl ester and sulfonated methyl ester products were determined by x-ray fluorescence (XRF). The results were shown in Table 4.15.

Table 4.15 The components of methyl ester and sulfonated methyl ester from palm oil and rice bran oil soapstock at measured wavelength.

Composition	Wavelength (Å)	
	Methyl ester	**Sulfonated methyl ester**
S	-	5.373
Cl	4.724	4.730
Cr	2.294	2.292
Mn	2.104	2.104
Fe	1.937	1.938
Cu	1.542	1.542

From the XRF spectrum of methyl ester product (Figure A31) as comparing with sulfonated methyl ester (Figure A32), it could be seen that at wavelength 5.373 Å belonged to the sulfur from the spectrum of sulfonated methyl ester.

4.5 Determination of sulfur content of sulfonated methyl ester from palm oil and rice bran oil soapstock.

The sulfur content of palm oil and rice bran oil soapstock were 1.3707 % and 2.5545 % by weight, respectively.

According to the fragmentation ion peak of methyl ester from palm oil and rice bran oil soapstock in Table 4.13 and 4.14, it could be observed that rice bran oil methyl ester gave the unsaturated fatty acid methyl ester more than palm oil methyl ester. Moreover, rice bran oil methyl ester gave the area of unsaturated fatty acid methyl ester higher than palm oil methyl ester. Therefore, it could be concluded that more unsaturated fatty acid methyl ester gave the higher sulfur content in the products.

4.6 Analysis of blended base diesel fuel.

The physical properties of synthesized sulfonated methyl ester blended with base diesel fuel at concentration of 10% by weight are shown in Table 4.16.

Table 4.16 Physical properties of base diesel fuel blended with synthesized sulfonated methyl ester from soapstocks.

Properties	**Base**	**Base + 5% SMP**	**Base + 5% SMR**	**Base + 10% SMP**	**Base + 10% SMR**
Mid-Boiling Point (°C)	351.9	352.7	353.1	353.5	356.6
API Gravity @ 60 °F	38.52	38.38	38.04	37.04	36.52
Viscosity @ 40 °F	3.152	3.294	3.423	3.353	3.735
Pour Point (°C)	1	1	1	1	1
Flash Point (°C)	61	61	62	61	61
Total Acid Number (mgKOH/g)	0.0325	0.0346	0.0354	0.0362	0.0367
Density @ 15 °C	0.8282	0.8356	0.8382	0.8356	0.8382

The sulfonated methyl ester from soapstocks were easily soluble in base diesel fuel and did not change any physical properties within specification of diesel fuel at the concentration of 0.05% to 10.0 % by weight.

4.7 Determination of lubricity performance of base diesel fuel blended with sulfonated methyl ester compound.

The lubricity performance of the base diesel fuels blended with sulfonated methyl ester were investigated by using High Frequency Reciprocating Rig (HFRR) test procedure, according to CEC F-06-A-96. The lubricating efficiency of the fuels was estimated by measuring the mean wear scar diameter (WSD) value. If samples had higher lubricity performance, it could be given lower wear scar diameter value. Table 4.17 showed the lubricity performances of sulfonated methyl ester blended in base diesel fuel at the same concentration of 5% by weight. The results showed that the sulfonated methyl ester from rice bran oil soapstock gave the lower mean wear scar diameter than the sulfonated methyl ester from palm oil soapstock and less than 460 μm of standard.

Table 4.17 Lubricity performance of the blends of 5% by weight of sulfonated methyl ester with base diesel fuel.

Blended composition	**Lubricity performance (Mean wear scar diameter, μm)**
Base diesel fuel	416
Base + sulfonated methyl ester from palm oil soapstock	192
Base + sulfonated methyl ester from rice bran oil soapstock	192
Standard	< 460

According to sulfur content and lubricity performance in Table 4.16, it could be observed that sulfonated methyl ester from palm oil and rice bran oil soapstock gave lubricity performance. This result could be compared with the lubricity performance of base diesel fuel blended with methyl ester from palm oil soapstock and rice bran oil soapstock at 5% by weight, the results was shown the mean wear scar diameter of 373 μm and 472 μm respectively whereas the base diesel fuel of 421 μm. From these results, it could be concluded that both of sulfonated methyl ester from palm oil and rice bran oil soapstock could improve the lubricity performance as compared with base diesel fuel and methyl ester from palm oil soapstock and rice bran oil soapstock[30].