CHAPTER IV

RESULTS AND DISCUSSIONS

4.1 Synthesis of sulfurized palm oil.

In this research, reaction conditions for synthesized sulfurized palm oil were study in order to select the optimum condition. The major conditions that influenced the quality of total sulfur were following :

- reaction temperature
- reaction time
- concentration of sulfur

It has been found that sulfurized palm oil was simply prepared by addition reaction of double bond with sulfur. At the optimum condition,a dark-brown liquid product which had the most viscosity was obtained. The mechanism of this reaction is shown in Section 2.3 .

4.1.1 Effect of reaction temperature.

Sulfurized palm oil was prepared at various reaction temperatures from 160-220 ^{o} C. The dependence of total sulfur of the product on the reaction temperature while the other parameters were constant, i.e., the reaction time of 2 hrs., 190 g of palm oil and 10 g of sulfur, were listed and Table 4.1.

Table 4.1 Effect of reaction temperature

sample no.	reaction temp. (^{o} C)	product yield (g)	total sulfur (% by weight)
S1	160	170.70	4.43
S2	180	175.64	4.59
S3	200	167.27	4.76
S4	220	158.72	3.40

Effect of reaction temperature,shown in Table 4.1 and Figure 4.1, respectively. It can be seen that total sulfur of product continued increasing with increasing temperature. At this stage (after 200 ^{o} C) the loss of H_2S from sulfurized product was obtained from the desulfurization reaction because at high temperature, the bond between C-H and C-S was easily broken. At the low temperature, the reaction was not completed, thus the total sulfur was low. It could be concluded that the high total sulfur product of 4.76 % by weight was obtained at 200 ^{o} C.

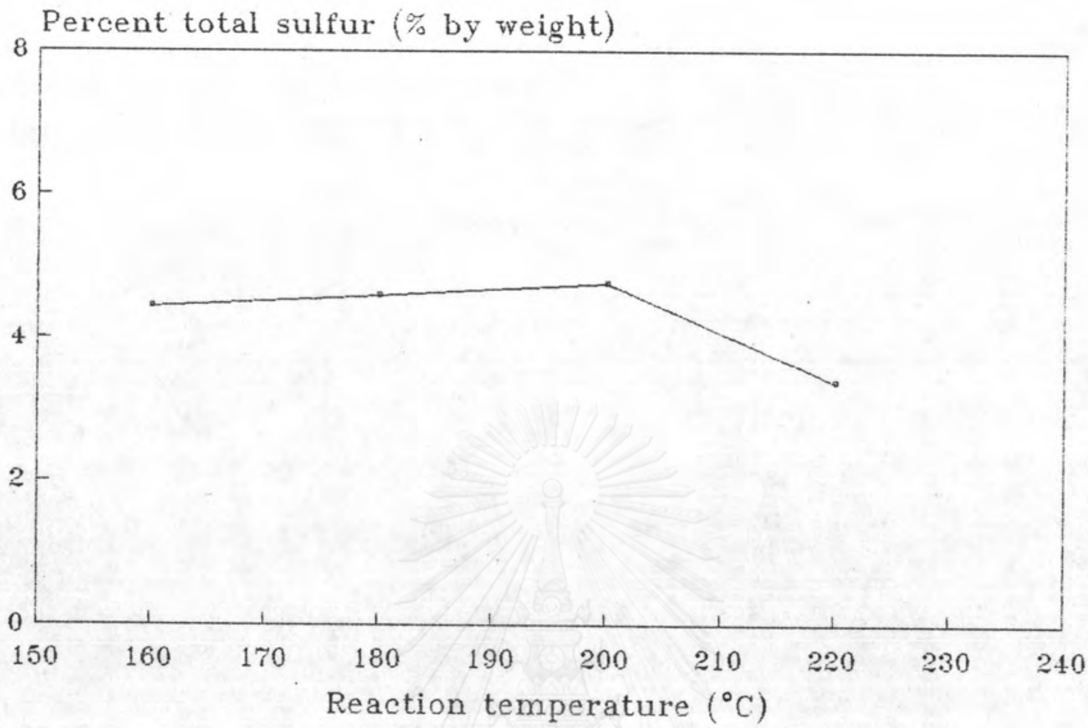

Figure 4.1 The total sulfur of sulfurized palm oil at various reaction temperature.

4.1.2 Effect of reaction time.

The reaction was carried out in various reaction time from 2-10 hrs. The dependence of total sulfur of the product on the reaction time was listed and shown in Table 4.2 and Figure 4.2, respectively, while the other parameters were constant..

It was found that at 2 hrs., the total sulfur of product was maximum. And the total sulfur continued constantly or was little decreased with time but at a shorter time, e.g. 1 hr, the reaction was not completed and resulted in the product being a yellow-brown liquid and sulfur which was not completely reacted in the reaction. It could be implied that the optimum reaction time was 2 hrs.

As can be seen for the samples S6 and S7, the product yields of both samples were exactly unable to determined since the products resulted in lots of was less yellow precipitation after 2 months. The precipitation was suspected to be unreacted sulfur and wax was possibly much higher molecular weight sulfurized palm oil.

Table 4.2 Effect of reaction time.

sample no.	reaction time (hrs.)	product yield (g)	total sulfur (% by weight)
S3	2	167.27	4.76
S5	4	200.66	4.77
S6*	8	-	4.39
S7*	10	-	3.75

* The yields were drastically decreased after letting stand for 2 months.

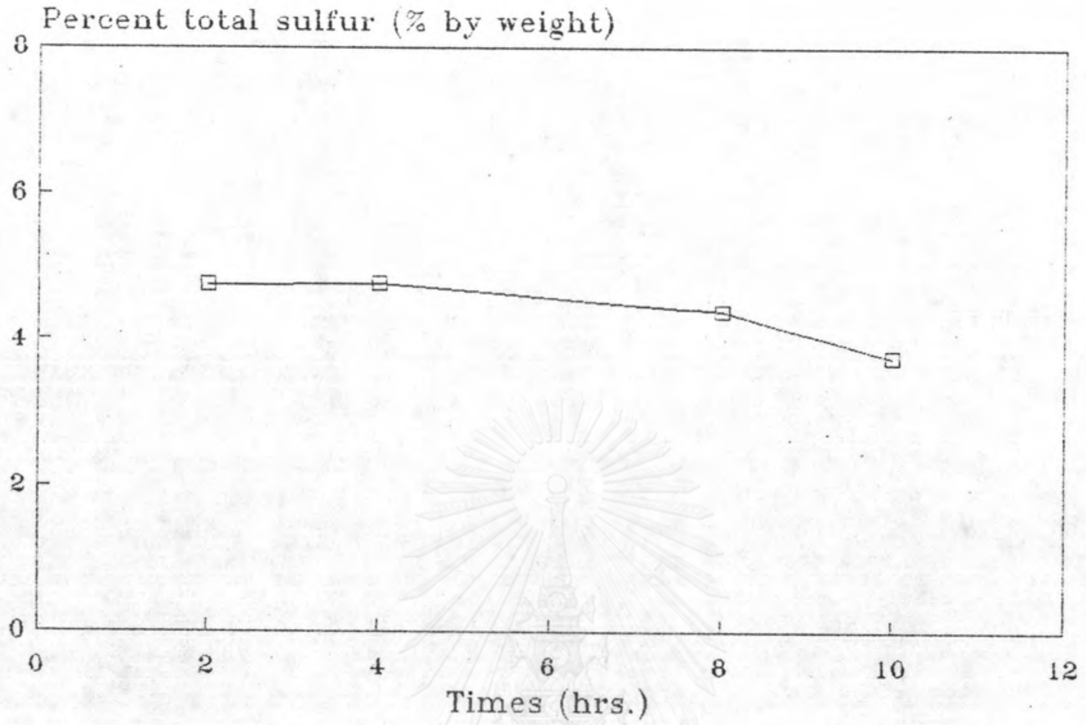

Figure 4.2 The total sulfur of sulfurized palm oil at various reaction time.

4.1.3 Effect of sulfur concentration

In this experimental, the concentrations of sulfur were varied. Since the total sulfur of product was limited by the doublebond of palm oil which was affected by the addition reaction, as listed and shown in Table 4.3 and Figure 4.3, respectively.

Table 4.3 Effect of sulfur concentration.

Sample no.	Sulfur conc. (% by weight)	Total sulfur (% by weight)	Viscosity at 100°C (cts)
S8	3.00	2.80	20.71
S3	5.00	4.80	28.77
S9	7.00	6.80	43.14
S10	9.00	8.38	51.42
S11	10.00	8.98	48.93
S12	11.00	9.15	53.73
S13	12.00	10.87	53.19
S14	13.00	11.36	53.64
S15	14.00	10.28	50.17
S16	15.00	11.68	60.80
S17	16.00	15.07	56.13
S18	18.00	13.20	61.24
S19	20.00	13.12	66.19
S20	25.00	15.01	66.32
S21	25.00	15.06	69.99
S22	25.00	15.00	78.98

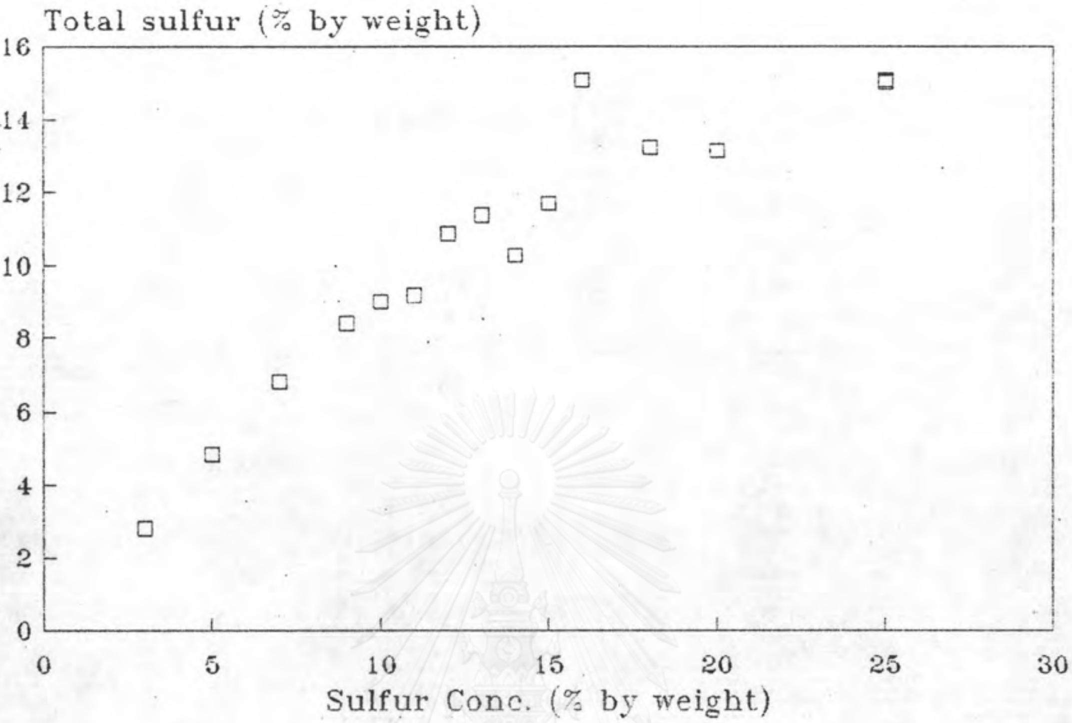

Figure 4.3 The total sulfur of sulfurized palm oil at various sulfur concentration

It can be seen that the total sulfur of product samples continued to increase with increasing sulfur concentration until thepoint, at which the curve flattened and continued constantly with conecntration was reached. At this stage (after 15% by weight of total sulfur) the total sulfur of product was optimum because of the limited numbers of the double bond in the palm oil. It was thus found thatthe unreacted sulfur was precipitated out at the bottom of the reaction flask. However, at low sulfur concentration (between 3-9 % by weight), it was found that the wax was floated above the product after 4 days later. A reason was possibly that the double bond of palm oil was not completely reacted so it can be react with oxygen from air to give an oxidized wax instead.

As a total aspect, the conclusion could be drawn that the appropiated sulfur concentration was 10-15 % by weight so that the double bond of palm oilcould be completely reacted and the reaction gave the maximum sulfur of the product. The optimum condition was 200 ^{o}C for 2 hrs.

Besides the total sulfur of product, the sulfur concentration also influenced on the viscosity of the product because the sulfur acted as a crosslinking agent in curring the molecule of fats (monomer) to give a higher molecular weight polymer which directly affected the viscosity of polymer, as shown in Figure 4.4 and the viscosity data was collected in Table 4.3

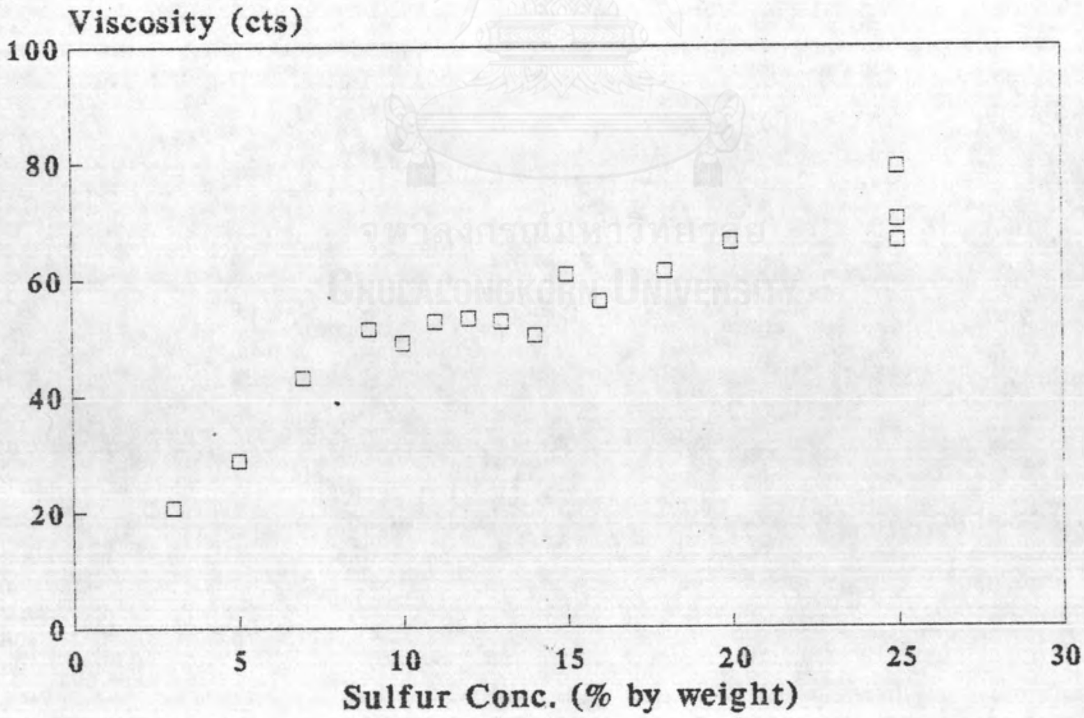

Figure 4.4 The viscosity of sulfurized palm oil at various sulfur concentration.

It can be seen that the viscosity of product increased with sulfur concentration until the point was, reached at which the curve flatted and continued constant. Similarly to the result from Figure 4.3, it can be explained that sulfur reacted with double bond of palm oil as a crosslinker and gave a polymer which had more molecular weight that directly influenced the viscosity. As summerized, the lower concentration ofthe sulfur, the lower molecular weight, consequently the lower viscosity. Contrarily, the higher concentration, the higher molecular weight, as a result the higher viscosity, as shown in Figure 2.3. Until the point which the viscositywas constant, it can be expected that the double bond of the palm oil was completely reacted, as describe previously, the molecular weight of polymer product was maximum so the viscosity was constant..

4.2 Characterization.

The palm oil and sulfurized palm oil could be characterized by nuclear magnetic resonance (NMR) techniques. ^{1}H-NMR spectra of palm oil was shown in Figure 4.5 .

Palm oil was a liquid wax that contains double bond in each constituent molecule. The hydrogen atoms at the double bond, the allylic carbons appeared at the chemical shifts of 5.3 ppm and 2.0 ppm, respectively. The hydrogen atoms in position to carboxylic group appeared at the chemical shifts of 4 and 2.3 ppm. The aliphatic hydrogen and those in the -CH2- groups appear with the shifts of 1.3 and 0.8 ppm, respectively, as can be seen in Table 4.4.

Table 4.4 The assignments for ^{1}H-NMR spectrum of palm oil.

Chemical shift δ (ppm)	Assignment
0.8	$-CH_3-$
1.3	$-CH_2-$
2.0	$-C=C-CH_2-$
2.3	$-CH_2-C(=O)-$
4.1 } 4.2	$-CH_2-O-$
5.3	$-CH=CH-$

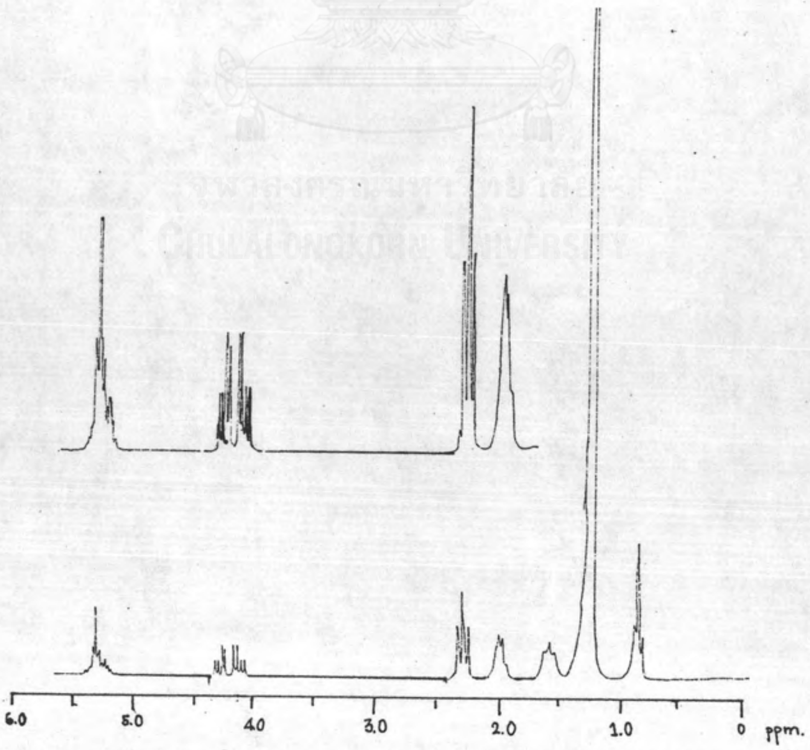

Figure 4.5 ^{1}H-NMR spectrum of palm oil.

The sulfurized palm oil product could also be characterized by NMR technique. Even though the technique could not detect C-S streching at 300 cm^{-1}, it could show the intensity of C=C bond which would be decreasing as the reaction went. The IR (NaCl) spectrum and the assignments of product listed and shown in Figure 4.6 and Table 4.5, respectively. ^{1}H-NMR Spectrum of sulfurized palm oil product and the assignments were shown and listed in Figure 4.7 and Table 4.6 , respectively.

Table 4.5 The assignment for IR(NaCl) spectrum of sulfurized palm oil.

Absorption frequency (cm-1)	Assignment
2850-2900	C-H stretching aliphatic
1740	C=O stretching
1450	$-CH_2-$
1375	$-CH_3-$
1180	C-O stretching
720	C-H rocking of $-(CH_2)_{\geq 4}-$

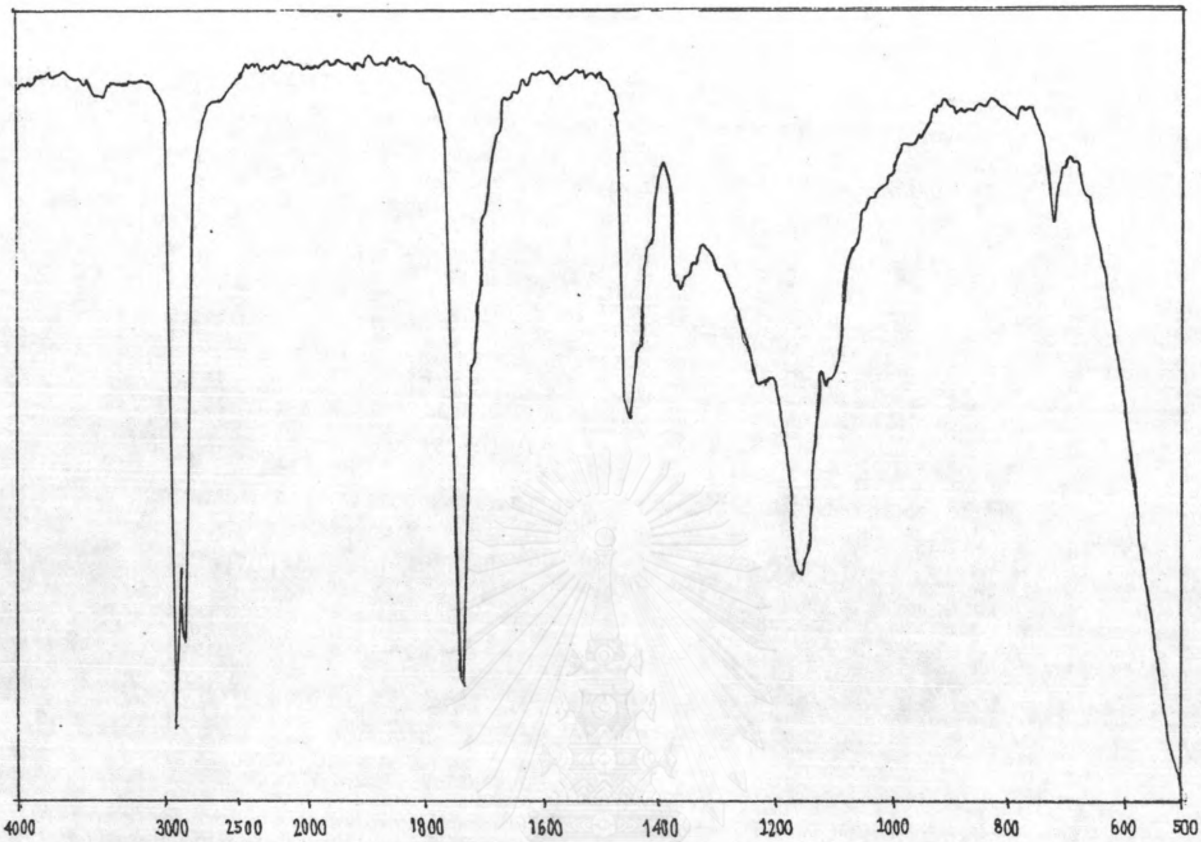

Figure 4.6 IR (NaCl) spectrum of sulfurized palm oil.

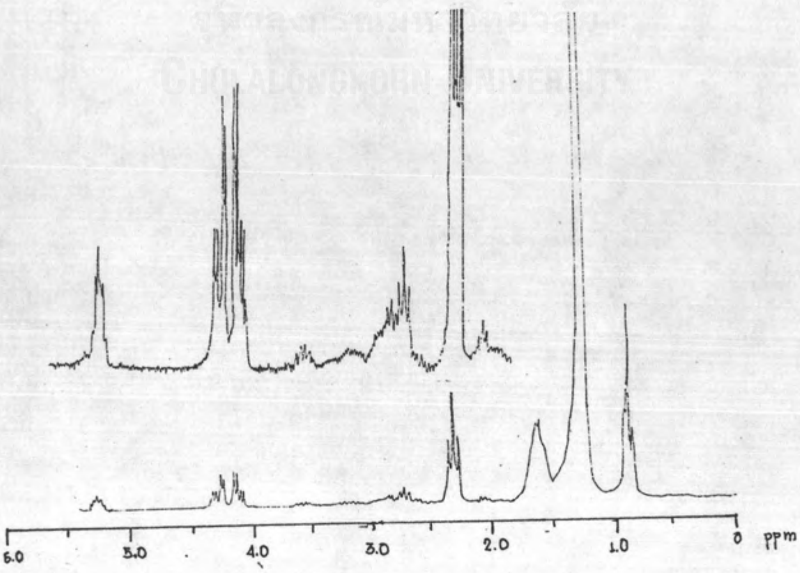

Figure 4.7 ^{1}H-NMR spectrum of sulfurized palm oil.

Table 4.6 The assignment for ^1H-NMR spectrum of sulfurized palm oil.

Chemical shift δ (ppm)	Assignment
0.9	$-CH_3-$
1.2-1.3	$-CH_2-$
2.2	$-CH_2-C(=O)-$
2.7 2.9 3.2 3.6	-CH-CH- | | Sx Sx | / -CH CH-
4.2 4.3	$-CH_2-O-$

4.3 The extreme-pressure property of sulfurized palm oil.

The EP property is the most important factor in this research because it can show the efficiency of the sulfurized palm oil synthesized by comparing the EP property with pure base oil in generalapplication. The following major conditions that influenced the quality of the EP property were studied :

- the amount of sulfurized palm oil.
- the viscosity of base oil.
- the concentration of sulfurized palm oil.

4.3.1 The effect of the amount of sulfurized palm oil.

The reaction was carried out in various amount of sulfurized palm oil from 1.5-30 g in 3 litres of base oil A. The influence on the amount of sulfurized palm oil was shown in Figure 4.8. The load carrying data of EP property was collected in Table 4.7.

Table 4.7 The EP property in various amount of sulfurized palm oil. (SPO)

sample no.	amount of SPO in base oil A. (g)	load carrying weight (lbs)
EP1	O	90
EP2	1.5	100
EP3	3	120
EP4	15	300
EP5	30	650

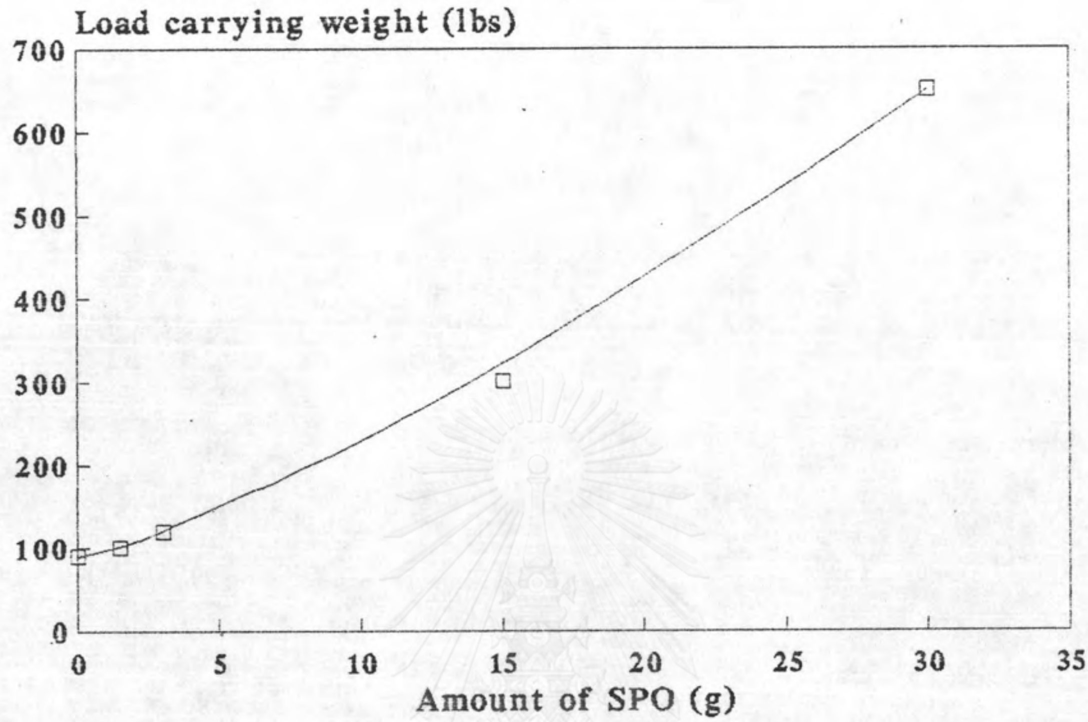

Figure 4.8 The EP property in various amount of sulfurized palm oil

It can be seen that the load carrying in EP property was increased from the starting value of pure base oil A. The higher amount of sulfurized palm oil, the higher load carrying obtained. It can be simply explained that the more sulfurized palm oil as an additive improved the property of base oil to form the thicker film on the metal surface. The higher load carrying weight was therefore obtained to break the film. The higher load carrying weight implies the higher efficiency of the sulfurized palm oil.

4.3.2 The effect of viscosity of base oil.

The load carrying weight data of viscosity of base oil was listed and shown in Table 4.8 and Figure 4.9. It is clear that the load carrying weight increased when the viscosity of base oil increased. Thus the higher viscosity which means the higher molecular weight, the thicker film occurred and obtained the higher load carrying weight to break that film. The increasing trend of load carrying weight of film containing 1.5 g and 15 g of sulfurized palm oil were similar to that of pure oil.

Table 4.8 The EP property in various viscosities of base oil.

sample no.	amount of SPO in base oil (g)	viscosity of base oil	load carrying weight (lbs)
EP1	0.0	base oil A	90
EP2	1.5	base oil A	100
EP4	15.0	base oil A	300
EP6	0.0	base oil B	100
EP7	1.5	base oil B	160
EP8	15.0	base oil B	300
EP9	0.0	base oil C	150
EP10	1.5	base oil C	200
EP11	15.0	base oil C	440

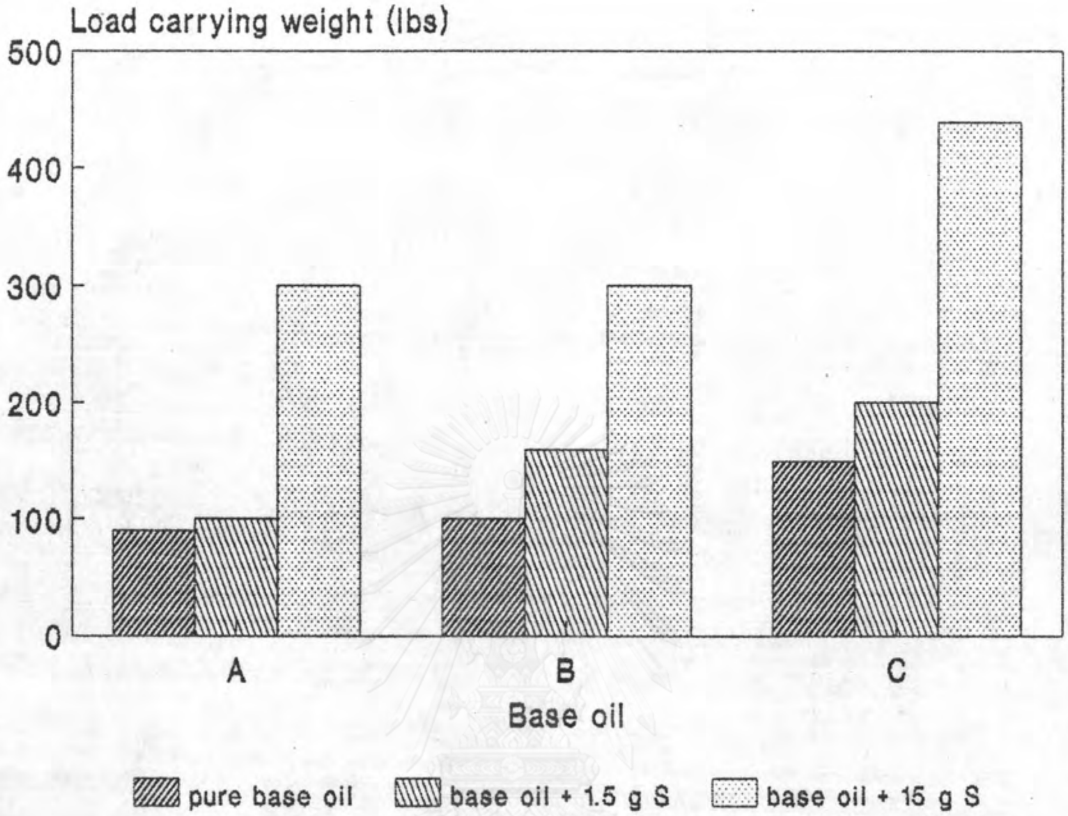

Figure 4.9 The EP property in various viscosity of base oil.

4.3.3 The effect of the concentration of sulfurized palm oil.

The reaction was carried out in various concentration of sulfurized palm oil from 6-15 percentage by weight in 3 litres of base oil A, The influence on the amount of sulfurized palm oil was shown in figure 4.10 and the load carrying weight data of EP property was collected in Table 4.9

Table 4.9 The EP property in various concentration of sulfurized palm oil.

Sample no.	concentration of SPO (% by weight)	amount of SPO in base oil (g)	load carrying weight (lbs)
EP_1	0	0	90
EP_{12}	6.8	1.5	80
EP_3	10.87	1.5	90
EP_{13}	12.14	1.5	140
EP_{14}	15.07	1.5	280

It can be seen that the load carrying weight increased when the concentration of sulfurized palm oil increased. Thus the higher concentration of sulfurized palm oil which means the thicker film on the metal surface occurred and obtained the higher load carrying weight to break that film.

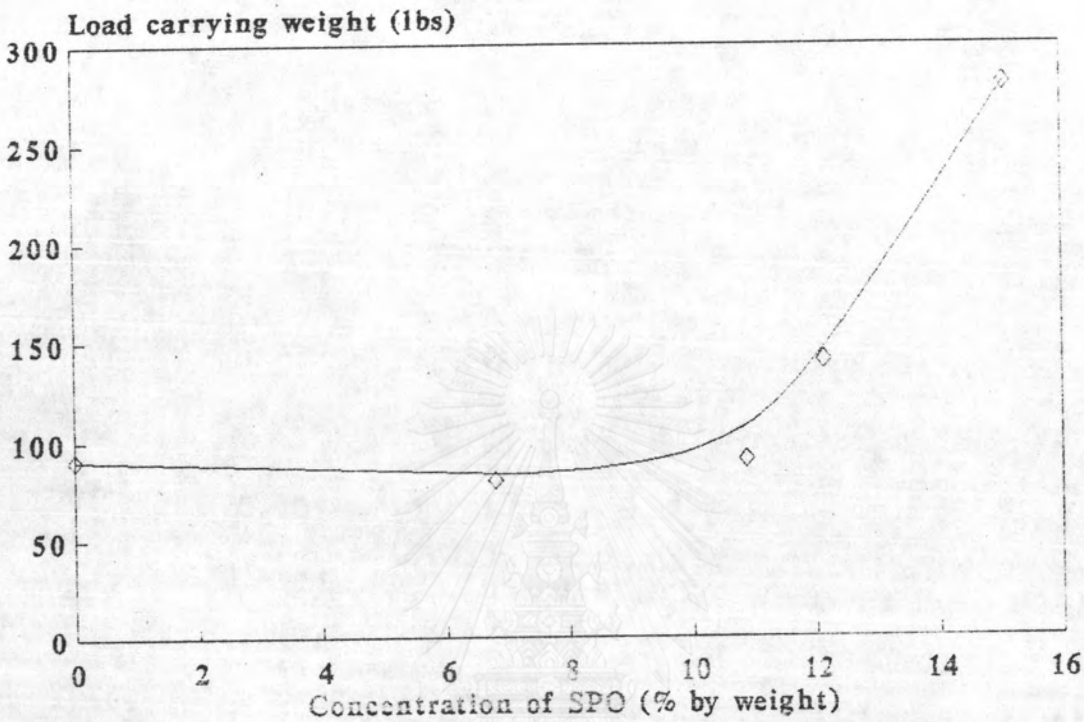

Figure 4.10 The EP property in various concentration of sulfurized palm.

4.4 The physical properties of sulfurized palm oil in base oil.

In this section, the conditions that affected the corrosion ofthe machine by sulfurized palm oil in base oil A were emphasized. Other properties of various concentrations of sulfur in palm oil were also studied, as follow :

4.4.1 Effect of amount of sulfurized palm oil on copper corrosion.

Similar to the effect of amount of sulfurized palm oil on EP property in section 4.3.1, the samples could be prepared in various percentages of sulfur in palm oil, ranging from 0.05-5.0 % by weight, while the other conditions were kept constant. The copper corrosion data of samples were shown in Table 4.9. It was found that in high concentration of sulfurized palm oil in base oil, the copper corrosion was increased. After using the sulfurized palm oil containing sulfur in the molecule, the acid were resulted and corroded the metal surface. In general application, the lower corrosion was accepted, so the optimum concentration in this section that gave the lowest corrosion was 0.05 % by weight.

Table 4.10 Corrosion in various concentration of sulfurized palm oil.

sample no.	concentration (% by weight)	copper corrosion
CR_1	0.05	1b
CR_2	0.5	2e
CR_3	1.0	3a
CR_4	5.0	4a

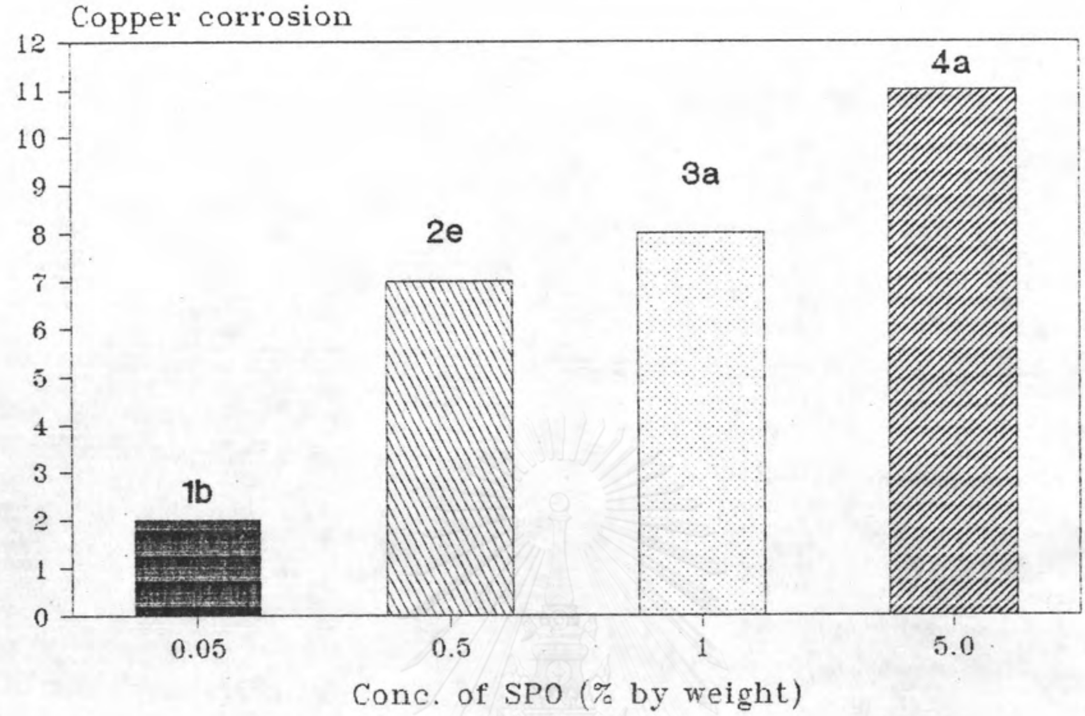

Figure 4.11 The corrosion in various concentration of sufurized palm oil

4.4.2 Other properties of sulfurized palm oil.

This section showed the results of sulfurized palm oil synthesized in base oils, as shown in Table 4.11 and Figure 4.12 .

Table 4.11 Properties of synthesis of sulfurized palm oil.

Sample no.	Total Sulfur	viscosity (cts)*								Flash Point*			Pour Point*		
	(%by weight)	Pure Sample		Base Oil A		Base Oil B		Base Oil C		Base Oil A	Base Oil B	Base Oil C	Base Oil A	Base Oil B	Base Oil C
		100 °C	40 °C	100 °C	40 °C	100 °C	40 °C	100 °C	40 °C						
S_8	2.87	20.71	147.83	4.54	23.51	11.66	104.77	30.97	473.88	230	266	312	-20.81	-12.4	-14.3
S_3	4.80	28.77	228.54	4.55	23.38	10.32	104.68	31.52	475.03	230	268	318	-20.60	-13.6	-13.2
S_9	6.80	43.15	401.11	4.54	23.44	11.63	105.24	31.42	473.99	230	264	326	-21.00	-13.6	-13.4
S_{31}	6.96	42.21	395.62	4.55	23.20	11.59	104.95	31.44	471.01	230	266	324	-18.20	-10.0	-12.0
S_{10}	8.38	51.42	517.12	4.56	23.08	11.49	104.55	31.15	480.22	220	268	310	-18.80	-11.0	-12.2
S_{30}	8.08	47.29	465.23	4.56	23.27	11.48	105.11	31.24	472.67	226	262	320	-21.20	-12.4	-14.3
S_{29}	9.85	48.93	486.67	4.54	23.16	11.51	105.13	-	-	222	268	-	-18.40	-10.8	-
S_{28}	7.54	32.34	284.94	4.54	23.41	14.83	104.11	31.29	476.62	226	268	316	-21.60	-13.7	-13.5
S_{27}	8.69	46.88	476.15	4.54	23.21	11.54	104.88	31.58	441.99	230	268	324	-21.60	-14.5	-14.4

* See Appendix (A) for specifications of base oils.

Sample no.	Total Sulfur	viscosity (cts)*								Flash Point*			Pour Point*		
	(%by weight)	Pure Sample		Base Oil A		Base Oil B		Base Oil C		Base Oil A	Base Oil B	Base Oil C	Base Oil A	Base Oil B	Base Oil C
		100 °C	40 °C	100 °C	40 °C	100 °C	40 °C	100 °C	40 °C						
S_{12}	9.15	52.73	540.98	4.54	23.15	11.60	104.48	31.71	472.39	220	258	316	-18.90	-11.0	-12.3
S_{13}	10.87	53.19	550.72	4.52	23.15	11.67	104.88	30.53	472.24	222	252	318	-18.70	-11.1	-12.4
S_{26}	10.58	51.23	532.28	4.55	23.23	11.56	104.94	31.59	443.57	220	258	320	-22.20	-13.8	-14.9
S_{14}	11.36	52.65	560.85	4.53	23.48	11.62	104.61	31.97	472.10	230	260	312	-19.10	-11.0	-12.9
S_{25}	10.17	47.60	492.34	4.55	23.15	11.64	104.80	30.93	472.81	222	252	310	-18.00	- 9.0	-12.0
S_{15}	10.28	50.16	520.64	4.54	23.13	11.55	104.72	31.68	473.37	222	260	-	-19.00	-10.0	-
S_{24}	11.10	49.69	516.73	4.54	23.49	11.58	104.77	30.97	472.86	226	256	324	-22.00	-14.6	-13.3
S_{17}	15.07	56.13	603.40	4.53	23.71	11.64	103.14	31.04	471.94	222	256	314	-18.00	- 9.0	-12.7
S_{18}	13.20	61.24	695.77	4.48	22.90	11.00	95.66	30.89	470.68	252	220	320	-19.00	-15.0	- 9.0

Sample no.	Total Sulfur	viscosity (cts)*								Flash Point*			Pour Point*		
	(%by weight)	Pure Sample		Base Oil A		Base Oil B		Base Oil C		Base Oil A	Base Oil B	Base Oil C	Base Oil A	Base Oil B	Base Oil C
		100 °C	40 °C	100 °C	40 °C	100 °C	40 °C	100 °C	40 °C						
S_{19}	13.12	66.19	786.55	4.56	23.15	11.56	104.74	31.11	472.41	226	266	308	-19.00	-10.9	-12.0
S_{23}	15.04	78.98	2.19	4.57	23.17	11.57	104.66	31.50	472.18	212	258	308	-19.50	-11.4	-19.2
S_{21}	15.06	69.99	824.54	4.55	23.29	11.52	104.88	31.03	472.20	228	266	314	-22.90	-14.9	-15.3
S_{20}	15.01	66.32	803.37	4.56	23.51	11.65	104.97	31.45	471.66	220	262	316	-22.20	-14.1	-14.8

Note

1. All sulfurized palm oil could be completely soluble in base oil.

2. The copper corrosion of all samples was not over 2a.

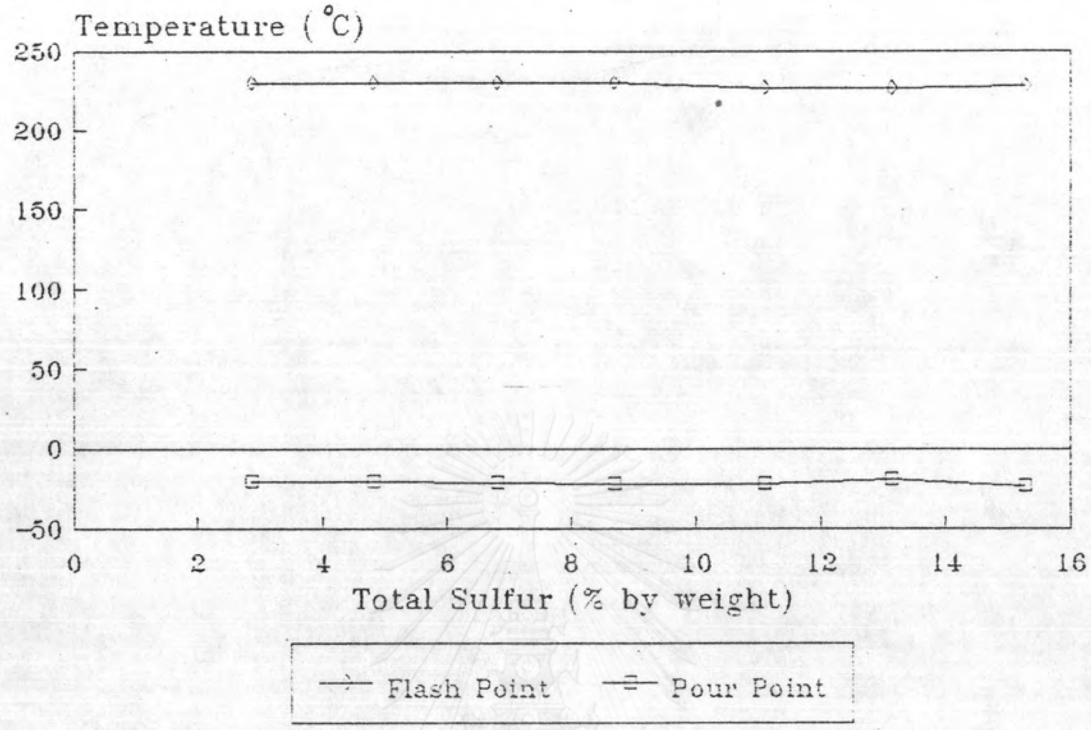

Figure 4.12 The flash point and pour point in various concentration sulfurized palm oil.