CHAPTER 4

RESULTS AND DISCUSSION

4.1 Analytical Result

4.1.1 Result of moisture content in sludge

Table 4-1 Results of Moisture Content

Sample Name	Moisture Content (%w/w)			S.D
	Portion 1	Portion 2	Average	
SSI No.1	17.77	18.03	17.90	7.19
SSI No.2	15.97	15.81	15.89	
SSI No.3	2.88	2.86	2.87	
SSI No.4	4.28	4.20	4.24	
SSM No.1	38.05	34.01	36.03	3.25
SSM No.2	35.42	35.64	35.53	
SSM No.3	36.12	38.22	37.17	
SSM No.4	30.10	29.68	29.89	
TCRSS No.1	73.99	73.52	73.76	1.08
TCRSS No.2	76.58	73.99	75.29	
TCRSS No.3	74.08	73.84	73.96	
TCRSS No.4	73.38	73.03	73.21	
SUS No.1	39.69	40.23	39.96	4.72
SUS No.2	47.35	45.24	46.30	
SUS No.3	33.76	35.01	34.39	
SUS No.4	42.81	42.97	42.89	

Table 4-1 showed the percent of moisture contents of initial sludge samples (the figures of raw sludge was shown in appendix A). The average moisture contents of SSI No. 1, 2, 3 and 4 were 17.90, 15.89, 2.87 and 4.24%, respectively. The average moisture contents of SSM No.1, 2, 3 and 4 were 36.03, 35.53, 37.17 and 29.89, respectively. The moisture content of TCRSS No.1, 2, 3 and 4 were 73.76, 75.23, 73.96 and 73.21%, respectively. The last sample, SUS No.1, 2, 3 and 4 were 39.96, 46.30, 34.39 and 42.89% of average moisture contents, respectively.

Average moisture contents of SSI No.1 and 2 were about 15-17% but the values of SSI No.3 and 4 were only 2-4%, so standard deviation of SSI was quite high (7.19). However, the standard deviation of SSM, TCRSS and SUS were lower than SSI's which were 3.25, 1.08 and 4.72, respectively. The moisture contents of each sample number were based on dewatered operation efficiency and dewatered method, which made the independent value of each sample.

Nevertheless, the results showed that water content in each sample number was a major component in this sludge type because of the high moisture content. Especially, TCRSS's sludges which were more than 70% of the total sample numbers(or 74.04% of average). SSI's sludges had the lowest moisture content in every samples and the average moisture of total sample portions and numbers was 10.23%. The average moisture contents of SSM and SUS's sludge were 34.65 and 74.04%, respectively.

The moisture contents of each sample number and each source were based on dewatered operation efficiency and dewatered method, which made the independent values of each number and each source .

4.1.2 Result of oil content with microwave extraction technique

4.1.2.1 Result of oil Content of Hot roll mill's sludge

Table 4-2 Extracted Oil content of SSI

Sample Name	Temperature Program (°C)	Extracted oil content (%w/w)			
		Acetone	Acetone + N-Hexane	N-Hexane	Petroleum Ether
SSI No.1	90	7.31	7.75	8.60	10.41
SSI No.2	90	4.98	8.62	8.99	8.91
SSI No.3	90	8.68	9.34	6.87	8.37
SSI No.4	90	6.68	8.45	8.19	8.14
Average	**90**	**6.91**	**8.54**	**8.16**	**8.96**
SD	**90**	**1.53**	**0.65**	**0.92**	**1.02**
SSI No.1	120	8.32	6.28	6.48	7.18
SSI No.2	120	7.51	6.29	7.43	4.27
SSI No.3	120	9.10	8.95	7.24	6.15
SSI No.4	120	7.49	7.62	6.59	5.92
Average	**120**	**8.10**	**7.29**	**6.94**	**5.88**
SD	**120**	**0.77**	**1.28**	**0.47**	**1.21**
SSI No.1	150	5.97	4.97	6.84	-
SSI No.2	150	5.21	5.07	6.92	-
SSI No.3	150	5.73	6.71	7.78	-
SSI No.4	150	7.14	6.18	6.34	-
Average	**150**	**6.01**	**5.73**	**6.96**	**-**
SD	**150**	**0.82**	**0.85**	**0.60**	**-**

Table 4-3 Extracted Oil content of SSM

Sample Name	Temperature Program (°C)	Extracted oil content (%w/w)			
		Acetone	Acetone + N-Hexane	N-Hexane	Petroleum Ether
SSM No.1	90	13.99	15.70	12.65	14.87
SSM No.2	90	12.66	16.77	15.26	12.64
SSM No.3	90	12.40	13.76	12.59	14.45
SSM No.4	90	13.56	14.08	13.26	14.66
Average	**90**	**13.15**	**15.08**	**13.44**	**14.16**
SD	**90**	**0.75**	**1.41**	**1.25**	**1.03**
SSM No.1	120	12.41	13.78	12.25	11.86
SSM No.2	120	14.32	13.94	13.35	12.16
SSM No.3	120	14.36	13.70	11.64	11.18
SSM No.4	120	17.33	11.90	11.85	10.00
Average	**120**	**14.61**	**13.33**	**12.27**	**11.30**
SD	**120**	**2.03**	**0.96**	**0.76**	**0.96**
SSM No.1	150	14.91	16.05	13.17	-
SSM No.2	150	19.92	17.16	15.05	-
SSM No.3	150	16.14	14.79	12.75	-
SSM No.4	150	14.84	15.80	12.93	-
Average	**150**	**16.45**	**15.95**	**13.47**	**-**
SD	**150**	**2.39**	**0.97**	**1.06**	**-**

Table 4-4 Extracted Oil content of TCRSS

Sample Name	Temperature Program (°C)	Extracted oil content (%w/w)			
		Acetone	Acetone + N-Hexane	N-Hexane	Petroleum Ether
TCRSS No.1	90	5.48	6.90	5.22	4.96
TCRSS No.2	90	4.92	8.89	7.24	4.64
TCRSS No.3	90	8.84	10.36	5.62	5.39
TCRSS No.4	90	6.09	6.36	5.99	4.25
Average	**90**	**6.33**	**8.13**	**6.02**	**4.81**
SD	**90**	**1.74**	**1.84**	**0.87**	**0.49**
TCRSS No.1	120	9.22	6.88	3.14	6.61
TCRSS No.2	120	9.51	7.66	2.34	5.42
TCRSS No.3	120	13.76	11.62	3.83	4.96
TCRSS No.4	120	10.52	6.11	2.79	4.49
Average	**120**	**1075**	**8.07**	**3.02**	**5.37**
SD	**120**	**2.08**	**2.45**	**0.63**	**0.91**
TCRSS No.1	150	6.54	6.15	8.16	-
TCRSS No.2	150	9.13	10.34	6.34	-
TCRSS No.3	150	9.70	11.75	8.87	-
TCRSS No.4	150	7.86	8.61	8.02	-
Average	**150**	**8.31**	**9.21**	**7.85**	**-**
SD	**150**	**1.41**	**2.41**	**1.07**	**-**

Table 4-5 Extracted Oil content of SUS

Sample Name	Temperature Program (°C)	Extracted oil content (%w/w)			
		Acetone	Acetone + N-Hexane	N-Hexane	Petroleum Ether
SUS No.1	90	43.95	84.52	84.46	54.04
SUS No.2	90	41.18	84.52	82.25	48.79
SUS No.3	90	46.55	85.85	84.26	53.29
SUS No.4	90	45.16	79.94	80.43	51.44
Average	**90**	**44.21**	**83.71**	**82.85**	**51.89**
SD	**90**	**2.28**	**2.59**	**1.90**	**2.34**
SUS No.1	120	51.32	86.14	81.13	60.00
SUS No.2	120	54.98	84.56	81.71	53.96
SUS No.3	120	52.45	82.79	86.94	54.17
SUS No.4	120	57.90	84.32	85.35	55.25
Average	**120**	**54.16**	**84.45**	**83.78**	**55.84**
SD	**120**	**2.92**	**1.37**	**2.82**	**2.83**
SUS No.1	150	55.12	82.89	87.14	-
SUS No.2	150	55.87	84.91	89.58	-
SUS No.3	150	56.51	86.25	91.50	-
SUS No.4	150	53.36	83.69	91.29	-
Average	**150**	**55.21**	**84.43**	**89.88**	**-**
SD	**150**	**1.36**	**1.47**	**2.02**	**-**

Table 4-2 to 4-5 showed the extracted oil content (%w/w) after drying the taken samples from all sources of rolling mill's sludge. (Detail as shown in appendix C)

At 150°C temperature program of petroleum ether, extracted oil content could not be analyzed because the solvent could not be heated up to 150°C

4.1.3 Suitable condition of microwave extraction for the de-watered sludge

4.1.3.1 Suitable microwave extraction condition for SSI's sludge

4.1.3.1.1 Effect of microwave temperature program

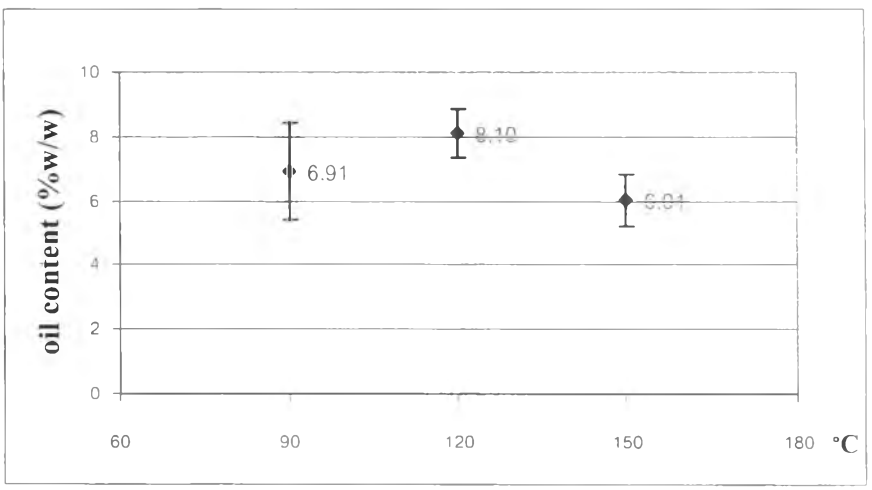

Figure 4-1 Relationship between extracted oil content and temperature program of a hot roll mill (SSI) in acetone

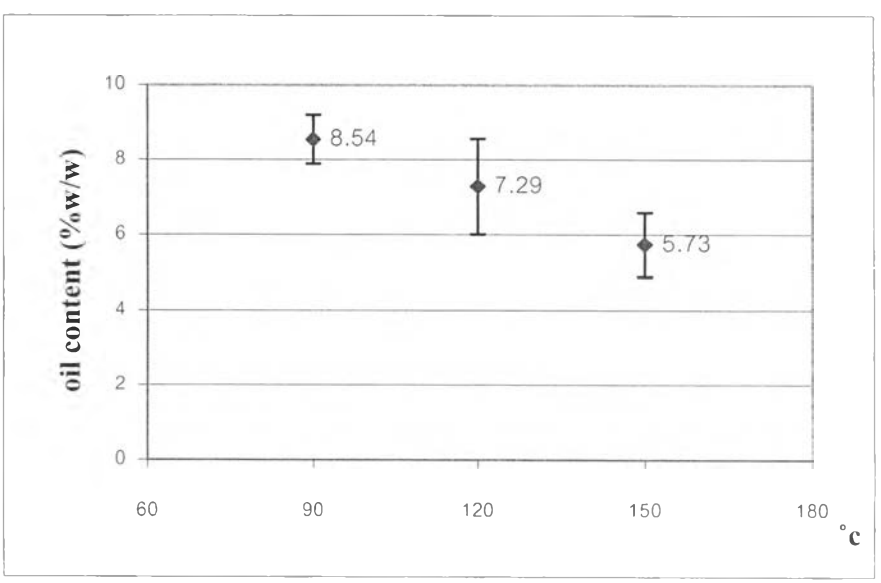

Figure 4-2 Relationship between extracted oil content and temperature program of a hot roll mill (SSI) in acetone and N-hexane mixture solution (1:1 v/v)

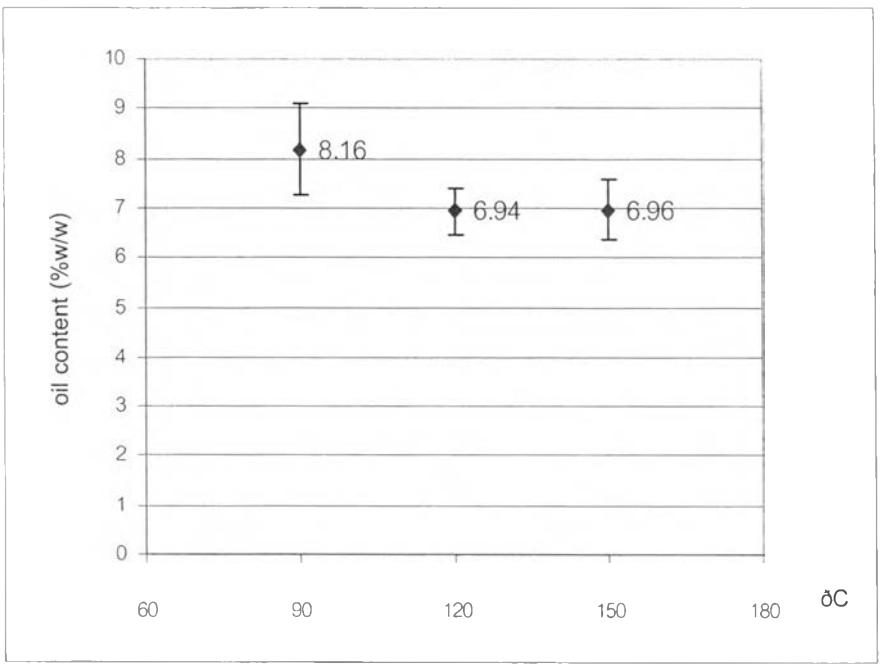

Figure 4-3 Relationship between extracted oil content and temperature program of a hot roll mill (SSI) in N-hexane

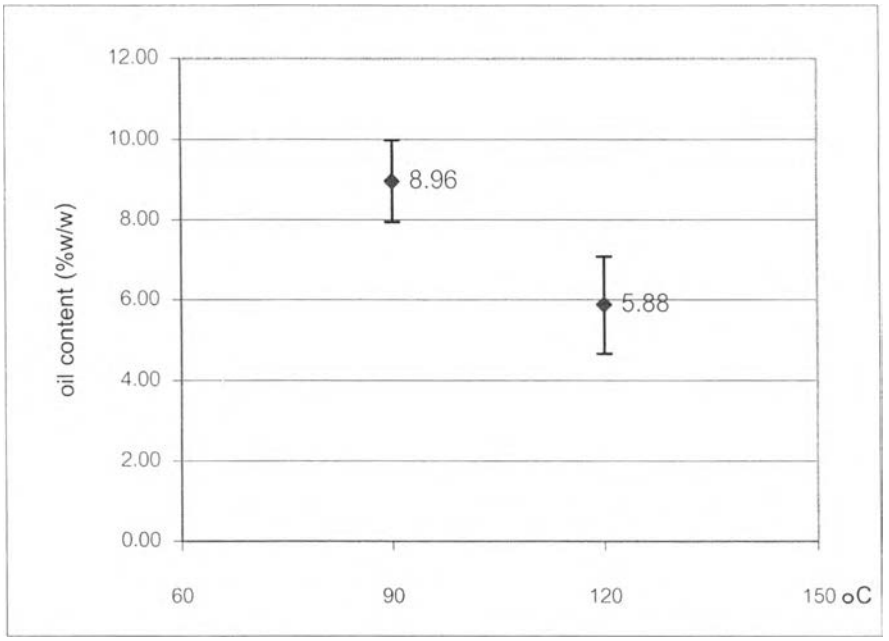

Figure 4-4 Relationship between extracted oil content and temperature program of a hot roll mill (SSI) in petroleum ether

Figure 4-1 to 4-4 represented the relationship between extracted oil content and temperature program in four solvent types from SSI's sludge. By varying temperature program with specific type of solvent, the extraction gave different percentage of extracted oil content. Figure 4-1 with acetone using as solvent, showed that the temperature program varying from 90, 120 and 150°C resulted in 6.91, 8.10 and 6.01 of average oil content percentage, respectively. While the standard deviation range from temperature program were 1.53, 0.77 and 0.82, respectively. It could be concluded that at 120°c with SSI' sludge gave the highest percentage of extracted oil content (8.10%) which the lowest standard deviation. Figure 4-2 depicted that mixture of Acetone and N-hexane gave percent of oil content as 8.54, 7.29 and 5.73, respectively. Figure 4-3 showed that mixture of N-hexane gave percent of oil content as 8.16, 6.94 and 6.96, respectively. Figure 4-4 represented that mixture of petroleum ether gave percent of oil content as 8.96 and 5.88, respectively.

4.1.3.1.2 Effect of solvent type

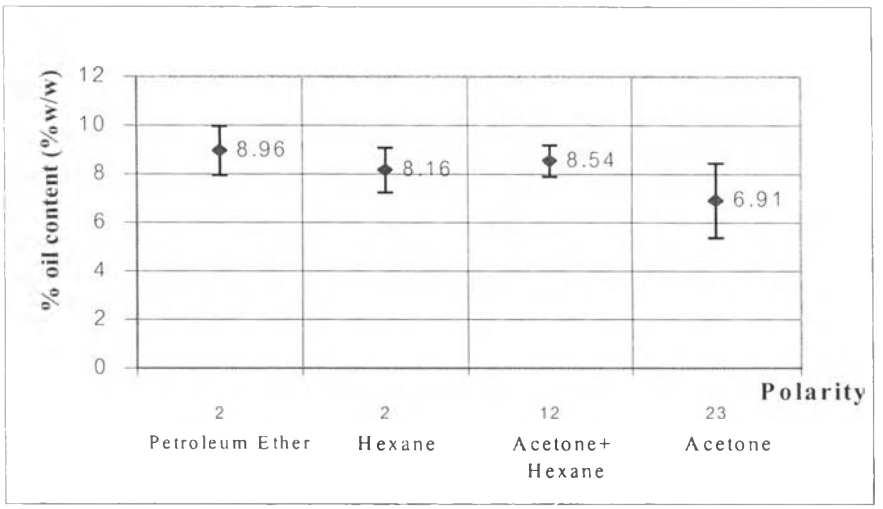

Figure 4-5 Relationship between extracted oil content and solvent polarity of a hot roll mill (SSI) at temperature program 90 °C

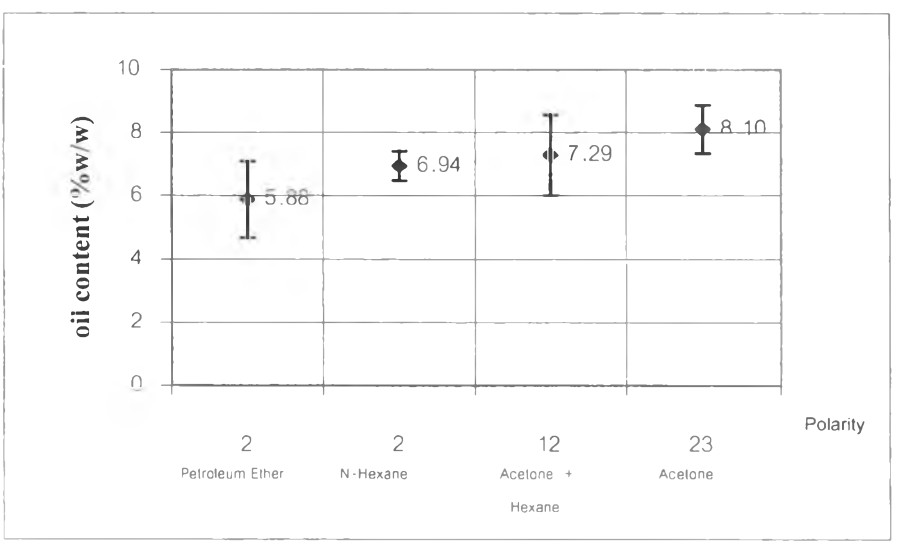

Figure 4-6 Relationship between extracted oil content and solvent polarity of a hot roll mill (SSI) at temperature program 120 °C

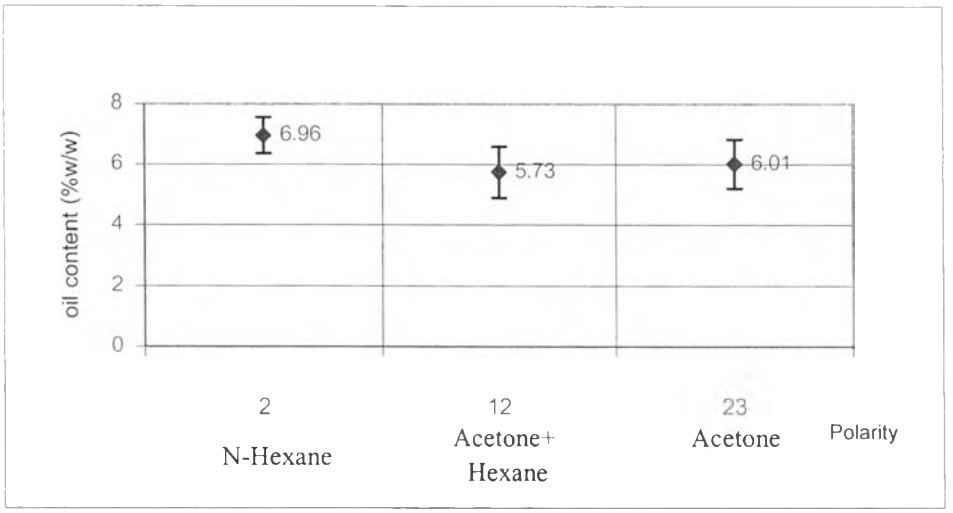

Figure 4-7 Relationship between extracted oil content and solvent polarity of a hot roll mill (SSI) at temperature program 150 °C

Figure 4-5 to 4-7 depicted the effect of solvent polarity used in SSI's sludge sample at selected temperature program. Different types of solvent which have different polarity values resulted in variation of percentage extracted oil contents. Figure 4-5 showed that at 90°C, petroleum ether, N-hexane, mixture of acetone and N-hexane, and acetone, which have 2, 2, 12 and 23 polarity values gave 8.96, 8.16, 8.54 and 6.91% extracted oil content, respectively. From Figure 4-6, 120 °C extraction temperature Petroleum Ether, N-hexane, mixture of Acetone and N-hexane, and acetone gave 5.88, 6.94, 7.29 and 8.10% extracted oil content, respectively. At 150 °C, petroleum ether, N-hexane, mixture of acetone and N-hexane, and acetone gave 6.96, 5.73, and 6.01% extracted oil content, respectively, as shown in figure 4-7.

4.1.3.2 Suitable microwave extraction condition for SSM's sludge

4.1.3.2.1 Effect of microwave temperature program

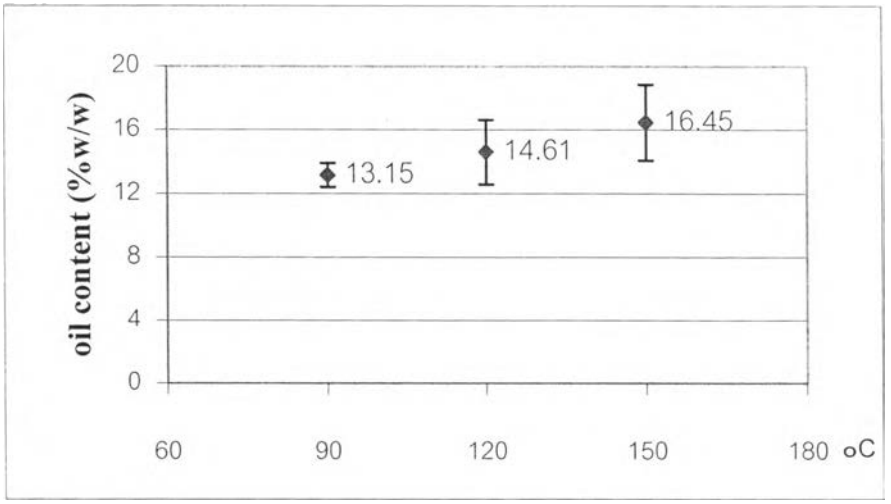

Figure 4-8 Relationship between extracted oil content and temperature program of a hot roll mill (SSM) in acetone

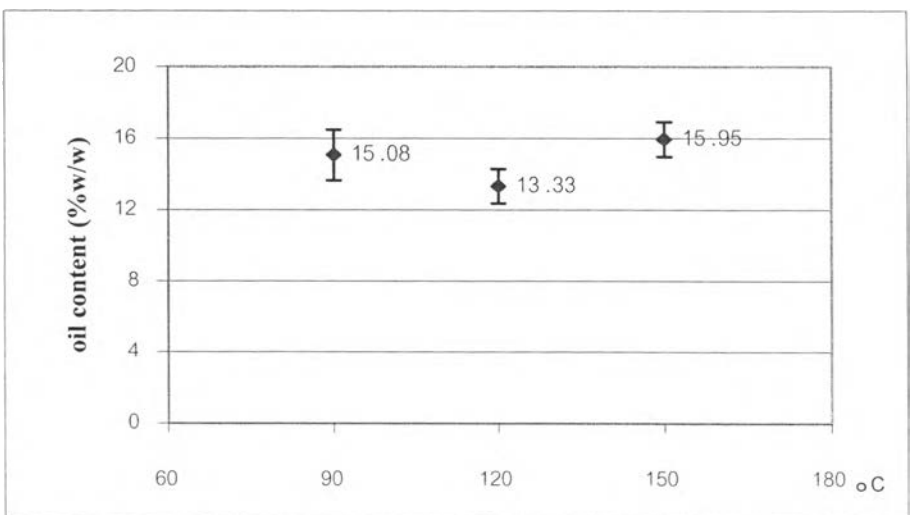

Figure 4-9 Relationship between extracted oil content and temperature program of a hot roll mill (SSM) in acetone and N-hexane mixture solution (1:1 v/v)

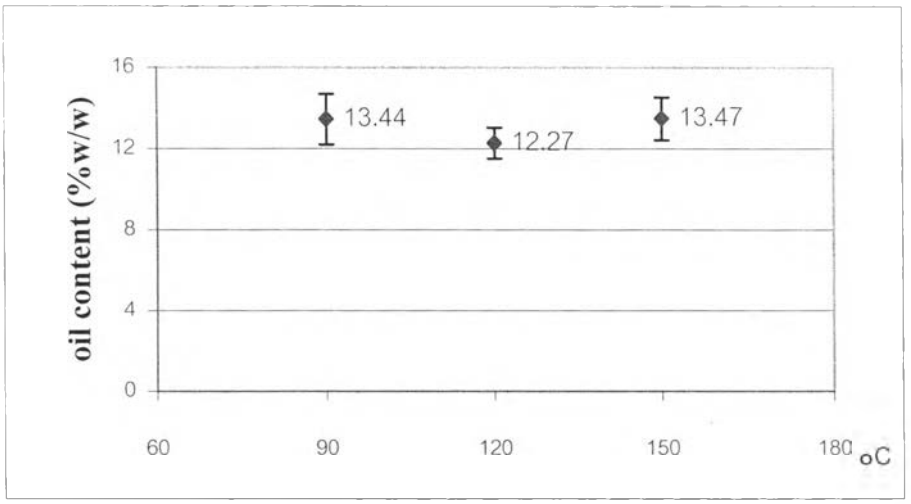

Figure 4-10 Relationship between extracted oil content and temperature program of a hot roll mill (SSM) in N-hexane

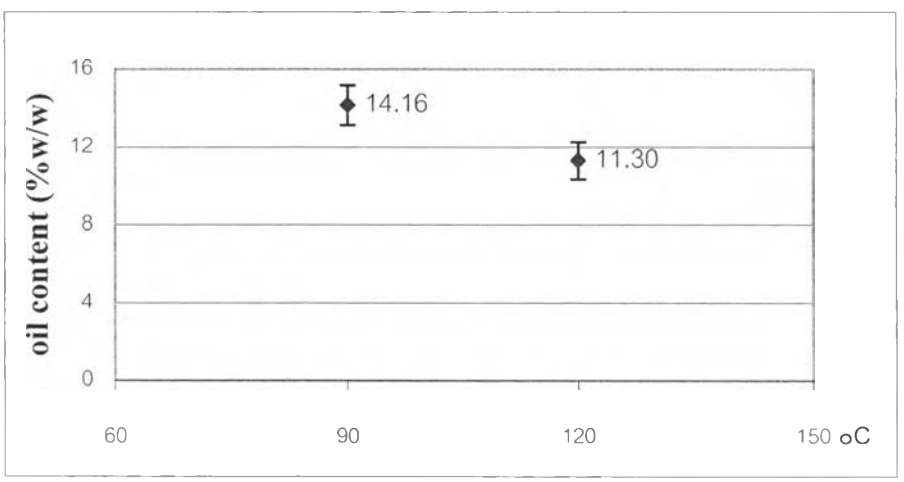

Figure 4-11 Relationship between extracted oil content and temperature program of a hot roll mill (SSM) in petroleum ether

Figure 4-8 to 4-11 represented the relationship between extracted oil content and temperature program in four solvent types from SSM's sludge. The extraction gave different percentage of extract oil content. Figure 4-8 with acetone using as solvent, it showed that the temperature program varying from 90, 120 and 150 °C resulted in 13.15, 14.61 and 16.45 of average oil content percentage, respectively. Figure 4-9 depicted that mixture of acetone and N-hexane gave percent of oil content as 15.08, 13.33 and 15.95, respectively. Figure 4-10 showed that

mixture of N-hexane gave percent of oil content as 15.08, 13.33 and 15.95, respectively. Figure 4-11 represented that mixture of petroleum ether gave percent of oil content as 14.16 and 11.30, respectively.

4.1.3.2.2 Effect of solvent type

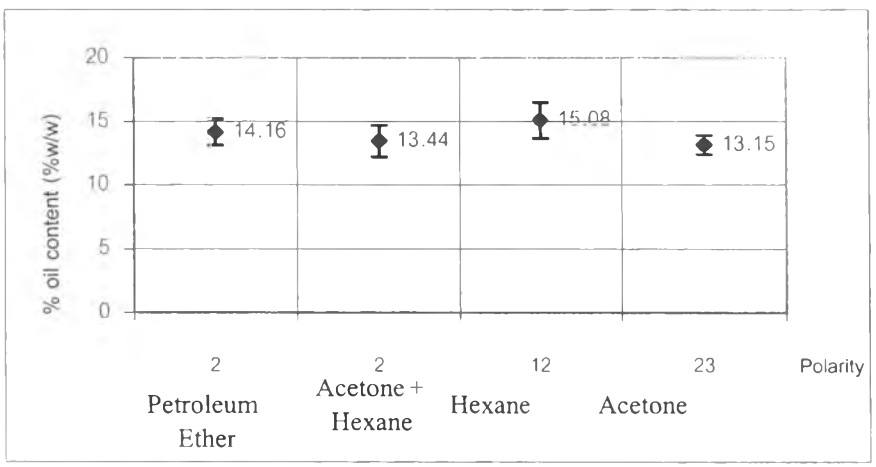

Figure 4-12 Relationship between extracted oil content and solvent polarity of a hot roll mill (SSM) at temperature program 90 °C

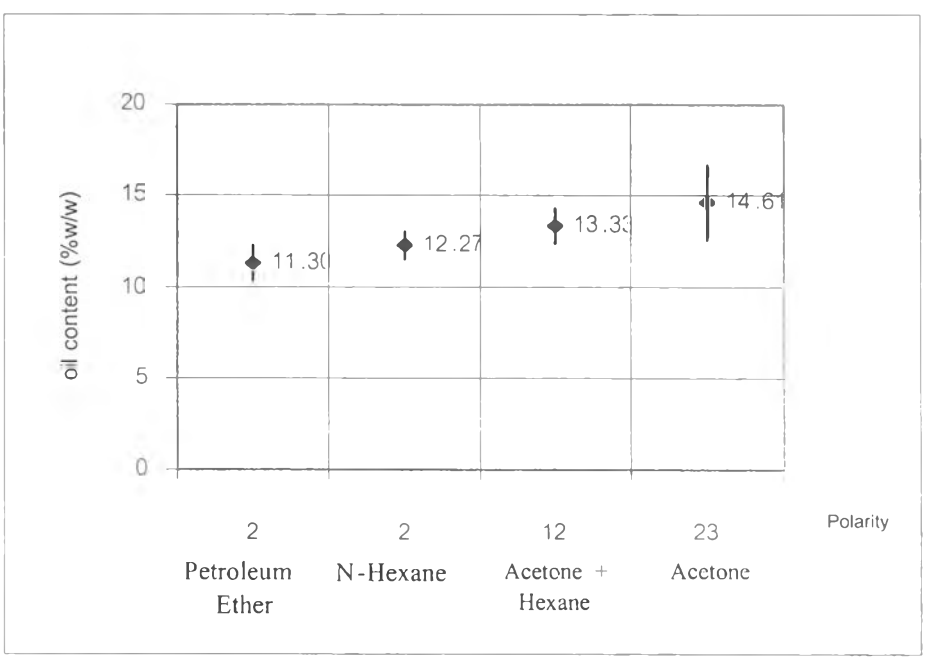

Figure 4-13 Relationship between extracted oil content and solvent polarity of a hot roll mill (SSM) at temperature program 120 °C

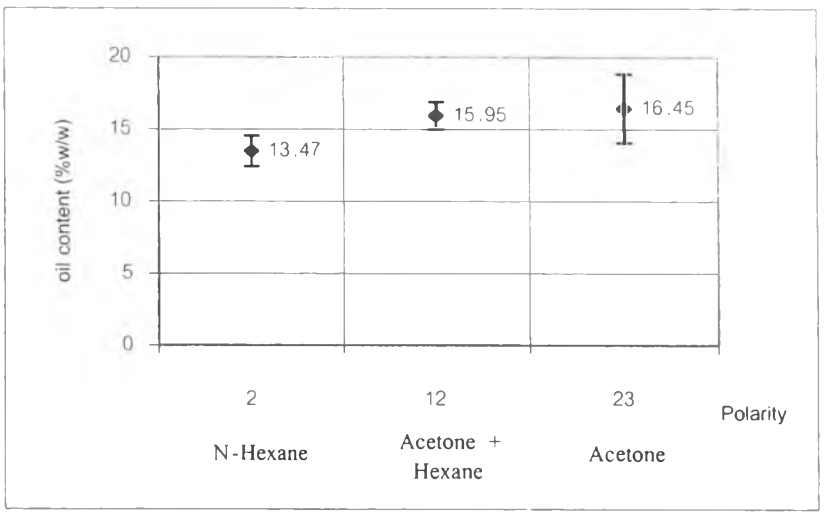

Figure 4-14 Relationship between extracted oil content and solvent polarity of a hot roll mill (SSM) at temperature program 150 °C

Figure 4-12 to 4-14 showed the effect of solvent polarity used with SSM's sludge sample at selected temperature program. Different types of solvent which have different polarity value resulted in variation of percent extracted oil content. Figure 4-12 showed that at 90 °C, petroleum ether, N-Hexane, mixture of acetone and N-Hexane, and acetone, which have 2,2,12 and 23 polarity value of respectively, gave 14.16, 13.44, 15.08 and 13.15% extracted oil content respectively. From figure 4-13, 120 °C extraction temperature Petroleum Ether, N-Hexane, mixture of Acetone and N-Hexane, and Acetone gave 11.30, 12.27, 13.33 and 14.61% extracted oil content respectively. At 150 °C, Petroleum Ether, N-Hexane, mixture of Acetone and N-Hexane, and Acetone gave 13.47, 15.95, and 16.45% extracted oil content respectively as shown in figure 4-14.

4.1.3.3 Suitable microwave extraction condition for TCRSS's sludge

4.1.3.3.1 Effect of microwave temperature program

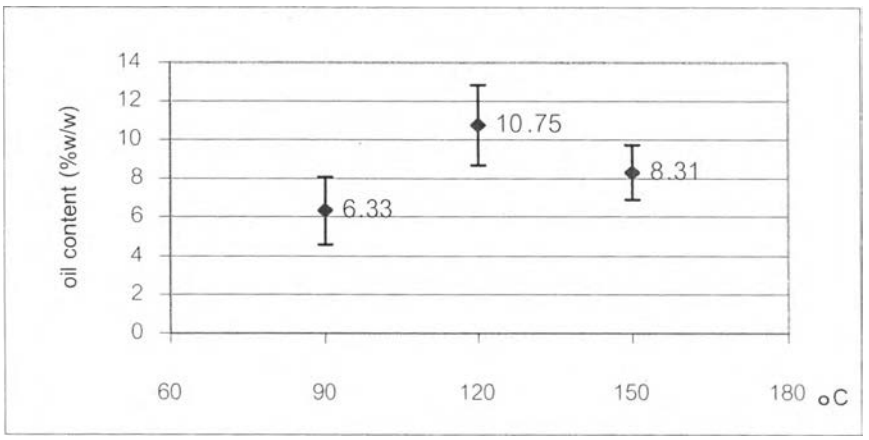

Figure 4-15 Relationship between extracted oil content and temperature program of a cold roll mill (TCRSS) in acetone

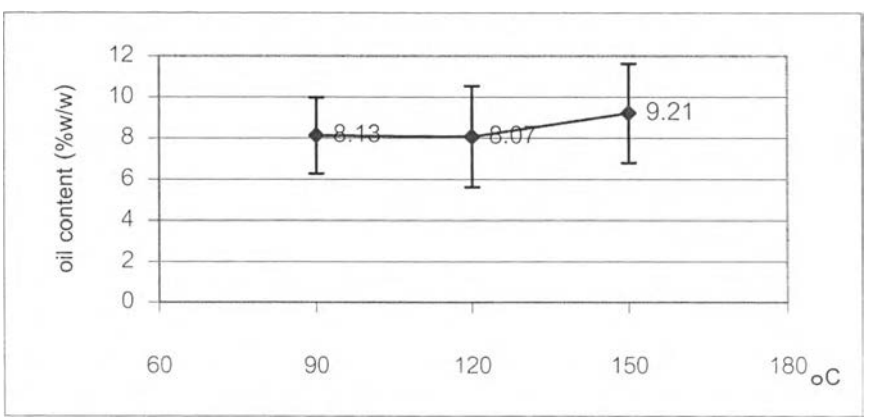

Figure 4-16 Relationship between extracted oil content and temperature program of a cold roll mill (TCRSS) in acetone and N-hexane mixture solution (1:1 v/v)

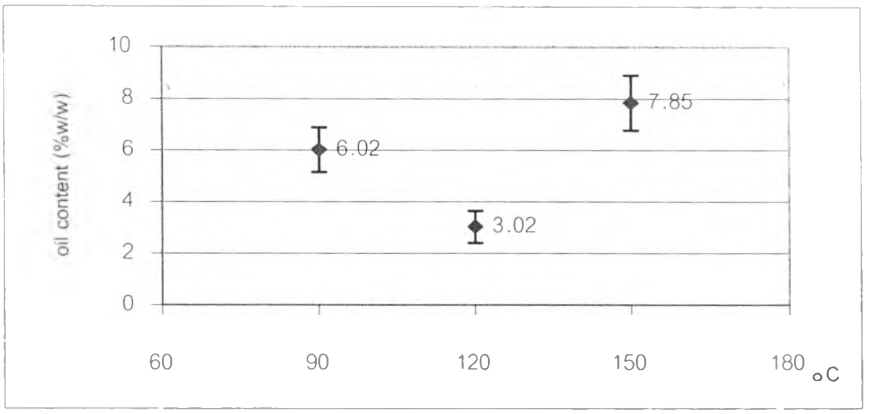

Figure 4-17 Relationship between extracted oil content and temperature program of a cold roll mill (TCRSS) in N-hexane

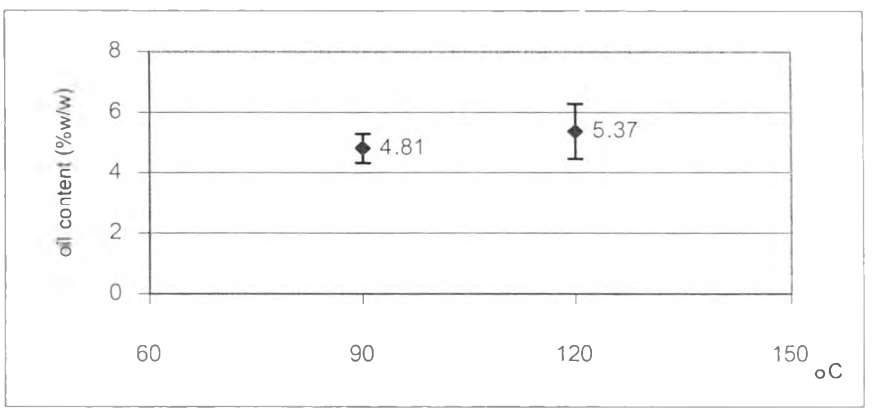

Figure 4-18 Relationship between extracted oil content and temperature program of a cold roll mill (TCRSS) in petroleum ether

Figure 4-15 to 4-18 represented the relationship between of extracted oil content and temperature program in four solvent types from TCRSS's sludge. The extraction gave different percentage of extract oil content. Figure 4-15 with the use of acetone as solvent, it showed that the temperature program varying from 90, 120 and 150 °C resulted in 6.33, 10.75 and 8.31 of average oil content percentage respectively. Figure 4-16 depicted that mixture of Acetone and N-Hexane gave percent of oil content as 8.13, 8.07 and 9.21, respectively. Figure 4-17 showed that mixture of N-Hexane gave percent of oil content as 6.02, 3.02 and 7.85, respectively. Figure 4-18 represented that mixture of Petroleum Ether gave percent of oil content as 4.81 and 5.37, respectively.

4.1.3.3.2 Effect of solvent type

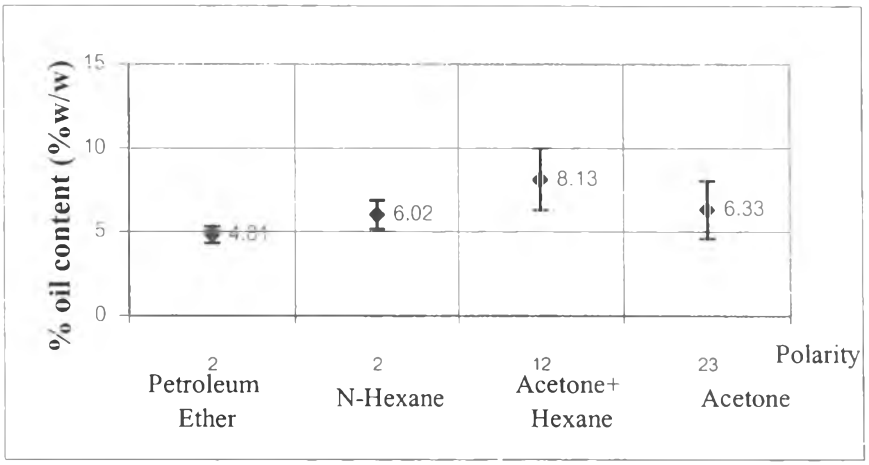

Figure 4-19 Relationship between extracted oil content and solvent polarity of a hot roll mill (TCRSS) at temperature program 90 °C

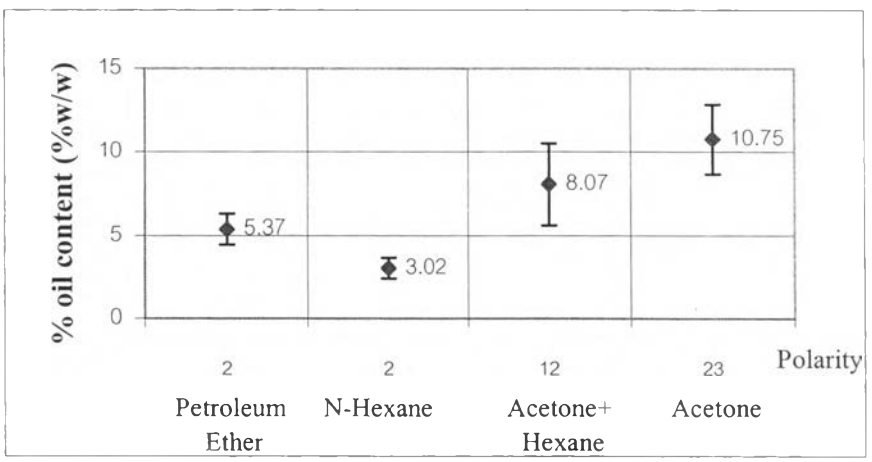

Figure 4-20 Relationship between extracted oil content and solvent polarity of a hot roll mill (TCRSS) at temperature program 120 °C

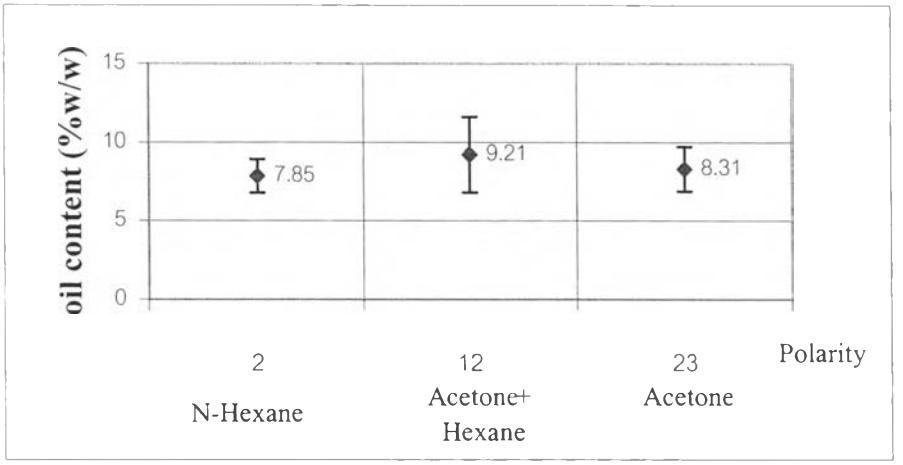

Figure 4-21 Relationship between extracted oil content and solvent polarity of a hot roll mill (TCRSS) at temperature program 150 °C

Figure 4-19 to 4-21 showed the effect of solvent polarity used with TCRSS's sludge sample at selected temperature program. Different types of solvent which have different polarity value resulted in variation of percentage extracted oil content. Figure 4-19 showed that at 90 °C, petroleum ether, N-Hexane, mixture of acetone and N-Hexane, and acetone, which have 2,2,12 and 23 polarity value of respectively, gave 4.81, 6.02, 8.13 and 6.33% extracted oil content respectively. From figure 4-20, 120 °C extraction temperature Petroleum Ether, N-Hexane, mixture of Acetone and N-Hexane, and Acetone gave 5.37, 3.02, 8.07 and 10.75% extracted oil content respectively. At 150 °C, Petroleum Ether, N-Hexane, mixture of Acetone and N-Hexane, and Acetone gave 7.85, 9.21, and 8.31% extracted oil content respectively as shown in figure 4-21.

4.1.3.4 Suitable microwave extraction condition for SUS's sludge

4.1.3.4.1 Effect of microwave temperature program

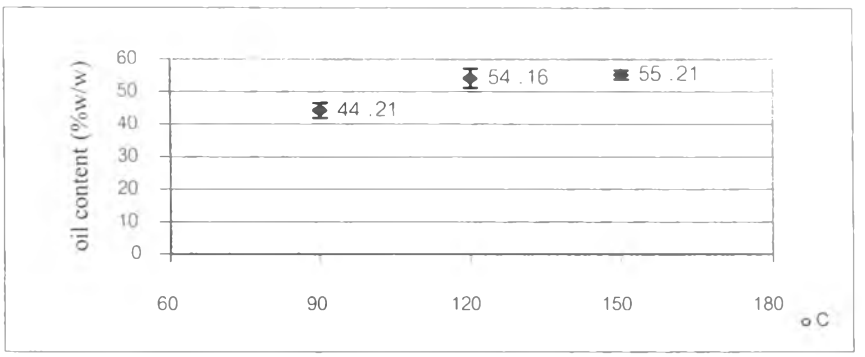

Figure 4-22 Relationship between extracted oil content and temperature program of a cold roll mill (SUS) in acetone

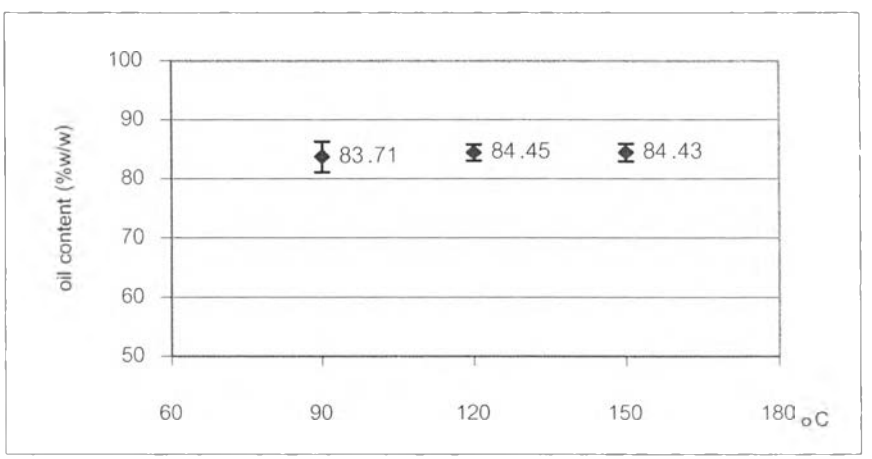

Figure 4-23 Relationship between extracted oil content and temperature program of a cold roll mill (SUS) in acetone and N-hexane mixture solution (1:1 v/v)

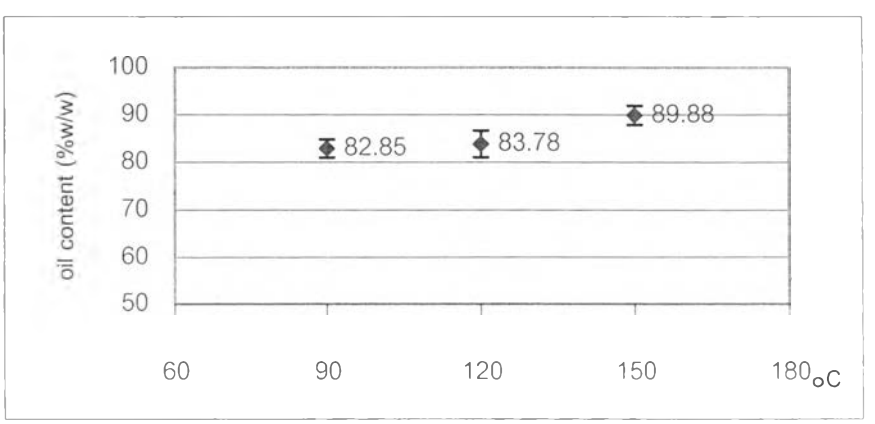

Figure 4-24 Relationship between extracted oil content and temperature program of a cold roll mill (SUS) in N-hexane

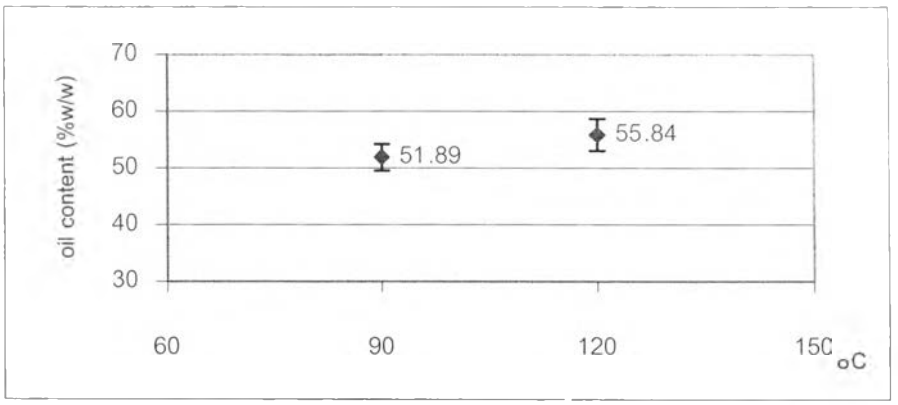

Figure 4-25 Relationship between extracted oil content and temperature program of a cold roll mill (SUS) in petroleum ether

Figure 4-22 to 4-25 represented the relationship between extracted oil content and temperature program in four solvent types from SUS's sludge. The extraction gave different percentage of extract oil content. Figure 4-22 with the use of acetone as solvent, it showed that the temperature program varying from 90, 120 and 150 °C resulted in 44.21, 54.16 and 55.21 of average oil content percentage respectively. Figure 4-23 presented that mixture of Acetone and N-Hexane gave 83.71, 84.45 and 84.43%, respectively. Figure 4-23 depicted that mixture of Acetone and N-Hexane gave percent of oil content as 83.71, 84.45 and 84.43%, respectively. Figure 4-24 showed that mixture of N-Hexane gave percent of oil content as 82.85, 83.78 and 89.88, respectively. Figure 4-25 represented that mixture of Petroleum Ether gave percent of oil content as 51.89 and 55.84, respectively.

4.1.3.4.2 Effect of solvent type

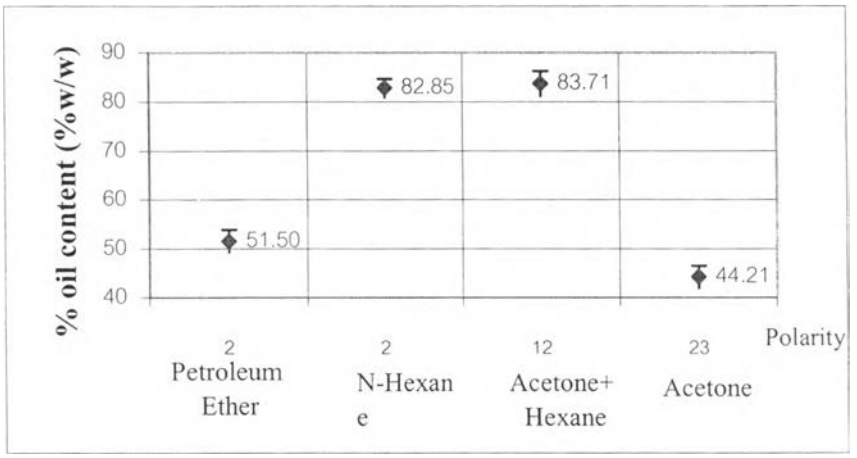

Figure 4-26 Relationship between extracted oil content and solvent polarity of a hot roll mill (SUS) at temperature program 90 °C

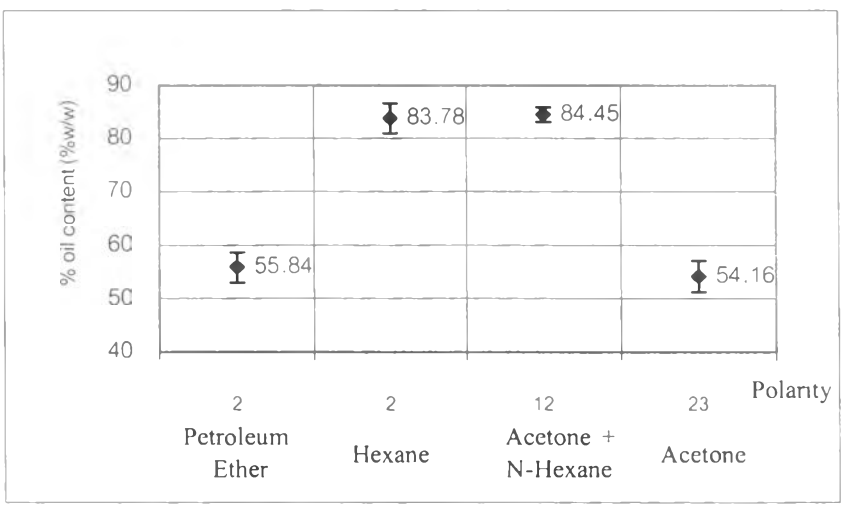

Figure 4-27 Relationship between of extracted oil content and solvent polarity of a hot roll mill (SUS) at temperature program 120 °C

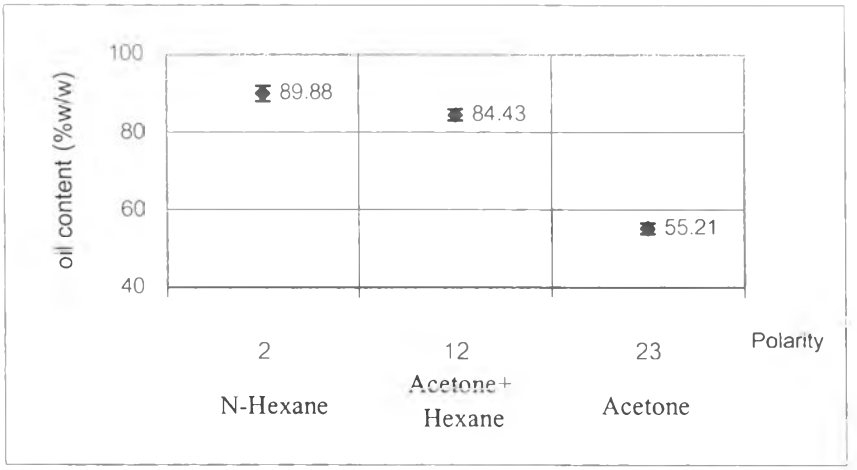

Figure 4-28 Relationship between extracted oil content and solvent polarity of a hot roll mill (SUS) at temperature program 150 °C

Figure 4-26 to 4-28 showed the effect of solvent polarity used with SUS's sludge sample at selected temperature program. Different types of solvent which have different polarity value resulted in variation of percent extracted oil content. Figure 4-26 showed that at 90 °C, petroleum ether, N-Hexane, mixture of acetone and N-Hexane, and acetone, which have 2,2,12 and 23 polarity value of respectively, gave 51.89, 82.85, 83.71 and 44.21% extracted oil content respectively. From Figure 4-27, 120 °C extraction temperature Petroleum Ether, N-Hexane, mixture of Acetone and N-Hexane, and Acetone gave 55.84, 83.78, 84.45 and 54.16% extracted oil content respectively. At 150 °C, Petroleum Ether, N-Hexane, mixture of Acetone and N-Hexane, and Acetone gave 89.88, 84.43, and 55.21% extracted oil content respectively as shown in Figure 4-28.

4.1.4 Recycling

4.1.4.1 Recycled fine iron oxide for re-melting

After filtration, the remaining solid was collected to be analyzed percentage of iron. The recommended value for re-melting process must be more than 70% (by dry weight) [Krissana, Marubeni]. Iron contents of all samples were shown in Table 4-6.

Table 4-6 Percent of iron content in the obtained solid after microwave extraction

Source	Iron Content (%)				Average of Iron Content (%)	Standard Deviation
	No.1	No.2	No.3	No.4		
SSI	95.736	95.922	95.575	95.508	95.7	0.18
SSM	81.838	83.29	84.332	85.532	83.7	1.57
TCRSS	57.835	58.221	51.617	55.778	55.9	3.03
SUS	79.15	74.657	79.7	79.507	78.3	2.41

According to the upper table, the percentage of iron (by dry weight) of SSI No.1, 2, 3 and 4 were 95.7, 95.9, 95.8 and 95.5%, respectively, and average iron content value was 95.7%. For SSM, another hot rolling mill, percentage of iron from No.1 to No.4, were 81.8, 83.3, 84.3 and 85.5, respectively, and the average value was 83.7%. The results of TCRSS were 57.8, 58.2, 51.8 and 55.8%, respectively, and the average value was 55.9%. And the last samples taken from SUS, the iron content of sample No.1, 2, 3 and 4 were 79.2, 74.7, 79.7 and 79.5%, respectively, and the average value was 78.3%. In term of the standard deviation value, it was quite low, which were 0.1 for SSI, 1.57 for SSM, 3.03 for TCRSS and 2.41 for SUS.

It could be noted that SUS, cold rolling mill, had higher iron content than the recommended value while all sample numbers of TCRSS had lower only at 55.9% of average iron content which could not be the raw material for re-melting process(Results of XRF was shown in appendix D).

4.1.4.2 Recycled oil used as fuel in cement kiln

The liquid phase, which had separated from solid phase by filtration, contained both oil and solvent. These two parts must be separated by evaporation, so the solvent was removed. Then the oil would be analyzed and compared with specified control parameters for fuel in cement kiln grade. The results were shown in Table 4-7

Table 4-7 Analytical Result of the Extracted Oil Compared with Specified Control Parameters for Fuels in Cement Kiln Grade

Parameter	SSI					TCRSS					SSM					SUS					Synthesis fuel	Lignite	Unit
	No.1	No.2	No.3	No.4	Avg.	No.1	No.2	No.3	No.4	Avg.	No.1	No.2	No.3	No.4	Avg.	No.1	No.2	No.3	No.4	Avg.	in cement kiln		
Heat value	10,614	10,615	10,544	10,330	10,526	10,798	10,613	10,723	12,151	11,071	10,510	10,368	10,433	10,251	10,391	8,093	8,321	8,613	8,710	8,434	> 500	> 4,000	cal/g
Sulfur content	0.68	0.52	0.45	0.89	0.63	0.37	0.25	0.23	0.37	0.31	0.81	0.59	0.9	0.8	0.78	0.49	0.07	0.48	0.14	0.29	< 4.0	-	%
Chloride content	0.0001	0.0005	0.0001	0.0003	0.0003	0.0003	0.0005	0.0005	0.0005	0.0005	0.0004	0.0006	0.0006	0.0006	0.0006	0.0002	0.0001	0.0001	0.0002	0.0002	< 1.0	-	%
7. Heavy metal content																							
- Chromium (Cr)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0014	0.0008	0.0011	0.0000	0.0008	< 0.1	-	%
- Vanadium (V)	0.0000	0.0007	0.0000	0.0000	0.0002	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0003	0.0001	< 0.1	-	%
- Nikel (Ni)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0033	0.0000	0.0000	0.0008	< 0.1	-	%
- Zinc (Zn)	0.0024	0.0014	0.0005	0.0017	0.0015	0.0003	0.0021	0.0033	0.0001	0.0015	0.0002	0.0034	0.0061	0.0094	0.0048	0.0032	0.0038	0.0045	0.0000	0.0029	< 0.1	-	%
- Copper (Cu)	0.0000	0.0000	0.0000	0.0005	0.0001	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0014	0.0000	0.0000	0.0004	0.0000	0.0000	0.0000	0.0000	0.0000	< 2.0	-	%
- Telenium (Tl)	0.0000	0.0000	0.0000	0.0082	0.0021	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	< 0.1	-	%
- Arsenic (As)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	< 0.1	-	%
- Lead (Pb)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	< 1.0	-	%
- Mercury (Hg)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	< 0.01	-	%
- Cadmium (Cd)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	< 0.1	-	%

As shown in the table, the specified control parameters for cement kiln fuels were calorific value, sulfur content, chloride content and ten heavy metals which including chromium (Cr), Vanadium (V), Nickel (Ni), Zinc (Zn), Copper (Cu), Tellurium (Tl), Arsenic (As), Lead (Pb), Mercury (Hg) and Cadmium (Cd).

Heating or calorific value of all samples showed that SSI's samples ranged from 10,330 to 10,615 cal/g and the average value was 10,526 cal/g. The heating values of SSM's clean oil were 10,251 to 10,510 cal/g with the average value was 10,391 cal/g. TCRSS's samples ranged from 10,613 to 12,151 cal/g and the average was 11,071 cal/g. The last sample was SUS, where heating values ranged from 8,093 to 8,710 cal/g and the average was 8,434 cal/g. The heating value of all samples was very high comparing to the synthetic fuel for cement kiln. For the major fuel in cement kiln, lignite, the heating value was the only considered parameter and Lignite got 4,000 cal/g. The result found that all samples gave higher heating value than lignite.(Results of heating value were shown in appexdix E)

All the samples displayed low sulfur content. In the first hot roll coil's sample, SSI, the results of No.1 to No.4 ranged from 0.45 to 0.89% and 0.63% was the average. In the clean oil sample of the another hot roll mill, SSM, the results ranged from 0.59 to 0.81% and the average was 0.78%. For TCRSS's clean oil samples, which were from cold roll mill, the sulfur content ranged 0.23 to 0.37% and the average was 0.31%. Another cold roll mill's sample from SUS, the sulfur contents ranged from 0.07 to 0.49% and the average was 0.29%

The characteristic of synthetic fuel for cement kiln was less than 4% sulfur content that results of all samples complied with the recommended value.

Chloride content, a characteristic of synthetic fuel for cement kiln, showed in table 4-1. The clean oil samples of SSI ranged from 1.49 to 4.96 ppm and the average was 2.73%.

The sample from another hot rolling mill, SSM, was 3.97 – 5.96% and the average was 5.58%. 3.47 – 5.46% was the result of TCRSS's cleaned oil sample and 4.71% was the average. 1.49 – 2.48% was the result of SUS's sample and the average was 1.86%.

There were ten heavy metals contributed in major characteristic of synthetic fuel in cement kiln. Table 4-7 showed that most of results were zero or

undetectable and the others were very low components. Chromium was found only in 2 samples out of all 16 samples. Both are SUS's samples (No.2 and No. 4) which contained 0.14 and 0.11% of Chromium, respectively. Vanadium was found only in two samples which SSI's sample No.2 was 0.0007% and SUS's sample No.4 was 0.0003%. Only sample SUS No.2 contained 0.0033% Nickel. Most samples were found low zinc content. Samples from SSI No.1 to No.4 gave 0.0024, 0.0014, 0.0005 and 0.0017% Zinc, respectively. SSM's samples were 0.0002, 0.0034, 0.0061 and 0.0094% Zinc, respectively. The zinc contents in TCRSS's samples were 0.003, 0.0021, 0.0033 and 0.0001%, respectively. SUS's samples were 0.0032, 0.0038, 0.0045 and 0.0000% zinc, respectively.

Copper content in the clean oil sample, shown in Table 4-1, two samples were found. The first one was SSI's sample No. 4 with 0.0005% copper and another was SSM's sample No. 2 with 0.0014% copper. Tellurium was found in only one sample in SSI No.4 at 0.0082% concentration. The other four heavy metals, which were arsenic, lead, mercury and cadmium, were undetectable from all samples. The recommendation values of synthetic fuel for Siam cement kiln were less than 0.1% of Chromium, Vanadium, Nickel, Zinc, Tellurium, Arsenic and Cadmium. The recommendation value was less than 2% copper, less than 1% Lead and less than 0.01% Mercury. All results were lower than Siam Cement's recommendation.

4.2 Discussion

4.2.1 Suitable condition of microwave extraction

4.2.1.1 SSI

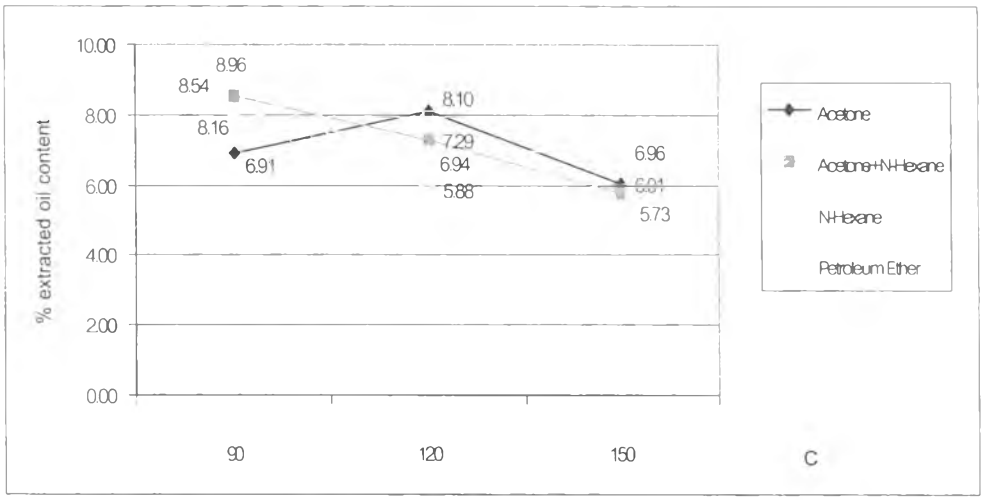

Figure 4-29 Extracted oil content (%) as a function of microwave temperature programming of a hot roll mill (SSI) by varying solvent types

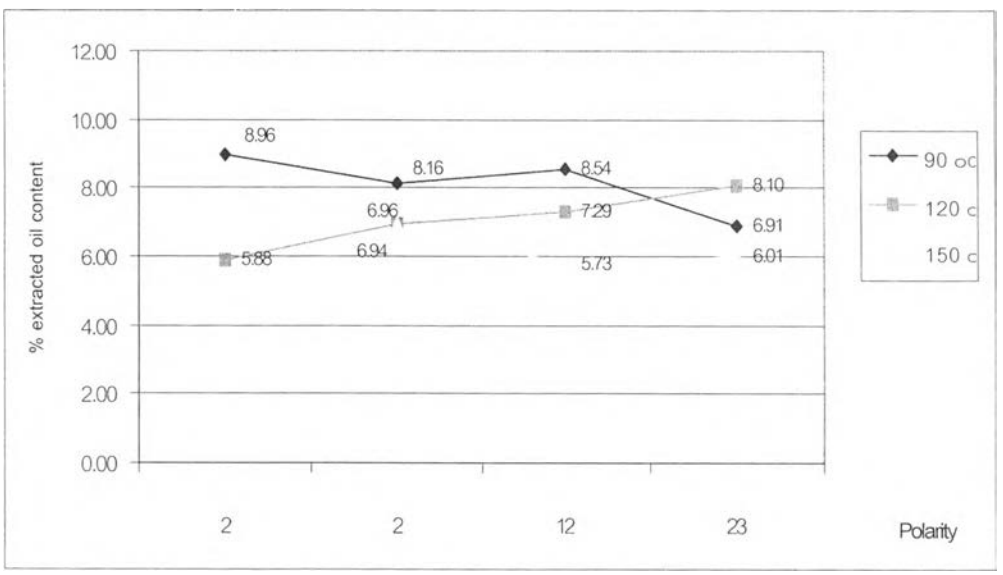

Figure 4-30: Extracted oil content (%) as a function of solvent type of a hot roll mill (SSI) by varying microwave temperature program

According to Figure 4-29, it could be observed that most of sludge samples except ones that were extracted with acetone gave higher extracted oil content with lower temperature program.

In the aspect of polarity of solvent, it could be noticed that there were no direct relationship between percentage of extracted oil content with polarity of solvent using in this research as shown in Figure 4-30. With temperature programs at 90 ^{o}C and 150 ^{o}C, better extraction results (high percentage of extracted oil) could be

achieved by using low or non-polar solvent. On contrary, with temperature program at 120 °C, extraction results (high in percentage of extracted oil) were proportion to polarity of extract solvents. By considering percentage of extracted oil, temperature program at 90 °C in combination with non-polar solvent was the optimum condition for oil extraction of SSI's sludge in this research as shown in Figure 4-29 and 4-30. Overall percent extracted oil from all SSI's sludge samples were considered a narrow range of output since extracted oil content were ranged from 5 to 8% (of dry weight).

4.2.1.2 SSM

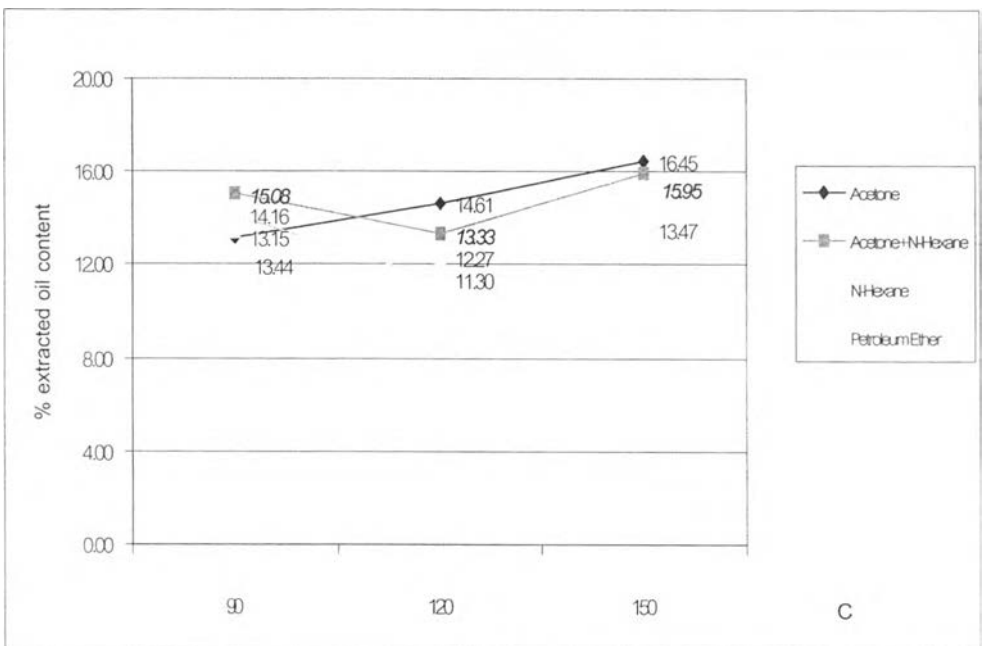

Figure 4-31: Extracted oil content as a function of microwave temperature programming of a hot roll mill (SSM) by varying solvent types

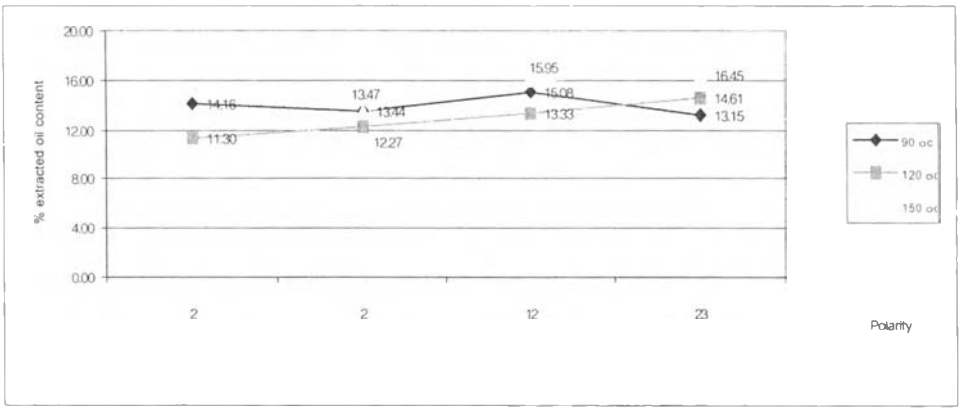

Figure 4-32: Extracted oil content as a function of solvent type of a hot roll mill (SSM) by varying microwave temperature program

From Figure 4-31, temperature program at 150 C gave the highest extracted oil. As shown in Figure 4-32, it can be concluded that percentage of extracted oil have a proportional relationship with polarity of solvent higher percentage of extracted oil gained from more polar solvent. Range of extracted oil was from 11-16% which could be considered as low yield of extraction. Also the effect of varying extraction condition were not significant, so cost of operation were another aspect should be considered.

4.2.1.3 Hot Rolling Mills

According to sample No. 4.2.1.1 and 4.2.1.2, they both are sludge from hot rolling operations. It could be considered that SSI and SSM source gave quite low extracted oil per dry weight of sample, but SSM gave a little higher than SSI but not significantly different. It was about 6-8% difference. The optimum condition for microwave extractions of each source were different as previously described in item No. 4.2.1.1 and 4.2.1.2. There were possible multi factors contributed to the suitable condition of extraction which could be

- Design of process pipeline-Hot rolling mill was high-pressure oil operation. Different type of process pipeline material and welding caused different level of oil leakage.
- Design of lubricating system-Some design caused high content lubricating in effluent.

- Types of lubricant used at plant-Different type of lubricants had different solubility to each solvent.

4.2.1.4 TCRSS

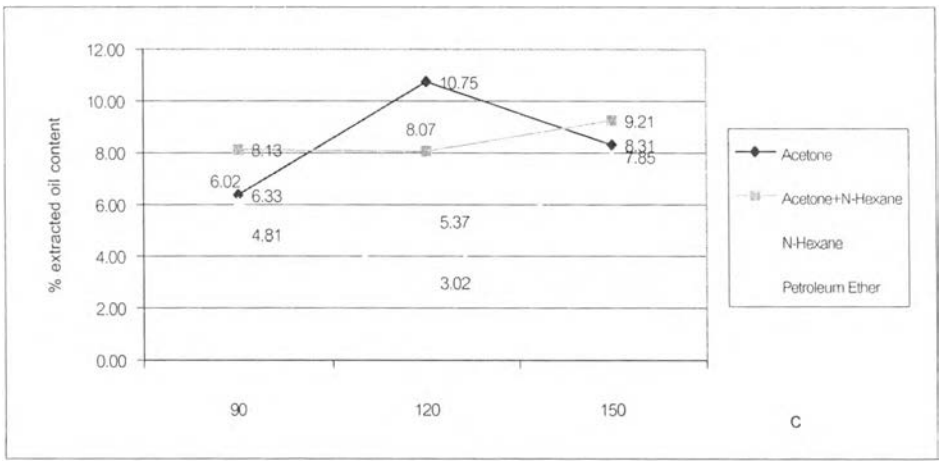

Figure 4-33: Extracted oil content as a function of microwave temperature programming of a cold roll mill (TCRSS) by varying solvent types

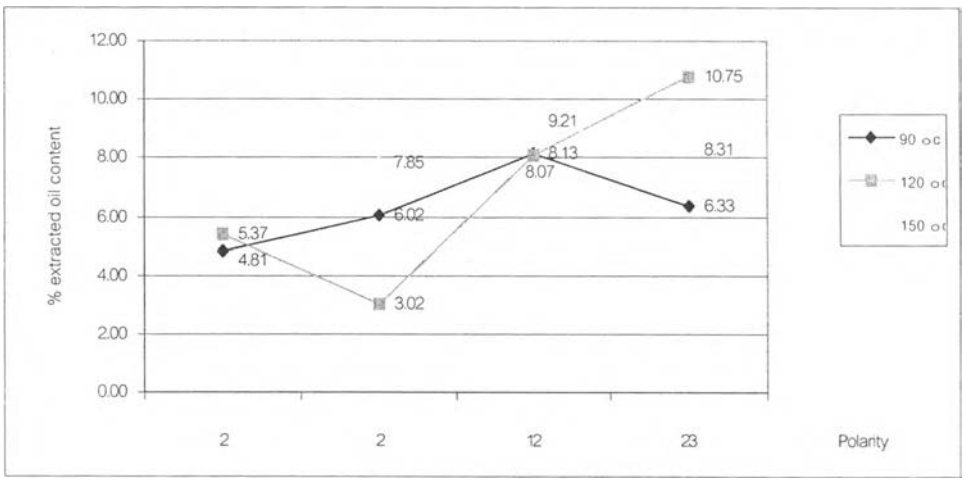

Figure 4-34: Extracted oil content as a function of solvent type of a cold roll mill (TCRSS) by varying microwave temperature program

It could be observed from figure 4-33 to 4-34 that percentage of extracted oil was quite low, from 3-11%. But percent extracted oil were significantly varied from different condition applied as seen from Figure 4-33. Standard deviation of extracted oil of all temperature programs from extractions with Acetone and mixture of Acetone with Hexane were 2.05 and 2.45 respectively. With these values of standard variation, the results gave us lower level of confidence. From overall point

of view, the use of N-Hexane and Petroleum Ether gave the highest results at 150 C microwave temperature program.

In the aspect of polarity of solvent which showed in Figure 4-34, mixture of acetone with N-Hexane and N-Hexane provided better results in oil extraction. However these values could not be used to conclude the effect of polarity since their low percentage of extract oil result with high standard deviation.

4.2.1.5 SUS

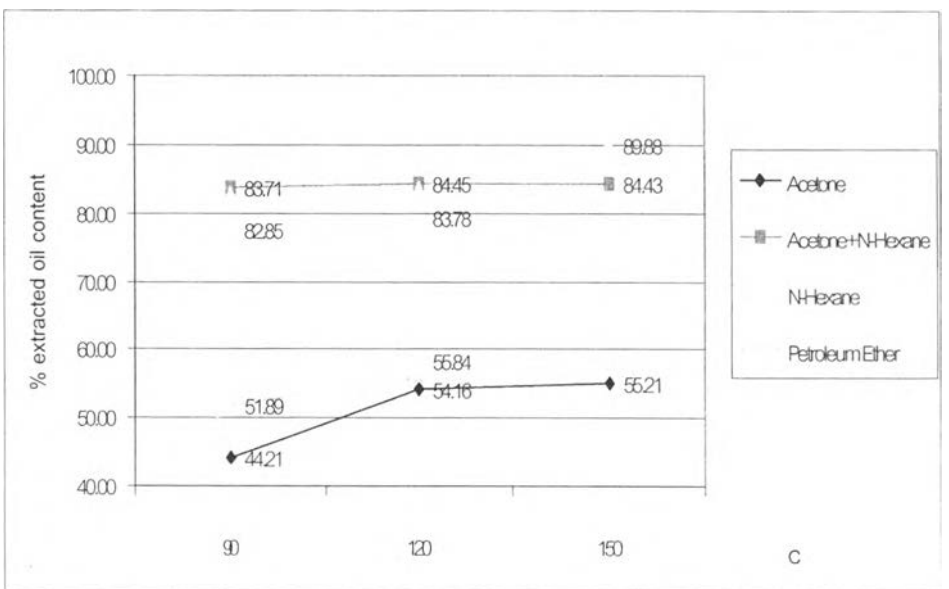

Figure 4-35: Extracted oil content as a function of microwave temperature programming of a cold roll mill (SUS) by varying solvent types

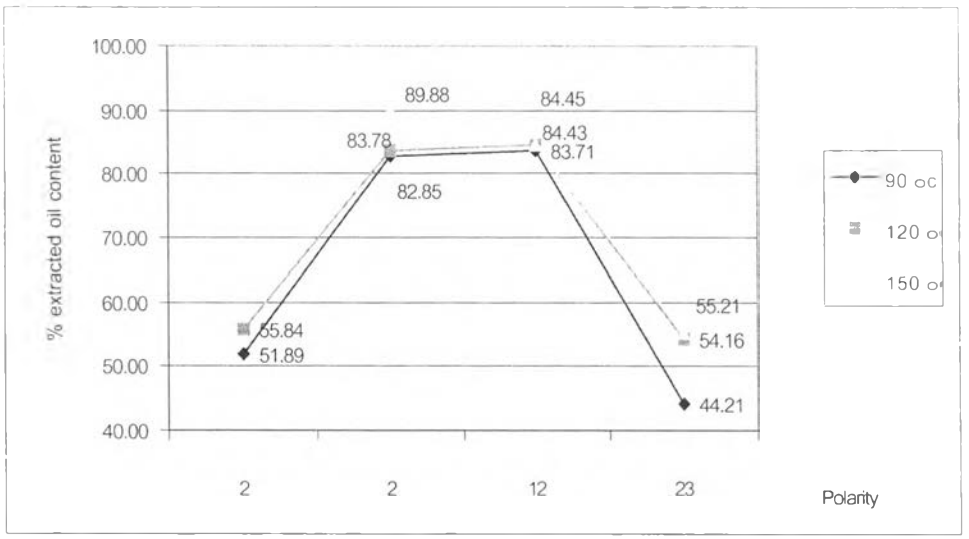

Figure 4-36: Extracted oil content as a function of solvent type of a cold roll mill (SUS) by varying microwave temperature program

Extracted oil content were significantly high comparing to other sample sources. The effect of temperature could be seen from Figure 4-35. It was found that higher temperature gave higher percent extracted oil. With regard to polarity of solvent, it could be clearly noticed that N-hexane and mixture of acetone with N-Hexane provided better results. However petroleum ether which is non-polar solvent similar to N-hexane gave the significantly lower result in percentage of extracted. The reason was that petroleum ether was a mixture of alkane substance of C4 to C6. The selected petroleum ether used in this research mostly composed of C4 as major ingredient with boiling temperature 40-60 C. Comparing to N-Hexane, the selected petroleum ether had a smaller molecular size which caused the lower solubility of extracted oil in the selected petroleum.

4.2.1.6 Cold Roll Mills

From item No. 4.2.1.4 and 4.2.1.5, they both were sludge from cold rolling operations. It was found that percent extracted oil from each source were significantly different. TCRSS samples gave low percent extracted oil content with high standard variation, while SUS sludge samples contained high percent extracted oil ranging from 44 to 90 % (dry weight). Considering condition of microwave extraction, SUS samples showed a trend of higher extraction with higher temperature for all solvent types and also the effect of solvent type and molecular size. Overall

result for cold rolling mill, the optimum condition of microwave extraction was 150 C temperature program and mixture of Acetone and N-Hexane. However, each cold rolling mill had individual technical of process and operation and several oil types, they could be significantly caused different extracted oil content and detailed condition of extraction as well.

4.2.2 Cost estimation

Cost of operation with microwave extraction were one of major factors that needed to be considered further than extracted oil, if the method would be brought into industrial environment. Different temperature program or types of solvent mean different cost of operation. However, cost of microwave extraction in the laboratory scale was very expensive which was shown the below. (Detail of calculation was shown in appendix F)

1. Cost of Electricity

• Microwave extraction equipment	1600	Watt
• Extraction time	30	Minute/12 samples
• Electricity price	2.5	B./unit
• Sample weight	1	g./sample
• **Total cost of electricity**	**0.167**	**B./gram of sample**

2. Cost of Solvent

• Acetone	380 B./2500 ml
• N-Hexane	630 B./2500 ml
• Petroleum Ether	400 B./1000 ml
• Mixture of acetone+N-hexane	505 B./2500 ml
• Solvent usage	30 ml/gram of sample
• Acetone cost	4.56 B./sample
• Mixture acetone and N-hexane	6.06 B./sample
• N-hexane cost	7.56 B./sample
• Petroleum ether cost	12 B./sample
• Solvent recovery	99 %

- **Total cost of acetone usage** **0.0456 B./sample**
- **Total cost of mixture acetone+N-hexane** **0.0606 B./sample**
- **Total cost of N-hexane** **0.0756 B./sample**
- **Total cost of petroleum ether** **0.12 B./sample**

Cost estimation in term of Baht/gram of obtained extracted-oil at various microwave temperature programming and different solvent types of each source could be explained in Figure 4-37 to 4-40.

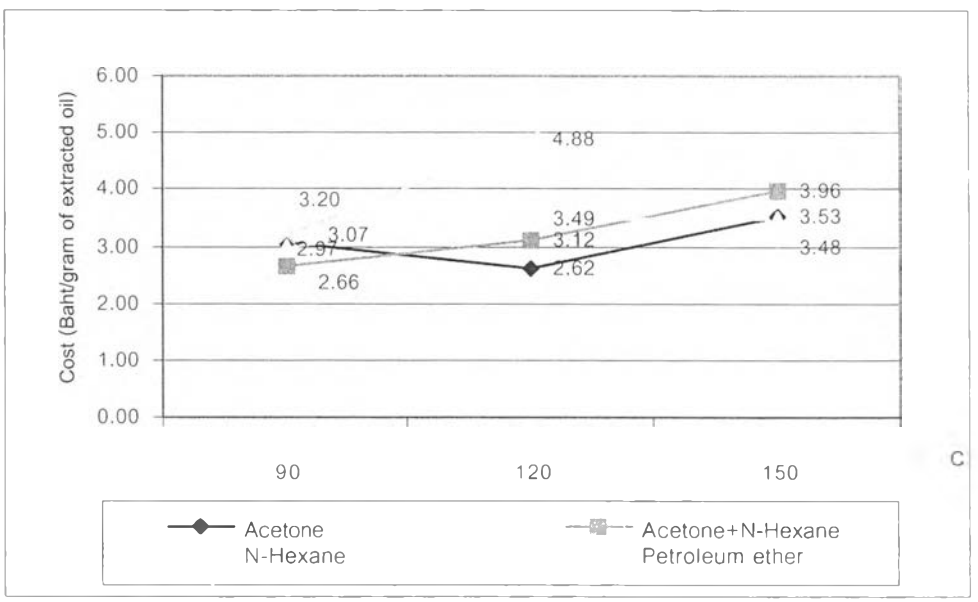

Figure 4-37 Cost Estimation in term of B./gram of obtained extracted-oil at various temperature programming and different solvent types of a hot roll mill (SSI)

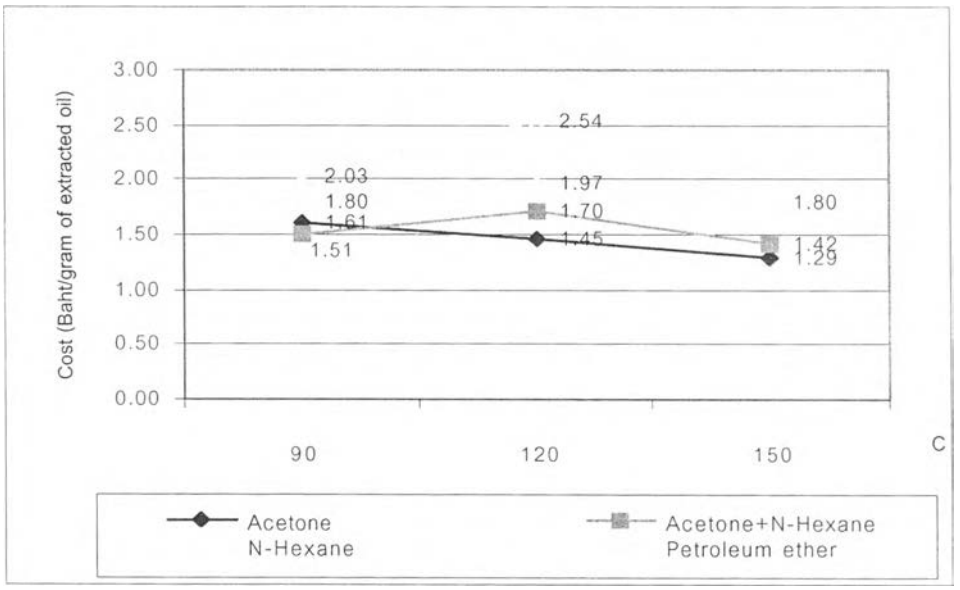

Figure 4-38 Cost Estimation in term of B./gram of obtained extracted-oil at various temperature programming and different solvent types of a hot roll mill (SSSM)

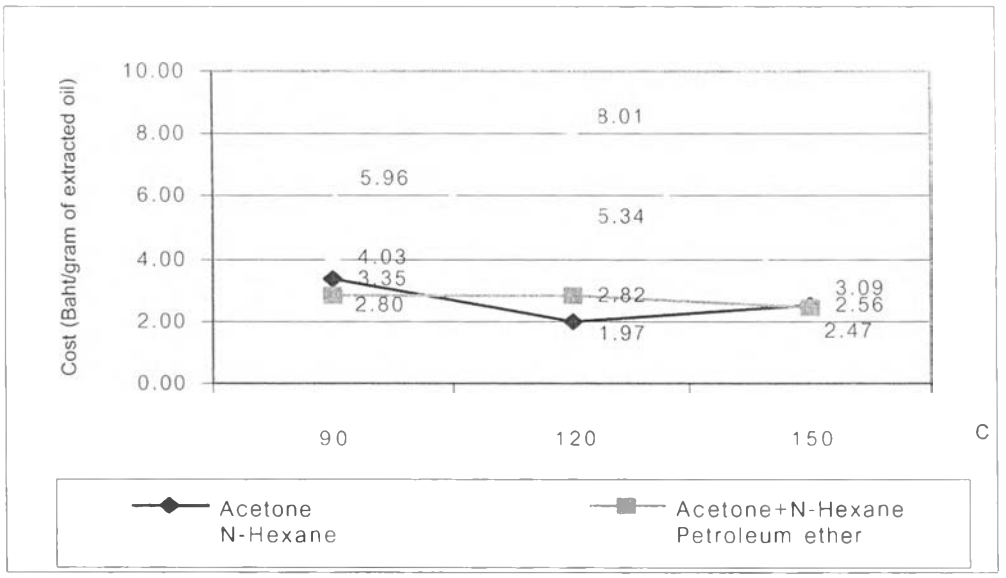

Figure 4-39 Cost Estimation in term of B./gram of obtained extracted-oil at various temperature programming and different solvent types of a cold roll mill (TCRSS)

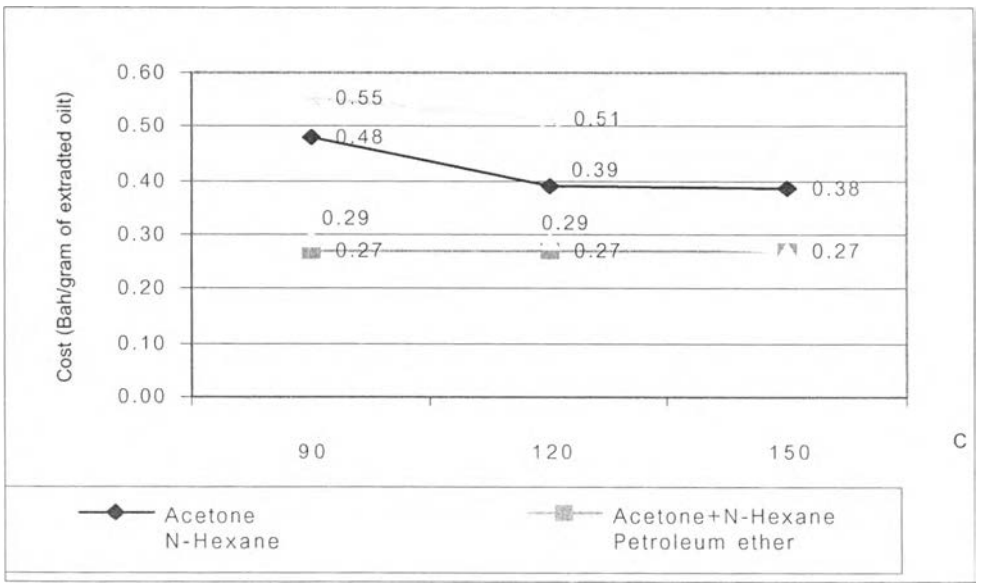

Figure 4-40 Cost Estimation in term of B./gram of obtained extracted-oil at various temperature programming and different solvent types of a cold roll mill (SUS)

From Figure 4-37 to 4-40, the results of operating cost from the aspect of solvent types were aligned for samples from SSI, TCRSS, and SSM. Acetone was the cheapest extract solvent (Baht per gram of obtained extracted oil content). Differ

from the other, SUS had the cost rank (from cheapest Baht per gram of obtained extracted oil) as following: mixture of acetone and N-hexane, N-hexane, acetone and petroleum ether, respectively. Even the cost of acetone which were only 75% of mixture of acetone and N-hexane price and 60% of N-hexane price, but it could not compensate with its deficiency in extraction comparing to mixture of acetone and N-hexane.

In term economy of scale, the cost of extraction from this research may not represent the actual cost of industrial environment. In industrial environment, solvents will be commercial grade and can be recovered from the process. Also the design of microwave system will be different and support a mass operation, which will significantly cost less than lab or research scale.

4.2.3 Obtained material recycling

4.2.3.1 Fine iron oxide material for re-melting

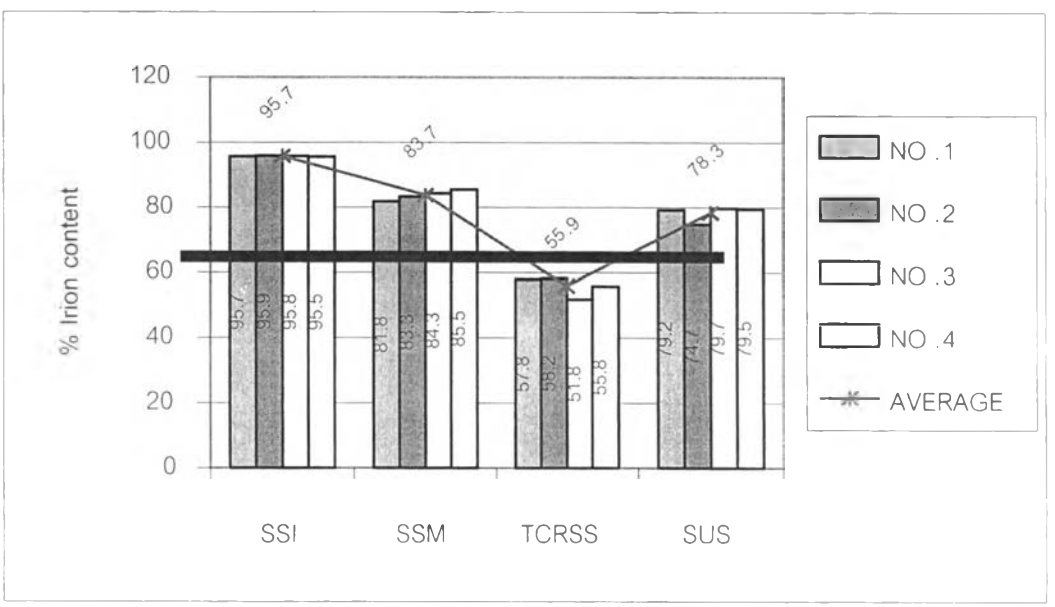

Figure 4-41 Percent of iron content in the obtained solid after extraction

As the Figure 4-41, three out of four extracted remains had percent iron content higher than 70%, which were SSI, SSM and SUS. It was clearly observed

that hot roll mill's extracted remains were significantly higher in percentage of iron content than cold roll mill's and also significantly higher than 70% which was the lowest minimum iron content could be used raw material in re-melting mill.

The obtained solid containing iron more than 70% could be sold for re-melting mill. Price of obtained solid containing high iron's raw material was 10$/ton

4.2.3.2 Extracted oil for used be fuel in cement kiln

Table 4-7: Result of major characteristic of recycled oil for being secondary fuel between rolling mills and cement kiln

Parameter	Extracted oil from SSI	Extracted oil from SSM	Extracted oil from TCRSS	Extracted oil from SUS	Allowable Characteristic for fuel using in cement kiln	
					Liquid fuel	Lignite
Heat value (cal/g)	10526	10391	11071	8434	> 500	> 4,000
Sulfur content (%)	0.63	0.78	0.31	0.29	< 4.0	N.D.
Chloride content (ppm)	0.0003	0.0006	0.0005	0.0002	< 1.0	N.D.
Heavy metal content (%)						N.D.
- Chromium (Cr)	0	0	0	0.0008	< 0.1	N.D.
- Vanadium (V)	0.0002	0	0	0.0001	< 0.1	N.D.
- Nikel (Ni)	0	0	0	0.0008	< 0.1	N.D.
- Zinc (Zn)	0.0015	0.0048	0.0015	0.0029	< 0.1	N.D.
- Copper (Cu)	0.0001	0.0004	0	0	< 2.0	N.D.
- Telenium (Tl)	0.0021	0	0	0	< 0.1	N.D.
- Arsenic (As)	0	0	0	0	< 0.1	N.D.
- Lead (Pb)	0	0	0	0	< 1.0	N.D.
- Mercury (Hg)	0	0	0	0	< 0.01	N.D.
- Cadmium (Cd)	0	0	0	0	< 0.1	N.D.

Noted: From Siam Cement Public Co., Ltd. (2000)

Fuels in cement kiln were 2 types, which were liquid fuel and solid fuel. The liquid fuel was called "synthetic fuel". As in the results in Table 4-7 found that all major characteristics of recycled oil including heating value, sulfur content, chloride content and ten heavy metals of all hot rolling and cold rolling samples from dry weight form could be liquid fuel in cement kiln. The other fuel type, main fuel in cement kiln, was called "Lignite" which concerned only heating value for being fuel. The heating value results of all samples were 8,434 – 11,071 cal/g which were about 2-3 times more than cement's specification of > 4,000 cal/g.

4.2.4 Compositions of the dewatered sludge

In this study, the major compositions of the de-watered sludge obtained from rolling mills were classified into four types of materials such as water, oil, iron and other solid material.

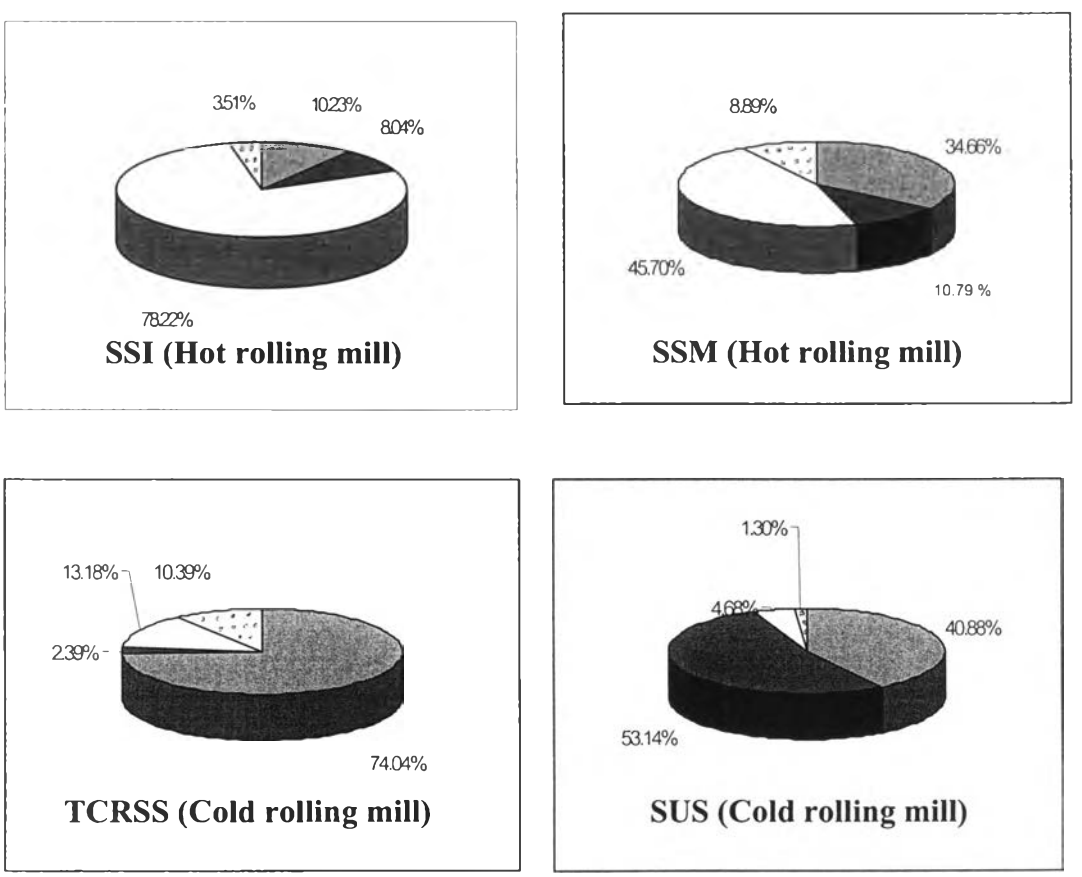

Figure 4-42: The composition of water, oil, iron and other solid in the sludges from various sources.

Based on the experimental results, percent of water, oil, iron and other solid material were illustrated in Figure 4-42, it was shown that only the de-watered sludge from SSI contains 78.22% iron content. There was higher than 70% iron content (The acceptable iron content for sale as remelting material), thus, the de-watered sludge from SSI could be sold for direct remelting without extraction.

Consideration of extraction cost, it was very expensive method. So It had to study in commercial scale before selected management method.

Consideration of water content in de-watered sludge, it was notified that moisture content of hot rolling sludges were less than those of cold rolling's sludges.

This may be attributed to the reason that the dewatering processes of hot rolling mills were more efficient than those of cold rolling mills.

Concerning oil content, it could be seen that oil contents of 8.04% and 10.79% in hot rolling sludges from SSI and SSM were comparable but oil contents in cold rolling sludges from TCRSS of 2.39% were obviously different to those of 53.14% from SUS. The factors used for making the explanations of such different value of oil contents in cold rolling sludges were not cleared.

According to Figure 4-42, the percentage of other solid material in de-watered sludge from both rolling operations were also investigated. The values of as low as 3.51-8.89% and 1.30-10.39% of other solid materials were found in hot rolling dewatered sludges and cold rolling de-watered sludges, respectively. The elements containing in other solid materials determined by X-ray fluorescence are depicted in Table 4-8 and detailed in appendix F)

Table 4-8: Elements in other solid material

Element	SSI	SSM	TCRSS	SUS
Na	<<	√	√	<<
Mg	√	<<	√	√
Al	√	√	√	√
Si	√	√	√	√
P	√	√	√	√
S	√	√	√	√
Cl	<<	√	√	<<
K	<<	<<	<<	<<
Ca	√	√	√	√
Cr	<<	√	<<	<<
Mn	<<	√	<<	<<
Fe	√	√	√	√
Ni	<<	<<	-	<<
Cu	<<	√	-	<<
Zn	-	<<	-	-
Mo	-	<<	-	-

Remark : √ - not less than 0.1 %
<< - less than 0.1 %
- - not detectable