



CHAPTER IV

RESULTS & DISCUSSION

4.1 Characterization of Waxes by GC

Petroleum wax contains many types of hydrocarbon structure, this investigation tried to establish a fractionation and analysis method that will enable purified wax fraction to be produced and characterized. In order to carry out analysis for carbon distribution of the wax fractions obtained from fractionation of slack waxes by using extraction and crystallization techniques, the most appropriate GC analysis method must be used. GC analysis method is convenient and accurate when compared with other methods (see in Chapter 2.6). This section provides a comparison on the GC analysis efficiency using the ASTM D 5442-93 and HT GC methods.

4.1.1 Comparison of Chromatographic Results Obtained According to ASTM D 5442-93 and by Using HT GC

The hydrocarbon contents in 500SW and 600SW slack waxes were determined by using standard GC analysis methods for petroleum waxes (ASTM D 5442-93) compared with HT GC. Both slack waxes were completely dissolved in an appropriate solvent, cyclohexane (for ASTM D 5442-93) and carbon disulfide (for HT GC). The samples prepared were introduced into a GC columns by using suitable operating condition for each. (see in Chapters 3.5.1 and 3.5.2). The chromatograms obtained from ASTM D 5442-93 & HT GC for 500SW & 600SW slack waxes are shown in Figures 4.1 to 4.4, respectively.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

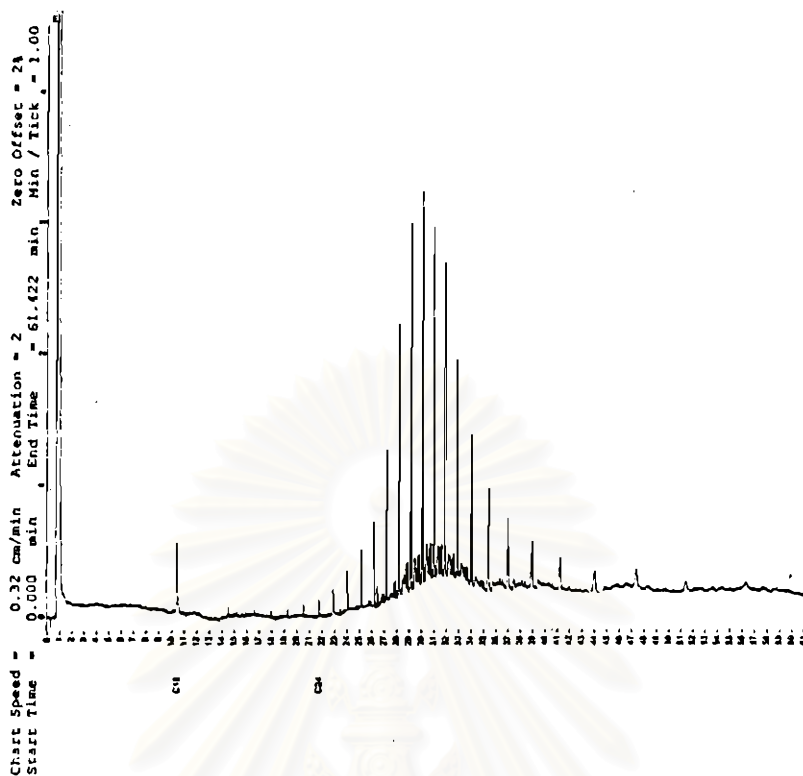


Figure 4.1 GC chromatogram of 500SW obtained according to ASTM D 5442-93

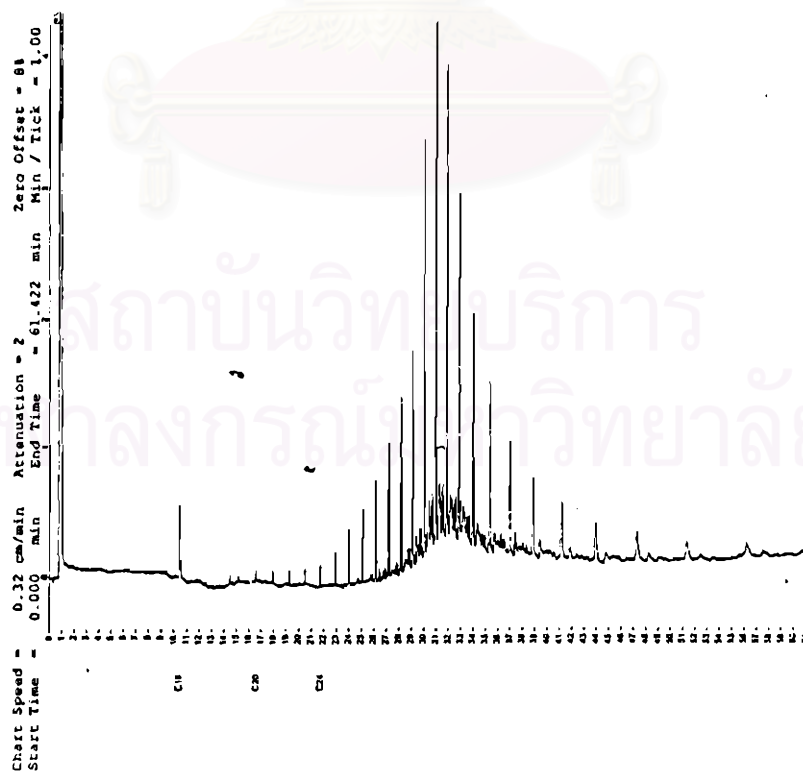


Figure 4.2 GC chromatogram of 600SW obtained according to ASTM D 5442-93

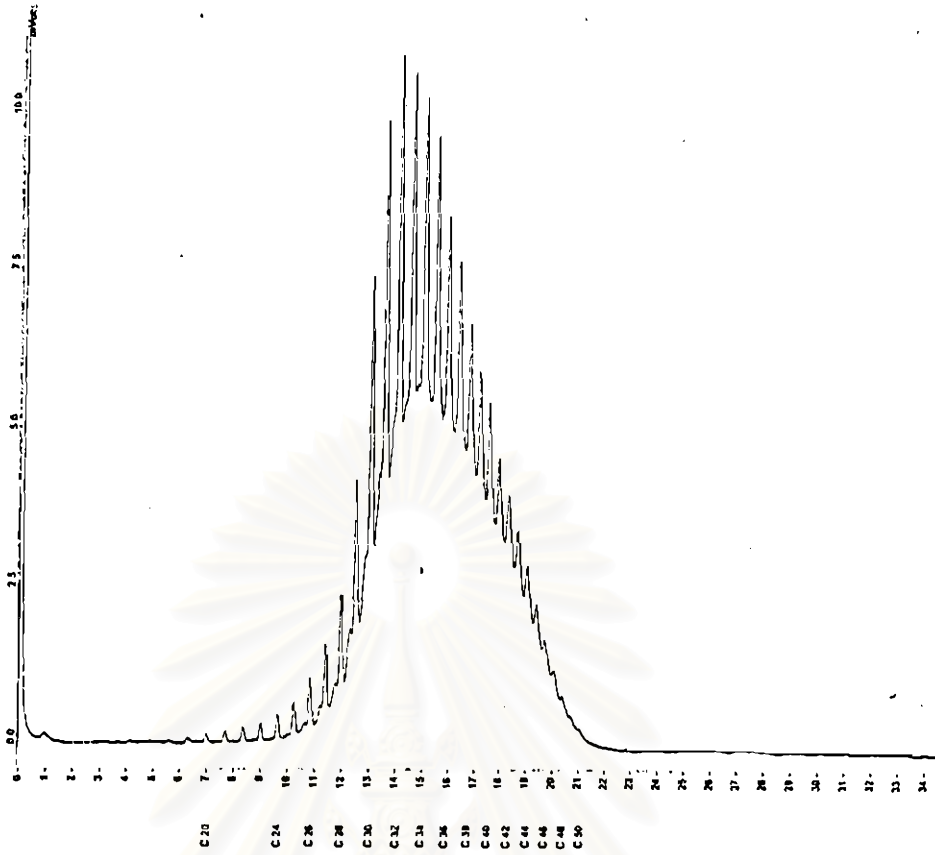


Figure 4.3 GC chromatogram of 500SW obtained using HT GC

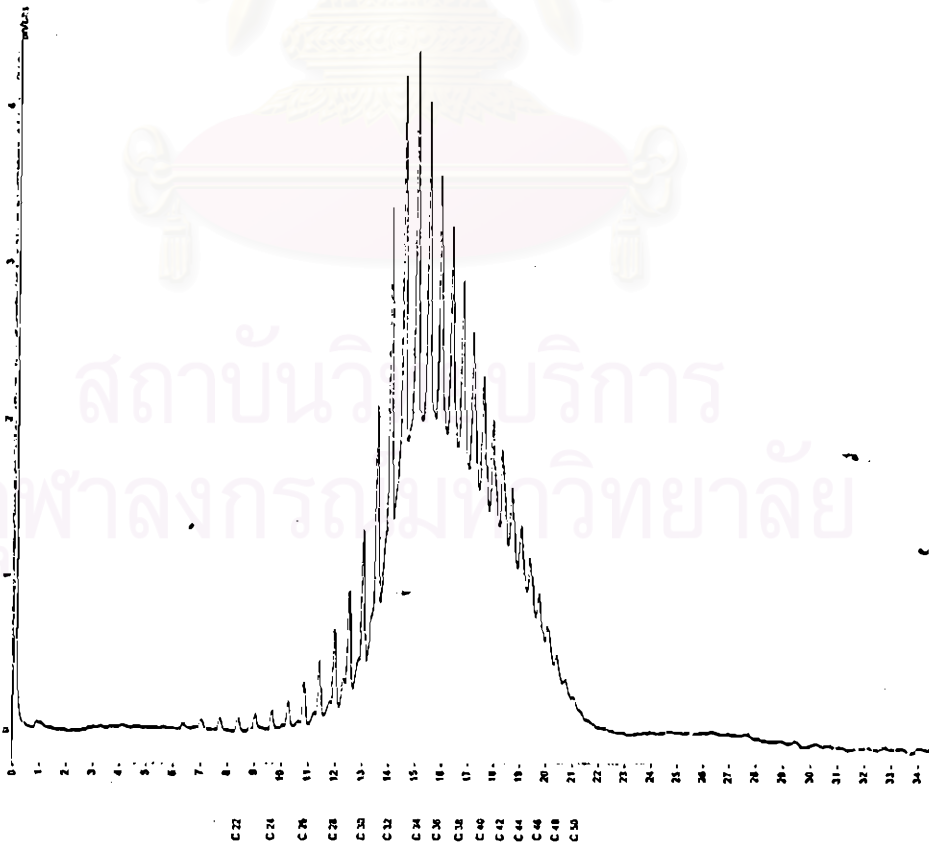


Figure 4.4 GC chromatogram of 600SW obtained using HT GC

The hydrocarbon numbers in each GC chromatogram were determined according to chromatographic identification procedure given in Sect. 3.3.3. The results indicated that :

- 1) **ASTM D 5442-93 method** could determine the hydrocarbon number from C₁₆ through C₄₄. For wax with hydrocarbon greater than C₄₅ complete elution of all components may not be achieved under the specified conditions. (see in Sect. 2.6).
- 2) **HT GC method** could determine the hydrocarbon number in waxes from C₁₆ to greater than C₉₂. (see in Figure A1).
- 3) Since the 500SW and 600SW slack waxes contained hydrocarbons which had carbon number greater than C₄₄ so the ASTM D 5442-93 method was not suitable. The HT GC method had a detection range which can cover the complete carbon number range of both slack waxes (C₁₉ to C₅₂), with both normal and non-normal hydrocarbon contents, so it was selected as the most appropriate method. Thus, all GC chromatograms of waxes in this research were obtained by using HT GC method. The residual waxes and oils in this research were characterized using the same procedure.

4.1.2 Composition of 500SW and 600SW Slack Waxes by HT GC

According to chromatographic identification (in Sect. 3.3.3) and percentage calculation for N and NON (in Sect. 3.3.4), the characterization of 500SW and 600SW slack waxes were obtained as shown in Table 4.1.

Table 4.1 The characterization of 500SW and 600 SW by HT GC

Slack Waxes	Hydrocarbons	Fractions, %		
		N	NON	Oil *
500SW	C ₁₉ to C ₅₂	19.53	51.66	28.81
600SW	C ₁₉ to C ₅₂	22.83	56.30	20.87

* Oil content was determined by ASTM D 721

4.2 Solubility Study of 500SW and 600SW Slack Waxes

This experiment identified factors that have an effect on the solubility of 500SW & 600SW slack waxes in MEK and toluene. The solubility data obtained was used in finding the most suitable method and best solvent for wax purification using solvent.

The solubility of 500SW & 600SW slack waxes in MEK and toluene was compared at various temperatures (0, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50 and 55 °C). Further to this, the solubility of “MEK-soluble-waxes” in MEK was also studied. The waxes which were obtained from the 1st extraction (see in Chapter 4.3.1) were called “solvent-soluble-wax”. The MEK-soluble-waxes obtained at optimum extraction condition of the first extraction for 500SW & 600SW slack waxes (55 °C) were selected for further study of their solubility in MEK at 40, 45, 50 and 55 °C, for comparison with the solubility of 500SW & 600SW slack waxes in MEK.

When the results in Tables 4.2 and 4.3 were plotted between the solubility against temperature, the curves in Figures 4.5 and 4.6, respectively, were obtained.

Table 4.2 Solubility of 500SW & 600SW slack waxes in MEK & toluene at various temperatures (Unit : Grams of wax in 100 ml. of solvent)

Solvent	E Debye	Wax	Temperature (°C)											
			0	5	10	15	20	25	30	35	40	45	50	55
Toluene	0.36	500SW	I	I	I	0.21	0.61	1.84	5.03	12.09	21.21	49.16	G	G
		600SW	I	I	I	0.10	0.41	1.05	2.89	8.58	18.77	36.25	G	G
MEK	2.77	500SW	I	I	I	I	I	I	I	I	0.17	0.48	1.39	11.60
		600SW	I	I	I	I	I	I	I	I	0.04	0.19	0.84	4.20

Notes : E = Dipole Moment of Solvent, I = Insoluble, G = Good solubility

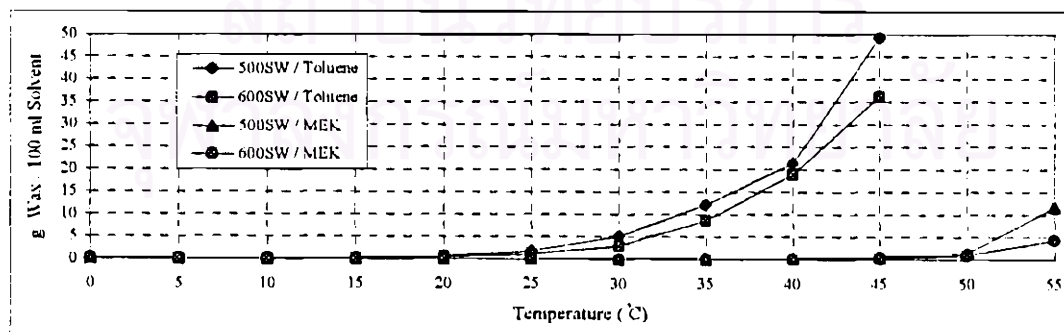


Figure 4.5 Temperature-solubility curves of 500SW & 600SW slack waxes in MEK and toluene

Table 4.3 Solubility of 500MEK- & 600MEK-soluble-waxes (from the 1st extraction) in MEK at various temperatures (Unit : Grams of wax in 100 ml. of MEK)

MEK Soluble Waxes	Temperature (°C)			
	40	45	50	55
500SW	Insoluble	1.07	3.99	Good solubility
600SW	Insoluble	0.68	2.29	Good solubility

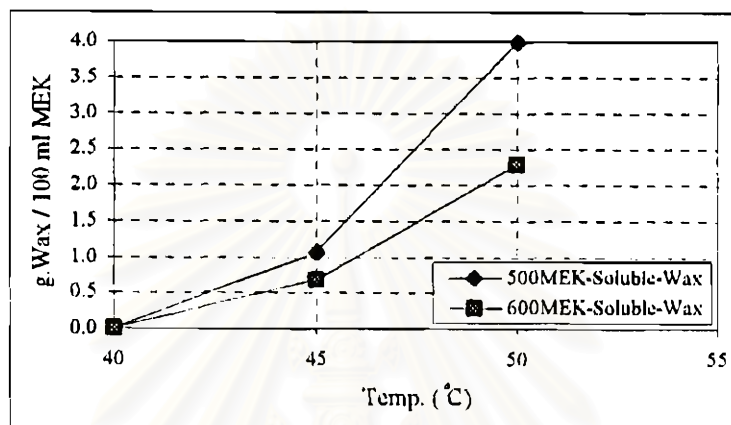


Figure 4.6 Temperature-solubility curves of 500MEK- & 600MEK-soluble-waxes (from the 1st extraction) in MEK

It was found that the solubility of waxes was depended upon the: temperature, solvent type, and wax composition (The solubility data are given in Figures 4.5 and 4.6):-

- 1) Solvent** The waxes were more soluble in toluene than in MEK. The polarities of toluene and MEK, measured using the dipole moment, were 0.36 and 2.77 Debye, respectively. Toluene is a hydrocarbon solvent without donor atoms and hydrogen-bond-forming capability, so there was better wax solubility in it than in MEK since the waxes contain only hydrocarbons. MEK, on the other hand, is a solvent that has donor atoms but no active hydrogen atom, therefore bonding between molecules of solute and solvent increased at higher temperature.
- 2) Temperature** Irrespective of solvent polarity, the solubility of all waxes increased rapidly as the temperature was increased.
- 3) Composition of waxes** An increase in the oil, microcrystalline wax and paraffin wax content corresponded with an increase in the wax solubility. The relationship of the wax composition and their solubility is summarized in Table 4.4 below.

Table 4.4 showed that the 600MEK-soluble-wax has similar oil content to the 500SW wax but it had higher solubility and microcrystalline wax content (57.60% vs 51.66 %). The oil content in the waxes had a profound effect on the wax solubility. Higher oil content increased the solubility in MEK. The solubility was also influenced by the amount of microcrystalline wax content since it has a similar structure to the oil. It was confirmed that solubility of oil in MEK was higher than solubility of wax in MEK at every temperature, as shown in Figure 2.2.

Table 4.4 Composition and solubility (g wax/100 ml MEK) of waxes

Type of Waxes * = (from 1 st extraction)	Composition, wt %		Solubility	
	Microcrystalline	Oil	45 °C	50 °C
500 MEK-Soluble-Wax*	46.63	37.86	1.07	3.99
600 MEK-Soluble-Wax*	57.60	28.97	0.68	2.29
500SW	51.66	28.81	0.48	1.39
600SW	56.30	20.87	0.19	0.84

4.3 The Effect of Temperature and Solvent on Slack Waxes Extraction

In order to increase understanding of the effect of the temperature and solvent type on the slack waxes' solubility (see Chapter 4.2), the objectives of this experiment are to study :-

- 1) The effect of the solvent extraction temperature and solvent (MEK & toluene) on the wax composition obtained from 500SW & 600SW slack waxes.
- 2) Changes in the wax composition after the 2nd extraction performed on the extracted wax which was obtained at optimum condition of the first extraction.

HT GC was used to monitor the changes in the extracted wax composition.

4.3.1 1st Extraction of 500SW and 600SW Slack Waxes at Different Temperatures Using MEK and Toluene as Solvents.

The first extraction of 500SW and 600SW slack waxes was performed at 15, 20, 25, 30, 35, 40 and 45 °C for toluene as a solvent, and 40, 45, 50 and 55 °C using MEK as a solvent.

Solvent-soluble-wax was obtained by evaporating the solvent from the filtrate. The wax cake was obtained by filtration and drying the solidified wax from the solvent-wax slurry. The oil content in all wax cakes and solvent-soluble-waxes was determined

according to ASTM D721-93. Analysis of n-paraffin and microcrystalline waxes composition in all waxes was obtained by using HT GC. The oil, n-paraffin & microcrystalline wax contents in both the solvent-soluble-waxes and wax cakes, extracted at various temperature by using MEK and toluene, are shown in Tables 4.5 and 4.6, respectively. Figures 4.7 to 4.10 show plots of the wax composition vs extraction temperature.

Table 4.5 Extraction of 500SW and 600SW slack waxes at various temperatures by using MEK (Unit = % by weight)

T (°C)	500 SW						600 SW					
	Soluble Wax			Wax Cake			Soluble Wax			Wax Cake		
	N	Mic.	Oil	N	Mic.	Oil	N	Mic.	Oil	N	Mic.	Oil
40	19.05	45.28	35.67	70.78	29.22	nil	21.37	51.61	27.02	69.31	30.69	nil
45	16.65	45.81	37.54	68.13	31.87	nil	20.64	52.25	27.11	66.61	33.39	nil
50	15.73	46.48	37.79	63.56	33.73	2.71	18.82	52.64	28.54	64.99	32.98	2.03
55	15.51	46.63	37.86	56.88	36.59	6.53	13.43	57.60	28.97	60.78	34.11	5.11

Table 4.6 Extraction of 500SW and 600SW slack waxes at various temperatures by using toluene (Unit = % by weight).

T (°C)	500 SW						600 SW					
	Soluble Wax			Wax Cake			Soluble Wax			Wax Cake		
	N	Mic.	Oil	N	Mic.	Oil	N	Mic.	Oil	N	Mic.	Oil
15	21.70	49.05	29.25	85.37	14.63	nil	24.51	47.25	28.24	79.31	20.69	nil
20	19.84	49.67	30.49	81.37	18.63	nil	22.87	47.47	29.66	76.74	23.26	nil
25	19.78	49.71	30.51	75.39	24.61	nil	21.76	48.29	29.95	75.33	24.67	nil
30	19.08	49.82	31.10	73.20	26.80	nil	21.61	48.34	30.05	75.11	24.89	nil
35	18.52	50.18	31.30	56.03	36.82	7.15	21.58	48.31	30.11	51.37	40.94	7.69
40	17.27	50.49	32.24	53.92	37.04	9.04	21.26	48.34	30.40	36.84	43.60	19.56
45	14.39	51.00	34.61	27.28	53.12	19.60	19.15	49.18	31.67	26.03	52.31	21.66

Figures 4.7 and 4.8 show that the composition of 500MEK- & 600MEK-soluble-waxes contained microcrystalline wax more than oil, and less of n-paraffin, while the 500 and 600 wax-cakes contained n-paraffin wax more than microcrystalline wax and less oil. The n-paraffin wax content in MEK-soluble-waxes decreased slowly with an increase in the temperature while the oil and microcrystalline wax contents increase. The oil and

microcrystalline wax contents of the wax cakes increased slowly with the temperature while the n-paraffin wax content decreased.

Figures 4.9 and 4.10 show that the composition of toluene-soluble-waxes was similar to MEK-soluble-waxes. The n-paraffin wax content in 500 and 600 wax-cakes from the extraction using toluene decreased slowly from 15 to 30 °C and then decreased rapidly from 30 to 45 °C, while the oil and microcrystalline wax contents increased at higher temperature.

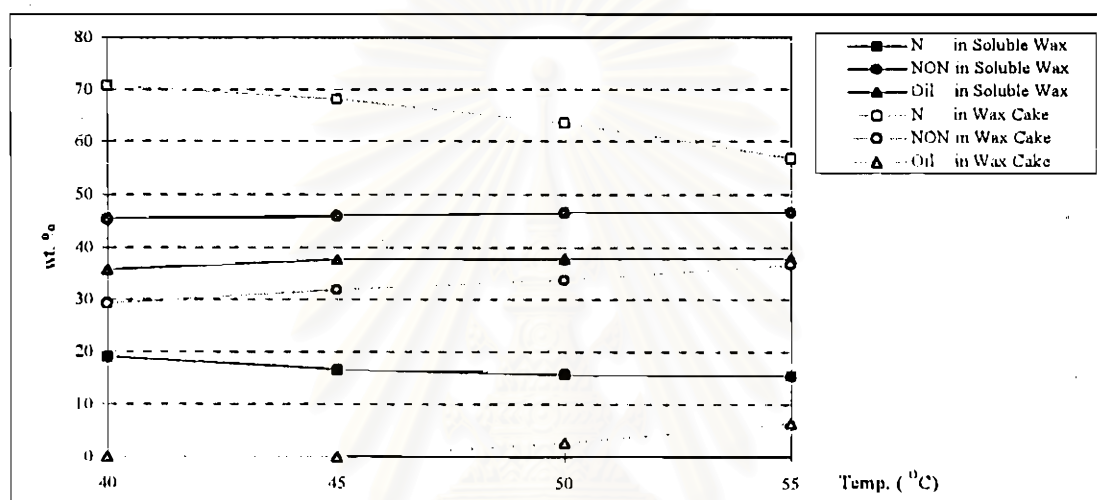


Figure 4.7 Wax composition vs temperature curves for 500MEK-soluble-wax and 500 wax-cake from 500SW using MEK as a solvent.

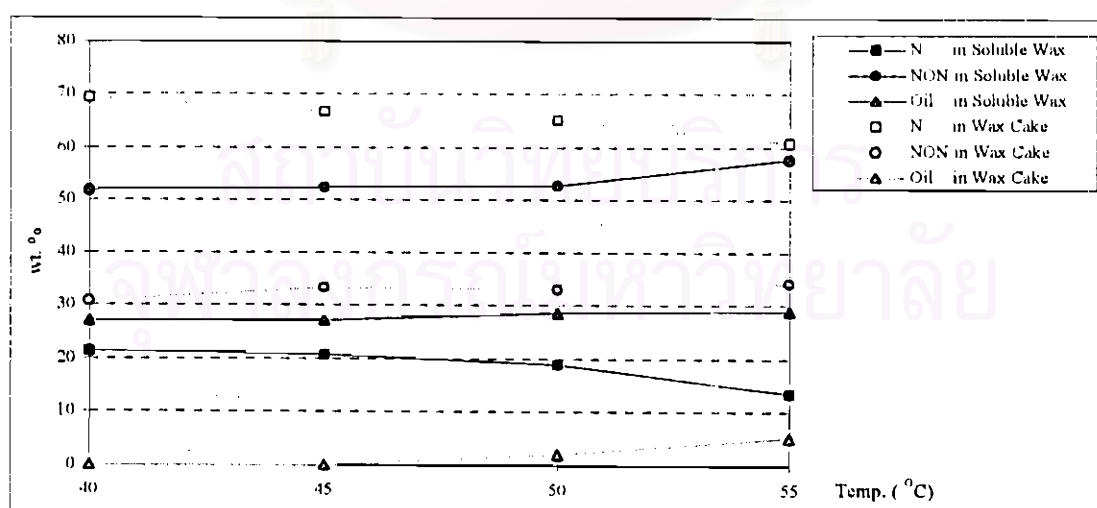


Figure 4.8 Wax composition vs temperature curves for 600MEK-soluble-wax and 600 wax-cake from 600SW using MEK as a solvent.

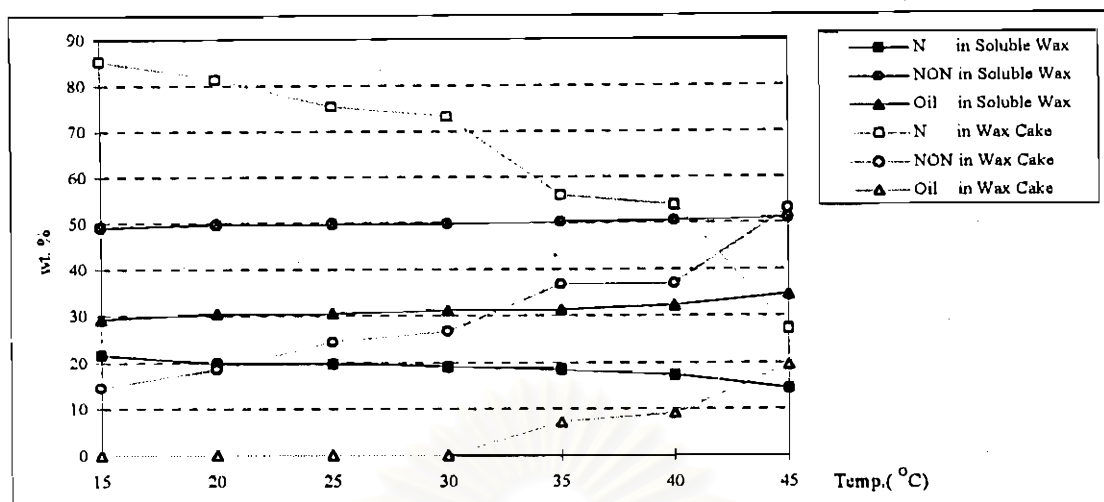


Figure 4.9 Wax composition vs temperature curves for 500toluene-soluble-wax and 500 wax-cake from 500SW using toluene as a solvent.

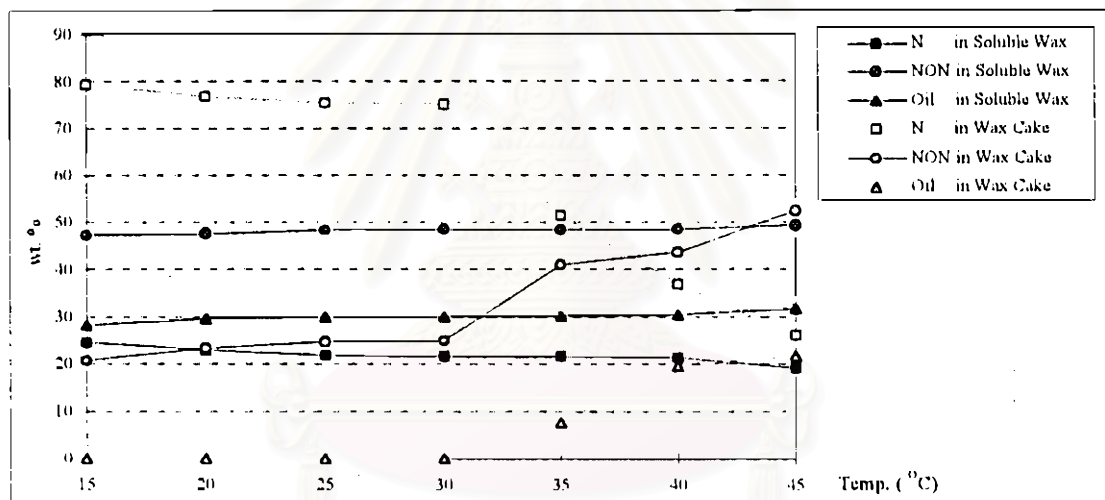


Figure 4.10 Wax composition vs temperature curves for 600toluene-soluble-wax and 600 wax-cake from 600SW using toluene as a solvent.

The results indicated that the microcrystalline and oil contents of the solvent-soluble-waxes, extracted using either MEK or toluene, increased with the extraction temperature while n-paraffin content decreased. This was considered to be because the oil and microcrystalline wax dissolved more readily in MEK and toluene than n-paraffin wax. The limited solubility of oil and microcrystalline wax in MEK and toluene probably caused an increase in the amount of microcrystalline and oil contents in the wax cakes with an increase in the temperature.

4.3.2 2nd Extraction of 500MEK- and 600MEK-Soluble-Waxes Using MEK

The solvent-soluble-waxes from the first extraction at optimum conditions were selected for the second extraction. The criteria for selection of the optimum extraction conditions were as follows. The solvent-soluble-wax should contain a large amount of microcrystalline wax and oil with small amount of n-paraffin wax, while the wax cake should have the opposite composition. The properties of solvent-soluble-wax and wax cake extracted at 55 °C using MEK satisfied these criteria (see Table 4.5).

The aim of the second extraction was to determine the efficiency of continuous extraction of 500MEK- and 600MEK-soluble-waxes using MEK. The efficiency of the second extraction was determined using criteria similar to the first extraction.

The 500MEK-and 600MEK-soluble-waxes obtained from the optimum conditions of the first extraction, were extracted using the same procedure as the first extraction using MEK (see in Chapter 4.3.1) at temperatures of 45 and 50 °C at which they were soluble in MEK (see in Table 4.3). The amount of oil, n-paraffin and microcrystalline waxes in MEK-soluble-waxes and wax-cakes, from the second extraction by MEK are given in Table 4.7.

The composition of MEK-soluble-waxes from the second extraction (Table 4.7) was similar to the composition in MEK-soluble-waxes from the first extraction (Table 4.5). The oil content of MEK-soluble-waxes from the second extraction increased rapidly at higher temperatures. Irrespective of the oil content, the n-paraffin of MEK-soluble-waxes from the second extraction was high (~ 17 to 25 wt. %).

Table 4.7 2nd extraction of 500MEK- and 600MEK-soluble-waxes (from 1st extraction) using MEK at 45 and 50 °C (Unit : % by weight).

T (°C)	500 SW						600 SW					
	Soluble Wax			Wax Cake			Soluble Wax			Wax Cake		
	N	Mic.	Oil	N	Mic.	Oil	N	Mic.	Oil	N	Mic.	Oil
45	14.88	43.04	42.08	71.36	28.64	nil	12.40	48.64	38.96	75.45	24.55	nil
50	11.33	44.08	44.59	43.50	43.19	13.31	10.35	50.27	39.38	58.25	37.47	4.28

The targeted wax composition was high level of microcrystalline wax in MEK-soluble-wax and high level n-paraffin wax in the wax cake. The extraction of MEK-soluble-wax and wax cake should be done over and over again in order to obtain different fractions at different extraction temperatures.

4.4 Study of Fractionation Crystallization

The relationship between the solubility of slack wax and its composition, which is sensitive to molecular structure and temperature, is important in the fractionation of slack wax by solvent extraction. Structural fractionation of slack wax was done by crystallization at low temperatures in order to study the effect of low temperature on the composition of crystalline waxes and solvents on the wax crystallization.

Fractionation crystallization of 500SW & 600SW slack waxes was done by dissolving slack wax at 40 °C in 100ml solvent according to its solubility (Table 4.2). The solution was cooled down step by step to 30, 20, 10, 0, -10 and -20 °C. The crystalline waxes at each temperature were separated by filtration. The solvent in the filtrate obtained from crystallization at -20 °C was allowed to evaporate out leaving only the oil. The composition of crystalline waxes and oils was analyzed by using HT GC. The oil content was determined according to ASTM D 721-93. The results are summarized in Tables 4.8 and 4.9 (for MEK & toluene based crystallization, respectively).

Table 4.8 Fractionation crystallization of 500SW and 600SW slack waxes by using MEK as a solvent (Unit = % by Weight)

T (°C)	500SW			600SW		
	N	Mic.	Oil	N	Mic.	Oil
30	66.87	33.13	nil	58.55	41.45	nil
20	51.78	48.22	nil	22.04	77.96	nil
10	26.07	73.93	nil	15.49	84.51	nil
0	17.58	82.42	nil	15.13	84.87	nil
-10	17.04	82.96	nil	14.00	86.00	nil
-20	15.23	84.77	nil	13.53	86.47	nil
Residual Oil	3.18	-	96.82	3.97	-	96.03

Table 4.9 Fractionation crystallization of 500SW and 600SW slack waxes by using toluene as a solvent (Unit = % by Weight).

T (°C)	500SW			600SW		
	N	Mic.	Oil	N	Mic.	Oil
30	29.48	70.52	nil	36.23	63.77	nil
20	43.27	56.73	nil	53.51	46.49	nil
10	60.58	39.42	nil	59.84	40.16	nil
0	44.35	55.65	nil	39.70	60.30	nil
Residual Oil	6.39	-	93.61	8.08	-	91.92

Note : The waxes did not solidify at -10 and -20 °C.

From the results obtained, the following conclusions can be drawn.

- 1) The crystalline waxes that, obtained by fractionation crystallization of slack waxes in MEK, contained more n-paraffin wax at higher crystallization temperature but at lower crystallization temperature contained more microcrystalline wax. In the toluene based crystallization using similar conditions, it is found that, the composition of the crystalline waxes was irregular at all crystallization temperatures. It is evident that, between -10 and -20 °C, the waxes did not solidify in the toluene solution.
- 2) It is well known that oils are miscible in MEK and toluene at all temperatures so the absence of oil in the crystalline wax extracted was expected.
- 3) In Tables B56 to B69 the carbon number distribution and temperature are collected to give Table 4.10. Similarly, in Tables B70 to B79 are collected the same factors to give Table 4.11.

Table 4.10 Carbon number distribution of crystalline waxes crystallized from 500SW and 600SW slack waxes at various temperatures by using MEK.

(Unit = % by Weight, C/No. = Carbon number of crystallized wax).

T (°C)	C/No of 500 SW crystallized-wax			C/No of 600SW crystallized-wax		
	N	Mic.	Oil	N	Mic.	Oil
30	C ₂₉ -C ₅₀	C ₃₁ -C ₄₉	-	C ₂₆ -C ₄₉	C ₂₉ -C ₅₁	-
20	C ₂₆ -C ₄₅	C ₂₉ -C ₅₀	-	C ₂₄ -C ₄₇	C ₂₈ -C ₅₁	-
10	C ₂₃ -C ₄₇	C ₂₉ -C ₅₁	-	C ₂₂ -C ₄₇	C ₂₇ -C ₅₁	-
0	C ₂₃ -C ₄₆	C ₂₇ -C ₅₀	-	C ₂₀ -C ₄₆	C ₂₆ -C ₅₁	-
-10	C ₂₁ -C ₄₄	C ₂₇ -C ₅₀	-	C ₂₀ -C ₄₄	C ₂₆ -C ₅₁	-
-20	C ₂₀ -C ₄₂	C ₂₆ -C ₅₀	-	C ₂₀ -C ₄₄	C ₂₅ -C ₅₁	-
Residual Oil	C ₁₉ -C ₂₃ & C ₂₆ -C ₄₀	-	C ₂₆ -C ₅₀	C ₁₉ -C ₂₂ & C ₂₇ -C ₄₀	-	C ₂₆ -C ₅₀

The carbon numbers of n-paraffin & microcrystalline waxes, which crystallized in MEK, were higher at higher temperatures (Table 4.10). The waxes crystallized in toluene contained n-paraffin and microcrystalline waxes which had similar carbon number at all temperatures (Table 4.11). The results showed clearly that the carbon distribution number of the wax components in the extracted wax is a function of the solvent polarity. The polarity of toluene and MEK, measured using the dipole moment, were 0.36 and 2.77 Debye, respectively. MEK is a solvent that has donor atoms, therefore, bonding between molecules of solute and MEK decreased at lower temperature. It was confirmed that lower molecular weight of hydrocarbons in wax was preferentially crystallized in MEK at lower crystallization temperature. Toluene, on the

other hand, is a hydrocarbon solvent without any donor atom, so there was better wax solubility in it than in MEK since the waxes contain only hydrocarbons. It was confirmed that the waxes crystallized in toluene had similar carbon number to obtained waxes at all crystallization temperatures.

Table 4.11 Carbon number distribution of crystalline waxes crystallized from 500SW and 600SW slack waxes at various temperatures by using toluene.

(Unit = % by Weight, C/No. = Carbon number of crystallized wax).

T (°C)	C/No of 500 SW crystallized-wax			C/No of 600SW crystallized-wax		
	N	NON	Oil	N	NON	Oil
30	C ₂₆ -C ₄₉	C ₂₉ -C ₅₁	-	C ₂₆ -C ₅₁	C ₂₉ -C ₅₁	-
20	C ₂₆ -C ₄₈	C ₂₉ -C ₅₁	-	C ₂₅ -C ₄₉	C ₃₁ -C ₅₀	-
10	C ₂₇ -C ₄₅	C ₂₉ -C ₅₁	-	C ₂₇ -C ₄₈	C ₃₂ -C ₅₀	-
0	C ₂₅ -C ₄₇	C ₃₀ -C ₅₁	-	C ₂₅ -C ₄₈	C ₃₁ -C ₅₀	-
Residual Oil	C ₂₀ -C ₄₅	-	C ₂₄ -C ₅₁	C ₂₀ -C ₂₅ & C ₂₈ -C ₄₅	-	C ₂₆ -C ₅₁

4.5 Solvent Selection

Before the fractionation of slack waxes was established, comparison on the suitability of MEK and toluene for use as solvents in the wax separation was made. The solubility, extraction temperature and fractionation crystallization data were used in the solvent selection slack-waxes fractionation. It was found that MEK was more suitable for the task than toluene by the following reasons :-

- 1) At higher extraction temperatures, n-paraffin content in the wax cake was used as a reference. At higher extraction temperature, n-paraffin wax was more pre-dominant in the wax cakes obtained in MEK than in toluene (Tables 4.5 and 4.6).
- 2) At lower fractionation crystallization temperature, the microcrystalline wax content in the crystallized waxes was used as a reference, the yield of microcrystalline wax was higher in MEK than in toluene (Tables 4.8 and 4.9).

4.6 Fractionation of 500SW and 600SW Slack Waxes

Previous study found that, n-paraffin waxes were preferentially separated at higher temperature but micro-crystalline waxes were preferentially separated at lower temperature, while oils were recovered by using solvent extraction. If both slack waxes were solvent extract at 20 °C to obtain wax cakes and filtrate, it was expected that a large proportion of the filtrate will contain micro-crystalline waxes and oils while the wax cakes will contain largely n-paraffin waxes with the remaining being microcrystalline waxes. Micro-crystalline waxes were obtained solutions after step cooling to 10, 0, -10 and -20 °C. The residual oils were recovered by distilling out the solvent. The solvent extraction method was used to produce oil-free waxes from the wax cakes which were obtained from both slack waxes by fractionating at 30, 40, 50 and 60 °C. The hydrocarbon number and structure of all wax fractions were determined by using HT GC as well as the specific gravity, melting point, viscosity, oil content and sulfur content. The structural group and carbon number of the residual oils were analyzed by using ASTM D 3238-95 and HT GC methods, respectively.

4.6.1 Relationship between Initial Amounts of Slack Waxes and Non-Normal Paraffin Waxes in Obtained-Wax-Cakes from Extraction by MEK at 20 °C

It was observed that there was little change in the wax content of the MEK-soluble-waxes at all extracting temperature between 40 to 55 °C (Figures 4.7 and 4.8). This means that all the wax fractions have relatively constant solubility in MEK between 40 to 55 °C. In order to maximize on the amount of microcrystalline wax extraction, there was a need to determine the solubility limit of microcrystalline wax in MEK by varying the initial amount of slack wax that was used in the extraction (1, 5, 10 and 15 g in 100 ml MEK, at 20 °C) The wax cake was filtered out from MEK-wax slurry before evaporating out the MEK.

The amount of n- and non-normal paraffin waxes in the obtained-wax-cakes and initial amount of slack waxes, from MEK extraction at 20 °C, are shown in Table 4.12.

Table 4.12 Normal and non-normal paraffin waxes in the wax cakes and initial amount of slack waxes in MEK, from extraction at 20 °C

Slack Wax Wt,*g	1		5		10		15	
Composition Types	N	NON	N	NON	N	NON	N	NON
500SW, %	56.24	43.76	42.00	58.00	36.39	63.61	33.12	66.88
600SW, %	51.39	48.61	44.43	55.57	35.65	64.35	35.57	64.43

* Initial weight of slack wax used for extraction in MEK (g. wax / 100 ml MEK)

The initial amount of slack waxes in MEK were plotted against non normal paraffin waxes content in the obtained-wax-cakes as shown in Figure 4.11.

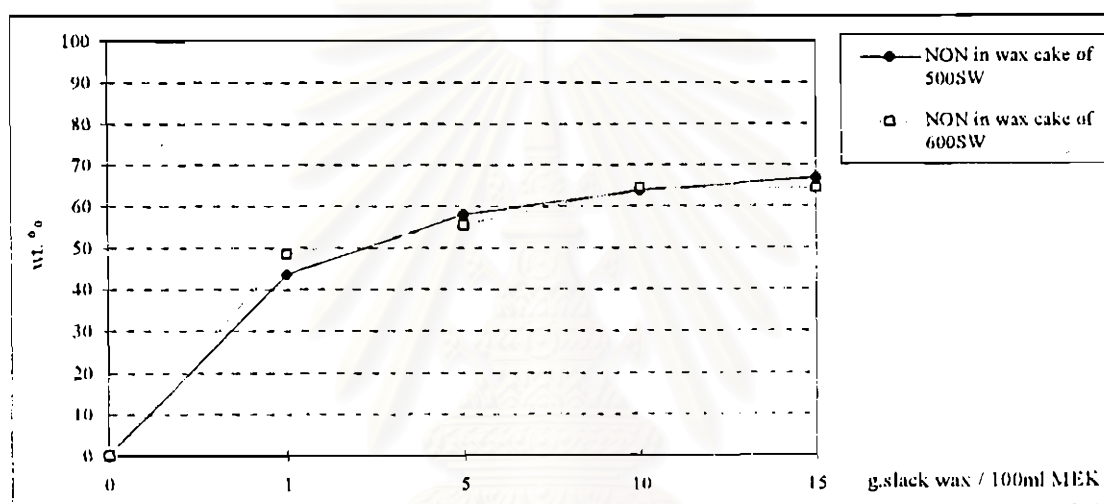


Figure 4.11 Curves of initial amount of slack waxes in MEK vs non-normal paraffin wax content in obtained-wax-cakes, from extraction at 20 °C.

When the initial amount of slack wax was 10 g or more in 100 ml MEK, the wax cake obtained had consistently high micro-crystalline waxes content. If micro-crystalline wax contents in the wax cakes were high, it was not possible to obtain pure components in subsequent extraction. So it was important to determine the most suitable amount of slack waxes for extraction at 20 °C. The solubility of mineral oil and n-paraffin in MEK are 29 and 0.4 % wt, respectively (Figures 2.2 and 2.3, at 20 °C, MEK density of 0.805 ± 0.003). There is no solubility data for other components of 500SW and 600SW slack waxes.

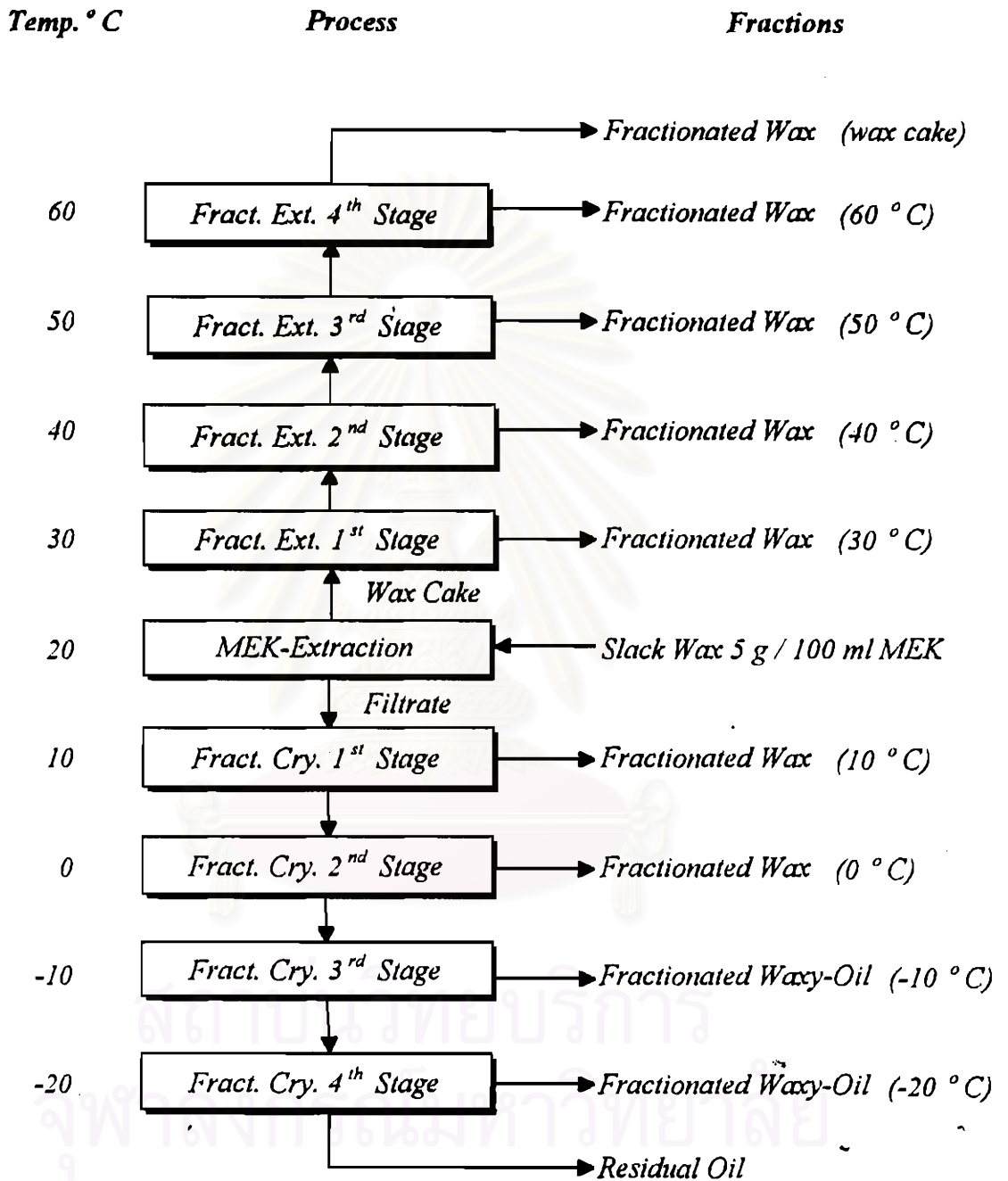
4.6.2 Fractionation Process of Slack Waxes

The separation of fractions such as n-paraffin, micro-crystalline waxes and oil from 500SW and 600SW slack waxes was done by dissolving 5 g of slack wax in 100 ml MEK at 20 °C. Wax cake and filtrate were obtained by filtering out the MEK-wax slurry before doing separation according to the following procedures.

- 1) All amounts of each wax cake were extracted in 100 ml MEK at various temperatures from 30, 40, 50 and 60 °C by fractionation. The fractionated wax cake from each extracting temperature was filtered at its extracting temperature and then dried MEK out. The fractionated waxes (or solvent soluble waxes) for each extracting temperature were obtained by evaporating out of MEK from its filtrates. Finally, the wax cakes from the extraction at 60 °C were evaporated MEK out, to fractionated wax cakes, which can extractable at temperature higher than 60 °C.
- 2) The filtrate of each MEK-soluble-wax, from Chapter 4.6.2, was crystallized at various temperatures from 10, 0, -10 and -20 °C by stepwise. The filtration of fractionated wax was performed at crystallizing temperature. The crystallized waxes at 10 and 0 °C were dried MEK out. The crystallized waxes from crystallizing temperature of -10 and -20 °C at room temperature their form were oil (was called waxy-oil). These waxy-oils were also dried MEK out. Finally, the residual oil in filtrate, from crystallizing temperature at -20 °C, was obtained by evaporating out of solvent.

Figure 4.12 show schematic flow diagram of fractionation process of slack waxes.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย



Note : *Fract. Ext.* = *Fractionation Extraction*
 Fract. Cry. = *Fractionation Crystallization*

Figure 4.12 Schematic flow diagram of fractionation process of slack waxes

4.6.3 Fractionated Waxes and Oils

The normal and non-normal paraffin wax compositions in fractionated waxes, waxy-oils and oils from each separating temperatures are given in Table 4.13.

Table 4.13 Normal and non-normal paraffin wax contents in fractionated waxes, oils and waxy oils from fractionation of 500SW and 600SW slack waxes.

T, °C	N, %	NON, %	Yield, %	T, °C	N, %	NON, %	Yield, %
500SW				600SW			
RO	0.00	100.00	20.14	RO	0.00	100.00	15.00
-20	0.99	99.01	6.38	-20	1.70	98.30	4.13
-10	0.00	100.00	2.70	-10	0.00	100.00	4.23
0	14.76	85.24	7.07	0	14.86	85.14	7.64
10	17.13	82.87	13.12	10	17.47	82.53	11.95
20	42.00	58.00	-	20	44.43	55.57	-
30	12.62	87.38	13.94	30	14.57	85.43	12.26
40	26.17	73.83	9.82	40	22.27	77.73	8.42
50	34.63	65.37	11.75	50	39.29	60.71	11.76
60	64.59	35.41	9.49	60	69.81	30.19	18.24
WC	73.44	26.56	2.09	WC	65.51	34.49	2.96
		Lost	3.50			Lost	3.77

RO = Residual Oils, **T** = Fractionation Temperature, **WC** = Wax cake

In addition to data in Table 4.13, the carbon distribution curves in Figures C1 to C22, give the carbon number of N and NON in fractionated waxes, waxy-oils and oils from fractionation of 500SW and 600SW slack waxes. These data indicated that :

- 1) The fractionated waxes (from separating temperatures of 30, 40, 50 and 60 °C) which contained n-paraffins with higher molecular weight were preferentially separated at higher temperatures. Thus, it was possible to purify the n-paraffin waxes, in the wax cake from fractionation of 600SW, at higher temperatures. This was similar to the results obtained by Katayama (1990) (Chapter 2.7.2).
- 2) N-paraffin waxes with low molecular weight, which were contained in these fractionated waxes, were preferentially separated at lower temperatures.
- 3) Fractionated waxes from low separating temperature at 10 and 0 °C, it contained n-paraffin waxes as same carbon number as non-normal paraffin waxes.

All obtained oils and waxy-oils were characterized in order to study the significance of fractionation of non-normal paraffin waxes from slack waxes at low temperatures.

In addition to characterization of residual oil and waxy-oils by using HT GC, there was structural group analysis following the ASTM D 3238-95. The composition can also be expressed in terms of a carbon distribution, that is, the percentage of the total number of carbon atoms that are present in aromatic ring structures ($\%C_A$), naphthene ring structure ($\%C_N$) and in paraffin chains ($\%C_P$). This test method calculates the carbon distribution of residual oils and waxy-oils from measurements of refractive index at 20 °C, density at 20 °C, sulfur content and kinematics viscosity. The molecular weight is estimated from measurements of viscosity at 37.8 and 98.9 °C by following ASTM D 2502-92. These data were then used to calculate the carbon distribution ($\%C_A$, $\%C_N$ and $\%C_P$) using the appropriate set of equations (see in Chapter 3.14). The structural group analysis of residual oils and waxy-oils from 500SW and 600SW slack wax fractionation is reported in Table 4.14.

Table 4.14 Structural groups of obtained oils from 500SW and 600SW slack waxes fractionation, by following ASTM D 3238-95

SW& Lube oil	T °C	ν , cSt		Sulfur ppm	RI 20°C	ρ 20°C	MW	S/ Group, %		
		37.8°C	98.9°C					C_A	C_N	C_P
500SW	-10	53.0	6.95	2,300	1.4843	0.8974	440	Nil	51.62	48.38
	-20	66.9	7.39	1,279	1.4780	0.9093	420	Nil	68.50	31.50
	RO	123	12.6	5,356	1.4880	0.9199	550	Nil	61.24	38.76
500N	-	110	10.9	2,600	1.4856	0.8801	500	5.65	27.78	66.57
600SW	-10	65.5	8.53	2,900	1.4817	0.9030	490	Nil	56.08	43.92
	-20	98.3	8.11	4,340	1.4811	0.9077	390	Nil	65.28	34.72
	RO	50.3	9.65	7,764	1.4909	0.9268	650	Nil	60.00	40.00
600N	-	124	11.8	4,400	1.4879	0.8855	510	5.76	29.08	65.16

SW = Slack wax, T = Fractionation temp., ν = Viscosity, RI = Refractive Index, ρ = Density, S/Group = Structural group, RO = Residual Oil

The results in Table 4.14 indicate that the structural groups of residual oils and waxy-oils, from 500SW and 600SW slack waxes fractionation, contained less paraffin waxes (about 32 to 48%) than naphthenes (about 52 to 68%) without any aromatics group. The structure of paraffin waxes in residual oils and waxy-oils was highly-branched chain as shown by its GC chromatograms in Figures A96 to A98, for

fractionation of 500SW, and A107 to A109, for fractionation of 600SW, by respectively. The 500SW slack wax was separated from dewaxed 500N-oil and the 600SW slack wax was separated from dewaxed 600N-oil. Lube oils, either 500N or 600N types, are made up of 65 to 66% paraffins, 28 to 29% naphthenes and 6% aromatics oils (Table 4.15). There were clear distinction in compositions of 500N and 600N lube oils compared to residual- and waxy-oils, from 500SW and 600SW slack wax fractionations. The lube oils were paraffinic oils but the residual oils and waxy-oils were naphthenic oils. It might be reasoned that the uniform distribution of components in residual oils and waxy-oils had profound effect on their structural group during fractionating process. It appeared from this study that naphthenes and highly-branched paraffins, by respectively, were invariant of solubility in MEK at low temperatures. The structural groups of fractionated waxes, from 500SW and 600SW slack waxes fractionation, were identified to be normal and non-normal paraffin waxes by HT GC chromatograms. Non-normal paraffins were iso-paraffin or slightly-branched chain hydrocarbon. Highly branched chain hydrocarbons and naphthenes were not identified separately since both hydrocarbon structures were co-eluted together offer the same retention time from the HT GC column and showed up as a large valley in the chromatogram. The structural groups found for fractionated waxes, waxy-oils and oils are shown in Table 4.15.

Table 4.15 Structural group of hydrocarbons in fractionated waxes and oils from 500SW and 600SW slack waxes fractionation at various temperatures

T °C	Paraffins			Naphthenes
	Normal	SB Chain	HB Chain	
RO			Medium	High
-20		Low	Medium	High
-10			Medium	High
0	Medium	Low	High	High
10	Medium	Low	High	High
20	Medium	Low	Medium	Medium
30	Low	Low	High	High
40	Medium	Low	High	High
50	Medium	Low	Medium	Medium
60	High	Medium	Medium	Medium
WC	High		Low	Low

SB Chain = Slightly Branched Chain, **WC** = Wax Cake
HB Chain = Highly Branched Chain, **RO** = Residual Oil

It is clear that the hydrocarbon structures found in the slack waxes exerted considerable influence on separation temperature and technique, as well as on the molecular weight distribution of the component. It was concluded that :

- 1) For fractionation crystallization at temperatures $\leq -10^{\circ}\text{C}$, naphthenic waxes made up the largest component of the fractionated waxy-oils and oils.
- 2) Normal paraffin waxes which had higher molecular weights were isolated by using fractionation extraction at temperatures $\geq 60^{\circ}\text{C}$.
- 3) Wax fractions which separated at 0, 10, 30 and 40 $^{\circ}\text{C}$, in each fractionated waxes were contained more highly-branched paraffin and naphthene waxes than n-paraffin waxes. There were two groups of normal paraffins appeared in these fractionated waxes (fractionating temperatures 0, 10, 30, and 40 $^{\circ}\text{C}$). The first of normal paraffins group isolated in front of the grater portion (highly-branched and naphthene waxes) of each fractionated waxes. The second of normal paraffins group isolated as same carbon number as the grater portion of each fractionated waxes. The two groups of normal paraffins are shown in Figures A90 to A95 for 500SW fractionation and Figures A101 to A106 for 600SW fractionation. In these Figures, it can be note that low carbon number of normal paraffins appeared at low fractionation crystallization temperatures (0 and 10 $^{\circ}\text{C}$). Conversely, high carbon number of normal paraffins appeared at high fractionation extraction temperatures (30 and 40 $^{\circ}\text{C}$).

Some physical properties of the fractions were studied the specific gravity at 25/25 $^{\circ}\text{C}$, melting point according to ASTM D 127-93, kinematic viscosity at 80 $^{\circ}\text{C}$ according to ASTM D 445-94, oil content according to ASTM D 721-93 and sulfur content according to ASTM D 3120-92. Some physical properties of the obtained-wax fractions discussed above are summarized in Table 4.16.

Table 4.16 Physical properties of fractionated waxes from 500SW and 600SW slack waxes fractionation.

Slack Wax	T °C	SG 25/25°C	MP °C	ν , 80°C cSt	Oil %wt	Sulfur ppm/wt	Appearance
500	-	0.8868	57	10.70	28.81	1,369	Soft, Pale yellow
	0	0.8580	36	9.07	Nil	445	Sticky, Colorless
	10	0.8596	41	9.11	Nil	285	Sticky, Colorless
	20	0.8746	64	9.21	Nil	522	Soft powder, White
	30	0.8887	44	8.38	Nil	826	Soft, Pale yellow
	40	0.8600	52	7.79	Nil	297	Soft, Pale yellow
	50	0.8443	62	7.71	Nil	67	Dry powder, Pale yellow
	60	0.8838	66	9.45	Nil	24	Dry powder, White
	WC	0.9074	68	11.11	Nil	16	Crystal, Glossy
600	-	0.8907	59	11.60	20.87	1,356	Soft, Pale yellow
	0	0.8295	34	8.84	Nil	1,285	Sticky, Colorless
	10	0.9036	42	9.12	Nil	666	Sticky, Colorless
	20	0.8843	65	10.40	Nil	338	Soft powder, White
	30	0.8874	45	10.10	Nil	847	Soft, Pale yellow
	40	0.9107	54	8.38	Nil	450	Brittle & soft, Colorless
	50	0.9067	61	8.74	Nil	195	Brittle & soft, Colorless
	60	0.9070	69	9.77	Nil	88	Brittle & hard, White
	WC	0.9173	76	9.95	Nil	51	Hard, White

T = Temperature, SG = Specific Gravity, MP = Melting Point,
 ν = Kinematic Viscosity WC = Wax Cake

The results showed that the separated waxes had a complex composition

- 1) The wax separated composed of different types of straight chains, branched chains and cyclic hydrocarbon structures. Thus, their specific gravity, melting point and viscosity varied with their hydrocarbon composition. For a given type of structure, such as straight chain, the SG, MP, ν , and MW values increase with the chain length
- 2) The sulfur content was higher in wax which contained higher percentage of naphthene hydrocarbons and was lower in wax which contained higher percentage of normal paraffin hydrocarbons.

The crystallization behaviors of each obtained-wax fractions were studied microscopically (200X) as the waxes were cooled down from high temperature at a set rate (Figures 4.13 to 4.16).

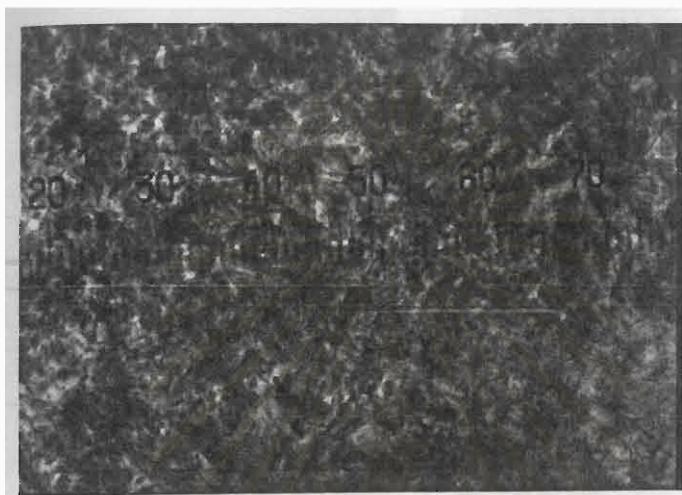


Figure 4.13 Photomicrograph of 500SW slack wax(100% plate, 3 μm)

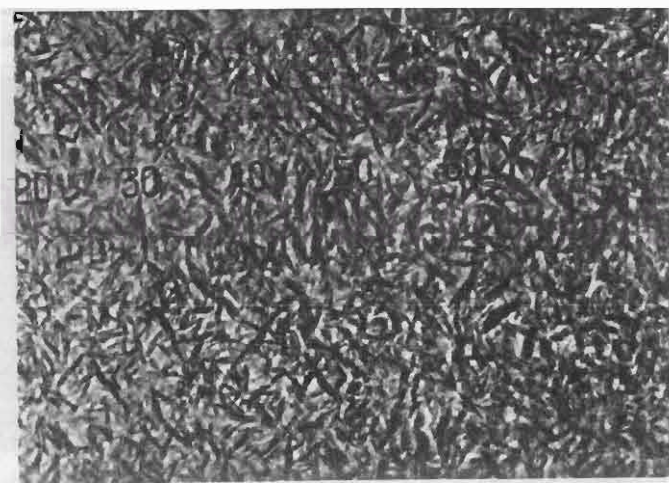
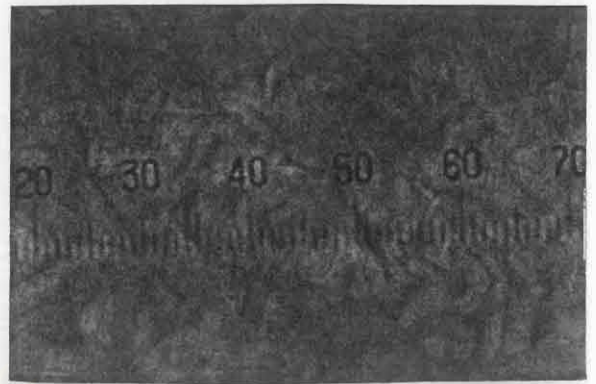


Figure 4.14 Photomicrograph of 600SW slack wax (100 % plate, 3 μm)



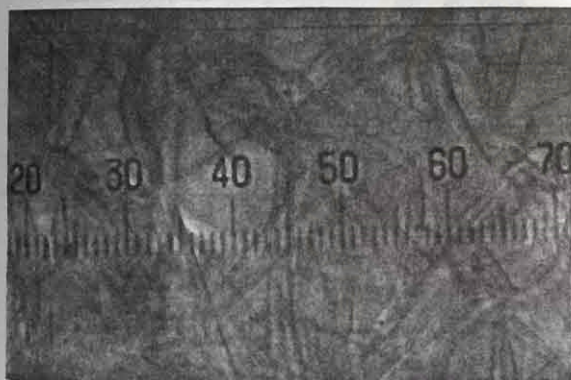
b) 60 °C (75% plate, 7 μm & 25% needle, 7 μm)



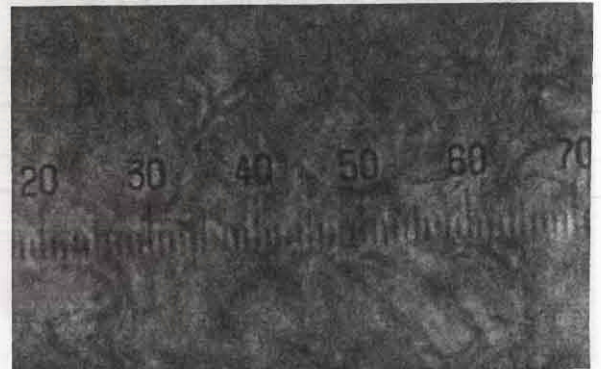
c) 50 °C (50% plate, 5 μm & 50% needle, 8 μm)



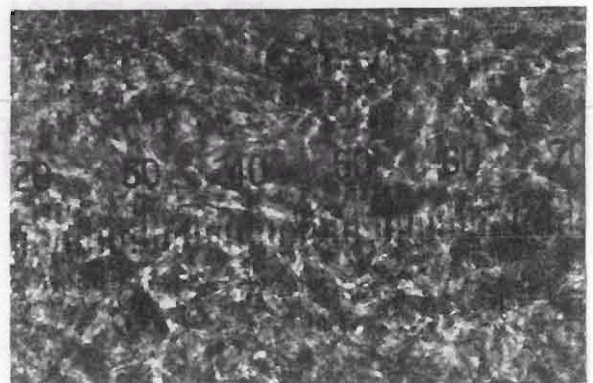
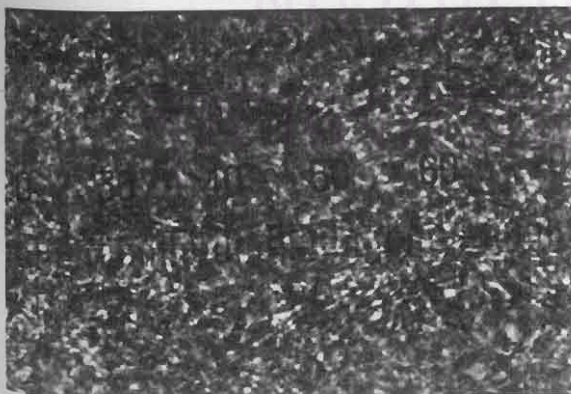
d) 40 °C (75% plate, 9 μm & 25% needle, 13 μm)



e) 30 °C (100% needle, 14 μm)



f) 20 °C (100% needle, 6 μm)

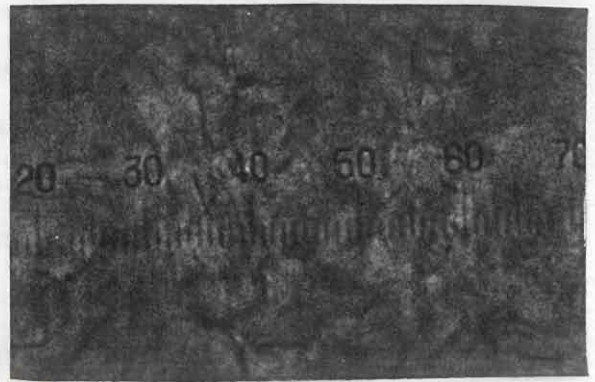


h) 0 °C (100% microscopic size, < 1 μm)

Figure 4.15 Photomicrographs of wax crystals from fractionation of 500SW at various temperatures



a) wax cake (100% plate, 8 μm)



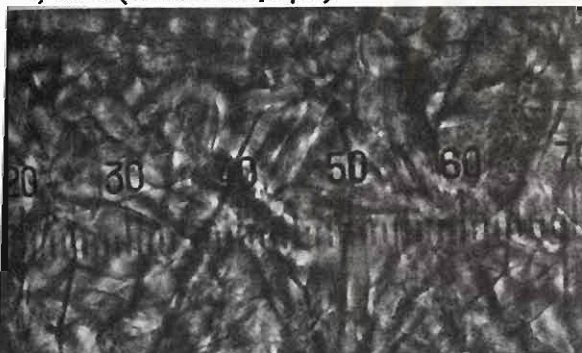
b) 60 °C (100% plate, 9 μm)



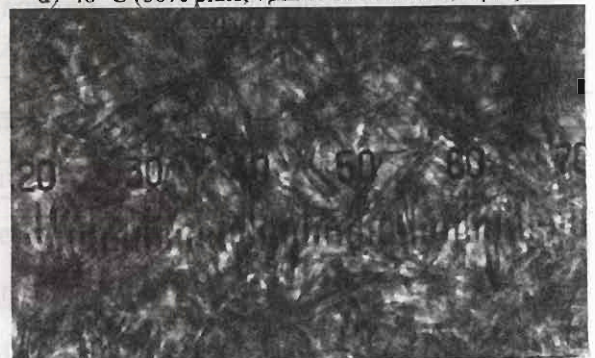
c) 50 °C (100% needle, 8 μm)



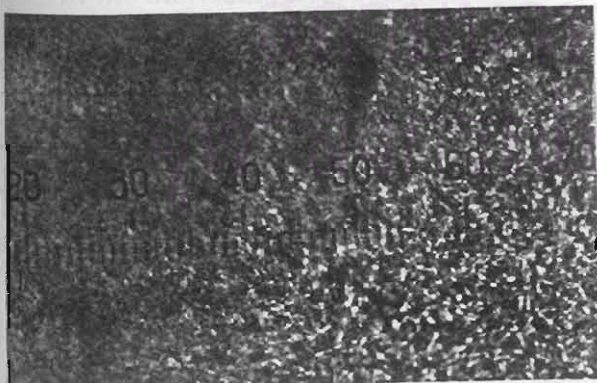
d) 40 °C (50% plate, 7 μm & 50% needle, 9 μm)



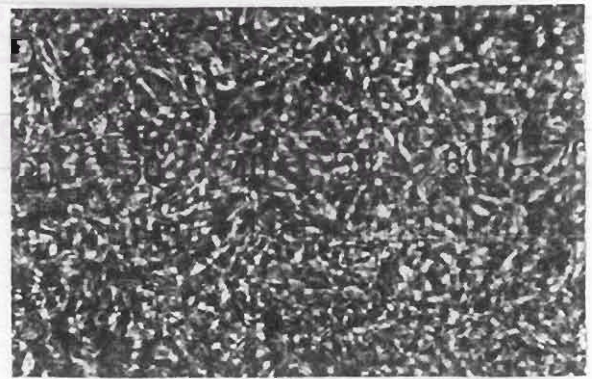
e) 30 °C (100% needle, 12 μm)



f) 20 °C (100% needle, 5 μm)



g) 10 °C (100% microscopic size, < 1 μm)



h) 0 °C (100% microscopic size, < 1 μm)

Figure 4.16 Photomicrographs of wax crystals from fractionation of 600SW at various temperatures

The wax crystals structures are used in the characterization of the waxes in that plate-type crystals represent straight-chain hydrocarbons, needle-type crystals represent branched-chain hydrocarbons, and fine crystals represent microcrystalline waxes (see in Chapter 2.5). The data of structural group in Table 4.15 contains structural analysis results that correspond with the crystal types that are shown in Figures 4.13 to 4.16. The relationship as follows :-

- 1) As normal paraffin wax content increased, the plate crystal type was found on the plate. This was observed for wax cakes and fractionated waxes from the fractionation extraction at 60 °C.
- 2) The amount of non-normal paraffin waxes in the fractionated waxes decreased with an increase in the extracting temperatures (30, 40 and 50 °C). Needle type wax crystals indicates higher proportion of non-normal paraffin waxes. This confirmed that the fractionated waxes obtained at the extracting temperatures, 30, 40 and 50 °C, contained more highly-branched chains than naphthenic hydrocarbons (Table 4.15).
- 3) The crystals of the fractionated waxes at 10 and 0 °C were largely fine crystals. This corresponded with a rapid increase in the amount of naphthenic hydrocarbons in the crystallized waxes obtained at 10 and 0 °C.
- 4) Higher content of normal paraffin waxes gave larger plate crystal size while the larger needle wax crystals indicate the predominance of the branched-chain hydrocarbons. If both needle and plate type crystals were present in the wax at the same time, both wax types will crystallize at the same temperature (Section 2.5).
- 5) The appearance of the wax crystals was dependent upon the crystallographic behavior of the individual hydrocarbon.