



CHAPTER III EXPERIMENTAL

The objective of this research was to study the possibility of fractionations of intermediate waxes into fractions. The fractionations were established by using solvent extraction and crystallization techniques. The extraction and crystallization procedures were developed by means of determination of oil in wax method (ASTM D 721-93). [20] The fractions obtained from fractionations of intermediate waxes were fractionated waxes, waxy-oils and residual oils. These fractions were analyzed hydrocarbon structures, some of components and some of physical properties by means of experiments according to the follows :-

1) Hydrocarbon structures of fractions

1.1) Carbon number distribution and hydrocarbon structures in every fractionated wax, waxy-oil and oil were determined by using High Temperature Gas Chromatography (HT GC) method.

1.2) Additionally, structural group analysis of fractionated waxy-oils and residual oils was also determined by according to ASTM D 3238-95 [21]. This method measured refractive index and density at 20 °C, also estimated the molecular weight from measurement of viscosity at 37.8 and 98.9 °C by following the ASTM D 2502 [22]. These data were then used to calculate the carbon distribution ($\%C_A$, $\%C_N$, $\%C_P$) using the appropriate set of equations.

2) Physical properties of fractionated waxes

Some physical properties of the wax fractions were determined such as solubility, specific gravity 25/25 °C, melting point by according to ASTM D 127-93 [23], kinematic viscosity at 80 °C by according to ASTM D 445-94 [24], microscopic study and appearance.

3) Other components

3.1) The determination of oil in slack waxes and fractionated waxes followed ASTM D 721-93.

3.2) Sulfur content was determined in waxes, waxy-oils and oils by following the ASTM D 3120-92 [25].

3.1 Apparatus and Instruments

1. Analytical Balance Mettler Toledo, model AG 204, readability to 0.1 mg
2. Cooling Bath Heto, model AT 110
3. Filter Bottle 250 ml capacity, with fine sintered glass disk
4. Gas Chromatography Varian, model star 3400 CX, detector type FID, with star chromatography workstation, auto sampler, model 8200 CX
5. GC Column High temperature Sim Dist, 6 m length, 0.53 mm inside diameter, 0.15 μ m film thickness
6. Microlitre Syringe 10 μ l capacity
7. Microscope Nikon, Optiphot-Pol-HFX-2A
8. N₂ Pressure Regulator Concoa, CGA fitting No. 580 single stage, delivery pressure range 0 to 1000 psi and cylinder pressure range 0 to 4000 psi
9. Refractometer Atago, type 1T
10. Rotary Evaporator Buchi, model B-178
11. Specific-Gravity Bottle Pycnometer, capacity 10 & 50 ml
12. Sulfur Analyzer Dohrmann, model MCTS-130 / 120
13. Temp. Controlled Bath Cannon, model CT-1000 for kinematics viscosity
14. Thermometer Temperature range from -40 °C to + 100 °C
15. Viscometer Cannon-Fenske, range 7 to 35 cSt, glass capillary type

3.2 Materials

1. Carbon disulfide supplied by Merck.
2. Cell electrolyte solution (for oxidative microcoulometer) was prepared by dissolving 0.5 g of KI and 0.6 g of NaN₃ in 500 ml of high purity water 5 ml of CH₃COOH was added and diluted to 1,000 ml. All chemicals were supplied by Merck.
3. Diethylene glycol supplied by Carlo Erba Reagenti.
4. High purity grade, argon, oxygen, air, hydrogen, nitrogen and helium (99.99% purity minimum) gases, supplied by Chuttrakorn Special Gases Co.,Ltd.
5. Intermediate waxes, type 500SW and 600SW slack waxes.
6. Iso-octane supplied by Carlo Erba Reagenti.
7. MEK (Methyl Ethyl Ketone) supplied by Carlo Erba Reagenti.
8. Normal butyl sulfide supplied by Carlo Erba Reagenti.
9. Normal paraffin standards supplied by Restek Corporation.
10. Toluene supplied by Carlo Erba Reagenti.

3.3 Characterization of Waxes by GC

The quantitative determination of the carbon number distribution of petroleum waxes in the range from C_{16} through C_{92} was characterized by gas chromatography. Cool on-column injection was used for sample introduction. The column temperature was linearly increased at temperature program rate until the sample was completely eluted from the column. The eluted components were detected by a flame ionization detector and recorded on computer system. The peak area could be measured by computer, and used blank baseline subtraction from the sample area. The individual carbon numbers were identified by standard curve of normal paraffins. The percentage of each hydrocarbon number from C_{16} through C_{92} was calculated by normalized areas of the GC peaks.

3.3.1 Operating Condition of HT GC

1. Column Name	High Temperature Sim Dist
2. Column Length	6 m
3. Column ID.	0.53 mm
4. Film Thickness	0.15 μm
5. Carrier Gas	Helium
6. Carrier Flow Rate	40 ml / min
7. Linear Velocity	25 cm / s
8. Spit Ratio	4 : 1
9. Back Pressure	5.0 psi
10. Column Temperature	Initial temperature 46 °C without holding time, temperature program rate 12 °C / min., final temperature 400 °C with holding time 5 min
11. Injector Temperature	Initial temperature 46 °C without holding time, temperature program rate 20 °C / min, final temperature 400 °C with holding time 5 min
12. Detector Temperature	400 °C
13. Sample Preparation	0.01 to 0.10 g of wax / 8 ml of CS_2 to give concentration 0.1 to 1.0 wt.%
14. Injection Volume	1.0 μl
15. Calculation	Area normalization

3.3.2 Operating Condition of Standard Test Method for Analysis of Petroleum Waxes by GC (ASTM D 5442-93) [9]

1. Column Name	HP-5 cross-linked 5% phenyl methyl siloxane
2. Column Length	30 m
3. Column ID.	0.32 mm
4. Film Thickness	0.25 μm
5. Carrier Gas	Helium
6. Back Pressure	22 psi
7. Column Temperature	Initial temperature 65 °C without holding time, temperature program rate 6 °C / min, final temperature 320 °C with holding time 10 min
8. Injector Temperature	Initial temperature 68 °C without holding time, temperature program rate 15 °C / min, final temperature 320 °C with holding time 5 min
9. Detector Temperature	375 °C
10. Sample Preparation	0.1 to 0.06 g of wax / 8 ml of cyclohexane to give concentration 0.1 to 1.0 wt.%

3.3.3 Chromatographic Identification for HT GC

Chromatographic identification involves comparing the retention time and adjusted retention time of a known n-paraffin to that of the unknown peak under identical chromatographic condition

Adjusted retention time and different adjusted retention time are calculated by Equations 3.1 and 3.2 respectively.

$$t'_{R(i)} = t_{R(i)} - t_{CS_2} \quad \text{-----} \quad \text{Equation 3.1}$$

$$\Delta t'_{R(i)} = t'_{R(i)} - t'_{R(\text{Standard } i)} \quad \text{-----} \quad \text{Equation 3.2}$$

Where : $t'_{R(i)}$ = Adjusted retention time of a peak i

$t_{R(i)}$ = Retention time of a peak i

t_{CS_2} OR t_m = Retention time of a solvent, CS_2

$\Delta t'_{R(i)}$ = Different adjusted retention time of a peak i

$t'_{R(\text{Standard } i)}$ = Adjusted retention time of a peak standard of i

This relationship is illustrated in Figure 3.1

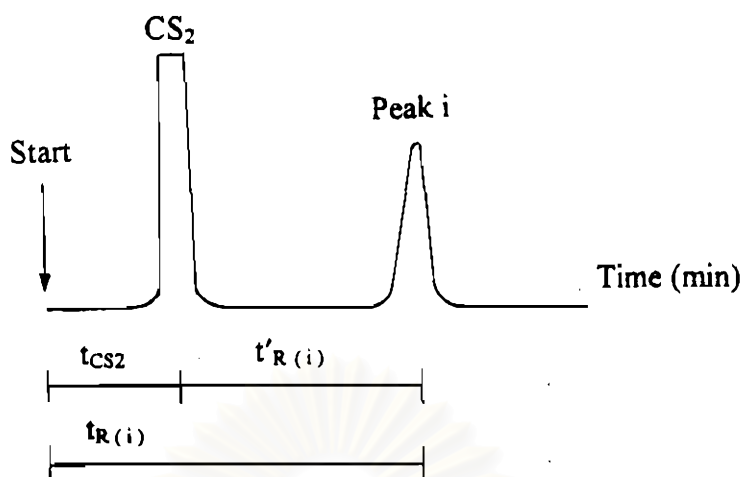


Figure 3.1 Chromatogram
Source : represented from reference number [26]

The hydrocarbon groups (by HT GC) in waxes, i.e. C_{16} to C_{92} hydrocarbons were identified by standard curve of normal paraffins, is shown in Figure 3.2. This curve obtained by plotting the $\text{Log } t'_R$ against carbon number from Table A-1

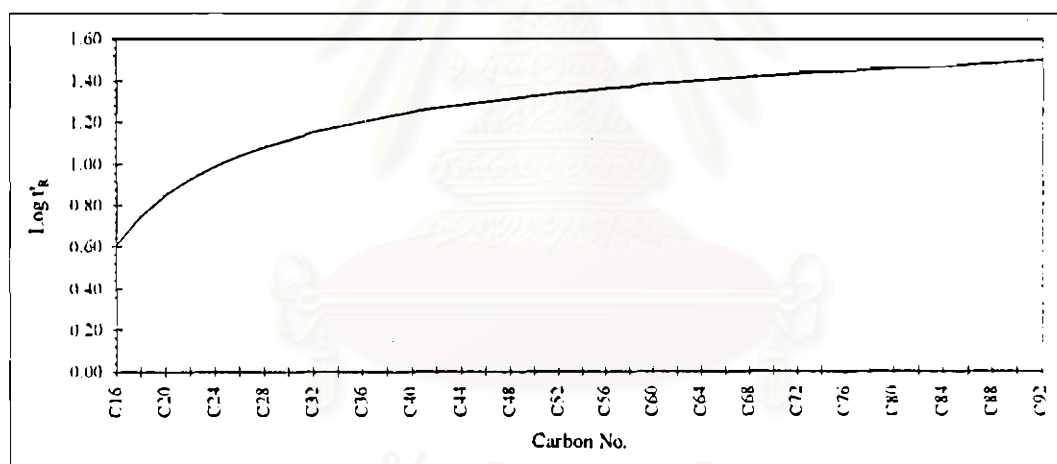


Figure 3.2 Standard curve of normal paraffins (C_{16} to C_{92} hydrocarbons)

The standard sample was prepared with even number n-paraffins only. Actual wax samples contained both odd and even number n-paraffins for which the odd number peaks were eluted between the known even number peaks.

Similarly, non-normal paraffin i (NON i) peaks should eluted between n paraffin i-1 (N_{i-1}) and n paraffin i (N_i) peaks.

This was confirmed by the results that the t_R of $C_{16}H_{34}$ (n-paraffin standard) showed at 4.091 min (see in Table A-1) while, the t_R of 1-phenyldecane (non-normal paraffin standard) showed at 3.767 min. (see in Figure 3.3)

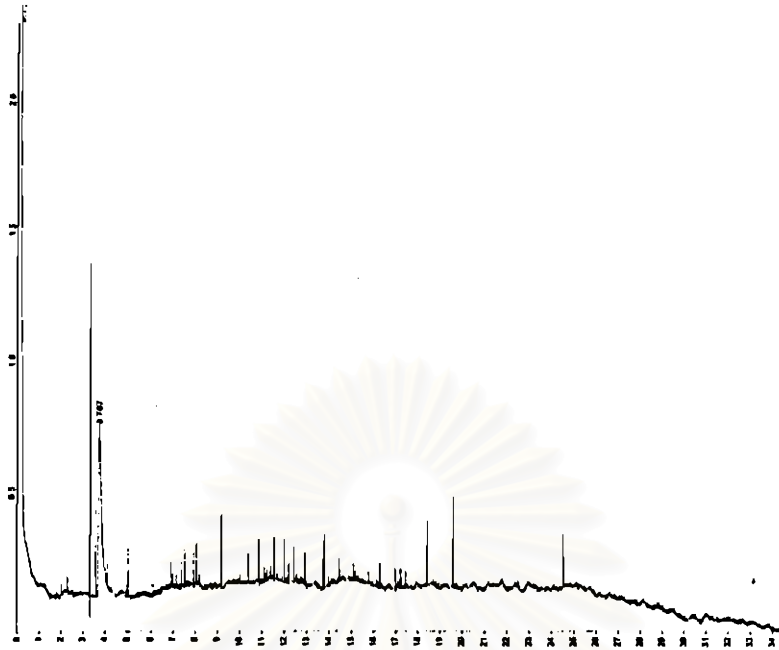


Figure 3.3 HT GC chromatogram of 1-phenyldecane (non-normal paraffin standard)

It can be expected that non-normal paraffins may be classified into two groups. The first group consisted of iso-paraffins with slightly-branched chains while the second one consisted of highly-branched chains with naphthenes. All these observations showed conclusively that peak of iso-paraffin i with slightly branched chain appeared in front of normal paraffin i peak as shown in GC chromatogram of paraffin wax type 150SW (see in Figure 3.4). While, distinction of GC chromatogram for highly-branched chains with naphthenes were appeared together at same retention time and then became huge valley as also shown in Figure 3.4

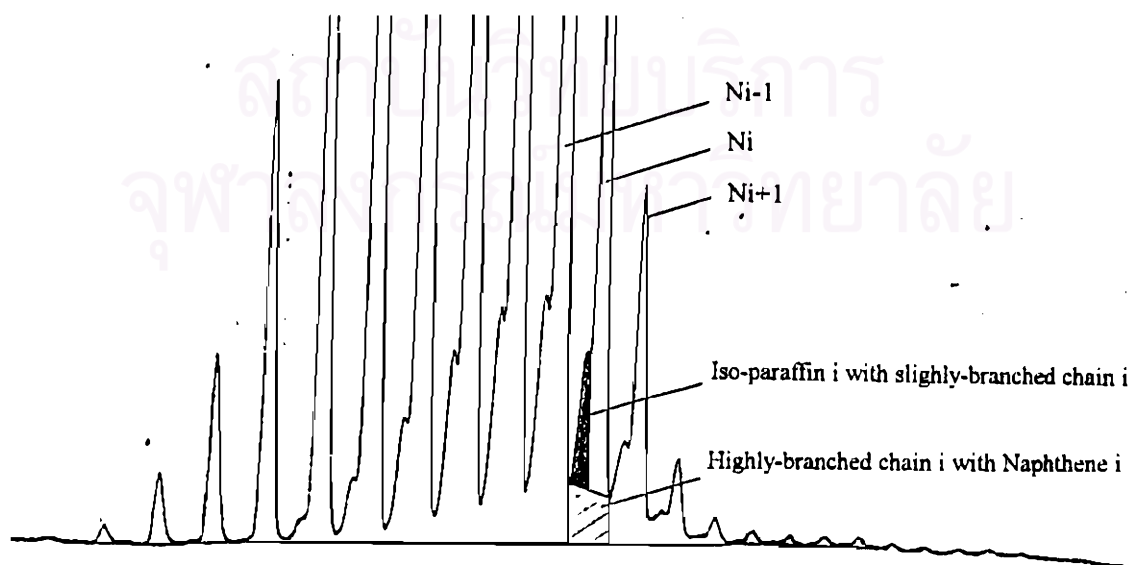


Figure 3.4 GC chromatogram of paraffin wax type 150 SW.

3.3.4 Percentage Calculation of N and NON for HT GC Chromatogram

All HT GC chromatograms in this research were integrated the stored signal twice, using the baseline construction as below.

- 1) Using a valley to valley baseline construction, integrate the detector signal to obtain a area for each peak in the chromatogram (see Figure 3.4). Identify the normal paraffin (N) peaks and tabulate their areas.
- 2) Using a vertical drop to a horizontal baseline construction, integrate the detector signal (see Figure 3.5). Sum the area of all the peaks of each carbon number and tabulate these totals. The peaks assigned the carbon number n are those that elute between the valley immediately following the normal paraffin peak (C_{n-1}) and the corresponding valley following the next normal paraffin peak (C_n).

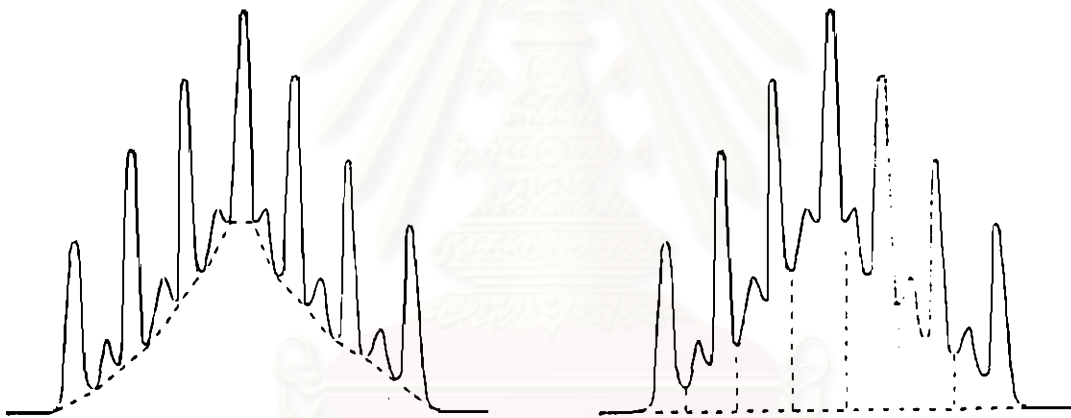


Figure 3.5 Valley to valley integration Figure 3.6 Vertical drop to horizontal baseline

- 3) Normal paraffin (N_i). Calculate the mass % of each normal paraffin from the individual areas using area percent :

$$\text{Area \%} = [A_i / \sum A] \times 100 \quad \text{----- Equation 3.3}$$

Where, A_i = area of individual peak i

$\sum A$ = sum of all peak areas

- 4) Each carbon number (C_i). Calculate the mass % for each carbon number determined in step 2 using Equation 3.3.
- 5) Non-normal paraffin (NON_i). The non normal paraffins are calculated as the difference between the mass percent of hydrocarbons with carbon number i (C_i) and the mass percent of the n-paraffin with carbon number i (N_i) :

$$NON_i = C_i - N_i \quad \text{----- Equation 3.4}$$

Microcrystalline wax = NON - Oil ----- Equation 3.5

where oil was determined by according to ASTM D 721-93

Carbon distribution curves as shown in Appendix C were obtained by plotting the percentage of N and NON against carbon number of N and NON from each chromatographic data as shown in Appendix B.

3.4 Extracting Procedure

Solvent extraction of waxes was performed by using the extracting unit as shown in Figure 3.7. Wax was dissolved in 100 ml. MEK in a glass bottle. The amount used was greater than the wax solubility limit in MEK at room temperature (solubility data is shown in Table 4.2, Chapter 4.2). Immerse glass bottle into water bath maintained at defined extracting temperature. During this extracting operation, the wax-solvent slurry was stirred continuously for 30 min and then immerse in the mixture the filter stick which had previously been heated by placing it in a glass bottle and holding at the same extracting temperature for 10 min. The filtrate was collected in the receiving beaker by applying air pressure into the filtration assembly with flow rate around 500 ml/min. The solvent was evaporated from the filtrate by using rotary evaporator, the condition of solvent evaporation for toluene used pressure of 50 mbar at 50 °C and MEK used pressure of 30 mbar at 50 °C, to obtain solvent-soluble-wax. The wax cake was obtained by drying the extract in the oven at 40 °C for 2 hours, and left at room temperature for overnight.

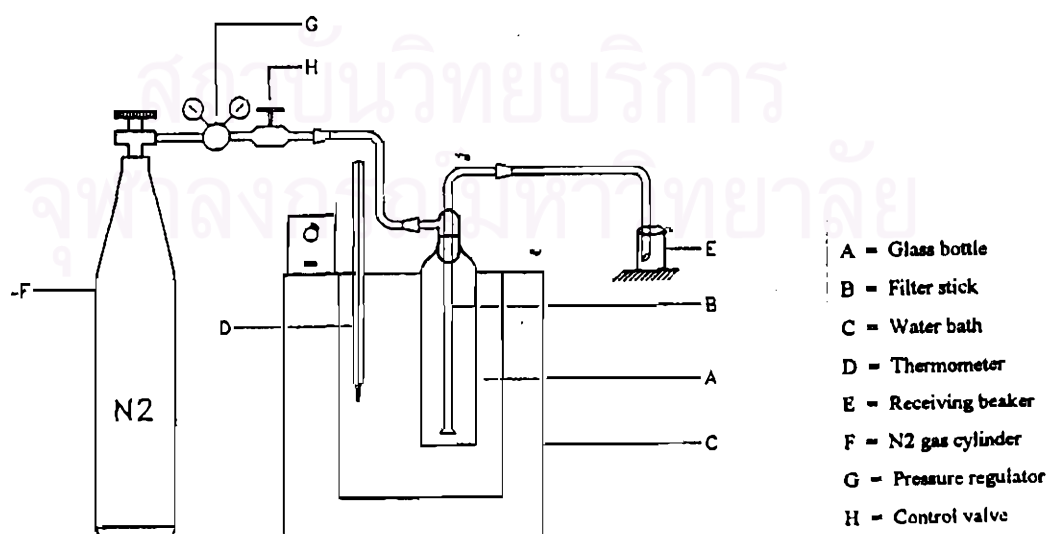


Figure 3.7 Schematic drawing of extracting, crystallizing, and separating unit

3.5 Crystallizing Procedure

Crystallization of waxes was performed by using the crystallization and separation unit as shown in Figure 3.7 (same as extracting unit). Wax was dissolved in 100 ml MEK in a glass bottle. The amount used was greater than the wax solubility limit in MEK at room temperature (solubility data is shown in Table 4.2, Chapter 4.2). Heat the solution at above crystallizing temperature by stirring until a homogeneous solution was obtained. Immerse glass bottle into cooling bath maintained at defined crystallizing temperature. Operating temperature from 0 to -20 °C, fluid in cooling bath should be filled with diethylene glycol. Stir the solution to maintain uniform consistency as the wax precipitate. The filter stick, which had previously been cooled by placing it in a glass bottle and holding at the same crystallizing temperature for 10 min, was immersed into a glass bottle. The filtrate was collected in the receiving beaker by applying approximately 500 ml/min of air flow rate. For fractionation crystallization, the filtrate was cooled down step by step to 30, 20, 10, 0, -10 and -20 °C. The solvent was evaporated from the crystallized waxes by heating in the oven at 40 °C for 2 hours and left at room temperature for overnight. The wax was nearly completed to precipitate at -20 °C, finally, to obtain the residual oil, the filtrate at -20 °C was evaporated solvent out by using rotary evaporator. The condition of solvent evaporation for toluene used pressure of 50 mbar at 50 °C and MEK used pressure of 30 mbar at 50 °C.

3.6 Determination of Solubility

Solubility of petroleum waxes in this research was studied by using MEK and toluene at various temperatures (0, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50 and 55 °C) Unit of the solubility was reported in grams of wax per 100 ml of each solvent.

3.7 Determination of Specific Gravity

Specific gravity of petroleum waxes in this research was determined by using a Pycnometer specific-gravity bottle, capacity 50 ml, having a ground glass stopper with small hole in center. Wax was melted at 70 °C and poured into a porcelain dish, of 2 mm of the melted wax. Wax slap was left at 25 °C for 2 hours, and cut a piece of the wax slap, approximately 0.5 x 4 cm. The wax specimen was weighed accurately to 0.0001 g at 25 °C. The bottle was filled with water stoppered and wiped dry, weighed at 25 °C, submerged the wax specimen in the water slowly so that no air bubbles cling to surface

of the wax, and weight the whole. The specific gravity, at 25/25 °C, of the wax specimen was calculated as follows :

$$\text{Sp Gr} = \frac{\text{weight of wax}}{[A - B + \text{weight of wax}]} \text{----- Equation 3.6}$$

Where : A is weight of the bottle filled with water,

B is weight of the bottle filled with wax and water.

3.8 Determination of Drop Melting Point

Melting point of petroleum waxes in this research was studied by following ASTM D 127-93. The waxes were deposited on two thermometer bulbs by dipping chilled thermometers into melted waxes. The thermometers bearing the waxes were placed in test tubes and heated by means of water bath until the waxes melted and first drop fell from each thermometer bulb. Average of temperatures at which these drops fall was the drop melting point of the wax.

3.9 Determination of Kinematic Viscosity

Kinematic viscosity (ν) of petroleum waxes in this research was determined by following ASTM D 445-94

The wax was heated at 70 °C for flow freely to fill fixed volume of calibrated glass capillary viscometer (in range 7 to 35 cSt.). The viscometer with liquided-wax was immersed in temperature-controlled bath at 80 °C. The volume of liquided-wax was adjusted to coincide with the filling mark of viscometer. Time was measured in seconds from the first timing mark to the second. The kinematic viscosity was product of the measured flow time and calibration constant of the viscometer.

Calculate the kinematic viscosity, ν , from the measured flow time, t , and the viscosity constant, C , by means of the following equation :

$$\nu = C \cdot t \text{----- Equation (3.7)}$$

Where : ν is kinematic viscosity, mm²/s or cSt,

C is calibration constant of the viscometer, (mm²/s)/s, and

t is mean flow time, s.

3.10 Determination of Oil Content in Wax

The oil content of petroleum waxes was determined by following ASTM D 721-93. The oil content in waxes was performed by using the separating unit as shown in Figure 3.1. A 1 g. of wax was dissolved in 15 ml. of MEK into a test tube, solution was homogenized by stirring in a heating bath. The solution was cooled by a cooling bath, wiped dry on outside test tube with a cloth, and weighed to the nearest 0.1 g. The solution was cooled to -32 °C to precipitate the wax, immersed in the mixture with filter stick which had previously been cooled by placing it in the test tube and holding at -32 °C in the cooling bath for 10 min, and filtered by applying air pressure with flow rate approximately 500 ml/min to the filtration assembly. A 4 ml of filtrate was collected in a weighing bottle, and weighed it to the nearest 10 mg. The oil content of the filtrate was determined by evaporating the MEK at 35 °C with the air for 30 min, and weighing the residue at nearest 0.1 mg.

Calculate the amount of oil in the wax as follow :

$$\text{Oil in wax, weight \%} = (100 \cdot a \cdot b / c \cdot d) - 0.15 \text{ -----Equation 3.8}$$

Where :

- a is weight of oil residue, g,
- b is weight of wax, g,
- c is weight of solvent, g, obtained by subtracting weight of test tube plus wax from weight of test tube and contents,
- d is weight of solvent evaporated, g, obtained by subtracting weight of weighing bottle plus oil residue from weight of weighing bottle plus filtrate, and

0.15 is average factor correcting for the solubility of wax in the solvent at -32 °C.

3.11 Determination of Sulfur Content by Oxidative Microcoulometry

The sulfur content in petroleum waxes was determined by following ASTM D 3120-92. A 1 g. of wax or oil was weighed accurately into a 25 ml. volumetric flask and then dissolved with isooctane. Diluted to mark with isooctane and reweighed. Sulfur, standard stock solution was prepared approximately 300 µg/g by weighing accurately 0.5 g of n-butyl sulfide into a tared 500 ml volumetric flask, diluted to the mark with isooctane and then reweighed. Sulfur standard solution (approximately 30 µg/g) was

prepared by pipetting 10 ml of sulfur stock solution into a 100 ml volumetric flask and diluted to volume with isooctane. A 1 μ l. of wax-solution was introduced into a combustion tube maintained at 800 °C having a flowing stream of gas containing about 80% oxygen and 20% argon. Oxidative pyrolysis converts the sulfur to sulfur dioxide which flowed into a titration cell where it reacted with triiodide ion present in the cell electrolyte solution. The triiodide thus consumed, was coulometrically replaced and the total current required to replace it was a measure of the sulfur present in the wax-solution introduced. These microequivalents of triiodide (iodine) were equal to the number of microequivalents of titratable ion entering the titration cell.

Calculated the sulfur content of the waxes and oils in parts per million, μ g/g as follows :

$$\text{Sulfur, } \mu\text{g/g} = \left[\frac{\text{CR}}{\text{V} \cdot \text{D} \cdot \text{RF}} - \frac{\text{CB}}{\text{V} \cdot \text{D} \cdot \text{RF}} \right] \cdot \frac{(\text{W} + \text{S})}{\text{W}}$$

-----Equation 3.9

Where : V = Volume of wax-solution, μ l,
 CR = counts of wax readout,
 CB = counts of blank,
 W = g of wax,
 S = solvent,
 D = Density of wax-solution, g/ml, measure the density of solution by obtaining the mass of 10.0 ml (using a 10 ml volumetric flask) to the nearest 0.1g, and
 RF = Recovery factor, fraction of sulfur in standard that is titrated, ratio of ppm sulfur determined in standard divided by the known ppm sulfur in standard.

$$\text{RF} = \left[\frac{\text{CS}}{\text{M} \cdot \text{Cstd}} \right] - \left[\frac{\text{CB}}{\text{M} \cdot \text{Cstd}} \right] \text{----- Equation 3.10}$$

Where : M = mass of standard, g (volume x density)
 Cstd = Concentration of standard, ppm, and
 CS = count of standard readout

3.12 Determination of Molecular Weight for Oils from Viscosity Measurements

The estimation of molecular weight (relative molecular mass) of oils in this research was determined by following ASTM D 2502-92. This test method measured the kinematic viscosity at 37.8 and 98.9 °C of the oil. A function H of the 37.8 °C viscosity was established by reference to a tabulation of H function versus 37.8 °C viscosity as shown in Table 3.1. The H value and the 98.9 °C viscosity were then used to estimate the molecular weight from a correlation chart, shown in Figure 3.8.

Table 3.1 Tabulation of H function

Kinematic Viscosity, cSt. at 100°F (37.78°C)	H				
	0	0.2	0.4	0.6	0.8
2	-178	-151	-126	-104	-85
3	-67	-52	-38	-25	-13
4	-1	9	19	28	36
5	44	52	59	66	73
6	79	85	90	96	101
7	106	111	116	120	124
8	128	132	136	140	144
9	147	151	154	157	160
10	163	166	169	172	175
11	178	180	183	185	188
12	190	192	195	197	199
13	201	203	206	208	210
14	211	213	215	217	219
15	221	222	224	226	227
16	229	231	232	234	235
17	237	238	240	241	243
18	244	245	247	248	249
19	251	252	253	255	256
20	257	258	259	261	262
21	263	264	265	266	267
22	269	270	271	272	273
23	274	275	276	277	278
24	279	280	281	281	282
25	283	284	285	286	287
26	288	289	289	290	291
27	292	293	294	294	295
28	296	297	298	298	299
29	300	301	301	302	303
30	304	304	305	306	306
31	307	308	308	309	310
32	310	311	312	312	313
33	314	314	315	316	316
34	317	317	318	319	319
35	320	320	321	322	322
36	323	323	324	325	325
37	326	326	327	327	328
38	328	329	329	330	331
39	331	332	332	333	333

	H									
	0	1	2	3	4	5	6	7	8	9
40	334	336	339	341	343	345	347	349	352	354
50	355	357	359	361	363	364	366	368	369	371
60	372	374	375	377	378	380	381	382	384	385
70	386	387	388	390	391	392	393	394	395	397
80	398	399	400	401	402	403	404	405	406	407
90	408	409	410	410	411	412	413	414	415	415
100	416	417	418	419	420	420	421	422	423	423
110	424	425	425	426	427	428	428	429	430	430
120	431	432	432	433	433	434	435	435	436	437
130	437	438	438	439	439	440	441	441	442	442
140	443	443	444	444	445	446	446	447	447	448
150	449	449	449	450	450	450	451	451	452	452
160	453	453	454	454	455	455	456	456	456	457
170	457	458	458	459	459	460	460	460	461	461
180	461	462	462	463	463	463	464	464	465	465
190	465	466	466	466	467	467	468	468	468	469

Table 3.1 Tabulation of H function (Continued)

TABLE *Continued*

Kinematic Viscosity, cSt at 100°F (37.78°C)	H									
	0	10	20	30	40	50	60	70	80	90
200	469	473	476	479	482	485	487	490	492	495
300	497	499	501	503	505	507	509	511	512	514
400	515	517	518	520	521	523	524	525	527	528
500	529	530	531	533	534	535	536	537	538	539
600	540	541	542	543	544	545	546	547	547	548
700	549	550	551	551	552	553	554	554	555	556
800	557	557	558	559	559	560	561	562	562	563
900	563	564	565	565	566	566	567	567	568	569
	0	100	200	300	400	500	600	700	800	900
1 000	569	574	578	583	587	591	594	597	600	603
2 000	605	608	610	612	614	616	618	620	621	623
3 000	625	626	628	629	631	632	633	634	636	637
4 000	638	639	640	641	642	643	644	645	646	647
5 000	648	649	650	651	652	652	653	654	655	656
6 000	656	657	658	658	659	660	660	661	662	662
7 000	663	664	664	665	665	666	666	667	667	668
8 000	668	669	670	670	671	671	671	672	672	673
9 000	673	674	674	675	675	676	676	677	677	677
	0	1000	2000	3000	4000	5000	6000	7000	8000	9000
10 000	678	681	684	688	691	694	696	699	701	703
20 000	705	707	709	711	712	714	715	717	718	719
30 000	720	722	723	724	725	726	727	728	729	730
40 000	731	732	732	733	734	735	736	736	737	738
50 000	739	739	740	741	741	742	743	743	744	744
60 000	745	746	746	747	747	748	748	749	749	750
70 000	750	751	751	752	752	753	753	753	754	754
80 000	755	755	756	756	756	757	757	758	758	758
90 000	759	759	759	760	760	760	761	761	761	762
100 000	762	762	763	763	763	764	764	764	764	765

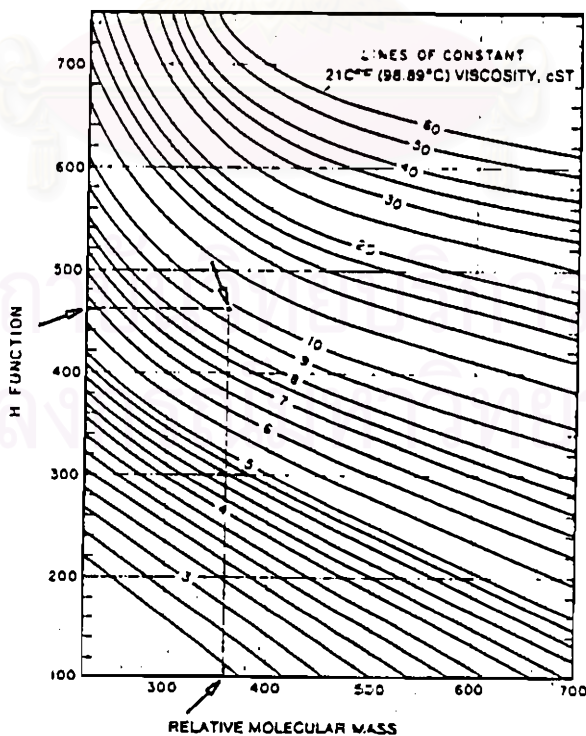


Figure 3.8 Viscosity molecular weight chart

3.13 Determination of Refractive Index of Oils

Refractive index of oils in this research was determined by measuring the critical angle method with Atago refractometer using monochromatic light. The oils shall be free of suspended solids or other materials that tend to scatter light. It can be removed by centrifuging or filtering. The measurement was reported to fourth decimal place at temperature 20 °C.

3.14 Determination of Structural Group Analysis for Oils

Structural groups of oils in this research were studied by following ASTM D 3238-95. This test method calculated the carbon distribution of oils, such as aromatic ring structures (%C_A), naphthene ring structures (%C_N) and in paraffin chains (%C_P), from measurements of refractive index at 20 °C (see in Chapter 3.13), density at 20 °C (measured by obtaining the mass of 10.0 ml, in pycnometer of 10 ml capacity, to the nearest 0.1 mg), sulfur content (see in Chapter 3.11) and kinematic viscosity (see in Chapter 3.9). The molecular weights of oils were estimated from measurements of viscosity at 37.8 and 98.9 °C (see in Chapter 3.12)

The data were then used to calculate the carbon distribution (%C_A, %C_N, and %C_P) using the appropriate set of equations. Calculate the factors ν and ω from the observed density (d) and the observed refractive index (n) using following equations :

$$\nu = 2.51 (n_D^{20} - 1.4750) - (d_4^{20} - 0.8510) \text{ ----- Equation 3.11}$$

$$\omega = (d_4^{20} - 0.8510) - 1.11 (n_D^{20} - 1.4750) \text{ ----- Equation 3.12}$$

Calculate the percentage of aromatic carbon (%C_A) from ν and the molecular weight (M) using one of the following equations :

$$\text{If } \nu \text{ is positive : } \%C_A = 430\nu + 3660 / M \text{ ----- Equation 3.13}$$

$$\text{If } \nu \text{ is negative : } \%C_A = 670\nu + 3660 / M \text{ ----- Equation 3.14}$$

Calculate the percentage of carbon in total (aromatic and naphthenic) ring structures (%C_R) from ω and the molecular weight.

$$\text{If } \omega \text{ is positive : } \%C_R = 820\omega - 3S + 10000 / M \text{ ---- Equation 3.15}$$

$$\text{If } \omega \text{ is negative : } \%C_R = 1440\omega - 3S + 10600/M \text{ ---- Equation 3.16}$$

Where : S = mass % sulfur

Calculate the percentage of naphthenic carbon ($\%C_N$) and the percentage of paraffinic carbon ($\%C_P$) as follows :

$$\%C_N = \%C_R - \%C_A \text{ ----- Equation 3.17}$$

$$\%C_P = 100 - \%C_R \text{ ----- Equation 3.18}$$

3.15 Determination of Microscopy of Waxes

The crystal habit of waxes in this research was performed by using microscopic study. The waxes were heated by electrical controller and cooled down from high temperature at a set rate. Photomicrographs were made of the crystal during the process of development by using magnification 200X.



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