CHAPTER IV RESULTS AND DISCUSSION

4.1 Characterization of Crude Oils

4.1.1 Distillation

The distillation curves obtained by conventional method (ASTM D86) and by simulated distillation gas chromatography (ASTM D2887) of the three crude oils are shown in Figure 4.1. The curves from the two methods were very close to each other. It was observed that the initial boiling point of Lankrabue crude oil was lower than that of Fang and U-thong crude oils, i.e. 75, 87 and 125 °C, respectively. The results indicate that Fang crude oil contained more lighter components than U-thong and Lankrabue crude oils. The compositions of these three crude oils as presented in the sim-dist GC chromatograms in Figure 4.2 show that major hydrocarbon concentrations in Lankrabue, U-thong and Fang crude oils were in the carbon atom ranges of 12 to 28, 12 to 36 and 5 to 36, respectively.

4.1.2 Other Properties

The physical properties, i.e. pour point, density, wax content, WAT, WDT, \leftrightarrows H_{WAT} and \leftrightarrows H_{WDT} are summarized in Table 4.1. Fang crude oil possessed lowest pour point, density, wax content, and thermodynamics properties relating to wax content. Detailed results are shown in Appendix F.

Based on the range of carbon atoms of three crude oils. All these properties show good correlation with the carbon atom range.

. The total enthalpy of precipitation or enthalpy of dissolution of crude oil is the total energy released during cooling or absorbed during heating process and is proportional to the areas under the exothermic or endothermic peaks, respectively. Glavaniri *et al.* (1973) confirmed that the total enthalpy is a linear relationship with n-paraffin content. Moreover, the total enthalpy is related to the transition state of liquid-solid or solid-solid that depends on component of each crude oil thus total enthalpy of the three crude oils as determined by DSC showed differences due to the differences in composition (i.e. molecular weight and molecular structure) and wax content in each crude oil as shown in Figure 4.3. Generally the dissolution enthalpy is higher than the corresponding enthalpy of precipitation. The enthalpy differences could not be explained thermodynamically as this evidence might be the result of experimental uncertainty as confirmed by Elsharkawy *et al.* (2000). From the result as shown in Table 4.1, WAT of three crude oils were 15 to 17 °C lower than WDT. The difference between WAT and WDT was due to undercooling and overheating that occurred in non-equilibrium conditions during fast temperature scanning (Elshakawy *et al.*, 2000). Moreover, it is also found that there are good correlation among WAT, wax content and pour point. For example, Fang crude oil had lowest pour point and wax content and 20.3 + 0.02 % respectively at 31.1 + 0.1 °C, and also lowest WAT at 32 + 1 °C while Lankrabue crude oil had highest pour point and wax content and 20.3 + 0.02 % respectively at 327.1 + 0.2 °C, and also highest WAT at 39 + 1 °C.

4.2 Wax Separation

4.2.1 <u>Sim-Dist GC</u>

Wax and asphaltene compositions in the crude oil samples were separated based on the methods suggested by Nguyen's and modified method (Wison, 2004). The separated fractions obtained by Nguyen's method were analyzed by the sim-dist GC as shown in Figures 4.4-4.5. From the chromatograms of the identified microcrystalline (branching paraffin) fractions (Fig. 4.4), there were 2-3 clusters of hydrocarbons, approximate carbon number lower than C_{17} , C_{17} - C_{24} and C_{25} - C_{38} . U-thong showed higher content of C_{25} - C_{38} cluster than Lankrabue crude oils while Fang showed a broad cluster of C_{17} - C_{30} . The overall microcrystalline fraction was accounted for about 4 % of the crude oil. The macrocrystalline (n-paraffin wax) fractions as shown in Figure 4.5 indicate similar carbon clusters to the microcrystalline fractions except these fractions contained larger amount of higher hydrocarbon content and the clusters of C_{15} - C_{26} and C_{22} - C_{38} of U-thong are more pronounced. The overall macrocrystalline fraction was approximately 30 % of the crude oil.



Figure 4.1 Comparison of distillation temperatures a) Lankrabue b) U-thong c) Fang crude oils.



Figure 4.2 Simulated distillation gas chromatograms a) Lankrabue b) U-thong and c) Fang crude oils.

Source	Range of C- atom	Pour point (°C)	Density (g/cm ³)	Wax content (%)	WAT (°C)	WDT (°C)	ΔH _{wat} (j/g)	ΔH _{wdt} (j/g)
Lankrabue	12-28	37.1 <u>+</u> 0.2	0.879±0.001	23.92+0.01	39±1	54+15	44.87+0.02	50.53+0.02
U-thong	12-36	35.7 <u>+</u> 0.1	0.855 <u>+</u> 0.002	21.82+0.02	34 <u>+</u> 1	51 <u>+</u> 17	33.95+0.01	39.97+0.01
Fang	5-36	31.1+0.1	0.846±0.001	20.13 <u>+</u> 0.02	32 <u>+</u> 1	49 <u>+</u> 17	32.45+0.01	38.59+0.02

 Table 4.1
 Properties of Crude Oils



Figure 4.3 Relationship between percent wax content and enthalphy of wax precipitation and dissolution obtained from DSC.



Figure 4.4 Simulated distillation chromatogram of micro-crystalline fraction as obtain from Nguyen separation method a) Lankrabue, b) U-thong, and c) Fang crude oils.



Figure 4.5 Simulated distillation chromatogram of macro-crystalline fraction as obtain from Nguyen separation method a) Lankrabue, b) U-thong, and c) Fang crude oils.

The fractions of micro- and macro-crystallines obtained from the modified method are shown in Figure 4.6 and Figure 4.7, respectively. A broad range of carbon cluster in the chromatograms and high hydrocarbon content in the macrocrystalline fraction were observed. This indicates that the chromatograms of the identified microcrystalline (branching paraffin) fractions (Fig. 4.6) showed a cluster of hydrocarbons, approximate carbon number C_{13} - C_{38} for Lankrabue and U-thong crude oils and C_{18} - C_{36} and lowest content for Fang crude oil. The overall microcrystalline fraction was accounted for about 3 % of the crude oil. The macrocrystalline (n-paraffin wax) fractions as shown in Figure 4.7 indicate similar carbon clusters to the microcrystalline fractions but these fractions. The overall macrocrystalline fraction was approximately 35 % of the crude oil. The calculation is shown in Appendix B.

These chromatograms give valuable information about the hydrocarbon ranges of each fraction of crude oils. There are clear differences in each fractions obtained from all three crude oils. From two methods of separation, the significant difference was in the first step used to remove resins and asphaltenes from crude oil. The modified method used n-heptane to precipitate asphaltene while the Nguyen's method used p-xylene to extract aphaltene and waxes. As p-xylene has higher polarity than n-heptane and the micro- and macro-crystalline wax obtained from modified method contained higher content of each hydrocarbon than Nguyen's method. One can conclude that polarity of solvent has the strong effect on the separation of the fractions.

4.2.2 <u>FTIR</u>

FTIR spectra of asphaltene fraction separated by the Nguyen's method and the modified method are shown in Figures 4.8-4.9. The peaks appear at 2940 cm⁻¹ for –CH- stretch, 2120 cm⁻¹ for C-S stretch, and 1585 cm⁻¹ for aromatic C=C stretch. The characteristic peak of asphaltenes showing the finger print of aromatic below 1000 cm⁻¹ that appears in the asphaltene fraction of each crude oil but these peaks were not clear due to low concentration of asphaltenes. In addition, the broad range of the absorption peak at 800-500 cm⁻¹ indicates the presence of



Figure 4.6 Simulated distillation chromatogram of micro-crystalline fraction as obtained from modified method a) Lankrabue, b) U-thong, and c) Fang crude oils.



Figure 4.7 Simulated distillation chromatogram of macro-crystalline fraction as obtained from modified method a) Lankrabue, b) U-thong, and c) Fang crude oils.



(d)

Figure 4.8 FTIR spectra of identified asphaltene fraction from the Nguyen's method a) Lankrabue, b) U-thong, c) Fang crude oil, and d) published (Suryanarayana *et al.*, 1990).



(d)

Figure 4.9 FTIR spectra of identified asphaltene fraction from the modified method a) Lankrabue, b) U-thong, c) Fang crude oil, and d) published (Suryanarayana *et al.*, 1990).

asphaltene in these fractions.

The FTIR spectra of micro-crystalline fractions shown in Figures 4.10-4.12 were identified by comparing with the microcrystalline wax spectrum reported by Suryanarayana et al. (1990). The characteristic peaks of microcrystalline wax appear at 1450 cm⁻¹ for alicyclic -CH₂- scissor and 1395 cm⁻¹ for symmetric CH₃ bending (iso- and tert- alkyl). The spectra of all micro-crystalline fractions were comparable with the spectrum reported by Survanarayana et al. (1990), C-S stretching at 2150 cm⁻¹ and boarding peak around 1500-1350 cm⁻¹ possibly belong to the solvent CS₂ residue and asphaltenes. The CS₂ peak in the chromatogram (Figure 4.10-4.12) indicated the presence of residue CS₂ and the aromatic finger print at 900-700 cm⁻¹ in the FTIR spectra of microcrystalline fractions indicated the presence of asphaltenes. The FTIR spectra of macrocrystalline fraction from Figures 4.13-4.15 were identified by comparing with the spectrum reported by Bouquet et al. (1982). The spectra of all micro-crystalline fractions were similar to this reported by Bouquetet al. (1982).; This confirms that after separation by solvent from both methods which Nguyen's use p-Xylene while modified method use n-pentane, all fractions of three crude oils from two methods are true micro-crystalline fractions but different in the amount.

From the FTIR findings, one can conclude that both separation methods can separate the micro-crystalline wax fraction the macro-crystalline wax fraction, and that the modified method is less time consuming than Nguyen's method.

4.3 Investigation of The Chemical Method to Integrate Wax Deposition Problem

4.3.1 Effect of Solvents

In this study, considerable effort was devoted to develop a chemical method to inhibit paraffin deposition. Several methods were used. One of the methods was dissolution in hydrocarbon solvents. N-pentane, n-hexane and nheptane were employed as the solvents at varying concentrations. Pour point



Figure 4.10 FTIR spectra of micro-crystalline fraction of Lankrabue crude oil identified by a) Nguyen's method, b) modified method, and c) published (Bouquet *et al.*, 1982).



Figure 4.11 FTIR spectra of micro-crystalline fraction of U-thong crude oil identified by a) Nguyen's method, b) modified method, and c) published (Bouquet *et al.*, 1982).



Figure 4.12 FTIR spectra of micro-crystalline fraction of Fang crude oil identified by a) Nguyen's method, b) modified method, and c) published (Bouquet *et al.*, 1982).



Figure 4.13 FTIR spectra of macro-crystalline fraction of Lankrabue crude oil identified by a) Nguyen's method, b) modified method, and c) published (Bouquet *et al.*, 1982).



Figure 4.14 FTIR spectra of macro-crystalline fraction of U-thong crude oil identified by a) Nguyen's method, b) modified method, and c) published (Bouquet *et al.*, 1982).



Figure 4.15 FTIR spectra of macro-crystalline fraction of Fang crude oil identified by a) Nguyen's method, b) modified method, and c) published (Bouquet *et al.*, 1982).

reduction as a function of solvent concentrations are shown in Figure 4.16. The effect of dissolution can be described as follows:

1) Pour point reduction with varying concentration of hydrocarbon solvents: the result indicats that pour point decreased as concentration of the solvents in the crude oils increased in a non-linear fashion, to a maximum of approximately 40 °C. Maximum reduction was achieved with 44.4 % (by weight) solvent addition. It was noted that there was no further reduction with further increase in solvent concentration beyond 44.4 %.

2) Pour point reduction with varying lengths of hydrocarbon solvent from n-pentane (C₅) to n-heptane (C₇): Figure 4.16 also shows that when carbon chain length of the solvent was varied from C₅ to C₇, pour point decreased only a few degree celcius, indicating slight effect of carbon chain length. Solvent type and composition showed the same trend in all crude oil samples. The light component such as n-pentane, n-hexane and n-heptane shows various degrees of success to remediate wax deposition in each crude oil.

In this work, the solvents considered have high capacity to dissolve wax and this solution has advantage more than hot-oiling and hot-watering methods.

4.3.2 Effect of Wax Inhibitors

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Wax inhibitors, i.e. polymer, are additives used in the chemical method to inhibit wax deposition. In this study, seven polymers were tested, namely; Poly(methyl methacrylate) or PMMA, poly(ethylene-co-vinyl acetate) (EVA), poly(ethylene -co-butyl acrylate -co-maleic anhydride) or PEBAMA, poly(ethylene -co-vinyl acetate) -graft-maleic anhydride or EVAGMA, poly(maleic anhydride-alt-1-octadecane or PMAO, poly(lauryl methacrylate-co-ethylene glycol or PLEGMA and poly(octadecyl methacrylate or POMA. The effects of polymer wax inhibitors on pour point reduction of Lankrabue, U-thong and Fang crude oils are shown in Figures 4.17-4.19.

- For Lankrabue crude oil, the best polymer wax inhibitor for pour point reduction was poly(maleic anhydride-alt-1-octadecane) (PMAO), at 800 ppm concentration.

- For U-thong crude oil, the best polymer wax inhibitor for pour point



Figure 4.16 Effect of solvents on pour point reduction, a) Lankrabue, b) U-thong, and c) Fang crude oil.



Figure 4.17 Pour point reduction as varied with types and concentration of EVA for a) Lankrabue, b) U-thong, and c) Fang crude oil.



Figure 4.18 Pour point reduction as varied with types and concentration of PMMA for a) Lankrabue, b) U-thong, and c) Fang crude oil.



Figure 4.19 Pour point reduction as varied with types and concentration of other wax inhibitors for a) Lankrabue, b) U-thong, and c) Fang crude oil.

reduction was poly(octadecyl methacrylate) (POMA) at 600 ppm concentration.

- For Fang crude oil, the best polymer wax inhibitor for pour point reduction was 18 % of vinyl acetate in poly(ethylene-co-vinyl acetate) (EVA) at 400 ppm concentration.

The combined effects of solvent and polymer wax inhibitor at maximum pour point reduction are shown in Tables 4.2-4.4. The results indicate that;

- For Lankrabue crude oil, the best condition was obtained when it was treated by 800 ppm poly(maleic anhydride-alt-1- octadecene) (PMAO) in 44 %(wt/wt) n-heptane solution.

- For U-thong crude oil, the best condition was obtained when it was treated by 600 ppm poly(octadecyl methacrylate) (POMA) in 44 %(wt/wt) n-heptane solution.

- For Fang crude oil, the best condition was obtained when it was treated by 600 ppm poly(maleic anhydride-alt-1- octadecane) (PMAO) in 44 %(wt/wt) n-heptane solution.

The results show that the polymers act as wax crystal modifiers that inhibit or alter wax crystal growth by preventing wax networking. The modifiers have structural segments that can interact with forming wax crystals at molecular level to accumulate on each other, thereby reducing the capacity of paraffin wax to network in the oil. The ability to act at the molecular level makes the modifier effective at concentrations in parts-per-million range.

To select a suitable wax inhibitor, one has to consider the solubility of wax inhibitor. The concentration of polymers are generally suggested related to their solubilites in crude oil. In Figure 4.17, percent of vinyl acetate in pcly(ethylene-co-vinyl acetate) (EVA) was varied from 18 to 40 % and the concentration of EVA from 100 to 1000 ppm (wt/wt) as suggested in literature (Zhang *et al.*, 2004 and Behar *et al.*, 2002). The appropriate fraction of vinyl acetate distributing in the polymer for the pour point reduction found in this work was between 18 and 25 % and the polymer concentration range was 200-800 ppm. Different compositions of VA and EVA concentrations are required for different crude oils because of different oil compositions.

		Pour point (°C)					
Chemical	Concentration (ppm)	Without solvent	44.4%(wt/wt) n-Pentane	44.4%(wt/wt) n-Hexane	44.4%(wt/wt) n-Heptane		
No chemical	-	37.1+0.1	-2.0+0.1	-2.5±0.2	-4.5+0.1		
25 %VA of EVA	800 ppm	26.8+0.2	-8.0±0.2	-9.0+0.1	-10.4+0.2		
PMMA (VH)	100 ppm	27.0+0.2	-8.5±0.3	-9.4+0.2	-10.9+0.1		
EVAGMA	1000 ppm	26.0+0.3	-14.0+0.2	-15.1+0.2	-16.1+0.3		
PMAO	800 ppm	19.9+0.1	-21.1+0.1	-22.3+0.1	-24.1+0.2		
PEBAMA	200 ppm	24.5+0.5	-17.1±0.2	-18.1+0.3	-19.6+0.2		
PLEGMA	1000 ppm	25.5+0.3	-14.5+0.2	-15.0+0.1	-16.0+0.2		
POMA	600 ppm	23.0+0.2	-18.0+0.2	-18.5+0.3	-19.1+0.2		

Table 4.2 Effects of wax inhibitors on pour point reduction of Lankrabue crude oil

 Table 4.3 Effects of wax inhibitors on pour point reduction of U-thong crude oil

		Pour point (°C)					
Chemical	Concentration (ppm)	Without solvent	44.4%(wt/wt) n-Pentane	44.4%(wt/wt) n-Hexane	44.4%(wt/wt) n-Heptane		
No chemical	-	35.7+0.1	-4.0+0.1	-4.5+0.2	-6.5+0.2		
25 %VA of EVA	200 ppm	20.9+0.1	-13.9+0.2	-15.8+0.1	-16.8+0.1		
PMMA (MD)	800 ppm	25.1+0.1	-8.9+0.1	-10.1+0.2	-11.5+0.1		
EVAGMA	400 ppm	19.6+0.3	-20.1+0.2	-20.6+0.1	-22.1+0.2		
PMAO	600 ppm	21.9+0.2	-17.1+0.3	-17.5+0.2	-20.1+0.1		
PEBAMA	1000 ppm	23.4+0.1	-16.1+0.1	-17.1+0.1	-19,4+0.3		
PLEGMA	1000 ppm	21.1+0.2	-18.8+0.1	-19.2+0.2	-20.5+0.2		
POMA	600 ppm	17.0+0.1	-22.5+0.1	-23.1+0.1	-24.1+0.2		

Table 4.4	Effects of	wax inhibi	tors on po	our point re	duction of	Fang crude	oil

		Pour point (°C)					
Chemical	Concentration (ppm)	Without solvent	44.4%(wt/wt) n-Pentane	44.4%(wt/wt) n-Hexane	44.4%(wt/wt) n-Heptane		
No chemical	1	31.1+0.1	-10.0+0.3	-10.5+0.2	-12.5+0.2		
18%VA of EVA	400 ppm	19.2+0.2	-20.0+0.2	-21.1+0.2	-22.6+0.1		
PMMA (VH)	200 ppm	24.4+0.1	-16.1+0.1	-17.0+0.1	-18.3+0.2		
EVAGMA	200 ppm	20.1+0.1	-21.1+0.1	-22.1+0.1	-23.0+0.1		
PMAO	600 ppm	19.9+0.2	-20.4+0.2	-21.6+0.2	-24.1+0.2		
PEBAMA	1000 ppm	20.9+0.3	-19.1+0.1	-20.1+0.1	-21.1+0.3		
PLEGMA	1000 ppm	24.4+0.2	-16.5+0.2	-17.5+0.2	-19.1+0.2		
POMA	600 ppm	21.1+0.1	-20.0+0.1	-21.1+0.2	-22,5+0,1		

EVA exerts interaction with molecules of wax in crude oil using the non-polar parts of the EVA molecules to perform excellent affinity with the alkane molecules and to keep distance between the wax molecules. The polar part gives a significant repulsion effect to the n-alkane molecules especially the polar ester group or VA content in the polymer. Generally the efficiency of wax inhibitor increases with VA content. However, if the VA content is too high, it might be hard to dissolve in crude oil. The loss of efficiency observed at high concentration may be ascribed to precipitation of the pure inhibitor instead of n-paraffin, or to wax crystallization with nucleation induced by the co-polymer.

From different chemical structures of wax inhibitors the effect to each crude oil can be compared, taking EVA, and PMMA as a typical example; PMMA has the same methacrylate group as EVA but it has only polar part while EVA has both polar and non polar part. The result shows that EVA resulted in higher pour point reduction than PMMA for three crude oils. It can be concluded that non polar part (hydrocarbons) in wax inhibitor help reducing the pour point. For PMMA, PLEGMA and POMA; they have the same structure, but differ only the length of hydrocarbons, acting as the non-polar part. The effects of hydrocarbon lengths to pour points reduction, from least to most are PMMA < PLEGMA < POMA. In the case of EVAGMA and PEBAMA, PEBAMA has longer hydrocarbon chains in substituted group than EVAGMA, thus one should expect to see lower pour points than EVAGMA. However, this is not true for U-thong crude oil as PEBAMA gives higher pour point than EVAGMA. It is possible that the polarity of solvents, EVAGMA and PEBAMA, come into play. EVAGMA has higher polarity than PMMA. EVAGMA is EVA grafted with maleic anhydride group which has ligher, polarity than EVA. The result shows that by increasing polarity of wax inhibitors, pour point reduction will increase, except for Fang crude oil. PMAO has higher polarity than POMA and showed more pronounced effect to reduce pour point lower than POMA. The result of U-thong crude oil shows the significant pour point reduction of PMAO less than POMA, thus for polarity effect, it shows no correlation between pour point reduction and polarity of wax inhibitor and it may depend on the structure of crude oil as well.

It can be summarized that the factors which affect pour point reduction of Lankrabue crude oil depend on non-polar part more than polar part of the wax inhibitor while these of U-thong crude oil depend on polarity of wax inhibitor more than non polar part of wax inhibitor. Comparison of macrocrystalline fraction in the two crude oils (Figure 4.4) shows the same ranges of hydrocarbon (C_{15} - C_{38}) but with different intensity. The higher intensity of macrocrystalline or higher wax content of U-thong might be an important factor in making the polar part of wax inhibitors more effective than the non-polar part in both main and substituted group. Again, the polarity of wax inhibitor plays a more important role than non polar part for Fang crude oil because the higher intensity of macrocrystalline.

The results show that effects of polymer alone can reduce the pour point within the range of 10-17 °C for Lankrabue and U-thong and 7-10 °C for Fang depending on the generic nature from different compositions in each crude oil. Thus, to identify the common influence responsible for wax inhibitation, the main requirements should be that the alkyl chain in crude oil interactions be treated consistently and with a non-polar part in wax inhibitors that gave at least a semiquantitative description of paraffin liquid and crystal structure.

The maximum effects of pour point reductions are summarized in Tables 4.2-4.4 indicating that different types of polymers exerted different dispersion effects to the wax component. In addition, the combined effects of polymer inhibitor and solvent show that the effects were additive, without synergism and the pour point reduction of crude oil depended on the crude composition.

In the combined wax inhibitor and solvent system, the solvent can reduce the pour point in the same, manner as the non polar part of wax inhibitor. The results show that the best condition was obtained when the solvent was used together with the inhibitor. The solvent and wax inhibitor cooperated together by solvent dissolving some wax and the remaining of wax interacting with the polar and non polar part of wax inhibitor.