CHAPTER IV
RESULTS AND DISCUSSION

4.1 Crude Oil Characterizations

4.1.1 Properties of Crude Oil

The physical properties, i.e. pour point temperature, viscosity, specific gravity, API gravity, WAT, and WDT, were determined and reported in Table 4.1. Generally, the WDT is somewhat higher than the WAT for all crudes. The difference between WAT and WDT might be due to undercooling and overheating that result in non-equilibrium conditions during fast temperature scanning (Elsharkawy *et al.*, 2000).

Table 4.1 Physical properties of Phet Crude

Pour point (°C)	Viscosity (cP) *	Specific gravity **	API gravity	WAT (°C)	WDT (°C)
30.8	248	0.805	40.45	31	46

Note * at 26.6°C and ** at 40°C

4.1.2 Crude Oil Composition

Normally, crude oil is a complex chemical system containing several kinds of hydrocarbons, such as n-paraffin, branched paraffin, naphthene, and aromatic. In this work, crude oil composition was analyzed by simulated distillation gas chromatography (Sim-Dist GC) following ASTM D2887. Due to a limitation of standard references, the analysis of hydrocarbons in crude performed on straight chain (paraffins) only. The chromatogram of crude and the crude oil composition show in Figure 4.1. The result shows that Phet crude consists of hydrocarbon with C number in the range of C_{11}-C_{24}. In addition, true boiling point curve shown in Figure 4.2 reveals new crude was lighter than previous crude (the data was obtained from last year) due to different production time period.

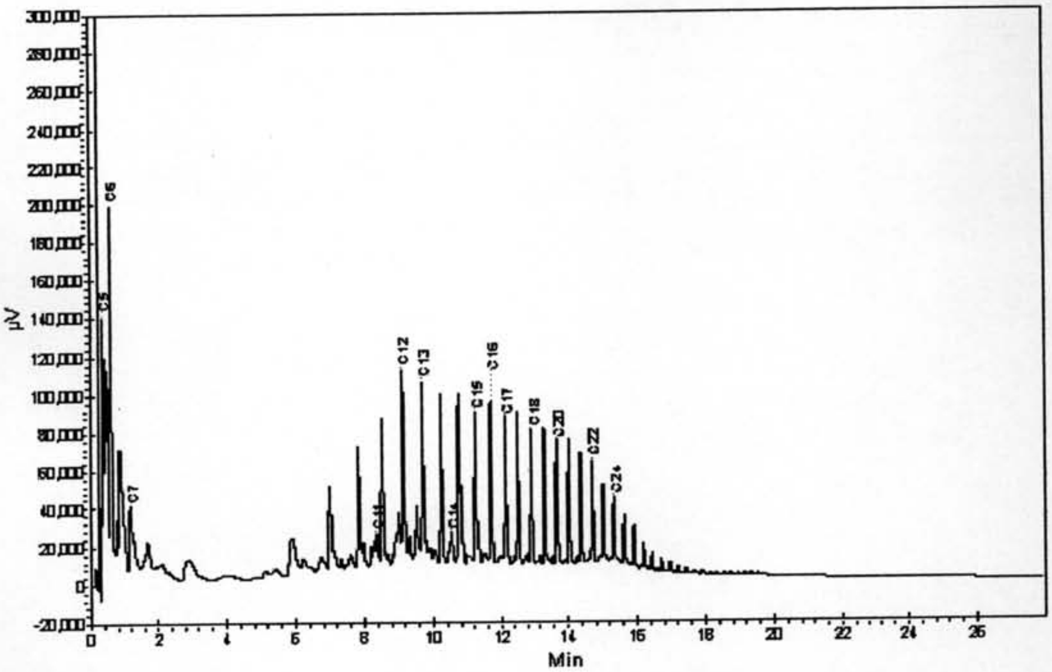


Figure 4.1 Chromatogram of Phet crude oil analyzed by Sim-Dist GC.

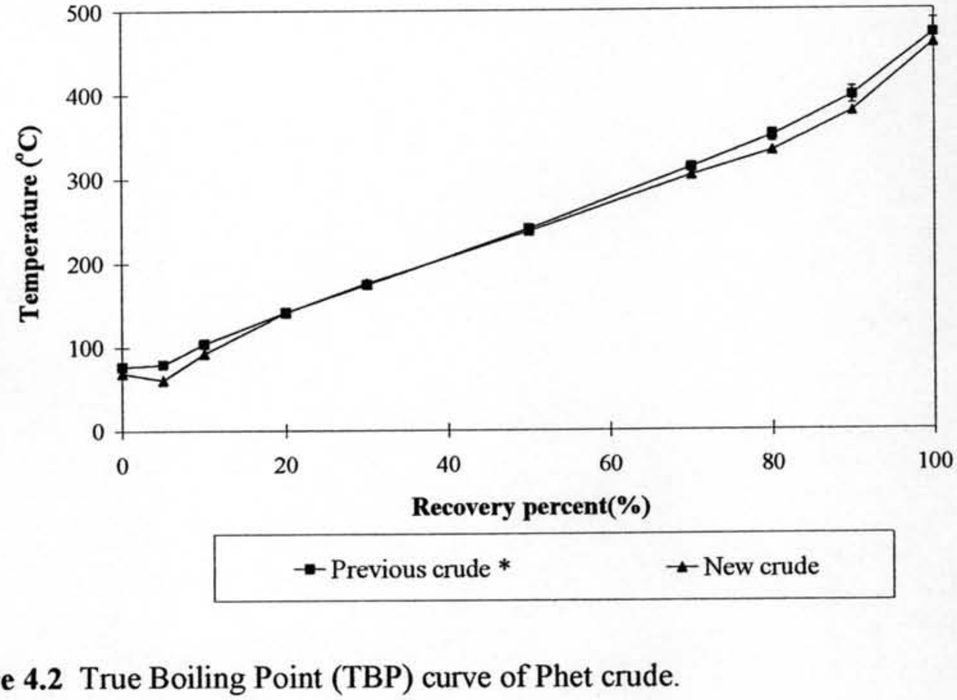


Figure 4.2 True Boiling Point (TBP) curve of Phet crude.

4.1.3 Fractionation of Crude Oil

Wax and asphaltene compositions in the crude oil sample were separated based on the methods suggested by modified Nguyen's method (Srisirivilaikul, 2004). The fractions of micro- and macro-crystallines obtained from the modified method are shown in Figure 4.3 and Figure 4.4, respectively. It is clearly seen that the chromatogram of identified microcrystalline (branched paraffin) fraction (Figure 4.3) showed a cluster of hydrocarbons with carbon number in the range of C_{18}-C_{28}. The macrocrystalline (n-paraffin wax) fraction, as shown in Figure 4.4, exhibited somewhat similar carbon clusters (C_{16}-C_{24}) to the microcrystalline fraction, but these fractions contain higher hydrocarbon content than the microcrystalline fraction.

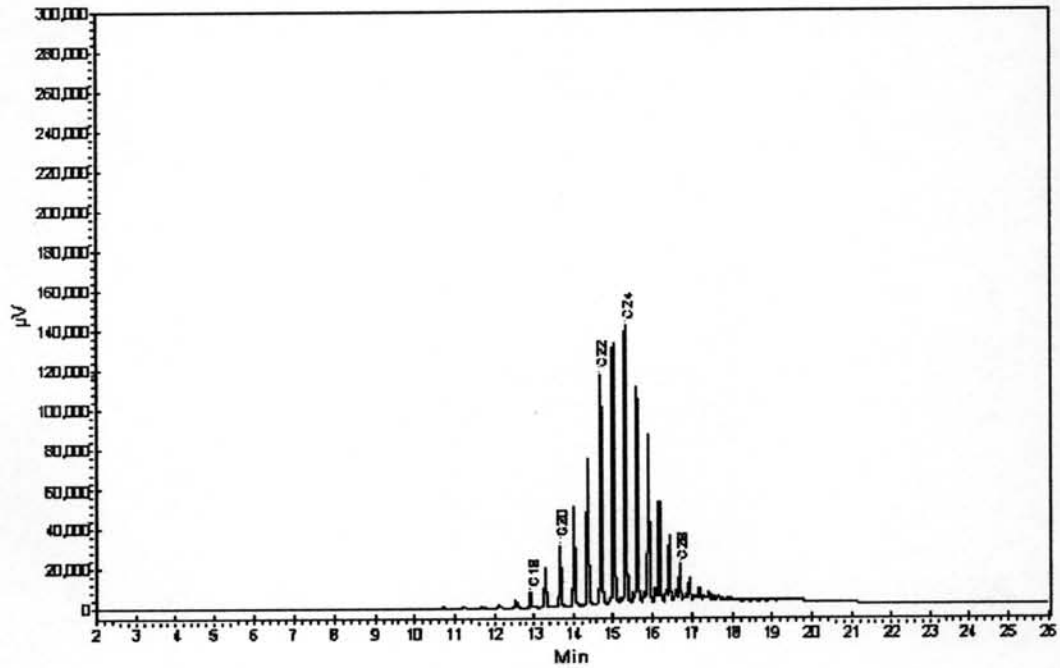


Figure 4.3 Simulated distillation chromatogram of microcrystalline (branched paraffin) fraction of Phet crude.

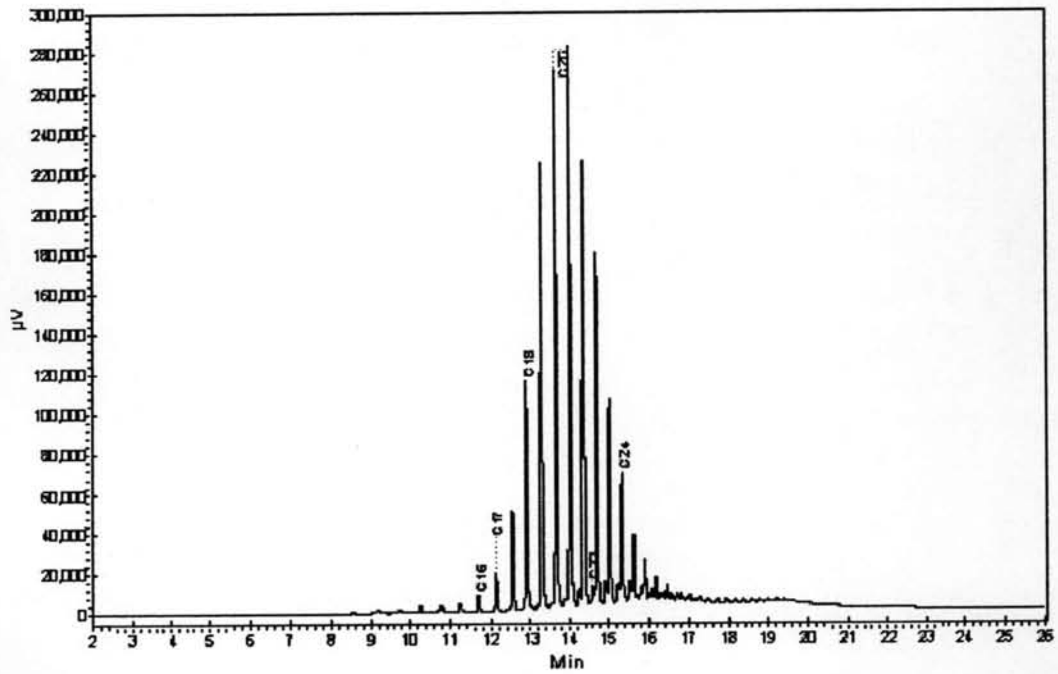


Figure 4.4 Simulated distillation chromatogram of macrocrystalline fraction of Phet crude.

4.2 Effect of Wax Inhibitors on Pour Point Reduction

4.2.1 Effect of Analytical Grade Polymer Inhibitors

Poly(ethylene-co-vinyl acetate) (EVA) and their derivatives were investigated as wax inhibitors at 60°C. The effect of EVA with 25, 33, and 40% vinyl acetate content on pour point of the crude oil is shown in Figure 4.5. The results show that the pour point decreased as the concentration increased. Furthermore, the EVA with 40% vinyl acetate content was the most effective polymer since it reduced the pour point to 16.3°C at 1,000 ppm. However, at a low concentration, EVA with 25% vinyl acetate content showed the best effect on pour point reduction to 21°C at 200 ppm.

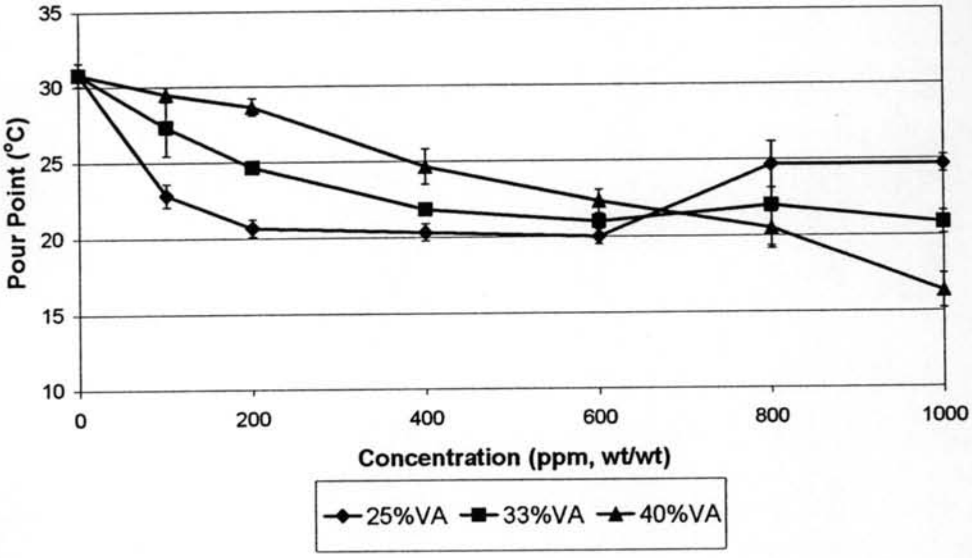


Figure 4.5 Pour point comparison of crude mixed with various types and concentrations of EVA (AR Grade) and preheated at 60°C.

4.2.2 Effect of Commercial Grade Polymer Inhibitors

The commercial grade poly(ethylene-co-vinyl acetate) or EVAFLEX was also used in this research. The effect of EVAFLEX with 28, 33, and 41% vinyl acetate content on the pour point reduction is shown in Figure 4.6. EVAFLEX with 33% vinyl acetate content was the most effective polymer because it could reduce the pour point from 30.8°C to around 18°C at 1,000 ppm. In addition, at a low concentration (400 ppm) of EVAFLEX, 28% vinyl acetate content showed the best effect since it could reduce pour point to 20°C. On the other hand, EVAFLEX with 41% vinyl acetate content was not appropriate as wax inhibitor.

When comparing analytical grade EVA with EVAFLEX, the results show that similar trend of pour point reduction was observed, except that commercial grade EVA with 41% vinyl acetate content was not as effective as analytical grade EVA with 40% vinyl acetate content. The commercial EVAFLEX was accepted for industrial use. The EVAFLEX with 25 and 33% vinyl acetate content was then selected for further experiments.

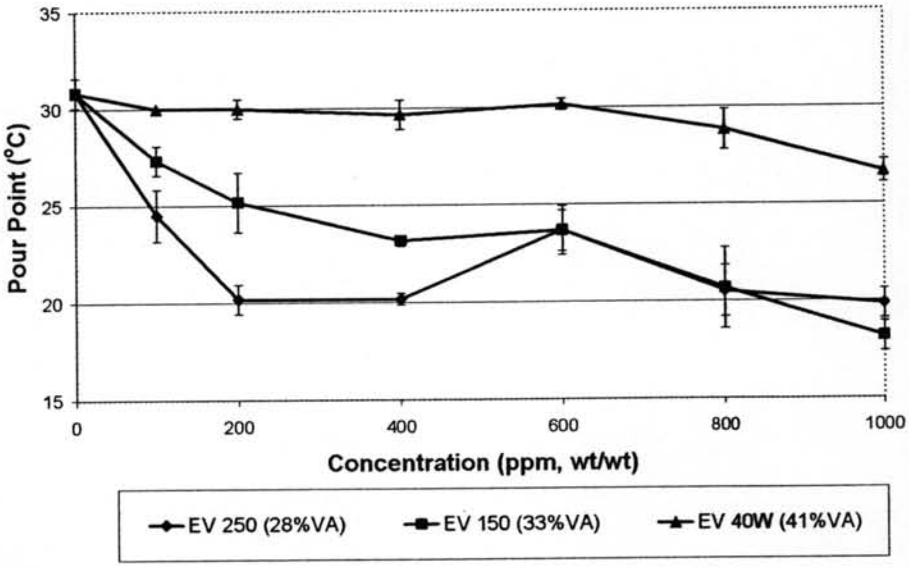


Figure 4.6 Pour point comparison of crude mixed with various types and concentrations of EVAFLEX and preheated at 60°C.

The results from analytical and commercial grade EVA indicated that the number of vinyl acetate distributing in the polymer is played an important role on the pour point reduction. EVA might exert interaction to molecules of wax by using the non-polar hydrocarbon backbone of its structure to attach the alkane molecules, whereas, the polar part of vinyl acetate groups provide a significant repulsion effect to the n-alkane molecules, for inhibiting the aggregation of the wax nuclei. Thus, wax molecules are dispersed.

4.3 Effect of Wax Inhibitor on Remaining-On-Board (ROB) Using Semi-Pilot Scale Test

4.3.1 Effect of Poly(ethylene-co-vinyl acetate) on ROB Reduction Using Steel and Glass Containers.

There was a technical restriction on using water aspirator as a vacuum pump to drain off the crude through the small outlet of the steel container, the crude oil could not be pumped out from the steel container, although the crude oil with the inhibitor present was a fluid. Thus, the experiment was not carried out further and the glass container was used instead. After the experiment was done in glass container, crude oil was poured out by gravity force for 30 min and the remaining was called the remaining-on-board (ROB). In addition, the efficiency of inhibitor was determined by using ROB reduction.

$$\text{ROB reduction} = \frac{\text{The amount of crude} - \text{The amount of ROB}}{\text{The amount of crude}}$$

In the lab test, the crude without the inhibitor was semisolid, which could not be pour out and then totally became ROB.

4.3.1.1 Effect of EVA and EVAFLEX on ROB Reduction

Analytical grade poly(ethylene-co-vinyl acetate), or EVA, and their derivatives were investigated at 60°C. ROB reduction as shown in Figure 4.7. EVA with 40% vinyl acetate content was the most effective at relatively high concentration of 1,000 ppm, since the ROB decreased 89.5%. However, at lower concentrations of EVA with 25% vinyl acetate content showed better ROB reduction of 93% at 200 ppm.

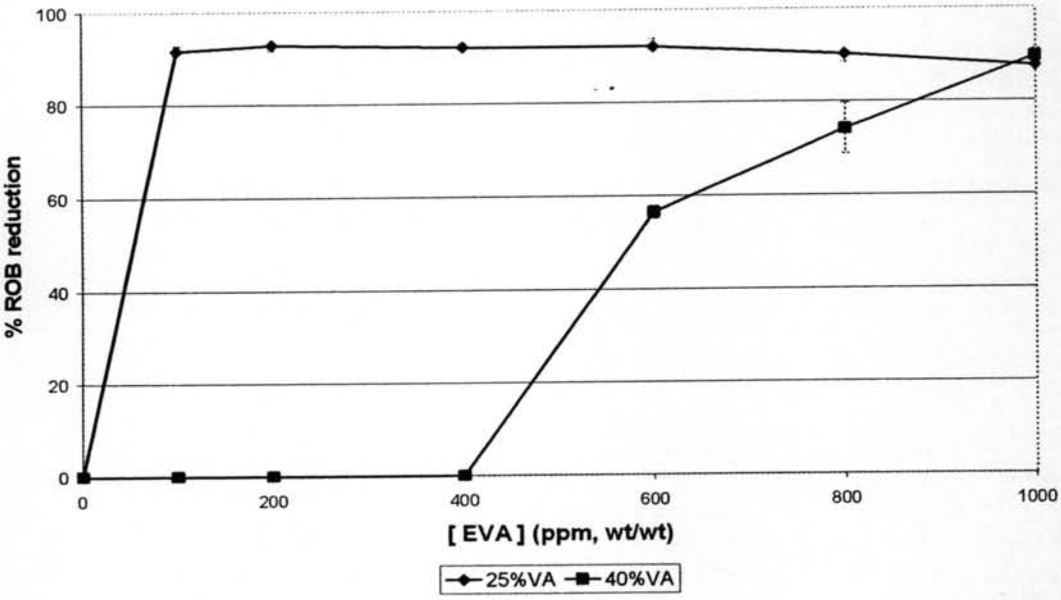


Figure 4.7 % Remaining-on-board comparison of crude using EVA at 60°C.

For the commercial grade EVAFLEX, the ROB reduction is shown in Figure 4.8. EVAFLEX with 33% vinyl acetate content was the most effective polymer with the ROB reduction of 96.5% at 1,000 ppm. In addition, at a low concentration of EVAFLEX, 28% vinyl content showed a good ROB reduction of 90.5% at 400 ppm.

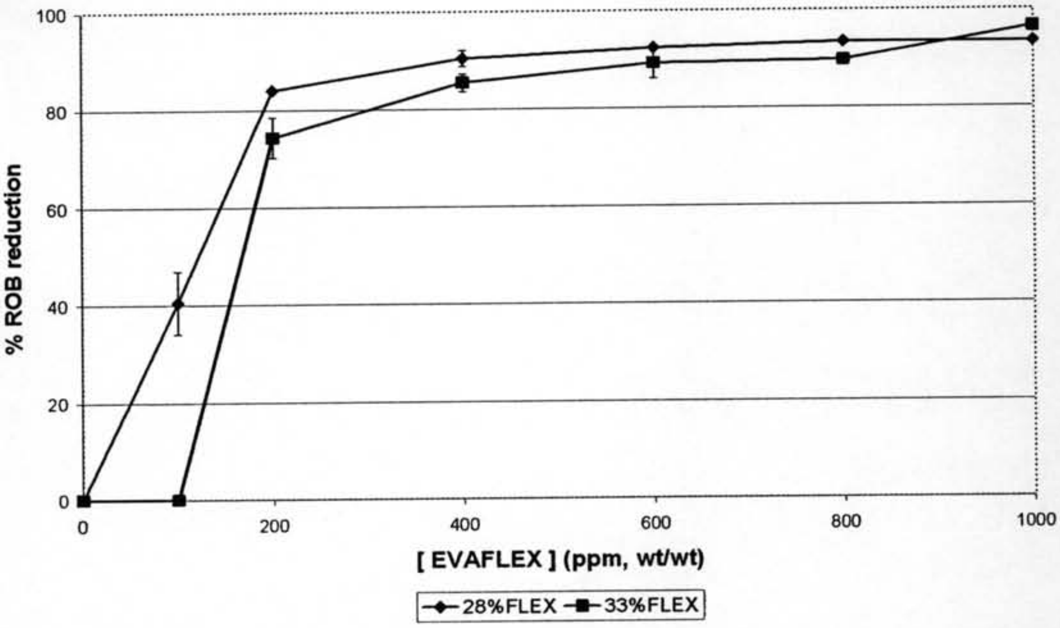


Figure 4.8 % Remaining-on-board comparison of crude using EVAFLEX at 60°C.

The obtained ROB was correlated to the pour point temperature as shown in Figures 4.9 and 4.10. The results show that the ROB decreased as the pour point decreased.

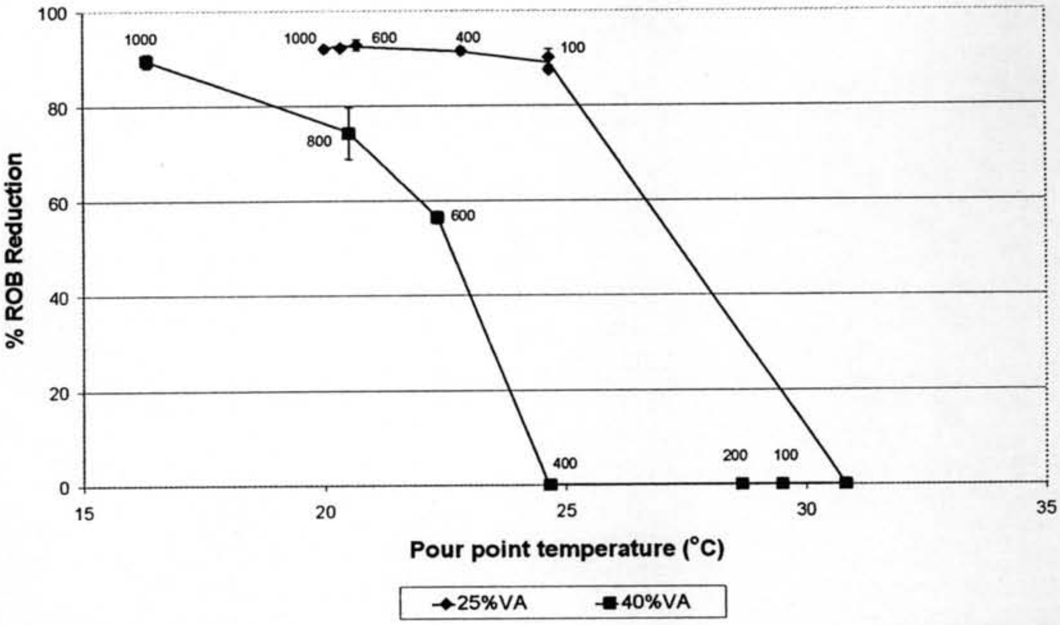


Figure 4.9 Correlation of ROB reduction with pour point temperature of crude using EVA inhibitor.

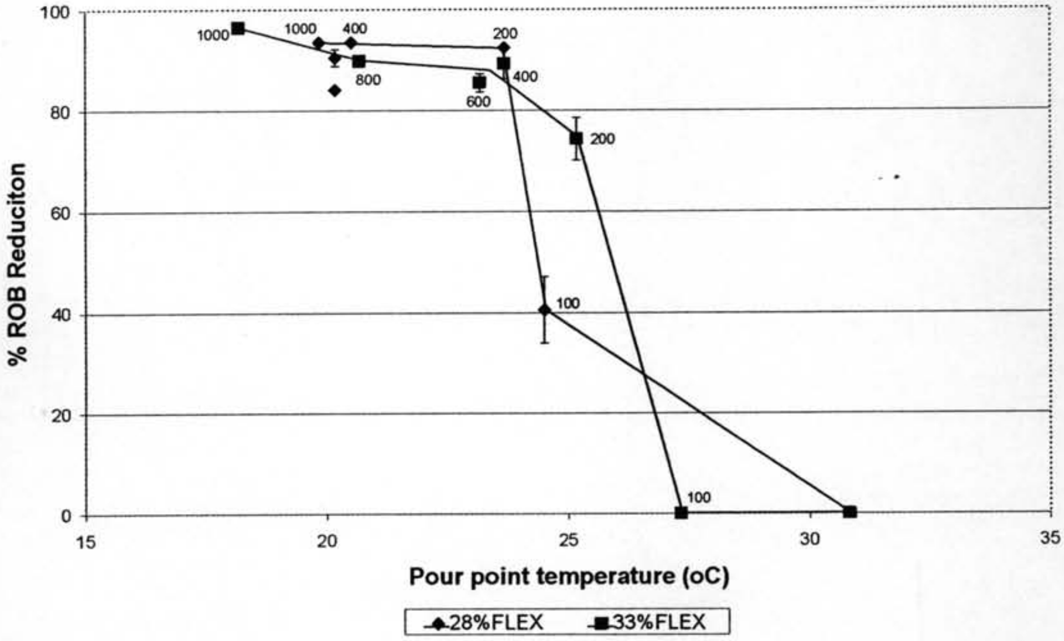
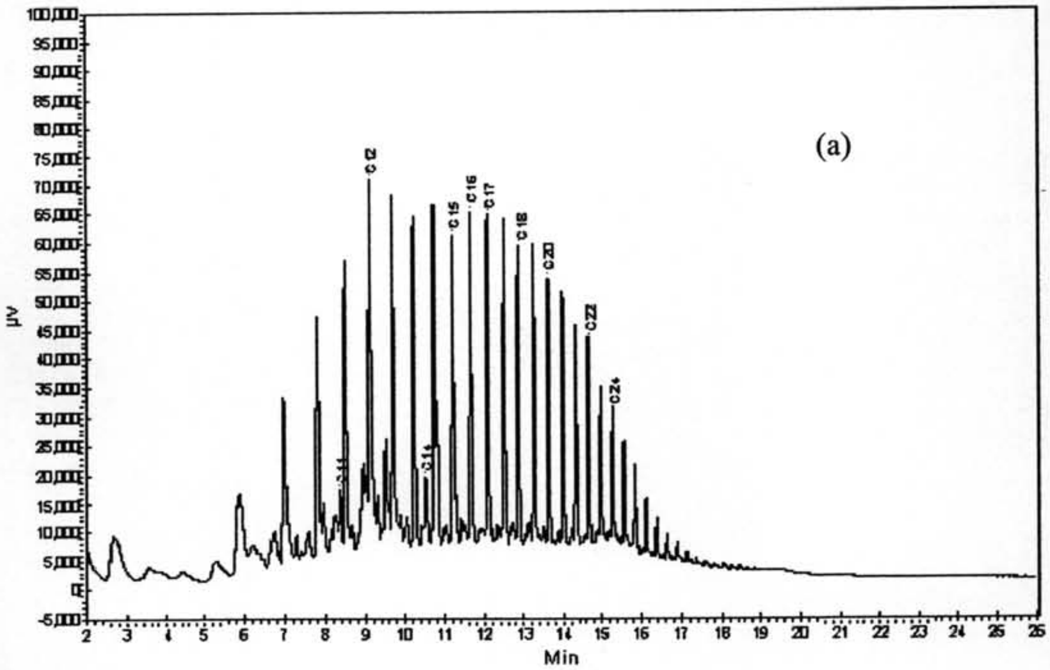


Figure 4.10 Correlation of ROB reduction with pour point temperature of crude using EVAFLEX inhibitor.

4.3.1.2 Pour Point Temperature of Oil and ROB Fractions from Semi-Pilot Scale Test (Glass Container)

When the experiments of semi-pilot scale test were done in glass container, the crude oil sample was divided into two fractions; oil and ROB. Both of these two fractions were separated to determine pour point temperature.

After the inhibitor was introduced into the crude oil in a glass container with shaking at 30°C for 12 h, the oil fluid was drained off as an oil fraction by gravity force for 30 min and the semisolid sticking in the glass container as ROB fraction. Chromatograms of the oil and ROB fractions are presented in Figure 4.11 a) and b) were not noticeably different. The pour point temperature of oil fraction and ROB fraction are shown in Figures 4.12, 4.13, 4.14, and 4.15. All results show that pour point of ROB are higher than that of the oil fraction. In addition, the pour point temperature of both oil and ROB fractions decreased as the concentration increased.



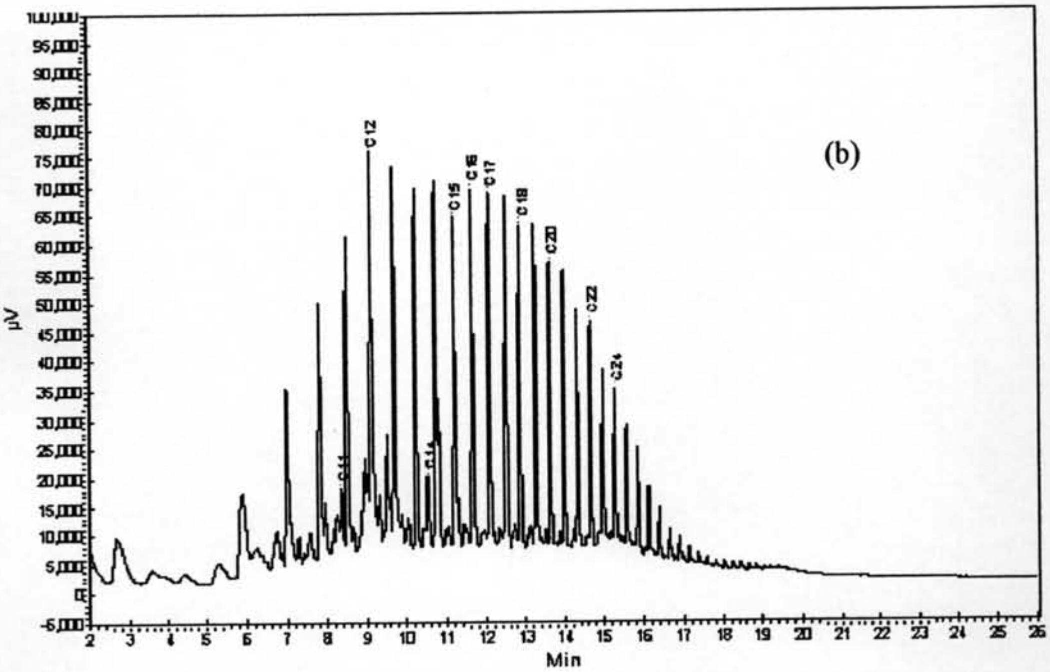


Figure 4.11 Chromatograms of (a) Oil (b) and ROB fraction with EVAFLEX with 28%VA content at 200 ppm.

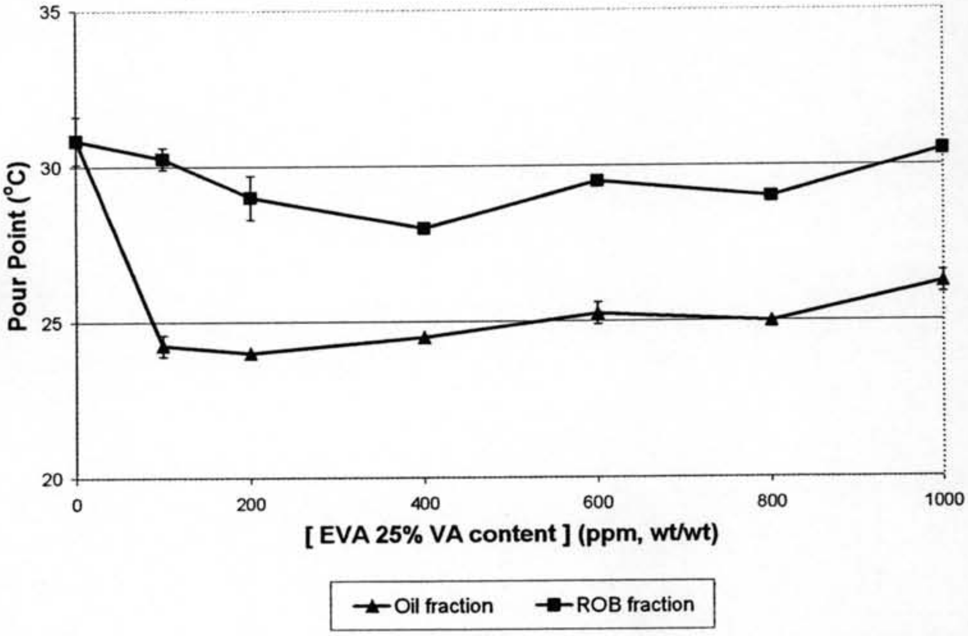


Figure 4.12 Pour point comparison of oil and ROB fractions mixed with EVA with 25% vinyl acetate content and preheated at 60°C.

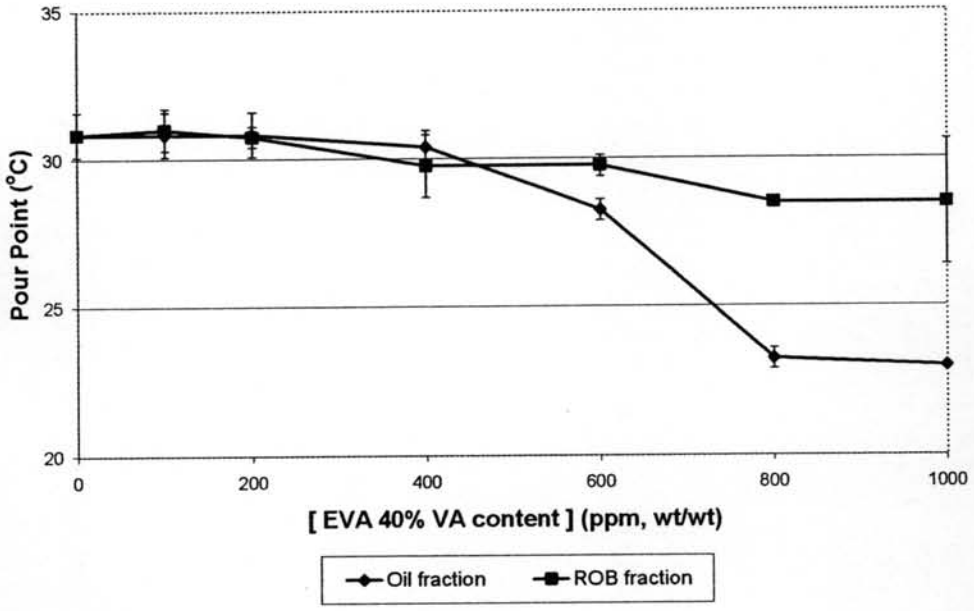


Figure 4.13 Pour point comparison of oil and ROB fractions mixed with EVA with 40% vinyl acetate content and preheated at 60°C.

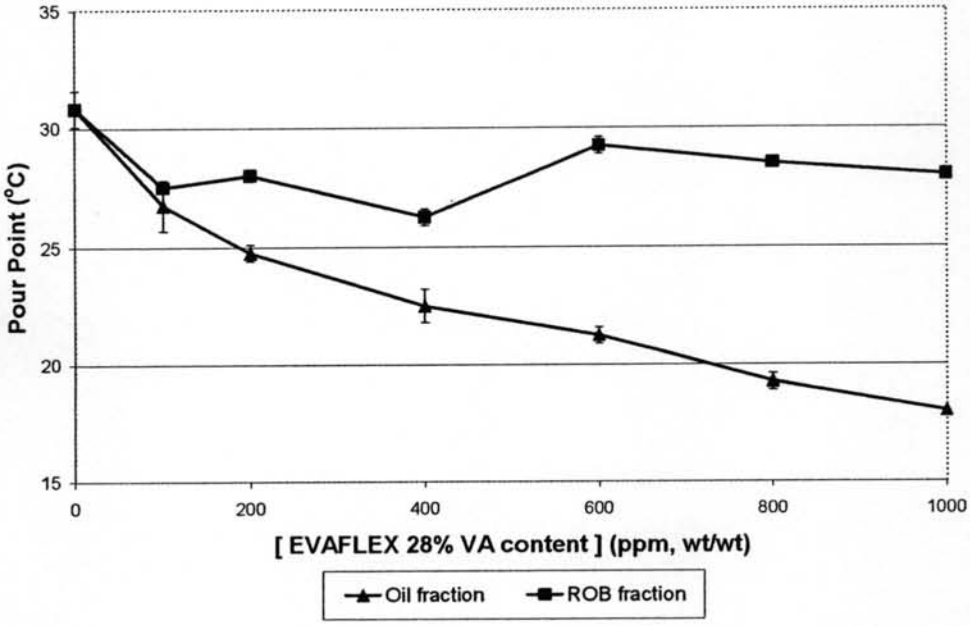


Figure 4.14 Pour point comparison of oil and ROB fractions mixed with EVAFLEX with 28% vinyl acetate content and preheated at 60°C.

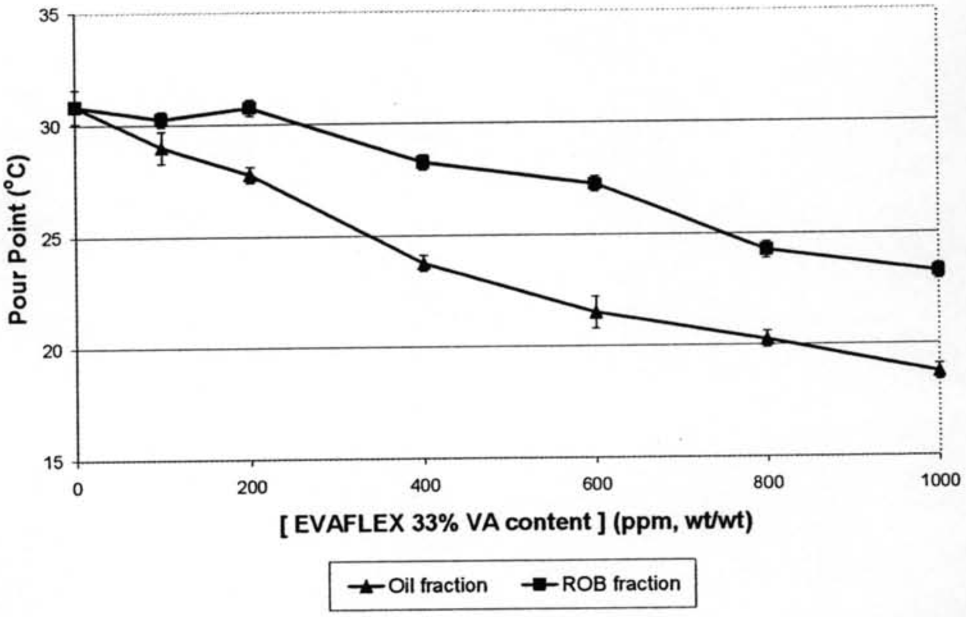


Figure 4.15 Pour point comparison of oil and ROB fractions mixed with EVAFLEX with 33% vinyl acetate content and preheated at 60°C.

4.4 Effect of Poly(ethylene-co-vinyl acetate) on ROB Using Actual Train Wagon Test

EVAFLEX with 33% vinyl acetate content was selected to use in the actual train wagon test at Bung Phra station and Bangchak refinery at the concentration of 400 ppm based on the experimental results in semi-pilot scale test (Figure 4.10), which the pour point temperature and % ROB reduction at this concentration were 23°C and 85.5%, respectively.

At Bung Phra depot loading point, the average loading temperature was 48°C and pour point temperature of crude with and without inhibitor was 28.5 and 30°C, while the pour point of the same crude measured in the lab at 60°C was 23 and 30°C, respectively (as shown in Figure 4.16). When crude was being loaded at Bung Phra depot, there were no oil and ROB fractions separated, only crude was sampling for pour point determination. When the empty wagons were sent back to Bung Phra depot for new loading, the ROB fraction occurs in the wagon, only ROB was sampling for pour point determination, which were 35.5 and 34°C for ROB with and without the inhibitor, respectively at preheated 48°C, while in the lab at preheated temperature of 60°C was 36 and 34°C, respectively (as shown in Figure 4.16). For the crude preheated at 60°C, the results showed significant effect of inhibitor on the pour point, while there was no different effect for ROB preheated at 48°C and 60°C.

The crude was transported about 10 hours by train to be unloaded at Bangchak refinery, where the crude may separate into oil and ROB fractions, therefore, the sampling was called an oil fraction and the unloadable crude called ROB fraction. The ROB was remeasured when the train wagon got back to Bung Phra depot. The pour point temperature of oil fraction conducted at 48°C were 28 and 30°C for oil fraction with and without the inhibitor, respectively, while measured in the lab at 60°C were 23 and 30°C, respectively (as shown in Figure 4.17), which were similar to the pour point of crude at Bung Phra loading point. The pour point temperatures of ROB preheated at 48°C with and without inhibitor were 34 and 31.5°C, while in the lab at 60°C were 34 and 32°C, respectively (as shown in Figure 4.17). However, the average pour point of the ROB at Bangchak was the same as that at Bung Phra.

The results from Simdist-GC showed that the composition of ROB with inhibitor consists of higher molecular fraction, but absent in the ROB fraction without inhibitor as shown in Figure 4.18 and 4.19, which may indicated ineffectively homogenizing of inhibitor in the crude and resulted in precipitation of inhibitor in the ROB.

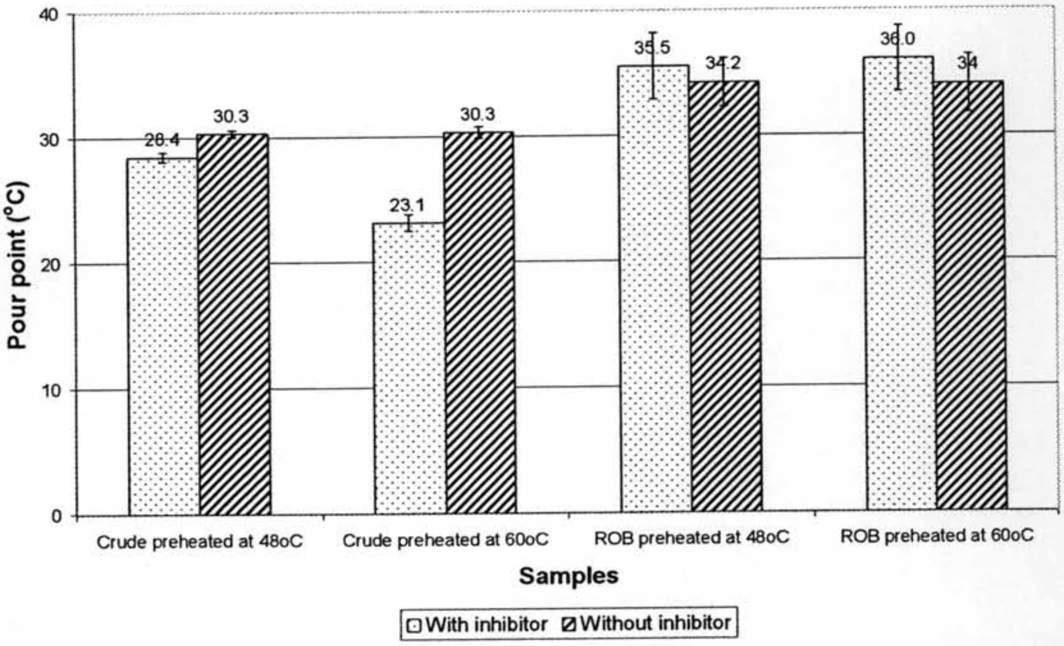


Figure 4.16 Pour point temperatures of crude and ROB at Bung Phra depot. The crude and ROB were preheated at 48°C and 60°C.

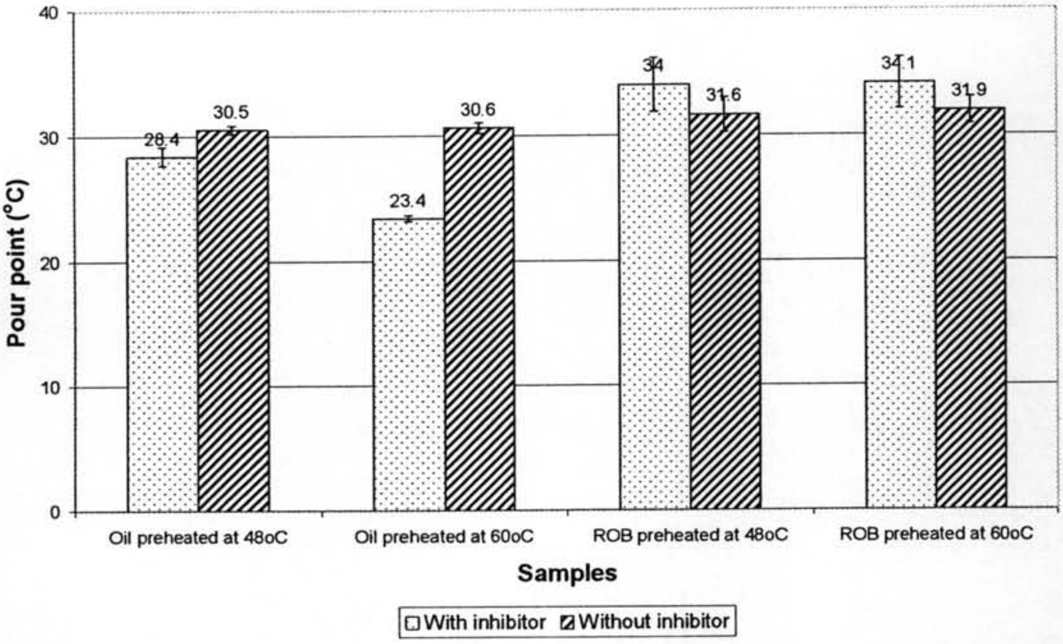
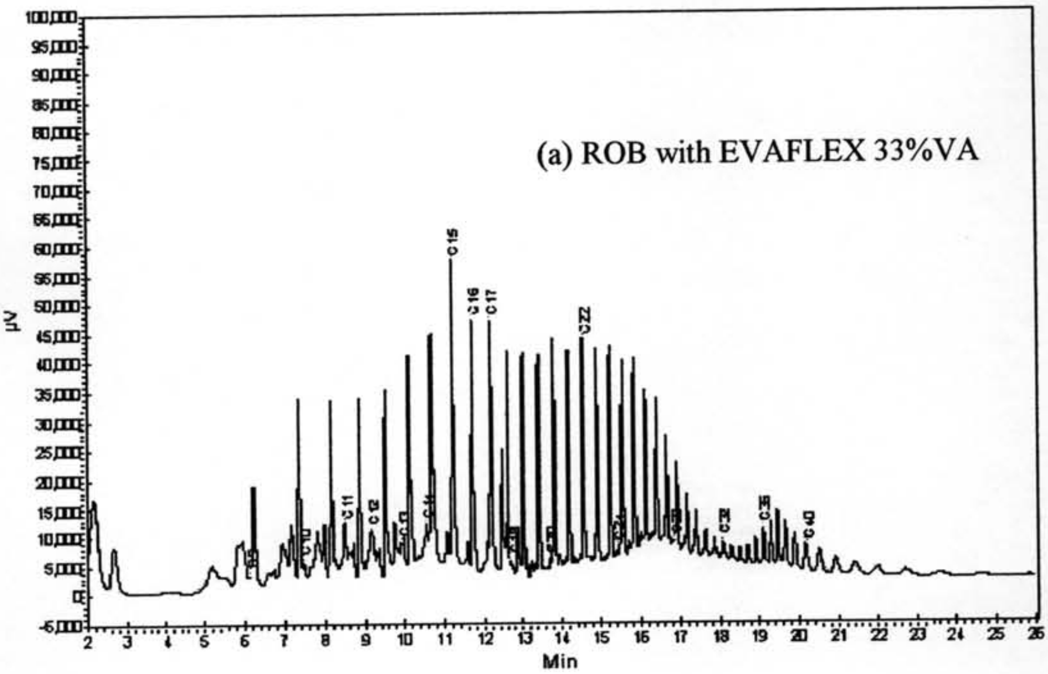


Figure 4.17 Pour point temperatures of crude and ROB at Bangchak refinery. The crude and ROB were preheated at 48°C and 60°C.



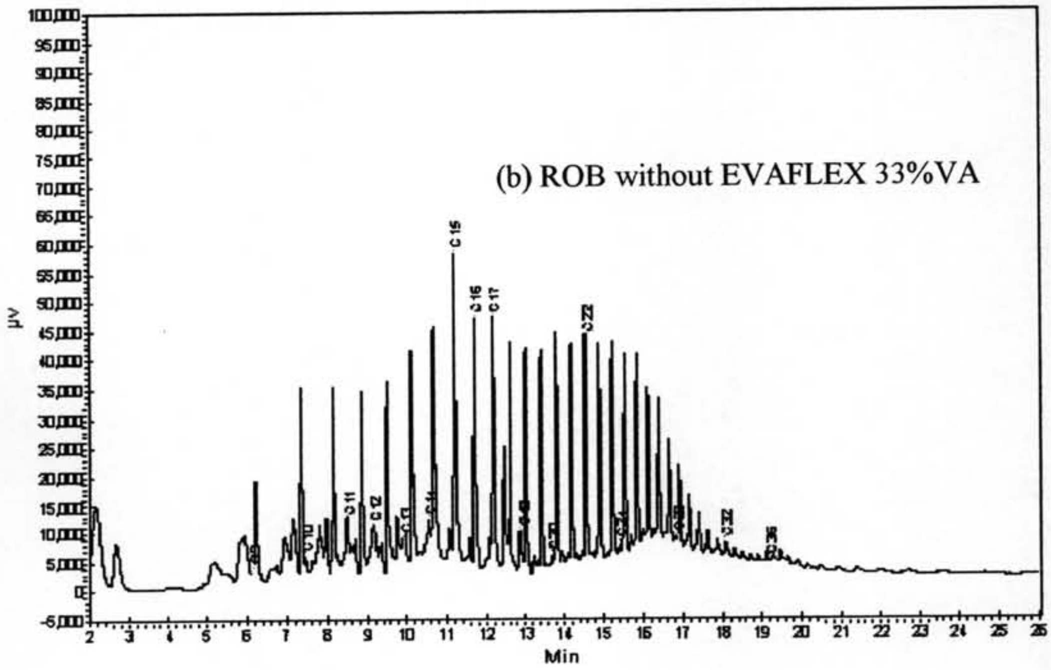


Figure 4.18 Chromatograms of ROB fraction.

4.4.1 Effect of Temperature on Inhibitor Efficiency

The effect of temperature on pour point and ROB reduction was studied at 48, 52, 56, and 60°C using EVAFLEX 28% vinyl acetate content at 400 ppm and 33% vinyl acetate content at 1,000 ppm. The results showed that the inhibitor decrease the pour point temperature above 52°C (Figure 4.19). Accordingly, the ROB reduction increase at the temperature higher than 52°C as shown in Figure 4.20. At the temperature below 52°C, the preheated crude appearance was semisolid which could not be drained off. As the result, the whole crude completely became ROB in the glass container. The results of ROB obtained from the lab test was completely different from the actual train wagon test in that the crude was semisolid in the lab and totally became ROB however the crude was still fluid in the train wagon at the same temperature of 48°C. Therefore, we attempt to fluidize the crude at 48°C in the lab test by varying the EVAFLEX concentration. As shown in Figure 4.21, the results showed that the pour point did not change with varying the inhibitor at 48°C. The result confirmed the ineffectiveness of the inhibitor that used in the train wagon operating at 48°C. At the temperature above 52°C, the crude was separated into two fractions, oil and ROB. Then, the pour points of the oil and ROB fractions were investigated. The results in Figures 4.22 and 4.23 show that the pour points of the oil fraction was lower than the ROB fraction probably due to different amount of the inhibitor distributing into the two fractions.

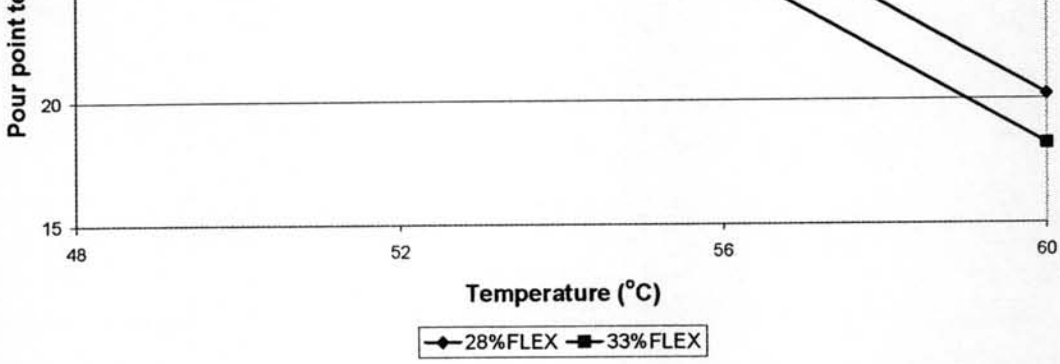


Figure 4.19 Pour point temperature of crude preheated at different temperature.

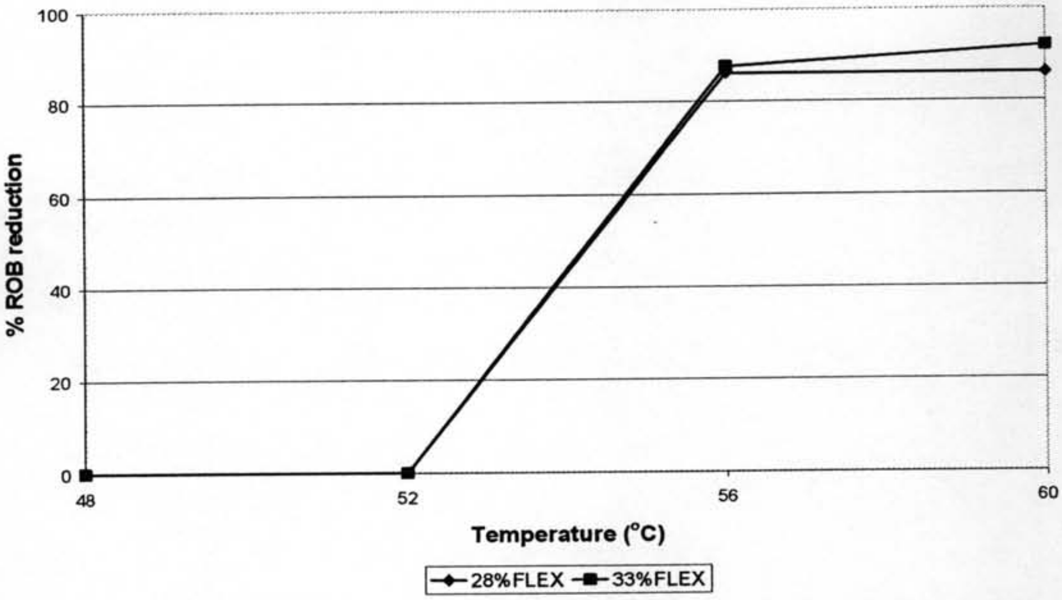


Figure 4.20 % Remaining-on-board of crude preheated at different temperature.

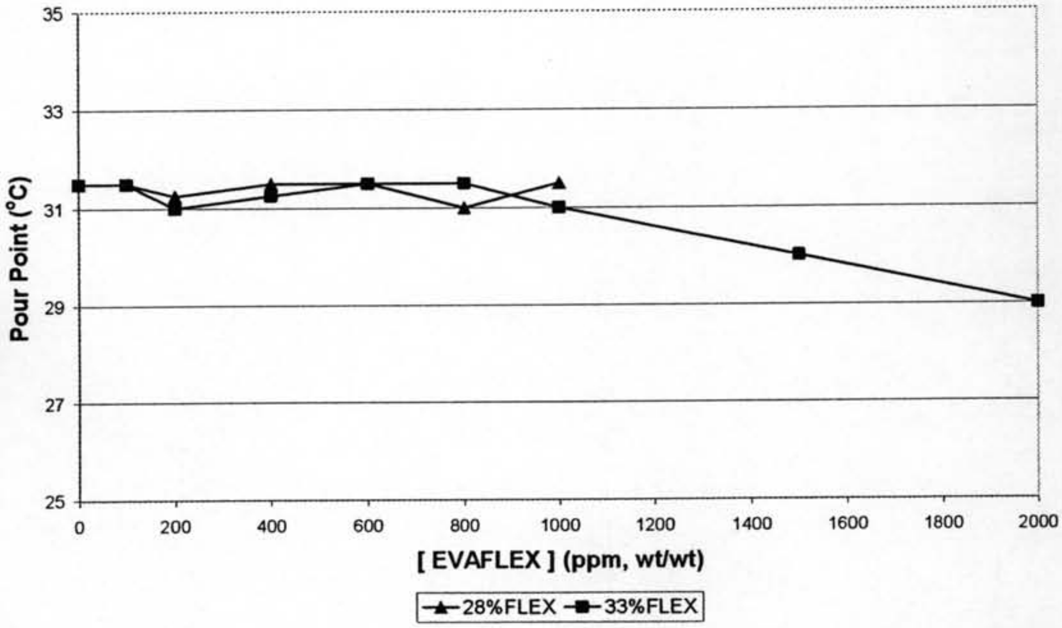


Figure 4.21 Pour point comparison of crude mixed with various types and concentrations of EVAFLEX and preheated at 48°C.

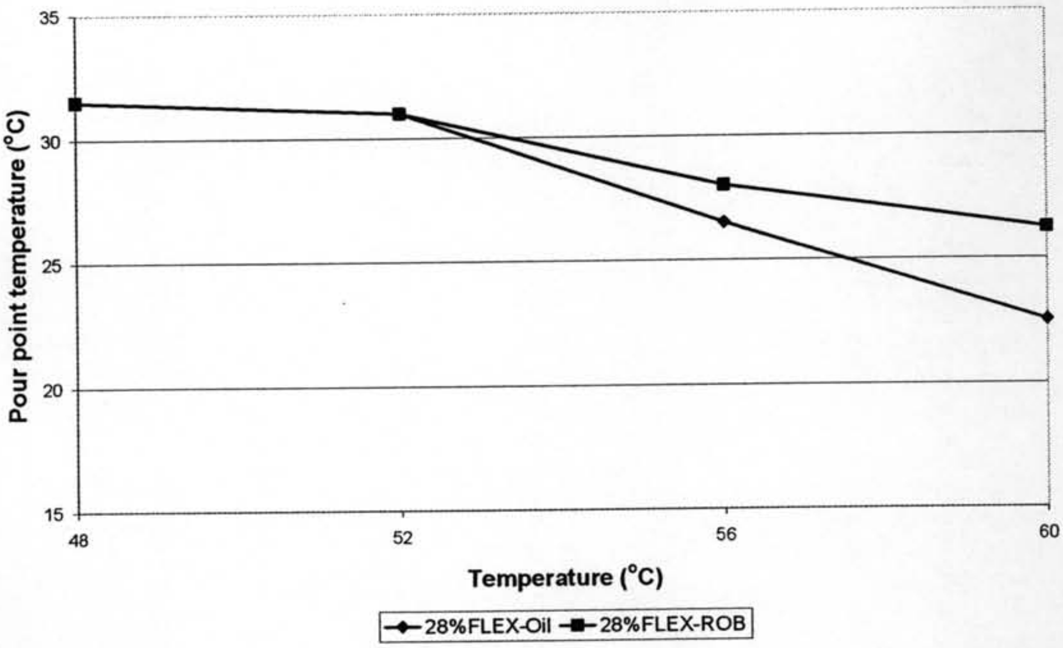


Figure 4.22 Pour point of oil and ROB fractions in the presence of 400 ppm EVAFLEX with 28% vinyl acetate content and preheated at different temperature.

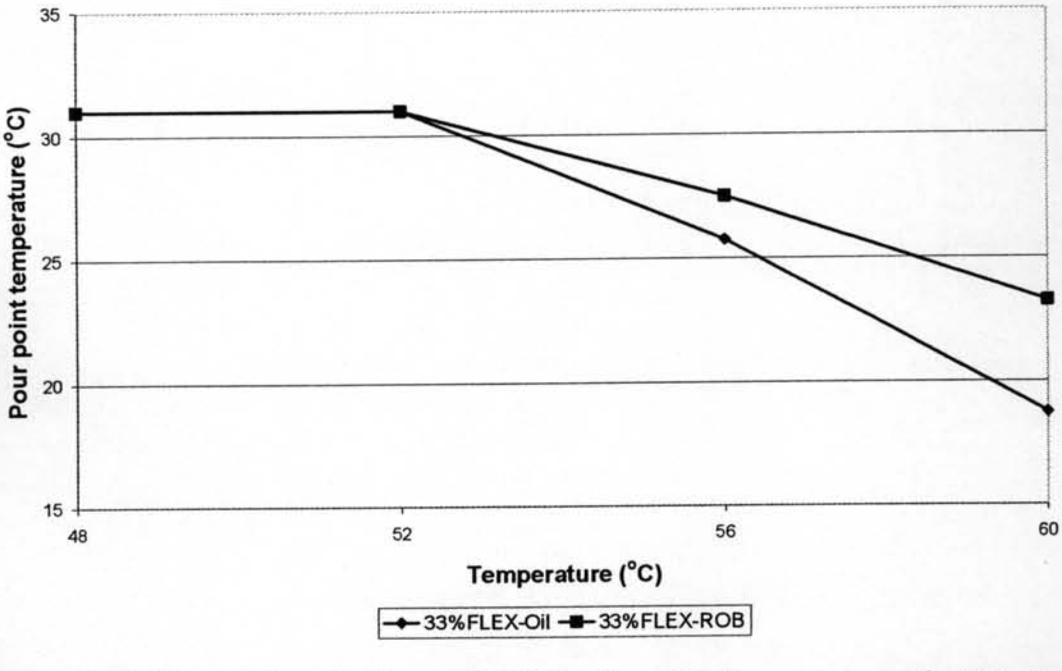


Figure 4.23 Pour point of oil and ROB fractions in the presence of 1000 ppm EVAFLEX with 33% vinyl acetate content and preheated at different temperature.

4.4.2 WAT and WDT Determination

WAT and WDT of crude, oil fraction and ROB fraction obtain from the lab test (glass container) and the train wagons with and without EVAFLEX 33%VA were determined as shown in Figure 4.24. The results showed that various fractions did not show significantly different in the WAT and WDT.

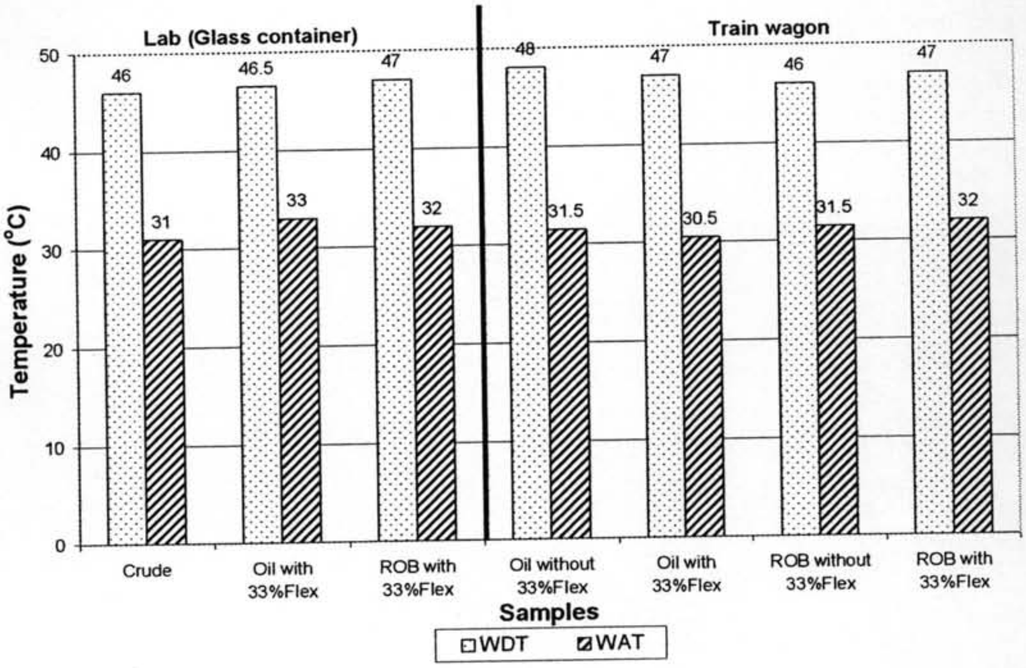


Figure 4.24 WAT and WDT of crude, oil fraction and ROB fraction with and without inhibitor (33% EVAFLEX) performed in lab and train wagon.

Furthermore, the total enthalpy of wax precipitation and dissolution corresponding to WAT and WDT in Figure 4.24 were also measured. The total enthalpy of precipitation (total energy released during cooling) or enthalpy of dissolution (absorbed during heating process) of crude oil is proportional to the areas under the exothermic or endothermic peak, respectively. The thermogram presenting heat releasing and WAT is shown in Figure 4.25. The total enthalpy required to change transition state of liquid-solid depends on composition present in crude as shown in Figure 4.26. The result showed that ΔH_{WAT} and ΔH_{WDT} of wax obtained from real wagon was significantly higher than the others.

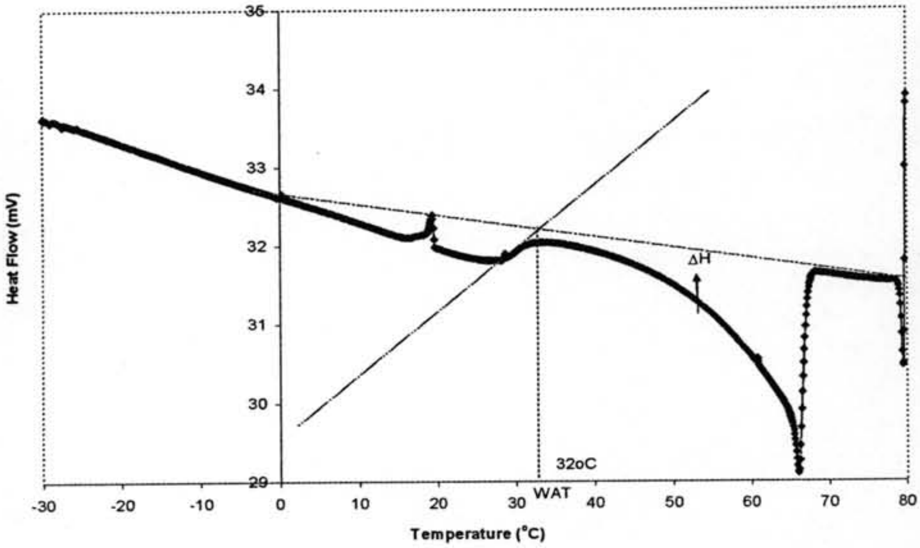


Figure 4.25 DSC thermogram of cooling from 80 to -30°C of wax obtained from train wagon with EVAFLEX with 33% vinyl acetate content at 400 ppm.

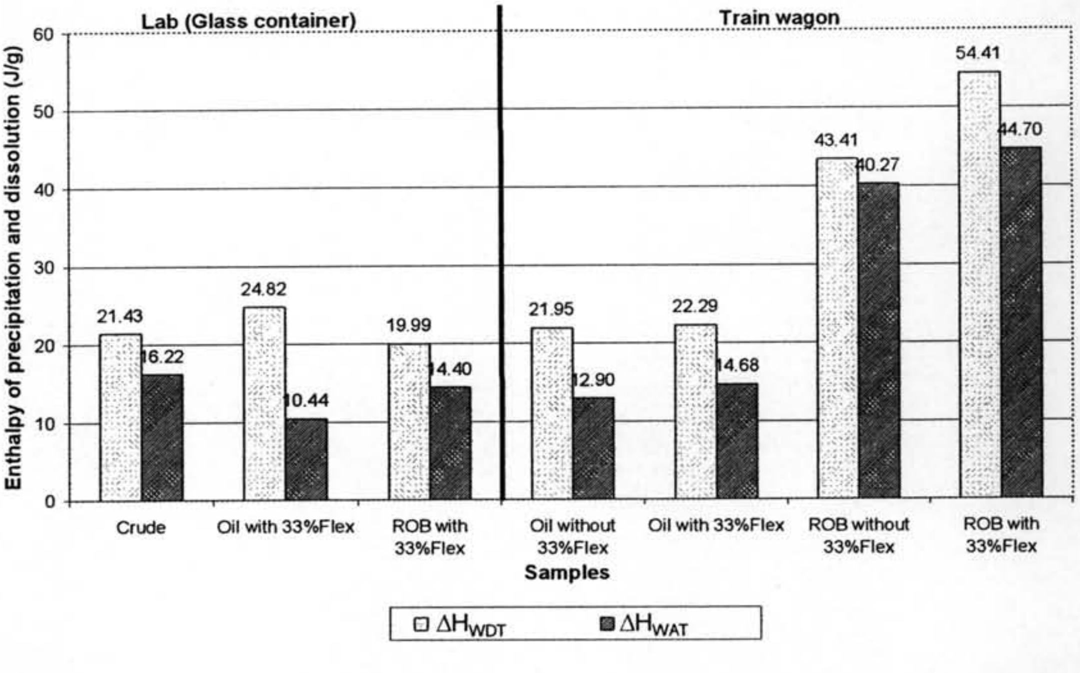


Figure 4.26 ΔH_{WAT} and ΔH_{WDT} of crude, oil fraction and ROB fraction with and without EVAFLEX 33%VA performed in lab and train wagon.

4.5 Effect of Wax Inhibitor on Enthalpy and Crystallization Temperature

In the lab test, it was not possible to separate oil and ROB fractions at 48°C in order to determine the amount of EVAFLEX in each fraction. Therefore, the condition had to be slightly modified. The oil and ROB fractions separated by 100 ppm EVAFLEX with 28% vinyl acetate content at 60°C was further investigated for distributing amount of EVAFLEX using differential scanning calorimeter. Varying concentration of EVAFLEX from 100 to 1000 ppm was added into the two fractions and the enthalpy and crystallization temperature of fractions were determined.

In the thermograms of oil and ROB fractions (Figure 4.27 and 4.28), the exothermic peak corresponds to crystallization temperature of n-paraffins (Faust *et al.*, 1978) and the area under the peak is a measured of the enthalpy of n-paraffins distribution. Chromatograms of the oil and ROB fractions are present in Appendix H. The results showed that the enthalpy of n-paraffins dissolution of the oil and ROB fractions decreased as the EVAFLEX concentration increased (Figures 4.29 and 4.30). Similarly, the crystallization temperature of n-paraffins decreased as the concentration increased (Figures 4.31 and 4.32).

In addition, the thermograms also showed that crystallization temperature was 46°C. According to the Sim-Dist GC results, the macrocrystalline wax (n-paraffin wax) wax showed a cluster of hydrocarbons with carbon number in the range of C18-C28 and the melting point of these hydrocarbons was similarly to the crystallization temperature. So, it can be concluded that the exothermic peak and the area under the peak corresponds to crystallization temperature and dissolution enthalpy of n-paraffins.

This is because when adding the inhibitor the crystallinity of n-paraffins was decrease when EVAFLEX concentration increased. So, the energy used to crystallize the n-paraffins decrease as the concentration increase.

The relationship of enthalpy change with EVAFLEX concentration seems to be linear with the best coefficient of determination (R^2) of 0.9863 and 0.8131 for oil and ROB fractions, respectively. The intercept corresponds to the enthalpy change of oil or ROB fraction at zero ppm of inhibitor in the plot in Figures 4.29 and 4.30. From the linear equation, the enthalpy change of the oil fraction (or ROB fraction) due to the distribution of EVAFLEX can be determined. The results showed that the amount of inhibitor in oil and ROB fraction was around 78 and 22 ppm, respectively (see detailed calculation in appendix I).

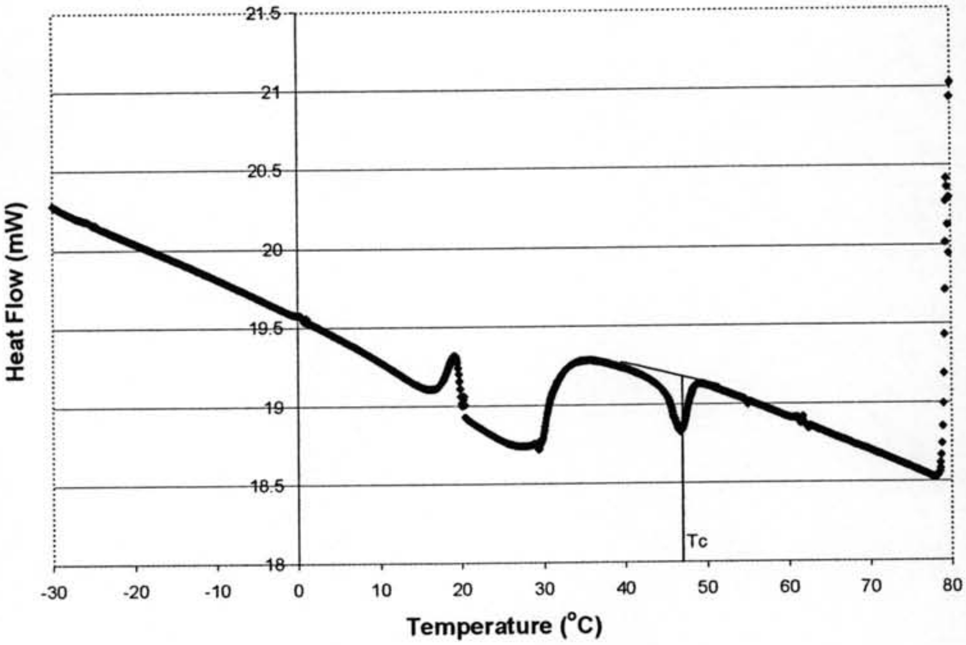


Figure 4.27 DSC thermogram obtained by cooling from 80 to -30°C of oil fraction with EVAFLEX with 28% vinyl acetate content at 100 ppm

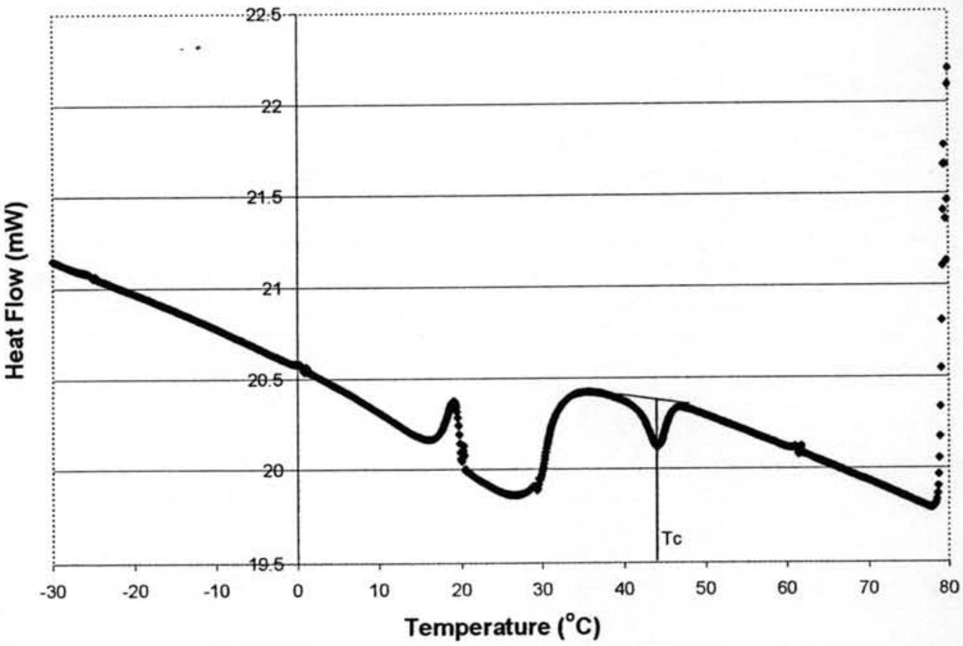


Figure 4.28 DSC thermogram obtained by cooling from 80 to -30°C of ROB fraction with EVAFLEX with 28% vinyl acetate content at 100 ppm

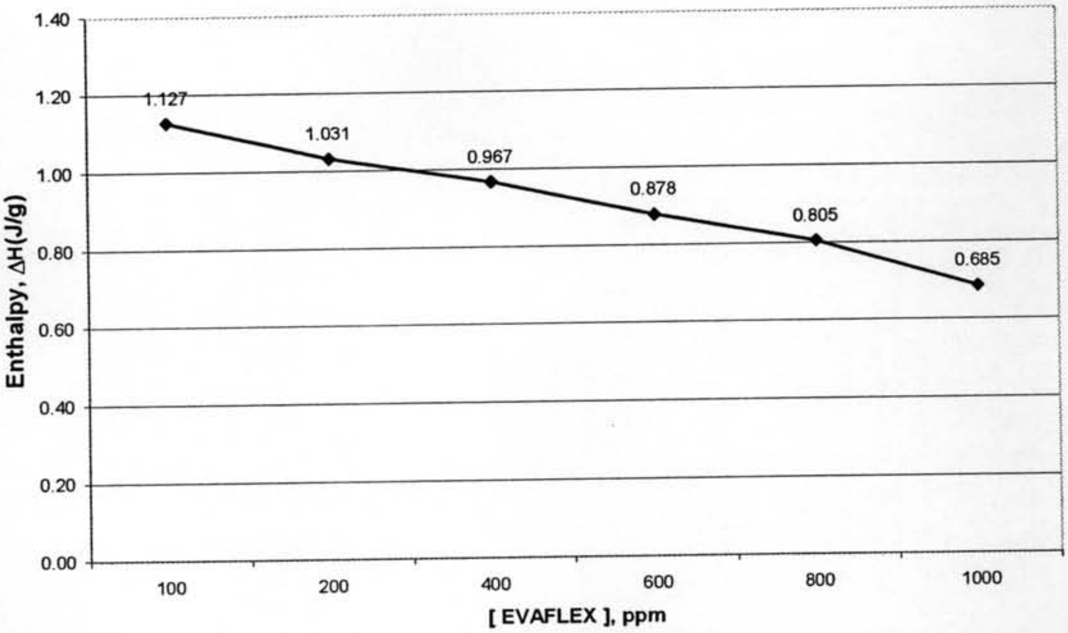


Figure 4.29 Enthalpy of n-paraffins dissolution of oil fraction in the presence of EVAFLX with 28% vinyl acetate content.

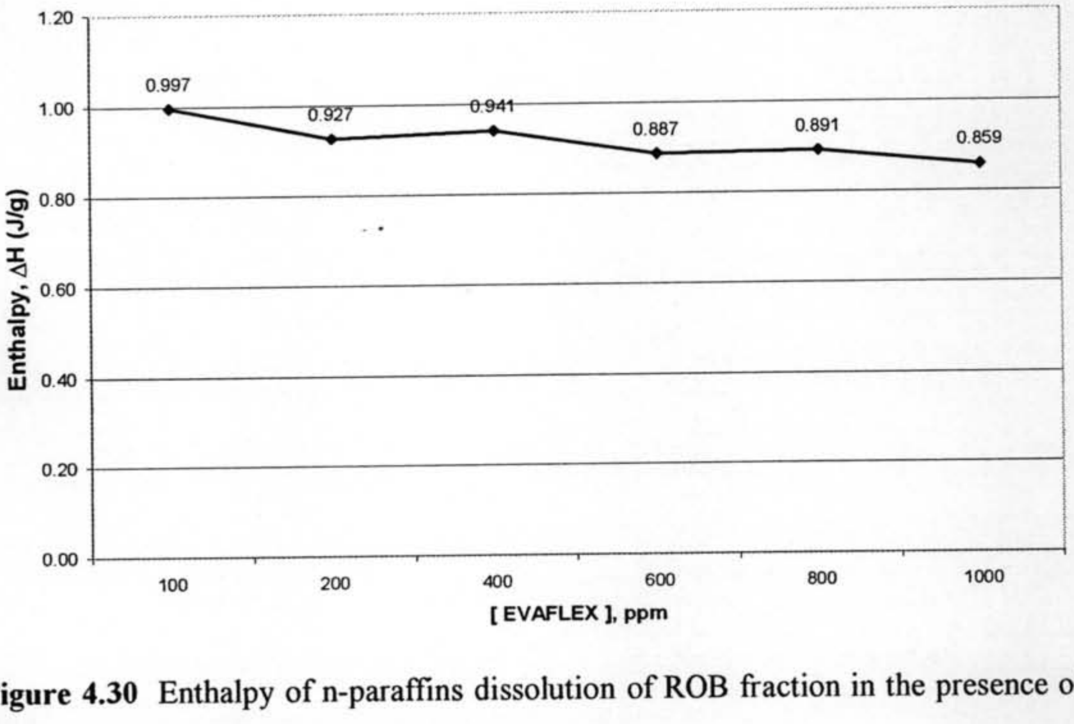


Figure 4.30 Enthalpy of n-paraffins dissolution of ROB fraction in the presence of EVAFLX with 28% vinyl acetate content.

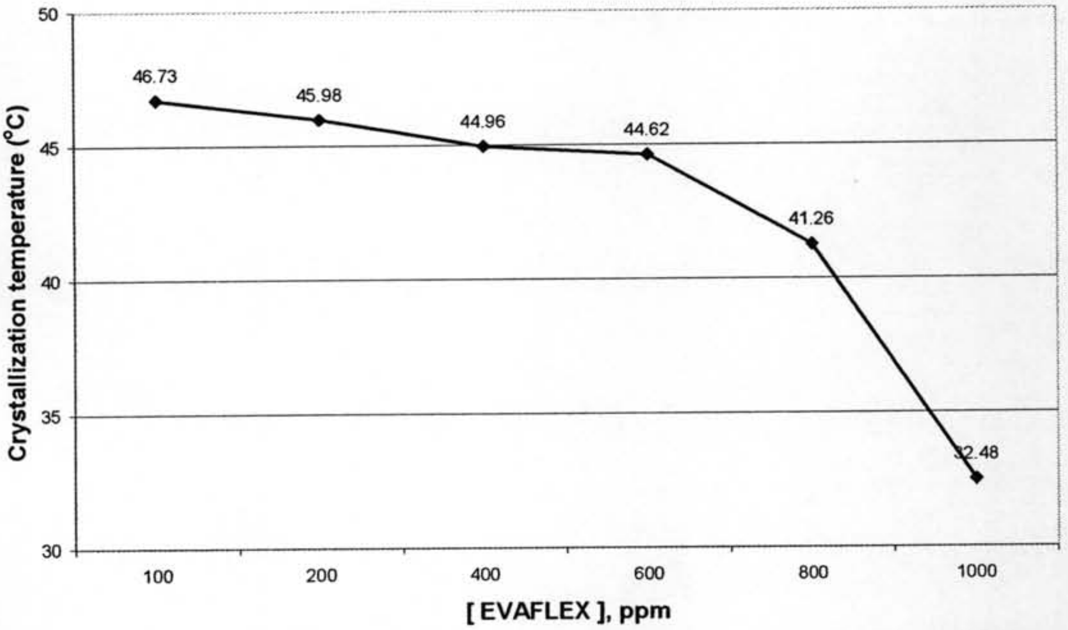


Figure 4.31 Crystallization temperature of oil fraction in the presence of EVAFLEX with 28% vinyl acetate content.

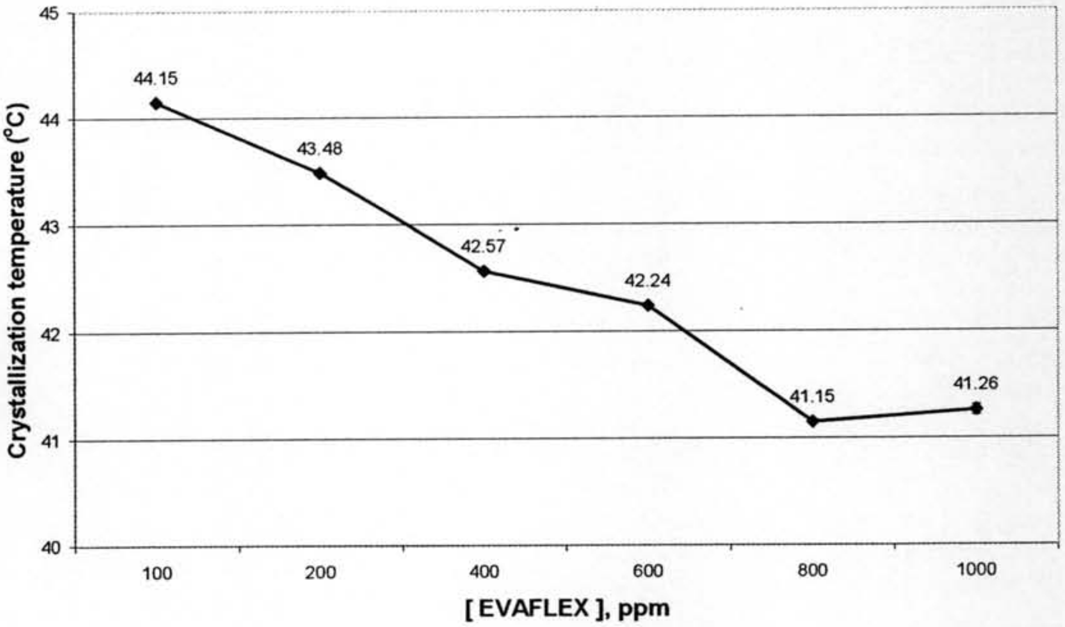


Figure 4.32 Crystallization temperature of ROB fraction in the presence of EVAFLEX with 28% vinyl acetate content.

4.6 Effect of Naphtha on Dissolution of Wax Deposition

An alternative method to reduce ROB was studied using dissolution of ROB with petroleum ether (as a naphtha). Figure 4.33 shows dissolution of ROB at various naphtha to ROB weight ratio of 0.5:1–1.5:1. Dissolution of ROB was 73-77%

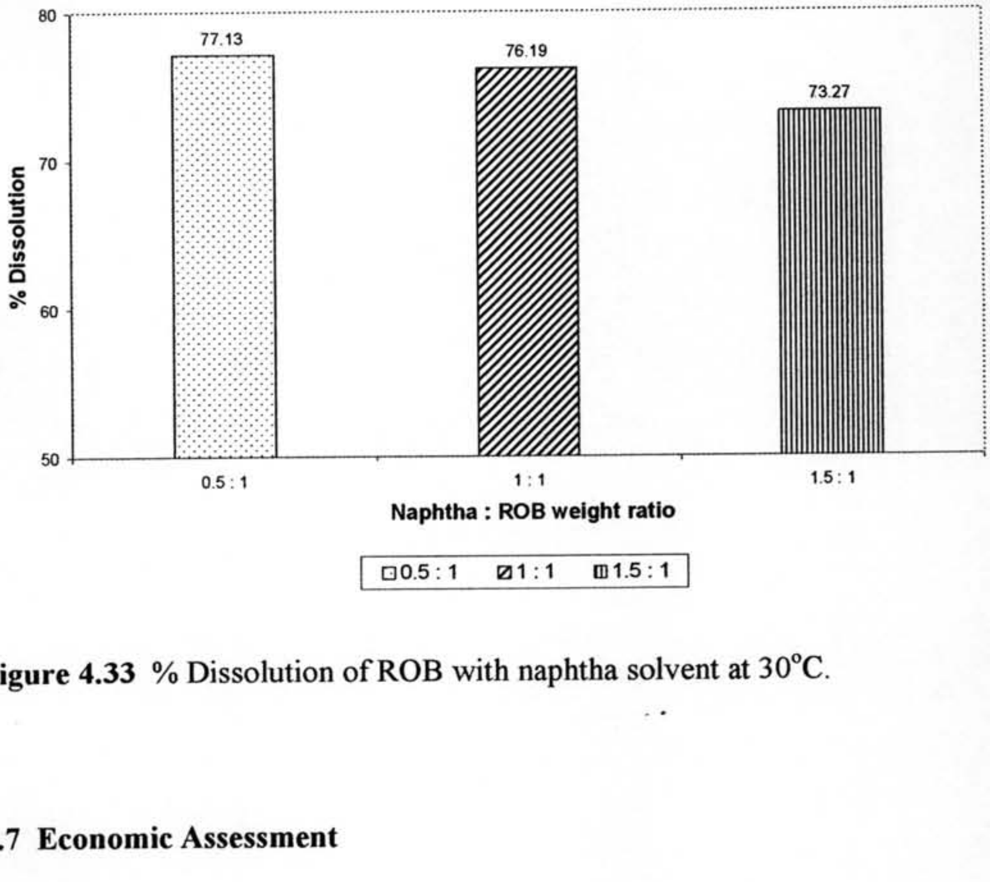


Figure 4.33 % Dissolution of ROB with naphtha solvent at 30°C.

4.7 Economic Assessment

ROB present in rail tanker causes losses to the company. The first loss is to clean the rail tanker every three months which becomes expenses related to costs of steam, wastewater transport and treatment. It is accounted for 7,880,000 baht or 47.90% as shown Table 4.2. The second loss is an expense for the rail freight cost, which the company has to pay in full capacity while transporting less crude volume due to accumulation of ROB in the bottom of the train tanker. The loss from the cost of rail freight is accounted for 8,568,923 baht (52.10%) annually. Therefore, it costs the company each year for about 16.45 million baht for total disposal (see Appendix J). Additionally, there is a loss called "opportunity loss" which is referred as ROB, The company not be able to sell it as crude. It is noted that the opportunity loss is not a cost. If the ROB can be sold as crude, it will be gained or credited to a crude recovery process (a change of ROB to crude) when the inhibitor is applicable.

Table 4.2 Current disposal cost for wax deposition

Disposal	Cost		
	Cost per unit*	Cost per year	
		Baht	%
Treatment cost			
- Steam cost	20,000 Baht per wagon	7,600,000	46.2
- Water treatment cost	2,500 Baht per ton	200,000	1.2
- Transport of waste water	1,000 Baht per ton	80,000	0.5
Transport cost			
- Rail freight cost	55.50 Baht per bbl.	8,568,923	52.1
Total disposal		16,448,923	100

* Data provided by the petroleum company (PTTEP) based on 2006.

The amount of ROB is a yearly average of 6.0% of the crude production (52,370 tons/year) and the minimum amount is around 2.25% (19,639 ton/year). However, the sludge wax solid estimated after steam cleaning is varied around 1,500 to 4,000 tons/year, which is accounted for about 11.44 million baht (up to maximum 30.5 million baht). Since there is no accurate ROB measured before the rail tanks are cleaned, the ROB data used in the economic calculation will be 1,500 to 4,000 tons/year. The different statistical data of these two sets will be referred to again later.

Economic Assessment for Using Wax Inhibitor in Rail Tank Wagon

Information for economic assessment is as follows:

1. Costs of EVAFLEX with 28% and 33% vinyl acetate content were 90 and 94 Baht/kg, respectively.
2. Cost of toluene was 990 US$/ton (36,135 baht/ton or 36 Baht/kg). Diesel was 31 Baht/kg, naphtha was 26.02 Baht/kg and heavy aromatic was 20.89 Baht/kg
3. Specific gravity of crude was 0.8.

When the inhibitor is applied, the ROB could be minimized to a level of dead stock. Ideally, 100% ROB reduction is equal to maximum ROB of 4,000 tons/year (6%), while practically, there is some reasonable amount of ROB remaining (dead stock), *i.e.* 1,500 tons/year (2.25%). Therefore, the actual working amount of ROB reduction is 2,500 tons/year (max. ROB of 4,000-min.ROB of 1,500 ton/year), which is accounted for a credit of 19,067,800 baht/ year from selling the ROB as crude as the calculation is shown in Table 4.3. The details of calculation are presented in Appendices J and K.

Table 4.3 Income credit gained from selling of ROB as crude

% ROB reduction	ROB gained as crude (ton/year)	Gain of selling ROB as crude (Baht/year)
100	2,500	19,067,800
95	2,375	18,114,410
90	2,250	17,161,020
85	2,125	16,207,630
80	2,000	15,254,240

Figure 4.34 (for 28%VA and 33%VA) show the cost of EVAFLEX (solid lines) in a toluene solution as a function of the inhibitor concentration. The cost of EVAFLEX with 33%VA is very slightly higher than that of 28%VA. The income credit from selling ROB as crude is, therefore, subtracted from the cost of inhibitor solution for the net expense as shown in dashed lines (opened labels). For example, the cost of 200 ppm EVAFLEX 28%VA in a toluene solution is 47.25 million bahts and the net

cost after subtracting the income credit from selling ROB as crude is 28.18 million bahts compared to the total disposal cost (16.45 million bahts) in Table 4.2. Therefore, it is not economic to use the inhibitor in a toluene solution to prevent wax precipitation.

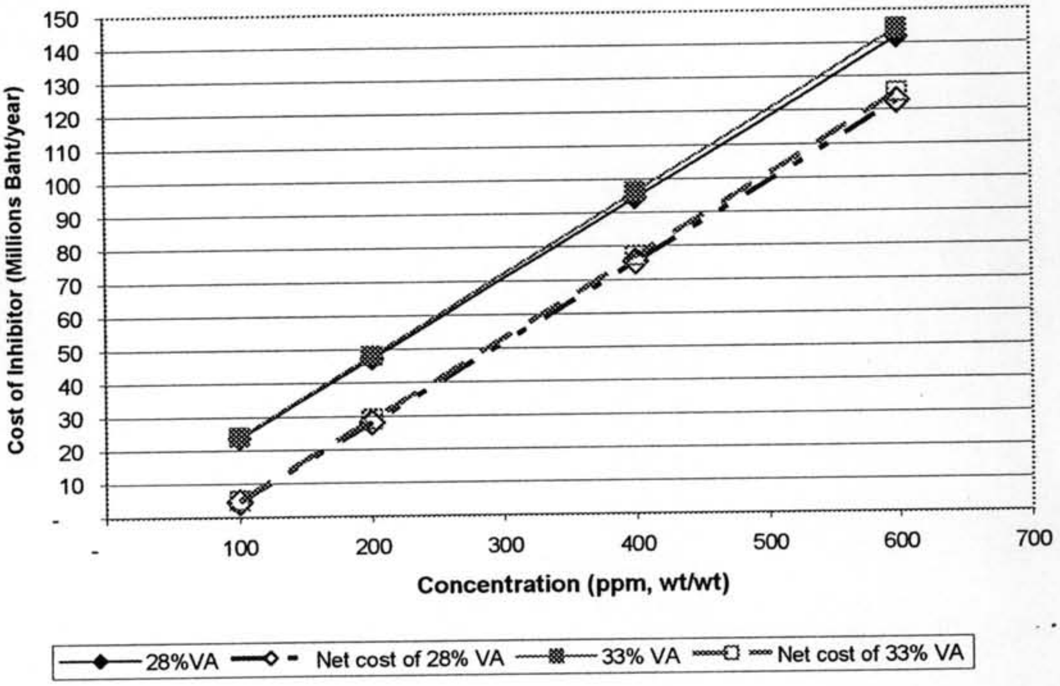


Figure 4.34 Cost of EVAFLEX with 28%VA and 33%VA in toluene solution with and without subtraction of ROB credit as crude (also see Appendices J and K).

An attempt to reduce the cost of the inhibitor solution is done by changing the solvent to diesel, heavy naphtha, and heavy aromatics, where the costs of diesel, naphtha, and heavy naphtha are 24, 26, and 20 baht/kg, respectively. Figure 4.35 shows the cost comparison of EVAFLEX 28%VA in different types of solvents, for example, at 200 ppm, the costs are 47.25, 36.27, is 38.42 and is 33.94 million baths/year in toluene, diesel, naphtha, and heavy aromatics solutions, respectively. After subtracting the income credit from selling ROB as crude (19.07 million bahts), the net costs are 28.19, 17.20, 19.35, and 14.88 million baths/year for toluene, diesel, naphtha and heavy aromatic solutions, respectively compared to the total disposal cost of 16.45 million bahts. The results showed slight advantage of using the inhibitor in heavy aromatic solution.

As mentioned earlier that the economic calculation is based on 1,500-4,000 ton/year of sludge wax solid, which is much lower than the ROB estimation of 2.25% (19,639 tons/year) to 6% (52,370 tons/year) of crude production. The economic assessment here demonstrates that the inhibitor solution could be applied and the company still gains the income from selling ROB as crude where the amount of working ROB (total ROB-dead stock ROB) should be at least 2500 tons/year.

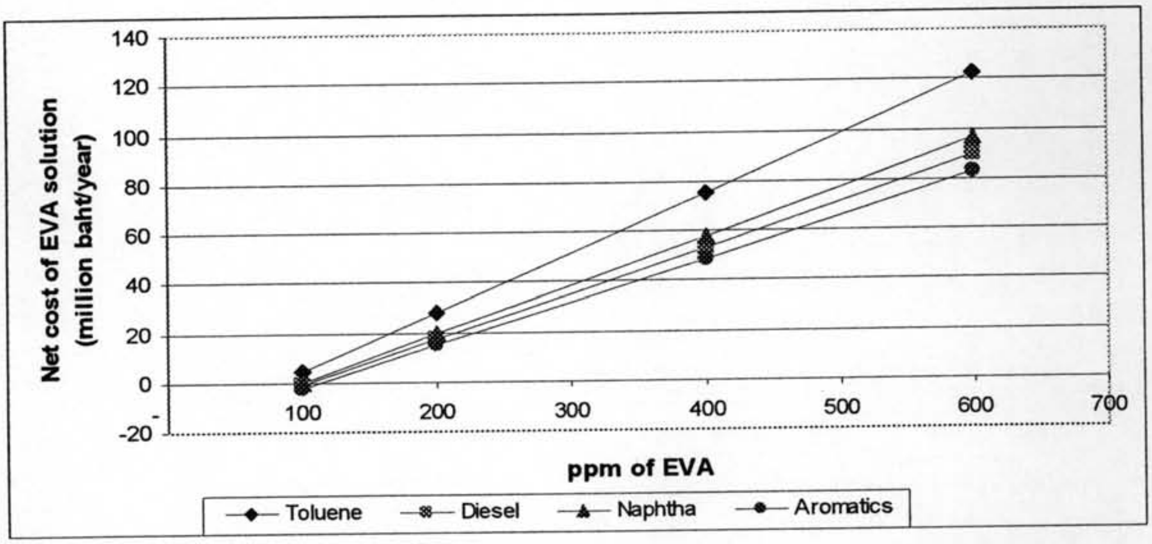


Figure 4.35 Net cost of EVAFLEX (28%VA) solution in various types of solvents.