CHAPTER III
EXPERIMENTAL

3.1 Materials

3.1.1 Crude Oil

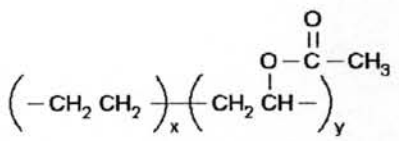
Crude oil from Lankrabue oil filed was supplied by PTT Exploration and Production Public Company Limited (PTTEP), Thailand.

3.1.2 Solvents

n-Pentane (99.5% purity), n-heptane (99.5% purity), toluene (AR grade), acetone (AR grade), and petroleum ether (AR grade) were supplied by Labscan Asia Company, Bangkok, Thailand. Methanol (commercial grade) was obtained from Reagent Chemical Industry, Bangkok, Thailand. Carbon disulfide (synthetic grade) was supplied by Merck KGaA Company, Germany.

3.1.3 Polymer Chemicals

Poly(ethylene-co-vinyl acetate) or EVA with 25%, 33%, and 40% vinyl acetate content (AR grade) were supplied by Aldrich Chemical Company, Milwaukee, USA. Commercial grade poly(ethylene-co-vinyl acetate) or EVAFLEX with vinyl acetate content of 28% (EV 250), 33% (EV 150), and 41% (EV 40W) were obtained from Dupont-Mitsui Polychemicals, Japan. The structure of poly(ethylene-co-vinyl acetate) is shown in schematic.



Poly(ethylene-co-vinyl acetate) (EVA)

Figure 3.1 Structure of poly(ethylene-co-vinyl acetate).

3.2 Characterization Techniques

Simulated distillation gas chromatograph. The hydrocarbon composition of crude was analyzed by a simulated distillation gas chromatograph (Sim-Dist GC, model Varian GC-3800), Varian, Holland. One microliter of crude in carbon disulfide solution was injected at injector temperature of 295°C with helium carrier gas at the flow rate of 18 ml/min. The GC column was Chrompak capillary column (CP 7512) with the length of 10 m, diameter of 0.53 mm, and thickness of 0.88 μm. The column was operated with a temperature program. The column temperature was initially kept constant at 20°C for 5 min, then increased with the ramping rate of 20°C/min for 14.5 min until reaching the final temperature of 320°C, and finally kept constant for 8.5 min. The chromatographic peaks were detected by a flame ionization detector at temperature of 320°C.

Differential scanning calorimeter. (DSC, model DSC7, Perkin Elmer, USA) was used to measure wax appearance temperature, wax dissolution temperature, enthalpy of crystallization and crystallization temperature. The DSC instrument was equilibrated for both temperature and heat flow using pure indium as a standard reference.

Brookfield DV III viscometer (USA, Brookfield Engineering Labs) was used to determine the viscosity of crude oil.

Stanhope-Seta pour point apparatus was used to determine pour point temperature of crude oil sample following ASTM D97.

3.3 Methodology

3.3.1 Characterization of Crude Oil

Crude oil composition: The crude oil composition was analyzed by using Sim-Dist GC. The chromatographic peaks were characterized following ASTM D2887 with straight chain hydrocarbon from C_5 to C_{44} as standard reference. The crude oil sample was heated to 48°C to obtain a homogenous phase and then dissolved in carbon disulfide (CS_2) with the weight ratio of 1:200. The solution was then kept in a sealed vial prior to the analysis.

Fractionation of crude oil: For crude oil fractionation, a novel method (Nguyen *et al.*, 1999) was modified and used in order to reduce separation time by replacing p-xylene used in asphaltene soxhlet extraction with n-heptane (Srisirivilaikul, 2004). Crude oil was separated into 4 major fractions: saturates asphaltenes, resins, and wax. The fractionation procedure is shown in Figure 3.2.

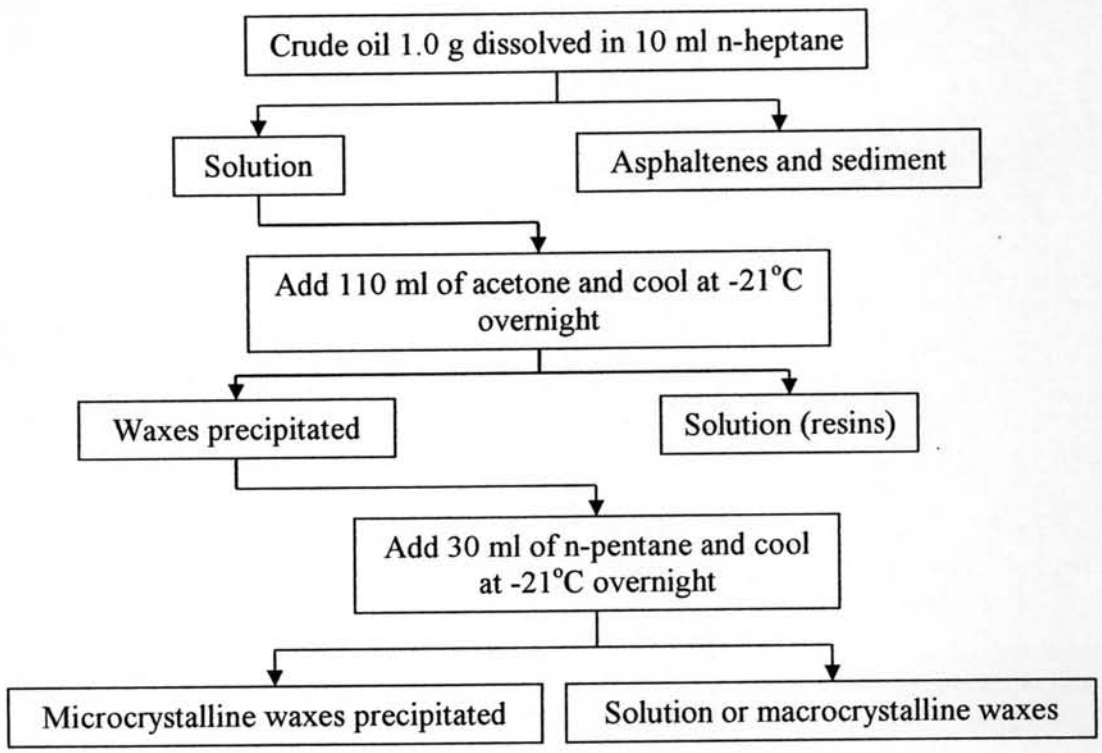


Figure 3.2 Experimental procedure for crude oil fractionation. (Srisirivilaikul, 2004)

Microcrystalline and macrocrystallline waxes can be separated by precipitation using n-pentane cooled at -21°C overnight.

Pour point testing: The pour point of crude oil was tested following ASTM D97 by using Stanhope-Seta pour-point apparatus.

Density and API gravity: Hydrometer was used to measure density of crude oil following ASTM D1298. And, API gravity of crude was determined by the following equation:

$$\text{API gravity} = (141.5/\text{sp.gr. at } 60^{\circ}\text{F}) - 131.5$$

Wax appearance temperature (WAT), wax dissolution temperature (WDT), enthalpy of crystallization and crystallization temperature: were measured by using a Perkin Elmer differential scanning calorimeter. Five to fifteenth milligrams of crude was placed into aluminum pans, and the filled pans were then closed with pan compressor. Temperature scanning of crude was performed from -30 to 80°C for both heating and cooling at a rate of 5°C/min.

Viscosity of crude oil: The viscosity measurement was conducted at 25-30°C with the spindle no. 21. The crude sample was added to a half level of the chamber, and the spindle was placed into the chamber. The rotation was then applied to the chamber. Percent of torque and viscosity were recorded. The exact value of viscosity was achieved when the percentage of torque exceeded 95%. To achieve more than 95% torque, either temperature or rotating speed adjustment could be done.

3.3.2 Effect of Wax Inhibitors

3.3.2.1 Inhibitor Preparation

The influence of wax inhibitors on the pour point reduction was investigated by varying the derivatives of EVA and their concentration from 100 to 1000 ppm. The polymer inhibitors were prepared by mixing with solvent (toluene) in the weight ratio of 1:5. Then, the polymer solution was heated and shaken at 45°C to obtain a homogeneous mixing. The criterion of polymer solution preparation was that the solvent was used in small amount in order to avoid the effect of solvent on pour point testing.

3.3.2.2 Inhibitor Efficiency

The pour point of crude without and with adding an inhibitor was measured at 60°C following the ASTM D97. Twenty five grams of crude and weighed inhibitor were added into a test cell. The crude was heated to 60°C, continuously stirred for 15 min, and held for another 15 min without stirring. Afterwards, the test cell was put in the Stanhope-Seta pour point apparatus, which contains cold water. Then, the pour ability was checked every 2°C. The pour point is the lowest temperature, at which crude oil shows no movement when the test cell is

held in a horizontal position for 5 seconds. The flow diagram for inhibitor efficiency determination is shown in Figure 3.3.

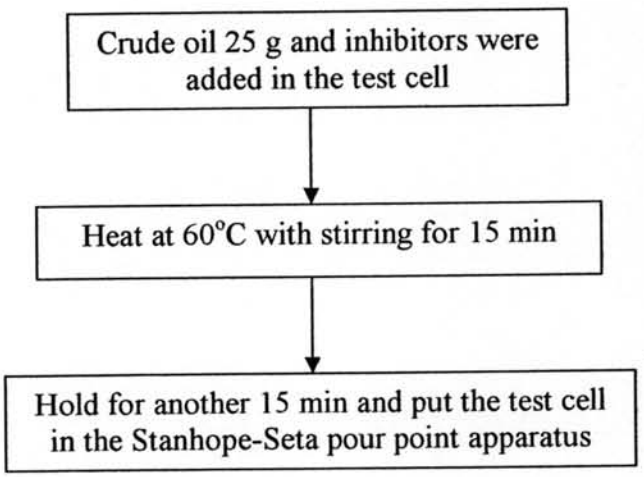


Figure 3.3 Experimental procedure for determination of inhibitor efficiency.

3.3.2.3 Semi-Pilot Scale Test

This part was to find the correlation among pour point temperature, concentration, and remaining-on-board by using two types of container material, steel and glass.

Steel container: a crude container with similar shape to a train wagon was made of steel with its capacity of 1.6 liter. As shown in Figure 3.4, inside the container, there are 3 buffer plates where its function is to reduce an impact of crude on the container surface. The buffers can be taken out and reinstalled.

(a)

(b)

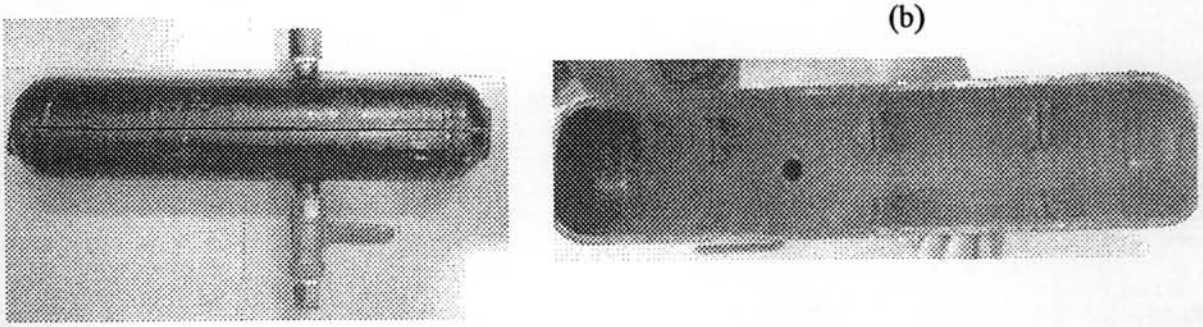


Figure 3.4 Semi-pilot scale container (a) and its inner configuration (b).

Procedure for steel container experiment:

1. The buffers were installed.
2. Crude was mixed with inhibitor (or without inhibitor), and the crude was weighed. After that, the crude was loaded into the container.
3. The container was shaken (simulated transporting action) at a controlled temperature for 12 h.
4. After the crude was drained, the weight and pour point of the drained crude were measured. Then, the remaining on board was calculated.
5. The buffers were taken out to examine the wax deposition and reinstalled again.
6. Steps 1 to 5 were repeated for many cycles with new crude for each cycle.

Procedure for glass container experiment:

Glass container: the bottle screw cap bottle of 500 ml was used as a container. There were no buffer plates inside the glass container. The procedure for the steel container was repeated.

1. Crude 240 g mixed with inhibitor (or without inhibitor) at 60°C for 2 h.
2. The glass container was shaken at 30°C for 12 h.
3. Oil fluid was drained off as oil fraction by pouring the glass container by using gravity force for 30 min. and the remaining in the glass container was called ROB. Then, the weight of ROB was measured
4. The pour point of oil and ROB fractions was measured.

3.3.2.4 Train Wagon Test

Two train wagons with their capacity of 32,500 liter were used for comparison, one with inhibitor and another without inhibitor addition.

The crude was loaded at Bung Phra depot, transported by train to Bangchak refinery where the crude was unloaded. Then, the train with empty crude in the wagon goes back to Bung Phra depot to load the new crude. The experiment was performed for five transportations. The ROB was measured after the crude was unloaded at Bangchak refinery and after the train got back to Bung Phra depot.

Procedure at Bung Phra depot (Loading station):

1. EVAFLEX with 33%VA of 400 ppm was prepared in toluene solution with the weight ratio of EVAFLEX to toluene equal to 1 to 5 corresponding to EVAFLEX 10.4 kg in toluene 52 kg. The solution was stirred until completely dissolved.
2. The solution was loaded into the train wagon while crude was being loaded.
3. Loading temperature, volume of crude being loaded, and volume of ROB (with and without inhibitor) were recorded.
4. Crude oil was sampled for 3 sampling points for pour point analysis.
5. ROB samples (with and without inhibitor) was withdrawn for analyses.

Procedure at Bangchak Refinery (Unloading station):

6. Both crude oil and ROB samples (with and without inhibitor) was withdrawn for analyses of pour point, WAT, and WDT.
7. Traveling time, unloading temperature, and volume of ROB (with and without inhibitor) were recorded using measuring stick which measures the ROB height accumulating at the bottom of the wagon at the different points and is converted to ROB volume.
8. Steps 1 to 9 were repeated for 5 transportations for the same wagon.

3.3.2.5 Effect of Temperature on Inhibitor Efficiency

Crude oil without and with adding an inhibitor was conducted at 48, 52, 56 and 60°C. The efficiency of inhibitor was determined by using pour point temperature following the ASTM D97 and the percent ROB decreased.

3.3.2.6 Effect of Inhibitor on Dissolution Enthalpy and Crystallization Temperature of n-Paraffins

Crude oil mixed with 100 ppm EVAFLEX of 28% vinyl acetate content was conducted at 60°C and shaking at 30°C for 12 hours. Then, the crude oil was separated into two fraction, oil and ROB. The inhibitor with varying concentration range of 100-1000 ppm was added into each fraction of oil and ROB, and the mixture was thoroughly mixed. After that the sample was examined by using DSC with scanning rate 5°C/min to find the relation between dissolution enthalpy,

crystallization temperature and EVAFLEX concentration and to determine the amount of inhibitor in oil and ROB fraction.

3.3.3 Effect of Solvent on Dissolution of Wax Deposition

Dissolution of wax remaining on board in the train wagon was studied with the glassware by adding hydrocarbon solvent at a controlled temperature. Petroleum ether was used as naphtha. The weights of the glass container and ROB were measured before and after solvent loading. The weight ratio of naphtha to ROB was varied from 0.5:1 to 1.5:1 at 30°C for 12 h. After the solvent dissolving a portion of ROB was drained, the weights of glass container and ROB remained were measured again.

3.3.4 Economic Assessment

For economic assessment, important information was obtained from the field as follows:

A.) Steam for cleaning ROB in RTW = 20,000 Baht/tank

B.) Water treatment for oil contaminated wastewater = 2500 Baht/ton water

C.) Transport of contaminated water = 6,000 Baht/trip equal to 6 ton/trip

D.) Minimum ROB produced = 2.25% of crude production

E.) Wagon cleaning = 380 tanks/year

F.) Contaminated water produced = 80 ton water/year

G.) Rail transport cost = 55.5 Baht/bbl.

H.) Sale of ROB as crude = 26.58 US$/bbl.

I.) Sludge wax loss = 1500 ton/year

From the data provided by PTTEP, the disposal cost is related to the remaining on board which is related to pour point of crude. The experiments with the semi-pilot container were therefore carried out to find the correlation between pour point temperature and the remaining on board. Afterwards, the economic assessment was performed using the inhibitor, and compared with present incurred losses.