

## **CHAPTER III**

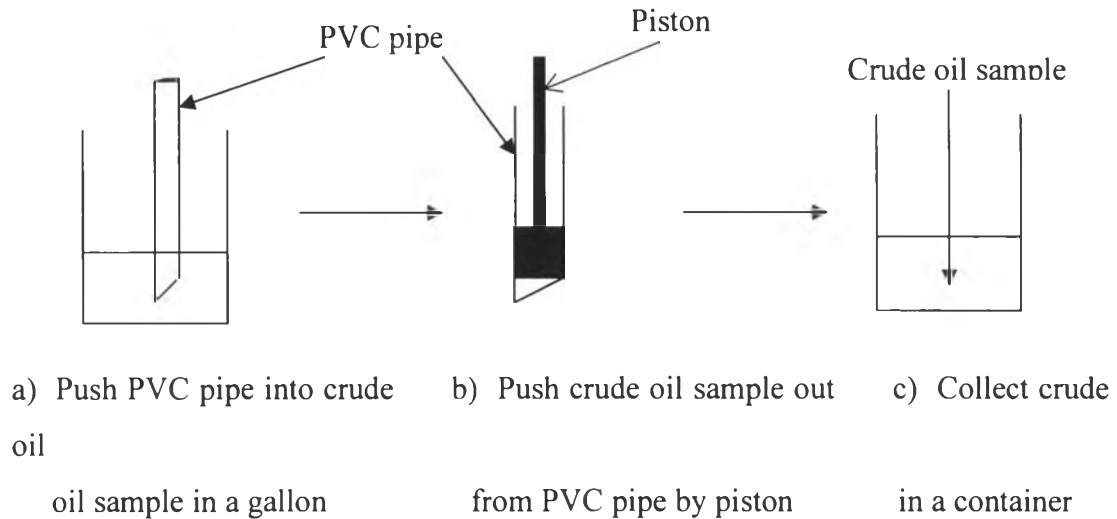
### **EXPERIMENTAL**

#### **3.1 Chemical**

Acetone (C<sub>3</sub>H<sub>6</sub>O), analytical reagent grade as obtained from Lab-Scan was used to precipitate the wax crystal. *n*-Heptane (C<sub>7</sub>H<sub>16</sub>), analytical reagent grade that was obtained from Lab-Scan was used to precipitate the asphaltene and resins from crude oil. For the separation of micro- and macro-crystalline wax, and the precipitation of asphaltene and other sediments in the wax content determination, *n*-pentane (C<sub>5</sub>H<sub>12</sub>), analytical reagent grade as obtained from Lab-Scan was used. In the part of analytical by Sim-Dist GC, carbon disulfide (CS<sub>2</sub>), 99.9% purity that was obtained from Merck was used to dissolve the sample of crude oil micro- and macro-crystalline wax. Toluene (C<sub>7</sub>H<sub>8</sub>), analytical grade, obtained from Lab-Scan, was used to wash the wax crystal in the procedure of wax content determination. The mixture of methanol, analytical reagent grade obtained from Lab-Scan and dry ice obtained from Praxair (Thailand) Co., Ltd., were used as coolant. In addition, the investigation chemical method to solve wax deposition problem, poly(ethylene-co-vinyl acetate) or EVA obtained from Italmar, and poly(methyl methacrylate) or PMMA, VH grade (m.p. 115 °C) and MD grade (m.p. 130 °C), obtained from Diapolyacrylate Co., Ltd. were used.

#### **3.2 Sampling Preparation**

Crude oils from Lankrabue oil field, Kumphangphet province, from Thaishaell Exploration and Production Co., Ltd., and U-Thong oil field, Suphanburi province, from PTT Exploration and Production Public Co., Ltd., respectively are semi-solid at room temperature. A modified sampling method employing PVC pipe (3 cm. diameter) was used as shown in Figure 3.1.



**Figure 3.1** Procedure of sampling preparation.

#### Procedure to sample crude oil

- 1) The PVC pipe was pushed into the crude oil gallon until it reached the bottom then pulled out.
- 2) The crude oil sample was pushed out from the pipe with a piston.
- 3) The procedure was repeated at the different locations across the surface of the crude oil in each gallon.
- 4) All crude oil samples were collected in a container.

### **3.3 The Study of Characteristics and Properties of Crude Oil**

#### 3.3.1 Testing

All tests for crude oil samples follow ASTM standards.

##### *3.3.1.1 Distillation*

Distillation curves of crude oil samples were determined following ASTM D86 by using Stanhope-Seta Distillation apparatus.

### Procedure

1) Apply heat to the distillation flask and contents. The heating stage followed Table 4 in ASTM D86.

2) Move the graduate so that the tip of the condenser touches its inner wall and regulate the heating so that the time from initial boiling to 5 or 10% recovered is as indicated in Table 4.

3) Observe and record the initial boiling point.

4) Continue to regulate heating so that the rate of obtained condensate is 4-5 ml per min.

5) Observe and record the final boiling point.

6) Report the percent recovery and the temperature.

#### *3.3.1.2 Pour Point Testing*

Pour point of crude oil were tested following ASTM D97 by using Stanhope-Seta pour point apparatus.

### Procedure

1) Heat the crude oil in a water bath until it is just sufficiently fluid to pour into the test jar.

2) Pour the crude oil into the test jar upto the marked level.

3) Close the test jar by the cork carrying the test thermometer.

4) In case of crude oil having pour point above  $-33\text{ }^{\circ}\text{C}$  (see more details in ASTM D97 procedure), the crude oil was heated to  $9\text{ }^{\circ}\text{C}$  above expected pour point without stirring but at least  $45\text{ }^{\circ}\text{C}$ . A bath should be maintained at  $12\text{ }^{\circ}\text{C}$  above the expected pour point, but at least  $48\text{ }^{\circ}\text{C}$ .

5) Insert the test jar into the jacket.

6) After the crude oil has cooled, take great care not to disturb the mass of oil nor permit the thermometer to shift the oil. Pour point is expressed in the integers that are positive or negative multiple of  $3\text{ }^{\circ}\text{C}$ .

7) Begin to examine the pour point when the temperature of oil is  $9\text{ }^{\circ}\text{C}$  above the pour point.

8) At each test thermometer reading that is multiple of  $3\text{ }^{\circ}\text{C}$  below the starting temperature remove the test jar from the jacket.

9) Observe the movement of crude oil in the test jar. If the crude oil shows any movement, replace the test jar immediately in the jacket and repeat the test at the next temperature 3 °C lower.

10) The complete operation of removal, wiping, and replacement shall require not more than 3 s.

#### *3.3.1.3 Density Testing*

Crude oil samples were tested for density by using ASTM D1298-85

##### Procedure

1) Heat the crude oil in a water bath until it is just sufficiently fluid to pour point into the cylinder without splashing.

2) Remove any air bubbles formed by touching them with a piece of clean filter paper before inserting the hydrometer.

3) Place the cylinder containing in a bath to avoid excessive temperature changes.

4) Lower the hydrometer gently into the sample in vertical position.

5) As soon as a steady reading is obtained, record the temperature of the sample and then remove the thermometer.

6) Depress the hydrometer scale divisions into the liquid and then release it.

7) Read the hydrometer scale approximately when the hydrometer has come to rest, floating away from the walls of cylinder by observing with the eye slightly above the plane of the surface of the liquid, the point on the hydrometer scale to which the samples rises.

### **3.4 Analysis**

#### 3.4.1 Identification of Hydrocarbon Composition in Crude Oil

The hydrocarbon composition of crude oil is identified by using Simulated Distillation Gas Chromatography (Sim-Dist GC), Varian, GC-3800 model.

##### *3.4.1.1 Condition*

- 1) Injector temperature 30 °C
- 2) Column oven temperature 295 °C
- 3) Flame ionization detector (FID) 320 °C
- 4) H<sub>2</sub> and air at a rate of 40 and 60 ml/min, respectively
- 5) Temperature program
  - Hold at 30 °C for 0.05 min.
  - Heat up to 295 °C at a rate of 10 °C
- 6) Carrier gas, He, at rate of 80 ml/min.

#### 3.3.1.2 Sample Preparation

- 1) The crude oil was heated to 80 °C.
- 2) It was then dissolved in carbon disulfide (CS<sub>2</sub>) in the concentration of 0.01 g/ml.
- 3) The solution (around 2 ml) was kept in a vial.
- 4) Finally, one microliter of sample was automatically injected to be analyzed by Sim-Dist GC.

### 3.4.2 Separation of the Composition in Crude Oil

In crude oil, the major compositions are saturates, asphaltenes, resin, and aromatics. The separation method that was used in this work provides a qualitative subdivision of the wax fractions into *n*-pentane soluble and insoluble wax which, when correlated with physical properties of crude oil such as pour point, viscosity, wax appearance temperature (WAT), etc., may help explain causes of wax deposition during production, transportation, and storage petroleum. In this work, two methods were employed: one from previous work (Nguyen *et al.*, 1999) and the other method which was modified from Nguyen's in this work. After that both results were compared to each other.

#### 3.4.2.1 *Crude Oil Separation Method from Previous Work (Nguyen et al., 1999)*

Nguyen *et al.* (1999) studied a novel method to separate the composition in crude oil and the work in this part was done following that. Detailed scheme is shown in Figure 3.2, and can be described as followed.

The initial step in this method involves the adsorption of asphaltenes and resins from the oil on alumina, using approximately 1.0000 g of oil dissolved in 10 ml of hot *p*-xylene for 48 hr., however this time period can be significantly reduced if the micro-crystalline wax content ( $>C_{40}$ ) of the oil is low. Following the extraction, the *p*-xylene extract is concentrated and the wax precipitated with acetone, 110 cm<sup>3</sup> was added to the precipitate and the solution allowed to stand overnight. Finally, two fractions are obtained with the macro-crystalline waxes being in solution and micro-crystalline waxes with predominance of high molecular weight hydrocarbons present as precipitate.

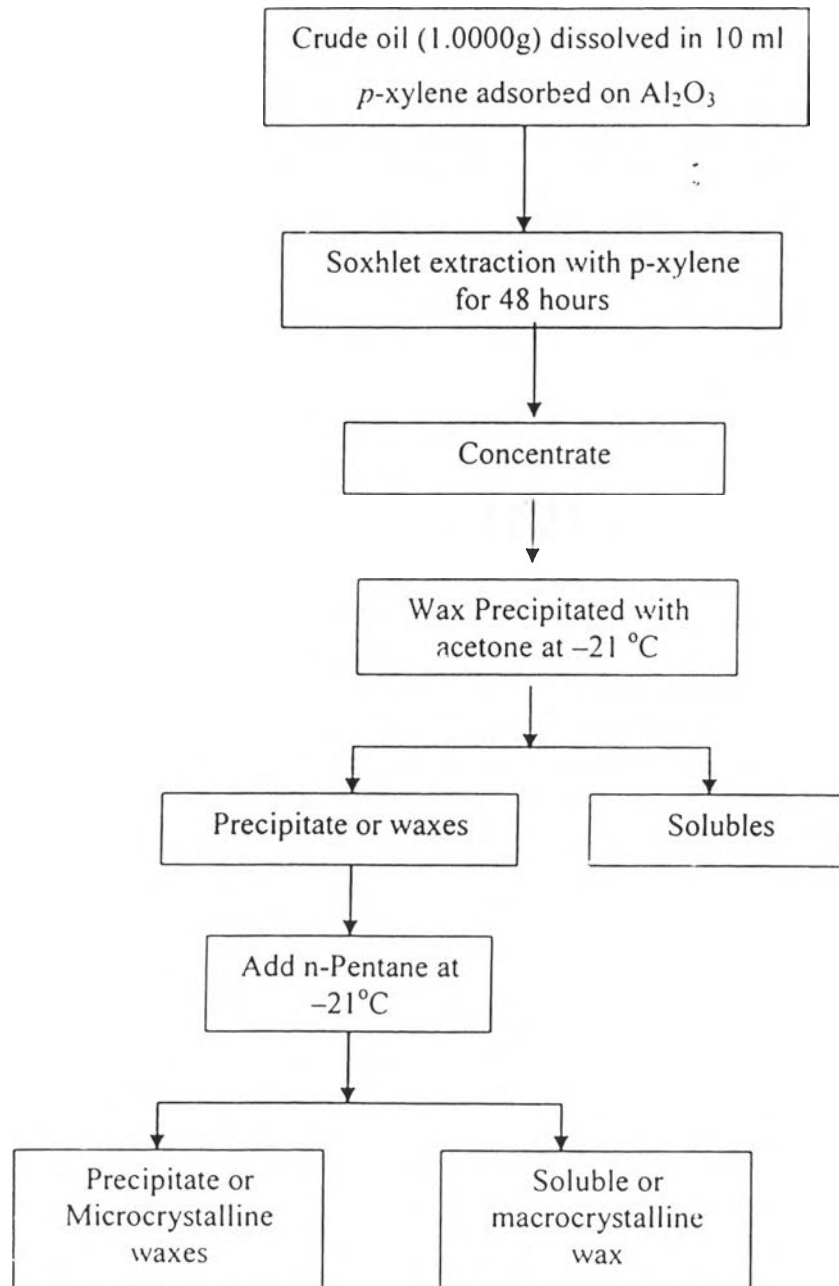
After the separation, both types of crystal waxes were analyzed for hydrocarbon composition by Sim-Dist GC, and were indicated whether both fractions were free from asphaltene by FTIR.

#### 3.4.2.2 Modified Method to Separate the Composition of Crude Oil

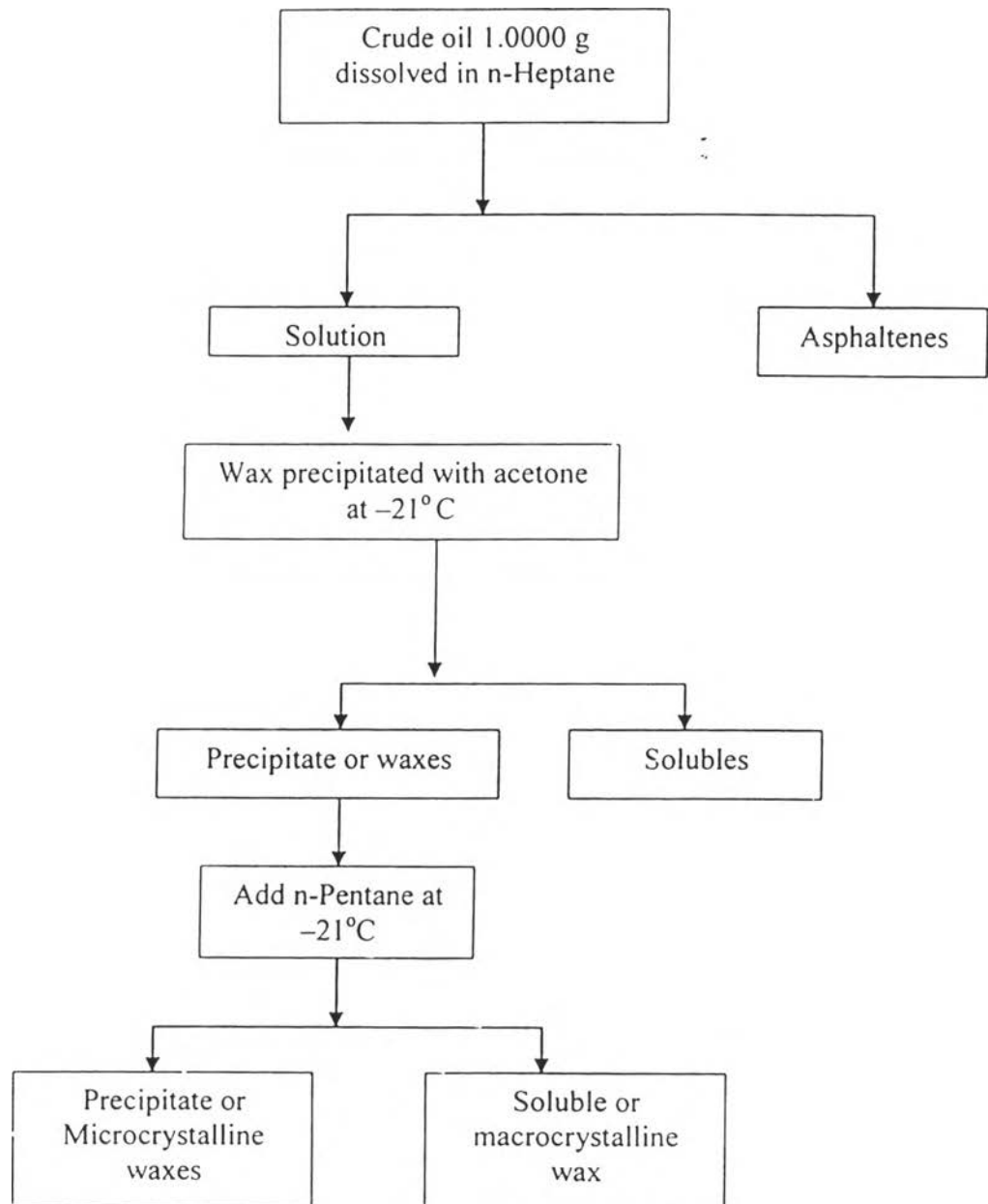
In this work, the method as developed by Nguyen *et al.* (1999) is modified to reduce the time-consuming and number of steps used to separate crude oil.

Approximately 1.0000 g of crude oil is mixed with *n*-heptane and then it is heated to at least 80 °C. The solution is cooled to 0 °C and left overnight. The asphaltenes in the solution is removed by filtration. The wax remained in the solution precipitated by acetone at -21 °C. Finally, micro- and macro-crystalline wax was separated from each other by cold *n*-pentane at -21 °C. Detailed scheme is shown in Figure 3.3.

After the separation, both types of crystal waxes were analyzed for hydrocarbon composition by Sim-Dist GC, and were indicated whether both fractions were free from asphaltene by FTIR.



**Figure 3.2** Qualitative separation scheme of asphaltenes, micro- and macrocrystalline wax (Nguyen *et al.*, 1999).



**Figure 3.3** Modified method from Nguye *et al.* (1999) for qualitative separation of asphaltenes, micro- and macro-crystalline wax.



### 3.4.3 Determination of Wax Appearance Temperature (WAT) and Wax Dissolution Temperature (WDT)

WAT during cooling and WDT during heating were measured using the differential scanning calorimeter (DSC, Perkin Elmer). It is a standard procedure in most research laboratories. In this work, DSC instrument was adjusted to both temperature and heat flow using pure Indium as standard reference.

Prior to any measurement, the crude oil sample was heated to temperature of 80 °C for 60 min. to ensure that all wax crystals has dissolved. A sample of 5-10 mg. was then transferred into an aluminium pan for liquid and sealed. During the cooling process, the sample was cooled at a rate of 5 °C/min from 80 °C to -30 °C. The crystallization onset temperature or WAT was determined as the onset of the exothermic peak corresponding to the liquid-solid transition. Under heating conditions, the sample was heated from -30 °C to 80 °C at a rate of 5 °C/min. The dissolution temperature on heating is taken as the temperature at which the solid-liquid exotherm reaches the baseline.

## 3.5 Quantification of the Amount of Wax

### 3.5.1 Determination of Wax Content

The wax content is determined by the modified UOP method 46-64 (Burger *et al.*, 1981) that is based on precipitation of wax by acetone.

#### *Procedure*

- 1) Crude oil sample was heated to 70 °C to ensure complete dissolution of all solid phases.
- 2) A laboratory/screw cap bottle and filter paper (Whatman. No.42) were weighed.
- 3) The oil (1.0000 g) was then mixed with 40 ml *n*-pentane (1:40 wt/vol), left overnight, and filtered to separate the asphaltene and other sediments.
- 4) A representative sample, 5 ml, was taken into a laboratory/screw cap bottle of suitable size.
- 5) A given volume of petroleum ether (35 cm<sup>3</sup>) was added to the sample and stirred until the sample is thoroughly dissolved.

6) Adequate volume of acetone (about 110 cm<sup>3</sup>) was added and stirred well.

7) The sample was cooled at  $-20\text{ }^{\circ}\text{C}$  to  $-30\text{ }^{\circ}\text{C}$  by using a bath that contained a mixture of dry ice and methanol and allowed to come to temperature for 2 hours.

8) The sample was filtered by vacuum filtration by pouring it slowly into a Buchner funnel, using a stirring rod as a guide. The stirring rod, bottle, and filter cake were washed well with the cold solvent mixture. The vacuum was disconnected, the filter paper was carefully removed from the funnel, and placed in the original bottle. Any wax crystals that remained in the filter funnel and the stirring rod were washed into the bottle weight, minus the weight of the filter paper used, was the weight of the wax crystals contained in the originally representative sample, 5 ml.

Detailed scheme as described is shown in Figure 3.4

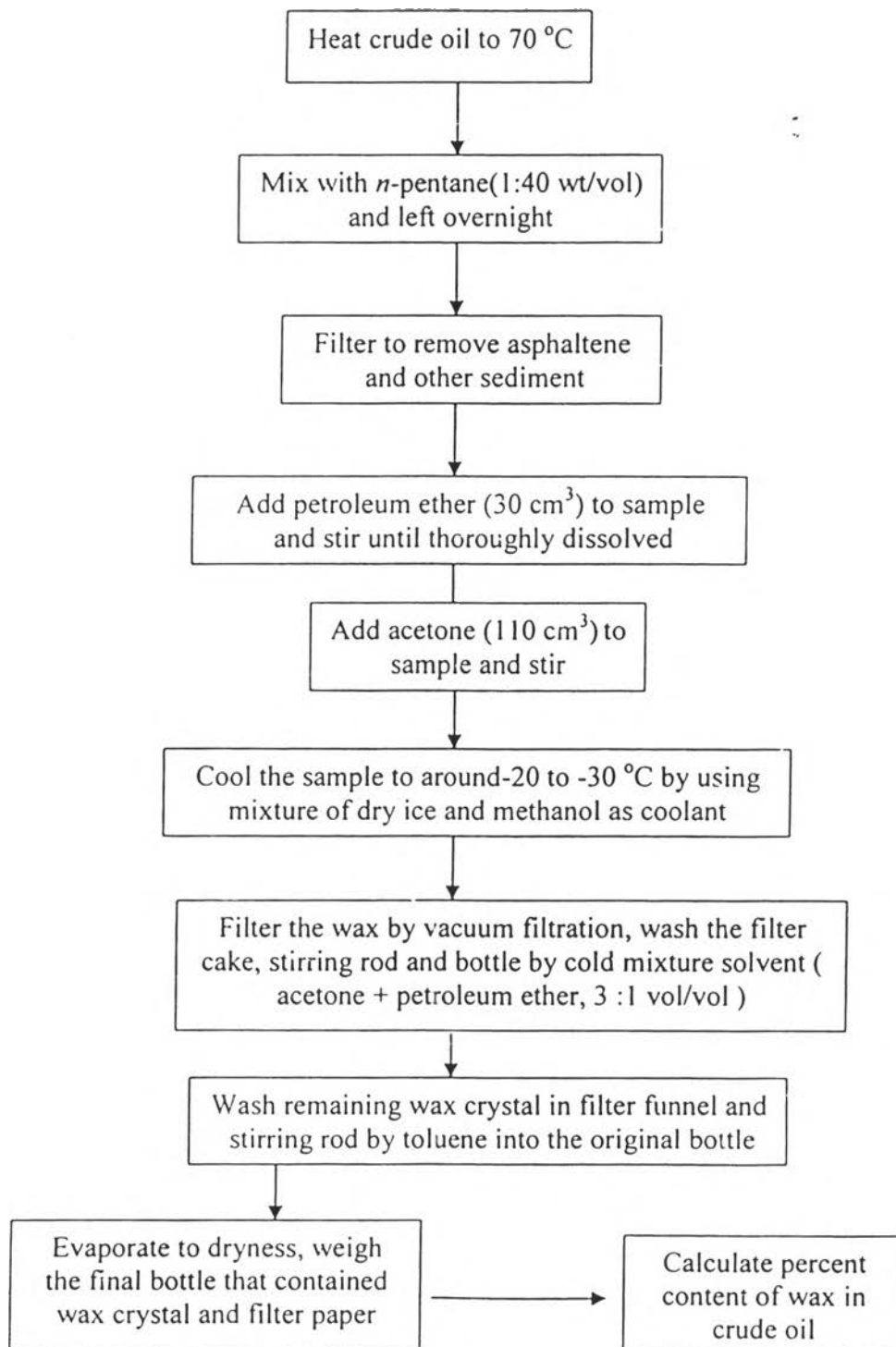


Figure 3.4 Method to determine wax content.

### 3.5.2 Expression of The Relationship between Temperature and The Amount of Wax

The relationship between the amount of wax and temperature can be expressed by using the combination of crystalline curve of DSC thermogram with wax content that obtained from the standard UOP 46-64.

## 3.6 Investigation of the Chemical Method to Solve Wax Deposition Problem

The influence of the EVA and PMMA on pour point of Thai crude oil was studied employing EVA that has various percent content of vinyl acetate of 18, 25, 33, and 40 wt%, and two commercial grades of PMMA, VH grade (m.p. 115 °C) and MD grade (m.p. 130 °C), obtained from Diapolyacrylate Co., Ltd. The concentration of EVA in each vinyl acetate content and of PMMA in each commercial grade was varied at 100, 200, 400, 600, 800, and 1,000 ppm (wt./wt.), as suggested by Andre *et al.* (1999).

#### Procedure

Example: Treated crude oil with EVA addition at 400 ppm

- 1) Pour point test tube was weighed and recorded.
- 2) Ten milligram (0.0100 g.) of EVA was added into the tube and the total weight was recorded.
- 3) Small amount of heated crude oil was added.
- 4) The mixture of crude oil and EVA, was heated to at least 80 °C ( but to at least 120 °C and 135 °C for the treated crude oil by PMMA, MD and VH grade, respectively) in an oil bath to obtain homogeneous solution by visual observation.
- 5) More crude oil was then added into the tube until the total weight of crude oil and EVA was 25.0100 g.
- 6) Finally, the mixture was heated to obtain homogeneous solution.