

## CHAPTER III EXPERIMENT

### 3.1 Materials

Solvents used for crystallization process were toluene, methyl ethyl ketone (MEK), and mixture of toluene and ketone (50:50 vol/vol). Toluene was an analytical reagent (A.R. grade) with 99.5 % purity and was obtained from Lab-Scan Analytical Science (Bangkok, Thailand). Methyl ethyl ketone, (GLC assay 99.5 %) was obtained from Carlo Erba Reagents (Strada Rivoltana, Rodano). Carbon dioxide for supercritical fluid extraction (SFE) was an industrial grade and was supplied by Thai Industrial Gas (Chachoengsao, Thailand). Carbon disulfide with 99.9 % purity was used as a reference in a simulation distillation gas chromatograph (SimDist GC) and was purchased from Merck (Darmstadt, Germany).

### 3.2 Equipment

#### 3.2.1 Continuous Supercritical Fluid Carbon Dioxide Extraction.

The wax purification by supercritical fluid was performed using a supercritical fluid extraction system (Sawangkeaw, R, 2004), consisting mainly of a high-pressure pump (Thar, model P-50-2) supplied by Applied Scientific Instrument (Bangkok, Thailand). The pump connected to ethylene glycol cooling bath (Heto, type CBN 18-30) and water bath (Heto, type OBN 18), which were manufactured by Heto-holten A/S (Allerød, Denmark). The reactor was a stainless steel tube with 19.05 mm in outside diameter, 12.7 mm in inside diameter, 190 mm in length, and 3.175 mm in thickness. The product was collected from the outlet of an automatic back-pressure regulator (model BP-1580-81), which was supplied by Jasco (Maryland, USA).

### 3.2.2 Batch Dissolution Using Supercritical Solvent (Toluene, MEK, and Mixture of Toluene and MEK)

The temperature of the supercritical solvent reactor was controlled by fluidization sand bath (Omega, model FSB-4), which was manufactured by Engineering Inc, (Stamford, Connecticut) and supplied by Pennyful Thailand (Bangkok, Thailand). The reactor was a stainless steel tube with 9.525 mm in outside diameter, 200 mm in length, and 1.588 mm in thickness.

### 3.2.3 Simulation Distillation Gas Chromatograph

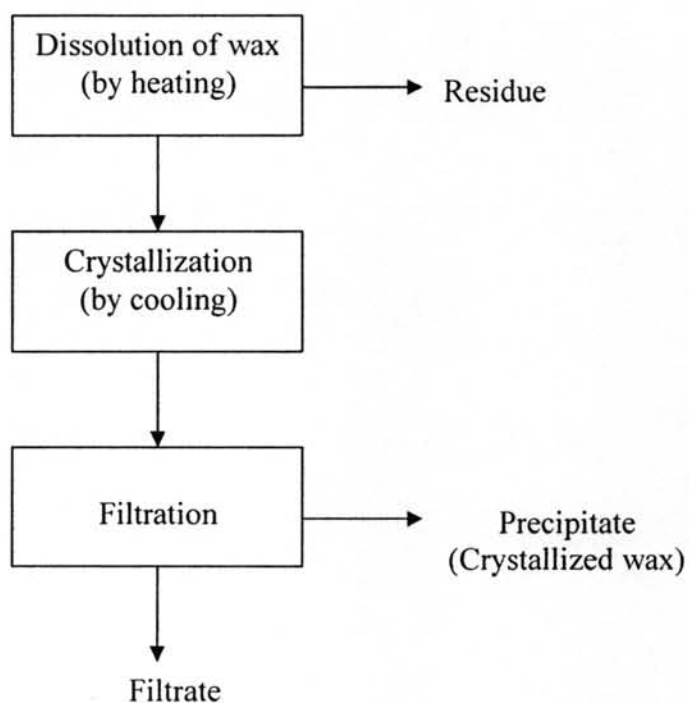
A Varian CP-3800 simulation distillation gas chromatograph (SimDist GC) model GC-3800 (Holland) was used, with the operating conditions following ASTM D2887, to analyze the hydrocarbon compositions. One microliter of sample in carbon disulfide solution was injected at 295°C injector temperature with helium carrier gas at the flow rate of 18 ml/min. The column was Chrompak capillary column (CP 7512) with the length of 10 m, diameter of 0.53 mm, and thickness of 0.88  $\mu\text{m}$ . The programmed column temperature was operated at the constant temperature of 30°C for 5 min, then increased at the rate of 20°C/min for 14.5 min until reaching the final temperature of 320°C and finally held constant for 8.5 min. The chromatographic peaks were detected by flame ionization detector (FID) at temperature of 320°C.

## 3.3 Methodology

### 3.3.1 Crystallization by Using Solvents

A 0.6 g of sludge wax was dissolved in 30 ml (ratio of solvent:wax = 50:1 vol/wt%) of toluene, methyl ethyl ketone, and mixed solvent (toluene to methyl ethyl ketone = 50:50 vol/vol%). The solution was then heated to 80°C, held constant for 15 min, and filtered to separate the insoluble part, which was collected as a residue. The filtrate was cooled down at the temperature of -21°C overnight until the crystallized wax was precipitated out. The crystallized wax was separated from the filtrate by filtration using suction funnel equipped with a pump. The crystallized wax and

filtrate were analyzed for their composition and oil content by the SimDist-GC. The process is shown diagrammatically in Figure 3.1



**Figure 3.1** Diagram of the crystallization process.

*Effect of solvent type.* The sludge wax was brought into contact with toluene, methyl ethyl ketone, and toluene-MEK mixture (ratio of 50:50 vol/vol%) to study the effect of type of solvents on a purification of wax. A wax was dissolved in a solvent in a ratio of solvent:wax = 50:1 vol/wt% at 80°C and then crystallized at -21°C. The residue, precipitate, and filtrate were analyzed by GC-SimDist.

*Effect of solvent composition (MEK to Toluene ratio).* Toluene-MEK mixtures with different mixed ratios of 20, 40, 60, 80, and 100 vol% MEK were used. A wax was dissolved in a toluene-MEK mixture in a ratio of solvent to wax =

50:1 vol/wt% at 80°C and crystallized at -21°C, respectively, and then the residue, precipitate, and filtrate were analyzed by GC-SimDist.

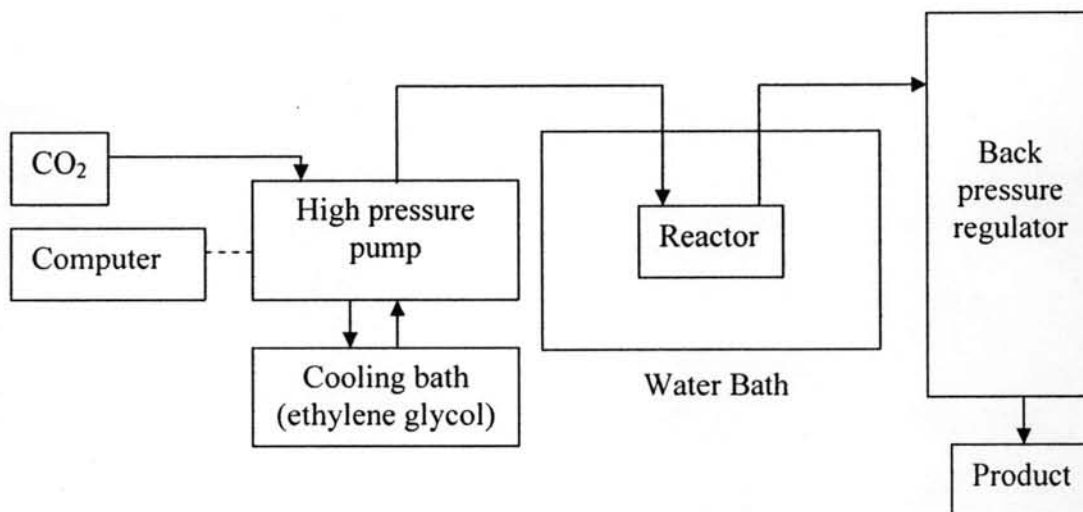
*Effect of solvent amount (solvent to wax ratio).* A toluene-MEK mixture (ratio of 50:50 vol/vol%) was used to dissolve sludge wax in different ratios of 30:1, 40:1, 50:1, 60:1, 70, and 80:1 vol/wt%. A dissolution and crystallization temperature were 80°C and -21°C respectively. The residue, precipitate, and filtrate were collected and analyzed by GC-SimDist.

### 3.3.2 Crystallization by Using Supercritical Solvents

A 0.05 g of wax was dissolved in 0.03 mol of toluene and methyl ethyl ketone (solvent:wax ratio of 50:1). The solution was loaded into the reactor, placed in the fluidization sand bath, and heated to 340°C to reach the supercritical pressure of the solvents for 10 min (The calculation is shown in Appendix A). For supercritical condition, the pressure of the solution was 133.969 atm for toluene, and 85.153 atm for MEK. Then, the reactor was taken off the fluidization bath and cooled in a water bath at room temperature. The solution was unloaded from the reactor, and a portion of the resulting mixture was taken to analyze for the composition by SimDist-GC. The solution was also further cooled down at the temperature of -21°C until the crystallized wax was precipitated. The crystallized wax was separated from the filtrate by filtration, using suction funnel equipped with pump. The crystallized wax and filtrate were analyzed for their composition and oil content by SimDist-GC.

### 3.3.3 Supercritical Fluid Carbon Dioxide Extraction of The Sludge Wax

Sludge wax of 0.04 g was loaded into the reactor, of which the temperature was controlled at 40°C in the water bath. Then, the supercritical carbon dioxide with a flow rate of 3 g/min at pressure of 250 bar was allowed to pass through the reactor for 30 min. The extracted product was collected, while the supercritical fluid (CO<sub>2</sub>) was released through back-pressure regulator. Next, the remaining wax in the reactor was unloaded. Both the extracted product and the remaining wax were analyzed by SimDist-GC. The schematic diagram of the supercritical fluid CO<sub>2</sub> extraction system is shown in Figure 3.2.

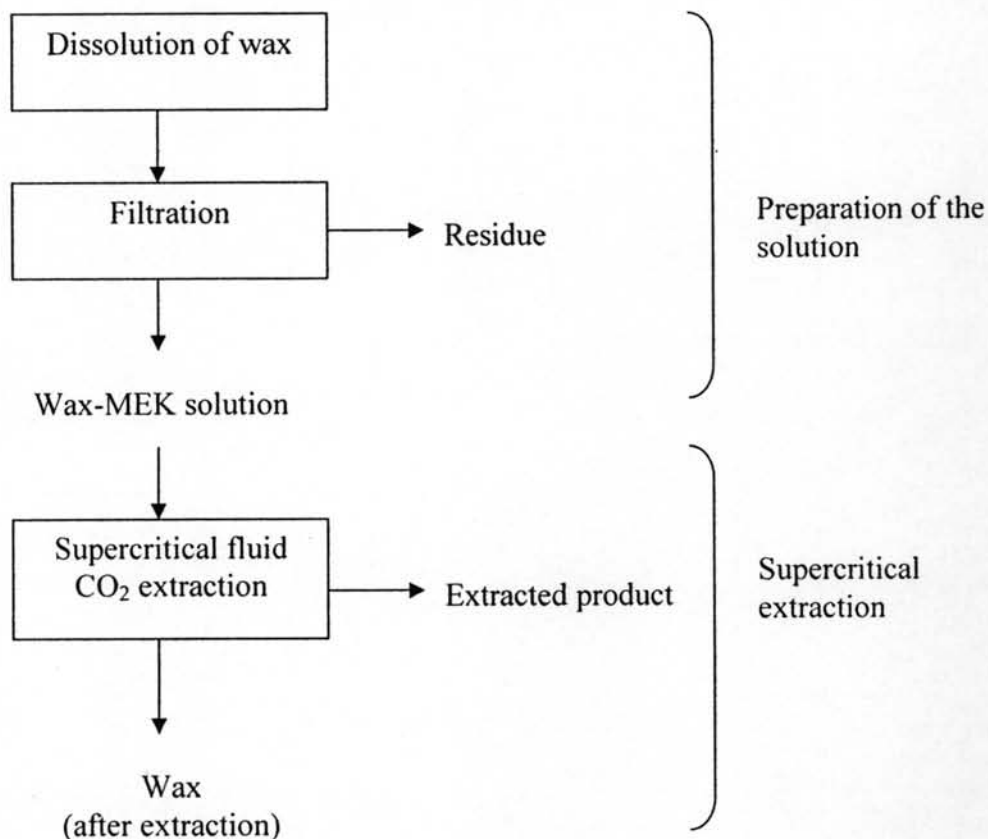


**Figure 3.2** Schematic of the supercritical fluid CO<sub>2</sub> extraction apparatus.

### 3.3.4 Supercritical Fluid (CO<sub>2</sub>) Extraction of The Wax in Methyl ethyl ketone Solution

*Preparation of wax in methyl ethyl ketone solution.* One gram of sludge wax was dissolved in 50 ml of methyl ethyl ketone (solvent:wax ratio = 50:1 wt/vol%) at the temperature of 75°C for 15 min. Then, the solution was filtered to separate an insoluble residue, which the residue was also further analyzed for the composition by SimDist-GC. The MEK solution (filtrate) was further extracted with the supercritical fluid CO<sub>2</sub>.

*Extraction of wax in methyl ethyl ketone solution with supercritical fluid (CO<sub>2</sub>).* The wax in MEK solution was loaded into a reactor, of which the temperature was controlled at 40°C in the water bath. Then, the supercritical carbon dioxide with a flow rate of 3 g/min at pressure of 250 bar was allowed to pass through the reactor for 40 min. The extracted product was collected for every 30 min, while the supercritical fluid (CO<sub>2</sub>) was released through a back-pressure regulator. The composition of the product was analyzed by SimDist-GC. The diagram of the supercritical fluid (CO<sub>2</sub>) extraction of the wax-methyl ethyl ketone solution is shown in Figure 3.3



**Figure 3.3** Diagram of the supercritical fluid (CO<sub>2</sub>) extraction of the wax-methyl ethyl ketone solution.

### 3.4 The Experimental Design

#### 3.4.1 Supercritical Fluid Carbon Dioxide Extraction

Experimental design method was applied to this section of the experiment, which involved the study of the effect of two or more factors. In general, *factorial designs* are the most efficient for this type of experiment. Wax was purified by using supercritical fluid carbon dioxide extraction. In this work, the  $2^k$  *factorial design* was applied. The  $2^k$  factorial design is particularly useful in the early states of experimental works, when they are likely to have many factors to be investigated. It provides the smallest number of run, with which  $k$  factor can be studied in the complete factorial design.



This work focused on the effect of 3 factors on the extraction efficiency, which were pressure, CO<sub>2</sub> flow rate, and extraction time. Each factor was studied at 2 levels of interest, so the design is called 2<sup>3</sup> factorial design. The data of 2 levels of each factor are shown in Table 3.1.

**Table 3.1** Two levels of the three investigated factors

Factor	Symbol	Level	
		Low level	High level
Extraction time (min)	A	30	120
Pressure (bar)	B	250	350
CO <sub>2</sub> flow rate (g/min)	C	3	5

Not only the main effect contributed from each sole factor, but also the interaction effect between each factor was studied. Generally, a capital letter is always used to denote the effect of each factor. Thus, "A", "B", "C" and "AB" refer to the effects of extraction time, Pressure, CO<sub>2</sub> flow rate, and interaction between A and B, respectively. In the 2<sup>3</sup> factorial design, the low and high levels of A and B are denoted by "-" and "+" signs, respectively.

The eight treatment combinations in the design are usually represented by lowercase letters. The high level and low level of any factor in the treatment combination are denoted by the corresponding lowercase letter and the absence of the letter. For example, "a" represents the treatment combination of A at high level, B and C at low level. "b" represents the treatment combination of B at the high level, and A and C at low level, and "ab" represents the treatment combination of A and B at the high level, and C at the low level. In addition, "(1)" denotes all factors at the low level, all treatment combinations with corresponding to the experimental condition are shown in Table 3.2. The eight runs in the 2<sup>3</sup> design are also listed, as shown in Table 3.3. This is sometimes called the design matrix. It is often convenient to write down the treatment combinations in the order of (1), a, b, ab, c, ac, bc, and abc. This is referred to as standard order.

**Table 3.2** All treatment combinations corresponding to the experimental condition

Treatment combination	Extraction time (min)	Pressure (bar)	CO <sub>2</sub> flow rate (g/min)
(1)	30	250	3
a	120	250	3
b	30	350	3
ab	120	350	3
c	30	250	5
ac	120	250	5
bc	30	350	5
abc	120	350	5

**Table 3.3** Total number of run and label in the 2<sup>3</sup> design

Run	A	B	C	Label
1	-	-	-	(1)
2	+	-	-	a
3	-	+	-	b
4	+	+	-	ab
5	-	-	+	c
6	+	-	+	ac
7	-	+	+	bc
8	+	+	+	abc

By using this standard order, the contrast coefficients used for estimating the effects are just the product of the corresponding coefficients for the two main effects. The contrast coefficient is always either +1 or -1, and a table of plus and minus signs, as shown in Table 3.4, can be used to determine the proper sign for the treatment combination. The column headings in Table 3.4 represent the main effect,



the interaction effect, and I, which represents the total or average of the entire experiment. To find the contrast for estimating any effect, the signs in the appropriate column of the table are simply multiplied by the corresponding treatment combination. For example, to estimate A, the contrast is  $-(1) + a - b + ab - c + ac - bc + abc$ . The larger the estimated contrast, the more pronounced the effect of the factor on the experiment.

**Table 3.4** Algebraic signs for calculating the effects in  $2^3$  design

Treatment combination	Factorial effect							
	I	A	B	AB	C	AC	BC	ABC
(1)	+	-	-	+	-	+	+	-
a	+	+	-	-	-	-	+	+
b	+	-	+	-	-	+	-	+
ab	+	+	+	+	-	-	-	-
c	+	-	-	+	+	-	-	+
ac	+	+	-	-	+	+	-	-
bc	+	-	+	-	+	-	+	-
abc	+	+	+	+	+	+	+	+

The method of analysis provided a simple way to determine the factor effects. A normal probability plot of the estimates of the effects was suggested. The effects that are negligible are normally distributed, with mean zero and variance  $\sigma^2$ , and tend to fall along the straight line on this plot, whereas significant effects have non-zero means and do not lie along the straight line. Thus, the preliminary model is specified to contain those effects that are apparently non-zero, based on the normal probability plot. The apparently negligible effects are combined as an estimate of error.

Sums of squares for the effect are easily computed, because each effect has a corresponding single degree of freedom contrast. In the  $2^3$  design with  $n$  replicates, the sum of square for any effect is:

$$SS = \frac{(Contrast)^2}{8n}$$

Then, to confirm the magnitude of these effects, the analysis of variance table was built to see *Mean square*,  $F_0^*$ , and *P-value*\*\* . In order to see the effect of each factor, if the calculated p-value is higher than 0.05, and the null hypothesis is not rejected, this experiment can thus be stated as being "not statistically significant at the 5 % level". If the p-value is lower than 0.05, and the null hypothesis is rejected, this experiment can be oppositely stated as being "statistically significant at the 5 % level".

\* F-value = Mean square sample/mean square residue.

\*\*P- value = the smallest level of significance that would lead to rejection of the null hypothesis.