

## CHAPTER IV

### RESULTS AND DISCUSSION

#### 4.1 Characterization of Sludge Wax

*Sludge wax.* Characterization of sludge wax by SimDist GC showed the oil content of 68.7%, and wax content of 31.3% (Raw data on oil and wax content are also shown in Appendix B, and Table B1). Oil content is defined as hydrocarbon compound with carbon number less than 20, while wax as those with carbon number greater than 20. The chromatogram of original sludge wax is shown in Figure 4.1.

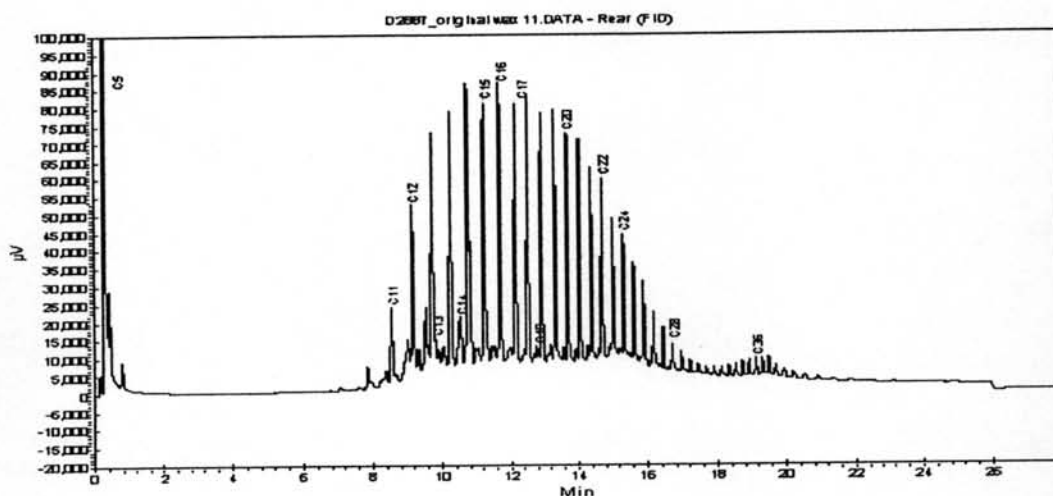


Figure 4.1 Chromatogram of the original sludge wax.

#### 4.2 Wax Purification by Crystallization

##### 4.2.1 Wax Purification by Crystallization Using Solvents

##### 4.2.1.1 *Effect of solvent types.*

The sludge wax was brought into contact with toluene, methyl ethyl ketone, and toluene-MEK mixture. The residue obtained after dissolution of sludge wax in the solvent, the precipitate (crystallized wax), and the filtrate after crystallization were analyzed by SimDist-GC. The oil and wax content, which were

related to original content of each fraction, accounted for only n-paraffin hydrocarbons according to a standard solution, as shown in Table 4.1, the yield, amount of wax, and purity of the precipitate are shown in Table 4.2, and the chromatograms for various fractions are shown in Figure 4.2 (Raw data on oil and wax content are also shown in Appendix B, and Table B2).

The results show that a residue from MEK solvent has lower oil content than toluene. It is clear that because MEK has higher polarity than toluene, larger amount of oil were dissolved by MEK, resulting in lower percentage of oil remained in a residue.

Similar to a residue, the oil and wax content in a precipitate can also be explained by the effect of solvent polarity. Another interesting and important evidence is that the precipitate of crystallized wax from mixed solvent solution contained most wax with least oil content, while MEK or toluene alone did not provide good wax separation. So, attention was focused on mixed solvent, and the optimum ratio of mixed solvent was also studied.

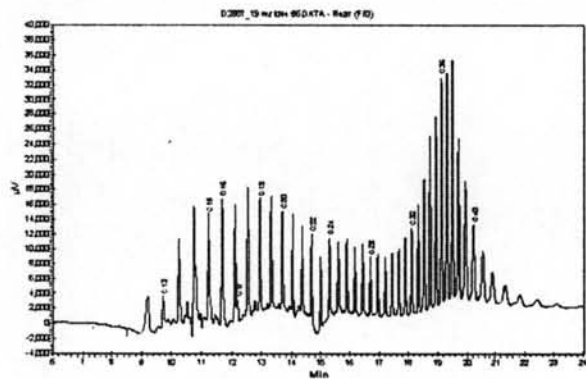
The filtrate obtained after crystallization appeared as a clear solution, which was dark yellow when MEK was used, brown when mixed solvents was used, and darker brown when toluene was used. Since most of oil fractions were presented in a filtrate, this can be rationalized by the fact that an oil content could be dissolved by the solvents and separated as a filtrate fraction.

**Table 4.1** The oil and wax content in each fraction obtained from different solvents

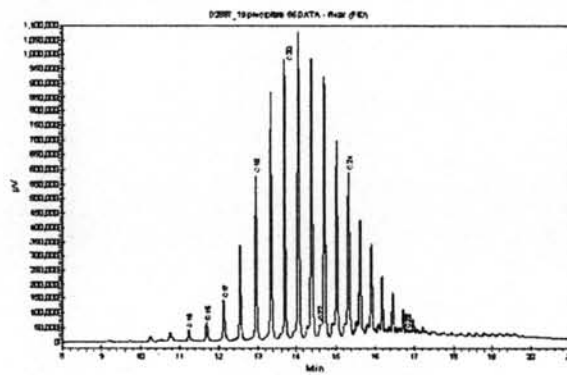
| Solvent       | Residue    |                 |                 | Precipitate (Crystallized wax)  |                 |                 | Filtrate     |                 |                 |
|---------------|------------|-----------------|-----------------|---------------------------------|-----------------|-----------------|--------------|-----------------|-----------------|
|               | Appearance | Oil content (%) | Wax content (%) | Appearance                      | Oil content (%) | Wax content (%) | Appearance   | Oil content (%) | Wax content (%) |
| MEK           | Brown      | 8.26            | 27.90           | Dark yellow soft slurry         | 3.41            | 7.22            | Dark yellow  | 53.22           | 0.00            |
| Toluene       | Black      | 12.94           | 23.32           | Darker brown and stiffer        | 3.15            | 2.68            | Darker brown | 39.38           | 18.52           |
| Mixed solvent | Dark brown | 10.62           | 30.94           | Darker yellow and quite stiffer | 0.51            | 4.96            | Brown        | 48.80           | 4.17            |

**Table 4.2** The yield, amount of wax ,and purity of the desired product (precipitate) obtained from different solvents.

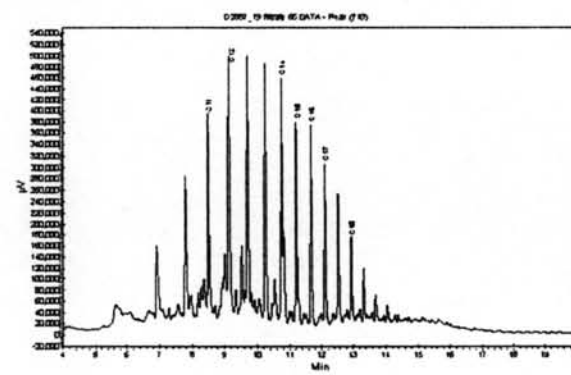
| Solvents      | Yield (precipitate) |       | Amount of wax |      | Purity of wax (%) |
|---------------|---------------------|-------|---------------|------|-------------------|
|               | Weight (g)          | %     | Weight (g)    | %    |                   |
| MEK           | 0.0639              | 10.62 | 0.04          | 7.22 | 67.92             |
| Toluene       | 0.0355              | 5.84  | 0.02          | 2.68 | 45.92             |
| Mixed solvent | 0.0331              | 5.48  | 0.03          | 4.96 | 90.63             |



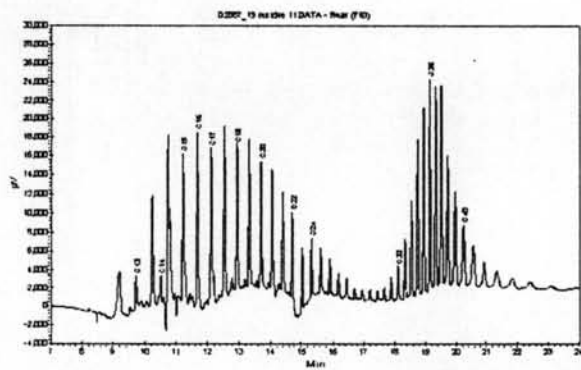
(a) Residue from MEK solution



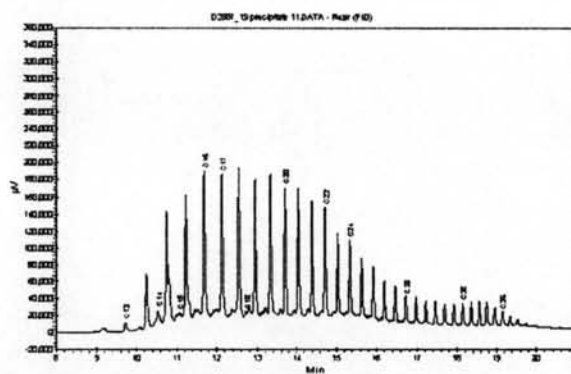
(b) Precipitate from MEK solution



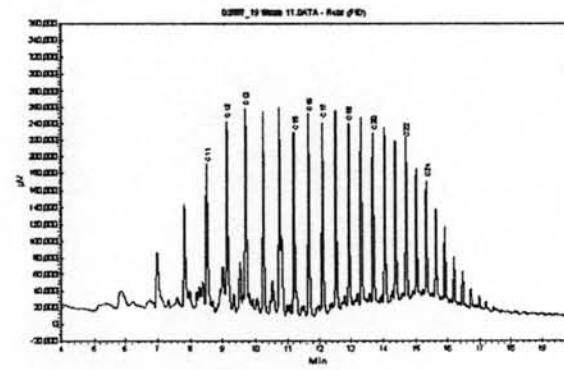
(c) Filtrate from MEK solution



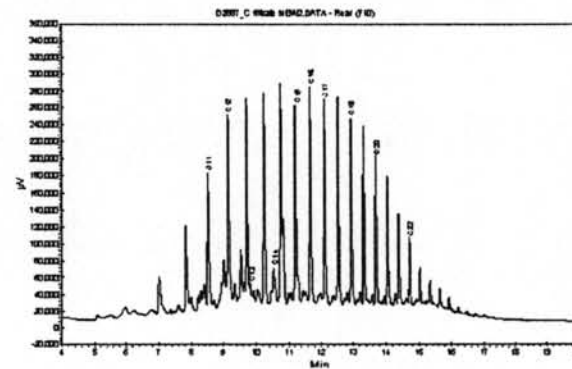
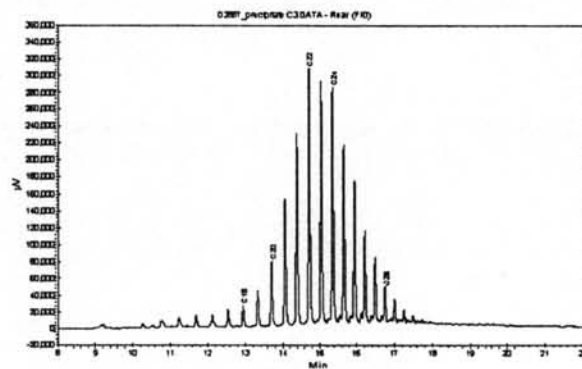
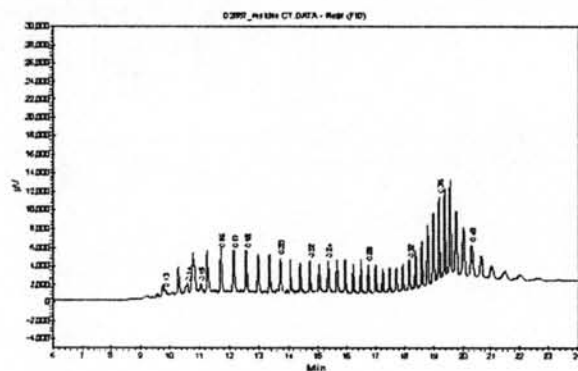
(d) Residue from toluene solution



(e) Precipitate from toluene solution



(f) Filtrate from toluene solution



(g) Residue from mixed solvent solution

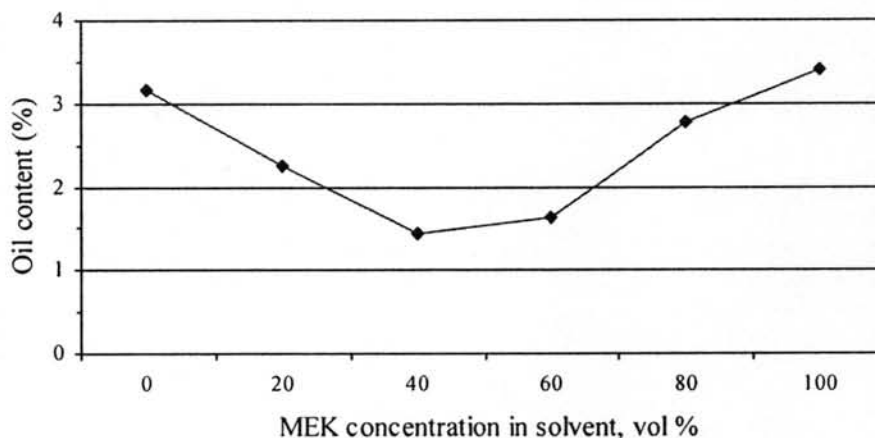
(h) Precipitate from mixed solvent solution

(i) Filtrate from mixed solvent solution

**Figure 4.2** Chromatograms of a residue, precipitate, and filtrate from different solvents: (a) residue from MEK solution, (b) precipitate from MEK solution, (c) filtrate from MEK solution, (d) residue from toluene solution, (e) precipitate from toluene solution, (f) filtrate from toluene solution, (g) residue from mixed solvent solution, (h) precipitate from mixed solvent solution, and (i) filtrate from mixed solvent solution.

#### 4.2.1.2 Effect of solvent composition (MEK to Toluene ratio).

After dissolving sludge wax in a MEK to toluene mixture, with various ratios of 0, 20, 40, 60, 80, and 100 vol% MEK, the oil content in a precipitate was examined by GC-SimDist.



**Figure 4.3** Oil content in a precipitate compared to the original sludge wax obtained from different MEK to toluene ratios.

Figure 4.3 shows the plot of the oil content remained in a precipitate against the various ratios of mixed solvent. The results indicate that the oil content in the precipitate decreased with increasing % MEK in the mixture until approximately 40-50 vol%, because the solubility of wax in MEK is quite low, and higher in toluene. So, during 0-50 vol% MEK, most of oil fractions were dissolved resulting in the percentage of oil remained in precipitate decreased. On the contrary, if the concentration of MEK in a solvent higher than 50 vol%, a higher polarity in a solvent were unable to dissolve fraction of oil which is non polar, resulting in percentage of oil remained in precipitate increased. Eventually, the optimum mixed solvent ratio is at 50%vol MEK.

#### 4.2.1.3 Effect of solvent amount (solvent to wax ratio).

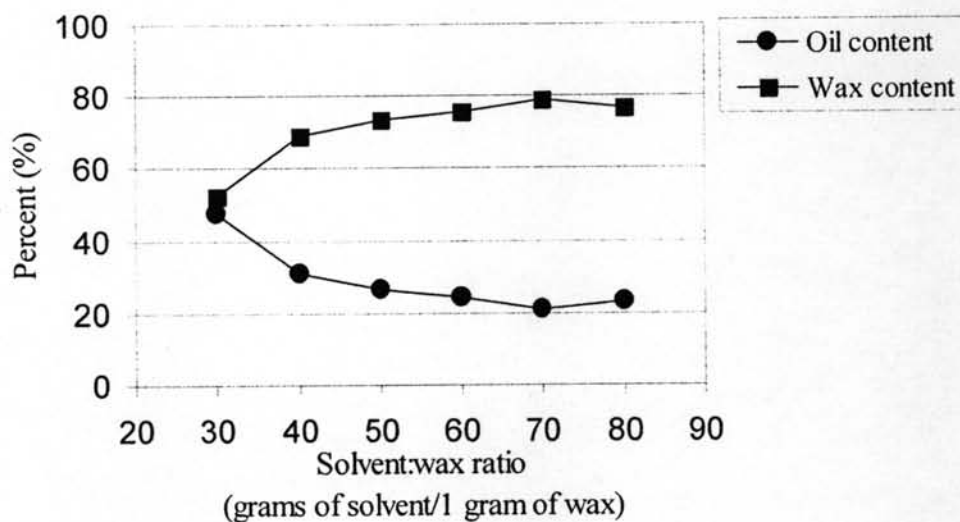
A crystallization of wax in a MEK to toluene mixture, 50%vol MEK, with various solvent to wax ratios of 30:1, 40:1, 50:1, 60:1, 70:1, and 80:1 was also carried out. The oil and wax content, related to original sludge wax, in a residue, precipitate, and filtrate, obtained from different solvent to wax ratios are shown in Table 4.3, the yield, amount of wax, and purity of the precipitate are shown in Table 4.4, and the percentage of oil and wax in each fraction is graphically shown in Figures 4.4-4.6, respectively.

**Table 4.3** The oil and wax content in each fraction obtained from different solvent to wax ratio

| Solvent to wax ratio | Residue         |                 | Precipitate<br>(Crystallized wax) |                 | Filtrate        |                 |
|----------------------|-----------------|-----------------|-----------------------------------|-----------------|-----------------|-----------------|
|                      | Oil content (%) | Wax content (%) | Oil content (%)                   | Wax content (%) | Oil content (%) | Wax content (%) |
| 30:1                 | 26.31           | 28.85           | 1.05                              | 7.24            | 17.76           | 17.79           |
| 40:1                 | 13.44           | 30.13           | 1.27                              | 8.85            | 23.90           | 22.45           |
| 50:1                 | 11.20           | 31.05           | 0.55                              | 10.87           | 26.64           | 19.66           |
| 60:1                 | 10.12           | 31.84           | 0.58                              | 12.32           | 60.73           | 17.72           |
| 70:1                 | 8.48            | 31.44           | 0.34                              | 13.87           | 26.92           | 18.95           |
| 80:1                 | 9.30            | 30.82           | 0.18                              | 15.83           | 27.55           | 16.32           |

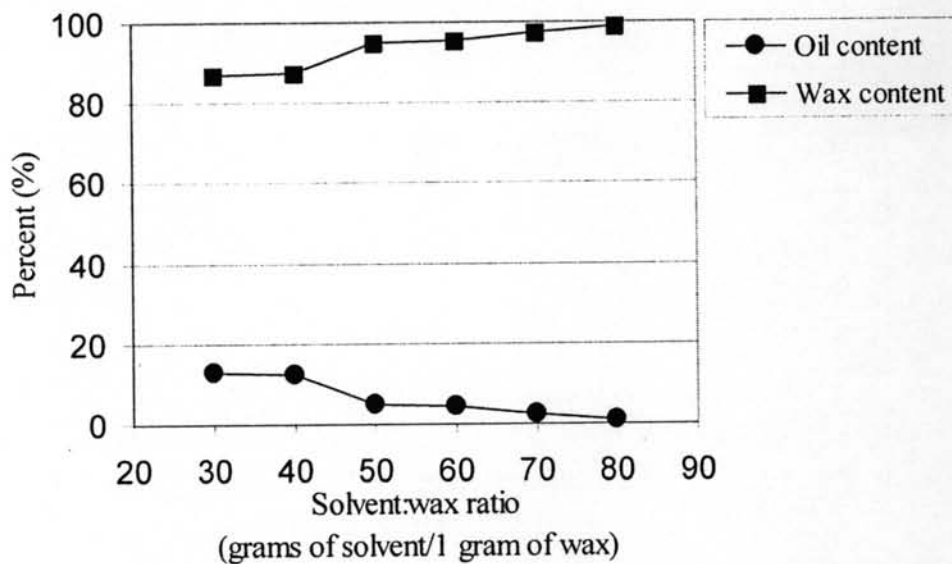
**Table 4.4** The yield, amount of wax ,and purity of the desired product (precipitate) obtained from different solvent to wax ratio.

| Solvent to wax ratio | Yield (precipitate) |       | Amount of wax |       | Purity of wax (%) |
|----------------------|---------------------|-------|---------------|-------|-------------------|
|                      | Weight (g)          | %     | Weight (g)    | %     |                   |
| 30:1                 | 0.0499              | 8.29  | 0.0436        | 7.24  | 87.33             |
| 40:1                 | 0.0613              | 9.62  | 0.0536        | 8.85  | 87.45             |
| 50:1                 | 0.0691              | 11.42 | 0.0658        | 10.87 | 95.18             |
| 60:1                 | 0.0779              | 12.9  | 0.0744        | 12.32 | 95.50             |
| 70:1                 | 0.0859              | 14.21 | 0.0838        | 13.87 | 97.61             |
| 80:1                 | 0.0973              | 16.01 | 0.0962        | 15.83 | 98.88             |

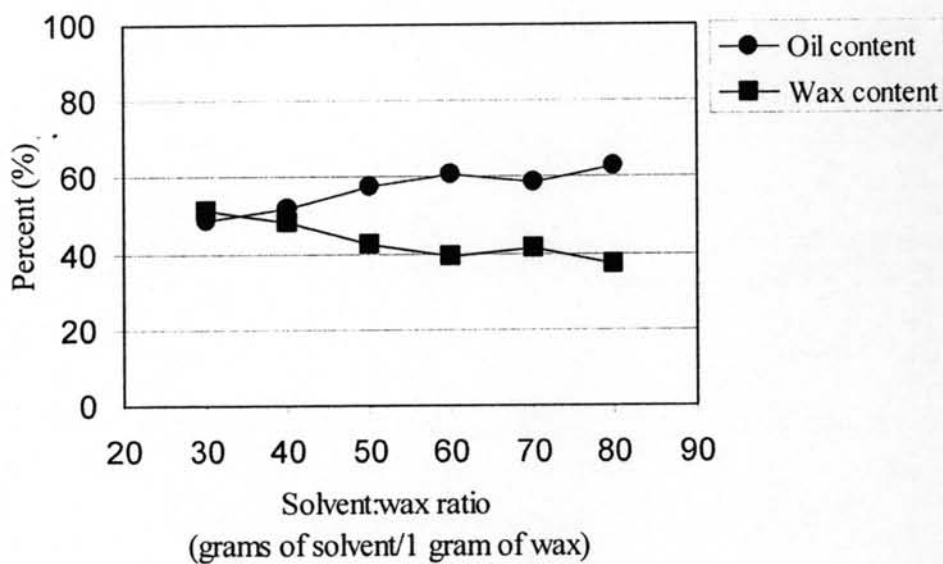


**Figure 4.4** Percentage of oil and wax content in residue obtained from different solvent to wax ratios.





**Figure 4.5** Percentage of oil and wax content in precipitate obtained from different solvent to wax ratios.



**Figure 4.6** Percentage of oil and wax content in filtrate obtained from different solvent to wax ratios.

The results indicate that for the residue, the oil content decreased continuously with increasing the solvent to wax ratio. It can be seen that the more solvent used, the more solubility of oil and more oil was washed out, the percentage of oil content decreased until reaching the certain solvent to wax ratio of approximately 70:1, where the oil solubility was limited. Then the oil content became constant. On the contrary, the percentage of wax content increased with increasing the solvent to wax ratio. For the precipitate, similar to the residue, the oil content decreased with increasing the solvent to wax ratio. Especially, at the ratio of solvent to wax of about 50:1, the amount of oil remained in precipitate substantially decreased. When increasing solvent to wax ratios, larger amount of oil in sludge were dissolved due to the increase in its solubility. So, most of oil fractions were present in a filtrate and increased with increasing the solvent to wax ratio.

### 4.3 Wax Purification by Crystallization Using Supercritical Solvents

A product obtained after dissolution of the sludge wax in supercritical solvents was a wax-solvent mixture, which was colloidal, dark yellow color when using MEK as a solvent, brown when using mixed solvent, and very dark brown when using toluene. The crystallization was then applied to the mixtures to obtain wax. The originally obtained mixture, precipitate (crystallized wax), and filtrate were analyzed by SimDist-GC (Raw data of oil and wax content are also shown in Appendix B, and Table B3). The results of oil and wax content, related to original content of sludge wax, and chromatograms are presented in Table 4.5 and Figure 4.7, the yield, amount of wax, and purity of the precipitate are shown in Table 4.6 respectively.

After dissolution of the sludge wax in a supercritical solvent under an extremely high temperature and pressure, the higher hydrocarbon may possibly crack to smaller molecules resulting in a higher percent content of oil in a solution, comparing to the original wax.

The precipitate obtained from the MEK solution was soft slurry with dark yellow color, while that obtained from the toluene solution was darker in color and stiffer. The filtrate obtained after crystallization and filtration appeared in a dark yellow color when the dissolution was performed in the supercritical MEK, brown in the supercritical mixed solvent, and very dark brown in the supercritical toluene.

From the result, there are no wax content in a precipitate obtained from toluene and MEK, It can be presumed that the higher hydrocarbon molecules might crack to smaller molecules. As a result, the oil fractions in a filtrate are higher than wax fraction for every filtrate obtained from different supercritical solvent.

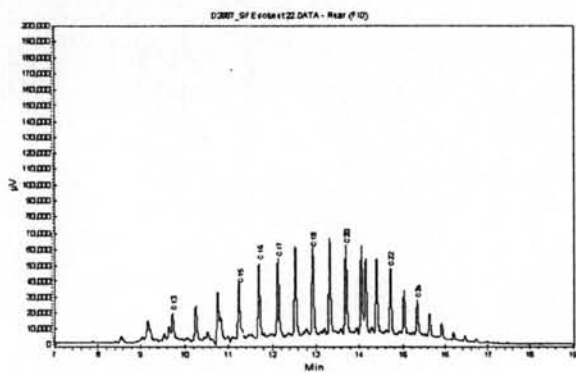
The chromatograms in Figure 4.7 show that the hydrocarbon compositions are different when compared to those obtained from crystallization at normal conditions.

**Table 4.5** The oil and wax content in wax-supercritical mixtures, precipitate, and filtrate obtained from different supercritical solvents

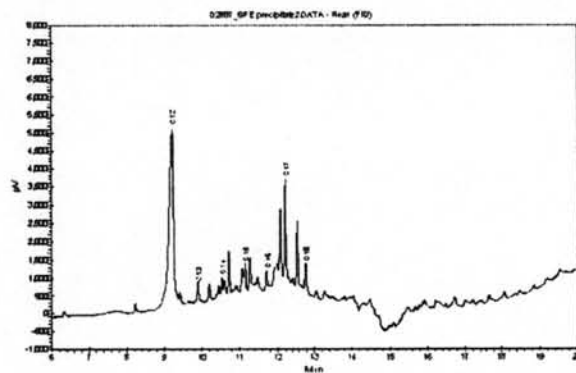
| Solvents      | Wax-supercritical solvent mixture |                 |                 | Precipitate (Crystallized wax) |                 |                 | Filtrate        |                 |                 |
|---------------|-----------------------------------|-----------------|-----------------|--------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|               | Appearance                        | Oil content (%) | Wax content (%) | Appearance                     | Oil content (%) | Wax content (%) | Appearance      | Oil content (%) | Wax content (%) |
| MEK           | Dark yellow colloid               | 65.18           | 34.82           | Dark yellow soft slurry        | 13.28           | 0               | Dark yellow     | 71.96           | 14.76           |
| Toluene       | Dark brown                        | 85.94           | 14.06           | Dark brown and stiffer         | 39.40           | 0               | Very dark brown | 38.94           | 21.66           |
| Mixed solvent | Brown                             | 95.13           | 4.87            | Brown and stiffer              | 27.05           | 22.27           | Brown           | 27.95           | 22.73           |

**Table 4.6** The yield, amount of wax, and purity of the desired product (precipitate) obtained from different solvents.

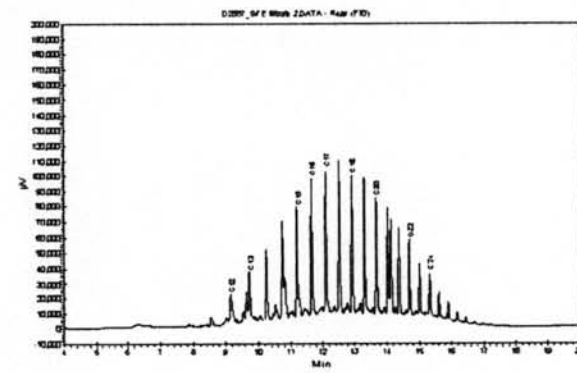
| Solvents      | Yield (precipitate) |       | Amount of wax |       | Purity of wax (%) |
|---------------|---------------------|-------|---------------|-------|-------------------|
|               | Weight (g)          | %     | Weight (g)    | %     |                   |
| MEK           | 0.0036              | 13.28 | 0             | 0     | 0                 |
| Toluene       | 0.0171              | 39.40 | 0             | 0     | 0                 |
| Mixed solvent | 0.0217              | 49.32 | 0.0098        | 22.27 | 45.15             |



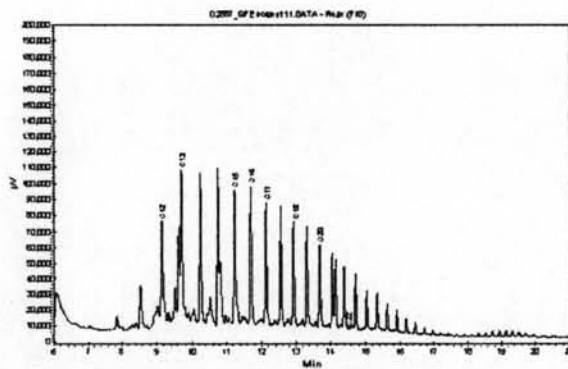
(a) Wax- supercritical MEK mixture



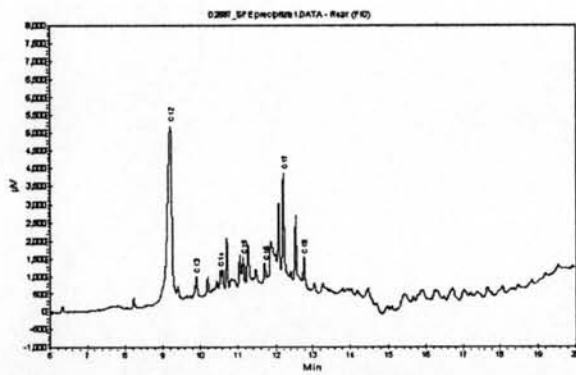
(b) Precipitate from Wax-supercritical MEK mixture



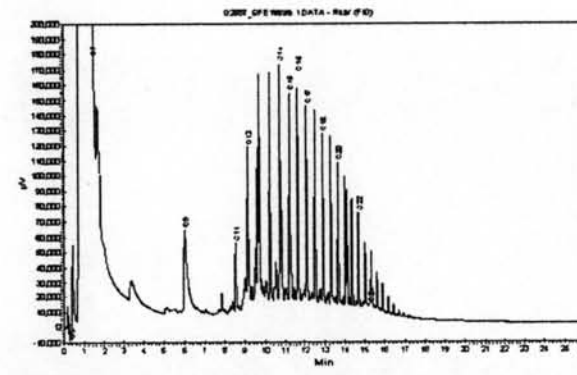
(c) Filtrate from Wax- supercritical MEK mixture



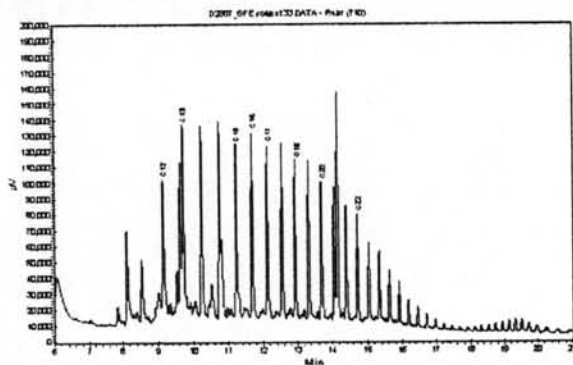
(d) Wax- supercritical toluene mixture



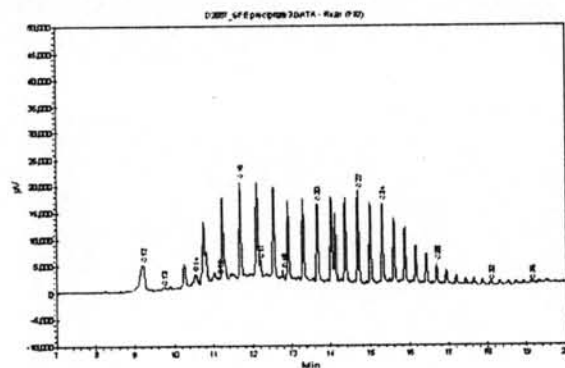
(e) Precipitate from Wax- supercritical toluene mixture



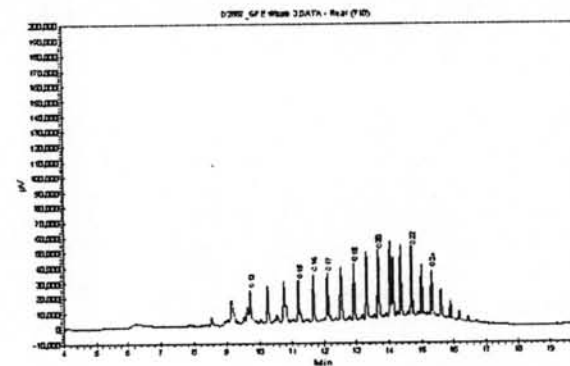
(f) Filtrate from Wax- supercritical toluene mixture



(g) Wax- supercritical mixed solvents



(h) Precipitate from Wax- supercritical mixed solvent



(i) Filtrate from Wax- supercritical mixed solvent

**Figure 4.7** Chromatograms of a wax- supercritical solvent mixture, precipitate, and filtrate obtained from different supercritical solvents: (a) wax- supercritical MEK mixture, (b) precipitate from supercritical MEK mixture, (c) filtrate from supercritical MEK mixture, (d) wax- supercritical toluene mixture, (e) precipitate from supercritical toluene mixture, (f) filtrate from supercritical toluene mixture, (g) wax- supercritical mixed solvents, (h) precipitate from wax- supercritical mixed solvent, and (i) filtrate from wax- supercritical mixed solvent.

## 4.4 Wax Purification by Supercritical Fluid Extraction

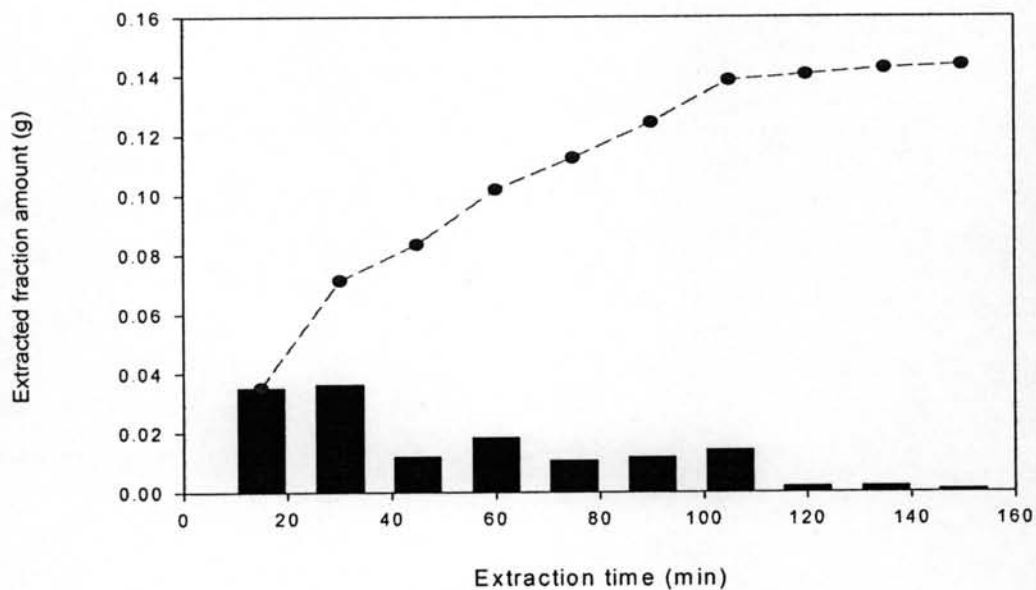
### 4.4.1 Wax Purification by Supercritical Fluid Carbon Dioxide Extraction of The Original Sludge Wax

The original sludge wax was directly purified by supercritical fluid carbon dioxide. Two fractions of product were obtained. First, the extracted fraction was yellow colloid; and second, the remaining fraction in the reactor was black solid mixed with dark brown color. The wax after the extraction was less sticky and drier as compared to the original one.

This experiment involved the study of the effect of two or more factors. Since many experiments needed to be investigated, the factorial design was applied to see how the factors affect the extraction (Douglas, C.M, 1997).

#### 4.4.1.1 *Effect of extraction time*

In order to determine an appropriate extraction time, the experimental was done under mild condition at pressure of 250 bar and CO<sub>2</sub> flow rate of 3 g/min. The effect of extraction time on the amount and accumulated amount of extracted fraction is shown in Figure 4.8. As shown in the line plot of the accumulated amount of extracted fraction, the extracted amount increased, with increasing the extraction time. Especially during the first 30 min, the amount of the extracted fraction dramatically increased. After that, it gradually increased until reaching the constant value at that extraction time of approximately 120 min. The bar chart indicates that the amount of the extracted fraction decreased with increasing the extraction time. It can also be said that increasing the extraction time provided a long contacting period between sludge wax and supercritical carbon dioxide. Oil Contained in the sludge was continuously extracted, and the amount of the extracted fraction was remarkably increased. These results would allow to set the extraction time between 30 and 120 minutes for further experiments.



**Figure 4.8** The effect of extraction time on the amount and accumulated amount of extracted fraction (Bar: amount; Line: accumulated amount).

After the supercritical extraction was done under several conditions, according to the  $2^3$  design, the amount of the extracted fraction was collected and calculated, and percentage of oil remaining in a purified wax was determined by the SimDist-GC. These two data are shown in Table 4.7, as a response of the experimental design.



**Table 4.7** The observed response of all experiments at several conditions

| Treatment combination | Conditions            |                |                   | Responses                        |                             |
|-----------------------|-----------------------|----------------|-------------------|----------------------------------|-----------------------------|
|                       | Extraction time (min) | Pressure (Bar) | Flow rate (g/min) | Amount of sludge wax extract (g) | Percentage of oil remaining |
| (1)                   | 30                    | 250            | 3                 | 0.1054                           | 35.239                      |
| a                     | 120                   | 250            | 3                 | 0.2570                           | 21.096                      |
| b                     | 30                    | 350            | 3                 | 0.0757                           | 28.637                      |
| ab                    | 120                   | 350            | 3                 | 0.1227                           | 11.341                      |
| c                     | 30                    | 250            | 5                 | 0.0755                           | 29.529                      |
| ac                    | 120                   | 250            | 5                 | 0.1373                           | 3.4630                      |
| bc                    | 30                    | 350            | 5                 | 0.0968                           | 21.846                      |
| abc                   | 120                   | 350            | 5                 | 0.1106                           | 20.004                      |

#### 4.4.1.2 Effects of Factor on The Extracted Amount

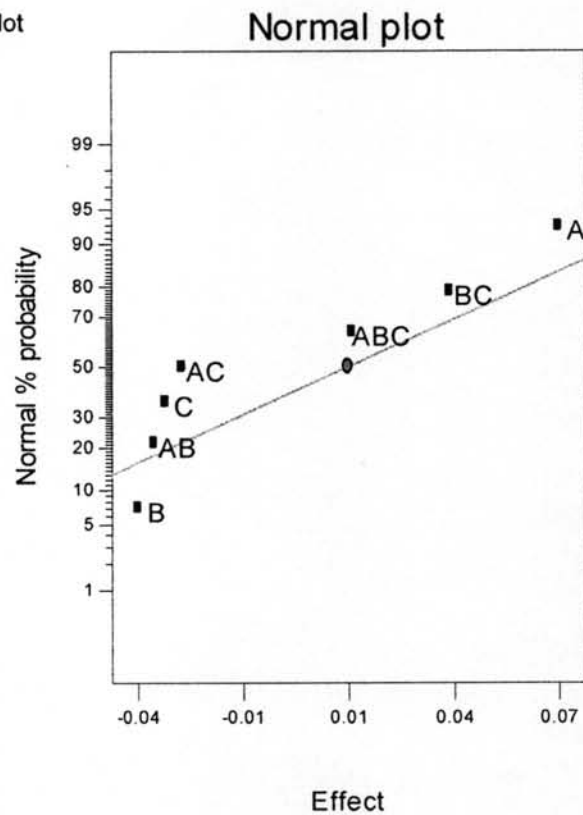
A normal probability plot was used as a method of analysis, which provided a simple way to determine the factor effects to the observed response, extracted amount, as shown in Figure 4.9. The estimate of the effects showed that there are seven effects, which do not lie along the straight line. Thus, the preliminary model has to contain those seven effects that are not normally distributed. Based on the normal probability plot, the extraction time (effect A), pressure (effect B), CO<sub>2</sub> flow rate (effect C), interaction effect between extraction time and pressure (effect AB), interaction effect between extraction time and CO<sub>2</sub> flow rate (effect AC), and interaction effect between pressure and CO<sub>2</sub> flow rate (effect BC) are all the factors that could affect on the extracted amount.

The analysis of variance was used to confirm the magnitude of these effects. The analysis of variance for the extracted amount is shown in Table 4.8. It can be noted that although the seven factors could affect on the extracted amount, there was no main factor effect, which is statistically significant at the 5%

level. However, the lowest p-value of the extraction time implied that among all the factors, the extraction time had the most effect on the extracted amount.

DESIGN-EXPERT Plot  
extracted amount

A: time  
B: pressure  
C: flow rate



**Figure 4.9** Normal probability plot of all effects on the extracted amount.

**Table 4.8** Analysis of variance for the extracted amount

| Source   | Sum of Squares | DF * | Mean Square | F-Value ** | P-value *** |
|----------|----------------|------|-------------|------------|-------------|
| Model    | 0.023403       | 6    | 0.0039      | 9.74021    | 0.2405      |
| A        | 0.009398       | 1    | 0.009398    | 23.4694    | 0.1296      |
| B        | 0.003587       | 1    | 0.003587    | 8.957647   | 0.2053      |
| C        | 0.002471       | 1    | 0.002471    | 6.170748   | 0.2436      |
| AB       | 0.002911       | 1    | 0.002911    | 7.269026   | 0.2261      |
| AC       | 0.001891       | 1    | 0.001891    | 4.722559   | 0.2746      |
| BC       | 0.003144       | 1    | 0.003144    | 7.851877   | 0.2182      |
| Residual | 0.0004         | 1    | 0.0004      |            |             |
| Total    | 0.023803       | 7    |             |            |             |

\* DF = Degree of freedom.

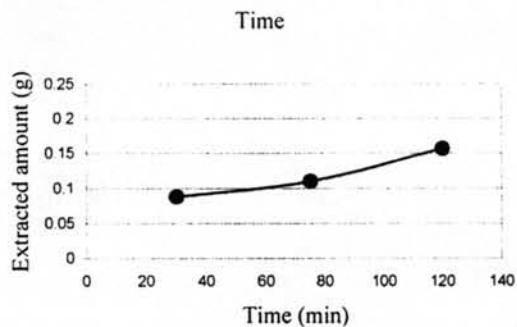
\*\* F-value = Mean square sample/mean square residue.

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

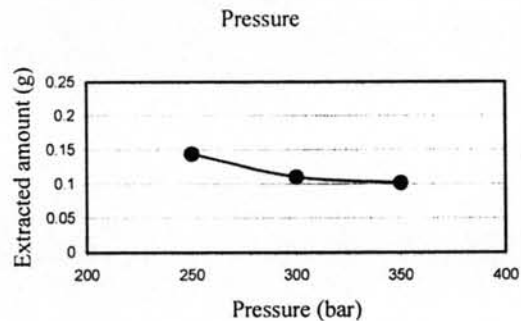
To assist the practical interpretation of the experimental design, Figure 4.10 presents plots of the effects of the extraction time, pressure, CO<sub>2</sub> flow rate, extraction time-pressure, extraction time-CO<sub>2</sub> flow rate, and pressure-CO<sub>2</sub> flow rate on the extracted amount.

It can be seen that the extraction time had a positive effect on the extracted amount because an increase in the extraction time resulted in the larger amount of the extracted fraction. On the other hand, the pressure and CO<sub>2</sub> flow rate had a fairly negative effect on the extracted amount since the amount of the extracted fraction gradually decreased with increasing these two factors. A possible explanation might be that an extremely high pressure could more easily remove the lower molecular hydrocarbon and result in loss of some of the extracted fraction. Because a long extraction time at less severe condition gave long contacting period, sludge containing oil were then extracted more continuously, and the extracted amount simultaneously increased.

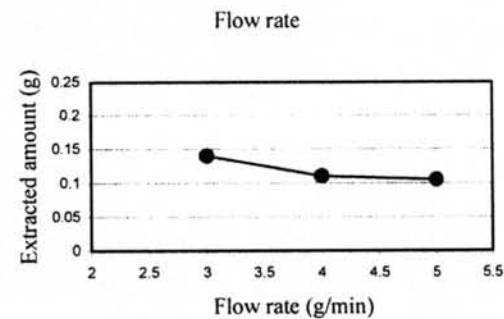
For the interaction effect, the extraction time-pressure interaction shows that the effect of extraction time was comparatively small when operating the system at high pressure level of 350 bar and became higher when lowering the system pressure to a low level of 250 bar. On the contrary, the time-CO<sub>2</sub> flow rate interaction implies that time effect was quite small when operate at high flow rate and higher at low flow rate. One of the possible reasons is that at low flow rate, long extraction time gave much more contacting period. This means that the extraction time did not give much effect at high flow rate. The pressure-CO<sub>2</sub> flow rate interaction indicates that the pressure effect was quite large when operating at low flow rate, and no pressure effect was observed when operating at high flow rate. However, all of the effects were not statistically significant at the 5% level.



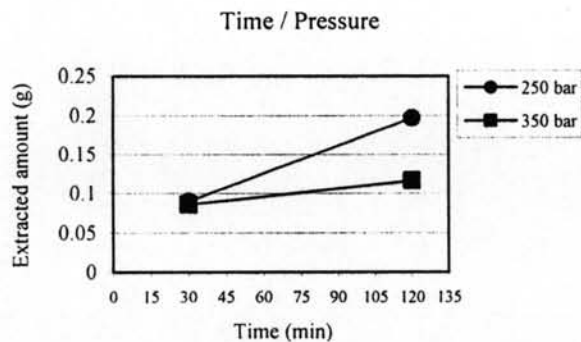
(a) Extraction time



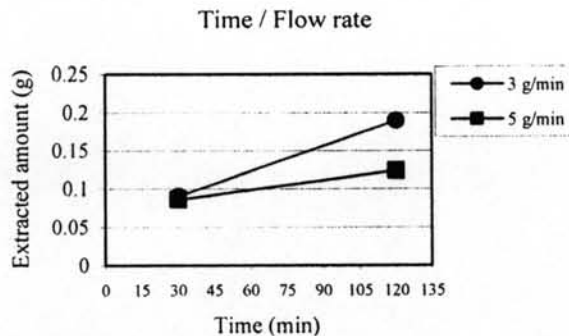
(b) Pressure



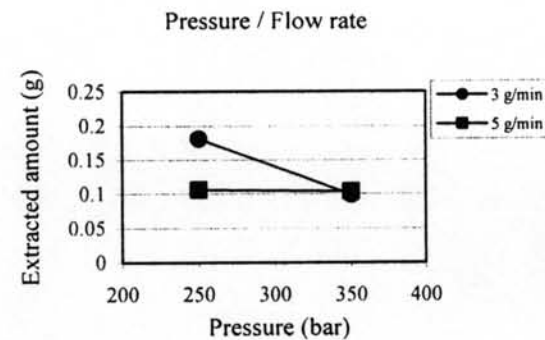
(c) CO<sub>2</sub> flow rate



(d) Time-pressure interaction



(e) Time-CO<sub>2</sub> flow rate interaction



(f) Pressure-CO<sub>2</sub> flow rate interaction

**Figure 4.10** Main effects and interaction plots for (a) extraction time, (b) pressure, (c) CO<sub>2</sub> flow rate, (d) time-pressure interaction, (e) time-CO<sub>2</sub> flow rate interaction, and (f) pressure-CO<sub>2</sub> flow rate interaction.

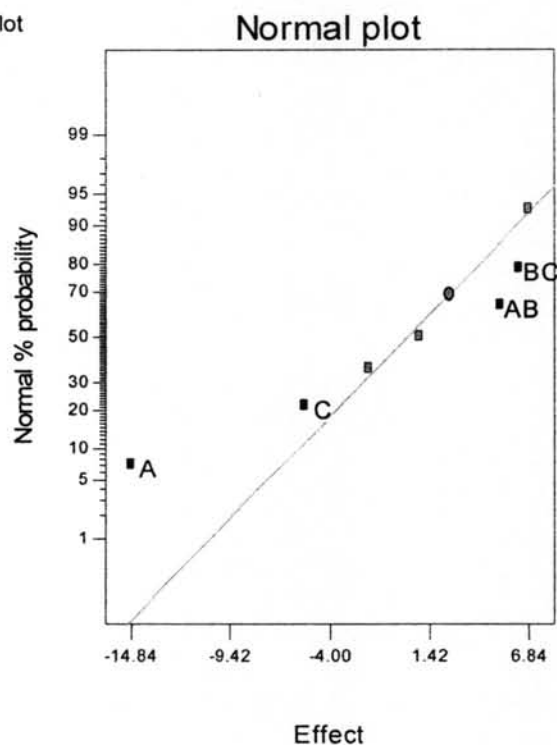
#### 4.4.1.3 Effects of Factor on The Percentage of Remaining Oil

A normal probability plot was used as a method of analysis, which provided a simple way to determine the factor effects to the observed response, percentage of remaining oil, as shown in Figure 4.11. The estimate of the effects showed that there are four effects which do not lie along the normal distributed. Thus, the preliminary model has specified to contain those four effects that are not normally distributed. Based on the normal probability plot, the extraction time (effect A), CO<sub>2</sub> flow rate (effect C), interaction effect between extraction time and pressure (effect AB), and interaction effect between pressure and CO<sub>2</sub> flow rate (effect BC) are all the factors that could affect on the percentage of remaining oil.

The analysis of variance was used to confirm the magnitude of these effects. The analysis of variance for the percentage of remaining oil is shown in Table 4.9. It can be noted that the extraction time was the main factor that have affected on the percentage of remaining oil, which is statistically significant at the 5% level.

DESIGN-EXPERT Plot  
remaining oil

A: time  
B: pressure  
C: flow rate



**Figure 4.11** Normal probability plot of all effects on the percentage of remaining oil.

**Table 4.9** Analysis of variance for the percentage of remaining oil

| Source             | Sum of Squares | DF* | Mean Square | F-Value** | P-value*** |
|--------------------|----------------|-----|-------------|-----------|------------|
| Model              | 632.8567       | 4   | 158.2142    | 4.640828  | 0.1189     |
| Time               | 440.2583       | 1   | 440.2583    | 12.91391  | 0.0369     |
| Flow rate          | 57.62548       | 1   | 57.62548    | 1.690303  | 0.2844     |
| Time/Pressure      | 55.49838       | 1   | 55.49838    | 1.62791   | 0.2918     |
| Pressure/Flow rate | 79.47453       | 1   | 79.47453    | 2.331192  | 0.2242     |
| Residual           | 102.2754       | 3   | 34.0918     |           |            |
| Total              | 735.1321       | 7   |             |           |            |

\* DF = Degree of freedom.

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

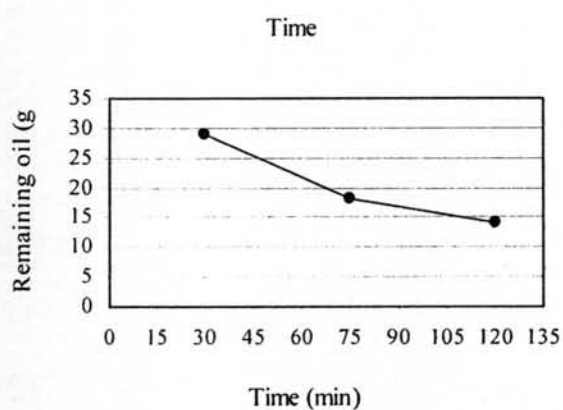
\*\*\* P- value = the smallest level of significance that would lead to rejection of the null hypothesis.

To assist the practical interpretation of the experimental design, Figure 4.12 presents plots of the effects of extraction time, CO<sub>2</sub> flow rate, extraction time-pressure, and pressure-CO<sub>2</sub> flow rate on the percentage of oil remaining.

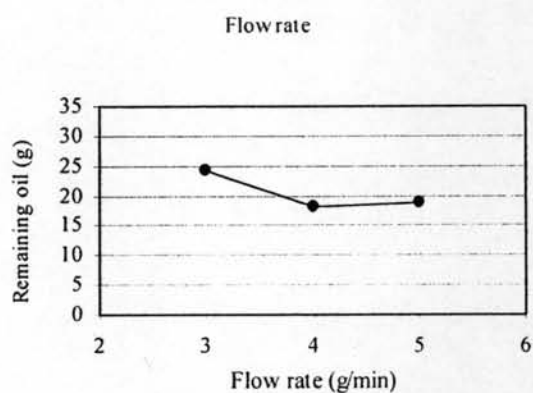
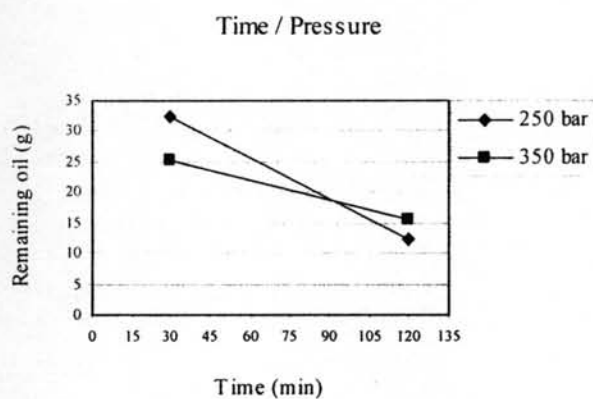
Notice that there was only one main effect that is statistically significant at the 5% level, the extraction time with p-value < 0.05, which had a negative effect on the percentage of remaining oil because an increase in the extraction time resulted in the significant decrease of the percentage of remaining oil. Similar to an extraction time, CO<sub>2</sub> flow rate also had a negative effect, but not statistically significant. Another point that can be observed in this effect was that is high CO<sub>2</sub> flow rate can contribute to replace the previously entering solvent with new solvent in a reactor all the time. Then, the oil remaining in sludge apparently increased.

For the extraction time-pressure interaction, it was found that the effect of the extraction time was comparatively large when operating the system

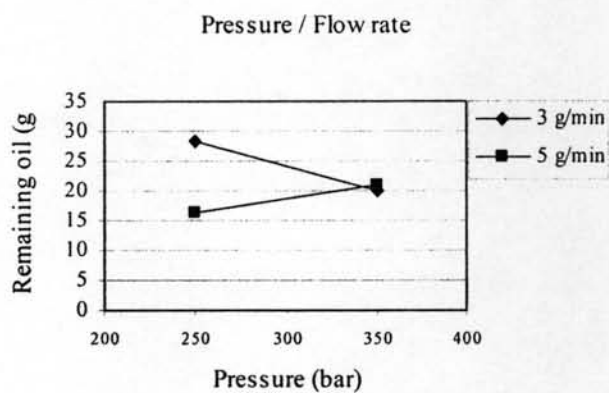
at low pressure level of 250 bar, with the best results obtained from long extraction time and low level of pressure. The pressure-CO<sub>2</sub> flow rate interaction indicates that at low level of pressure, a high CO<sub>2</sub> flow rate of 5 g/min resulted in decreased the percentage of oil. This would allow the expansion of flow rate used and reduction of pressure for a long period of extraction time for further experiments.



(a) Extraction time

(b) CO<sub>2</sub> flow rate

(d) Time-pressure interaction

(e) Pressure-CO<sub>2</sub> flow rate interaction

**Figure 4.12** Main effects and interaction on remaining oil (a) Extraction time, (b) Pressure, (c) CO<sub>2</sub> flow rate, (d) Time-pressure interaction, (e) Time-CO<sub>2</sub> flow rate interaction, and (f) Pressure-CO<sub>2</sub> flow rate interaction.



#### 4.4.1.4 Supercritical Fluid Carbon Dioxide Extraction with The Optimum Condition

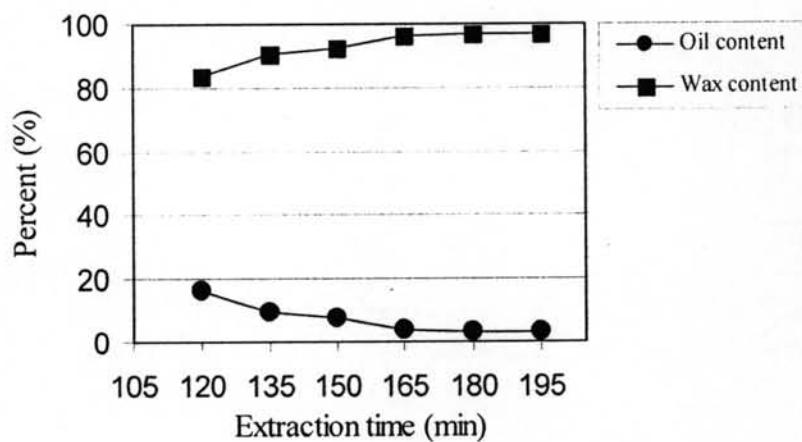
According to the factorial design, extraction time was found to be the main factor that gave a significant effect on the extracted amount of oil. When operating at high level of flow rate and low level of pressure, a long extraction time could lower percentage of oil remaining in a wax after extraction (remaining fraction). The experimental was then operated at the pressure of 250 bar, and CO<sub>2</sub> flow rate of 5 g/min for different extraction times. The data on the oil and wax content of extracted and remaining fraction obtained from different extraction times are shown in Table 4.10, and the chromatogram of a remaining and extracted fraction are graphically shown in Figures 4.13, and 4.14, the yield, amount of wax, and purity of the remaining wax are shown in Table 4.11, respectively.

**Table 4.10** Oil and wax content in extracted and remaining fractions obtained from different extraction times

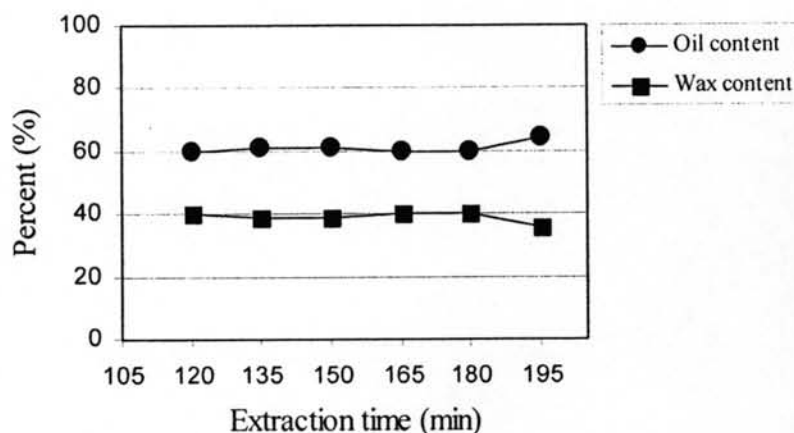
| Extraction time<br>(hr) | Extracted fraction    |                       | Remaining fraction    |                       |
|-------------------------|-----------------------|-----------------------|-----------------------|-----------------------|
|                         | Oil<br>content<br>(%) | Wax<br>content<br>(%) | Oil<br>content<br>(%) | Wax<br>content<br>(%) |
| 2.00                    | 22.03                 | 14.61                 | 10.27                 | 53.09                 |
| 2.15                    | 23.29                 | 14.94                 | 5.83                  | 55.89                 |
| 2.30                    | 24.52                 | 15.70                 | 4.68                  | 55.10                 |
| 2.45                    | 24.78                 | 16.44                 | 2.27                  | 56.50                 |
| 3.00                    | 26.11                 | 17.34                 | 1.94                  | 54.61                 |
| 3.15                    | 29.37                 | 16.27                 | 1.68                  | 52.68                 |

**Table 4.11** The yield, amount of wax ,and purity of the desired product (precipitate) obtained from different extraction times

| Extraction time<br>(hr) | Yield<br>(remaining wax) |       | Amount of wax |       | Purity of wax<br>(%) |
|-------------------------|--------------------------|-------|---------------|-------|----------------------|
|                         | Weight (g)               | %     | Weight (g)    | %     |                      |
| 2.00                    | 0.2264                   | 63.36 | 0.1897        | 53.09 | 83.79                |
| 2.15                    | 0.2121                   | 61.72 | 0.1975        | 55.89 | 90.55                |
| 2.30                    | 0.2094                   | 59.78 | 0.1930        | 55.10 | 92.17                |
| 2.45                    | 0.2016                   | 58.77 | 0.1938        | 56.50 | 96.14                |
| 3.00                    | 0.1980                   | 56.55 | 0.1912        | 54.61 | 96.57                |
| 3.15                    | 0.1914                   | 54.36 | 0.1855        | 52.68 | 96.91                |

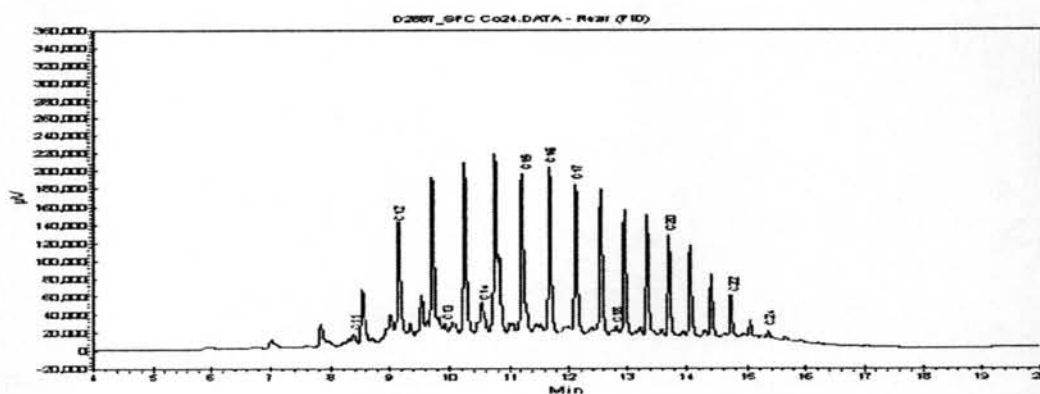


**Figure 4.13** Percentage of oil and wax in a remaining fraction obtained from supercritical fluid CO<sub>2</sub> extraction with different extraction time.

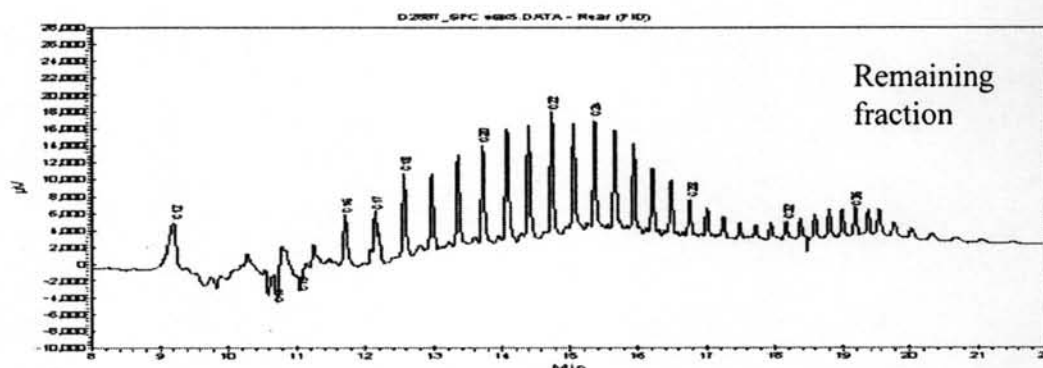


**Figure 4.14** Percentage of oil and wax in an extracted fraction obtained from supercritical fluid CO<sub>2</sub> extraction with different extraction time.

The results indicate that the amount of oil content in a remaining fraction gradually decreased with increasing extraction time, after reaching a certain period of 165 min, the amount of remained oil was quite constant. Due to the limited amount of oil contained in a sludge wax, more extraction time did not give a significant change to an oil content. Therefore, only a slight difference in the value of oil content was observed at comparatively high extraction time. The results obviously demonstrated that wax could be more purified when increasing the extraction time. The GC chromatograms of the extracted fraction and the remaining fraction are shown in Figure 4.15.



(a) The extracted fraction after supercritical fluid carbon dioxide extraction



(b) Wax in remaining fraction after supercritical fluid carbon dioxide extraction

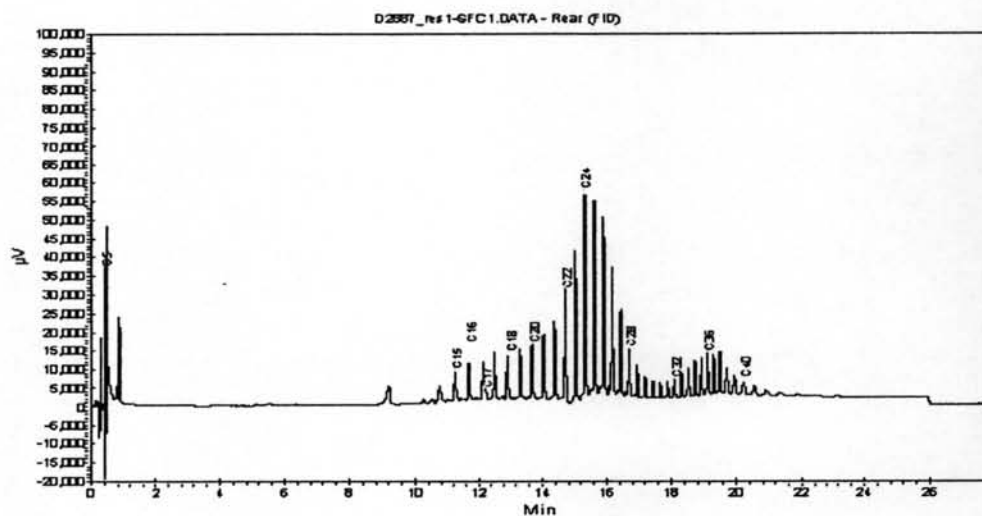
**Figure 4.15** Chromatograms of (a) the extracted fraction, and (b) wax after supercritical fluid carbon dioxide extraction.

#### 4.5 Wax Purification by Supercritical Fluid Carbon Dioxide Extraction of The Wax-Methyl ethyl ketone Solution.

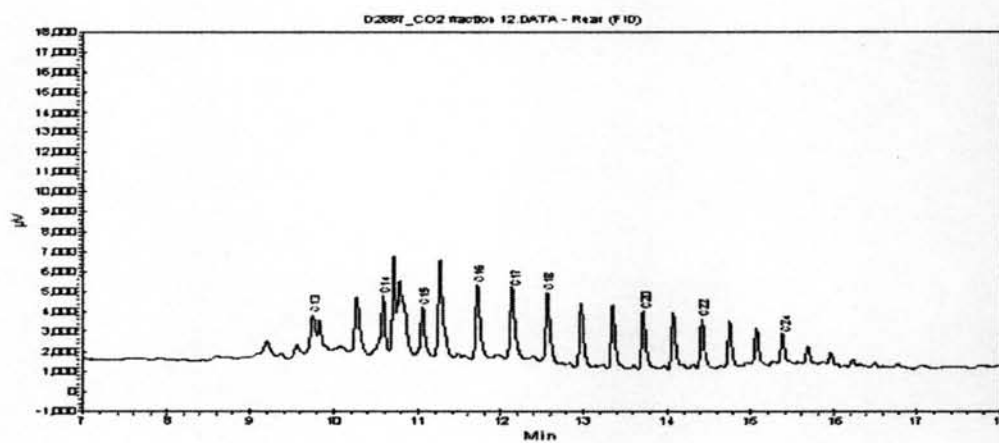
After dissolution of wax in methyl ethyl ketone by heating, the residue was separated out and analyzed by SimDist-GC. The filtrate was extracted by supercritical fluid carbon dioxide. Two fractions were obtained, i.e. the first fraction collected during 25-30 min, and second fraction collected after 30 min. The analysis of each fraction is shown in Table 4.12 (Raw data on oil and wax content are also shown in Appendix B, and Table B4). And, the chromatograms of a residue and both extracted fractions are shown in Figure 4.16.

**Table 4.12** The oil and wax content obtained from supercritical fluid carbon dioxide extraction of the wax-methyl ethyl ketone solution

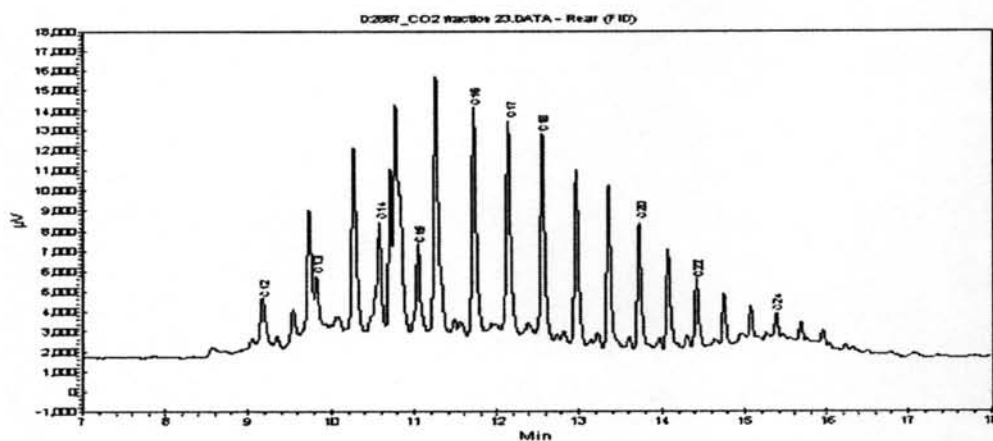
| Solvent | Residue before extraction |                 |                 | 1 <sup>st</sup> Fraction during 25-30 min |                 |                 | 2 <sup>nd</sup> Fraction after 30 min |                 |                 |
|---------|---------------------------|-----------------|-----------------|---|-----------------|-----------------|---------------------------------------|-----------------|-----------------|
|         | Appearance                | Oil content (%) | Wax content (%) | Appearance                                | Oil content (%) | Wax content (%) | Appearance                            | Oil content (%) | Wax content (%) |
| MEK     | Dark brown                | 2.25            | 10.86           | Clear brown solution                      | 67.35           | 8.63            | Dark yellow colloid                   | 10.01           | 0.90            |



(a) Chromatogram of a residue obtained from supercritical fluid carbon dioxide extraction of the wax-methyl ethyl ketone solution.



(b) Chromatogram of first fraction obtained from supercritical fluid carbon dioxide extraction of the wax-methyl ethyl ketone solution.



(c) Chromatogram of a second fraction obtained from supercritical fluid carbon dioxide extraction of the wax-methyl ethyl ketone solution.

**Figure 4.16** Chromatograms of the (a) residue, (b) first fraction (clear brown solution), and (c) second fraction (dark yellow colloid) obtained from supercritical fluid carbon dioxide extraction of the wax-methyl ethyl ketone solution.

The results show that the 1<sup>st</sup> fraction contained the majority of all products with mostly oil fraction. Moreover, both of 1<sup>st</sup> and 2<sup>nd</sup> fractions were liquid phase. It can be noted that a supercritical fluid carbon dioxide extraction of the wax-methyl ethyl ketone solution was not quite suitable to be used for purification of wax because an extracted fraction was liquid containing mainly oil composition, and there was no wax separated as the desired product.