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APPENDICES

Appendix A Calculation

1. Calculate the amount of solvent used in supercritical state

In order to calculate the amount of solvent required at supercritical temperature and supercritical pressure, the equation of state was then used. Redlich Kwong's equation was selected. A critical temperature of each solvent was fixed, and moles of solvent were iterated to reach a supercritical pressure.

Redlich Kwong's equation

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m \sqrt{T}(V_m + b)}$$

Where

V_m = molar volume (cm^3/ mol)

$$a = \frac{0.42748 R^2 T_c^{2.5}}{P_c}$$

$$b = \frac{0.08664 R T_c}{P_c}$$

2. Calculate the specific amount of wax used with supercritical toluene

The amount of solvent used with supercritical toluene was calculated by using a Redlich Kwong's equation.

Properties of toluene

Critical temperature (T_c) = 320 °C

Critical pressure (P_c) = 41 atm

Molecular weight (Mw) = 92.14 g/mol

Density (ρ) = 0.867 g/cm^3

Calculate the constant, a

$$a = \frac{0.42748(82.058 cm^3 atm/molK)^2 (593K)^{2.5}}{41 atm}$$

$$= 601188317.8\ (cm^6)(atm)(K^{0.5})/mol^2$$

Calculate the constant, b

$$b = \frac{0.08664(82.058 cm^3 atm/mol\,K)(593K)}{41 atm}$$

$$= 102.828\ cm^3/mol$$

Substitute a and b into the Redlich Kwong's equation.

Calculate the pressure, using 0.01mol of solvent pack in 5.5 cm^3 reactor at critical temperature.

$$P = \frac{\left(82.058(cm^3 atm/mol\,K)(593K)\right)}{\left(\frac{5.5cm^3}{0.01mol} - 102.828 cm^3/mol\right)} - \frac{\left(601188317.8(cm^6)(atm)(K)^{0.5}/(mol)^2\right)}{\left(\sqrt{593}K^{0.5}\left(\frac{5.5cm^3}{0.01mol}\right)\left(\left(\frac{5.5cm^3}{0.01mol}\right) + 102.828 cm^3/mol\right)\right.}$$

= 40.06 atm

By using toluene 0.01 mol at critical temperature, the pressure could not reach the critical state. So, the number of mole was varied to find the pressure, which was above the critical pressure of toluene.

Table A1 Pressure in a reactor by using different moles of toluene

Moles of toluene (mol)	0.01	0.02	0.03	0.04
Pressure (atm)	40.060	45.021	133.969	655.790

The specific amount of wax was then calculated from the amount of solvent used to reach the supercritical state (solvent to wax ratio = 50:1), as shown in a table below.

Table A2 Amount of the original wax used with difference moles of toluene

Moles of toluene (mol)	Amount of toluene (grams)	Amount of wax (grams)	Pressure (atm)
0.01	0.9214	0.0184	40.060
0.02	1.8428	0.0369	45.021
0.03	2.7642	0.0553	133.969
0.04	3.6856	0.0737	655.790

So, the amount of toluene of 0.03 mol was used with original sludge wax of 0.0553 g to reach the supercritical state at 320 °C and 133.969 atm.

3. Calculate the specific amount of wax used with supercritical methyl ethyl ketone

The amount of solvent used with supercritical methyl ethyl ketone was calculated by using the same procedure as the case of toluene, with changes in solvent properties

Properties of methyl ethyl ketone

Critical temperature (T_c) = 262.7 °C

Critical pressure (P_c) = 41.6 atm

Molecular weight (Mw) = 72.11 g/mol

Density (ρ) = 0.805 g/cm^3

With the same procedure, the constants in Redlich Kwong's equation for methyl ethyl ketone are;

a = 460231457.2

b = 91.603

Substitute a and b into the Redlich Kwong's equation and calculate the pressure, using 0.01 mol of methyl ethyl ketone pack in 5.5 cm^3 reactor at critical temperature. The pressure is 39.612 atm

However, the pressure could not reach to the critical state. So, the number of mole was varied to find the pressure, which was above the critical pressure of methyl ethyl ketone.

Table A3 Pressure in a reactor by using different moles of methyl ethyl ketone

Moles of MEK (mol)	0.01	0.02	0.03	0.04
Pressure (atm)	39.612	42.643	85.153	327.254

The specific amount of wax is then calculated from the amount of solvent used to reach the supercritical state (solvent to wax ratio = 50:1), as shown in a table below.

Table A4 Amount of the original wax used with different moles of methyl ethyl ketone

Moles of MEK (mol)	Amount of MEK (grams)	Amount of wax (grams)	Pressure (atm)
0.01	0.7211	0.0144	39.612
0.02	1.4422	0.0288	42.643
0.03	2.1633	0.0432	85.153
0.04	2.8844	0.0577	327.254

So, the amount of methyl ethyl ketone of 0.03 mol was used with original sludge wax of 0.0432 g to reach the supercritical state at 262.7 °C and 85.153 atm.

Appendix B Hydrocarbon Composition of The Original Sludge Wax

Table B1 Hydrocarbon compositions of the original sludge wax

Index	Name	Height	Area	Area %
		[μV]	[μV.Min]	[%]
3	C5	115862.3	7632.0	5.886
5	C11	23645.9	1947.4	1.502
8	C12	52058.9	4224.2	3.258
13	C13	14514.9	1077.2	0.831
16	C14	20963.9	2384.0	5.057
19	C15	80258.9	6557.7	4.805
20	C16	86169.9	6231.2	4.486
21	C17	80372.9	5816.8	0.956
23	C18	12780.9	1240.3	3.863
28	C20	72184.9	5008.9	2.944
32	C22	59714.9	3817.4	2.944
34	C24	43709.9	3586.3	2.766
39	C28	13097.9	1364.1	1.052
45	C36	9247.9	1040.6	0.802
Total		1666840.1	129670.5	100.000

Appendix C The oil and wax content in each fraction from different processes

Table C1 The oil and wax content in residue, precipitate, and filtrate from different solvent solution (from crystallization by using solvent)

Solvent	Residue		Precipitate (crystallized wax)		Filtrate	
	Oil content (%)	Wax content (%)	Oil content (%)	Wax content (%)	Oil content (%)	Wax content (%)
MEK	22.86	77.14	32.06	67.94	100	0
Toluene	35.70	64.30	54.21	45.79	68.02	31.98
Mixed solvent	25.55	74.45	9.27	90.73	92.12	7.88

Table C2 The oil and wax content in residue, precipitate, and filtrate from different MEK to toluene ratio

MEK concentration in solvent (vol%)	Residue		Precipitate (crystallized wax)		Filtrate	
	Oil content (%)	Wax content (%)	Oil content (%)	Wax content (%)	Oil content (%)	Wax content (%)
0	35.70	64.30	54.21	45.79	68.02	31.98
20	41.83	58.17	49.59	50.41	79.94	20.06
40	33.51	66.49	17.07	82.93	92.33	7.67
60	38.03	61.97	18.10	81.90	90.46	9.54
80	33.75	66.25	29.94	70.06	98.12	1.88
100	22.86	77.14	32.06	67.94	100	0

Table C3 The oil and wax content in residue, precipitate, and filtrate from different solvent to wax ratio

Solvent to wax ratio	Residue		Precipitate (crystallized wax)		Filtrate	
	Oil content (%)	Wax content (%)	Oil content (%)	Wax content (%)	Oil content (%)	Wax content (%)
30:1	47.71	52.29	12.72	87.28	48.59	51.41
40:1	30.85	69.15	12.60	87.40	51.61	48.39
50:1	26.50	93.50	4.79	95.21	57.54	42.46
60:1	24.12	75.88	4.45	95.55	60.74	39.26
70:1	35.01	64.99	2.47	97.53	58.69	41.31
80:1	23.16	76.84	1.15	98.85	62.78	37.22

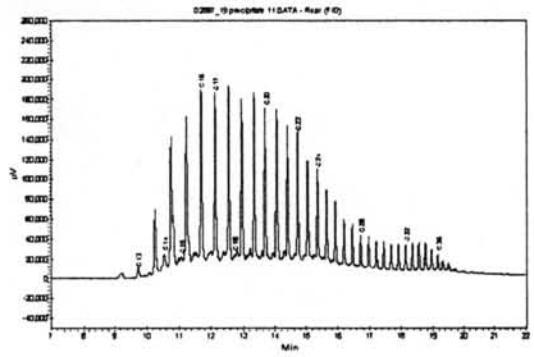
Table C4 The oil and wax content in wax-solvent mixtures (supercritical solution), precipitate, and filtrate from different solvent (from crystallization by using supercritical solvents

Solvent	Supercritical solution		precipitate (crystallized wax)		Filtrate	
	Oil content (%)	Wax content (%)	Oil content (%)	Wax content (%)	Oil content (%)	Wax content (%)
MEK	61.80	38.20	100	0	83.14	16.86
Toluene	48.79	51.21	100	0	64.21	35.79
Mixed solvent	82.45	17.55	55.01	44.99	55.23	44.77

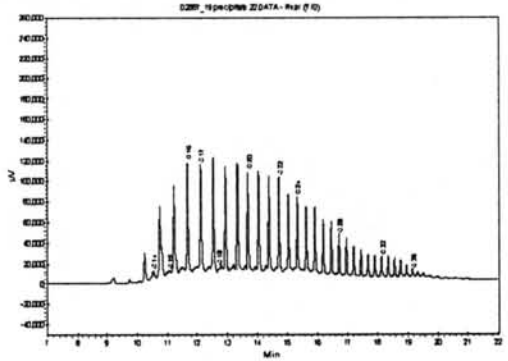
Table C5 The oil and wax contents in residue and a fraction from supercritical fluid carbon dioxide extraction of the wax-methyl ethyl ketone solution

Solvent	Residue		1st Fraction (25-30 min)		2nd Fraction after 30 min	
	Oil content (%)	Wax content (%)	Oil content (%)	Wax content (%)	Oil content (%)	Wax content (%)
MEK	17.15	82.85	88.64	11.36	91.76	8.24

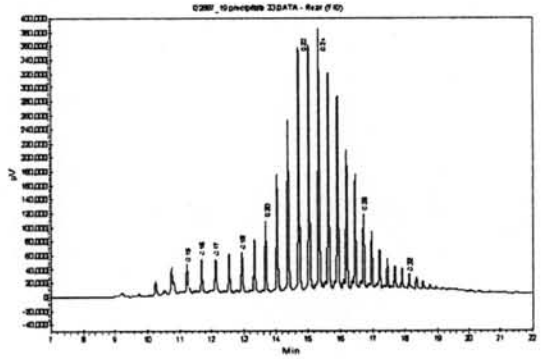
Appendix D Chromatogram of a purified wax obtain from difference process



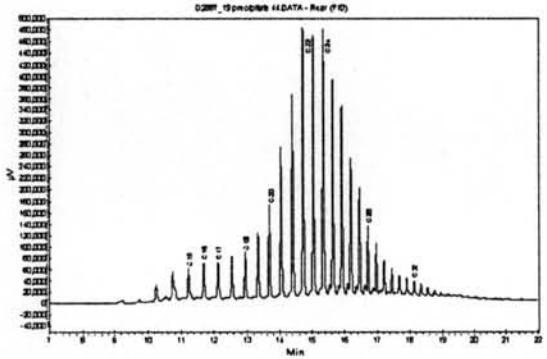
(a) 0 %vol MEK



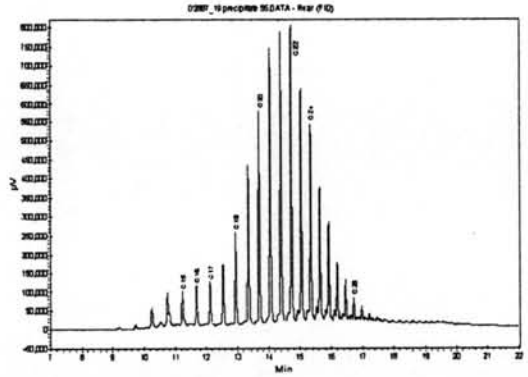
(b) 20 %vol MEK



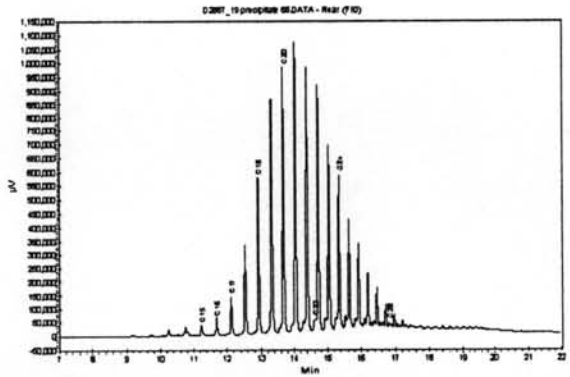
(c) 40 %vol MEK



(d) 60 %vol MEK

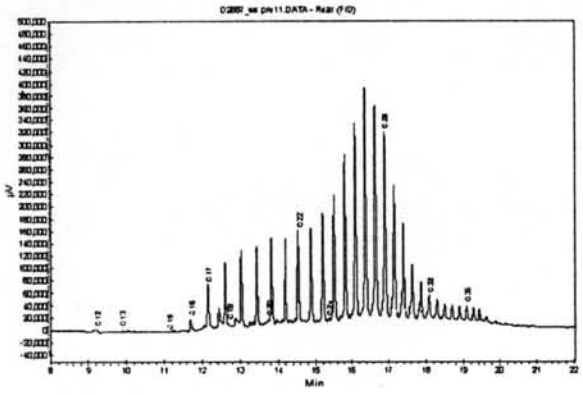


(e) 80 %vol MEK

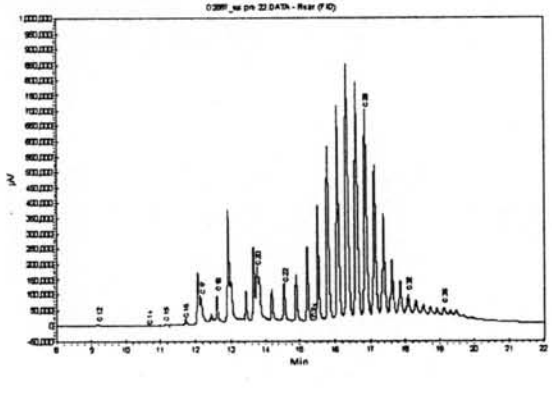


(f) 100 %vol MEK

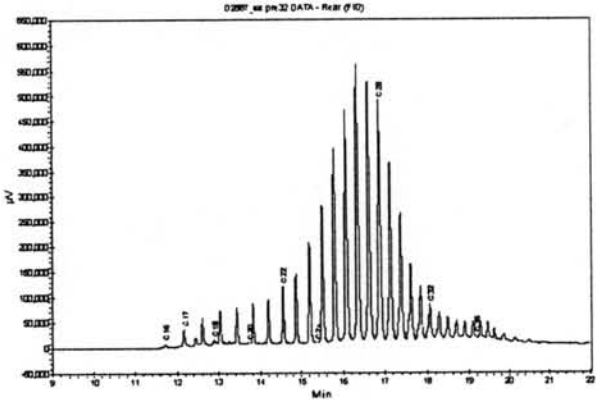
Figure D1 Chromatograms of a precipitate (purified wax) obtain from difference MEK to toluene ratio: (a) 0 %vol MEK, (b) 20 %vol MEK, (c) 40 %vol MEK, (d) 60 %vol MEK, (e) 80 %vol MEK, and (f) 100 %vol MEK.



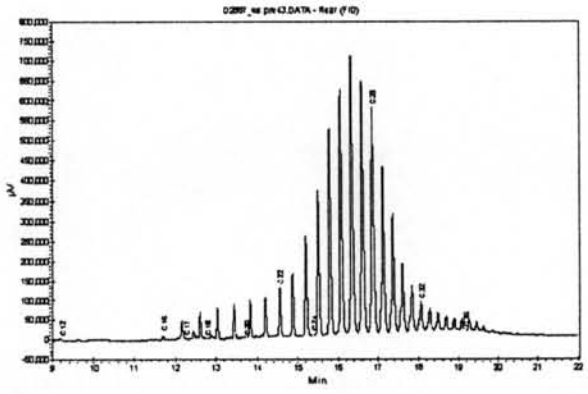
(a) 30:1 %vol/wt



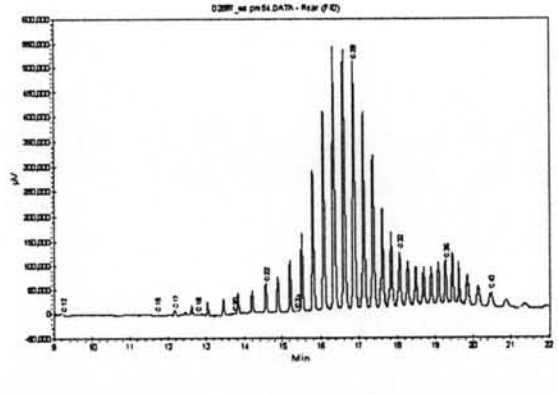
(b) 40:1 %vol/wt



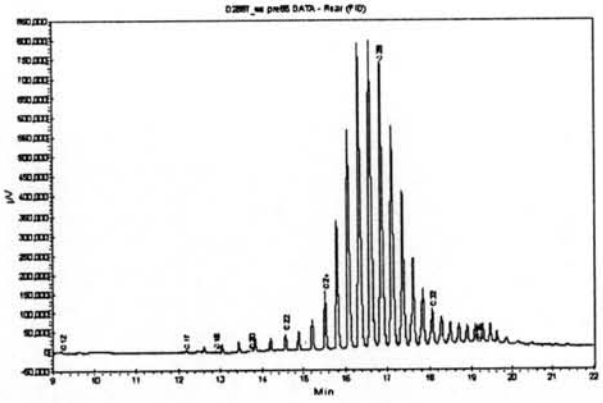
(c) 50:1 %vol/wt



(d) 60:1 %vol/wt

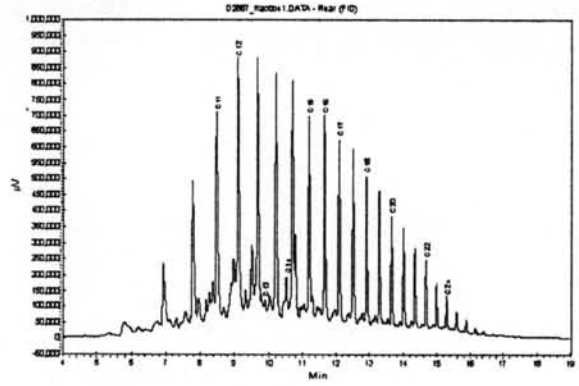


(e) 70:1 %vol/wt

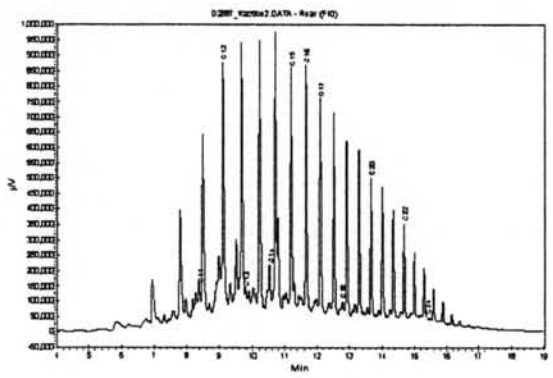


(f) 80:1 %vol/wt

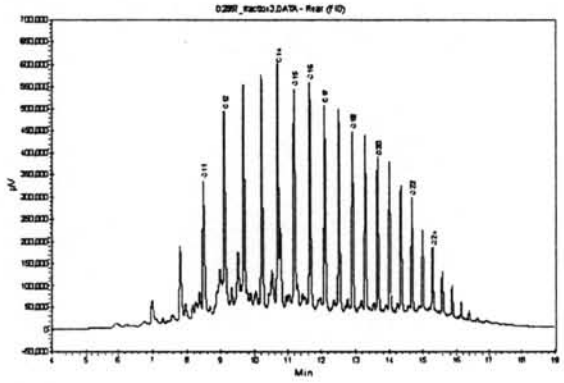
Figure D2 Chromatograms of a precipitate (purified wax) obtain from difference solvent to wax ratio: (a) 30:1 %vol/wt, (b) 40:1 %vol/wt MEK, (c) 50:1 %vol/wt, (d) 60:1 %vol/wt, (e) 70:1 %vol/wt, and (f) 80:1 %vol/wt.



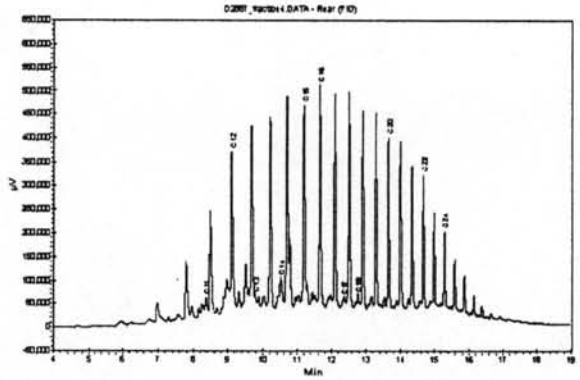
(a) 15 min



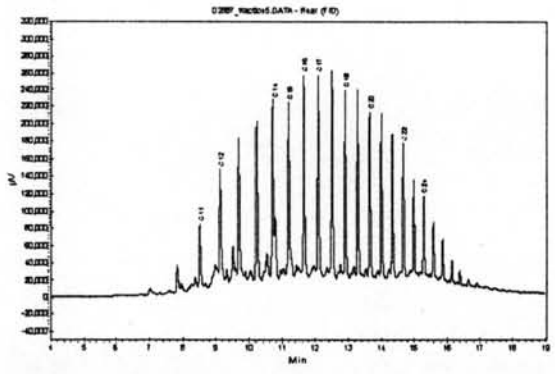
(b) 30 min



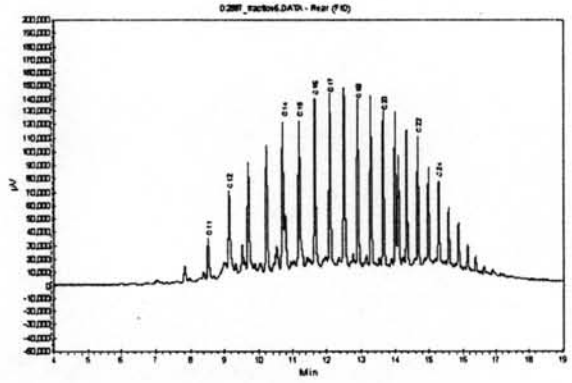
(c) 45 min



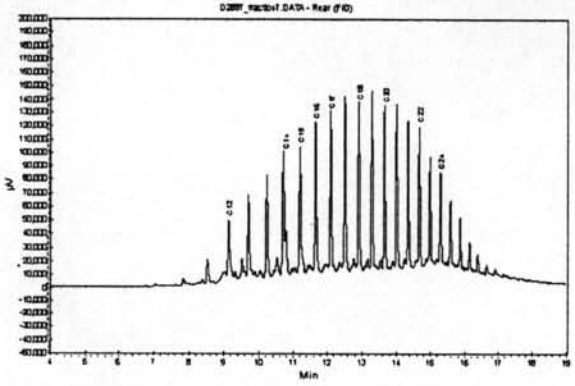
(d) 60 min



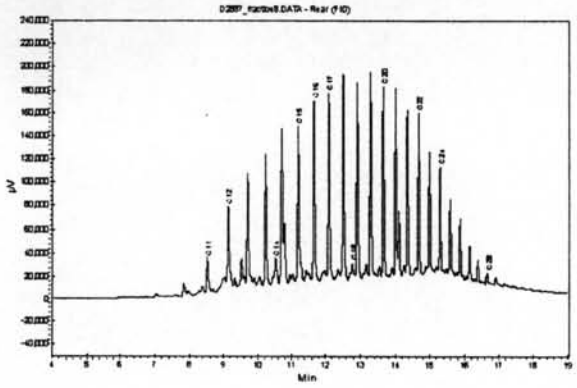
(e) 75 min



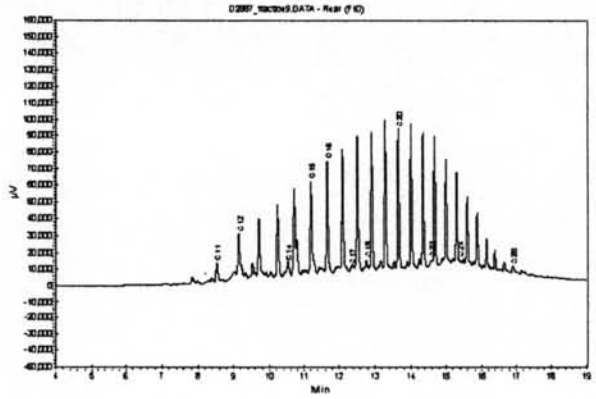
(f) 90 min



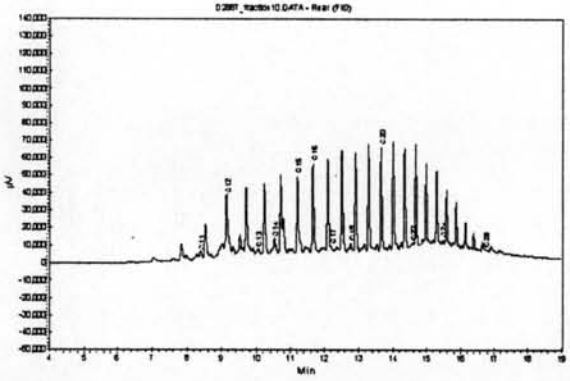
(g) 105 min



(h) 120 min

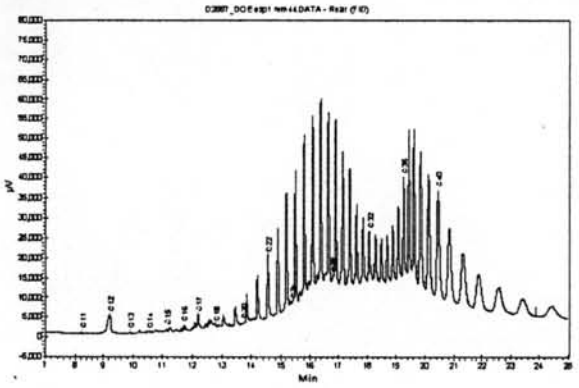


(i) 135 min

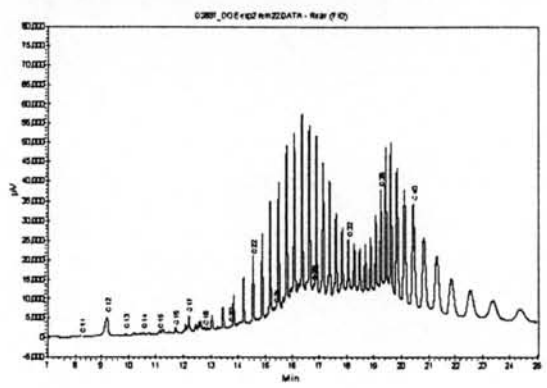


(j) 150 min

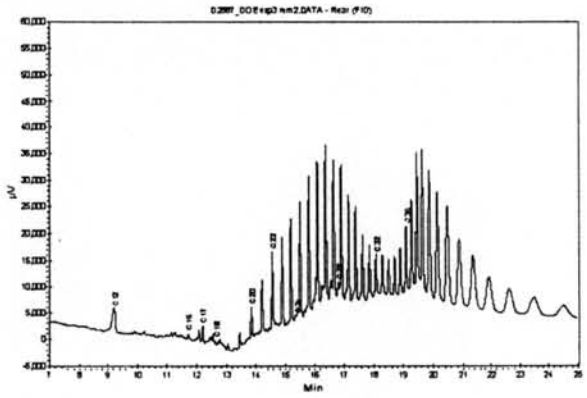
Figure D3 Chromatograms of an extracted fraction obtain from difference extraction time in a supercritical CO_2 extraction: (a) 15 min, (b) 30 min, (c) 45 min, (d) 60 min, (e) 75 min, (f) 90 min, (g) 105 min, (h) 120 min, (i) 135 min, and (j) 150 min.



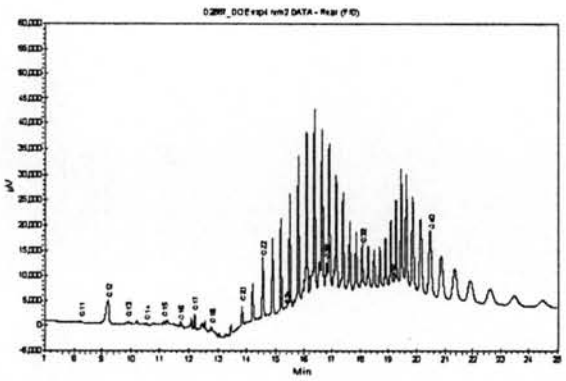
(a) 120 min



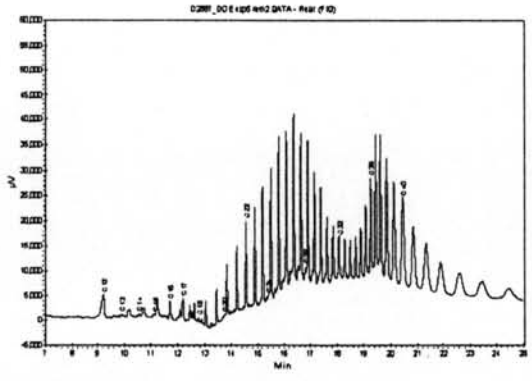
(b) 135 min



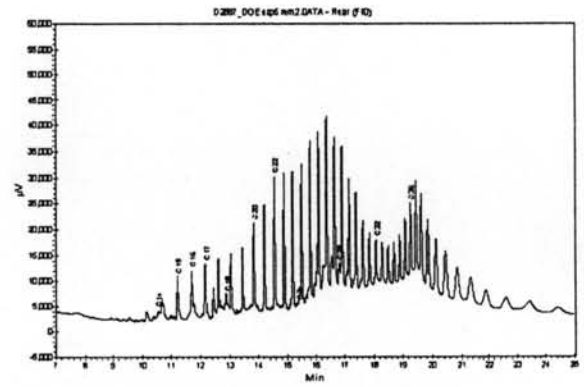
(c) 150 min



(d) 165 min



(e) 180 min



(f) 195 min

Figure D4 Chromatograms of a remaining fraction (purified wax) obtain from supercritical CO_2 extraction with the optimum condition from difference extraction time: (a) 120 min, (b) 135 min, (c) 150 min, (d) 165 min, (e) 180 min, and (f) 195 min.

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Presentations:

1. S. Rangsansvasti, C Saiwan, T. Sreethawong, and E. Behar (2006, December 3-5) Purification of Phet Wax: using Crystallization and Supercritical Carbon Dioxide Extraction process Oral presented at the 13th Regional Symposium on Chemical Engineering 2006, Nanyang Technological University, Singapore.