

Extraction of Crude Palm Oil Using Supercritical CO₂

Masturah Markom, Harcharan Singh
Masitah Hasan

ABSTRACT

The effects of changing the operating pressure and temperature on the solvating strength of supercritical carbon dioxide and the solubility of crude palm oil in the solvent were discussed. The operating temperatures and pressures investigated are 40, 50 and 60°C, and 110, 140 and 200 bars. Changes in pressure showed a stronger influence on palm oil solubility in CO₂ compared to temperature. The rate of extraction and the solubility of palm oil increased when the system pressure was increased (at constant temperature) or when the system temperature was decreased (at constant pressure). These results are comparable with the reported results of solubility of other vegetable oils such as soybean and olive oils. The change in the physical behaviour and the colour of the oil extracts and residues were also observed. It was discovered that the initial fractions of palm oil extracted were solid like while the latter fractions were semi-liquid. As the extraction progressed, the orange colour of the fractions became progressively more intense at 200 bars. At lower pressures of 140 and 110 bars, however, the colour intensity was reduced, indicating decreasing density and solvating strength of the supercritical CO₂.

Keywords: supercritical CO₂, palm oil, solubility, extraction

ABSTRAK

Kesan perubahan tekanan dan suhu operasi ke atas kuasa pengsolvasan superkritikal karbon dioksida dan kebolehlarutan minyak sawit mentah di dalam pelarut dibincangkan. Suhu operasi yang dikaji adalah pada 40, 50 dan 60°C serta tekanan adalah pada 110, 140 dan 200 bar. Tekanan memberi kesan yang lebih ketara ke atas kebolehlarutan minyak kelapa sawit di dalam CO₂ berbanding suhu. Kadar pengekstrasian dan kebolehlarutan minyak kelapa sawit meningkat apabila tekanan bertambah (pada suhu malar) atau suhu berkurang (pada tekanan malar). Keputusan ini adalah setara dengan keputusan yang dilaporkan untuk kebolehlarutan minyak sayuran lain seperti minyak kacang soya dan minyak zaitun. Perubahan ke atas sifat fizikal dan warna ekstrak dan baki minyak juga diperhatikan. Didapati hasil ekstraksi awal minyak sawit adalah berbentuk pepejal manakala hasil ekstraksi akhir berbentuk separa cecair. Semakin pengekstrasian bertambah, keamatan warna jingga ekstrak bertambah pada 200 bar. Namun begitu, keamatan warna berkurangan pada 140 dan 110 bar, menunjukkan penurunan ketumpatan dan kuasa pengsolvasan bagi superkritikal CO₂.

Kata Kunci: superkritikal CO₂, minyak sawit, kebolehlarutan, pengekstrasian

INTRODUCTION

Separation and fractionation of compounds used in food preparations, such as edible oils using supercritical fluids has become a subject of growing interest. The demand for high quality consumable products has led researchers to use improved and residual free extraction techniques while at the same time reducing thermal degradation of the product. The strength of a separation process also depends on achieving high solubility and/or selectivity for the desired components present in the matrix. This is usually difficult to achieve for vegetable oils because of their low volatility and narrow differences between molecular weights and component volatilities.

One of the major edible oils consumed worldwide is the palm oil. Crude palm oil is a semi solid material at a room temperature and has a boiling point of 36°C (Gunstone 1987). It is composed of more than 90% triglycerides, 2 to 7% diglycerides, less than 1% monoglycerides, 3 – 5% free fatty acids, and about 1% minor components (Choo et al. 1996). Nutritional qualities of palm oil can be further enhanced by the presence of important minor components such as the carotenes and Vitamin E. Unfortunately, these valuable components are destroyed or lost during the bleaching and refining processes.

Supercritical fluid extraction (SFE) of palm oil, using carbon dioxide as solvent, offers potential advantages for processing under milder conditions. Furthermore, carbon dioxide is non-toxic, readily available at low costs, and has low critical temperature (31.1°C) and pressure (73.8 bar). The solvent density can be varied continuously from gas-like to liquid-like densities by simply changing either the temperature or pressure. Other advantages of using SFE are easy separation of the extracted solute from the supercritical fluid by simple expansion, low operating temperature, which prevents degradation of valuable components, improved product yield by increasing solubility and/or selectivity and easy removal and recovery of the solvent. This study investigated the temperature and pressure effects on the physical state and colour of various fractions extracted from crude palm oil using supercritical CO₂. The extract yield and composition profiles as a function of temperature, pressure and CO₂ consumed were also studied.

MATERIALS AND METHODS

Crude palm oil was obtained from Jomalina Sdn. Bhd. (Banting, Malaysia). The solvent used for extraction was liquid carbon dioxide of 99.9% purity and was supplied by Sit Tatt Sdn. Bhd. (Petaling Jaya, Malaysia).

The extraction of palm oil was carried out in a simple apparatus shown in Figure 1. In a typical run, approximately 5 to 7 g of crude palm oil sample was placed in a 50-mL high-pressure liquid extraction vessel immersed in a water bath which temperature was controlled by a heater (Techne, model TE-8D) to within $\pm 0.1^\circ\text{C}$. System pressure was controlled by a back pressure regulator (Jasco, model 880-81) to within ± 0.1 bar. The sample was equilibrated at system temperature and pressure for half an hour before proceeding with a run.

A constant liquid CO₂ flow rate of 2.5 ml/min was delivered by a HPLC pump (Jasco, model PU-980). At this flow rate, saturation condition was

assumed because the palm oil solubility at 50°C was found to be similar to that obtained by Ooi et al. (1996). Expansion of CO₂ occurred at the back pressure regulator which was heated to 70°C to prevent oil precipitation. A surge vessel was used to dampen any pressure fluctuations. An in-line filter (7 mm) was installed to prevent any physical carry over of the palm oil out of the extraction vessel. The volume of CO₂ used was determined by a wet gas meter (Alexander Wright & Co.).

For each run, the palm oil sample was fractionated into various fractions (3 to 12 fractions) and one oil residue (raffinate). The fractions were collected in a 10-mL glass vial which, was immersed in a cold trap to avoid solute losses. Each fraction weighed between 0.3 to 2.0 g which was determined using a Mettler Toledo balance (± 0.0001 g). The run was terminated when it was observed that very little palm oil was being fractionated (i.e. deposited) at the vial. Typically more than 95% of the palm oil was extracted and is termed as an exhaustive extraction. For these extraction runs, each fraction took between 3 to 20 hours to extract. At some conditions such as at 50°C and 110 bar, and 60°C and 140 bar, palm oil samples were not exhaustively extracted because of the very low solubility.

RESULTS AND DISCUSSION

This work investigated the potential of extracting and fractionating crude palm oil at temperatures of 40°, 50° and 60°C and at pressures of 110, 140 and 200 bar using carbon dioxide. The seven conditions investigated are shown in Table 1. The palm oil samples were exhaustively extracted except at the conditions of 50°C and 110 bar, and 60°C and 140 bar. The total percentage of triglycerides loss during the extraction was found to be less than 4% for all of the exhaustive extractions. At 60°C and 140 bar, the extraction was terminated at about 42% weight of oil extracted because of its time-consuming run. The long extraction time might contribute to the relatively high percentage loss (13%) because some of the palm oil

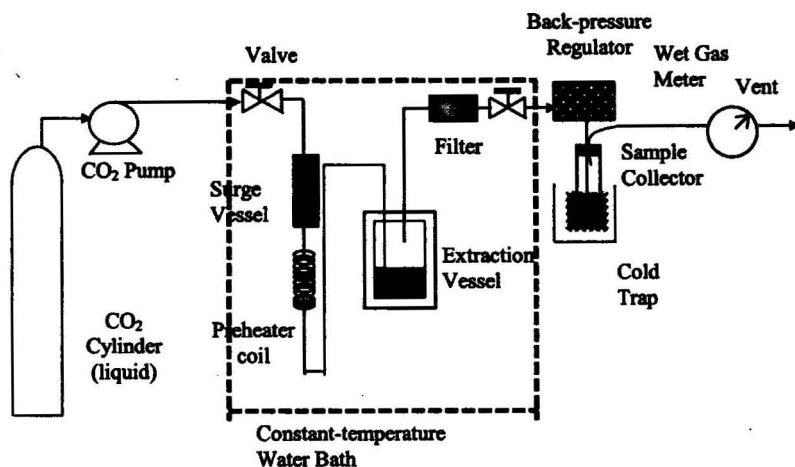


FIGURE 1. Schematic diagram of Supercritical Fluid Extraction (SFE) apparatus

TABLE 1. Extraction of palm oil using supercritical CO₂ at different conditions

P (bar)	T (°C)	Feed Sample (g)	Total Extract (g)	Raffinate (g)	Flushing (g)	% Lost
140	40	5.0220	4.9331	0.0081	0.0033	1.5
200	40	4.7539	4.7201	0.0031	0.0075	0.5
110	50	5.7681	0.1287	-	-	-
140	50	7.0744	6.7952	0.0057	0.0086	3.7
200	50	5.1489	4.9540	0.0055	0.0166	3.4
140	60	5.1509	2.2128	2.1360	0.1369	12.9
200	60	5.4944	5.3788	0.0065	0.0110	1.8

^a The amount of palm oil precipitated in tubing and was flushed with a large amount of CO₂.

- No readings were recorded.

components might have vaporized with the CO₂ during recovery, which could be observed by the oily yellow substance outside the collection vial and the tubing connecting the back-pressure regulator to the vial. The existence of this substance was more pronounced at longer extraction time.

EFFECTS OF P AND T ON THE SOLUBILITY OF PALM OIL

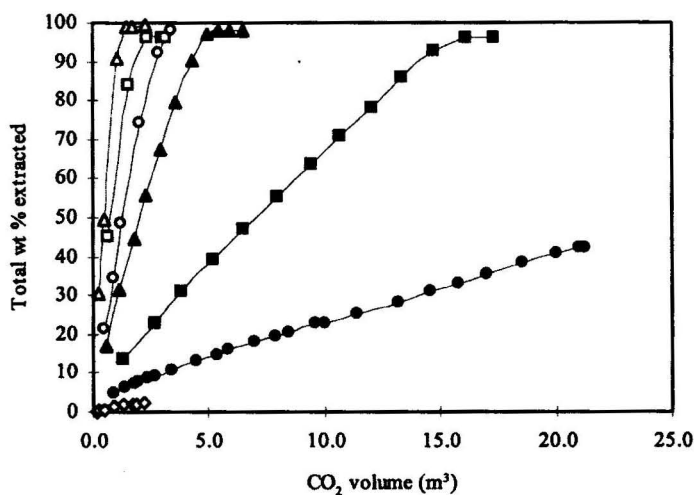
Table 2 to 4 show the amount (g) of oil extracted and visual observations of fractions extracted at 40°C, 50°C, and 60°C respectively. At each isotherm, the system pressures studied were 140 and 200 bar, except for the 50°C isotherm, where the extraction at 110 bar was also studied. At each condition, various fractions were collected. At some conditions, the quantity of fractionated palm oil collected was too small to be analysed further, thus a few fractions (or sub-fractions) were combined. It was found that CO₂ was able to extract more than 95% of crude palm oil. Since the liquid CO₂ flow rate used in this experiment was constant (at 2.5 mL/min), the CO₂ gas volume was proportional to the extraction time. The extraction of crude palm oil in terms of CO₂ volume (in m³) instead of extraction time would be used for further discussions.

The cumulative weight percentage of palm oil extracted at various conditions studied was plotted against the CO₂ volume and is shown in Figure 2. All the plots show an almost linear increase in palm oil extracted with CO₂ volume before levelling off. This behaviour is similar to the trend observed in other related studies on the oil and fat extraction using supercritical CO₂ (Chao et al. 1993; Lee et al. 1991).

In addition, it can be seen from Figure 2 that pressure has a strong effect on the rate of palm oil extraction. For example, at 50°C a quantity of 2 m³ of CO₂ extracted about 85% of palm oil at 200 bar but only about 18% and 2% at 140 and 110 bar, respectively. From Figure 2, it can be seen that an increase in temperature from 40 to 60°C at both 140 and 200 bar resulted in a decrease in the amount of palm oil extracted per cubic meter of CO₂ consumed. In addition, as temperature increased, a modest decrease in the quantity of palm oil extracted was seen at 200 bar compared to that at 140 bar.

TABLE 2. Fractionation of palm oil using supercritical CO₂ at 40°C

P (bar)	Fraction No.	Sub-fraction	Weight of oil extracted (g)	Total CO ₂ Volume (m ³)	Cumulative wt%	Physical at 25°C	Color Observed
140	1		0.8606	0.5	17.1	S	Y
	2		0.7176	1.1	31.4	S	Y
	3	a.	0.6575	1.8	44.5	S	Y
		b.	0.5727	2.3	55.9		
	4	a.	0.5729	2.9	67.3	S	Y
		b.	0.6186	3.6	79.7		
	5	a.	0.5313	4.3	90.2	SL	LY
		b.	0.3556	4.9	97.3		
		c.	0.0260	5.5	97.8		
		d.	0.0122	5.9	98.1		
		e.	0.0061	6.5	98.2		
	Raffinate		0.0081			S/L	DB
200	1		1.4432	0.3	30.4	S	O
	2		0.9184	0.5	49.7	S	O
	3		1.9442	1.0	90.6	S	O
	4	a.	0.4039	1.5	99.1	SL	DO
		b.	0.0092	1.7	99.3		
		c.	0.0012	2.2	99.3		
	Raffinate		0.0031			S/L	DB

FIGURE 2. Extraction of palm oil triglycerides using supercritical CO₂

The thermodynamic relationship between supercritical CO₂ and palm oil can be further explained by two contributing factors: solvent density and the solute vapour pressure. Changes in the temperature and pressure of the supercritical CO₂ will affect the solvent density as discussed by Eisenbach (1984). A pressure increase increases the solvent density, thereby reducing

TABLE 3. Fractionation of palm oil using supercritical CO₂ at 50°C

P (bar)	Fraction No.	Sub- fraction	Weight of oil extracted (g)	Total CO ₂ Volume (m ³)	Cumulative wt%	Physical at 25°C	Color Observed
110 ^N	1	a.	0.0077	0.1	0.1	S	LY
		b.	0.0074	0.2	0.3		
		c.	0.0177	0.5	0.6		
		d.	0.0375	0.9	1.2		
		e.	0.0310	1.3	1.8		
		f.	0.0140	1.7	2.0		
		g.	0.0087	1.9	2.2		
		h.	0.0047	2.2	2.2		
	Raffinate		-	-	-	S	DO
140	1		0.9543	1.3	13.5	S	Y
	2		0.6727	2.7	23.0	S	Y
	3		0.5784	3.9	31.2	S	Y
	4		0.5854	5.2	39.5	S	Y
	5		0.5451	6.5	47.2	S	Y
	6		0.5621	8.0	55.1	S	Y
	7		0.6101	9.4	63.7	S	Y
	8		0.5115	10.7	71.0	S	Y
	9		0.5206	12.0	78.3	S	Y
	10		0.5513	13.3	86.1	SL	Y
	11		0.4659	14.7	92.7	SL	Y
	12	a.	0.2348	16.1	96.0	SL	Y
		b.	0.0039	17.3	96.1		
	Raffinate		0.0057			S/L	DB
200	1		2.3188	0.7	45.0	S	O
	2		2.0120	1.6	84.1	S	O
	3	a.	0.6140	2.4	96.0	SL	DO
		b.	0.0092	3.0	96.2		
		c.	0.0009	3.2	96.2		
	Raffinate		0.0055			S/L	DB

the intermolecular distance of the solvent molecules and increasing the interactions between the palm oil molecules and the CO₂ molecules. On the other hand, temperature is an inverse function of solvent density and as the temperature was increased, the solvent density decreased accordingly. An increase in temperature, however, also causes the component vapour pressure to increase and therefore increases the solubility (Tilly et al. 1990).

Typically, as the system pressure is increased, the magnitude increase in solubility decreases. This is because the maximum solubility increase occurs near the critical point of CO₂. Figure 2 shows that as the pressure increases, the solubility is less sensitive to the temperature change, indicating a more pronounced competing effect between the solvent density and the solute vapour pressure. However, palm oil is a multicomponent mixture and the individual components have different physical and chemical characteristics, thus may behave differently as a function of temperature.

TABLE 4. Fractionation of palm oil using supercritical CO₂ at 60°C

P (bar)	Fraction No.	Sub- fraction	Weight of oil extracted (g)	Total CO ₂ Volume (m ³)	Cumulative wt%	Physical at 25°C	Color Observed
140 ^N	1	a.	0.2420	0.9	4.7	S	Y
		b.	0.0782	1.4	6.2		
		c.	0.0561	1.8	7.3		
		d.	0.0195	2.0	7.7		
		e.	0.0482	2.4	8.6		
		f.	0.0348	2.7	9.3		
		g.	0.0756	3.4	10.8		
	2	a.	0.1093	4.5	12.9	S	Y
		b.	0.0917	5.3	14.7		
		c.	0.0615	5.9	15.9		
		d.	0.1049	7.0	17.9		
		e.	0.0869	7.9	19.6		
		f.	0.0529	8.5	20.6		
		g.	0.1062	9.6	22.7		
	3	a.	0.1170	11.4	25.1	S	O
		b.	0.1623	13.2	28.1		
		c.	0.1408	14.6	31.0		
		d.	0.1137	15.8	33.2		
		e.	0.1142	17.0	35.4		
	4	a.	0.1458	18.6	38.2	S	W
		b.	0.1257	20.0	40.6		
		c.	0.0858	21.0	42.3		
		d.	0.0083	21.3	42.5		
	Raffinate		2.1360		41.5	L	W
	200	1	1.1812	0.5	21.5	S	Y
		2	0.7250	0.9	34.7	S	Y
		3	0.7480	1.2	48.3	S	Y
		4	1.4218	2.0	74.2	SL	O
		5	0.9814	2.8	92.1	SL	O
		6	0.3214	3.4	97.9	SL	DO
	Raffinate		0.0065			S/L	DB

^N = non-exhaustive

Notations:

S = Solid

SL = Semi-liquid

L = Liquid

S/L = Solid and Liquid

Mixture

W = Whitish

LY = Light Yellow

Y = Yellow

O = Orange

DO = Dark Orange

DB = Dark Brown

Solubility behavior of palm oil in supercritical CO₂ as a function of the solvent density is shown in Figure 3. The solubility data for palm oil were obtained from Markom (1998) and Ooi et al. (1996) at 50°C. It can be seen that the solubility increases with the density of supercritical CO₂. When the solubility was plotted on a log scale, the data give an approximately linear

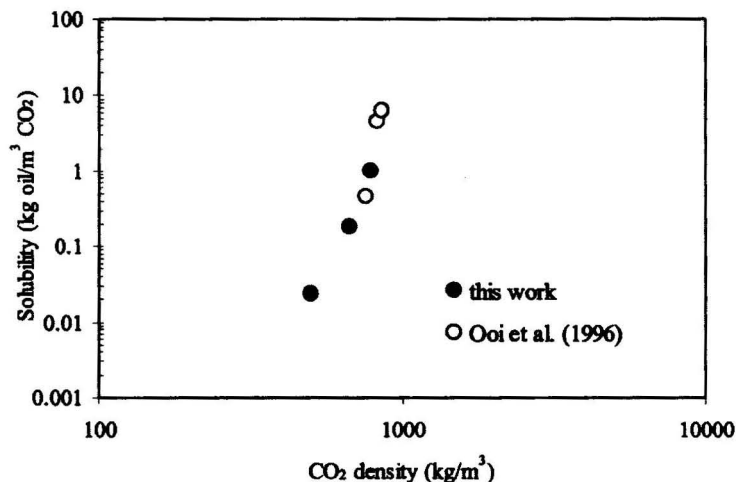


FIGURE 3. Solubility of palm oil in supercritical CO₂ at 50°C

relationship with the density. This behavior is similar to studies of other vegetable oils such as soybean and olive oils (List et al. 1993; Brunetti et al. 1989).

PHYSICAL CHANGES OF PALM OIL

The physical state of the extracted fractions and raffinates were observed in this study as shown in Table 2 to 4. At 40°, 50°, and 60°C, the feed palm oil sample was a liquid since the melting temperature of palm oil is about 36°C. For the exhaustive extractions (i.e. all runs except at 50°C and 110 bar, and 60°C and 140 bar), it was observed that the initial fractions collected at room temperature (25°C) were solid like. The latter fractions extracted (after or more than 60% of oil extracted) appeared to be more liquid like. This change in the physical state of the palm oil fractions may be attributed to the changing composition of the palm oil components.

Supercritical fluids extract components based on their molecular weights, volatilities and specific interactions. The tendency is to extract the lighter and shorter chain molecules first followed by the heavier and longer chain molecules. In palm oil, both saturated and unsaturated triglycerides are present. Therefore, the solid like appearance of the initial fractions is possibly due to a higher concentration of lighter and saturated triglycerides such as tripalmitin (PPP) being extracted. On the other hand, the semi-liquid fractions extracted towards the end of extraction contain a higher concentration of unsaturated and heavier triglycerides such as palmitodiolein (POO). For all the exhaustive extractions, the raffinate was found to consist of a very small amount of viscous liquid. A thin film of solid matter was also observed on the wall of the extraction vessel.

COLOUR CHANGES OF PALM OIL

The colour of the fractions extracted was also observed in this study. The initial colour of crude palm oil was dark orange. It was noted that the colour of the fractions extracted changed with the amount of CO₂ consumed. At 200

bar, the colour intensity of the extracted fractions increases as more palm oil sample was extracted, for example, from yellow to orange to dark orange. This was expected since the orange colour indicates the present of carotenes, and since carotenes are high molecular weight compounds, the concentration of these compounds should increase towards the end of the extraction. It was also observed that the colour of all fractions collected appeared darker at higher extraction pressures compared to the lower pressures at the same temperature.

At 140 bar and temperatures of 40 and 50°C, lighter colour intensity of the extracted triglycerides was observed as the extraction progressed as shown in Table 2 and 3. The colour of the extracts was observed to be yellow from initial to the end of extraction. At a lower pressure of 110 bar and 50°C, the extracted palm oil was observed to be a very light yellow (Table 2). At lower pressures, the CO₂ density is reduced, resulting in the lower solvating strength of CO₂ and thus, reducing the solubility of palm oil in the CO₂. The run at 140 bar and 60°C was expected to exhibit a similar observation. However, the raffinate collected at this condition was white, as shown in Table 4. This observation suggests that at this condition, the CO₂ was able to extract all of the yellow coloured components in the palm oil and therefore, should warrant further investigations.

CONCLUSIONS

This study shows that CO₂ is able to extract crude palm oil components at conditions not too far removed from the critical conditions of the solvent. The initial solid like fractions and the latter semi-liquid fractions extracted indicate that some degree of fractionation could be achieved. The coloured components such as carotenes are generally extracted towards the end, once the triglycerides have depleted. Pressure is shown to be more dominant over temperature in increasing the solubility of palm oil in supercritical carbon dioxide.

ACKNOWLEDGEMENTS

This project was funded by University of Malaya under Vote F Research Grant (F210/97). We would also like to thank Jomalina Sdn. Bhd. for the free crude palm oil samples provided.

REFERENCES

- Brunetti, L., Daghetta, A., Fedeli, E., Kikic, I. & Zandarighi, L. 1989. Deacidification of olive oils by supercritical carbon dioxide. *J. Am. Oil Chem. Soc.* 66(2): 209-217.
- Chao, R. R., Mulvaney, S. J. & Huang, H. 1993. Effects of extraction and fractionation pressures on supercritical extraction of cholesterol from beef tallow. *J. Am. Oil Chem. Soc.* 70(2): 139-143.
- Choo, Y. M., Ma, A. N., Yap, S. C., Hamid, H. A. & Ooi, K. E. 1996. Separation of crude palm oil components by semipreparative supercritical fluid chromatography. *J. Am. Oil Chem. Soc.* 73(40): 18-25.

- Eisenbach, W. 1984. Supercritical fluid extraction: a film demonstration. *Ber. Busenges. Phys. Chem.* 88: 882-887.
- Gunstone, F. D. 1987. *Palm oil*, London: Society of Chemical Industry.
- Lee, B. C., Kim, J. D., Hwang, K. Y. & Lee, Y. Y. 1991. Extraction of oil from evening primrose seed with supercritical carbon dioxide. *Supercritical Fluid Processing of Biomaterials: Basics of Process Design and Applications Symposium*, Toronto, 168-180.
- List, G. R., King, J. W., Johnson, J. H., Warner, K. & Mounts, T. L. 1993. Supercritical CO₂ degumming and physical refining of soybean oil. *J. Am. Oil Chem. Soc.* 70(5): 473-476.
- Markom, M. 1998. *Supercritical Fluid Extraction of Palm Oil Using Carbon Dioxide*. MSc. Thesis, University Malaya, Kuala Lumpur.
- Ooi, C. K., Bhaskar, A., Yener, M. S., Tuan, D. Q., Hsu, J. & Risvi, S. S. H. 1996. Continuous supercritical carbon dioxide processing of palm oil. *J. Am. Oil Chem. Soc.* 73(2): 233-237.
- Tilly, K. D., Chaplin, R. P. & Foster, N. R. 1990. Supercritical fluid extraction of the triglycerides present in vegetable oils. *Sep. Sci. Tech.* 25(4): 357-367.

Masturah Markom
Department of Chemical and Process Engineering
Universiti Kebangsaan Malaysia
43600 Bangi, Selangor
Malaysia

Harcharan Singh and Masitah Hasan
Department of Chemical Engineering
Universiti Malaya,
50603 Kuala Lumpur
Malaysia