Continuous Supercritical Carbon Dioxide Processing of Palm Oil

C.K. Ooi[a,*], A. Bhaskar[b], M.S. Yener[b], D.Q. Tuan[b], J. Hsu[b], and S.S.H. Rizvi[b]

[a]Palm Oil Research Institute of Malaysia, Kuala Lumpur, Malaysia, and
[b]Institute of Food Science, Cornell University, Ithaca, New York 14853

ABSTRACT: Crude palm oil was processed by continuous supercritical carbon dioxide. The process reduces the contents of free fatty acids, monoglycerides and diglycerides, certain triglycerides, and some carotenes. The refined palm oil from the process has less than 0.1% free fatty acids, higher carotene content, and low diglycerides. Solubility of palm oil in supercritical carbon dioxide increased with pressure. A co-solvent improves the refining process of palm oil.
JAOCS 73, 233–237 (1996).

KEY WORDS: Carotenes, co-solvent, diglycerides, free fatty acids, monoglycerides, palm oil, solubility of palm oil, supercritical carbon dioxide, vitamin E.

Supercritical fluid extraction (SFE) has been used in commercial production of decaffeinated coffee and concentrated hop extract (1). However, its economic viability in other areas of food and pharmaceutical production is still being evaluated. In the oils and fats industry, numerous studies on the application of SFE in processing have been conducted. Among them are the degumming of soybean oil (2), deodorization and deacidification of peanut oil (3), fractionation of thermally oxidized canola oil (4), processing and fractionation of milk fat (5), refining of olive oil (6), and others (7–10).

The SFE process has a number of advantages over conventional extraction. These are low-temperature operation, pollution-free operation, inert solvent, selective separation and fractionation of tailor-made end-product, and extraction of high-value product or new product with improved functional or nutritional characteristics. Some of the solvents used in SFE are carbon dioxide, ethylene, propane, nitrogen, nitrous oxide, and monochlorofluoromethane. The most common solvent is carbon dioxide because it possesses a number of desirable properties, such as nonexplosivity, low cost, ready availability, and nontoxicity, which makes it ideal for food processing.

Presently, palm oil is refined through physical or chemical refining. This involves degumming, alkaline wash, and steam distillation at high temperature under vacuum. The process removes free fatty acids (FFA) and deodorizes the oil. However, it also reduces the tocopherol content and destroys all carotenes present in palm oil. This paper describes refining of palm oil by SFE with carbon dioxide.

MATERIALS AND METHODS

Materials. Commercial-grade carbon dioxide (Pipe Welding Supply Co., Elmira, NY) was used. Crude palm oil was obtained from Jomalina Sdn. Bhd. (Selangor, Malaysia).

Apparatus. A continuous supercritical fluid pilot-plant system with packed column was used to process palm oil. A schematic of the system is shown in Figure 1. The extraction column is 61 cm long and has an internal diameter of 1.75 cm. It is packed with Goodloe knitted-mesh stainless-steel packing (Glitsch Inc., Dallas, TX). The packing surface area and void fraction are 19.2 cm^2/cm^3 and 0.95, respectively. The column is wrapped with heating tapes (Model N-03114-40; Cole-Palmer Instrument Co., Chicago, IL), and the tempera-

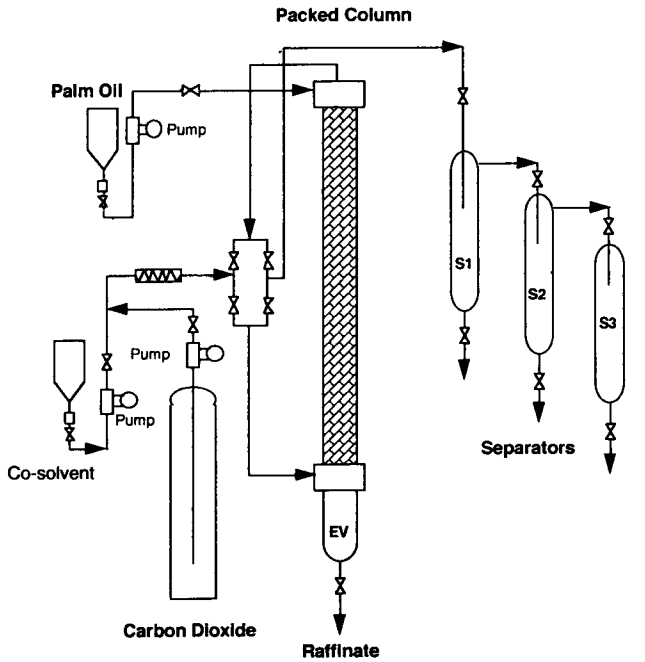

FIG. 1. Schematic diagram of continuous supercritical carbon dioxide processing of palm oil; S1, S2, S3: Separator 1, 2, 3, respectively; EV, extraction vessel.

*To whom correspondence should be addressed.

ture is controlled by a proportional controller (CN9000; Omega Engineering Inc., Stamford, CT). Thermocouples (sheath diameter 0.32 cm, J type; Omega Engineering Inc.) are attached at the top, middle, and bottom of the column. It is insulated with woven glass tapes (Model 17-1711, thickness 0.42 cm; Wales Apparatus Co., Hellertown, PA). The pumps used to transport palm oil, ethanol, and supercritical carbon dioxide (SC-CO_2) are high-pressure positive-displacement pumps (Model 396; Milton Roy Co., Riveria Beach, FL). A bolted-closure packless pressure vessel, extraction vessel (EV), is attached to the extraction column to collect the raffinate. The vessel has a volume of 300 cm^3. The separators (S1, S2, and S3) are 316 stainless-steel, 150-cm^3 cylinders (Model 50DF4; Whitey Co., Highland Heights, OH). The separators were wrapped with temperature-regulated heating tapes and insulated with woven glass tapes, so that the extracted material does not freeze and stick to the inner wall of the separators. The temperature of the separators is controlled by variable voltage transformers (Model N-01575-00; Cole-Palmer Instrument Co.). Pressure in the separators is controlled by pressure reduction valves (Model 44-1124-24-001; Tescom Co., Elk River, MN) and back pressure regulators (Model 26-1722-24-04; Tescome Co.). The whole apparatus was enclosed in a containment box except for the carbon dioxide pressurization subsystem and the carbon dioxide flow monitoring subsystem. A stable temperature environment was provided by a cascaded heating system. The temperature of the box was maintained at a constant temperature through three finned strip heaters (model 2#924; Grainger Inc., Rochester, NY) and controlled by a proportional controller (CN9111; Omega Engineering Inc.). The air in the box was circulated by ten fans (Model 81F8113; Newark Electronics, Rochester, NY). The separator containment box was partitioned from the main containment box and was controlled by two finned strip heaters with proportional controllers (Model 5GX220P; Oven Industries, Mechanicsbury, PA).

Refining procedures. A countercurrent process was performed on crude palm oil with SC-CO_2. Crude palm oil was continuously fed into the top of the extraction column at a rate of 60 g/h. SC-CO_2 was then pumped into the bottom of the column at a rate of 2400 g/h. Ethanol was pumped into the SC-CO_2 line before going into the extraction column. The countercurrent process was conducted at 50°C and 24.0 MPa. The raffinate was collected in the EV, and the extracts were collected in the separators (S1, S2, and S3). The pressures of the separators S1, S2, and S3 were 17.1, 10.3, and 3.4 MPa, respectively.

The extraction column pressures were varied from 10.3 to 27.4 MPa, solvent-to-feed (S/F) ratios from 10 to 110 at 50 and 60°C. The pressures of the separators (S1, S2, S3) varied from 3.4 to 20.6 MPa. The refining procedure was repeated three times for each condition.

Analytical methods. FFA, carotene content, and slip melting point were determined according to PORIM Test Method p 2.5, p 2.6, and p 4.2 (11), respectively. Glyceride contents were determined by gas–liquid chromatography (Model HP 5890; Hewlett-Packard, Avondale, PA) with a capillary column, 30 m × 0.32 mm, BD-5HT (J&W Scientific Co., Folsom, CA).

RESULTS AND DISCUSSION

The research was conducted to study SC-CO_2 processing parameters to produce refined palm oil.

Influence of pressure, temperature, and co-solvent on the FFA content of raffinate. Results showed that the process was able to reduce the FFA content of palm oil. At 24.0 MPa/50°C and S/F ratio of 58.2, FFA was reduced from 2.35 to 0.19% (Table 1). Although the FFA level was reduced, the level observed was considered high for a refined palm oil. Normal refined palm oil has a FFA level of less than 0.1%. Increasing the extraction pressure increases the solvent power of the supercritical fluid. But increasing the pressure to 27.4 MPa with S/F ratio of 62.8 at 50°C did not reduce the FFA level. Fatty acids are polar compounds; hence ethanol was added to SC-

TABLE 1
Effect of Pressure, Temperature, and Co-Solvent on the Free Fatty Acid (FFA) Content of the Raffinate and Solubility of Palm Oil in SC-CO_2 at Solvent-to-Feed Ratio (40 ± 5)

	Temperature (°C)							
	50	50	50	65	65	50	50	65
	Ethanol ± 0.3 (mole%)							
	—	3.7	6.3	4.6	8.0	—	3.7	8.0
Column pressure ± 0.1 (MPa)	FFA ± 0.01%					Solubility 0.01 (%)		
27.4	0.25[a]	—	—	—	0.08	0.74[a]	—	2.01
24.0	0.19[b]	0.08	0.06	0.09	0.07	0.55[b]	1.11	1.38
20.6	—	0.09	0.08	—	—	—	0.95	—
17.1	—	0.18	0.04	—	—	—	0.51	—
13.7	1.21[c]	0.13[d]	—	0.44	0.29	0.06[c]	0.22	0.13
10.3	2.02	—	—	—	—	0.00	—	—

[a]Solvent-to-feed (S/F) ratio 62.8.
[b]S/F ratio 58.2.
[c]S/F ratio 88.7.
[d]S/F ratio 54.7; SC-CO_2, supercritical carbon dioxide.

CO_2 to increase its polarity. The addition of ethanol as a co-solvent during the process did reduce the FFA level to less than 0.1% (Table 1). However, this was achieved at 20.6 MPa and above, with 3.7 mole% ethanol at 50°C. Increasing the ethanol level to 6.3 mole% at 17.1 MPa/50°C, the process was able to reduce the FFA level to 0.04%. But at pressures below 13.7 MPa, increasing temperature and ethanol level were not able to reduce the FFA level to 0.1% or less. This showed that it is possible to refine palm oil with SC-CO_2 by varying the pressure, temperature, and S/F ratio.

Influence of pressure, temperature, and co-solvent on the yield and solubility of palm oil. SC-CO_2 pressure affects the yield and solubility of palm oil. The yield decreases with increase in pressure (Fig. 2). This is expected because an increase in SC-CO_2 pressure increases its density and solvent power. The yield of the raffinate obtained ranged from 90.2% at 13.7 MPa to 72.8% at 27.4 MPa. The addition of ethanol to SC-CO_2 further reduced the yield of the raffinate, from 86.5% at 13.7 MPa to 47.6% at 27.4 MPa. The presence of ethanol increases the polarity of SC-CO_2. This will increase the solubility of palm oil in SC-CO_2. As observed with the addition of 3.7 mole% ethanol, the solubility increases from 0.55 to 1.11% at 24.0 MPa/50°C (Fig. 2). However, a slight increase in the solubility was observed when the temperature of SC-CO_2 was increased from 50 to 65°C, as higher temperature reduces the density of SC-CO_2.

Generally, the solubility of palm oil in the equilibrium state is higher than under continuous processing conditions. At equilibrium, the solubility of palm oil was 0.74% at 23.9 MPa/50°C, compared to 0.50% under continuous processing conditions (Fig. 2). Similarly, the solubility of palm oil in the presence of ethanol in SC-CO_2 in the equilibrium state was higher, 1.38% compared to 1.11% during processing.

Influence of pressure on yield, FFA, and carotene content of extracts. The yield of extract in the two separators varies with the pressure of the extraction column and the separators. Higher extraction column pressure gave higher yield of the extract. However, the yield of the extract in each separator varies. The yield of extract in separator 1 (S1) decreases with increase in S1 pressure and vice-versa, whereas the yield in S2 increases with S1 pressure (Fig. 3). In most cases, the FFA content of the extract in S2 was much higher than in S1 (Fig. 3 and Table 2). This is due to the comparatively higher solubility of the FFA compared to the triglycerides. Crude palm oil has a carotene content of 500–600 ppm. With SC-CO_2, some of the carotenes were extracted together with FFA and triglycerides. However, the amount of carotenes extracted was low (Table 2). The presence of ethanol in SC-CO_2 did not affect the extraction of carotenes from the oil (Table 2). The carotene content of the extracts obtained was between 110–322 ppm.

Characteristics of SC-CO_2 refined palm oil and extracts. The refined palm oil from SC-CO_2 processing at 24.0 MPa/50°C has a similar triglyceride composition but reduced FFA, monoglycerides, and diglycerides contents (Table 3). However, the addition of ethanol during the process under the same conditions produced a refined oil with FFA of 0.04%, trace amounts of monoglycerides, and a much reduced diglycerides content (Table 4). Higher processing temperature produced a different refined oil with lower C_{48} and C_{50} triglycerides, much reduced diglycerides (0.66%), and higher carotene content (Table 5). The diglycerides content in the oil is important because its presence affects the crystallization behavior of the oil. Berger and Wright (12) and Persmark *et al.* (13) reported that the presence of diglycerides in palm oil slowed down the transformation from α to β′ during crystallization. Its presence caused the formation of a mixture of crystals of different shapes and sizes. This causes problems in filtration and results in low yield of the liquid fraction. It is known that palm oil crystallizes in three major forms, the α, β′, and β, in order of increasing stability. The α form crystallizes faster than β′, which in turn is faster than the β form. Hence, it is desirable to prevent the formation of α crystals

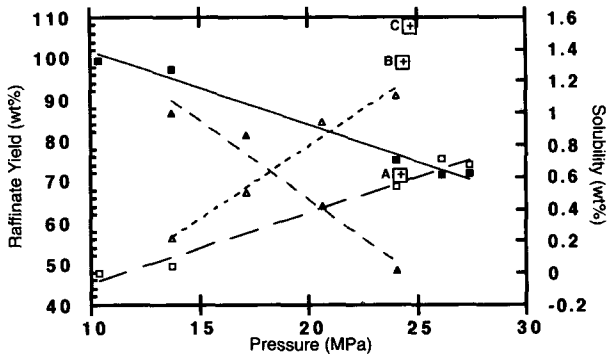

FIG. 2. Effect of pressure and 3.7 mole% ethanol on the yield of raffinate and solubility of palm oil in supercritical carbon dioxide (SC-CO_2) at 50°C and solvent-to-feed ratio (40 ± 5): ▲, yield with ethanol; ■, yield without ethanol; △, solubility with ethanol; □, solubility without ethanol; A, solubility of palm oil in equilibrium conditions; B, solubility of palm oil in SC-CO_2 with 3.4 mole% ethanol in equilibrium conditions; C, solubility of palm oil in SC-CO_2 with 4.6 mole% ethanol in equilibrium conditions.

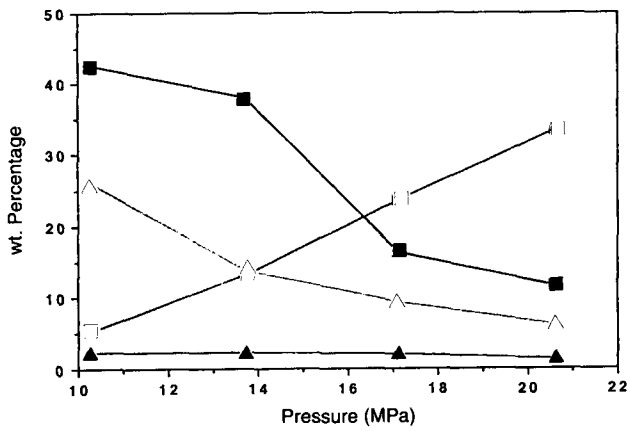

FIG. 3. Effect of S1 pressure on the yield and free fatty acids (FFA) of fractions at 24.0 MPa/50°C with 3.7 mole% ethanol: ■, S1 yield; □, S2 yield; ▲, S1 FFA; △, S2 FFA. Abbreviations as in Figure 1.

TABLE 2
Effect of Column Pressure[a] on the Yield, FFA, and Carotene Content of S1 and S2[b] at 50°C and S/F Ratio (40 ± 5)

		Sample			
		S1	S2	S1	S2
		Ethanol ± 0.3 (mole%)			
		3.7		6.4	
Column pressure ± 0.1 (MPa)					
24.0	Yield (%)	42.5 ± 3	5.2 ± 0.5	49.8 ± 3	6.6 ± 0.5
	FFA ± 0.05 (%)	2.67	27.74	2.32	25.97
	Carotene ± 10 (ppm)	162	110	180	322
20.6	Yield (%)	30.9 ± 3	4.8 ± 0.5	31.0 ± 3	6.7 ± 0.5
	FFA ± 0.05 (%)	3.19	28.94	3.20	20.22
	Carotene ± 10 (ppm)	186	124	186	141
17.1	Yield (%)	14.3 ± 3	4.2 ± 0.05	25.0 ± 3	8.1 ± 0.5
	FFA ± 0.05 (%)	4.94	31.45	3.08	23.96
	Carotene ± 10 (ppm)	169	119	185	123

[a]Pressure S1, 10.3 MPa, pressure S2, 6.9 MPa. See Table 1 for abbreviations.
[b]S1, S2, Separators 1 and 2.

TABLE 3
SC-CO_2 Processing of Crude Palm Oil at 50°C and S/F Ratio (58 ± 5)[a]

Sample	Crude palm oil	Raffinate	Separator 1	Separator 2
Pressure ± 0.1 (MPa)	—	24.0	17.1	6.9
Yield (%)	—	68.5 ± 3.0	7.7 ± 0.5	24.4 ± 0.5
FFA (%)	2.35 ± 0.05	0.19 ± 0.01	2.41 ± 0.05	9.46 ± 0.05
Monoglycerides ± 0.05 (%)	0.33	0.10	0.40	1.55
Diglycerides ± 0.05 (%)	5.07	2.80	6.53	7.89
Triglyceride Composition ± 0.05 (%)				
C_{48}	9.18	9.17	10.41	11.65
C_{50}	42.29	43.34	45.41	45.49
C_{52}	39.19	38.73	36.71	35.64
C_{54}	9.34	8.76	7.47	7.22
Carotene ± 10 (ppm)	540	690	196	147

[a]See Table 1 for abbreviations.

TABLE 4
SC-CO_2 Processing of Crude Palm Oil at 50°C with 6.1 Mole% Ethanol and S/F Ratio (40 ± 5)[a]

Sample	Crude palm oil	Raffinate	Separator 1	Separator 2
Pressure ± 0.1 (MPa)	—	17.1	10.3	6.9
Yield (%)	—	70.3 ± 3.0	25.0 ± 0.5	8.1 ± 0.5
FFA (%)	2.35 ± 0.05	0.04 ± 0.01	3.08 ± 0.05	23.96 ± 0.05
Monoglycerides ± 0.05 (%)	0.33	0.03	0.65	2.75
Diglycerides ± 0.05 (%)	5.07	2.35	9.29	3.42
Triglyceride Composition ± 0.05 (%)				
C_{48}	9.18	8.22	10.88	11.11
C_{50}	42.29	42.94	45.64	44.04
C_{52}	39.19	39.64	36.24	36.70
C_{54}	9.34	9.40	7.24	8.15
Carotene ± 10 (ppm)	540	674	185	123

[a]See Table 1 for abbreviations.

TABLE 5
SC-CO_2 Processing of Crude Palm Oil at 65°C with 7.5 Mole% Ethanol and S/F Ratio (40 ± 5)[a]

Sample	Crude palm oil	Raffinate	Separator 1	Separator 2
Pressure ± 0.1 (MPa)	—	24.0	10.3	6.9
Yield (%)	—	23.3 ± 0.5	72.8 ± 3.0	2.2 ± 0.05
FFA (%)	2.35 ± 0.05	0.07 ± 0.01	3.07 ± 0.05	16.08 ± 0.05
Monoglycerides ± 0.05 (%)	0.33	0.02	0.34	1.21
Diglycerides ± 0.05 (%)	5.07	0.66	5.79	5.88
Triglyceride Composition ± 0.05 (%)				
C_{48}	9.18	6.70	10.09	10.59
C_{50}	42.29	39.60	44.53	43.73
C_{52}	39.19	42.05	37.32	37.03
C_{54}	9.34	11.66	8.06	8.66
Carotene ± 10 (ppm)	540	1225	189	159

[a]See Table 1 for abbreviations.

and enhance the formation of β′ crystals. The β′ crystals generally agglomerate into large aggregates that are firm and of uniform spherical size, and they give good separation. Crystallization results in the formation of β′ crystals. The low diglycerides content of the SC-CO_2-refined palm oil is preferred compared to physical-refined palm oil. The monoglycerides content in palm oil is normally less than 1% and, at this level, has no significant effect on crystallization or separation.

The extracts from the SC-CO_2 process with or without ethanol have higher C_{48} and C_{50} triglycerides. The extracts in S2 have higher mono- and diglycerides compared to crude palm oil (Tables 3, 4, and 5). However, the monoglycerides content in S1 was comparable to crude palm oil, although its diglycerides content was much higher.

This study has shown that the conditions to refine crude palm oil economically in terms of yield and FFA is at a pressure of 17.1 MPa and 50°C, with 6.1 mole% of ethanol and a S/F ratio of 40 ± 5. However, to prepare high-carotene refined palm oil or low-diglyceride oil, the process will have to be carried out at higher pressure (24 MPa), temperature (65°C), 7.5 mole% of ethanol, and an S/F ratio of 40 ± 5.

ACKNOWLEDGMENTS

The project was supported by Asian Development Bank and Palm Oil Research Institute of Malaysia. The authors thank Jomalina Sd. Bhd. and Normah Samad for their contributions to the project.

REFERENCES

1. Volbrecht, R., *Chem. Ind.*:397 (1982).
2. List, G.R., J.W. King, J.H. Johnson, K. Warner, and T.L. Mounts, *J. Am. Oil Chem. Soc. 70*:473 (1993).
3. Ziegler, G.R., and Y.J. Liaw, *Ibid. 70*:947 (1993).
4. Hansen, S.L., and W.E. Artz, *Ibid. 71*:615 (1994).
5. Lim, S.B., G.B. Lim, and S.S.H. Rizvi, *Proc. 2nd Int. Conf. Supercritical Fluid*:292 (1991).
6. Bondioli, P., C. Mariani, A. Lanzani, E. Fedeli, A. Mossa, and A. Muller, *J. Am. Oil Chem. Soc. 69*:477 (1992).
7. Chao, R.R., S.J. Mulvaney, and H. Huang, *Ibid. 70*:139 (1993).
8. Bharath, R., T. Adschiri, H. Inomata, K. Arai, and S. Sato, *Proc. 2nd Int. Conf. Supercritical Fluid*:288 (1991).
9. Ikawa, N., S. Furuta, R. Fukuzato, N. Imanishi, H. Kawana, M. Mitsuiki, and H. Suzuki, in *Solvent Extraction*, edited by T. Sekine, Elsevier Science Publishers, 1992, p. 1707.
10. De Haan, A.B., and J. De Graauw, in *Solvent Extraction*, edited by T. Sekine, Elsevier Science Publishers, 1992, p. 1713.
11. *PORIM Test Methods*, Vol. 1, Palm Oil Research Institute of Malaysia, Kuala Lumpur, 1995, p. 2.5–2.7.
12. Berger, K.G., and W.B. Wright, *PORIM Occasional Paper*:17 (1986).
13. Persmark, U., K.A. Melin, and P.O. Stahl, *Riv. Ital. Sost. Grasse 53*:301 (1976).

[Received February 13, 1995; accepted November 20, 1995]