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Phase Equilibrium Study of Triacylglycerols from Crude Palm Oil Using CO_2

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Abstract: Two-phase equilibrium data was measured for carbon dioxide with triacylglycerols from crude palm oil using a phase equilibrium loading re-circulating high-pressure type apparatus at various pressures and at temperatures of 80, 100 and 120°C. According to this research, it concluded that the highest extraction in term of vapor phase was carried out at a middle pressure (P=5.4 MPa) and at temperature of 120°C. It also calculated that the extracted triacylglycerols (TAGs) percentage were about 2.27%. This gives a good opportunity to have these materials extracted using supercritical CO_2 method in order to scale up the system.

Key words: Crude palm oil · Phase behavior · Carbon dioxide · Triacylglycerols

INTRODUCTION

Palm oil is a main export product from Malaysia which has about 1.9 million hectares of plantations. The main product from palm fruits usually is palm oil. In order to get a palm oil, the palm fruits are first treated with steam and thereafter the oil-containing parts are separated from the bunch. By mechanical extraction of these parts, crude palm oil (CPO) is obtained. CPO is a semi solid material at a room temperature and has melting point of ~ 36°C [1].

Conventional methods based on the solvent extraction from the natural products are time consuming. These methods require multiple extraction steps and large amounts of organic solvents, which are often expensive and potentially harmful. Extraction with carbon dioxide under supercritical conditions constitutes an emerging technology in terms of environmental impact. The advantages of using carbon dioxide include its lack of toxicity, chemical inertness, low cost and ready availability [2]. Furthermore, the use of carbon dioxide is also beneficial in adding quality to the products obtained since this technique does not give rise to excessive heating, which usually has a negative effect on the thermolabile compounds [3].

Palm oil approximately has an equal amount of saturated and unsaturated fatty acids [4]. Most of the fatty acids of palm oil are present as triacylglycerols (TAGs). The different placement of fatty acids and fatty acid types on the glycerol molecule produces a number of different TAGs. There are 7-10% of saturated TAGs, predominantly tripalmitin [5]. The fully unsaturated triglycerides constitute 6 to 12% [5, 6]. The TAGs in palm oil partially define most of the physical characteristics of the palm oil such as melting point and crystallization behavior [4]. Several Malaysian tenera palm oil TAGs with their percentages have been reported in detail in the literature [4, 6, 7].

However, measurements of phase equilibrium in multicomponent mixtures of natural oils in supercritical carbon dioxide provide the necessary data for process evaluation, but measurements of phase equilibrium data in binary systems of supercritical carbon dioxide with a single triacylglycerols are also of importance, as model systems to determine the parameters [8, 9].

There are several researches related to the TAGs extraction using CO_2. Supercritical extraction of TAGs from buffalo butter oil using CO_2 solvent has been studied by Fatouh *et al.* [10]. According to this research, it concluded that increasing the pressure and temperature of the extraction led to increasing the solvating power of supercritical carbon dioxide. TAGs were extracted during the early stage of the fractionation, thereby creating low-melting fractions. Conversely, TAGs were concentrated in the fractions (i.e., high-melting fractions) obtained towards the end of the process [10].

Solubility data for several systems such as CO_2-tricaprilin [8], CO_2-trilaurin and CO_2-trimiristin [11], CO_2-tripalmitin, CO_2-tristearin and CO_2-olein [12] and

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mixtures of these with CO_2 [11] were already measured. Furthermore, several researchers have studied the solubilities of some multicomponent systems such as CO_2-blackcurrant oil [13], CO_2-canola oil [14], CO_2-corn oil, CO_2-sunflower seed oil, CO_2-babassu fat and CO_2-ucuuba fat [9].

Sovová *et al.* studied the solubility of CO_2-blackcurrant oil system, at pressures up to 29 MPa and at temperatures of 40-60°C [13].

A maximum yield of triglycerides and lipids containing phospholipids in supercritical carbon dioxide was obtained at pressure of 62 MPa and at temperature of 70°C with ethanol (as an entrainer) at an initial level of 5% by Temelli [14].

Soares *et al.* studied the solubility of refined corn and sunflower seed oils, babassu and ucuuba fats in supercritical carbon dioxide in a temperature range from 40 to 80°C and pressure between 20 and 35 MPa. Under working conditions, the values of solubility showed retrograde behavior [9]. In this research also the Chrastil's equation was also applied to correlate the solubility of oils in CO_2 as a function of the temperature and density of the supercritical CO_2.

Bravi *et al.* developed a rapid extraction method for analysis of fatty acids in brewing raw materials (malt and corn grits) [15]. According to this study, it concluded that the extraction of total fats achieved by a 60-min run with pure CO_2 at 65 MPa and at 100°C was 43% higher than that produced by Soxhlet performed for 9 h for malt.

Tan *et al.* studied supercritical fluid extraction of triacylglycerols from cocoa butter using CO_2 at pressures of 10-45 MPa, at temperatures of 35-75°C and extraction times of 1-12 h [16]. They concluded that the higher yield of triacylglycerols was obtained at higher values of pressure, temperature and extraction time. The smaller particle size produced a higher yield of cocoa butter. 1,3-Dipalmitoyl-2-oleoyl-glycerol (POP), 1-palmitoyl-2-oleoyl-3-stearoyl-glycerol (POS) and 1,3-distearoyl-2-oleoyl-glycerol (SOS) were the major TAGs present in the extracted cocoa butter, with POS being the highest (>30%) for all treatments studied.

In this study, mutual solubilities of TAGs [involving: 1, 3-dipalmitoyl-2-oleoyl-glycerol (POP), 1, 2-dioleoyl-3-palmitoyl-rac-glycerol (POO) and 1, 2-dioleoyl-3-stearoyl-rac-glycerol (SOO)] from crude palm oil using CO_2 solvent were determined. The amount of these components in Malaysian tenera palm oil has been reported around 20.02% (or 23.7%), 20.54% (or 21.5%) and 1.81% (or 1.40%) for POP, POO and SOO substances respectively [4]. The other TAGs percentages in palm oil have been reported in the literature [4].

EXPERIMENTAL

Materials: Crude palm oil was purchased from United Oil Palm Industries Sdn. Bhd, Nibong Tebal, Malaysia and CO_2 (99.9%) was purchased from MOX Sdn. Bhd. 1, 3-dipalmitoyl-2-oleoyl-glycerol (99%, Sigma), 1, 2-dioleoyl-3-palmitoyl-rac-glycerol (99%, Sigma) and 1, 2-dioleoyl-3-stearoyl-rac-glycerol (99%, Sigma) as standards were used.

Acetone (99.80%, J.T. Baker) and acetonitrile (99.99%, Fisher) were also used for analysis.

Calculations Method: The calculations for the mole fraction of carbon dioxide in the liquid phase (x) and in the vapor phase (y) of each system were carried out using the following equations:

$$x_1 = \frac{(nx_1)^L}{\left[(nx_1)^L + (nx_2)^L\right]} \quad (1)$$

$$y_1 = \frac{(nx_1)^G}{\left[(nx_1)^G + (nx_2)^G\right]} \quad (2)$$

$$y = \frac{(ny)^G}{\left[(nx)^G + (ny)^G\right]} \quad (3)$$

$$(1-x) = \frac{(nx)^L}{\left[(ny)^L + (nx)^L\right]} \quad (4)$$

$$(ny)^G = VP_2\left(\frac{1-(\frac{P_1}{P_2})(\frac{RT+B_vP_2}{RT+B_vP_1})}{(RT+B_vP_2)}\right) = \frac{V\times\Delta P}{RT+B_v\times\Delta P} \quad (5)$$

where:

$(nx_1)^L$: Number of moles of TAG in the liquid phase on a carbon dioxide free basis.

$(nx_1)^G$: Number of moles of TAG in the vapor phase on a carbon dioxide free basis.

$(nx_2)^L$: Number of moles of palm oil in the liquid phase on a carbon dioxide free basis.

$(nx_2)^G$: Number of moles of palm oil in the vapor phase on a carbon dioxide free basis.

where:

$(ny)^G$: Number of moles of carbon dioxide in the vapor sample bomb.

$(nx)^G$: Number of moles of heavy component in the vapor sample bomb.

$(ny)^L$: Number of moles of carbon dioxide in the liquid sample bomb.

$(nx)^L$: Number of moles of heavy component in the liquid sample bomb.

B_v: second virial coefficient, P_1 and P_2: expansion vessels pressures before and after expansion process, R: gases constant, T: system temperature.

The number of moles of carbon dioxide in the liquid sample bomb, $(ny)^L$, was calculated using the same procedure as given above except that the total volume of the expansion system (V) was taken as 7 liters instead of 35 liters which is used for vapor sample bomb calculations.

Experimental Procedure: As shown in Fig. 1, the equipment used in this study was a custom fabricated re-circulation high-pressure type phase equilibrium apparatus which has been described in detail and the reliability of the data was already proposed in the literature [17-20]. The current apparatus was equipped with a pressure gauge (model: Stainless Steel Miniature Gauge, brand: Swagelok, England. The pressure range is $0 < P/bar < 250$, with accuracy ±2.5% of span ASME B40.1 Grade C, EN 837-1 Class 2.5, JIS B7505 Class 2.5). This apparatus was also equipped with two sensitive Japanese-made OMRON digital temperature indicators (model: E5CN) with accuracy of ±0.3% of indicated value or ±1°C, whichever is greater.

The operating temperatures were set at 80°C, 100°C and 120°C. Then system pressure was allowed to increase. The samples containing the vapor and liquid phases from each run were collected, diluted by acetone and analyzed by a HPLC (model: Shimadzu, Japan) which equipped with a capillary column: Agilent Lichrosphere RP-18250×4 mn id and refractive index (RI) detector. The oven temperature was set on 50°C and a mixture involving 75% acetone and 25% acetonitrile were used as mobile phase. As an example HPLC chromatogram at pressure of 5.4 MPa for vapor phase is shown in Fig.s 2. The number of moles and the mole fractions based on CO_2 in the vapor and liquid phases were calculated by applying the procedure mentioned in the Experimental (Calculations Method) section.

The experimental data was produced based on the average of the two repeated runs which were performed for each data point. The repeated runs ensured that the experiments could be repeated within a maximum experimental error of ±2%. The precision of the effective parameters in compositions determination such as samples weight which were determined by a digital balance up to six places, operating temperature and pressure increment due to pre and post- expansion vessel which were measured with a mercuric manometer (based on mmHg) caused the mentioned error.

RESULTS AND DISCUSSION

The system carbon dioxide-heavy components (TAGs) were studied at temperatures of 80, 100 and 120°C and at relevant pressures.

Figure 3-5 show two-phase equilibrium data for POP at temperatures of 80, 100 and 120°C. Figure 3 clearly shows that POP mole fractions in the vapor phase increased by increasing the pressure at temperature of 80°C. This trend was also observed for liquid phase mole fractions. However, a regular trend was not observed in vapor and liquid phases at 100°C (Fig. 4) and at 120°C (Fig. 5), but maximum extraction of POP was obtained at pressure of 4.2 MPa, at temperature of 100°C and at pressure of 5.4 MPa, temperature of 120°C. The optimum condition around this operating range for the most extraction of POP was 120°C and 5.4 MPa.

Figure 6-8 show two-phase equilibrium data for POO at temperatures of 80, 100 and 120°C. Figure 6 shows that POO mole fractions in the vapor phase increased by increasing the pressure at temperature of 80°C. This trend was also observed in the liquid phase. However a regular trend was not observed in vapor and liquid phases at 100°C (Fig. 7) and at 120°C (Fig. 8), but maximum extraction of POO was observed at pressure of 7.6 MPa, at temperature of 100°C and at pressure of 5.4 MPa, at temperature of 120°C. The optimum condition around this operating range for the most extraction of POO was 120°C and 5.4 MPa.

Figure 9-11 show two-phase equilibrium data for SOO at temperatures of 80, 100 and 120°C. Figure 9 shows that SOO mole fractions in the vapor phase increased by increasing the pressure at temperature of 80°C. This behavior was also observed in the liquid phase. However an irregular trend was observed in the vapor and liquid phases at 100°C (Fig. 10) and at 120°C (Fig. 11), but maximum extraction of SOO was observed at pressure of 7.6 MPa, at temperature of 100°C and at pressure of 5.4 MPa, at temperature of 120°C. The optimum condition around this operating range for the most extraction of SOO was obtained 120°C and 5.4 MPa.

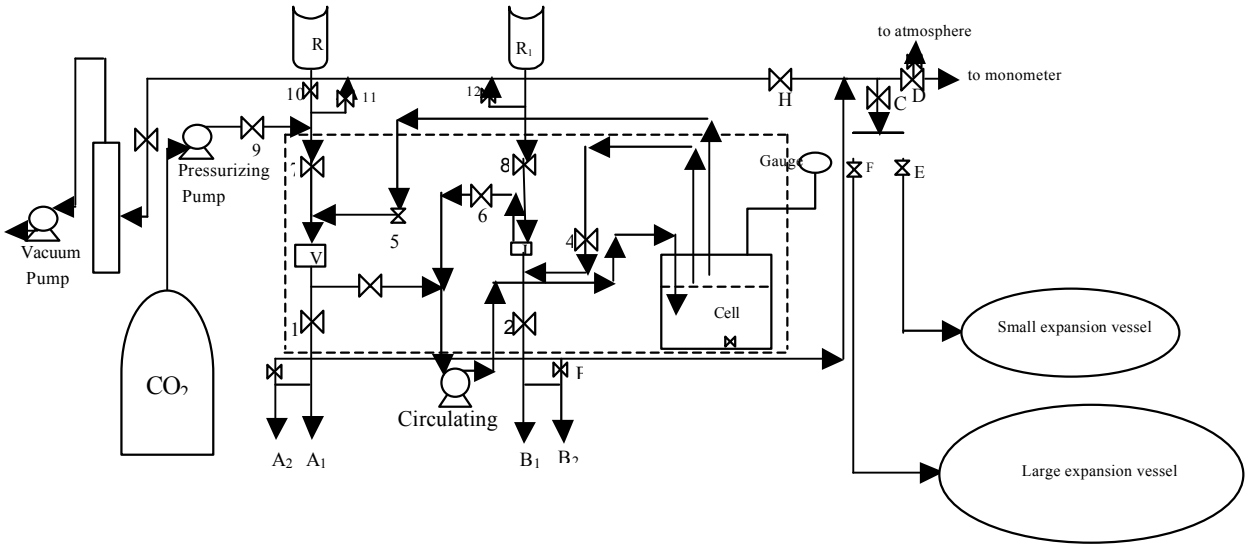

Fig. 1: Supercritical extraction apparatus schema

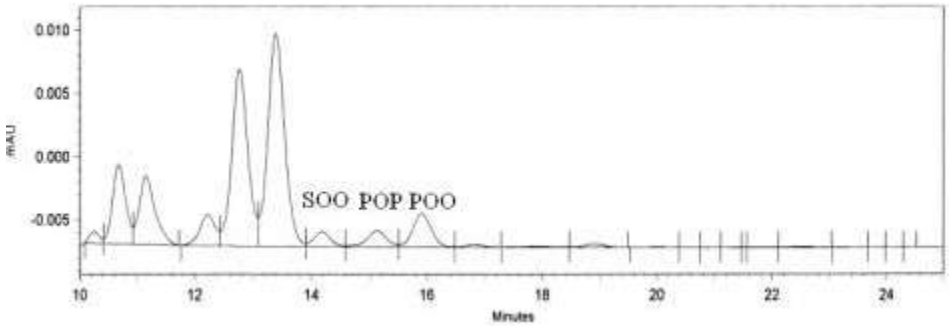

Fig. 2: HPLC chromatogram of crude palm oil TAGs for vapor phase at pressure of 5.4 MPa and at temperature of 120°C

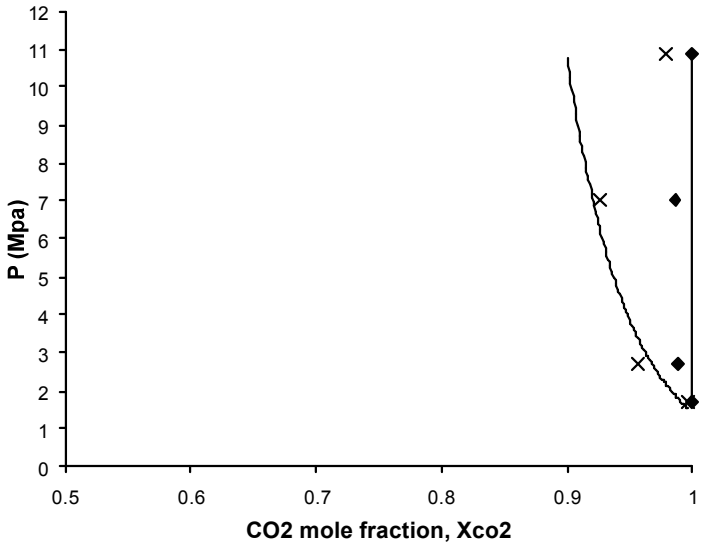

Fig. 3: Two-phase equilibrium diagram for POP at temperature of 80ºC
♦ : vapor phase, ×: liquid phase

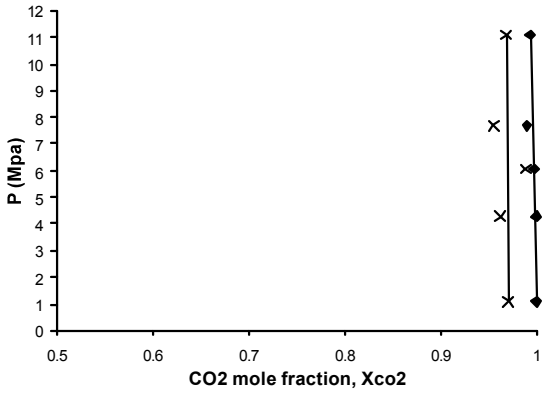

Fig. 4: Two-phase equilibrium diagram for POP at temperature of 100ºC
♦ : vapor phase, ×: liquid phase

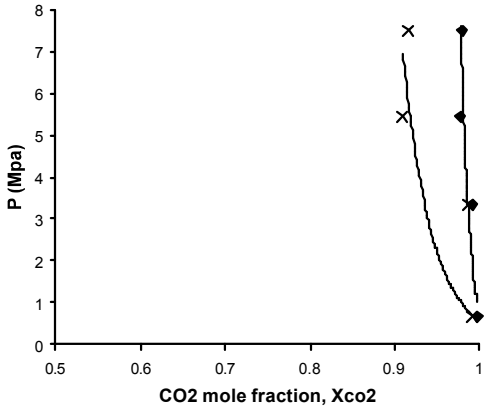

Fig. 5: Two-phase equilibrium diagram for POP at temperature of 120ºC
♦ : vapor phase, ×: liquid phase

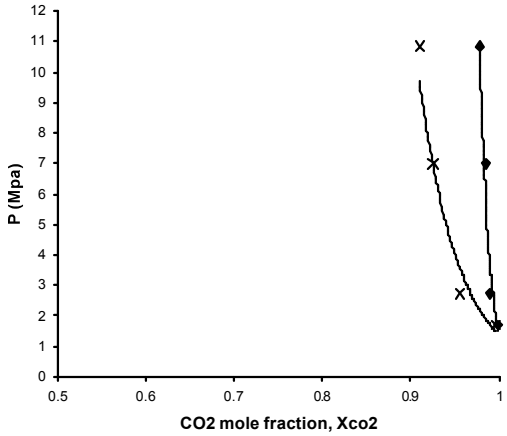

Fig. 6: Two-phase equilibrium diagram for POO at temperature of 80ºC
♦ : vapor phase, ×: liquid phase

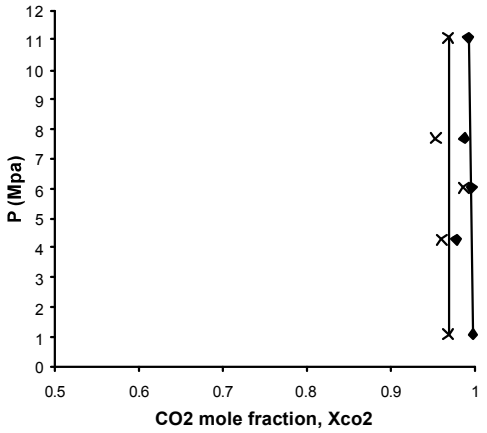

Fig. 7: Two-phase equilibrium diagram for POO at temperature of 100ºC
♦ : vapor phase, ×: liquid phase

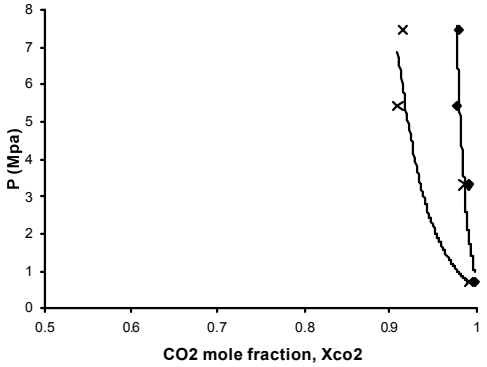

Fig. 8: Two-phase equilibrium diagram for POO at temperature of 120ºC
♦ : vapor phase, ×: liquid phase

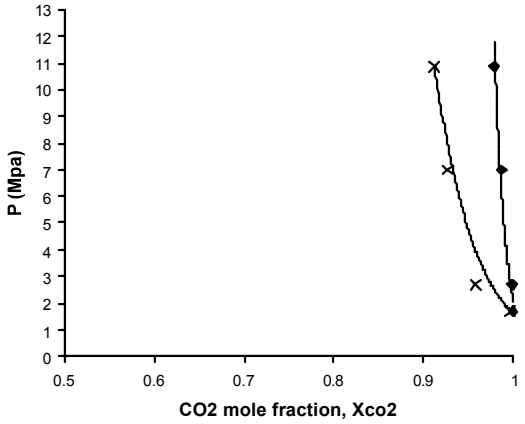

Fig. 9: Two-phase equilibrium diagram for SOO at temperature of 80ºC
♦ : vapor phase, ×: liquid phase

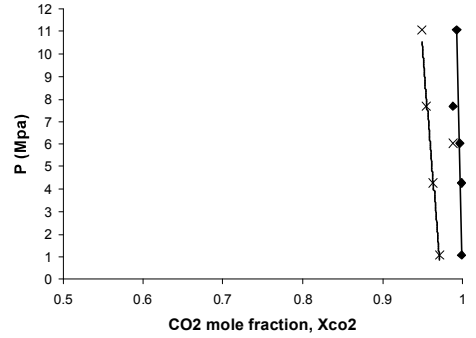

Fig. 10: Two-phase equilibrium diagram for SOO at temperature of 100°C
◆: vapor phase, ×: liquid phase

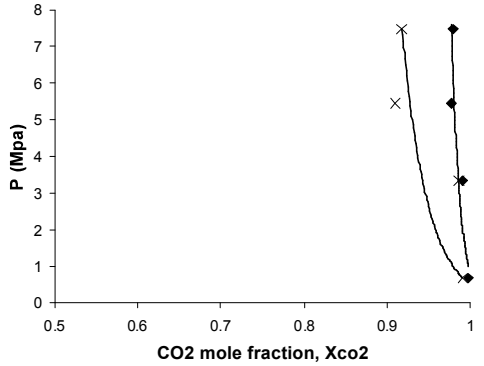

Fig. 11: Two-phase equilibrium diagram for SOO at temperature of 120°C
◆: vapor phase, ×: liquid phase

On the other hand, experimental results showed that although highest extraction using CO_2 was observed at 120°C and at 5.4 MPa for all of the substances but, maximum solubilities at the mentioned operating conditions were obtained for POP (y=0.977303094), POO (y=0.977318187) and SOO (y=0.977321253) respectively. The obtained result was confirmed by the overall conclusion which stated that the fats and oils composed of shorter chain fatty acids are more soluble than those with longer chain fatty acids [10]. Soares *et al.* also illustrated that high temperature had a desired effect on TAGs solubility in CO_2 as this output was obtained from the current research as well [9].

Tan *et al.* also confirmed that high temperature had a positive effect on TAGs extraction using CO_2 [16]. In order to this research, monounsaturated fatty acids (such as POP) had a maximum yield of extraction in supercritical CO_2 as this output was obtained from our research. Although they proposed high pressures for supercritical extraction of TAGs but they conducted their experiments at operating pressures more than 10 MPa and they studied yield of extraction.

CONCLUSION

In this study, it shows that high pressure carbon dioxide is a useful solvent for producing crude palm oil fractions that differ markedly in their properties. It concludes that the best condition for TAGs supercritical extraction related to the vapor phase is obtained at pressure of 5.4 MPa and at temperature of 120°C. Therefore, a maximum extraction was obtained by applying a middle pressure and rather high temperature in equilibrium condition. Furthermore, it concludes that the lighter TAG is more soluble than the heavier ones. Consequently, the resultant fractions may be a potential candidate in a wide variety of food applications. For example, use of high-melting fractions in palm oil in solid form would enhance its melting properties and a low-melting fraction may be used in the preparation of liquid palm oil. Supercritical extraction process using CO_2 is introduced as a safe and efficient method to reduce some of the TAGs from palm oil to make it as general oil. Even this refined oil from TAGs can be consumed by people who suffer from high fatty properties in their blood. Furthermore, this method is found as a safe source for providing the necessary fatties in some industries such as cosmetic industries.

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REFERENCES

1. Gunstone, F.D., 1987. Palm Oil. Society of Chemical Industry, UK.
2. Hawthorne, S., 1990. Analytical-scale Fluid Extraction. Anal. Chem., 62 (11): 533A-642A.
3. Macías-Sánchez, M.D., C. Mantell, M. Rodríguez, E. Martínez de la Ossa, L.M. Lubián and O. Montero, 2005. Supercritical Fluid Extraction of Carotenoids and Chlorophyll *a* from Nannochloropsis Gaditana. J. Food Eng., 66 (2): 245-251.

4. Sambanthamurthi, R., K. Sundram and Yew-Ai Tan, 2000. Chemistry and Biochemistry of Palm Oil. Progress in Lipid Res., 39 (6): 507-558.
5. Ucciani, E. and A. Debal, 1996. Chemical properties of fats. In: Oils & Fats Manual, Eds. Karleskind A and J.P. Wolff. Intercept Ltd. Andover, pp: 325-443.
6. Kifli, H., 1981. Studies on palm oil with special reference to interesterification, PhD thesis, University of St. Andrews, UK.
7. Sow, H.P., 1979. Modification in the chemical composition of palm oil by physical, chemical and biochemical treatment, Ph.D thesis, Universiti Sains Malaysia, Malaysia.
8. Maheshwari, P., Z.L. Nikolov, T.M. White and R. Hartel, 1992. Solubility of Fatty Acids in Supercritical Carbon Dioxide. J. Am. Oil Chem. Soc., 69 (11): 1069-1076.
9. Soares, B.M.C., F.M.C. Gamarra, L.C. Paviani, L.A.G. Gonçalves and F.A. Cabral, 2007. Solubility of Triacylglycerols in Supercritical Carbon Dioxide. J. Supercrit. Fluids, 43 (1): 25-31.
10. Fatouh, A.E., A. Mahran, M.A. El-Ghandour and R.K. Singh, 2007. Fractionation of Buffalo Butter Oil by Supercritical Carbon Dioxide. LWT-Food Sci. Tech., 40 (10): 1687-1693.
11. Bamberger, T., J.C. Erickson, C.L. Cooney, S.K. Kumar, 1988. Measurement and Model Prediction of Solubilities of Pure Fatty Acids, Pure Triglycerides, and Mixtures of Triglycerides in Supercritical Carbon Dioxide. J. Chem. Eng. Data, 33(3): 327-333.
12. Weber, W., S. Petkov and G. Brunner, 1999, Vapour–liquid-equilibria and Calculations Using the Redlich–Kwong–Aspen–equation of State for Tristearin, Tripalmitin, and Triolein in CO_2 and propane. Fluid Phase Equilib., 158 (1): 695-706.
13. Sovová, H., Z. Marie, V. Miroslav, S. Karel, 2001. Solubility of Two Vegetable Oils in Supercritical Carbon Dioxide. J. Supercrit. Fluids, 20 (1): 15-28.
14. Temelli, F., 1992. Extraction of Triglycerides and Phospholipids from Canola with Supercritical Carbon Dioxide and Ethanol. J. Food Sci., 57 (2): 440-457.
15. Bravi, E., G. Perretti, L. Montanari, F. Favati and P. Fantozzi, 2007. Supercritical Fluid Extraction for Quality Control in Beer Industry. J. Supercrit. Fluids, 42 (3): 342-346.
16. Tan, T.J., S. Jinap, A.E. Kusnadi and N.S. Abdul Hamid, 2008. Extraction of Cocoa Butter by Supercritical Carbon Dioxide: Optimization of Operating Conditions and Effect of Particle Size. J. Food Lipids, 15: 263-276.
17. Kassim, K.M., R. Davarnejad and A. Zainal, 2008. Phase Equilibrium Studying for the Supercritical Fluid Extraction Process Using Carbon Dioxide Solvent with 1.35 Mole Ratio of Octane to Ethanol Mixture. Chemical Eng. J., 140 (1-3): 173-182.
18. Davarnejad, R., K.M. Kassim, A. Zainal and A.S. Suhairi, 2008. Mutual Solubility Study for 94.2: 5.8 of Ethanol to Octane with Supercritical Carbon Dioxide Solvent. J. Chinese Inst. Chem. Eng., 39 (4): 343-352.
19. Kassim, K.M. and R. Davarnejad, 2007. Supercritical Fluid Extraction of Binary Systems of Monoolein, Diolein and Triolein, Using Carbon Dioxide Solvent. Int. J. Chemical Reactor Eng., 5 (A45): 1-9.
20. King, M.B., D.A. Alderson, F.H. Fallah, D.M. Kassim, K.M. Kassim, J.R. Sheldon and R.S. Mahmud, 1983, Chemical Engineering at Supercritical Fluid Conditions (Chapter 1), Paulaitis, M.E., J.M.L. Penninger, R.D. Gray Jr., P. Davidson (Eds.). Ann Arbor Science. Ann Arbor, MI.

NOMENCLATURE

Symbol	Description
$(nx_1)^L$	Number of moles of TAG in the liquid phase on a carbon dioxide free basis.
$(nx_1)^G$	Number of moles of TAG in the vapor phase on a carbon dioxide free basis.
$(nx_2)^L$	Number of moles of palm oil in the liquid phase on a carbon dioxide free basis.
$(nx_2)^G$	Number of moles of palm oil in the vapor phase on a carbon dioxide free basis.
x_1	Mole fractions of TAG in the liquid phase on a carbon dioxide free basis.
y_1	Mole fractions of TAG in the vapor phase on a carbon dioxide free basis.
x	Mole fraction of carbon dioxide in the liquid phase.
y	Mole fraction of carbon dioxide in the vapor phase.
$(ny)^G$	Number of moles of carbon dioxide in the vapor sample bomb.
$(nx)^G$	Number of moles of heavy component (TAG) in the vapo sample bomb.
$(ny)^L$	Number of moles of carbon dioxide in the liquid sample bomb.
$(nx)^L$	Number of moles of heavy component (TAG) in the liquid sample bomb.
V	System volume.
B_v	Second virial coefficient.
P	System pressure.
P_1	Expansion vessel pressure before expansion.
P_2	Expansion vessel pressure after expansion.
T	System temperature.