

Phase Behaviour of Palm Oil Fatty Acid Components in Supercritical Carbon Dioxide

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Abstract: In the supercritical CO₂ method of extraction of palm oil, many processes in conventional method, such as degumming, deodorization, refining and bleaching processes, are eliminated. The supercritical method allows palm oil to be extracted and fractionated simultaneously, which not only reduces the cost of processing, but also provides a more environmental-friendly processing alternative. In this research, the high-pressure phase behaviour of the binary system between supercritical carbon dioxide (SC-CO₂) and palm oil fatty acid components were investigated. The phase transition is observed from a camera which is connected to a high-pressure variable-volume view cell. Carbon dioxide has high solvating power, nontoxic, inflammable and low critical points. The determination of phase behaviour could offer an insight to the right operating condition of palm oil supercritical fluid carbon dioxide extraction process in order to acquire the desired extraction selectivity and an optimum yield. The phase boundaries of some fatty acids components, lauric acid (C12), stearic acid (C18), and oleic acid (C18) in compressed supercritical carbon dioxide were determined at temperatures of 313.15 K, 323.15 K, 333.15 K, 343.15 K and 353.15 K under pressures between 10 MPa and 60 MPa.

Key words: Fatty acid; Palm oil; Phase behaviour; Phase equilibrium; Supercritical fluid CO₂.

INTRODUCTION

Supercritical extraction of vegetable oil provides a short-cut process compared to the conventional process. The steps in the phase behaviour process that was performed with binary mixtures using supercritical CO₂ can eliminate degumming process, deodorization process, refining process, and bleaching process because the oil can be extracted and fractionated simultaneously. From phase behaviour data, thermodynamic modeling can be done and some refinery process such as clarification, degumming, bleaching, and deodorization can be replaced with a single unit operation by utilizing supercritical CO₂.

Supercritical fluids are substances at pressure and temperature above their critical values. In the supercritical region of a fluid, the phase state resembles one of a dense gas with properties that are generally intermediate to those of a gas and liquid. In the supercritical state, liquid like density is approached, while viscosity is near that of normal gases, and diffusivity is about two orders of magnitude higher than in typical liquid [1].

Supercritical carbon dioxide (SC-CO₂) has been attracting research activity around the globe due to its relatively low critical temperature (31.1°C) and

critical pressure (7.34 MPa). Using SC-CO₂ as a solvent, allows extraction processes to operate near ambient temperature. Furthermore, SC-CO₂ is nontoxic, and can be used in food grade form for food processing, and is considered to be an environmentally friendly solvent. Several articles have been published in the application of supercritical CO₂ in palm oil and palm kernel oil processing. Bisunadan [2] examined supercritical extraction of oil from palm fruits. Extraction and fractionation of palm kernel oil has been reported by Hassan et al. [3]. The extraction of palm kernel oil using supercritical CO₂ to produce cocoa butter equivalent fat has been reported by Md Zaidul et al. [4] and Nik Norulaini et al. [5].

Studies on fatty acid phase behaviour have also been reported. Bharath et al. [6] examined phase equilibrium data of triglyceride (C24, C36, C48)-CO₂ and fatty acid (C6, C12, C16)-CO₂. Chen et al. [7] measured phase equilibrium of linoleic acid, α -tocopherol and triolein in supercritical CO₂.

The application of the supercritical fluid CO₂ (SF-CO₂) has been reported as an alternative to palm oil/palm kernel oil conventional extraction process. The optimization of extraction efficiency and its selectivity generally concentrate on varying the temperature and pressure as well as the solvent modifier.

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The scope of the research included experiments conducted using static synthetic method in a high-pressure variable-volume view cell which examines the phase behaviour within the temperature and pressure ranges from 313.15 to 353.15 K and from 10 to 50 MPa, respectively. The phase transitions, which are observed as bubble point's data, were determined. The bubble point is the point at which the first bubble of gas forms.

The objectives of the research are to determine the phase behaviours of crude palm oil (CPO) and its fatty acid components (Oleic, Stearic and Lauric) in compressed carbon dioxide.

Phase Behaviour of Palm Oil and Its Components with CO₂:

In supercritical extraction, the solutes are mixed with supercritical carbon dioxide. It is important to understand the phase behaviour of mixtures of solutes since the solvent properties affect the solute solubility, mixture density, viscosity and mass transfer which consequently affect the extraction efficiency. When pressure is varied at constant temperatures, the density of CO₂ changes greatly especially in the critical region of carbon dioxide (more than 31°C, 7.3 MPa). Demonstration of data for the phase diagram of carbon dioxide calculated from the Equation of Span and Wagner is discussed in the literature [8]. For example, at 40°C when pressure is increased from 2 MPa to about 25 MPa, the CO₂

solvent density changes from about 40 kg/m³ to 880 kg/m³ as reported by Span and Wagner [8]. The change in density occurs without phase change, indicating that other properties such as viscosity; thermal conductivity etc. can be varied in a similar manner. Hence, it is important to understand the properties and behaviour of these mixtures in order to understand the extraction mechanism which subsequently can be used in developing extraction correlations and models.

In the extraction of palm oil using supercritical CO₂, it is important to understand the phase behaviour of palm oil and carbon dioxide that occurs in the process. Palm oil consists of the five major components which are palmitic acid, oleic acid, stearic acid, lauric acid, and myristic acid. However, in this paper, only results of oleic, stearic and lauric acid are reported.

EXPERIMENTAL

Materials and Chemicals: Palm oil was collected from Wilmar Sdn. Bhd., Penang. Chemically Pure (CP) grade liquidified carbon dioxide (purity, 99.995%) was purchased from MOX-Linde Gases Sdn. Bhd., Penang. The fatty acids, n-hexane, and other chemicals were obtained from Sigma, and R&M marketing (Kuala Lumpur).

Table 1: Table of fatty acid constituents, formulas, and types

Chemicals	Formula	Type
Lauric Acid	C ₁₂ H ₂₄ O ₂	Saturated
Myristic Acid	C ₁₄ H ₂₈ O ₂	
Palmitic Acid	C ₁₆ H ₃₂ O ₂	
*Stearic Acid	C ₁₈ H ₃₆ O ₂	
Oleic Acid	C ₁₈ H ₃₄ O ₂	
		Monounsaturated

Apparatus and Method: The phase equilibrium data (cloud points) were measured employing synthetic method in high-pressure variable-volume-view cell. The measured weights of the samples were introduced into the view cell. Before CO₂ was introduced, the cell vent valve was opened and CO₂ was allowed to flow for about 15 seconds before being purged. CO₂ was introduced from a cylinder to the cell until the cell is completely filled. Experiments were carried out at isothermal condition. Pressures were varied by turning the pump piston wheel at constant temperature. Naked-eye observations and camera recordings were conducted using a video camera which was connected to a computer. The phase transition which was observed visually through the computer screen was recorded in a compact disc or hard disk.

Fig. 1 shows a schematic diagram of a high-pressure variable-volume-cell of the supercritical fluid system. This equipment allows observation of phase behaviour of any solutions, including binary mixture of palm oil

and its components with carbon dioxide. The figure shows all the main components of experimental system which are CO₂ cylinder, view cell chamber (sample feeder 30 mL), manual hand pump, video camera, and computer. The CP Grade CO₂ was introduced to the sample view-cell-chamber from CO₂ cylinder tank. The sample view-cell-chamber can hold 30 mL mixture of solutions. The purpose of the hand pump is to vary the pressure pressed into the sample feeder so that the changes of phases can be observed. The pressure rate purged into the sample feeder was maintained below 15 psi/second so that there were no drastic changes on the phase behaviour. The video camera recorded all the activity observed in the view-cell. These records were then saved in the computer hard disk.

Fig. 2 shows the phase behaviour experimental set-up. The system consists of a CO₂ cylinder tank, weighting scale, SFT Phase Monitoring Equipment, and the computer.

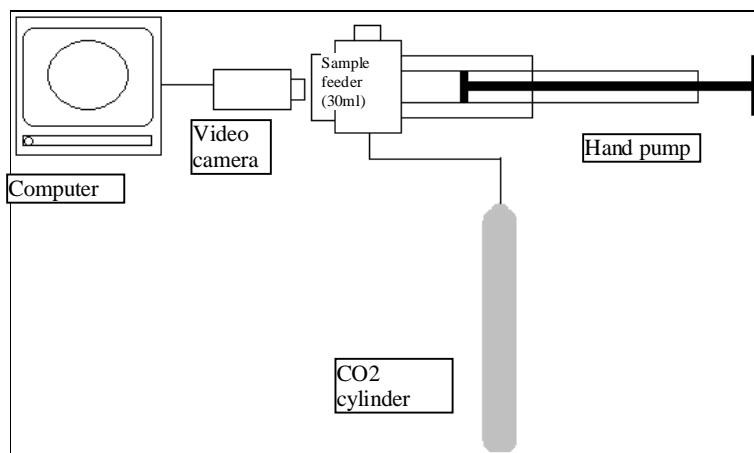


Fig. 1: Schematic diagram of high-pressure variable-volume-cell of supercritical fluid technology system



Fig. 2: Supercritical fluid technology phase behaviour monitoring system

RESULTS AND DISCUSSION

The binary mixture of palm oil and its components with supercritical carbon dioxide were observed through video camera. Once the mixtures achieved equilibrium phase at fixed temperature (K) and already varied pressure, the data obtained were recorded in the computer (values, pictures or videos). Fig. 3 shows the bubbling of oleic acid and CO₂, viewed from the camera.

Phase Equilibrium Data of Fatty Acids: Table 2 shows the data of temperature, pressure, and CO₂ mole fraction at phase equilibrium for binary mixture of oleic acid in carbon dioxide. Figs. 4(a) and 4(b) show the trend of the phase based on the pressure, temperature, and mole fraction. Fig. 4(a) shows that the higher the temperature, the higher pressure is required to achieve phase equilibrium. On the other hand, Fig. 4(b) shows that the higher the mole fraction of CO₂, the lower pressure is required to achieve phase equilibrium.

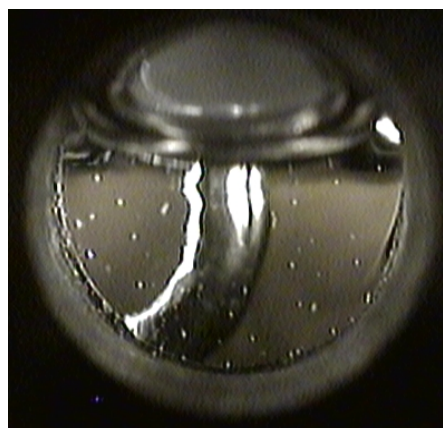
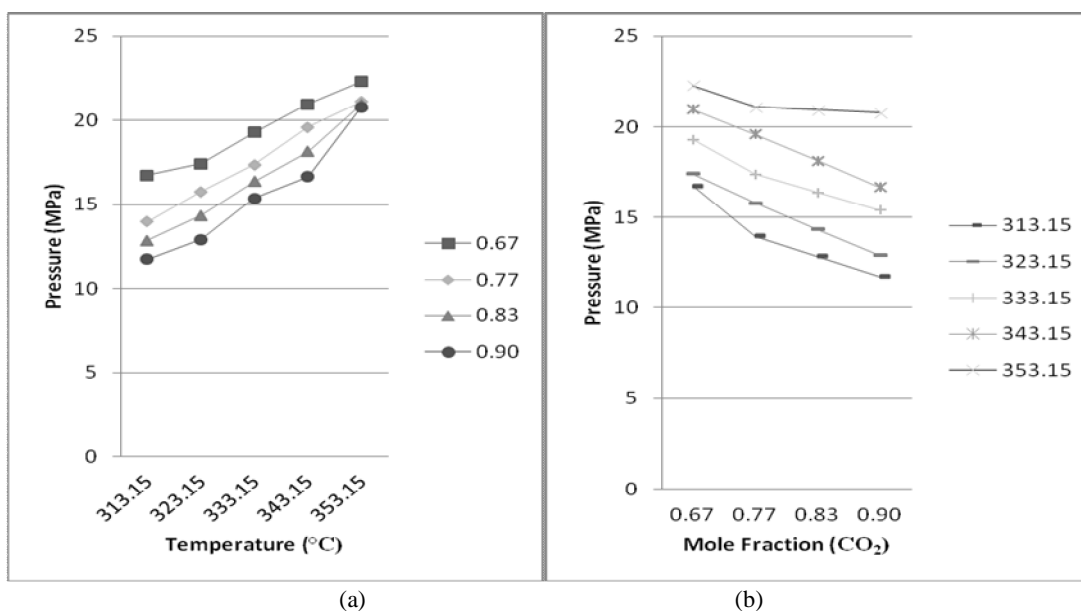


Fig. 3: Visual of oleic acid with CO₂ viewed from the camera at 40.0°C, 16.75 MPa

Table 2: Oleic acid (C18) + carbon dioxide phase equilibrium data

x_{CO_2}	0.67		0.77		0.83		0.90	
T (K)	P		P		P		P	
	psi	MPa	psi	MPa	psi	MPa	psi	MPa
313.15	2429	16.75	2026	13.97	1864	12.85	1701	11.73
323.15	2525	17.41	2288	15.78	2080	14.34	1872	12.91
333.15	2797	19.28	2520	17.37	2375	16.37	2230	15.38
343.15	3041	20.97	2841	19.59	2629	18.13	2417	16.66
353.15	3235	22.30	3061	21.10	3037	20.94	3013	20.77

Fig. 4: Phase equilibrium cloud points of pressure (MPa) vs temperature (°C) and mole fraction (CO_2) for oleic acid

The same trend is observed on the binary mixture containing stearic acid and CO_2 , as shown in Table 3 and Fig. 5. However, there are differences in the actual pressure and temperature equilibrium values. At $x_{CO_2} = 0.67$ and $T = 323.15$ K, the pressure needed by oleic

acid to achieve phase equilibrium is 17.41 MPa compared to that of stearic acid which is at 20.50 MPa. At $x_{CO_2} = 0.67$ and $T = 353.15$ K, the pressure required to achieve equilibrium is at 22.30 MPa for oleic acid and for stearic acid, 28.25 MPa.

Table 3: Stearic acid (C18) + carbon dioxide phase equilibrium data

x_{CO_2}	0.67		0.77		0.83		0.90	
T (K)	P		P		P		P	
	psi	MPa	psi	MPa	psi	MPa	psi	MPa
313.15	-	-	-	-	-	-	-	-
323.15	2974	20.50	2515	17.34	1966	13.96	1860	12.82
333.15	3458	23.84	2942	20.28	2348	16.19	2046	14.11
343.15	3748	25.84	3369	23.23	2557	17.63	2125	14.65
353.15	4098	28.25	3725	25.68	2825	19.48	2305	15.89

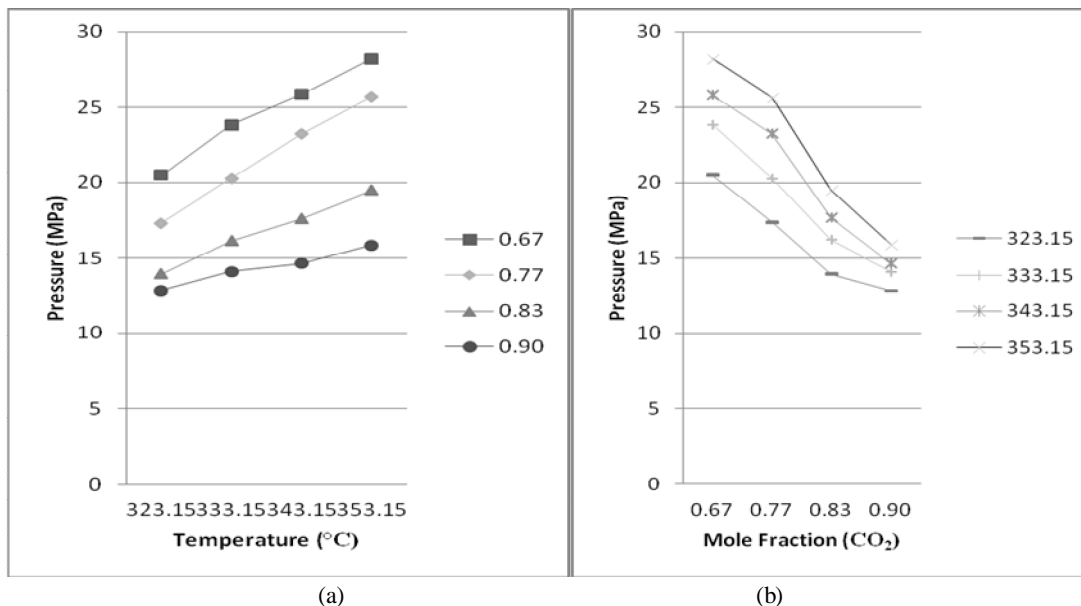


Fig. 5: Phase equilibrium cloud points of pressure (MPa) vs temperature (°C) and mole fraction (CO₂) for stearic acid

The differences in the equilibrium data between stearic acid and oleic acid is actually due to the differences in the molecular structure of both acids. Oleic acid is a monounsaturated acid with the molecular formula of C₁₈H₃₄O₂ while stearic acid is a saturated molecule with the molecular formula of C₁₈H₃₆O₂. The number of hydrogen bonds in stearic acid is more than that of oleic acid, thus more energy is required to weaken the hydrogen bonds in stearic acid as compared to oleic acid.

Table 4 and Fig. 6 show the phase equilibrium data for a mixture of lauric acid and CO₂. Lauric acid is categorized as saturated type, the same as stearic acid, but compared to oleic acid, it has a lower carbon and hydrogen molecules (C₁₂H₂₄O₂). Therefore, the pressure needed to achieve equilibrium is lower than that of oleic acid, as evident in Fig. 6. For example, at $x_{CO_2} = 0.67$ and $T = 353.15$ K, the pressure needed to achieve equilibrium is at 18.46 MPa for lauric acid, while the pressure needed by oleic acid is 22.30 MPa.

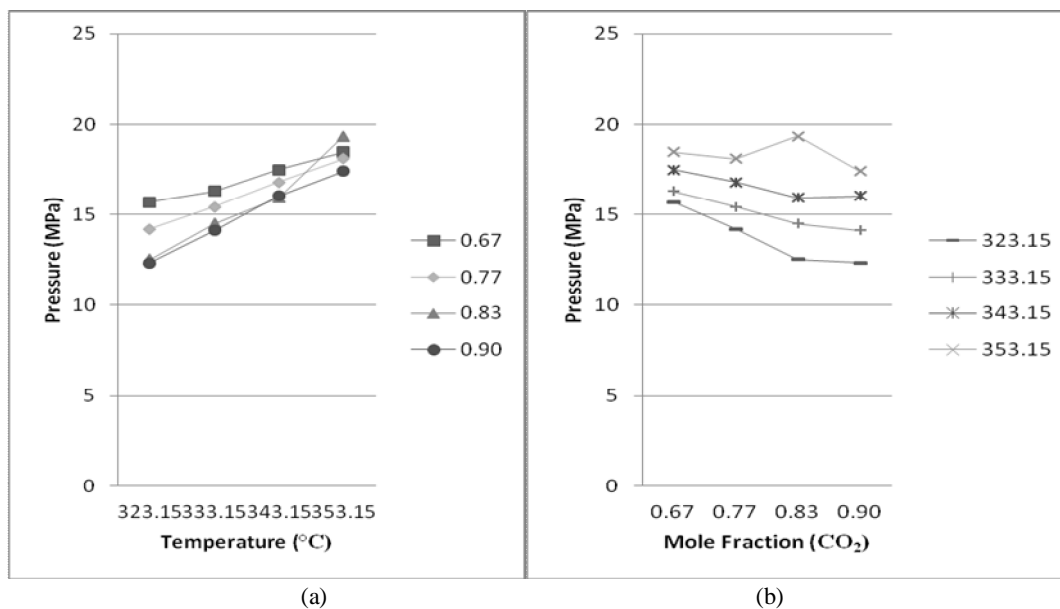


Fig. 6: Phase equilibrium cloud points of temperature (°C) and mole fraction (CO₂) versus pressure (MPa) for lauric acid

Table 4: Lauric acid (C12) + carbon dioxide phase equilibrium data

x_{CO_2}	0.67		0.77		0.83		0.90	
T (K)	P		P		P		P	
	psi	MPa	psi	MPa	psi	MPa	psi	MPa
313.15	-	-	-	-	-	-	-	-
323.15	2275	15.69	2059	14.2	1817	12.53	1788	12.33
333.15	2362	16.29	2235	15.41	1747	12.05	2075	14.13
343.15	2535	17.48	2436	16.80	2309	15.92	2324	16.02
353.15	2677	18.46	2625	18.10	2805	19.34	2525	17.41

Phase Equilibrium Data for Crude Palm Oil: The trend for the binary mixture of crude palm oil and CO_2 is similar to the trend of its fatty acid components. Fig. 7(a) shows that the higher the temperature, the higher pressure is required to achieve phase equilibrium. Fig. 7(b) shows that the higher the mole fraction of CO_2 , the lower pressure is required to achieve phase equilibrium. However, the trend was a bit different because at $x_{CO_2} = 0.77$ and $x_{CO_2} = 0.83$, the trend shows reverse data of

phase equilibrium points for each temperature range from 313.15 K to 353.15 K.

The pressure needed to achieve phase equilibrium for CPO at every temperature is the highest compared to other fatty acids components discussed above, i.e. lauric, oleic and stearic acids. For example, at $x_{CO_2} = 0.67$ and $T = 353.15$ K, the pressure needed by crude palm oil is 30.92 MPa, while the pressure needed by lauric acid is 18.46 MPa, oleic acid is 22.30 MPa, and stearic acid is 28.25 MPa to achieve the phase equilibriums.

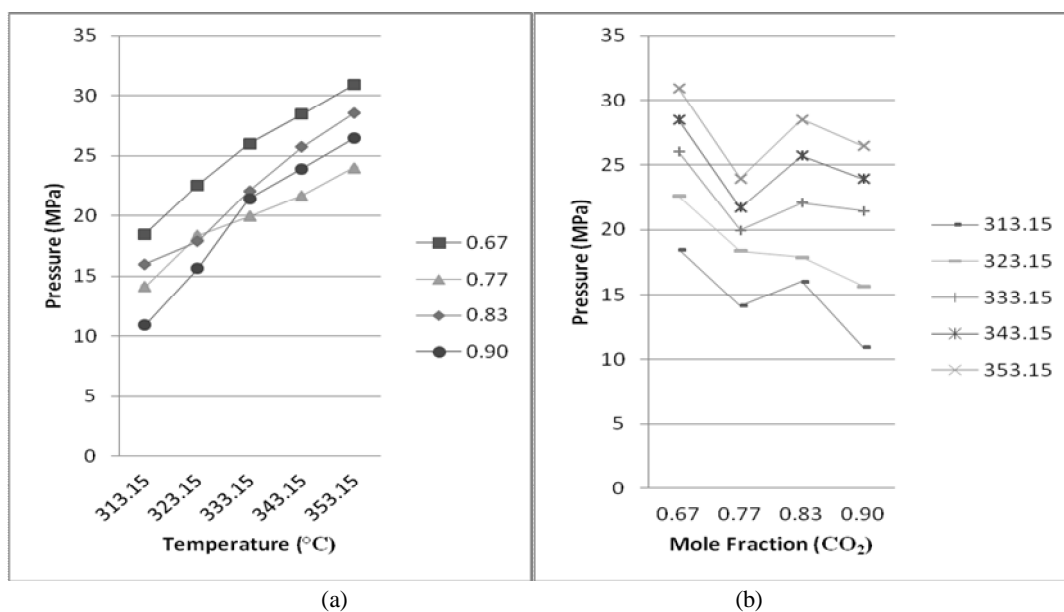


Fig. 7: Phase equilibrium cloud points of temperature ($^{\circ}C$) and mole fraction (CO_2) versus pressure (MPa) for crude palm oil

Table 5: Crude palm oil + carbon dioxide phase equilibrium data

x_{CO_2}	0.67		0.77		0.83		0.90	
T (K)	P		P		P		P	
	psi	MPa	psi	MPa	(psi)	(MPa)	psi	MPa
313.15	2680	18.48	2048	14.12	2322	16.01	1585	10.93
323.15	3274	22.57	2662	18.35	2539	17.88	2268	15.64
333.15	3773	26.01	2894	19.95	3203	22.08	3108	21.43
343.15	4125	28.44	3145	21.68	3729	25.71	3471	23.93
353.15	4484	30.92	3478	23.98	4133	28.50	3835	26.44

CONCLUSION

In extraction processes with supercritical carbon dioxide, the phase behaviour of palm oil and its components with CO₂ is one of the most important factors that influence extraction results. In this study, fundamental equilibrium data for palm oil and its fatty acid components, with supercritical CO₂ were determined.

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