초임계 이산화탄소를 이용한 Palm oil /Palm kernel oil 의 상평형 실험

홍승아, 김재덕*, 강익중 [1]
한국과학기술연구원, [1] 경원대학교
(jdkim@kist.re.kr*)

Phase Equilibria of Palm Oil and Palm Kernel Oil with Supercritical Carbon Dioxide

Seung-A Hong, Jae-Duck Kim*, Ik-Joong Kang[1]
Supercritical Fluid Research Laboratory, Korea Institute of Science and Technology (KIST),
[1]Dept. of Chemical & Bioengineering, Kyungwon Univ.
(jdkim@kist.re.kr*)

1. INTRODUCTION

More than 90% of the world production of fats and oils are used for foodstuff [1]. One of the major edible oils consumed worldwide is palm oil / palm kernel oil. Although it lies within the palm nut, palm kernel oil and palm oil differ greatly in their characteristics and properties.

Supercritical fluid extraction is a promising method to manufacture diet food from fatted raw material because CO_2 as a supercritical (SC) solvent is non toxic, cheap and clean. Phase equilibria data are necessary to develop the manufacturing process to produce the defatted food by SC carbon dioxide. Unfortunately, phase equilibria data between palm kernel oil and SC carbon dioxide are scarce at various ranges of temperature and pressure.

2. MATERIALS AND METHODS

2.1. Materials

The palm oil / palm kernel oil and CO_2, used in this experiment, was provided by Lotte Samgang Co. and Shinhan Sanso Co. respectively. The purity of CO_2 was 99.95 (wt%). Table. 1 shows the palm oil / palm kernel oil's property.

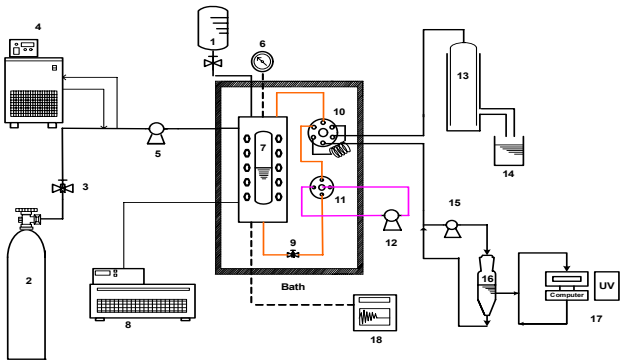
Table. 1. Palm oil / palm kernel oil's property

	Acid Value	Saponification Value	Peroxide Value	Refractive Index (40.2℃)	Specific Gravity (40℃/25℃)
Palm oil	0.22	192	412	1.46	0.91
Palm kernel oil	0.87	241	41.7	1.45	1.04

2.2. Apparatus and procedure

A new circulation type experimental apparatus for measuring mutual solubilities between palm oil / palm kernel oil and SC carbon dioxide was installed. The schematic flow diagram of the experimental apparatus is shown in Figure 1. Experimental procedure is as follows: First,

palm oil was fed into the equilibrium cell and followed by CO_2. After confirming the temperature of the cell and bath were maintained constant (± 0.1°C), CO_2 was supplied once more to the cell until it reach the desired pressure. CO_2 phase was selected and circulates first for six hours. As shown in Figure 2, it seems that six hours circulation is enough to reach the equilibrium.



1. Oil Storage Tank
2. CO_2 Cylinder
3. CO_2 Cylinder Valve
4. Low Temperature Circulator
5. Feed Pump
6. Pressure Gauge
7. Equilibrium Cell
8. Constant Temperature Circulator
9. Valve
10. Sampling Valve
11. Switching Valve
12. Circulation Pump
13. Vapor Holder
14. Water Receiver
15. Solvent Pump
16. Solvent Reservoir
17. UV Detector
18. Temperature recorder

Figure 1. A schematic diagram of the experimental setup for phase equilibrium measurement

After convincing the equilibrium, sample was taken by sampling valve and determined the quantities of CO_2 and palm oil. CO_2 was depressurized to atmospheric pressure and measured the gas volume in the vapor holder. Palm oil, remained in sampling valve after CO_2 depressurization, was dissolve by n-Hexane and was analyzed by UV-VIS Spectrophotometer (Jasco V-500). Meanwhile, palm oil phase with dissolved CO_2 of the cell was selected and circulated secondly as that of carbon dioxide phase. The experiment on palm kernel oil is made in the same way of palm oil experiment.

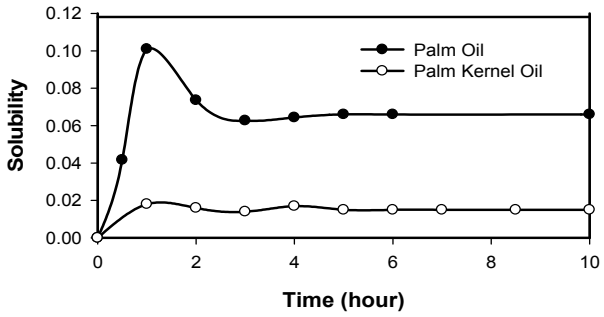


Figure 2. Solubility for the system Palm oil, Palm kernel oil with carbon dioxide

2.3. Fatty acid analysis

The fatty acid were analysed using a Hewlett Packard gas chromatography (Model HP5890)

equipped with an FID detector. The column used for the GC analysis was a 100/120 mesh Chromosorb W-HP packed column (10% Silar 7CP 1/8" 3.0 m coating). The oven temperature was 185℃ and raised to 240℃ at a gradient of 1.3℃/min. The injector temperature was set at 250℃. The detector temperature was set at 280℃.

3. RESULTS AND DISCUSSIONS

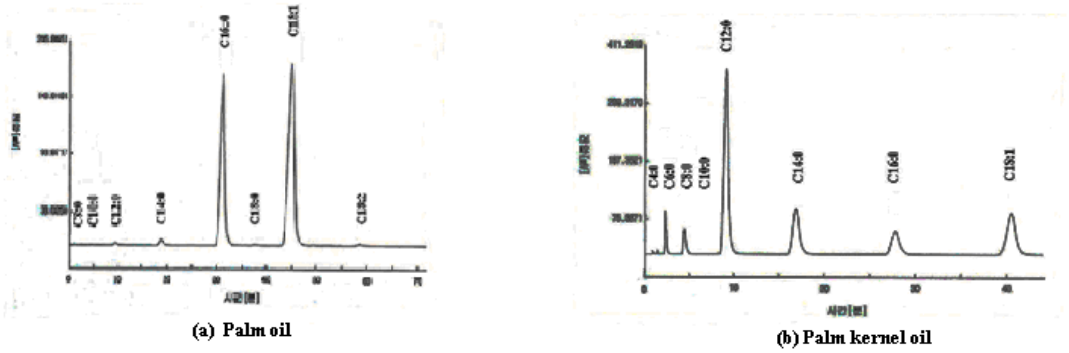


Figure 3. GC chromatogram of palm oil (a) / palm kernel oil fatty acid (b)

Main fatty acids of palm oil was: C8:0(0.04%), C10:0(0.01%), C12:0 (0.01%), C14:0(1.08%), C16:0(43.3%), C18:0(0.01%), C18:1(55.3%), C18:2(0.33%). Main fatty acids of palm kernel oil was: C4:0(0.11%), C6:0(3.57%), C8:0(3.43%), C12:0(47.0%), C14:0(16.4%), C16:0(9.69%), C18:1(19.7%). Figure 4 shows the results of experimental data of the palm oil / palm kernel oil with SC carbon dioxide system at 333.15, 353.15 and 373.15 K and 85 ~ 350 bar. For all isotherms condition in this experiment, the solubility of palm oil / palm kernel oil with SC carbon dioxide is increasing meanwhile the solubility of carbon dioxide in palm oil / palm kernel oil is decreasing at higher pressure. This phenomenon is always occurred in the phase equilibria data of the oil and SC carbon dioxide system [2].

Phase equilibria data were correlated using the Peng-Robinson EOS[3] with the van der Waals mixing rule for binary interaction parameters.:

$$P=\frac{RT}{V-b}-\frac{\Theta(T)}{V(V+b)+b(V-b)}$$

The van der Waals mixing rules with the combining rules for two binary interaction parameters are given by the following equations:

$$a_m=\sum\sum x_i x_j a_{ij} \qquad b=\sum\sum x_i x_j b_{ij}$$

$$a_{ij}=\sqrt{a_{ii}a_{jj}}(1-k_{ij}) \qquad b_{ij}=\frac{1}{2}(b_{ii}+b_{jj})$$

The lines in the Figure 4 were calculated by the Peng-Robinson EOS. As shown in Figure 4, experimental data were well correlated by the Peng-Robinson EOS with reasonable errors. Figure 5 presents the interaction parameter obtained when the equillibria data were optimized

by the Peng-Robinson EOS modeling.

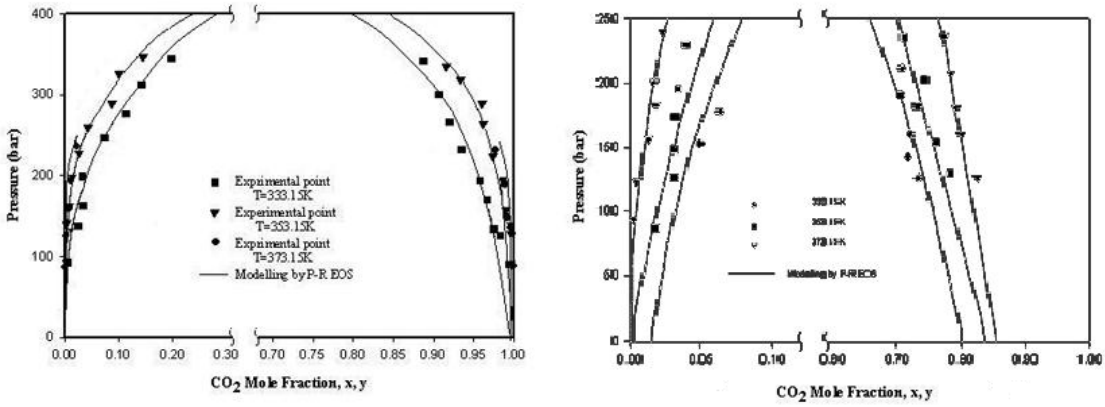


Figure 4. Experimental and calculated equilibrium data of palm oil(1) / palm kernel oil (2) and SC CO_2 system correlated with Peng-Robinson EOS

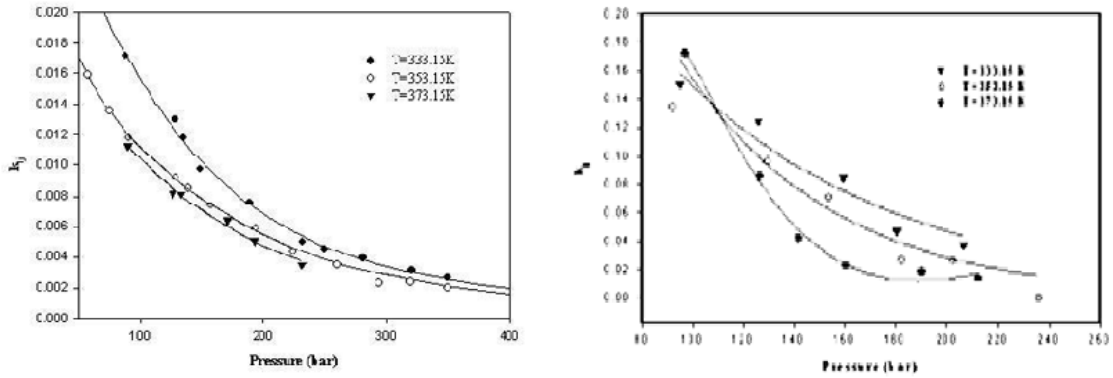


Figure 5. Binary interaction parameter of Peng-Robinson EOS

4. CONCLUSIONS

In this work, mutual solubilities of palm oil and palm kernel oil with carbon dioxide were measured in the new circulation type equilibria apparatus. The solubilities of palm oil and palm kernel oil in carbon dioxide were higher at lower temperature and higher pressure. The experimental data were well correlated with the Peng-Robinson EOS with van der Waals mixing rule.

REFERENCES

[1] SWERN(Ed.), D., Bailey's Industrial Oil and Fat Products, Wiley, New York, Vol.1, **1979**.

[2] RODRIGUES, J.E., ARAUJO, M.E., AZEVEDO, F.F.M. and MACHADO, N.T., "Phase equilibrium measurements of Brazil nut oil in supercritical carbon dioxide", J. of Supercritical Fluids, Vol.34, **2005**, p.223-229.

[3] PENG, D. Y., ROBINSON, D. B., "A new two-constant equation of state", Ind. Eng. Chem. Fundam. Vol.15, **1976**, p.58-64.