Modeling of *Moringa Oleifera* Oil Solubility in Supercritical Carbon Dioxide

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Abstract

*Moringa oleifera* (MO) oil solubility behavior in supercritical carbon dioxide (SC-CO2) was investigated at temperature range from 35 to 60°C and pressure from 15 to 30MPa. It was observed that pressure played key role on solubility while temperature has minor effect on solubility relative to that of pressure. Solubility was invariant with temperature. Solubility effect with temperature shifted to opposite behavior when pressure has reached the crossover pressure point at 26.38MPa. At p < 26.38MPa, an increased temperature has reduced the solubility. While at p ≥ 26.38MPa, the increased temperature led to an enhanced solubility. Fractionation of the oil during extraction period was observed too. Short chain fatty acids (C14:0, C16:0, C16:1) reduced by 21.87, 7.94 and 9.49% while long chain fatty acids (C20:0, C20:1, C22:0, C24:0) increased by 22.43, 11.42, 21.76 and 35.71% respectively. All C18 fatty acids (stearic, oleic, linoleic, linolenic) were not fractionated significantly during extraction period. Furthermore, modeling of MO oil solubility in SC-CO2 was conducted. Del Valle-Aguilera model with root mean square percentage deviation of 6.18% is recommended for high oleic oil solubility in SC-CO2.

Keywords: Modeling; *Moringa oleifera* oil; Solubility; Supercritical carbon dioxide

Introduction

*Moringa oleifera* (MO) is well known in Asian countries, Africa, South America, the Caribbean and Oceania [1,2]. Its popularity stems from the fact that the plant is a source of high nutritional food [3,4], medicine [5-8], cosmetic [9] and environmental application [10].

In recent years, supercritical fluids extraction using supercritical carbon dioxide (SC-CO2) has been widely attended by researchers and their successes cited in the fields of pharmaceuticals, food processing, environment, polymer and cosmetic. The green technology was applied widely because not only carbon dioxide is a non-toxic, cheap and non-flammable gas with low critical temperature of 35°C and relatively critical pressure of 7.4MPa, but its solvation power can also be varied widely with the change in pressure and temperature. An increase in pressure may results to increase in density, consequently, enhances the solvation power of SC-CO2. Thereby, solute solubility increases. The elevation of temperature leads to reduce solvation power due to decrease in density. Also, an contrast behavior is observed that the increased temperature may lead to enhance vapor pressure, consequently, improves solubility [11-15]. Solubility is commonly measured either dynamic or static method, in which, solvent is directly in contact with either liquid oil or ground material.

In this work, the dynamic method was employed where SC-CO2 was in direct contact with the ground MO kernels. The solubility behavior of MO oil in SC-CO2 was studied. The effects of pressure in the range from 15 to 30MPa and temperature from 35 to 60°C on the solubility behavior were investigated. Furthermore, modeling of solubility of the oil in SC-CO2 was conducted.

Materials and Methods

Materials

Air dried *Moringa oleifera* seeds (humidity 8.7%w/w) were used and sourced from Ilocos Norte and Ilocos Sur, Southern part of the Philippines. The seeds were de-coated and the good quality kernels, those are not moldy or breached were selected. MO kernels were ground few hours before extraction to minimize the effect of oxidation of the oil. Average particle size of the kernels at 0.64mm was used in the study.

Commercial CO2 was supplied by SUGECO (a local company). For fatty acid analysis, standard fatty acid methyl ester of myristic acid (C14:0), palmitic acid (C16:0), palmitoleic acid (C16:1), stearic acid (C18:0), oleic acid (C18:1), linoleic acid (C18:2), linolenic acid (C18:3), arachidic acid (C20:0), cis-11-eicosenoic acid (C20:1), behenic acid (C22:0), tetracosanoic acid (C24:0) and other chemicals such as n-hexane (GC analytical grade), methyl acetate (99.5%), acetic acid (99.7%), dehydrated diethyl ether (99.5%), sodium methoxide (0.5M) in dry methanol, solid sodium were all supplied by Sigma-Aldrich, Inc. and Wako Pure Chemical Industries, Ltd, Japan.


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Experiments

The extraction of MO oil using SC-CO₂ was carried out in the supercritical fluid extraction pilot plant (Akico, Japan) at the Department of Chemical Engineering Technology at MSU-IIT in Northern Mindanao, Philippines.

Figure 1A illustrates the multiple stages packed bed loaded with 70 g of the ground kernels in a 500 ml extractor arranged in four layers at 25 mm in thickness and 10 mm gap in between layers. The schematic of the pilot plant is shown in Figure 1B. The CO₂ from CO₂ tank was initial liquified prior to entering the high pressure pump (with maximum capacity of 35MPa). The CO₂ liquid was then heated by a heat transfer apparatus (maximum capacity of 100°C) to become SC-CO₂. In this work, the pressure of the SC-CO₂ was varied from 15 to 30 MPa and temperature was from 35 to 60°C. The SC-CO₂ flowed in the extractor and was directly in contact with the ground kernels. The CO₂ – oil solution from the extractor passed through the expansion valve where the oil was separated from CO₂. The oil was collected via a collector vessel and the CO₂ was released to the atmosphere at the flow rate of 0.45kg/h adequate to maintain the solvent saturated. For solubility determination, each experiment was performed in duplication and for about 20min in the first stage (the linear stage) of the supercritical fluids extraction. The solubility was based on the amount of oil and CO₂ by weight measurement.

GC analysis

To analyze the fatty acid components of MO oil, the oil was converted to fatty acid methyl esters using the method of Christie [16]. Up to 2mg of oil was dissolved by mixing 0.5mL sodium-dried diethyl ether, 20µL methyl acetate and 40µL sodium methoxide. After five minutes, the reaction was stopped by adding 2µL acetic acid. Nitrogen was used to evaporate the solvent and 1mL hexane was then added. The solid precipitate was separated from the solution by using centrifuge Hitachi CRG Series R20A2 at 4000 r/min for five minutes. The solution was injected into the capillary column SP-2560 (100m x 0.25mm ID, 0.25µm film) of the Gas Chromatograph GC-17A Shimadzu with helium as carrier gas. Operating temperature program for column was set at 140°C for 5 minutes then increased to 240°C at 4°C/min and withheld for 15 minutes.

Results and Discussion

Effect of pressure on solubility

Figure 2 indicates the effect of pressure on MO oil solubility in SC-CO₂. Pressure was varied from 15MPa to 30MPa while temperature was fixed. Three isothermal curves were generated at temperatures of 35°C, 47.5°C and 60°C.

It can be observed, that solubility increases at elevated pressure up to 30 MPa which can be attributed to enhance density, and therefore, improves the solvation power [12].

There was a convergence of the isotherms termed as crossover pressure point is approximately at 26.38MPa. The result agreed with the previous studies. Stahl and Quirin [17] reported that the crossover pressure point of solubility of soy-bean, rich in C18 fatty acid content, in SC-CO₂ was below 30MPa. The crossover pressure point of high oleic sunflower oil in SC-CO₂ was higher than 25MPa, reported by Kiriamiti [18]. In addition, Ozkal et al. [19] reported that the crossover pressure point of Hazelnuts oil (79% oleic acid) in SC-CO₂ was in between 15 and 30MPa.

Effect of temperature on solubility

The effect of temperature on MO oil solubility in SC-CO₂, is shown in Figure 3. The temperature was varied from 35°C to 60°C at constant pressure. Three isobaric curves were plotted at pressure of 15MPa, 22.5MPa and 30MPa.

At pressure lower than the crossover pressure point, 26.38MPa, the solubility was contra-varient with temperature change as illustrated in the isobaric curves at 15 and 22.5MPa. However, at the pressure of 26.38MPa and higher, the solubility increased at elevated temperature as indicated in the isobaric curve at 30MPa. This could be attributed to density decrease as temperature increases. Thereby, solvent solvation power decreases and consequently, reduces solubility. In other hand, increasing temperature improves the vapor pressure therefore solubility increases [20].

Moreover, the temperature contributed less impact on solubility compared with pressure. At low pressure, 15MPa, and increasing temperatures, the highest solubility achieved was lower than 2g/kg. While, in the care of high pressure, 30MPa, the lowest solubility was higher than 6g/kg.

Fractionation

Fractionation of oil in SC-CO₂ during the extraction period was reported by Sovova et al. [21] and Norulaini et al. [22]. Fatty acid composition of palm kernel oil varied with fractionation performed...
at pressure of 48.3 MPa and temperature of 80°C [22]. The percentage of short chain fatty acids (C8:0, C10:0, C12:0) in the oil was reduced during the extraction period. However, the amount of myristic acid (C14:0) did not change significantly. In the case of longer chain fatty acids (C16:0, C18:0, C18:1, C18:2), its yield was enhanced. Sovova et al. [21] reported that at temperature of 40°C and pressure up to 29 MPa, the percentage of free fatty acids, monoglycerides and diglycerides in grape seed oil decreased from first to last fraction but opposite phenomenon on triglycerides was observed, it was enhanced with time.

Ozkal et al. [19] reported that at pressure of 30 MPa and temperature of 40, 50 and 60°C, the hazelnut oil was not fractionated with time. The main fatty acid composition of hazenut oil such as stearic (C18:0, 2%), oleic (C18:1, 79%), linoleic (C18:2, 11%), palmitic (C16:0, 6%) and palmitoleic (C16:1, 0.15%) remained constant during the extraction period. However, the amount of myristic acid (C14:0) did not change significantly. In the care of longer chain fatty acids (C16:0, C18:0, C18:1, C18:2), its yield was enhanced. Sovova et al. [21] reported that at temperature of 40°C and pressure up to 29 MPa, the percentage of free fatty acids, monoglycerides and diglycerides in grape seed oil decreased from first to last fraction but opposite phenomenon on triglycerides was observed, it was enhanced with time.

In this work, three fractions were collected in the first 30 min, between 30 and 160 min, and from the first 160 min until the end of extraction after 7 hours. The experiments were conducted in duplication at pressure of 30 MPa, temperature of 60°C and CO2 flow of 0.45 kg/h. The fatty acid composition of MO seed oil in SC-CO2 of three fractions is shown in Table 1. Oleic (C18:1) was found as a main component with percentage of approximately 70%. The variation in the fatty acid composition of MO seed oil upon fractionation is highly noticeable. The percentage of deviation in fatty acids during extraction period was counted as the variation of those between the first fraction and last fraction. Short chain fatty acids such as myristic (C14:0), palmitic (C16:0) and palmitoleic (C16:1) decreased by 19.04, 8.40 and 12.87% during extraction time, respectively. All C18 fatty acids (stearic, oleic, linoleic and linolenic) did not change significantly. Longer chain fatty acids such as arachidic (C20:0), cis 11 eicosenoic (C20:1), behenic (C22:0) and tetracosanoic (C24:0) increased by 22.43, 16.15, 21.76 and 30.95%, respectively. In general, the results of this work agree with Norulaini et al. [22] where the shorter chain fatty acids were found to be more soluble than the longer one. The difference in the variation with fractionation of fatty acid in particular case between this work and others resulted in the difference in proportion of fatty acids, free fatty acid, monoglycerides, diglycerides and triglycerides in the oils. In addition, the difference in experimental conditions (pressure, temperature) may possibly led to the difference in solvent density and solute vapor pressure and consequently, generated variation in solubility of components.

Though the variation of some fatty acids composition with fractionation is significant, the impact on solubility is however minimal because the unchanged C18 fatty acids were predominant in the oil in [21].

**Model of solubility**

Chrastil [23] presented a model of solubility based on the proposition linear relationship between the logarithmic solubility and that of solvent density. Chrastil model also expressed the dependence of solubility on temperature. The expression of Chrastil model is:

\[ c = d^n \exp\left(a + \frac{a}{T}\right) \]  
(1)

where c is oil solubility (kg/m³), d is solvent density in kg/m³ and T is absolute temperature (K).

In 1983, Adachi-Lu [24] modified Chrastil model by improving the effect of density on solubility as follows:

\[ c = d^n \exp\left(a + \frac{a}{T}\right) \]  
(2)

Adachi-Lu model’s parameters units are same as in the Chrastil.

In 1988, Del Valle and Aguilera [25] developed Chrastil model to be more flexible with variation of temperature as shown below:

\[ c = d^n \exp\left(\frac{a}{T^2} + \frac{a}{T} + a\right) \]  
(3)

Del Valle-Aguilera model expresses solvent density (d) in kg/dm³ while c is in kg/m³ and T (K) is absolute temperature.

In this work, density CO2 was computed based from Peng-Robinson equation of state as follows:

\[ p = \frac{RT}{V-b} - \frac{aa}{V^2+2bV-b^2} \]  
(4)

\[ a = 0.45724R^2T^2 \]  
(5)

\[ b = 0.0778RT \]  
(6)

\[ \alpha = (1 + \frac{0.37464 + 1.54226\omega}{-0.26992\omega^2}) \left[1 - T_i^{a\alpha}\right]^{2} \]  
(7)

\[ T_i = \frac{T}{T_i} \]  
(8)
where, \( p \) is pressure (MPa), \( T \) is absolute temperature in K, \( V \) is molar volume (L/mol), \( T_c, p_c \) are critical temperature (K) and pressure (MPa), respectively, \( R \) is ideal gas constant and \( \omega \) is acentric factor of CO\(_2\) [26].

The exponent of density in Eqs. (1,2 and 3) is the slope of the log-log plot of MO oil concentration in SC-CO\(_2\) vis-à-vis that of CO\(_2\) density. The slope varied from 8.162 to 8.922 as indicated in Figure 4. The combination of the slope value and a set of experimental data in the models resulted the coefficients of the models as shown in Table 2.

The three models above were used to describe the solubility behavior of MO oil in SC-CO\(_2\). The agreement of the models versus experimental data was evaluated by means of the root mean square percentage deviation (RMSD). The RMSD is given as

\[
RMSD = 100 \left( \frac{1}{n} \sum_{i=1}^{n} \left( \frac{c_{cal} - c_i}{c_i} \right)^2 \right)^{0.5}
\]

where \( c_{cal} \) stand for the calculated solubility in kg/m\(^3\), \( c_i \) is experimental solubility in kg/m\(^3\) and \( n \) is number of experiment points.

The calculated results of del Valle-Aguilera, Adachi-Lu and Chrastil models in comparison with experimental data of MO oil solubility are presented in Figure 5, 6 and 7, respectively. Del Valle-Aguilera model showed the best fit with experimental data with RMSD of 6.18%. While those of Chrastil and Adachi-Lu model are 7.17% and 6.31%, respectively. Moreover, in Figure 5 the crossover pressure point was indicated clearly between 25MPa and 30MPa as the convergent point of the isotherms of Del Valle-Aguilera model. While, the isotherms of Chrastil and Adachi-Lu models did not converge in all cases. It suggests that Del Valle-Aguilera model should be applied for high oleic oil solubility in SC-CO\(_2\).

**Conclusion**

Effect of process parameters on Moringa oleifera oil solubility in supercritical carbon dioxide were studied within the range of temperature from 35 to 60°C, range of pressure from 15 to 30MPa.

Pressure played key role on solubility. In relative to pressure, temperature has minor effect on solubility. Increasing the pressure resulted to increase in solubility. For temperature, two opposing results on solubility were observed either an increase or decrease in solubility occurred depending on the relative between the pressure applied and...
the crossover pressure point (26.38 MPa). Fractionation of the oil during extraction period was observed. Short chain fatty acids such as myristic, palmitic and palmitoleic decreased by 19.04, 8.40 and 12.87%, respectively. All C18 fatty acids (stearic, oleic, linoleic and linolenic) did not fractionate significantly. While, long chain fatty acids such as arachidic, cis 11 eicosenoic, behenic and tetracosanoic increased by 22.43, 16.15, 21.76 and 30.95%, respectively. However, the effect of the fractionation on the solubility was insignificant. Three models were used to describe MO solubility behavior in SC-CO2. Del Valle-Aguilera model showed the best fit with experimental data with RMSD of 6.18%. While those of Chrastil and Adachi-Lu model are 6.31 and 7.17% respectively. Del Valle-Aguilera model is recommended for high oleic oil solubility in SC-CO2.

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