EXTRACTION AND SOLUBILITY STUDIES OF VIRGIN COCONUT OIL FROM COCONUT (*Cocos nucifera*) FLESH USING SUPERCRITICAL CARBON DIOXIDE

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by

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LIST OF ABBREVIATIONS

AAPD	average absolute percent deviation
ANOVA	analysis of variance
CER	constant extraction rate
CP	critical point
DOE	design of experiment
EOS	equation of state
FAME	fatty acid methyl ester
FID	flame ionization detector
GC	gas chromatography
MCTs	medium chain triglycerides
MS	mass spectroscopy
MW	molecular weight
OF	objective function
RBD	refined, bleached and deodorized
RSM	response surface methodology
SC-CO_2	supercritical carbon dioxide
SEM	scanning electron microscope
TP	triple point
VCO	virgin coconut oil

LIST OF SYMBOLS

A	molecule of solute
B	molecule of solvent/gas/supercritical CO_2
A' and B'	temperature independent constants in Equation 2.13
A'', B'' and C''	temperature independent constants in Equation 2.15
A_i	area under the peak corresponding to component i
a, b, c, d	constants in the density based model
b_s	coefficients in the multiple regression analysis
K_{eq}	equilibrium constant
K_i	correction factor of component i
k	association number
M_A	molecular weight of the solute
M_B	molecular weight of the gas solvent
m_i	weight percentage of component i in the FAME standard solution
n	number of data point
P	pressure
P_c	critical pressure
P^{sub}	sublimation pressure of solute
R	gas constant
T	temperature
T_c	critical temperature
x_s	independent variables (pressure, temperature and CO_2)

Y^*	solute solubility in solvent
$Y^*_{calc.}$	calculated solubility using the model
$Y^*_{\text{exp.}}$	solubility experimental data
y_s	dependent variables (extracted yield and the MCTs content) in the multiple regression analysis
ΔH	total reaction heat of dissolution (heat of solvation and heat of solute vaporization)
ΔH_{solv}	heat of solvation
ΔH_{vap}	heat of vaporization
ρ	density of the gas/supercritical fluids solvent (CO_2)

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PENYARIAN DAN KAJIAN KETERLARUTAN MINYAK KELAPA DARA DARI ISI KELAPA (*Cocos nucifera*) MENGGUNAKAN KARBON DIOKSIDA LAMPAU GENTING

ABSTRAK

Minyak kelapa yang disari dari isi kelapa segar dikenali sebagai minyak kelapa dara (MKD). Minyak kelapa dara adalah sumber semulajadi trigliserida rantai sederhana (TRS) yang mana telah dikenali sebagai minyak sihat. Sehingga ke hari ini, penyelidikan berkaitan penyarian MKD menggunakan karbon dioksida lampau genting (CO_2- LG) dari segi dasar pengekstrakkan masih lagi kurang. Objektif kajian ini adalah untuk menentukan kesan faktor-faktor pengekstrakan MKD menggunakan (CO_2- LG), dan mengkaji keterlarutan minyak tersebut dalam (CO_2- LG).

Penilaian kesan-kesan interaksi bagi parameter pengekstrakan telah dilakukan menggunakan Kaedah Tindakbalas Permukaan (RSM). Kajian ini telah dijalankan berdasarkan reka bentuk Box-Behnken. Tekanan (20.7 - 34.5 MPa), suhu (313 - 353 K) dan jumlah penggunaan karbon dioksida (10 - 60 g) telah dipilih sebagai parameter. Respon yang terlibat adalah hasil pengekstrakan dan kandungan TRS dalam minyak yang diekstrak. Hasil pengekstrakan dikira melalui kaedah gravimetrik dan analisis kandungan TRS dilakukan menggunakan analisis gas kromatografi (GC). Satu hubungkait telah dibangunkan dengan p-value untuk kedua-dua respon pada 95% aras keyakinan. Pengukuran keterlarutan dijalankan menggunakan kaedah dinamik pada julat tekanan dari 20.7 hingga 34.5 MPa dan suhu dari 313 hingga 353 K. Analisis keterlarutan minyak dilakukan secara

gravimetrik dan analisis lengkung. Keterlarutan minyak meningkat dengan suhu pada tekanan di antara 31.0 dan 34.5 MPa dan berkurang dengan suhu pada tekanan di antara 20.7 dan 24.1 MPa. Data keterlarutan yang diperolehi daripada eksperimen dikolerasikan menggunakan model *Chrastil* dan *del Valle-Aguilera* iaitu berdasarkan ketumpatan karbon dioksida (CO_2). Keterlarutan kawasan-lintasan boleh diperhatikan dalam julat tekanan 27.5 hingga 30.5 Mpa dan pada sekitar 29 MPa, yang menunjukkan keterlarutan MKD dalam CO_2- LG tidak dipengaruhi oleh suhu secara praktikalnya. Kesahihan data keterlarutan telah dilakukan melalui perbandingan dengan data keterlarutan trigliserida tulen dalam CO_2- LG yang pernah dilaporkan dan ujian ketekalan-diri dilakukan dengan kaedah *Méndez-Santiago* dan *Teja*.

EXTRACTION AND SOLUBILITY STUDIES OF VIRGIN COCONUT OIL FROM COCONUT (*Cocos nucifera*) FLESH USING SUPERCRITICAL CARBON DIOXIDE

ABSTRACT

Coconut (*Cocos nucifera*) oil which is extracted from fresh coconut flesh is known as virgin coconut oil (VCO). The oil is a natural source of medium chain tryglycerides (MCTs) which has been well known as healthy oil. It is remarkable that very few reports on the extraction of the VCO using SC-CO_2 have been published hitherto the fundamental insights on the SC-CO_2 extraction processes of the coconut oil are much lacking. The objectives of this work are evaluating the parameters effects of VCO extraction using SC-CO_2 and examination of the oil solubility in SC-CO_2.

The assessment of interaction effects of extraction parameters was performed using a Response surface methodology (RSM). The study was carried out according to Box-Behnken design. Pressure (20.7 – 34.5 MPa), temperature (313 – 353 K) and CO_2 consumption (10 – 60 g) were chosen as the parameters. The responses were the extraction yield and the MCTs content of extracted oil. The yield was calculated by gravimetric and the MCTs content analysis was performed using GC analysis. A correlation was established with p -value for both responses at 95% confident level. The Solubility measurement was performed by dynamic method at the pressures and temperatures range of 20.7 to 34.5 MPa and 313 to 353 K respectively. Oil solubility analysis was performed using gravimetric and curve

analysis. The oil solubility increases with temperature at pressures between 31.0 and 34.5 MPa and decreases with temperature at pressures between 20.7 and 24.1 MPa. The solubility experimental data obtained was correlated with Chrastil and del Valle-Aguilera model, which are based on the CO_2 density. A solubility cross-over region was observed in the pressure range of 27.5 to 30.5 MPa and at around 29 MPa, the solubility of VCO in SC-CO_2 is practically independent of temperature. The validity of the solubility data was performed by its comparison with previous reported data of pure triglyceride solubility in SC-CO_2 and performing a self-consistency test with the method of Méndez-Santiago and Teja.

CHAPTER 1

INTRODUCTION

1.1 Introduction

Coconut (*Cocos nucifera*) oil that is extracted from fresh coconut flesh is known as virgin coconut oil (VCO). The extraction involves a process that does not use thermal treatment or food preservatives. Coconut oil obtained from copra, dried coconut, has no taste or fragrance, due to the refining process; whereas, VCO has the fragrance and taste of coconut. The absence of heating and chemical treatment in the oil makes it tasty and healthy. The antioxidant activity of VCO is superior to that of regular coconut oil, which is extracted from copra, and also of groundnut oil (Nevin and Rajamohan, 2005). The existing production process of VCO is basically conducted through oil separation from coconut. Coconut milk can be obtained by either pressing of fresh coconut flesh without additional water or grating the coconut flesh followed by extraction of the water-oil emulsion with water. The oil can be separated from the emulsion by means of fermentation, enzymatic extraction, refrigeration or mechanical centrifuge (Marina et al., 2009). Separation of the oil from the water-oil emulsion can also be accomplished by breaking the emulsion and creating an oil-oil emulsion, in which pure coconut oil must be added to the coconut milk to extract the oil from the emulsion, and then the oil must be separated from the water and protein with decantation. The process requires 24 to 48 hours and produces an oil yield of about 40% of the oil available in the coconut (Sukartin and Sitanggang, 2005).

The VCO is a natural source of medium chain tryglycerides (MCTs) in terms of fatty acids constituents with approximately 60% of the total oil content which are regarded as C_8 to C_{12} fatty acids constituents. The MCTs constituents have been reported to be beneficial for the human health. The MCTs constituents are mainly utilized as a nutritional supplement for patient suffering from mal absorption caused by intestinal resection and also as a component of infant feeding formulation (Nandi et al., 2005). It is also reported that MCTs constituents have beneficial effect on weight control and glucose as well as lipid metabolism (Marten et al., 2006).

The technology of supercritical carbon dioxide (SC-CO_2) extraction was proposed to enhance the existing production process of virgin coconut oil. Supercritical fluids are substances at pressure and temperature above their critical values. Figure 1.1 shows a Pressure-temperature (P-T) diagram of pure CO_2. At the P-T diagram there are sublimation, melting and vaporization line. The three curves intersect at the triple point (TP), where the solid, liquid and gaseous phases coexist in equilibrium state. The vaporization line ends at critical point (CP). The corresponding pressure and temperature to the CP is called critical pressure (Pc) and critical temperature (Tc) respectively. Above the critical point, condensation and vaporization will not occur with change in pressure and temperature. This region of pressure and temperature above Pc and Tc is identified as supercritical region.

In the supercritical region of a fluid, the phase state resembles one of the dense gases 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 order of magnitude higher than

in typical liquid (Brunner, 2005). A specific feature of the supercritical state of a fluid is its dense and highly compressible nature. This means that properties can be changed greatly with small changes in temperature or pressure. The tremendous variation in characteristics due to various conditions is causing differences in effects on solutes within the state conditions.

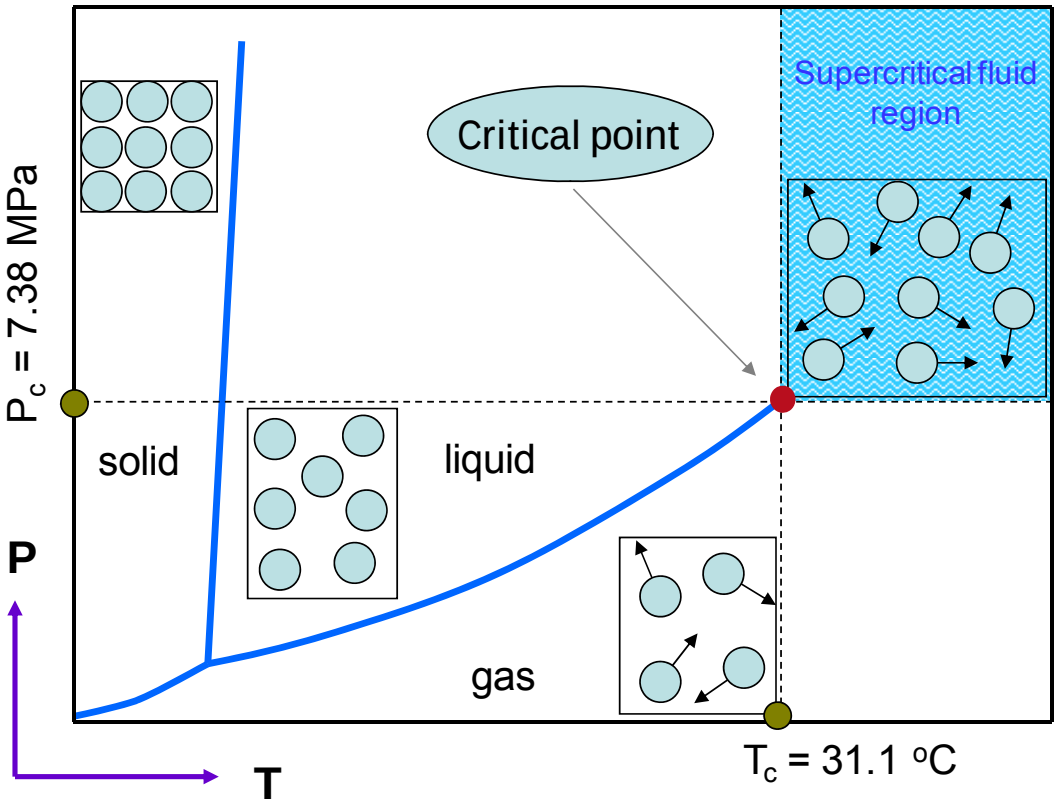


Figure 1.1 : Pressure–temperature phase diagram of pure CO_2 (Dean, 1993).

The SC-CO_2 provides an attractive technology which is being applied in many research activities around the globe due to its relatively low critical temperature (31.1 ^oC) and critical pressure (7.38 MPa) (McHugh and Krukonis, 1994). Using SC-CO_2 as solvent allows the extraction processes to operate near the ambient temperature which is useful for thermally labile natural material.

Furthermore, SC-CO_2 is a non-toxic material which can be used even in food-grade form for food processing, and is considered to be an environmentally friendly solvent (Prausnitz et al., 1999). Separation of extracts from SC-CO_2 is relatively simple, because it is done by reducing the pressure of the flowing mixture through an expansion valve.

Despite the fact that the extraction of natural compound using SC-CO_2 has been reported as a promising technique by many researchers (Favati et al., 1991, Ferreira et al., 1999, França and Meireles, 2000, Reverchon and Marrone, 2001, Smith Jr et al., 2003, Setianto et al., 2003, Nik Norulaini et al., 2004, Michielin et al., 2005, Westerman et al., 2006, Reverchon and De Marco, 2006, Machmudah et al., 2007, Zaidul et al., 2007a, Nik Norulaini et al., 2008, Nik Norulaini et al., 2009, Setianto et al., 2009), it is remarkable that very few reports on the extraction of coconut oil using SC-CO_2 have been published. Brannolte et al. (1983) reported on the extraction of coconut oil from copra with CO_2 over the range of 40 – 60 ^{o}C and 30 - 90 MPa. They found that extraction at higher pressure and temperature could reduce CO_2 consumption and extraction time required. For example at a pressure of 90 MPa and 60 ^{o}C, the oil could be extracted with 10% of the amount of CO_2 needed at 30 MPa and 40 ^{o}C. Celestino et al. (2006) analyzed oil content of copra extracted using SC-CO_2 extraction. It was reported that about 100% of coconut oil could be extracted from the copra within 1 hour at 120 ^{o}C and 51.7 MPa.

Gupta and Shim (2007) collected and compiled solubility data of various compounds in SC-CO_2 from over 1200 data. The solute including lipids, solids, polymer, food, drugs, pesticides, dyes, metal complexes have been reported. The

review of solute solubility study in SC-CO_2 found that the solubility of the coconut oil in SC-CO_2 has not been reported yet.

Nevertheless, review on this subject indicated that very few reports on the extraction of coconut oil using SC-CO_2 have been published hitherto the fundamental insights on the SC-CO_2 extraction process of the coconut oil is much lacking.

1.2 Objectives of The Study

The objectives of this study are :

- To examine the effects of supercritical carbon dioxide extraction parameters on virgin coconut oil yield and medium chain triglycerides content of the extracted virgin coconut oil.
- To study the virgin coconut oil solubility in supercritical carbon dioxide.

1.3 Scope of the Study

To achieve the objectives, the folowing scopes of the study were performed:

- Examination of the effects of supercritical CO_2 parameters on virgin coconut oil yield.
- Examination of the effects of supercritical CO_2 parameters on medium chain triglycerides content in the extracted virgin coconut oil.
- Measurement of the solubility of virgin coconut oil in supercritical CO_2.
- Application of solvent density based models on the solubility of virgin coconut oil in supercritical CO_2.

- Comparison the solubility of virgin coconut oil in supercritical CO_2 to those of pure triglycerides.
- Application of self-consistency test on the data of virgin coconut oil solubility in supercritical CO_2 using the method of Mendez-Santiago and Teja.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

In this chapter, literature reviews regarding the SC-CO_2 as solvent is presented. It includes: the solvent properties and characteristic, the application of the solvent for extraction processes, solute solubility measurements and modeling of the solubility of solute in SC-CO_2. Moreover, some published literatures regarding VCO are also reviewed.

2.2 Properties and Characteristics of Supercritical CO_2 as Extraction Solvent

The SC-CO_2 extraction process is a process that involves the bmixture of CO_2 and the solute. The density of CO_2 is one of the important properties of the solvent. Variation of pressure at constant temperature of the solvent CO_2 causes the density to change greatly especially in the critical region (> 31 ^oC, > 7.3 MPa). This can be seen in Figure 2.1. For example, at 40 ^oC, when the pressure is increased from 2 MPa to about 25 MPa, the CO_2 solvent density changes from about 40 kg/m^3 to 880 kg/m^3. The adjustment of the density by changing the pressure and temperature plays an important role in the extraction using SC-CO_2. Solute solubility, mixture density, viscosity and mass transfer, which are affected by the density, are affecting the extraction results. Moreover, such a density change occurs without phase change. That is the SC-CO_2 can be considered a continuously adjustable solvent.

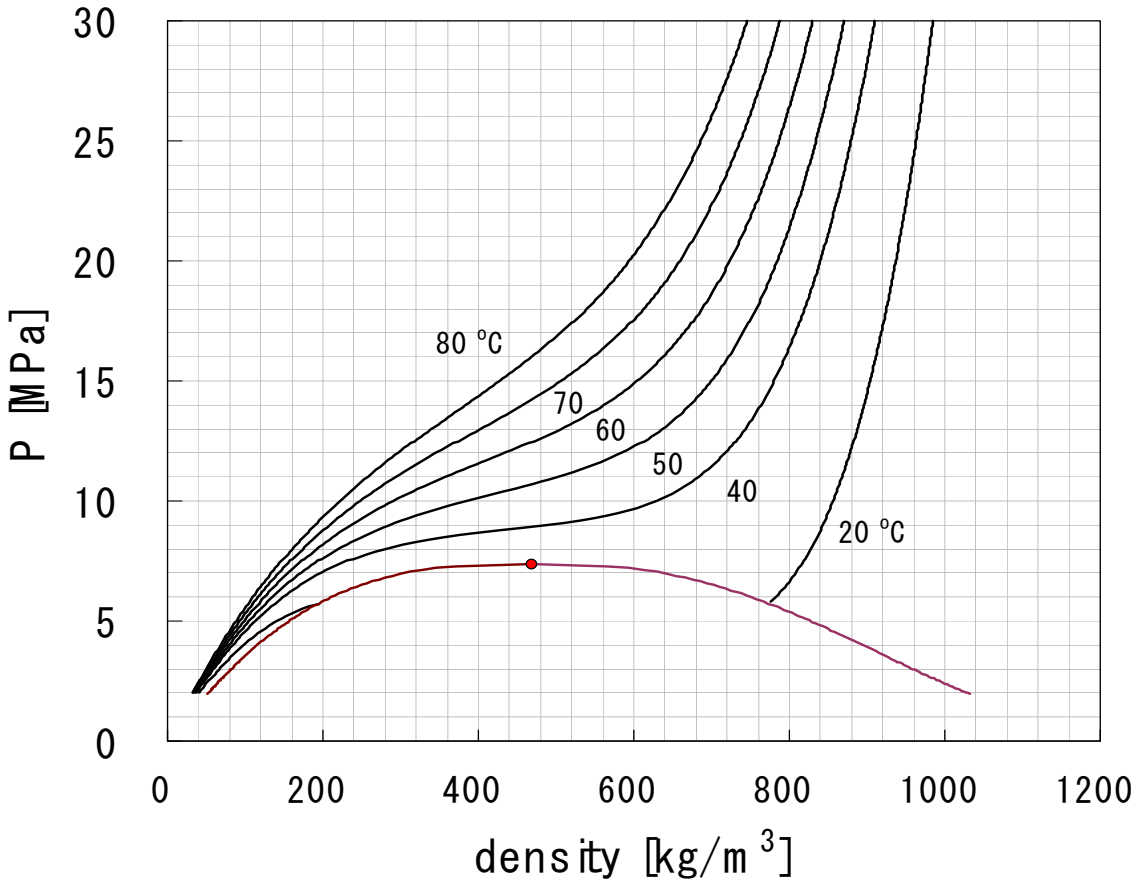


Figure. 2.1 Phase diagram of CO_2 calculated from the equations of Span and Wagner (Span and Wagner, 1996).

To illustrate how supercritical fluids compare to gases and liquids, Table 2.1 compiles some of the more important physicochemical properties of each (McNally and Bright, 1992).

The density of supercritical fluids is 100 to 1000 times greater than that of its gas and approaching to that of its liquid. This makes the solvating power of supercritical fluid near to that of its liquid. On the other hand diffusivity of supercritical fluid is higher than that of its liquid by a factor up to several hundred times. The viscosity of supercritical fluid shows a great difference than that of its

liquid by hundreds times. These properties make supercritical fluids turn into interested solvent extraction.

Table 2.1 : Properties of Supercritical Fluid vs. Gases and Liquids*.

	Gas	Supercritical fluid	Liquid
Density (g/cm^3)	10^{-3}	0.1 - 1	1
Diffusion coefficient (cm^2/s)	10^{-1}	$10^{-3} – 10^{-4}$	$< 10^{-5}$
Viscosity (g/ cm s)	10^{-4}	$10^{-3} – 10^{-4}$	10^{-2}

*Source : (McNally and Bright, 1992)

Among others substances, CO_2 is convenient for supercritical extraction. It has advantage of allowing extraction at temperatures near ambient temperature, and is useful for thermally labile natural material. A major advantage of CO_2 derives from its environmentally-friendly properties: it is not toxic; it is does not burn or explode; it is easily vented into atmosphere; and it is inexpensive (Prausnitz et al., 1999).

Due to the properties of SC-CO_2, many characteristics and advantages of using the fluids as solvent extraction have been reported. Sahena et al. (2009) reviewed the advantage of SC-CO_2 as solvent as follows (Sahena et al., 2009) :

1. SC-CO_2 has relatively low viscosity and high diffusivity (the diffusivity of SCFs is $\sim 10^{-4}$ cm^2 s^{-1} while that of liquid solvents is $\sim 10^{-5}$ cm^2 s^{-1}). Therefore, they can penetrate into porous solid materials more effectively than liquid solvents, and may render much faster mass transfer resulting in faster extractions.

2. In SC-CO_2 extraction, a fresh fluid is continuously forced to flow through the samples; therefore, it can provide quantitative or complete extraction.
3. In SC-CO_2 extraction, the solvation power of the fluid can be manipulated by changing pressure (P) and/or temperature (T); therefore, it may achieve a remarkably high selectivity. This tunable solvation power of SC-CO_2 is particularly useful for the extraction of complex samples such as plant materials
4. Solutes dissolved in SC-CO_2 can be easily separated by depressurization. Therefore, SC-CO_2 can eliminate the sample concentration process, which is usually time-consuming and often results in loss of volatile components.
5. Due to the critical point of SC-CO_2, using he solvent allows extraction usually is performed at low temperatures, so it may be an ideal technique to study thermally labile compounds and may lead to the discovery of new natural compounds.
6. A small sample can be utilized for component analysis. About 100 volatile and semi-volatile compounds could be extracted and detected by gas chromatography (GC)–mass spectroscopy (MS), of which more than 80 compounds were in sufficient quantity for accurate.
7. SC-CO_2 extraction uses no or significantly less environmentally hostile organic solvents. A SC-CO_2 method may need no or only a few m Liters.

8. SC-CO_2 extraction may allow direct coupling with a chromatographic method, which can be a useful means to extract and directly quantify highly volatile compounds.
9. In large scale SC-CO_2 extraction processes, the solvent can be recycled or reused thus minimizing waste generation.
10. SC-CO_2 extraction can be applied to systems of different scales, for instance, from analytical scale (less than a gram to a few grams of sample), to preparative scale (several hundred grams of sample), to pilot plant scale (kilograms of sample) and up to large industrial scale (tons of raw materials, such as SC-CO_2 extraction of coffee beans).

2.3 Extraction of Natural Compound Using Supercritical CO_2

Due to the properties and characteristics of SC-CO_2 as solvent, many advantages of its application for extraction of natural compound can be acquired. Supercritical fluids have been used widely in industrial extractions such as coffee decaffeination, hops and tea extraction, and flavor extraction (McHugh and Krukonis, 1994). Saito (1995) reviewed research and Reverchon and De Marco (2006) suggested that there are still many opportunities in industry for replacing organic solvents with supercritical fluids. For example, CO_2 has been suggested as a replacement for n-hexane or toluene in de-solventation of polymer solutions by Inomata et al. (1999). CO_2 has been proposed to be used in a process for improving the digestion properties of cellulosic material by Kim and Hong (2001). CO_2 in its supercritical state has been used for fractionating thermally sensitive natural oils (Suzuki et al., 1997, Riha and Brunner, 2000) as well as for extraction of anacardic

acid rich cashew nut shell oil without destroying the chemical content (Smith Jr et al., 2003, Setianto et al., 2009).

Several works on the application of SC-CO_2 extraction on vegetable oils such as sunflower oil, coriander oil, grape seed oil, tomato seed oil, peanut seed oil, almond oil, fennel oil (Reverchon and Marrone, 2001), amaranth seed oil (Westerman et al., 2006), rosehip seed oil (Machmudah et al., 2007), palm oil (França and Meireles, 2000) and palm kernel oil (Zaidul et al., 2007b, Zaidul et al., 2007a). Others application of the SC-CO_2 extraction on vegetable oil has been reviewed by Egger (1996). The author summarized the SC-CO_2 extraction process of oil that was extracted from soybean, rape seed, sun flower, corn germ, cotton seed, lupine seed, *oenothera* seed lupine seed, jojoba, wheat germ, wheat bran, copra, castor, peanut olive, and oat (Eggers, 1996).

Recent publication on the review on utilization of SC-CO_2 in food industry has been reported (Sahena et al., 2009). It includes extraction of lipid and cholesterol, extraction of natural color, extraction of natural flavorings extraction of antioxidants, extraction of hops and decaffeination of coffee and tea.

The principles of SC-CO_2 extraction apparatus are shown in the Figure 2.2. In the extraction process, firstly, the CO_2 was liquefied in the cooler and then its pressure is elevated using the pump to above its critical pressure according to the required condition. Then, the pressurized CO_2 is flown to a high pressure vessel. The vessel was heated in a jacket heater, and the temperature is adjusted at above the critical temperature according to the required condition. The CO_2, which is in a

supercritical condition, then flows to the sample inside the vessel and form a mixture/solution with the analyte in the sample matrices. The mixture then flows to the expansion valve. Due to the depressurization, the analyte will be separated from the CO_2 and it s collected in a trap. The mass of CO_2 that used in the extraction is measured using a gas meter.

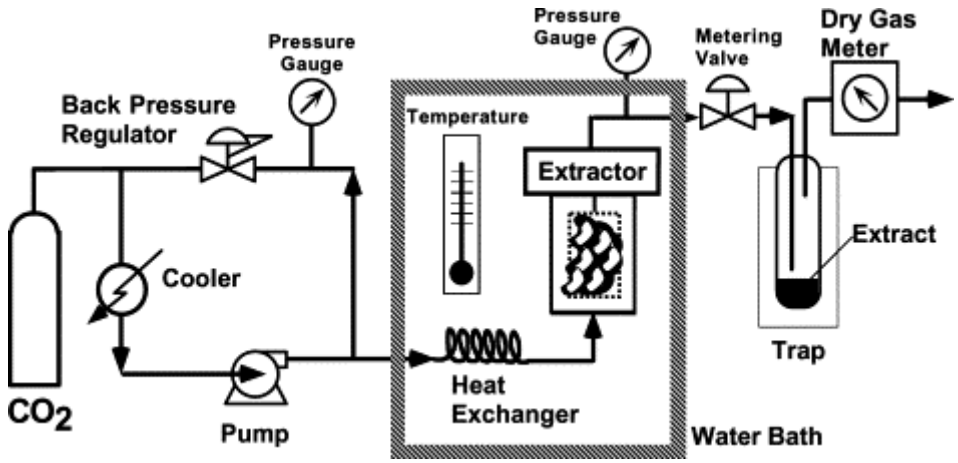


Figure 2.2 : The principle of SC-CO_2 extraction apparatus (Smith Jr et al., 2003).

2.4 Box-Behnken Design of Experiment

Box-Behnken designs (Myers and Montgomery, 2002) are a class of rotatable or nearly rotatable second-order designs based on three-level incomplete factorial designs. For three factors, its graphical representation can be seen in two forms (Figure 2.3).

The number of experiments required for the development of BBD is defined as :

$$N = 2x_s(x_s - 1) + C_0 \qquad (2.1)$$

where

N = Number of experiments required

x_s = Independent variables

C_0 = Number of centrals points

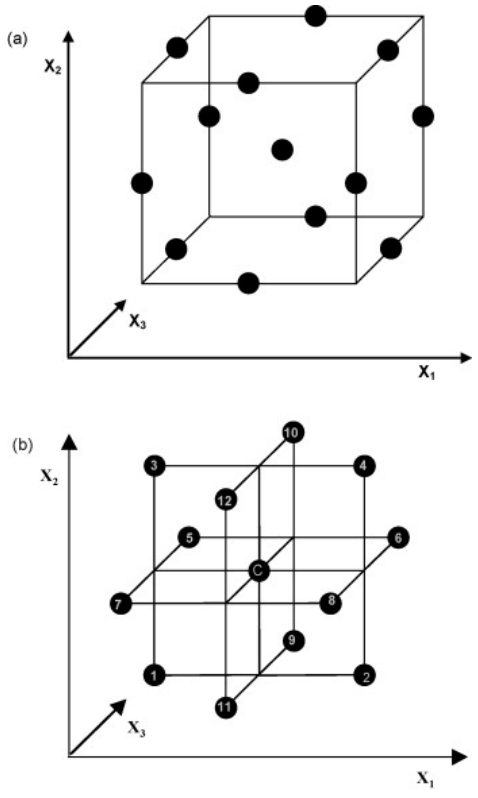


Figure 2.3 : Three factors graphical representation of Box-Behnken DOE. (a) The cube for BBD and three interlocking 2^2 factorial design. (b) The figure of three interlocking 2^2 factorial designs and a central point. (Ferreira et al., 2007).

Table 2.2 : Coded Factors Levels for a Box-Behnken Design of Three-variable System.*

Experiment	x_1	x_2	x_3
1	-1	-1	0
2	1	-1	0
3	-1	1	0
4	1	1	0
5	-1	0	-1
6	1	0	-1
7	-1	0	1
8	1	0	1
9	0	-1	-1
10	0	1	-1
11	0	-1	1
12	0	1	1
13	0	0	0
14	0	0	0
15	0	0	0
16	0	0	0
17	0	0	0

*(Myers and Montgomery, 2002)

There are advantages for using the Box-Behnken Design. Ferreira et al. (2007) explained that a comparison between the Box-Behnken design and other response surface designs (central composite, Doehlert matrix and three-level full

factorial design) has demonstrated that the Box-Behnken design and Doehlert matrix are slightly more efficient than the central composite design but much more efficient than the three-level full factorial designs. Another advantage of the BBD is that it does not contain combinations for which all factors are simultaneously at their highest or lowest levels. So these designs are useful in avoiding experiments performed under extreme conditions, for which unsatisfactory results might occur. Table 2.2 contains the coded values of the factor levels three for Box-Behnken Design.

2.5 Measurement of Solute Solubility in Supercritical CO_2

For developing extraction or other processes using SC-CO_2, the knowledge of solubility is essential. The design of supercritical fluid process requires the solubilities of each component in the supercritical fluid (Prausnitz et al., 1999). Many of the solubility/phase equilibrium measurements have been made to meet the need for fundamental data for process design purposes as well as analytical application. The data are important in determining the optimal operating condition, the solvent to feed ratio, and the selectivity of the extracted solute in engineering-scale supercritical fluid extraction. The experimental data may also be used to develope solubility correlation model (Maxwell, 1996).

Solubility and phase equilibrium measurement methods have been presented in McHugh and Krukonis (1986). The measurements can be performed by two procedures that are dynamic method and static method (Figure 2.4).

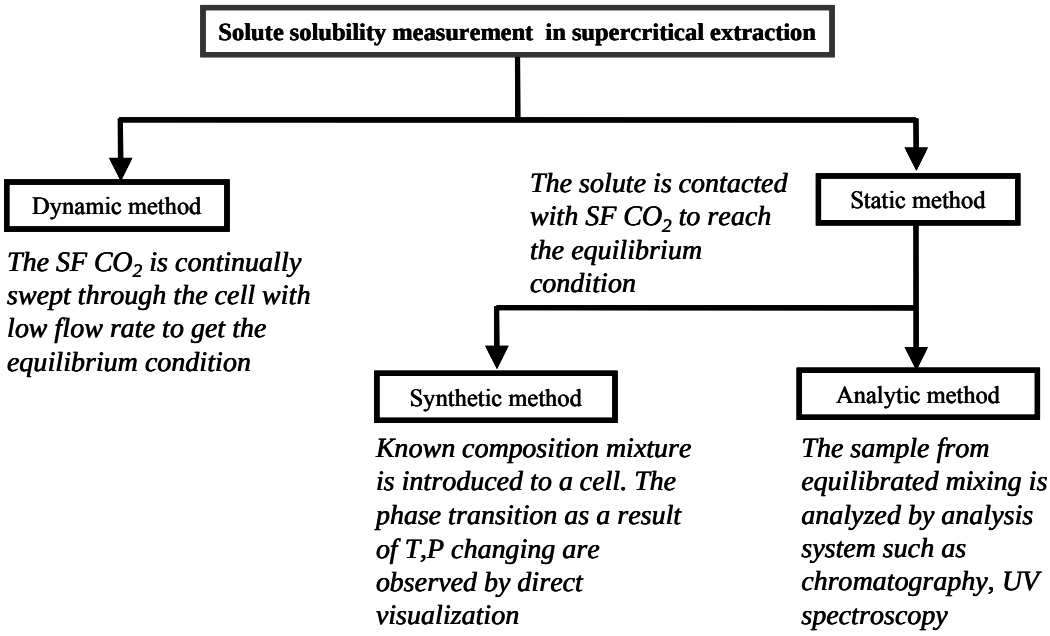


Figure 2.4 : Method of solubility measurement.

In the dynamic method, the supercritical fluid is continually swept through the cell using a set of equipment that can ensure the equilibrium condition between supercritical CO_2 and the solute. Therefore the measurement involved the formation of a saturated solution by passing the supercritical fluid over the solute in an extraction cell, decreasing the pressure to precipitate the solid or liquid solute, and analysis of the resulting solution is usually accomplished using a gravimetric method. One of the dynamic method equipment of solubility measurement is shown in Figure 2.5**.**

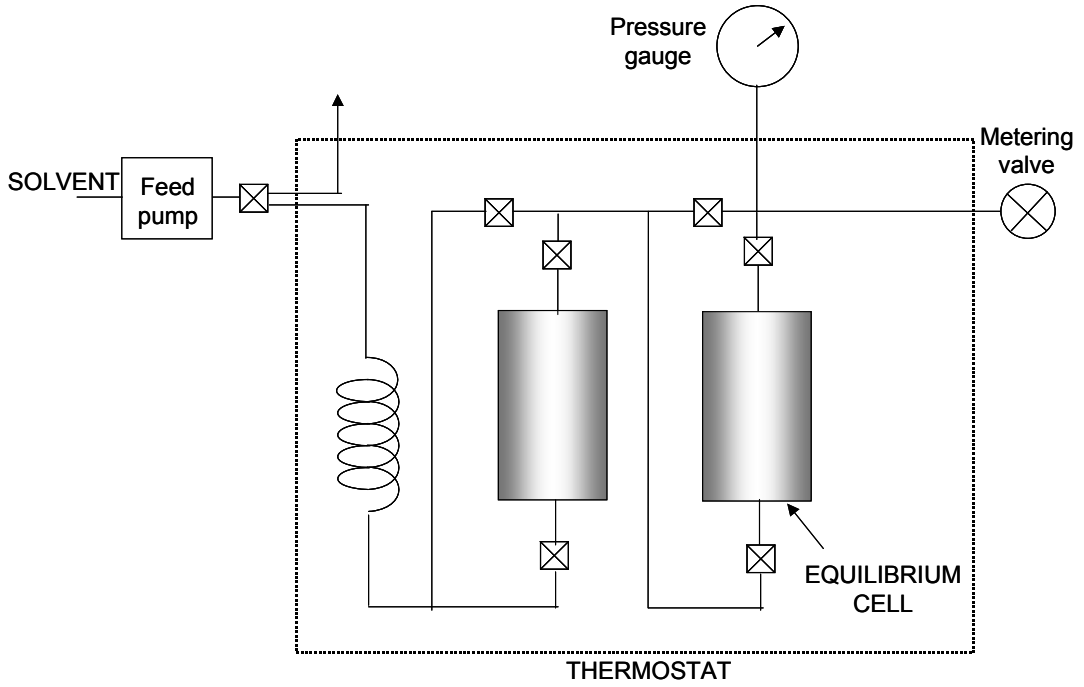
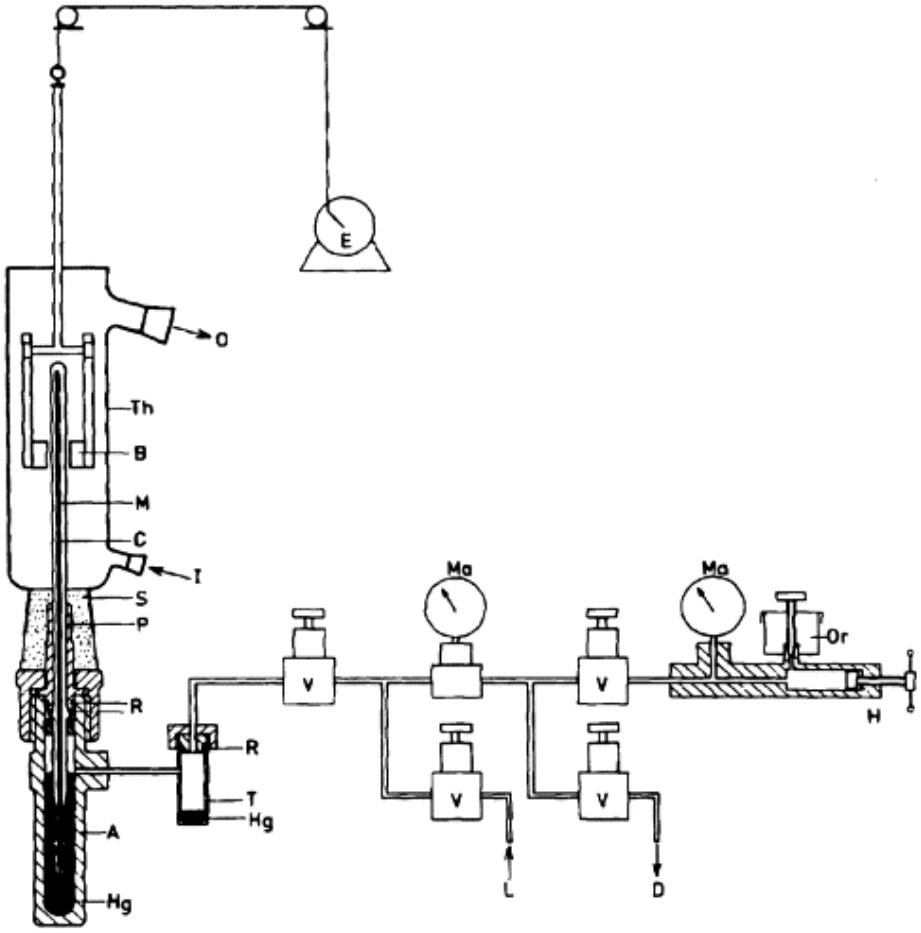


Figure 2.5 : Apparatus for dynamic method solubility measurement (McHugh and Krukonis, 1994).

In static method, the observation could be performed by analytical procedure or synthetic procedure. In static analytical method, the composition of the mixture (CO_2 and solute), which was brought to equilibrium condition, was analyzed using analysis system such as chromatography or UV spectroscopy, and in the most case, sampling of liquid phase as well as those of gas was performed. In the static synthetic method, known composition mixture is introduced in a view cell. The phase transitions as a result of change of temperature or pressure are observed by direct visualization through a camera that is connected by a monitor system. Schematic equipments used in this method, is shown in Figure 2.6.



A, autoclave; B, magnets; C, capillary glass tube; D, drain; E, motor; H, rotating hand pump; Hg, mercury; I, thermostat liquid in; L, line to dead weight pressure gauge; M, mixture being investigated; Ma, manometers; O, thermostat liquid out; Or, hydraulic oil reservoir; P, closing plug; R, Viton-O-rings; S, silicone rubber stopper; T, mercury trap; Th, glass thermostat; V, valve.

Figure 2.6 : The cailletet, apparatus for static method solubility measurement (Raeissi and Peters, 2001).

Figure 2.6 was reported as equipment for measurement of solubility and phase behavior of solutes in SC-CO_2. For example, determination of bubble-point pressures of the binary system carbon dioxide+linalool (Raeissi and Peters, 2001), examination of high-pressure phase equilibrium of the ternary system carbon dioxide + limonene + linalool (Raeissi and Peters, 2005) and measurement of pressure and

temperature of CO_2 that is saturated with cashew nut shell liquid (Setianto et al., 2009).

Solubility measurement according to dynamic method can be carried out through a "like extraction process" method. The supercritical CO_2 is allowed to flow through the solute in the cell. The flow rate of the CO_2 must be very low to ensure the saturation of CO_2 with solute. Mass of the extracted solute versus the total mass of supercritical CO_2 used to dissolve the solute are plotted. In the extraction process, the extraction curves can be described by a three-step process (Brunner, 1994). The first linear portion is denoted by constant extraction rate (CER) period and is characterized by the convective mass transfer between the solid material surface and the fluid phase. In this period, the amount of free-oil in the plant oil bearing cell was sufficient to allow for solvent saturation. The second part of the extraction curve represents the falling rate period. At this step both convection and diffusion in the solid must be considered. For the third step or the diffusion-controlled rate period the diffusion in the solid controls the rate of mass transfer.

The CER period indicates an equilibrium condition of the system is achieved. The extract concentration at the exit of the extractor represents the solubility of the solute. Therefore, the slope of the CER is the measured solubility at the temperature and pressure of the solute in SC-CO_2 at the correspondence operation condition (Favati et al., 1991, Sovova, 1994, Ferreira et al., 1999, de França and Meireles, 2000, Sovová et al., 2001, Sovová, 2005, Danielski et al., 2007).

2.6 Solubility Model

2.6.1 Chrastil Model

Empirical models for solubility determination are advantageous since they discharge the use of physical–chemical properties, normally difficult to obtain (Danielski et al., 2007). A density based model was proposed by Chrastil (Chrastil, 1982). The model related the solubility of solute to the density of solvent and the temperature of solvent. The model based on a physic chemical model where one molecule of solute associates with k molecules of solvent to form a solvato-complex which is in equilibrium condition.

Chrastil derived a solubility model as follows (Chrastil, 1982) :

In an ideal case if one molecule of solute A associate with k molecule of gas B to from one molecule of a solvato-complex AB_k in equilibrium with the system, it can be written as :

$$A + kB \rightleftarrows AB_k$$

$$K = \frac{[AB_k]}{\left([A][B]^k\right)} \tag{2.2}$$

$$\ln K + \ln[A] + k \ln[B] = \ln[AB_k] \tag{2.3}$$

where,

A = molar vapor concentration of solute

B = molar concentration of gas

AB_k = molar concentration of the solute in gas

K_{eq} = equilibrium constant, which can be expressed as (Chrastil, 1982) :

$$\ln K = \frac{\Delta H_{solv}}{RT} + q_s \tag{2.4}$$

ΔH_{solv} = heat of solvation

q_s = a constant

The vapor concentration of the solute $[A]$ can be approximated by the Clapeyron-Clausius equation :

$$\ln K = \frac{\Delta H_{vap}}{RT} + q_v \tag{2.5}$$

where,

ΔH_{vap} = heat of vaporizationof the solute

q_v = contant

Usually $[A] \ll [AB_k]$ combining into Equation 2.2, it can be expressed:

$$\frac{\Delta H}{RT} + q + k \ln[B] = \ln[AB_k] \tag{2.6}$$

where,

ΔH = total heat of dissolution, $\Delta H = \Delta H_{solv} + \Delta H_{vap}$ and $q = q_s + q_v$

q_v = constant

The concentration of the solute in gas (Y^*) and the density of gas (ρ) were expressed in [g/L]. and thus :

$$\left[AB_k\right] = \frac{Y^*}{\left(M_A + kM_B\right)} \text{ and } \left[B\right] = \frac{\rho}{M_B} \tag{2.7}$$

where,

Y^* = solute solubility in solvent (saturated concentration of a solute in a gas)

ρ = density of the gas

M_A and M_B = molecular weight of the solute and gas

Then the equation can be expressed as:

$$\frac{\Delta H}{RT} + q + k \ln \rho - k \ln M_B = \ln Y^* - \ln\left(M_A + kM_B\right) \tag{2.8}$$

And thus :

$$Y^* = \rho^k \exp\left(\frac{a}{T} + b\right) \tag{2.9}$$

where,

k = an association number

$a = \frac{\Delta H}{R}$

$b = \ln\left(M_A + kM_B\right) + q - k \ln M_B$

In an experimental data fitting, the solubility could be expressed in [g/g] (Vasconcellos and Cabral, 2001, Soares et al., 2007).

2.5.2 del Valle-Aguilera Model

Del Valle and Aguilera proposed a model that was improved from the Chrastil model (del Valle and Aguilera, 1988). Equation 2.8 was re expressed as:

$$\ln Y^* = q - \ln\left(\frac{\left[M_B\right]^k}{\left[M_A + kM_B\right]}\right) + \frac{\Delta H}{RT} + k \ln \rho \qquad (2.10)$$

According to Equation 2.10 plot of $\ln Y^*$ vs $\ln \rho$ for isothermal condition should give straight line with slope k and intercept b.

Furthermore if Y^* values for different isotherm are plotted against $\frac{1}{T}$, straight line with a slope k and intercept a will be obtained.

$$Y^* = b + \frac{a}{T} \qquad (2.11)$$

where,

$$b = q - \ln\left(\frac{[M_B]^k}{[M_A + kM_B]}\right)$$

$$= \ln(M_A + kM_B) + q - k \ln M_B$$

$$a = \frac{\Delta H}{R}$$

Hence, an empirical modification was introduced to Equation 2.10 to compensate the variation of ΔH_{vap} with temperature by introducing a constant, c. The equation expressed as:

$$\ln Y^* = k \ln \rho + \frac{a}{T} + \frac{c}{T^2} + b \qquad (2.12)$$

where,

c = constant introduced in the del Valle-Aguilera model

2.6.3 Méndez-Santiago and Teja model for Self-Consistency Data

Méndez-Santiago and Teja have proposed a correlation can be used to correlate solubility data of solutes in supercritical carbon dioxide (Méndez-Santiago and Teja, 1999, Méndez-Santiago and Teja, 2000)**.** The correlation was based on theory of dilute solution. In the theory, it is assumed that the solution in a infinite dilution that allow the solute molecule has no contact each other, so the mutual interaction between molecule of the solutes can be neglected. A correlation