

CHAPTER 2 BACKGROUND AND LITERATURE REVIEW

This chapter will begin by giving background of the key concepts necessary to the understanding of the ideas presented in this dissertation and supercritical extraction fluid process. Literature review will be investigated mathematical modelling of solubility and extraction yield using supercritical fluid proposed from many literatures.

2.1 Supercritical Fluids

Supercritical fluid is a substance above its critical values of temperature and pressure (T_c and P_c). The critical point (CP) represents the highest temperature and pressure at which the substance can exist as a vapour and liquid in equilibrium. A compound's liquid-vapour phase boundary no longer exists (Figure 2.1) and its fluid properties can be tuned by adjusting the pressure or temperature. A three dimensional pressure–volume–temperature (PVT) diagram and the pressure-temperature (P-T) projections (as shown in Figure 2.1) show the different physical states of a pure substance.

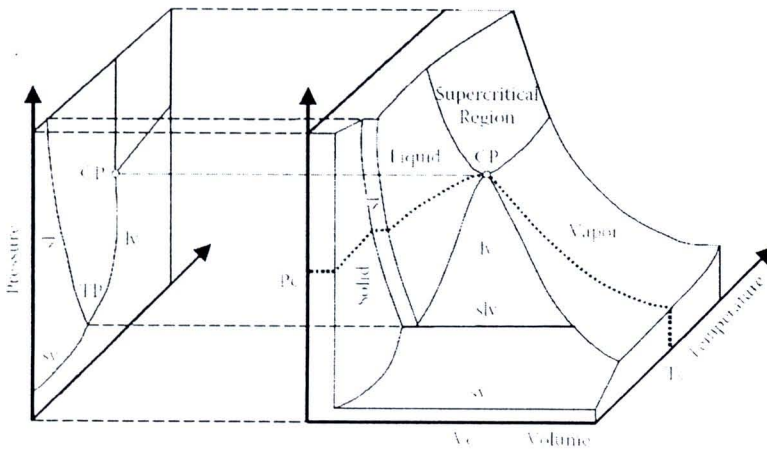


Figure 2.1 Pressure–Volume–Temperature (PVT) diagram of a pure substance and its projection on Pressure–Temperature plane (Martinez, 2008).

At critical point (CP), for a pure fluid:

$$\left(\frac{\partial P}{\partial V}\right)_T = \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0 \quad \text{at } P = P_c \text{ and } T = T_c \quad (2.1)$$

The region around the critical point ($1.4 > T/T_c > 0.9$ and $5 > P/P_c > 1.0$) is called the near critical region. In this region the pressure/volume isotherms shows the small changes in pressure can produce quite large changes in density.

2.1.1 Physical Properties of Supercritical Fluids

The physical properties of SCFs are in-between those of a gaseous and liquid states. Typical values of different physical properties for each fluid are listed in Table 2.1. Density and viscosity of SCFs are lower than those of liquids; however, diffusivities are higher. Thermal conductivities are relatively high in the supercritical state and have very large values near the CP because, in principle, the heat capacity of a fluid tends to approach infinity at the CP. Interfacial tension is close to zero in the critical region. In general, the physical properties in the critical region enhance mass and heat transfer processes. All salient properties of supercritical fluids are summarised in Figure 2.2.

Table 2.1 Comparison of the physical properties of gas, liquid, and supercritical fluids (Martinez, 2008).

Physical Property	Gas ($T_{ambient}$)	SCF (T_c, P_c)	Liquid ($T_{ambient}$)
Density, ρ (kg/m ³)	0.6-2	100-1,000	1,000-1,600
Dynamic viscosity, μ (mPa.s)	0.01-0.3	0.01-0.03	0.2-3
Kinematic viscosity, η ^a (10 ⁶ m ² /s)	5-500	0.2-0.1	0.1-5
Thermal conductivity, λ (W/m·K)	0.01-0.025	Maximum ^b	0.1-0.2
Diffusion coefficient, D (10 ⁶ m ² /s)	10-40	0.07	0.0002-0.002
Surface tension, σ (dyne/cm ³)	-	-	20-40

$T_{ambient}$: ambient temperature, T_c : critical temperature, and P_c : critical pressure

^a Kinematic viscosity defined as $\eta = \mu/\rho$

^b Thermal conductivity presents maximum values in the near-critical region, highly dependent on temperature

Usually, the SCF is applied at a temperature close to its critical value and at a pressure high enough for its density to become greater than the gas density. The design of processes using supercritical solvents is strongly dependent on the phase equilibrium scenario, which is highly sensitive to changes in operating conditions. Therefore, phase equilibrium plays a key role in the synthesis and design of SFE processes. The critical temperatures and pressures of materials vary quite significantly (Table 2.2). Generally, substances that are very polar at room temperature will have high critical temperature

since a large amount of energy is needed to overcome the polar attractive energy. In many applications, low critical temperature (T_c) solvents are preferred to be used because they are easily separated from the extract. Ideal substitute for hazardous and toxic solvent are preferred to apply with the food processing. One of the most commonly used supercritical fluids is CO_2 . It is gaseous at ambient temperature and pressure, which makes analyte recovery very simple and provides solvent-free extracts. Also, important for food and natural products extraction, is the ability of SFE using CO_2 at low temperatures which allows the extraction of thermally labile or easily oxidized compounds (Mendiola et al., 2007).

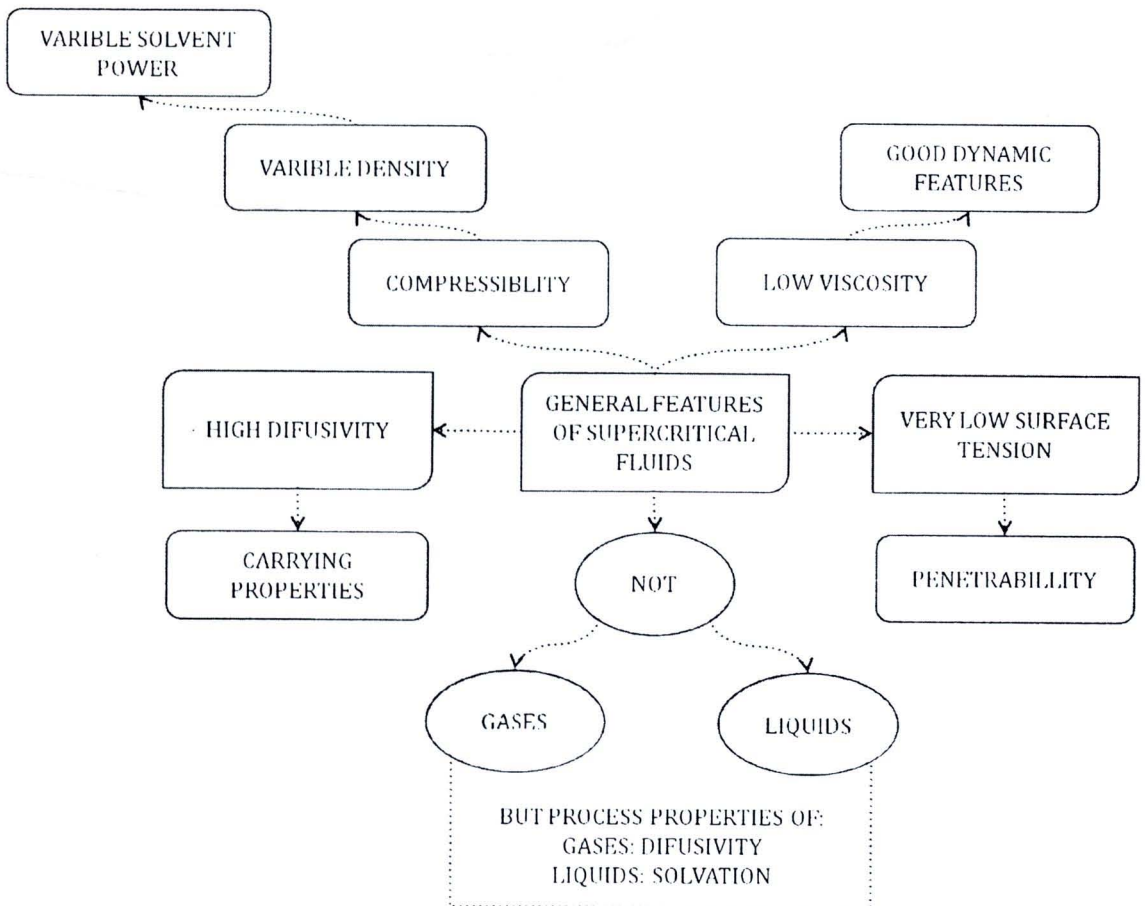


Figure 2.2 Salient properties of supercritical fluids

2.1.2 Supercritical Carbon Dioxide

Carbon dioxide (CO_2) is in its supercritical fluid state when both the temperature and pressure equal or exceed the critical point of 31°C and 73 atm (or 7.4 MPa), respectively (Figure 2.3). However, CO_2 is nonpolar, a polar organic cosolvent (or a

modifier) should be added to the supercritical fluid for separating polar compounds. By controlling the level of pressure/ temperature/ modifier, supercritical carbon dioxide (SCCO₂) can dissolve a broad range of compounds, both polar and nonpolar (Herrero et al., 2010).

Table 2.2 Critical conditions for various materials (Poling, Prausnitz and O'Connell, 2001).

Fluids	Critical Temperature (T_c , °C)	Critical Pressure (P_c , MPa)
Carbon Dioxide	30.97	7.37
Methane	-82.75	4.60
Ethane	32.15	4.87
Ethylene	32.20	5.04
Isopropanol	235.20	4.76
Propane	96.65	4.25
Propylene	91.90	4.62
Ammonia	132.50	11.28
Benzene	289.00	4.89
Toluene	318.60	41.10
n-Hexane	234.35	3.02
Cyclohexane	280.30	4.07
Water	374.20	22.12
Methanol	239.45	8.09
Ethanol	240.75	6.14

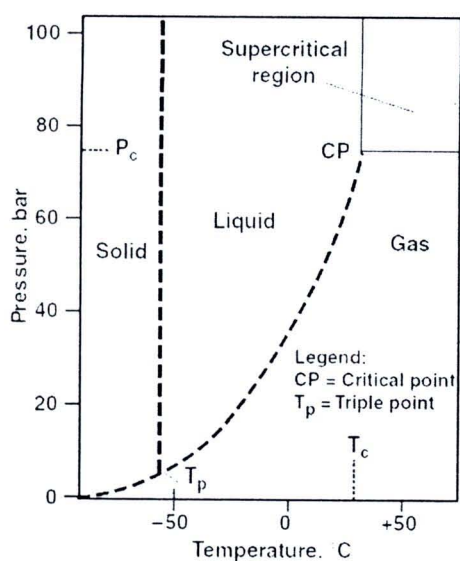


Figure 2.3 The phase diagram for carbon dioxide shows its supercritical region

2.1.3 Cosolvent

The solubility of the compound is higher for a higher mole fraction of cosolvent because the addition of a cosolvent generally increases the bulk density of the SCF mixture. Choice of cosolvent for a specific application requires a good understanding of effects of cosolvent addition on the solubility behaviour, mass transfer, and economics of the process. Typically, ethanol is preferred cosolvent for food application due to its safe. Both extraction rate and yield are larger under high density conditions (high pressure and low temperature). Further, when cosolvents are used, higher values of both variables are attained at softer operating pressures. Regarding the effect of cosolvents on these variables, it was found to follow this order: ethanol > methanol > acetone > hexane (Mahgerefteh, Denton and Rykov) .

2.1.4 Solid-Supercritical Fluid Phase Equilibrium

The conditions of phase equilibrium between a SCF and a solid component (i) are formulated on the basis of the isofugacity criterion. If the solid phase is assumed to be a pure component i , the solubility of solid (y_i^*) in the gas phase can be directly obtained as (Prausnitz, Lichtenthaler and de Azevedo, 1998):

$$y_i^* = E \frac{P_i^{sub}}{P} \quad (2.1)$$

where E is the enhancement factor over the ideal solubility. P and P_i^{sub} are the operating pressure and sublimation pressure of the solute. For a low-volatility, incompressible solid solute, the enhancement factor can be calculated as follows (Prausnitz, Lichtenthaler and de Azevedo, 1998):

$$E = \frac{\exp\left(\frac{(P - P_i^{sub})v_i^s}{RT}\right)}{\phi_i} \quad (2.2)$$

where ϕ_i is the fugacity coefficient of the solid solute in the gas phase which is strongly dependent on the SCF density. v_i^s is the solid molar volume, R is a universal gas constant and T is the operating temperature.

Figure 2.4 illustrates the relationships of the supercritical fluid density and solid solubility with pressure. The region of SCF is characterized by a strong variation of fluid density with pressure, at temperature close to the critical temperature. For a given isotherm, the increase in solubility closely follows the increase in density. The influence of temperature on the solid solubility is the result of two competing effects: the increase of solid volatility and the decrease of solvent density with temperature rise. Near the critical pressure, the effect of fluid density is predominant. Therefore, a moderate increase in temperature leads to a large decrease in fluid density and a consequent reduction in solute solubility. However, at higher pressure, the increase of the solid sublimation pressure with temperature exceeds the density reduction effect, therefore, the solubility increases with temperature. This behaviour leads to retrograde behaviour of the solid solubility, as illustrated in Figure 2.5. At pressure well above the critical pressure, the isotherms exhibit a maximum in solubility. This maximum is usually observed in the range of 30 to 100 MPa when the partial molar volume of the solute in the fluid phase is equal to its solid molar volume in the supercritical fluid – solid system (Poling, Prausnitz and O'Connell, 2001).

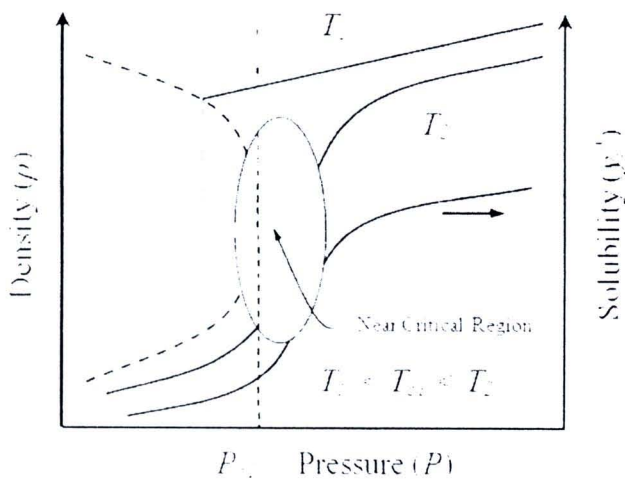


Figure 2.4 Supercritical fluid density (ρ) and solid solubility (y_i^*) in fluid phase as a function of pressure (P) (Martinez, 2008).

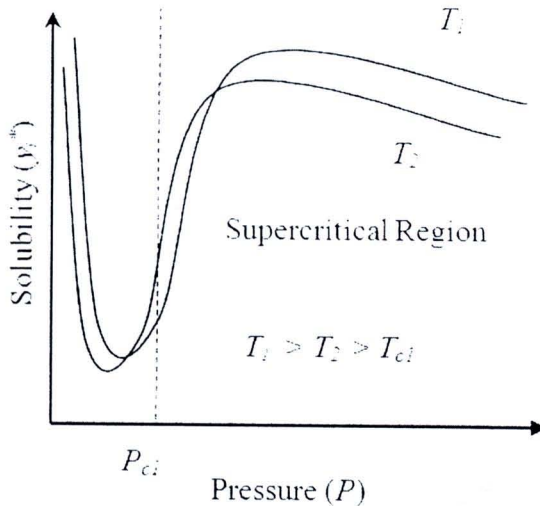


Figure 2.5 Typical isotherms of solid solubility in supercritical fluid (Martinez, 2008).

2.2 Supercritical Fluid Extraction Process

Supercritical fluid extraction (SFE) is a separation process where the substances are dissolved in a fluid which is able to modify its dissolving power under specific conditions in supercritical region. In the next section, its process description will be provided to describe how the SFE works.

2.2.1 Process Description

The process of SFE consists of two essential steps: extraction of the components soluble in a supercritical solvent and separation of the extracted solutes from the solvent. The SFE can be applied to a solid, liquid, or viscous matrix. Based on the objectives of the extraction, two different scenarios can be considered:

2.2.1.1 Carrier Material Separation

In this case, the feed material constitutes the final product after undesirable compounds are removed, for example, dealcoholisation of alcohol beverages, removal of off-flavours, removing fats from foods, or decaffeination of coffee.

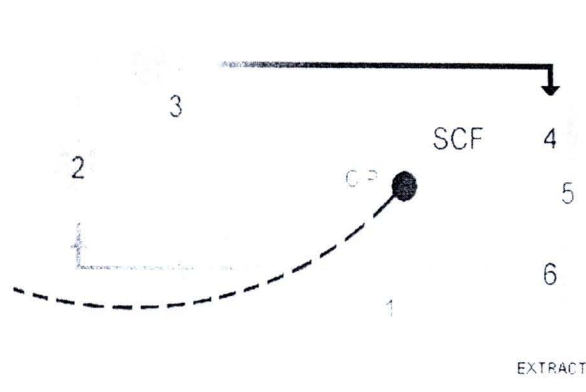
2.2.1.2 Extract Material Separation

The compounds extracted from the feed material constitute the final product, for example, essential oil or antioxidant extraction. The application of the supercritical fluid

technology was for the recovery of various compounds from natural resources and till present time this area is still widely studied (Reverchon and De Marco, 2006). Consequently, SFE of compounds from a solid matrix is attractive and it is chosen to study and model in this research. Most of the development and industrial implementation in supercritical fluid extraction has been performed on solid feed materials. Figure 2.6 showed basic steps of supercritical fluid extraction related to pressure-temperature diagram of fluid (Alimentarias, 2006).

Figure 2.7 illustrates a general flow diagram of a supercritical extraction process from solids. The solvent is subcooled prior to the pump, assuring a liquid phase to avoid cavitations. The pressurized solvent is heated above its critical temperature to the extraction temperature prior to the extraction vessel. The extraction vessel, which is filled with the feed material, is electrically heated to the extraction temperature. The supercritical solvent flows through the fixed bed and the soluble compounds are extracted from the carrier material. The supercritical fluid plus the extract leaves the extraction vessel from the top, through a pressure reduction valve. The solvent power decreases with pressure reduction, so the compounds precipitate. To assure total precipitation, the supercritical solvent is heated above the saturation temperature to reach the gas phase. Under those conditions, the solvent power is negligible. Then the material is collected in a separator while the solvent in gas phase leaves the separator vessel from the top and is recirculated back to the extraction vessel. Once the raw material is fully extracted, the following steps are required in the extraction vessels:

- Depressurization
- Opening of the extraction vessel
- Unloading the spent material
- Loading with fresh material
- Closing the extraction vessel
- Pressurizing to operating conditions



- | | |
|-----------------|--------------|
| 1 Condensation | 2 Pumping |
| 3 Heating | 4 Extraction |
| 5 Decompression | 6 Separation |

Figure 2.6 Basic steps of supercritical fluid extraction related to pressure-temperature diagram of fluid (Alimentarias, 2006).

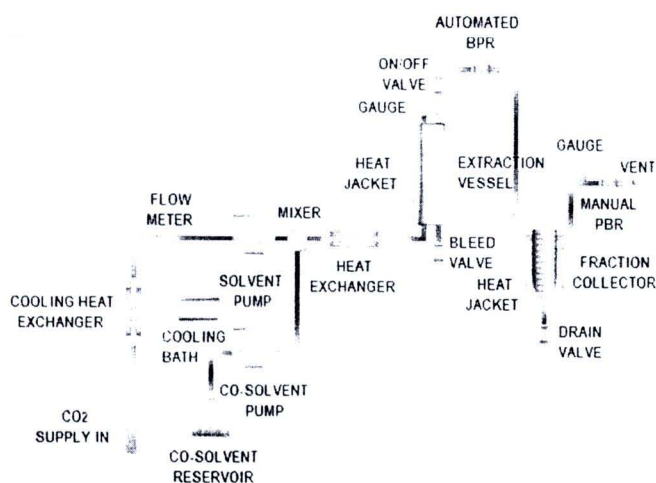
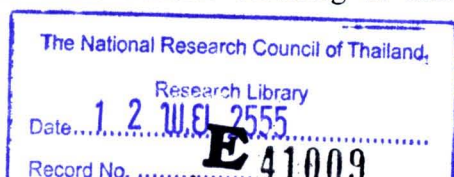


Figure 2.7 Flow diagram of the supercritical fluid extraction apparatus for solid materials (Martinez, 2008).

2.2.2 Advantages of SFE Technique

SFE has several distinct properties. Therefore, it is regarded as a promising alternative technique to conventional solvent extraction methods. Some of its major advantages are summarized as follows:

- SCFs can penetrate into porous solid materials more effectively than liquid solvents and, consequently, it may render much faster mass transfer resulting in faster extractions.



- In SFE, a fresh fluid is continuously forced to flow through samples; therefore, it can provide high quantity of solutes or complete extraction.
- In SFE, salvation power of SCFs can be manipulated by changing pressure and/or temperature.
- Solutes dissolved in SCCO₂ can be easily separated by depressurization.
- SFE is usually performed at low temperatures, so SCFs may be an ideal solvent for extracting thermally sensitive materials.
- SFE uses no or significantly less environmentally hostile organic solvents. SFE may need no or only a few millilitres of an organic solvent while a typical liquid-solid extraction method would require tens to hundreds of millilitres.
- CO₂ can be recycled or reused thus minimizes waste generation.
- SFE can be applied to systems of different scales, for instance, from analytical scale (less than a gram to a few grams of samples), to pilot plant scale (kilograms of samples) and up to large industrial scale (tons of raw materials).

2.2.3 Extraction Conditions

For successful SFE, several factors must be taken into consideration. These factors include type of sample, method of sample preparation, type of fluid, choice of modifiers, method of fluid feeding and extraction conditions including pressure, temperature, flow rate and extraction time as shown in Figure 2.7 (Lang and Wai, 2001).

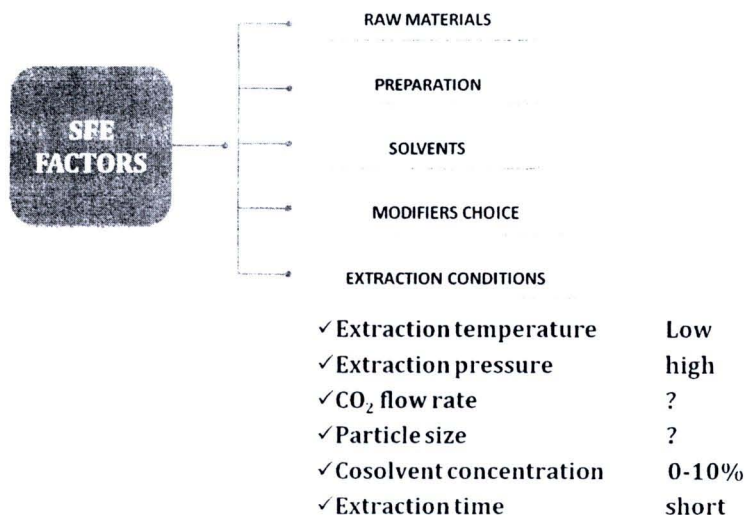


Figure 2.8 Factors of supercritical fluid extraction (Lang and Wai, 2001).

2.2.4 Processing Parameters in the Supercritical Fluid Extraction of Solids

Parameters affecting the supercritical fluid extraction of solids are listed in Table 2.3. The solubility of a target compound in a SCF is a major factor determining extraction efficiency. The influence of the process parameters on SFE can be summarised as follows:

- At pressure close to the critical pressure, the solubility of compounds increases by decreasing temperature. However, at high pressures, the solubility of compounds increases by increasing the temperature. This crossover effect is due to the competing effects of the reduction in solvent density and the increase of vapour pressure.
- The working temperature of SFE has to be fixed between 35 and 60 °C in the vicinity of the critical point for SFE using carbon dioxide as a solvent with and without cosolvent. Consequently, the degeneration of thermolabile compounds is avoided and the natural balance (to maintain quality of target biomolecules in material preparations) of extraction could be preserved.
- The solvent-feed ratio depends on many factors, such as concentration of the solute in feed material, the solubility in supercritical solvent, type of feed. Generally, the industrial processes target solvent-feed ratios are lower than 30.
- The solvent mass flow rate or the residence time of a solvent in an extraction vessel is usually optimized. Even though, high mass flow rates increase production capacity but capital costs also increase.
- The size and morphology of solid materials have a direct effect on the mass transfer rate. In general, increasing surface area increases extraction rate. Therefore, smaller particle size generally favours higher mass transfer and decreasing batch time. However, very small particles cause a channelling effect which decreases the extraction rate. Particles with mean diameters ranging approximately between 0.25 and 2.0 mm are typically used.

- High content of moisture is usually not desirable because moisture acts as a mass transfer barrier.

The scheme in Figure 2.9 indicates how individual extraction conditions (solvent and cosolvent types, temperature and pressure, solvent mass flow rate, and particle size) affect the process (phase equilibrium, flow pattern, and external and internal mass transfers). The thick lines mark the strongest influence. For example, the phase equilibrium is strongly dependent on temperature, pressure, and solvent and cosolvent types. Apparently, temperature and pressure have an influence on all processes. Moreover, the extraction mechanism must be highlight to explain the limitation of extraction step as described in the next section.

Table 2.3 Processing parameters in the extraction of solid (Martinez, 2008).

Raw material related	
<ul style="list-style-type: none"> • Particle morphology and size • Moisture • Chemical reactions for setting free the extract compounds • Cell destruction • Palletisation 	
Operating conditions	
<u>Extraction</u>	
<i>Extraction conditions:</i>	<i>Extraction operation:</i>
<ul style="list-style-type: none"> • Pressure • Temperature • Time • Solvent <ul style="list-style-type: none"> ○ Solvent flow ○ Solvent-feed ratio • Cosolvent <ul style="list-style-type: none"> ○ Cosolvent flow ○ Cosolvent type 	<ul style="list-style-type: none"> • Fractional extraction • Constant conditions
<u>Separation</u>	
<i>Separation conditions:</i>	<i>Separation operation:</i>
<ul style="list-style-type: none"> • Pressure • Temperature 	<ul style="list-style-type: none"> • Single stage • Fractional separation

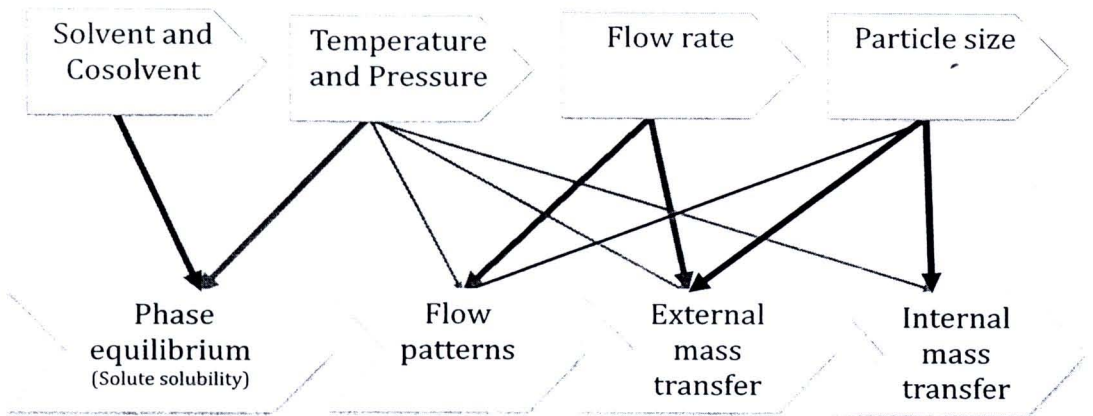
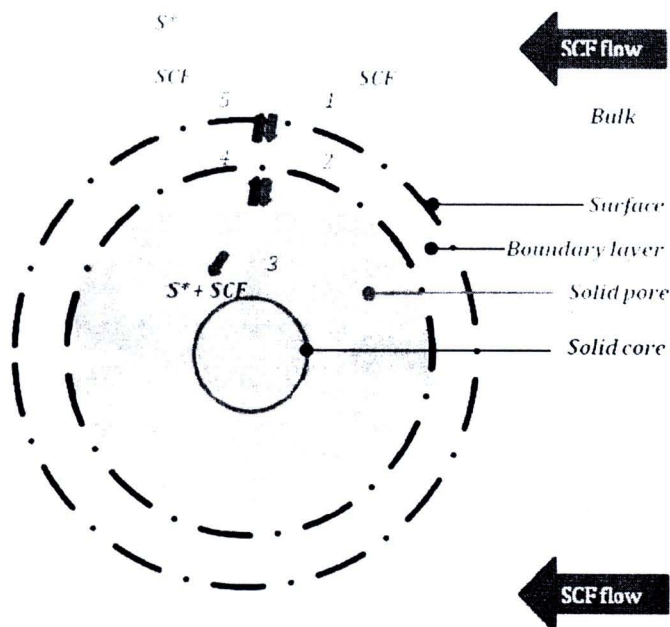


Figure 2.9 Effects of external conditions on equilibrium and kinetics of supercritical fluid extraction processes (Poling, Prausnitz and O'Connell, 2001).

2.2.5 Extraction Mechanism

In general, an extraction system involves a solid phase and a bulk fluid phase. Adsorption, diffusion, solubilisation, and desorption must be taken into consideration for mass transfer mechanisms in the SFE system (Leitner and Jessop, 1999). The mechanisms of SFE can be divided into five steps as can be seen in Figure 2.10.



- Step 1: CO_2 diffusion in SCF film around solid particles
- Step 2: CO_2 penetration and diffusion into particle
- Step 3: Compound solubilisation
- Step 4: Product diffusion through solid particles
- Step 5: Product diffusion through SCF

Figure 2.10 Mechanisms of supercritical fluid extraction.

2.2.6 Extraction Curve

An extraction process is most easily characterised by an extraction curve, a plot of accumulated extract against solvent mass passed through an extractor per unit mass of feed. In general, there are two mechanisms controlling this process, equilibrium-controlled and diffusion-controlled mechanisms. Figure 2.11 shows a typical extraction curve for extraction of solid matrices, which is formed by a straight line in the first period (equilibrium-controlled period) and by a bowed curve in the second extraction period (diffusion-controlled period). Both sections are smoothly connected by a short transition section.

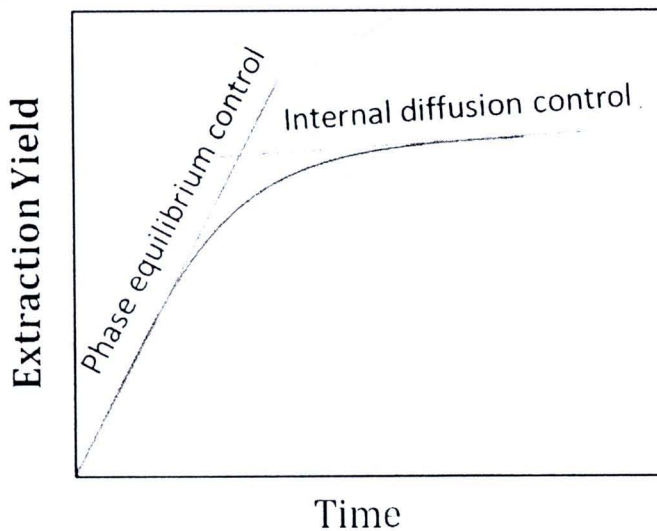


Figure 2.11 Characteristics of extraction curve by film and diffusion controlled mass transfer (McHugh and Krukonis, 1994).

Figure 2.12 (a) shows a typical diffusion controlled extraction curve. The extraction is initially rapid, until the concentration of solute at particle surface drops to zero, then the extraction rate becomes much slower. Figure 2.12 (b) shows a curve for a solubility limited extraction. The extraction rate is almost constant, and only flattens off towards the end of the extraction process. Figure 2.12 (c) shows an extraction curve where matrix effects are significant. There is some sort of reversible interaction with the matrix, such as desorption of solutes from active sites on solid surface.

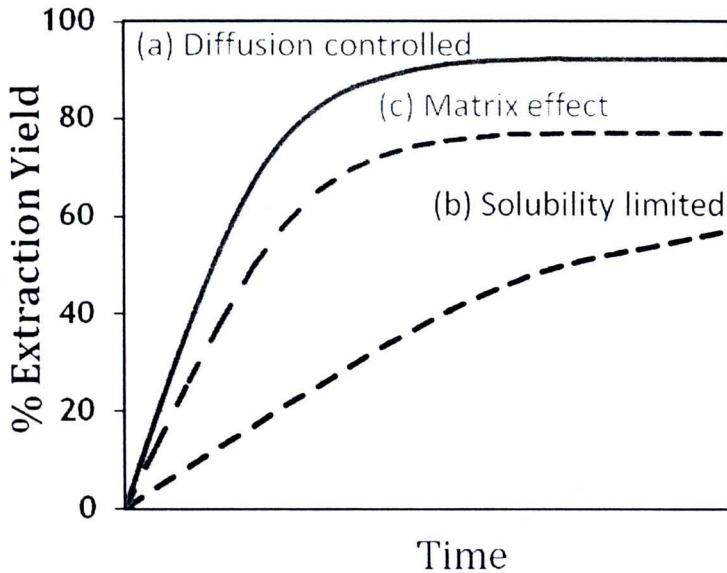


Figure 2.12 Extraction profile percent recovery versus time (Taylor and Larry, 1996).

2.3 Supercritical Fluid Extraction Model

Mathematical modelling for supercritical fluid extraction is one of tools that can help process design decision. In general, extraction models are based on mass transfer mechanisms and equilibrium relationships. Yield predictions require establishment of model predicting phase behaviour, equilibrium, solubility, adsorption, and desorption. Different approaches can be adopted in to describe kinetic behaviour of SFE. When a model describes well phenomena occurred in extractor vessels, it can safely be used for process designing and process scale-up. From a mathematical point of view, all models proposed can be categorized into three groups:

2.3.1 Models Based on Heat Transfer Analogy

A unit of extraction is a single spherical particle. Extension to a whole bed is immediate, since all particles are assumed to be identical. The underlying assumption is that there is no solute accumulation in a bulk fluid. A driving force of extraction is diffusion according to Fick's second law. By analogy with a problem of immersion of a hot sphere into a cold fluid, concentration profile inside particles is assumed to be uniform distribution. For this reason, this model considers ideal extraction behaviour for each single particle because the interactions between the particles can be neglected. However, the extrapolation of the concentration to a fixed bed of particles is overestimated (Reverchon, Donsi and Sesti Osseo, 1993; Esquivel, Bernardo-Gil and King, 1999).

2.3.2 Models based on Mass Transfer Balance

Phenomenological models developed using physical principles such as mass and energy conservations are accurate in representing chemical processes. However, the development of such models is a nontrivial exercise. They take into account the characteristics of the plant matrix, namely the particle size and the bed porosity. Mass balances equation for solute in solid phase and in fluid phase must be described. By integration of these differential equations time dependent concentration profiles in both phases are obtained and the extraction curve is calculated from fluid phase concentration at the extractor outlet. Different mass transfer or equilibrium mechanisms have been hypothesized as controlling the SFE. Three main groups of models based on differential mass balances can be devised. The first considers that the external mass transfer resistance controls the extraction. It was assumed that mass transfer resistance occurred only in the solvent phase (Reverchon, Donsi and Sesti Osseo, 1993; Esquivel, Bernardo-Gil and King, 1999). The second demonstrates that the diffusion inside the particle (internal mass transfer resistance) is the controlling step (Reverchon and Marrone, 1997). The last one points out that the resistance lies in both the fluid and solid phases. The external mass-transfer resistance of fluid phase and internal mass transfer resistance of particle can have a controlling role. However, in this model equilibrium relationship have to propose between the concentration of the particle and bulk phase. In most of SFE processes, the solid particles are porous and thus the solute is present both in the solid phase and in the fluid inside the pores. Due to the lack of experimental phase equilibrium data (Reverchon, Donsi and Sesti Osseo, 1993), two linear driving force approximations are employed (Figure 2.13): one between the fluid phase and the fluid phase in the pores of the solid, the other between the fluid phase in the pores and the solid phase (Sovová, Kucera and Jez, 1994; Reverchon, 1996).

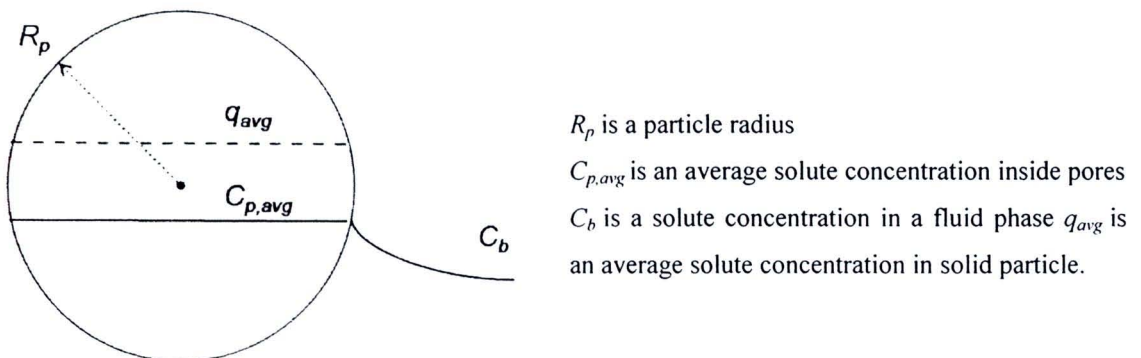
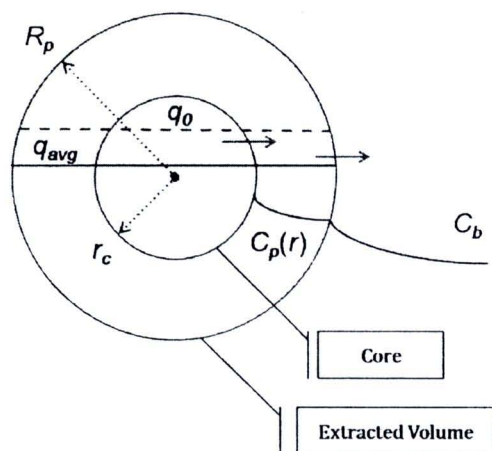


Figure 2.13 Bi-linear driving force of a porous solid (Peker et al., 1992).

2.3.3 Shrinking Core Model

Shrinking core model (SCM) describes a situation of an irreversible desorption followed by diffusion in a porous solid through pores (as illustrated in Figure 2.14). When mass transfer rate of a solute in a non-extracted inner part is much slower than that in outer part where most of the solute has been extracted, or solute concentration is much higher than solubility of a solute in a solvent phase, a shape boundary may exist between outer and inner region. Solid phase solute exists within a core, of which the inner region shrinks with extraction progress. The model will give well prediction if mass transfer mechanisms such as diffusion and solubility are well described (Peker et al., 1992). Solid and fluid phase balances are coupled with an equilibrium relationship to evaluate a mass transfer coefficient of extraction processes. SCM can be adopted when solubility equilibria or external diffusion are limiting steps. Important model parameters are thermophysical properties that need to be determined as the first step of SFE modelling more precisely (Goto, Roy and Hirose, 1996). Mass transfer coefficients can be obtained by many correlations (Poletto and Reverchon, 1996) but the solubility of a solute in supercritical fluids is normally limited to pure supercritical fluids because experimental data are not available. Moreover, evaluation of a separation process using supercritical fluids relies heavily on an ability to model the solute-supercritical solvent equilibrium behaviour (Mongkholkhajornsilp et al., 2005). Therefore, solubility modelling of solids in supercritical fluids is developed in this work.



r is a radial coordinate of a particle,
 r_c is a core radius
 $C_p(r)$ is a solute concentration in a pore network
 q_0 is an initial solute concentration in the solid particle.

Figure 2.14 Shrinking core particle (Goto, Roy and Hirose, 1996; Döker et al., 2004; Ajchariyapagorn et al., 2009).

2.4 Solubility Modelling of Solids in Supercritical Fluids

Knowledge of solute solubility in supercritical fluids is essential for efficiently designing supercritical fluid processes. Due to difficulties of experimental measurements and also time-consuming and costly techniques, it is desirable to develop predictive methods for estimating phase behaviour of SFE system. A literature survey shows that available models fall into two main categories (Huang et al., 2007):

2.4.1 Semi-Empirical Models

Semi-empirical or density based models are based on linear relationship between logarithm of solute solubility and logarithm of solvent density within a certain range of pressure and temperature. Generally, the semi-empirical models give fast estimation and good results for a solvent-density region used in the experiments. For most of the semi-empirical models, there is no need to use physicochemical a property because none of the mechanisms occurred in the process is taken into consideration. Therefore, no mechanistic insight can be obtained. Simple error minimization using least squares method may occur thus the model is applicable for interpolation of unmeasured solubility data after training the model by calculating the model constants. However, it needs to improve the semi-empirical models with regards to accuracy and wider applicability range (Lucien and Foster, 2000).

2.4.2 Theoretical Models

Theoretical models can be divided into 2 groups: Infinite dilute solution models and equations of state.

2.4.2.1 Infinite Dilute Solution Models

An Infinite dilute solution model is based on the regular solution theory. In SFE process, SCCO₂ is treated as an expanded liquid solvent, therefore, in this approach, solid pharmaceutical compounds were assumed to be in phase equilibrium with liquid SCCO₂ solvent. A deviation of solid solubilities using the same formulation as those in liquid phase is applied. An infinite dilution activity coefficient was employed for non-ideal behaviour of solid–liquid equilibrium with low solubility (Chrastil, 1982; Su and Chen, 2007). The parameters of this model generalized as a function of properties of compounds. For solids of low solubility (usually those with high melting points), solute-

solvent interactions are significant, and an appropriate activity coefficient must be chosen. Molar volumes of solid solutes in SCCO₂ are taken as the empirical parameters. The logarithms of the molar volumes of solutes are correlated as a linear function of the logarithms of the densities for SCCO₂ (Su and Chen, 2007).

2.4.2.2 Equations of State

Models derived from equations of state (EOS) need complicated computational procedures. These models employ solute properties, such as critical properties, acentric factor, solid molar volume, and vapour pressure. Numerical values of solute properties can affect solubility predictions using the models derived from EOS. Reasonable estimations of critical constants as well as sublimation pressures of solid are crucial to calculate precise roots of EOS. These properties can be determined by experiment or group contribution methods. Due to several drawbacks in both cases, an error is produced in solubility estimations (Su and Chen, 2008). Various EOSs and mixing rules are successfully applied in solid solubility calculation. The model derived from EOS requires adjustable parameters, interaction parameters, and size of solutes, which must be correlated from experimental solubility data. The model development of SFE system is accompanied by mathematical relationships as well as iterative calculations (Poling, Prausnitz and O'Connell, 2001).

Six different cubic EOSs, i.e. van der Waals (vdW), Redlich–Kwong (RK), Mohsen-Nia–Moddaress–Mansoori (MMM), Peng-Robinson (PR), Patel-Teja (PT), and modified PR-EOSs, were used to predict solubilities of cholesterol and β -carotene in supercritical fluids (carbon dioxide and ethane). All of them require two adjustable parameters and one interaction parameter calculated by minimizing the percentage of average absolute deviation except the MMM-EOS requires only one adjustable parameter. The MMM equation is in much better agreement with the experimental data than the other equations (Ajchariyapagorn et al., 2008; Yazdizadeh, Eslamimanesh and Esmaeilzadeh, 2011). Estimations of density of SCCO₂ from Lee-Kesler-Plöcker (LKP), Zudkevitch-Joffe (ZJ), Peng-Robinson (PR), Peng-Robinson modified by Stryjeck and Vera (PRSV), and Soave-Redlich-Kwong (SRK) EOSs were compared with experimental results from some previous studies for a pressure range of 20-60 MPa and a wide range of temperature. LKP equation had less error in comparison with most of the EOSs studied (Hartono, Mansoori and Suwono, 2001).

Ajchariyapakořn et al. (2009) applied LKP and MMM-EOSs to estimate PVT behaviour of solvents and a fugacity coefficient of solutes in solute-solvent mixtures. The LKP-EOS provides the best fit for β -carotene and nimodipine in SCCO_2 . On the other hand, the MMM-EOS is best for cholesterol in SCCO_2 and SCC_2H_6 as well as for nimbin in SCCO_2 . Aromaticity Index (AI) was used as a criterion for the model selection. One should use the LKP-EOS when $\text{AI} > 0.3$, otherwise use the MMM-EOS (Esamaeili, 2010).

Critical properties, sublimation pressures, acentric factors of all components, and molar volumes of solid components in the system are required for calculating the solubility and phase equilibrium of a solute in a supercritical fluid using EOS. When some of these values are not available, as is the case here, estimation techniques must be employed. When neither critical properties nor acentric factors are available in the literature, compound normal boiling point and molecular structure can be used for the estimation.

2.5 Physical Property Estimation

The basis for simulation of many chemical processing units is a set of physical and thermodynamic properties of compounds in process. It is not always possible to find experimental values of properties for the compounds of interest in the literature. Therefore, estimation methods are generally employed. Group contribution methods such as Joback and Reid (Ajchariyapagorn et al., 2008), Lydersen (Joback and Reid, 1987), Ambrose (Lydersen, 1955), Lyman (Poling, Prausnitz and O'Connell, 2001), and Gani (Lyman, Reehl and Rosenblatt, 1982) methods have been widely used to estimate critical properties. In these methods, the property of compound is a function of structurally dependent parameters, which are determined by summing the frequency of each group occurring in the molecule times its contribution. These methods provide an advantage of quick estimates without requiring substantial computational resources. Many of these methods are, however, of questionable accuracy, and are unable to distinguish among isomers and have limited applicability due to an oversimplification of molecular structure representation as a result of use of a simple group-contribution approach (Constantinou and Gani, 1994). In practical, interested compounds have high

molecular weight and complex structure molecules. A group contribution method which has a comprehensive data bank for all structure molecular groups is preferred. This will lead to minimum error in SFE model (Poling, Prausnitz and O'Connell, 2001).

Gani method developed from Joback method has been widely used to estimate critical properties of high molecular biomolecules because it gave smaller error than other group contribution methods (Poling, Prausnitz and O'Connell, 2001). However, the Gani method did not provide group contributions as much as Joback method (Garnier et al., 1999). The critical properties estimated by Joback method have higher values than those estimated by Gani method. The latter is fairly reliable for all critical properties' estimation although there are important errors for smaller substances (which is not the case of this research). On the other hand, Joback method is usually quite reliable for the prediction of critical temperatures but only if an experimental value for normal boiling temperature was used (which is not the case because normal boiling temperature was also estimated by Joback method). Furthermore, Joback method can originate large errors in the estimation of critical pressure, especially for large molecules such as fluorinated species and organic acids (Fornari, 2007). In addition, Coimbra et al. (2006) illustrated the key-role played by critical properties on the correlation of solid/SCF equilibrium. It appeared that, to obtain good correlation results using the SRK-EOS, the critical properties and Pitzer's acentric factor were preferable to be estimated using the Gani method (Poling, Prausnitz and O'Connell, 2001).

Besides critical properties, sublimation pressures of solids also play a dominant role to calculation results of fluid-solid separation process. The predicted solubilities are affected significantly by the value used for the sublimation pressure of the solid. The sublimation pressure values, which gave reasonably accurate predictions, were found to be 3-4 orders of magnitude lower than ones reported in the literature (Coimbra, Duarte and de Sousa, 2006). Generally, sublimation pressure of high molecular weight compound is too small for accurate experimental measurement and is very difficult to perform the experiment although sublimation pressures are of most importance in the process evaluation. Some researchers recommended that sublimation pressures should be considered as an adjustable parameter (Coutsikos, Magoulas and Kontogeorgis, 2003). In case of no experimental data is available in the literature, so sublimation pressure is often estimated by empirical correlations (Reverchon et al., 1995). Watson

correlation (Lyman, Reehl and Rosenblatt, 1982) was successfully used to estimate molar solid volumes of flurbiprofen, ketoprofen, naproxen and ibuprofen (Tuřrk and Kraska, 2009). Molar solid volumes may be determined experimentally by weighting from crystallography studies or from an extension of group contributions to a crystalline state when there are no available data in the literature (Coimbra, Duarte and de Sousa, 2006; Ajcharyapagorn et al., 2008).

The next chapter will present theoretical models of solid solute and their relevance is solubility and extraction yield in SFE systems.