STUDIES ON MASS TRANSFER CHARACTERISTICS OF PALM KERNEL OIL EXTRACTION USING SUPERCRITICAL CARBON DIOXIDE

by

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Thesis submitted in fulfillment of the requirements
for the degree of
Doctor of Philosophy

May 2005

DEDICATION

This thesis is especially dedicated to the memory of my dear father, Hj Ismail bin Hj Mohamad, whose love was sorely missed. This thesis is also dedicated to my loved ones; mother, Hajjah Khadijah bt Abdullah, husband, Zulkifle bin Mat Bah and children, Nur Sakinah, Nur Shahirah, Nur Shafiqah, Muhammad Zahid Hatim and Muhammad for their continuous love, support, and prayer..............................

ACKNOWLEDGEMENTS

Glory is to Allah and all praise is to Allah. It is only with His help, blessings and guidance and only by His will that I finally managed to complete my thesis. I would like to take this opportunity to thank my supervisor Prof. Ir Dr Mohd Omar Abdul Kadir for his kind help in whichever way that he could. Special thanks are due to Associate Professor Dr Mohammad Hakimi Ibrahim, Head of Environmental Technology Division, for all his kind help, guidance and valuable advice. Special thanks and appreciation also goes to Associate Professor Dr Jamaluddin Bin Mohd Ali from the School of Mathematics, Associate Professor Dr Abdul Karim and family, Dr Ruzitah bt. Mohd Salleh from Faculty of Chemical Engineering University Technology MARA, and Cik Rabeah Hussein from MPOB for helping me in whichever way that they could. I also wish to express my heartiest thanks and deep gratitude to my kind-hearted friend En Ahmad Kamarulnajuib b. Che Ibrahim (Malacca DOE State Director) for his constructive comments, guidance and assistance especially in this thesis writing and also during this study. Also to my colleagues the supercritical group member, En.Anuar, En.Rahmad Setia Budi, En Azizi, En Adel Banana, Dr Zaidul, and En Wahyu. Not forgotten Pn Asyirah, Dr Norli, Dr Zarina, Cik Afidah and others for all the kind help that they had given to me during my studies here in U.S.M. I also wish to express my thanks to all the Environmental Technology staffs. Special thanks and appreciation also goes to all Hj Ismail family members for their kind support, motivation, advice and prayer. Finally, I would like to thank my employer, University Technology MARA for giving me the opportunity to pursue my studies as well as sponsoring my studies here.

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LIST OF ABBREVIATIONS

PKO	Palm Kernel Oil
CPKO	Crude Palm kernel Oil
RBDPKO	Refined Bleached Deodorized Palm Kernel oil
SCF	Supercritical Fluid
$SC\text{-}CO_2$	Supercritical Carbon Dioxide
SEM	Scanning Electron Microscope
TEM	Light Electron Micrograph

LIST OF SYMBOLS

		Unit
V	Volume	m
D	Diameter	m
r	Radius	m
H	Height	m
ν_o	Solvent Flow Velocity	m/h
m_s	Mass Flow of CO_2	kg/h
Q	Volumetric Flow rate	m^3/h
ρ_b	Bulk Density	kg/m^3
ρ_p	Particle Density	kg/m^3

KAJIAN CIRI-CIRI PEMINDAHAN JISIM DALAM PROSES PENGEKSTRAKAN MINYAK ISIRUNG SAWIT MENGGUNAKAN BENDALIR LAMPAU GENTING KARBON DIOKSIDA

ABSTRAK

Untuk terus mengeksplotasi pengekstrakan Bendalir Lampau Genting Carbon Dioksida (BLG-CO_2), sebagai satu kaedah ringkas dan berteknologi bersih, maka kajian terhadap jumlah atau hasil minyak isirung sawit, kajian asas terhadap fenomena pemindahan jisim meliputi koefisien peresapan dan pemindahan jisim minyak isirung sawit bagi sebutir isirung sawit dan dan juga bagi lapisan terpadat isirung sawit dijalankan. Di samping itu, kajian ini juga membangunkan model matematik untuk menerangkan fenomena permindahan jisim minyak isirung sawit dalam lapisan terpadat isirung sawit dalam keadaan lampau genting. Oleh itu, kajian ini hanya memberi tumpuan kepada pengekstrakan isirung sawit yang bersaiz 6 mm pada garispusat luar menggunakan peralatan BLG-CO_2. Bagi pengekstrakan sebutir isirung sawit, keadaan lampau genting bagi komponen CO_2 pada julat suhu 40 °C, 50 °C, 60 °C, 70 °C dan 80 °C dan juga pada julat tekanan 27.6 MPa, 34.5 MPa, 41.4 MPa dan 48.3 MPa dipilih. Bagi pengekstrakan lapisan terpadat isirung sawit, julat suhu 50 °C, 60 °C dan 80 °C dipilih dengan mengekalkan julat tekanan yang sama.

Penemuan hasil kajian menunjukkan pertama, minyak isirung sawit yang paling maksima yang dapat diekstrak dari ***sebutir isirung sawit*** menggunakan BLG-CO_2 adalah sebanyak 5 peratus pada suhu dan tekanan paling maxima yang digunakan ia itu 80 °C dan 48.3 MPa. Kedua, kelarutan minyak isirung sawit dalam BLG-CO_2 juga di dapati bertambah dengan peningkatan suhu pada tekanan tetap, dan sebaliknya. Ketiga, kajian terhadap koefisien peresapan minyak isirung sawit di dalam sebutir isirung sawit menunjukkan bahawa koefisien peresapan bagi minyak isirung sawit di dalam sebutir isirung begantung kuat kepada tekanan.dan tidak kepada suhu pada julat tekanan 27.6 MPa hingga 48.3 MPa pada suhu tetap 50 °C dan 60 °C. Koefisien peresapan bagi minyak isirung sawit dalam sebutir isirung sawit di dapati tidak banyak berubah pada suhu tetap 40 °C, 70 °C dan 80 °C pada julat tekanan yang sama. Kajian ke atas koefisien pemindahan jisim keseluruhan bagi minyak isirung sawit bagi sebutir isirung sawit pula menunjukkan bahawa, pada suhu tetap 50 °C dan 60 °C, koefisien pemindahan jisim keseluruhan bertambah dengan tekanan dari 27.6 MPa hingga 48.3 MPa. Walau bagaimana pun, pada suhu tetap 40 °C, 70 °C dan 80 °C di dapati bahawa tekanan tidak memainkan peranan penting dalam meningkatkan koefisien pemindahan jisim keseluruhan.

Kajian lain terhadap pengekstrakan minyak isirung sawit di dalam ***lapisan terpadat isirung sawit*** menunjukkan jumlah maxima minyak isirung sawit yang dapat diekstrak adalah sebanyak 15 peratus pada suhu dan tekanan maksima 70 °C dan 48.3 MPa. Kajian juga mendapati bahawa, koefisien peresapan bagi minyak isirung sawit dalam lapisan terpadat isirung sawit adalah fungsi kepada tekanan, dan tidak kepada suhu.

Kajian terhadap koefisien pemindahan jisim keseluruhan bagi minyak isirung sawit dalam lapisan terpadat isirung sawit pula menunjukkan bahawa koefisien pemindahan jisim keseluruhan bagi minyak isirung dalam lapisan terpadat isirung sawit merupakan funsi kepada suhu dan tekanan. Kajian ini juga telah berjaya membangunkan model korelasi bagi pemindahan jisim untuk lapisan terpadat isirung sawit. Model korelasi Sh = 0.980 $ReSc^{1/3}$ merupakan model korelasi terbaik yang dapat menghubungkan nombor Sherwood, nombor Reynolds dan nombor Schmidt pada julat tekanan dan suhu masing-masing dari 27.6 MPa hingga 48.3 MPa dan julat suhu dari 50 °C hingga 70 °C.

ABSTRACT

To exploit further the application of supercritical carbon dioxide (SC-CO_2) extraction, as a simplified and environmental friendly process, a study on the palm kernel oil yield, fundamental of diffusivity and mass transfer coefficients of palm kernel oil in situation of overall single palm kernel and a packed-bed column of the overall single palm kernels was studied. The study also incorporated mathematical models formulation for describing the mass transfer phenomena of palm kernel oil at the supercritical conditions. Thus, this study has focused on the candidate sample of overall single palm kernels of size 6 mm (outside diameter) by using a laboratory Supercritical Carbon Dioxide (SC-CO_2) equipment. The experimental runs of the supercritical conditions considered in this study vary in a range of temperatures and pressures of 40 °C, 50 °C, 60 °C, 70 °C and 80 °C and pressures of 27.6 MPa, 34.5 MPa, 41.4 MPa and 48.3 MPa respectively for an overall single palm kernel, and at a constant temperature of 50 °C, 60 °C and 70 °C and within the same pressure range for a packed bed of overall single palm kernels.

The findings of this study on ***an overall single palm kernel***, demonstrated that first, the laboratory SC-CO_2 extraction process managed to extract a maximum yield of 5 percent PKO at the best supercritical conditions of temperature 80 °C and pressure 48.3 MPa respectively. Secondly, the solubility of PKO in SC-CO_2 increases with temperatures at a particular constant pressure, and likewise increases with pressures at a particular constant temperature. Thirdly, the study shows that the diffusion coefficients of PKO at the supercritical condition, based on an overall single palm kernel, is strongly dependent on

pressures from 27.6 MPa to 48.3 MPa, at each constant temperature of 50 °C, and 60 °C. Nevertheless, a weak correlation between diffusion coefficients with pressures was found at each constant temperature of 40 °C, 70 °C and 80 °C. Similarly, findings from this study also showed that at a constant temperature of 50 °C, and 60 °C, the overall mass transfer coefficients increases with pressures from 27.6 MPa to 48.3 MPa. But, at a constant temperature of 40 °C, 70 °C and 80 °C, no increasing trend of the overall mass transfer coefficients of PKO with pressure could be observed.

In another SC-CO_2 studies, for extraction of PKO from ***a packed bed of palm kernels*** in a laboratory scale extractor, show that a maximum amount of 15 percent PKO can be extracted at the best supercritical conditions of temperature 70 °C and pressure 48.3 MPa. The studies also demonstrated that the diffusion coefficients of PKO in a packed bed of overall single palm kernels are dependent on pressures rather than temperatures. In a similar study, it was found that the overall mass transfer coefficients of PKO from a packed bed of overall single palm kernels, dependent on both temperatures and pressures at supercritical conditions with temperature range from 50 °C to 70 °C and pressure range from 27.6 MPa to 48.3 MPa respectively. A mass transfer correlation model was developed for palm kernel oil extraction in a packed bed of overall single palm kernels. The mathematical empirical model developed is given by $Sh = 0.980\ ReSc^{1/3}$. This is the best-fit equation for correlating the experimental results of the Sherwood, Schmidt and Reynolds numbers for PKO extraction over the entire range of pressures and temperatures of 27.6 MPa to 48.3 MPa and 50 °C to 70 °C respectively.

CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

Efforts to optimize or increase extraction yield of palm kernel oil (PKO) in Malaysia is a new focus in the current research. A number of reasons have been put forward to motivate research in this area. First, the increase in price of commodity (PKO) in the world market has persuaded Malaysian government to formulate new strategies in order to maintain Malaysia as the world palm oil producer and exporter. At the same time, the growing global economy has driven consumption and demand for this commodity. Secondly, the current research and technology, has successfully demonstrated that PKO has multi applications, edible and non-edible uses. Examples of edible uses include margarine, cooking fats, coffee whiteners, confectionary, and artificial cream fillings. Non-edible uses like personal care products, soaps and detergents. Thirdly, to keep up to date with the new technology of production, and competition in global market, it is timely for Malaysia to review the current method of PKO extraction and to investigate a new extraction technology available in present world market and also research for its effectiveness in the current practices in the world, so that it can be adapted and adopted for Malaysian palm oil millers. Fourthly, due to environmental and social factors have also motivated Malaysian palm oil industries to search and apply a safer extraction and separation technology.

The fourth reason is also a result of the recent interest and development of new regulations and policy globally in order to scrutinize the safer solvent and fugitive hydrocarbons in the environment and also to enhance edible food products safely which commonly generated from the use of the solvent extraction method. The global warming issues and Kyoto Protocol, which Malaysia is a party, has prepared Malaysia to be proactive and abide with the new environmental policy directives ahead.

Current method of PKO extraction involved various methods such as screw press, solvent extraction and a combination of screw press with solvent extraction which normally remove the insoluble oil impurities like fruit fibres, nut shells and free moisture. However, other useful constituents available in PKO like oil soluble non glycerides which include free fatty acids, phospholipids, trace metals, carotenoids, tocopherols /tocotrienols, oxidation products and sterols, that are much more difficult to be removed. Thus, the oil needs to undergo further stages of refining in order to yield refined bleached and deodorized palm kernel oil (RBDPKO).

Further stages of refining techniques consisted of processes like degumming, bleaching, deodorization; fractionation and hydrogenation may also needed additional technological unit operations or processes to produce different types of the food uses. Consequently, each of these technological processes may affect the nature of the extracted oils. Therefore, an alternative up to date technology of PKO extraction with less or no effects to the extracted oil should be further research in particular, to understand it is fundamental on the phenomena of the oil mass transfer behavior or properties.

It has been well known that, one alternative method and also among the most recent technology possible for extraction and separation of oil in particular, palm kernels is the Supercritical Carbon Dioxide (SC-CO_2) method. According to Bruno and Ely (1991), the SC-CO_2 extraction method has emerged as an ideal separation processes in applications in food products manufacturing, pharmaceutical, and chemical and oil industries.

A supercritical fluid (SCF) is defined as any compound at a temperature and pressure above its critical values. The critical temperature of compound however, is defined as the temperature above which a pure, gaseous component cannot be liquefied regardless of the pressure applied, and the critical pressure is defined as the vapor pressure of the gas at the critical temperature. Thus, it is reasonable to assume that the fluid is neither a gas nor a liquid, and is best described as intermediate of the two extremes. It is interesting to note that at a certain combination of temperature and pressure, fluids reach their critical point, beyond which their solvent properties are greatly altered. These properties make extraction feasible. In fact, these properties make extraction more rapid and efficient (Mc Hugh and Krukonis, 1986).

It is therefore; very vital to exploit further the SC-CO_2 extraction method whether it provides an alternative and opportunities for extraction of PKO which maybe be feasible for commercial production. With this intention, research on the properties of SC-CO_2 in relation to the phenomena of mass transfer and separation of PKO within palm kernels and the effectiveness of its SFE column scale- up for the extraction of PKO is an essential knowledge for future decisions.

1.2 Statement of Problems

The ultimate aim of this study is to investigate the feasibility of evaluating an acceptable extraction yield of PKO for industrial scale production based on overall 'single' palm kernel or a set of the kernels by using SC-CO_2 extraction method. In this study, the term "overall or whole single palm kernel" and "single palm kernel" was taken to be synonymous. It is important to emphasize the term 'overall single palm kernel' at this point, because the original form or state of the kernels throughout this study has never been distorted to other forms such as ground, sliced, flaked and chopped. This study approach is unique for three main reasons:

(i) To maintain a condition similar to the current practice of PKO extraction, which normally involved the collection of the whole or overall single palm kernels, obtained immediately after fresh fruit bunches (FFB) are processed and leftover, and then it is transferred into conventional method-screw presses for further oil extraction. In this manner, the management and handling of the overall palm kernels, that include its total time of extraction processes per cycle, is kept to minimum.

(ii) The size of the palm kernels are small, almost spherical in shape and appropriate for PKO to be extracted by a 'packed-bed' in an extractor column. However, this manner of extraction particularly for palm kernels still provide some gaped for further research on its fundamental aspects such as the issues of supercritical conditions on diffusivity and mass transfer in its packed bed column to be scale up to industrial scale. The possibility of avoiding further grinding process can save extra unit operations. For that reason, this study is important to investigate the feasibility of modifying the current practice of palm oil extraction processes by replacing with the supercritical (SC-CO_2) extraction method instead of entirely dependent on the current conventional practice by using either screw press method, solvent extraction or a combination of both.

(iii) The palm kernels (a cross breed of Dura and pisifera varieties) itself originated from the oil palms (the Elaeis guineensis family) which is the Malaysian indigenous crop, and Malaysia, still the world exporter of palm oil.

1.3 Significant Contributions

The novel part of this study is related to the development of mass transfer empirical model which relates the Sherwood (Sh), Schmidt (Sc) and Reynolds (Re) number under the influence of supercritical conditions, for extracting palm kernel oil (PKO) from overall single palm kernels. In this case, the fundamental behavior of the mass transfer and diffusivity coefficients of PKO extraction, under the supercritical conditions based on overall single palm kernels will be well understood. Thus, a better prediction to an overall PKO extraction can be made with certain conditions of accuracy and validity for the purpose of scale-up, which involved a large amount of the overall single palm kernels.

In addition, the study can broaden the understanding on the behavior or effects of oil extraction yield, the properties of fluid flow and the problems that may limit the transport and separation processes of PKO. Further, an inventory to the database of SC-CO_2 literatures will be enhanced since PKO is a valuable commodity originated from the Malaysian native crop. Since previous studies on palm kernel oil extraction at supercritical conditions were merely concentrating on palm kernels that have undergo pre-treatment process (e.g. ground, sliced, flaked, chopped), therefore it is well-timed that studies on the overall single palm kernels should be conducted as it is still scarce in the literatures of supercritical fluid extraction (SFE).

1.4 Objectives of the Study

(a) To investigate the effects of supercritical extraction parameters by using the laboratory scale supercritical (SC-CO_2) on the extraction of palm kernel oil (PKO) from an overall single palm kernel;

(b) To investigate the transport and separation phenomena under the influence of supercritical conditions in particular, the diffusivity coefficient and the overall mass transfer coefficient on the extraction of palm kernel oil (PKO) from the overall single palm kernel by using the laboratory scale SC-CO_2 method;

(c) To investigate the effects of supercritical extraction parameters by using the laboratory scale supercritical (SC-CO_2) extraction method on the extraction of palm kernel oil (PKO) from a set of overall single palm kernels arranging in a packed bed column;

(d) To investigate the transport and separation phenomena under the influence of supercritical conditions in particular the diffusivity coefficient, the overall mass transfer coefficient, and the fluid flow conditions, for extraction of PKO from a set of overall single palm kernels arranging in a packed bed column by using the laboratory scale supercritical (SC-CO_2) extraction method;

(e) To develop supercritical conditions mathematical model on mass transfer of the palm kernel oil extraction with respect to the dimensionless numbers of Sherwood (Sh), Schmidt(Sc) and Reynolds (Re);

(f) To validate the observed and predicted mass transfer data of the palm kernel oil extraction at the supercritical conditions based on the mathematical models; and

(g) To determine an industrial scale-up of a packed-bed extraction column for palm kernel oil extraction under the influence of supercritical conditions by using data obtained from the laboratory scale experiments.

1.5 Limitations of the Study

The supercritical fluid extraction study emphasizes on candidate samples of overall single palm kernels, with each has specific size of outside diameter 6 mm and weight ranging between 0.20 to 0.25 g, based on wet weight. The kernels are selected amongst palm kernels of age around 7 years. The study excludes palm kernels in a form of ground, sliced, flaked and chopped.

The study conducted by using laboratory scale supercritical (SC-CO_2) equipment (Model: Isco, Inc., Lincoln, Nebraska U.S.A.) is entirely dependent on an extractor cell of size 7.5 mm internal diameter; and 56 mm in height and therefore, the palm kernels of size bigger than 7.5 mm outside diameter are excluded. For the study involving packed bed of overall single palm kernels, only a maximum of six (6) overall single palm kernel were considered during each experimental run at supercritical conditions.

CHAPTER 2

LITERATURE REVIEW

2.1 General

In this study, there are several different scientific and engineering literature topics of common subjects need to be reviewed. Although the ultimate intension of this study is to generate findings on the best acceptable yield of palm kernel oil for industrial production by using the supercritical carbon dioxide (SC-CO_2) extraction process, other important fundamental concepts and related subjects needed to be exploited. These include the principles of fluid mechanics, mass transport and separation phenomena for extracting palm kernel oil at supercritical conditions. Beside, mathematical modeling that correlates the mass transfer phenomena for palm kernel extraction at supercritical conditions is important to be established. The model can be useful tool for formulating an understanding on the general rules of scaling-up of an industrial supercritical conditions extraction column and the fundamental knowledge of diffusivity behavior of the palm kernels itself at the supercritical conditions.

2.2 History of Supercritical Fluids

As reported by Stahl et al (1988) and Mc Hugh and Krukonis (1986), supercritical fluids was evolved after the first observation report by Baron Cagniard de la Tour in 1822.

The observation report highlighted that a supercritical phase existed by noting the disappearance of the gas liquid when the temperature of certain materials was increased by heating each of them in a closed glass container. From these early experiments, the critical point of a substance was first discovered.

According to Stahl et al (1988), it was reported that in 1879, Hannay and Hogarth made some observations on the solubility of some inorganic salts in supercritical ethanol and later concluded that the solubility of substances having low vapor pressure in supercritical fluids conditions were dependent on pressure.

Larry (1996) reported that Buchner continued studies on the solubility of several solutes in supercritical fluids over a wide range of temperature since in 1906. He was the first to investigate the solubility of naphthalene in supercritical carbon dioxide and ethylene. However, due to considerable experimental problems, further investigations on the supercritical fluid of naphthalene solubility were hindered, until 1948; Diepen and Scheffer began their extensive publications on the phase behavior on naphthalene supercritical system in late 1940's.

As reported by Francis (1954), extensive studies were conducted on the phase behavior of ternary systems containing liquid carbon dioxide. Beside, the solubility of 261 compounds in near-critical liquid carbon dioxide was determined. This data was used to formulate general rules on the solubility behavior of compounds in supercritical carbon dioxide.

For the past 40 years ago, the use of supercritical fluid as solvents for extraction and separation purposes has been a tremendous interest. The real breakthrough in supercritical fluid extraction resulted from the work carried out by Zosel in 1964 at Max-Plank Institute on coal research. His work provided the incentive for extensive research in supercritical fluid. On the other hand, intensive study on extraction of food components by using supercritical fluid began in the early 1970's. Many patents resulted from these studies, such as, for the extraction of hops, decaffeination of coffee and tea, and tobacco and spices. Since then, supercritical fluid has been receiving increasing interest as a solvent extraction of solids and liquids, as reported by Mc Hugh and Krukonis (1986).

2.3 Principles of Supercritical Fluids

Mc Hugh and Krukonis (1986), also reported that at certain combination of temperature and pressure, fluids reach their critical point, beyond which their solvent characteristics are significantly changed. These characteristics make possible for extraction to take place rapidly. This principle can be explained more clearly by using solid, liquid and gas phase diagram.

Figure 2.1 shows a phase diagram of a pure component which differentiate between the gas, liquid and supercritical states. From the figure, if liquid and gas are in equilibrium, then the gas and liquid would coexist toward critical temperature (T_c), and increasing both the temperature and pressure, the liquid becomes less dense due to thermal expansion, and the gas become much denser due to the rising pressure. At the critical point C, the densities of the two phases become identical, the distinction between the gas and the liquid disappears, and therefore the substance becomes known as 'a supercritical fluid'.

The critical point is characterized by the intersection point between the critical temperature, (T_c), and critical pressure (P_c). Beyond critical temperature (T_c), the substance is described as a fluid, (F). However at lower pressures, the fluid has a gas-like property.

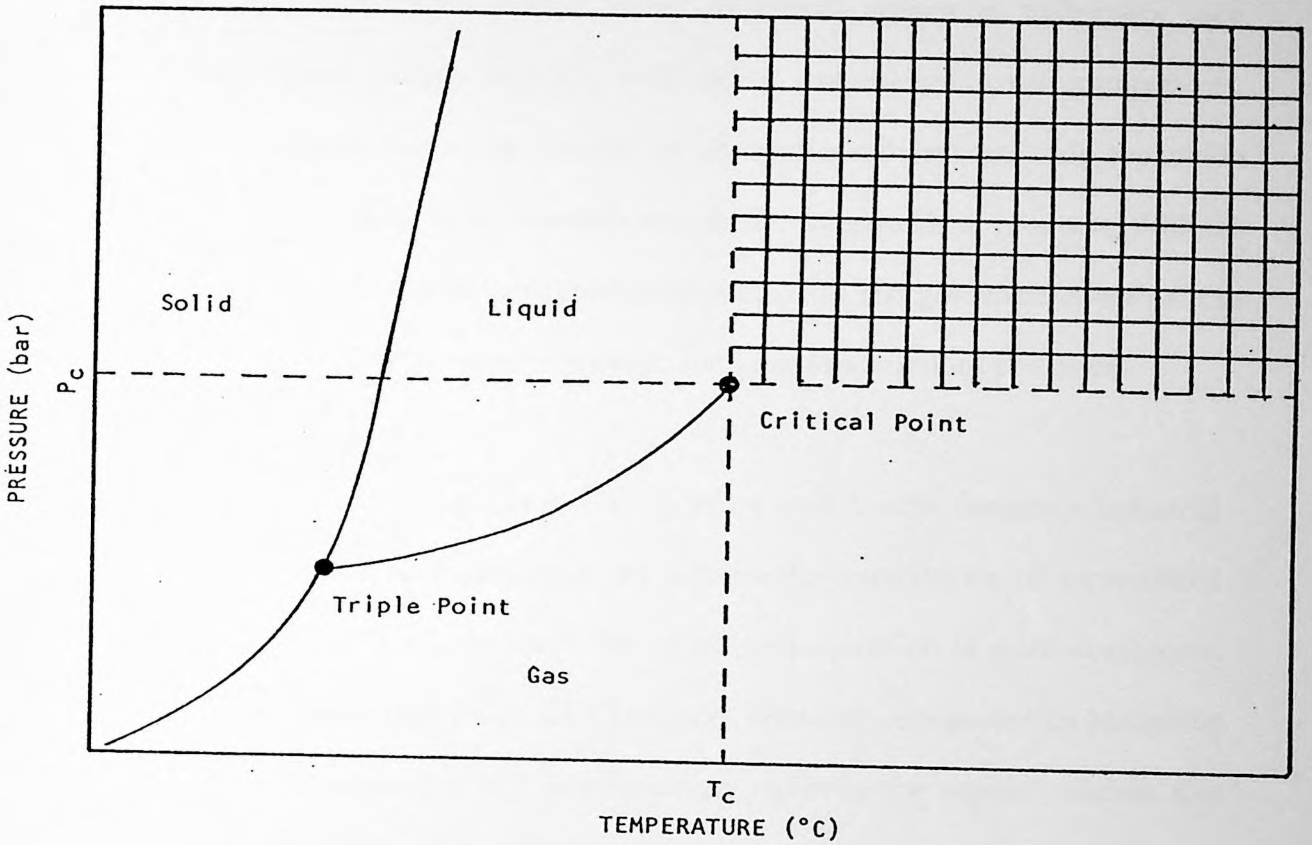

Figure 2.1 Typical pressure-temperature phase diagram for a pure component at a supercritical region denoted by the hatched area

Source: Dean, (1993)

2.3.1 Benefits of Supercritical Fluid Extraction

In accordance to Judie (1986), many traditional separation techniques used solvents, which cannot comply with the strict safety and environmental requirements. Thus, intensive research has to be focused on alternative efficient and safe separation techniques, in order to increase the demands on specific compounds or products. With the emergence of clean technologies have motivated companies and government laboratories to venture on effective solution to solve specific compounds separations problems.

In a recent report by Galia et al. (2002), in the past decade, numerous industrial and academic researches investigated on the solvents for applications of supercritical fluids. This interest was due to the feasibility of efficient separation of multi–component mixtures by using supercritical fluids (SCF) solvents. However, as reported by Mohamed and Mansoori (2001), currently, SCF is increasingly replacing the organic solvents that are used in industrial purification and recrystallization operations due to strict regulatory requirements and environmental pressures on the utilization of hydrocarbon and ozone-depleting substances.

SCF processes have an advantage over the use of hexane and methylene chloride as solvents. With stricter scrutiny of solvent residues in pharmaceuticals, and medical products due to high risk of volatile organic compounds (VOC) emissions, had driven industrial sectors to change to the use of SCF.

2.3.2 Properties of Supercritical Fluid Extraction

Important information on the properties of supercritical fluids are given by several researchers (Mc Hugh and Krukonis 1986; de Filippi 1982; Dean 1993; Moses 1982; and Westwood 1993). It is essential to discuss the properties of supercritical fluids in details since it determines the extractability of most compounds particularly those located remotely within solid matrices. The properties of supercritical fluids be discussed in accordance to the following classification:-

2.3.2.1. Solvent Power

Supercritical fluids begin to exhibit significant solvent strength when they are compressed to liquid – densities. The density of the SCF is typically 100 to 1000 times greater than that of gas and solvating characteristics approaching those of a liquid. Figure 2.2, shows the density of a pure solvent which changes in the region of its critical point.

The boundary of the coexistence of gas and liquid phases is shown by the convex curve. The region defined by reduced temperature (T_r), in the range 0.95 to 1.2 is defined as the near critical liquid region (NCL). The supercritical region lies in the reduced temperature and pressure which range above 1. For a reduced temperature from 0.95 to 1.2, reduced pressure above one (1), the density of solvent reduced to gas density and changes from about 0.1 to about 2.4, equivalent to a liquid density.

A liquid with reduced density begins to behave like a liquid solvent and thus, the solvent power of supercritical fluid (SCF) increases. When the temperatures are very high, the fluid density is reduced to a very small value due to the expansion of the fluid. This makes it necessary for a reduced pressure to be increased to a value above 10 to achieve liquid like densities.

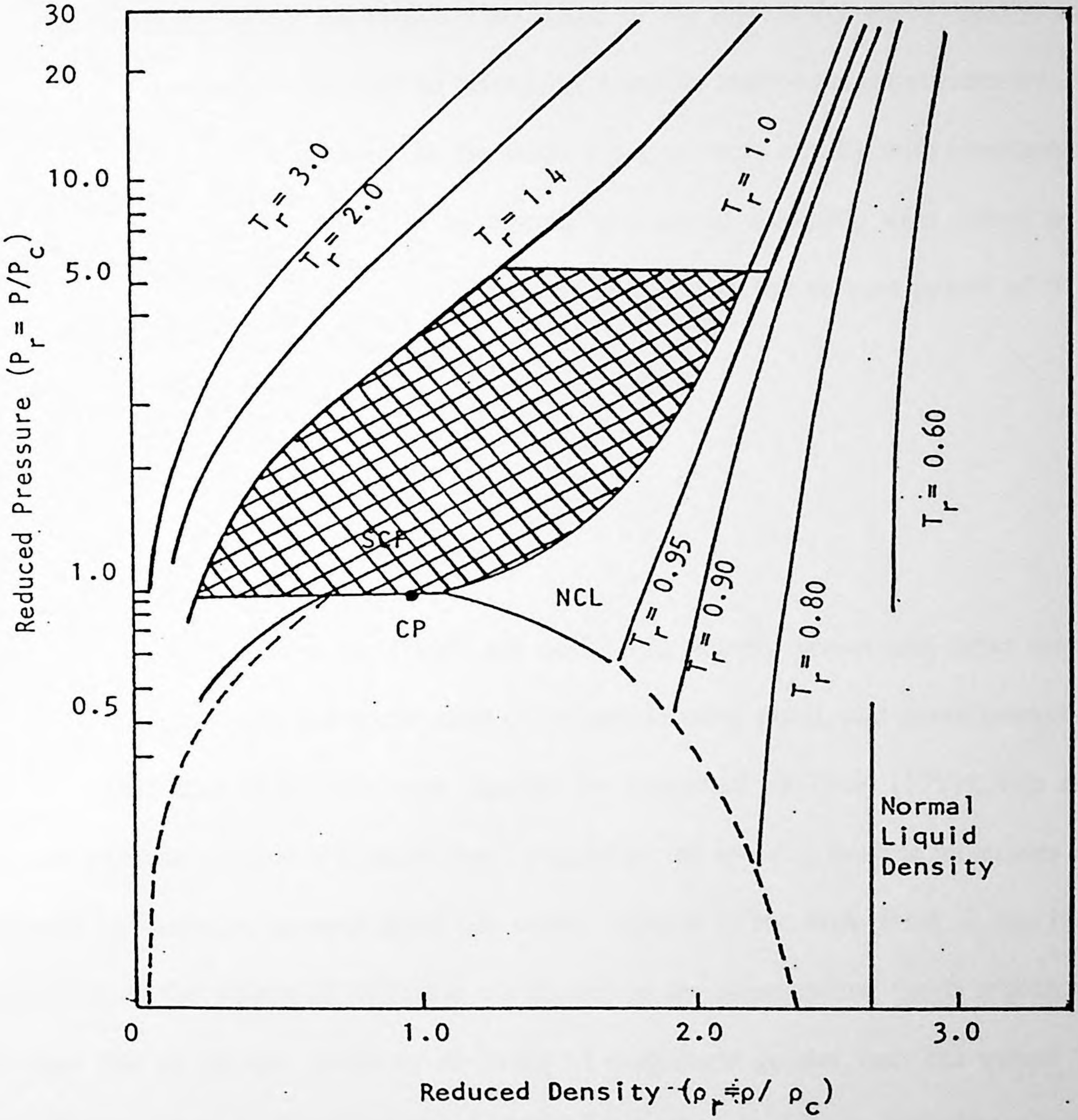

Figure 2.2 The reduced pressure-density diagram of SCF (Supercritical Fluid) and NCL (Near Critical Liquid)

Source: Mc Hugh and Krukonis (1986)

An explanation by Mc Hugh and Krukonis (1986), by operating in the critical region, as denoted by the cross hatched area as in Figure 2.2, the pressure and temperature can regulate the solvent power of a supercritical fluids. The clarification is that, as the temperature increases within this region, the density of the solvent decreases rapidly, and the solubility of a solute is expected to decrease though its vapour pressure increases. At higher pressures, the vapor pressure of the solute changes more rapidly with temperature than the solvent density, resulting in an overall increase in solubility of a solute with increasing temperature. However, as the pressure is reduced, the solvent power of SCF decreases in accordance to de Filippi (1982).

2.3.2.2. Rate of Mass Transfer

According to David et al. (1990) the liquid–like solvent power and rapid mass–transfer properties of SCF, can cause rates of extraction more rapid, and made extraction efficiency higher than if feasible with liquids. As supported by Dean (1993), this is a significant property as rates of extraction are limited by the speed as analyte molecules are transported by diffusion process from the matrix sample in the bulk fluid. It has been recognized that, the values of diffusion coefficient in the supercritical fluids region are lower than that in the gas phase by an order of magnitude greater than the values for normal liquids. Thus, it would be reasonable to state that the kinetics of mass transfer processes that involve limitation of diffusion in the extract phase would be favorable comparing it with conventional extraction technique, as supported by de Filippi and Moses (1982).

2.3.2.3. Low Viscosity

Dean (1993), explained that supercritical fluids exhibit significantly low viscosity than liquids, so it provides favorable flow properties. These properties allow supercritical fluids to penetrate matrices of species with low permeability more readily than conventional solvents because it does not exhibit surface tension limitations. Larry (1996) on the other hand, added that, the viscosities of supercritical fluids are 10 to 100 times lower than liquids.

2.3.2.4 Low Energy Utilization

As mentioned by Weatherley (1994), with respect to latent heat and heat capacity, fluids near their critical point exhibit unusual thermo physical properties. The latent heat at the critical point is zero due to the absence of any phase transition. As the critical point is approaching, the heat of vaporization decreases rapidly. This allows solvent and product separation with low energy utilization. The heat capacity of fluids in the supercritical regime can be several times the value of pure liquids and improvements in heat transfer efficiency may be expected during product recovery.

2.3.2.5 Ease of Removal from Analytes

Westwood (1993), mentioned that the commonly used supercritical fluids such as Carbon Dioxide (CO_2) and Nitrous Oxide (N_2O) are in gaseous form at room temperature and pressure, and can be easily separated from analytes by decompression.

2.3.2.6 Selectivity

The SC-CO_2 has high ability to dissolve the desired product largely than the other constituents of the mixture, and it can be varied to a certain extent by the nature of the solvent (Dean, 1993).

Table 2.1 shows values of physical properties for gas, supercritical fluid and liquid. This table also shows that the physical property of supercritical fluid (SCF) fall between those of gas and liquid. The density of SCF is similar to that of a liquid and therefore, SCF has a very good solvent power. On this basis, it is deduced that the physical properties like density is related to solvent power, viscosity is associated with flow rates, and diffusion coefficients, on the other hand, correlated with mass transfer within the fluid.

Because the viscosity and diffusivity of supercritical fluid are similar to that of a gas, therefore, the penetrating power of supercritical fluid in the solid matrix is good. These properties are important owing to the fact that, it enhances the mass transfer rates of solutes in the supercritical fluid phase compared to extraction carried out with a liquid. Hence, these unique properties of SCF, enhanced separation of constituents otherwise, without these properties, separation is difficult from their natural matrices (Larry, 1996).

Table 2.1 Values of physical property for gas, supercritical fluid and liquid.

Phase	Density ($g\ cm^{-3}$)	Viscosity ($gcm^{-1}sec^{-1}$)	Diffusion Coefficient (cm^2sec^{-1})
Gas 30 °C, 1 atmosphere	$(0.6\text{-}2) X 10^{-3}$	$(1\text{-}3) X 10^{-4}$	0.1-0.4
Supercritical fluid	0.2-0.9	$(1\text{-}9) X 10^{-4}$	$(0.2 – 0.7) X 10^{-3}$
Liquid 30 °C, 1 atmosphere	0.6-1.6	$(0.2\text{-}3) X 10^{-5}$	$(0.2\text{-}2) X 10^{-5}$

Source: de Castro et al (1994)

Table 2.2 shows critical conditions of selected supercritical solvents. It has been recognized that some gases are less suitable as supercritical solvents for application in large-scale practice such as chlorotrifluromethane, monofluoromethane and some other fluoro-(halo) hydrocarbons. According to Dick and Henry (1996), firstly, these gases are toxic and secondly, they are too expensive and suspected to be able to destroy the ozone layer of the earth's atom sphere. Nitrous oxide, on the other hand, should be used with care because it supports combustion and tends to spontaneous decomposition under certain condition.

Larry (1996) reported that, as for pure hydrocarbon, especially ethane and propane, even though they are suitable for some extraction processes under certain conditions, but they are flammable and form explosive mixtures with air. The cost of Xenon on the other hand is prohibitive. Water, besides having critical parameters that are not compatible with analytical extraction equipment, is also corrosive. Highly polar fluids such as ammonia are too reactive and toxic, while the solvating power of cycrohexanol is insufficient for all aromatic and polar analytes.

Further, Yoshiaki Fukushima (1999) reported that, trifluoromethane (CHF_3) has critical parameters lower than that of carbon dioxide (CO_2) yet exhibits a superior solvating power compare to CO_2 for some analytes. The compound CHF_3 has a dipole moment of 1.6 D, which is similar to the dipole moment of methanol, currently it is not thought to be an ozone depletion substance, however, and its cost may be prohibitive. It is also not readily available.

Table 2.2 Critical Conditions for Some Supercritical Solvents

Compounds	Critical Temperature T_c (°C)	Critical Pressure P_c (Bar)	Critical Density ρ_c (g /cm ^{3})
Carbon dioxide	**31.3**	**72.9**	**0.448**
Ammonia	132.4	112.5	0.235
Water	374.15	218.3	0.315
Nitrous Oxide	36.5	71.7	0.45
Xenon	16.6	57.6	0.118
Krypton	-63.8	54.3	0.091
Methane	-82.1	45.8	0.2
Ethane	32.28	48.1	0.203
Ethylene	9.21	49.7	0.218
Propane	96.67	41.9	0.217
Pentane	196.6	33.3	0.232
Methanol	240.5	78.9	0.272
Ethanol	243.0	63.0	0.276
Isopropanol	235.3	47.0	0.273
Isobutanol	275.0	42.4	0.272
Chlorotrifluoromethane	28.0	38.7	0.579
Monofluoromethane	44.6	58.0	0.3
Cycrohexanol	356.0	38.0	0.273

Source: Yoshiaki Fukushima (1999)

2.3.3 Rationale of Supercritical Carbon Dioxide (CO_2)

As mentioned by Mohamed and Mansoori (2001), it appears that no material with critical parameters as mild as CO_2. Its solvating power is high. Therefore, Carbon Dioxide (CO_2) is the most widely used solvent, suitable for analytical purposes, and widely applied in industries. In spite of a single automobile will exhaust more than 200 g of CO_2 per mile of travel, the use of SC-CO_2 is unlikely to contribute significantly to the increase in CO_2 in the atmosphere since it may originate from other sources.

The important of using carbon dioxide (CO_2) as solvent is attributed to the fact that at the best critical temperature and pressure (31.1 °C & 7.3 MPa), it is chemically stable, inflammable, radioactively stable and non-toxic. Thus, it is suitable alternative to hazardous organic solvents. Furthermore, it is available in large amounts under favorable conditions. It can be generated without depending on production from a petrochemical plant. Finally, large reserves in liquid form are technically available (Rizvi 1994).

As reported by Reverchon et al. (1993), in addition, carbon dioxide (CO_2) has a unique property for faster reactions, especially diffusion process since it control reactions involving gaseous reagents such as hydrogen, oxygen, or carbon monoxide. A faster reactions demonstrated by (CO_2) is possible due to its low viscosities, high miscibility, and high diffusivities properties.