

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

by

NORHUDA BT ISMAIL

**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 Kamarulnajib 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.

TABLE OF CONTENTS

	Page
Acknowledgement	iii
Table of Contents	iv
List of Figures	xi
List of Tables	xix
List of Plates	xxii
List of Abbreviations	xxiii
List of Symbols	xxiii
Abstrak	xxiv
Abstract	xxvii

CHAPTER 1 – INTRODUCTION

1.1	Introduction	1
1.2	Statement of Problems	4
1.3	Significant Contributions	5
1.4	Objectives of the Study	6
1.5	Limitations of the Study	8

CHAPTER 2 – LITERATURE REVIEW

2.1	General	9
2.2	History of Supercritical Fluids	9
2.3	Principles of Supercritical Fluids	11
2.3.1	Benefits of Supercritical Fluids	14
2.3.2	Properties of Supercritical Fluids	15
2.3.3	Rationale of Supercritical Carbon Dioxide as a Solvent	25
2.4	Review of SC-CO ₂ Extraction Literature	36
2.4.1	Review of Oil Seeds SC-CO ₂ Extraction Literature	36
2.4.2	Review of Oil Solubility by SC-CO ₂ Extraction Literature	40
2.4.3	Review of Palm Oil and Palm Kernel Oil by SC-CO ₂ Extraction Literature	42
2.5	Statistics and Processing of Palm Kernel and Palm Kernel Oil	46
2.5.1	Statistics of Production and Export	46
2.5.2	Types of Palm Kernel Oil Extraction Processes	48
2.5.3	Uses of Palm kernel Oil	51
2.5.4	Characteristics of an Overall Single Palm Kernel	52
2.6	Review on the Mass Transfer Phenomena of SC-CO ₂ Extraction Literature	60
2.6.1	Significance of diffusivity in solid mass	60

2.6.2	Methods of Determining Diffusivity	61
2.6.3	Significant of Mass Transfer Coefficient	62
2.7	Mathematical Modeling	65
2.7.1	Formulation of Mathematical Model for Supercritical Fluid Extraction	68
2.7.1.1	Formulation Based On Differential Equations	68
2.7.1.2	Formulation Based On Dimensional Analysis	69
2.7.2	Model Calibration and Validation Process	72
2.7.3	Review of Mathematical Modeling of SC-CO ₂ Literature	74
2.8	Scale- up	76

CHAPTER 3 – METHODOLOGY

3.1	Introduction	77
3.2	Field Sampling and Sample Preparation	77
3.2.1	Field Sampling	77
3.2.2	Sample Preparation	78
3.3	Experimental Set Up: Supercritical Fluid Extraction System	80
3.4	Method of Handling Palm Kernel	83
3.4.1	Method of Oil Extraction Based on Overall Single Palm Kernel	83

3.4.2	Method of Oil Extraction for Packed Bed of Palm Kernels	85
3.5	Determination of Moisture Content	88
3.6	Determination of Oil Content in a Single Palm Kernel	89
3.7	Determination of Porosity for Packed Bed of Palm Kernels	90
3.8	Quality Assurance and Quality Control	90
3.9	Statistical Analysis	91

CHAPTER 4 – RESULTS AND DISCUSSIONS

4.1	Effect of 30 Minutes Extraction on the Percentage of Palm Kernel Oil (PKO) Extracted for Different Sizes of an Overall Single Palm Kernel	92
4.2	Effect of Temperature, Pressure, Flow rates of CO ₂ and Extraction Time on PKO Extraction from an Overall Single Palm Kernel with Size 6 mm (Outside Diameter)	99
4.2.1	Effect of PKO extracted from an overall single palm kernel with time at constant pressure and a range of different temperatures and flow rates of CO ₂	101
4.2.2	Effect of PKO extracted from an overall single palm kernel versus extraction time at a constant temperature and corresponding to a range of different pressures and flow rates of CO ₂	105
4.2.3	Effect of Density of CO ₂ on Solubility of Palm Kernel Oil in SC-CO ₂ at Constant Pressure and Corresponding Range of Different in Temperatures	114
4.2.4	Effect of Density of CO ₂ on Solubility of PKO in SC-CO ₂ at a Constant Temperature and Corresponding Range of different in Pressures	120
4.2.5	Effect on of Different Pressures and Temperatures on the Amount of PKO Extracted for 30 Minutes of Extraction from an Overall Single Palm Kernel at Supercritical Conditions	124

4.2.5.1	Effect of Pressures and Temperatures on the Amount of PKO extracted from an Overall Single Palm Kernel for 30 minutes of extraction	125
4.2.5.2	Effect of Pressure and Temperature on the Solubility of PKO in SC-CO ₂	129
4.2.6	Effect of Pressure and Temperature on the Palm Kernel Seed Structure	134
4.2.7	Effect of 30 Minutes of PKO Extraction from a Single Palm Kernel on Volume of CO ₂ Consumed at Constant Pressure and Temperature	137
4.3	Determination of Diffusion Coefficient of PKO in a Single Palm Kernel	140
4.3.1	Effect of Diffusion Coefficient of PKO in a Single Palm Kernel with Temperature and Pressure	150
4.4	Determination of the Overall Mass Transfer Coefficient for Palm Kernel Oil Extracted from a Single Palm Kernel	158
4.4.1	Effect of Overall Mass Transfer Coefficient of Palm Kernel Oil (PKO) From Overall Single Palm Kernel at Different Conditions of Temperatures and Pressures	164
4.5	Effect of Pressures and Temperatures on Extraction of Palm Kernel Oil (PKO) From Overall Single Palm Kernels in a Packed Bed of Supercritical Extractor	170
4.5.1	Effect of increasing pressures within a range of 27.6 MPa to 48.3 MPa, at a constant temperature, on the amount of PKO extracted from a packed bed of overall single palm kernels in a supercritical extractor versus extraction times	172
4.6	Determination of Diffusion Coefficient of Palm Kernel Oil (PKO) Extracted From Overall Single Palm Kernels in a Packed Bed of Supercritical Extraction Column	175
4.6.1	Effect of Pressure on Diffusion Coefficient of PKO Extracted From Overall Palm Kernels in a Packed Bed of an Extractor at Constant Temperature	177

4.6.2	Effect of Temperature on Diffusion Coefficient of PKO Extracted From Overall Palm Kernels in a Packed Bed of an Extractor at Constant Pressure	180
4.7	Determination of the Overall Mass Transfer Coefficient of Palm Kernel Oil (PKO) of an Overall Palm Kernels Extracted in a Packed Bed of Extractor	185
4.7.1	Effect of Pressure on the Overall Mass Transfer Coefficient of PKO in a Packed Bed of Palm Kernels in an Extractor at Constant Temperature	188
4.7.2	Effect of Temperature on the Overall Mass Transfer Coefficient of PKO in a Packed Bed of overall single Palm Kernels in an Extractor at Constant Pressure	192
4.8	Determination of Viscosity of Carbon Dioxide (CO ₂) Gas	196
4.9	Determination of Density of CO ₂	197
4.10	Derivation of Mass Transfer Correlation for Extraction of PKO in a Packed Bed of Overall Single Palm Kernels in an Extractor by using Supercritical Carbon dioxide (SC-CO ₂)	198
4.10.1	Development of Mass Transfer Correlation Models	199
4.10.2	Model Validation	202
4.11	Scale-up Consideration	216
4.11.1	Scale up Basis	219
4.11.2	Scale up Calculations	221

CHAPTER 5 - CONCLUSIONS

5.1	Introduction	231
5.2	Mass Transfer Phenomena in the Extraction of an Overall Single Palm Kernel	231
5.3	Mass Transfer Phenomena in Extracting the Overall Single Palm Kernels in Packed Bed	233

5.4	Model Development and Mass Transfer Phenomena Modeling Study	235
5.5	Scale-Up of Supercritical Extraction Column	237
CHAPTER 6 - RECOMMENDATIONS		238
REFERENCES		240
APPENDICES		249
Appendix A -	Derivation of Mass Transfer Correlation for Palm Kernel Oil (PKO) Extracted from Overall Single Palm Kernels in a Packed Bed of Supercritical Extractor	250
Appendix B -	Statistical Description: t-Test: Paired Two Sample Means for Sherwood Number at temperatures of 50 °C, 60 °C and 70 °C. The Sherwood number (Sh) is calculated by using the empirical mass transfer correlation model $Sh = 0.9804Re Sc^{1/3}$	255
Appendix C -	Calculation for Scale up from Laboratory Scale to Production Scale	256
Appendix D -	Viscosity of Pure Gases and Hydrocarbon Vapor	264

LISTS OF FIGURES

	Page	
Figure 2.1	Typical pressure- temperature phase diagram for a pure component showing the supercritical region denoted by the hatched area	13
Figure 2.2	The Reduced pressure-density diagram of SCF (Supercritical Fluid) and NCL (Near Critical Liquid)	17
Figure 2.3	Diffusivity of CO ₂ in the supercritical fluid and near critical liquid regions	29
Figure 2.4	The solvent polarity (π^*), parameters for various supercritical fluids as a function of reduced density (ρ/ρ_c) at a reduced temperature of 1.03	31
Figure 2.5	Variation of the viscosity of CO ₂ with pressure at three different temperatures and critical pressure (P_c)	33
Figure 2.6	Influence of pressure on the dielectric constant and density of SC-CO ₂ at a constant temperature	35
Figure 2.7	Various Methods of Palm Kernel Oil Extraction	50
Figure 3.1	A schematic diagram showing process flowchart of SC-CO ₂ extraction system	81
Figure 4.1	Percentage of Palm Kernel Oil Extracted from Different Sizes of Palm Kernels at Different Pressures at a Constant Temperature of 50 °C for 30 Minutes of Extraction	94
Figure 4.2	Percentage of Palm Kernel Oil Extracted from Different Sizes of Palm Kernels at Different Pressures for a Constant Temperature of 60 °C for 30 Minutes of Extraction	94
Figure 4.3	Percentage of Palm Kernel Oil Extracted from Different Sizes of Palm Kernels at Different Pressures for a Constant Temperature of 70 °C for 30 Minutes of Extraction	95

Figure 4.4	Percentage of Palm Kernel Oil Extracted from Different Sizes of Palm Kernels at Different Pressures for a Constant Temperature of 80 °C for 30 Minutes of Extraction	95
Figure 4.5	Percentage of PKO extracted from an overall single palm kernel versus extraction times (minutes) at constant pressure of 27.6 MPa and corresponding to different temperatures and CO ₂ flow rates	101
Figure 4.6	Percentage of PKO extracted from an overall single palm kernel versus extraction times (minutes) at constant pressure of 34.5 MPa and corresponding to different temperatures and CO ₂ flow rates	101
Figure 4.7	Percentage of PKO extracted from an overall single palm kernel versus extraction times (minutes) at constant pressure of 41.4 MPa and corresponding to a range of different temperatures and CO ₂ flow rates	102
Figure 4.8	Percentage of PKO extracted from an overall single palm kernel versus extraction times at constant pressure of 48.3 MPa and corresponding to a range of different temperatures and CO ₂ flow rates	102
Figure 4.9	Percentage of PKO extracted from a single palm kernel versus time at a constant temperature of 40 °C and corresponding to a range of different pressures and CO ₂ flow rates	105
Figure 4.10	Percentage of PKO extracted from a single palm kernel versus time at a constant temperature of 50 °C and corresponding to a range of different pressures and CO ₂ flow rates	105
Figure 4.11	Percentage of PKO extracted from a single palm kernel versus time at constant temperature of 60 °C and corresponding to a range of different pressures and CO ₂ flow rates	106
Figure 4.12	Percentage of PKO extracted from a single palm kernel versus time at constant temperature of 70 °C and corresponding to a range of different pressures and CO ₂ flow rates	106

Figure 4.13	Percentage of PKO extracted from a single palm kernel versus time at constant temperature of 80 °C and corresponding to a range of different pressures and CO ₂ flow rates	107
Figure 4.14	Effect of density of CO ₂ on Solubility of PKO in SC-CO ₂ for an overall single palm kernel at constant pressure of 27.6 MPa and its corresponding range of different in temperatures	117
Figure 4.15	Effect of density of CO ₂ on Solubility of PKO in SC-CO ₂ for an overall single palm kernel at constant pressure of 34.5 MPa and its corresponding range of different in temperatures	117
Figure 4.16	Effect of density of CO ₂ on Solubility of PKO in SC-CO ₂ for an overall single palm kernel at constant pressure of 41.4 MPa and its corresponding range of different in temperatures	118
Figure 4.17	Effect of density of CO ₂ on Solubility of PKO in SC-CO ₂ for an overall single palm kernel at constant pressure of 48.3 MPa and its corresponding range of different in temperatures	118
Figure 4.18	Effect of density of CO ₂ on Solubility of PKO in SC-CO ₂ for an overall single palm kernel at constant temperature of 40 °C and its corresponding range of different pressures	120
Figure 4.19	Effect of density of CO ₂ on Solubility of PKO in SC-CO ₂ for an overall single palm kernel at constant temperature of 50 °C and its corresponding range of different pressures	120
Figure 4.20	Effect of density of CO ₂ on Solubility of PKO in SC-CO ₂ for an overall single palm kernel at constant temperature of 60 °C and its corresponding range of different pressures	121
Figure 4.21	Effect of density of CO ₂ on Solubility of PKO in SC-CO ₂ for an overall single palm kernel at constant temperature of 70 °C and its corresponding range of different pressures	121
Figure 4.22	Effect of density of CO ₂ on Solubility of PKO in SC-CO ₂ for an overall single palm kernel at constant temperature of 80 °C and its corresponding range of different pressures	122

Figure 4.23	Percentage of PKO extracted from an overall single palm kernel for 30 minutes extraction at different temperatures and pressures	125
Figure 4.24	Percentage of PKO extracted from a single palm kernel for 30 minutes duration along with temperatures at different pressures	125
Figure 4.25	Solubility of Palm Kernel Oil (PKO) in SC-CO ₂ for a single palm kernel versus pressure at different temperatures	132
Figure 4.26	Solubility of Palm Kernel Oil (PKO) in SC-CO ₂ for a single palm kernel versus temperature at different pressures	132
Figure 4.27	Mean volume of CO ₂ consumed for 30 minutes of PKO extraction as a function of pressure	137
Figure 4.28	Plot of $\ln m/m_0$ versus time at constant temperature of 40 °C at various pressures	146
Figure: 4.29	Plot of $\ln m/m_0$ versus time at constant temperature of 50 °C at various pressures	146
Figure 4.30	Plot of $\ln m/m_0$ versus time at constant temperature of 60 °C at various pressures	148
Figure 4.31	Plot of $\ln m/m_0$ versus time at constant temperature of 70 °C at various pressures	148
Figure 4.32	Plot of $\ln m/m_0$ versus time at constant temperature of 80 °C at various pressures	149
Figure 4.33	The diffusion coefficient of PKO in a single palm kernel versus pressures at different temperature of 50 °C and 60 °C	151
Figure 4.34	The diffusion coefficient of PKO in a single palm kernel versus pressures at different temperature of 40 °C, 70 °C and 80 °C	151
Figure 4.35	The diffusion coefficient of PKO in a single palm kernel versus temperature at different pressures	152

Figure 4.36	A plot of $-\ln(1-C/C^*)$ versus extraction time at a constant temperature of 40 °C and variation in pressures	161
Figure 4.37	A plot of $-\ln(1-C/C^*)$ versus extraction time at a constant temperature of 50 °C and variation in pressures	161
Figure 4.38	A plot of $-\ln(1-C/C^*)$ versus extraction time at a constant temperature of 60 °C and variation in pressures	162
Figure 4.39	A plot of $-\ln(1-C/C^*)$ versus extraction time at a constant temperature of 70 °C and variation in pressures	162
Figure 4.40	A plot of $-\ln(1-C/C^*)$ versus extraction time at a constant temperature of 80 °C and variation in pressures	163
Figure 4.41	Overall mass transfer coefficient (K) versus pressures at a constant temperature of 40 °C	167
Figure 4.42	Overall mass transfer coefficient (K) versus pressures at a constant temperature of 50 °C	167
Figure 4.43	Overall mass transfer coefficient (K) versus pressures at a constant temperature of 60 °C	168
Figure 4.44	Overall mass transfer coefficient (K) versus pressures at a constant temperature of 70 °C	168
Figure 4.45	Overall mass transfer coefficient (K) versus pressures at a constant temperature of 80 °C	169
Figure 4.46	Effect of increasing pressures within a range 27.6 MPa to 48.3 MPa, at a constant temperature of 50 °C, on the amount of PKO extracted from overall single palm kernels in a packed bed of a supercritical extractor versus extraction times	172
Figure 4.47	Effect of increasing pressures within a range 27.6 MPa to 48.3 MPa, at a constant temperature of 60 °C, on the amount of PKO extracted from overall single palm kernels in a packed bed of a supercritical extractor versus extraction times	173

Figure 4.48	Effect of increasing pressures within a range 27.6 MPa to 48.3 MPa, at a constant temperature of 70 °C, on the amount of PKO extracted from overall single palm kernels in a packed bed of a supercritical extractor versus extraction times	173
Figure 4.49	Diffusion coefficient of PKO in a packed bed of palm kernels in an extractor versus pressures at a constant temperature of 50 °C	177
Figure 4.50	Diffusion coefficient of PKO in a packed bed of palm kernels in an extractor versus pressures at a constant temperature of 60 °C	177
Figure 4.51	Diffusion coefficient of PKO in a packed bed of palm kernels in an extractor versus pressures at a constant temperature of 70 °C	178
Figure 4.52	Diffusion coefficient of PKO from overall palm kernels in a packed bed of an extractor at a constant pressure of 27.6 MPa and variation in temperatures	181
Figure 4.53	Diffusion coefficient of PKO from overall palm kernels in a packed bed of an extractor at a constant pressure of 34.5 MPa and variation in temperatures	181
Figure 4.54	Diffusion coefficient of PKO from overall palm kernels in a packed bed of an extractor at a constant pressure of 41.4 MPa and variation in temperatures	182
Figure 4.55	Diffusion coefficient of PKO from overall palm kernels in a packed bed of an extractor at a constant pressure of 48.3 MPa and variation in temperatures	182
Figure 4.56	Showing graph – $\ln(1-C/C^*)$ as a function of time at constant temperature of 50 °C and different pressures	186
Figure 4.57	Showing graph – $\ln(1-C/C^*)$ as a function of time at constant temperature of 60 °C and different pressures	186

Figure 4.58	Showing graph $-\ln(1-C/C^*)$ as a function of time at constant temperature of 70 °C and different pressures	187
Figure 4.59	Overall mass transfer coefficient of palm kernel oil (PKO) extracted from overall single palm kernels in a packed bed of an extractor at a constant temperature of 50 °C versus variation in pressures	189
Figure 4.60	Overall mass transfer coefficient of palm kernel oil (PKO) extracted from overall single palm kernels in a packed bed of an extractor at a constant temperature of 60 °C versus variation in pressures	189
Figure 4.61	Overall mass transfer coefficient of palm kernel oil (PKO) extracted from overall single palm kernels in a packed bed of an extractor at a constant temperature of 70 °C versus variation in pressures	190
Figure 4.62	Overall mass transfer coefficient of PKO extracted from overall single palm kernels arranged in a packed bed of an extractor at a constant pressure of 27.6 MPa versus variation in temperatures	193
Figure 4.63	Overall mass transfer coefficient of PKO extracted from overall single palm kernels arranged in a packed bed of an extractor at a constant pressure of 34.5 MPa versus variation in temperatures	193
Figure 4.64	Overall mass transfer coefficient of PKO extracted from overall single palm kernels arranged in a packed bed of an extractor at a constant pressure of 41.4 MPa versus variation in temperatures	194
Figure 4.65	Overall mass transfer coefficient of PKO extracted from overall single palm kernels arranged in a packed bed of an extractor at a constant pressure of 48.3 MPa versus variation in temperatures	194
Figure 4.66	Correlation between $Sh/Sc^{1/3}$ versus Re No at constant temperature of 50 °C and pressures ranging from 27.6 MPa to 48.3 MPa	203

Figure 4.67	Correlation between $Sh/Sc^{1/3}$ versus $Re No$ at constant temperature of 60 °C and pressures ranging from 27.6 MPa to 48.3 MPa	203
Figure 4.68	Correlation between $Sh/Sc^{1/3}$ versus $Re No$ at constant temperature of 70 °C and pressures ranging from 27.6 MPa to 48.3 MPa	204
Figure 4.69	Correlation between mass transfer coefficient (K) for model and experiment at a constant temperature of 50 °C	210
Figure 4.70	Correlation between mass transfer coefficient (K) for model and experiment at a constant temperature of 60 °C	211
Figure 4.71	Correlation between mass transfer coefficient (K) for model and experiment at a constant temperature of 70 °C	212
Figure 4.72	Correlation of mass transfer coefficient (K) with Reynolds number at 50 °C and pressure from 27.6 MPa to 48.3 MPa	214
Figure 4.73	Correlation of mass transfer coefficient (K) with Reynolds number at 60 °C and pressure from 27.6 MPa to 48.3 MPa	214
Figure 4.74	Correlation of mass transfer coefficient (K) with Reynolds number at 70 °C and pressure from 27.6 MPa to 48.3 MPa	215

LISTS OF TABLES

		Page
Table 2.1	Values of physical property for gas, supercritical fluid and liquid	22
Table 2.2	Critical conditions for some supercritical solvents	24
Table 2.3	Heat of vaporization of carbon dioxide	26
Table 2.4	Solubility of substances in SC-CO ₂ at a pressure of 200 bars and temperature of 60 °C	27
Table 2.5	Total Area Planted with Oil Palm (hectares) and Production of (CPO) and (CPKO)	47
Table 2.6	Malaysian Exports of Palm Kernel Oil by Products 1995 – 2000 (Tones)	48
Table 2.7	Composition of a single palm kernel (% wt)	59
Table 2.8	Cell Wall components	59
Table 3.1	Lists of models and suppliers of Supercritical Fluid (SC-CO ₂) Components	81
Table 4.1	Percentage of PKO Extracted (g oil/100 g palm kernel) from an Overall Single Palm Kernel of three Sizes for duration of 30 minutes at each Constant Temperature and Varying Pressures under the Supercritical Carbon Dioxide (SC-CO ₂) Conditions	96
Table 4.2	Percentage of PKO Extracted from an Overall Single Palm Kernel of Outside Diameter 6 mm for Various Extraction Time at a Constant Pressure and Corresponding to a Range of Different Temperatures	103
Table 4.3	Percentage of PKO Extracted from an Overall Single Palm Kernel of outside diameter 6 mm versus various Extraction Time at a Constant Temperature and Corresponding to a range of Difference in Pressures	108
Table 4.4	Effect of CO ₂ Density on Solubility of Palm Kernel Oil (PKO) in SC-CO ₂ at a Constant Pressure and Corresponding Range of Different in Temperatures	119

Table 4.5	Effect of CO ₂ Density and PKO Solubility in SC-CO ₂ at a Constant Temperature and Corresponding Range of Different in Pressures	123
Table 4.6	Percentage PKO Extracted from a Single Palm Kernel at different Pressures and Temperatures for 30 minutes of Extraction	126
Table 4.7	Solubility of PKO in SC-CO ₂ for Overall Single Palm Kernel with respect to various Pressures and Temperatures	133
Table 4.8	Mean Volume of CO ₂ Consumed as a function of Temperature and Pressure for 30 minutes extraction	138
Table 4.9	Variations in Diffusion Coefficient of PKO in a Single Palm Kernel for 6 mm (outside diameter) at constant Temperature and different Pressures	153
Table 4.10	Variations in Diffusion Coefficient of PKO in a Single Palm Kernel for 6 mm (outside diameter) at Constant Pressure and different Temperature	154
Table 4.11	The Overall Mass Transfer Coefficient of PKO from an Overall Single Palm Kernel by Using the SC-CO ₂ Extraction at various Temperatures and Pressures	166
Table 4.12	Percentage of PKO Extracted from Overall Single Palm Kernels of Size (Outside Diameter) 6 mm in the Packed Bed of Supercritical Extractor Column for Different Extraction Times at a Constant Temperature and Corresponding to a Range of Different Pressures	174
Table 4.13	Diffusion Coefficients of Palm Kernel Oil (PKO) of Overall Single Palm Kernels Extracted in a Packed Bed of Extractor at Consecutive Constant Temperatures and Variation in Pressures within 27.6 MPa to 48.3 MPa	179
Table 4.14	Diffusion Coefficients of Palm Kernel Oil of an Overall Palm Kernels in a Packed Bed of Extractor at Consecutive Constant Pressures and Variation in Temperatures Within 50 °C to 70 °C	183
Table 4.15	Variations in the Overall Mass Transfer Coefficient of PKO extracted from Overall Palm Kernels in a Packed Bed of an Extractor at Constant Temperature and variation in Pressures	191

Table 4.16	The Overall Mass Transfer Coefficient of PKO Extracted From Overall Single Palm Kernels in a Packed Bed of an Extractor at constant Pressures and variation in Temperature	195
Table 4.17	Validated empirical models of mass transfer correlations based on dimensionless numbers of Sherwood (Sh), Schmidt (Sc) and Reynolds (Re) for Supercritical Carbon Dioxide (SC-CO ₂) extraction of Palm Kernel Oil (PKO) at different temperatures and pressures	205
Table 4.18	Observed and Predicted Values of Dimensionless Numbers the Sherwood (Sh), the Schmidt (Sc) and the Reynolds (Re), for Extraction of Palm Kernel Oil (PKO)	208
Table 4.19	Statistical Description: Paired <i>t</i> -Test for mass transfer coefficient (K) values at a constant temperature of 50 °C and pressures ranges from 27.6 MPa to 48.3 MPa	210
Table 4.20	Statistical Description: Paired <i>t</i> -Test for mass transfer coefficient (K) values at a constant temperature of 60 °C and pressures ranges from 27.6 MPa to 48.3 MPa	211
Table 4.21	Statistical Description: Paired <i>t</i> -Test for mass transfer coefficient (K) values at a constant temperature of 70 °C and pressures ranges from 27.6 MPa to 48.3 MPa	212
Table 4.22	Expected Results for Extraction of 10 tones of Palm Kernels by using SC-CO ₂	230

LISTS OF PLATES

			Page
Plate	2.1	Picture showing the Fresh Fruit Bunches (FFB)	53
Plate	2.2	Picture showing the epicarp of fresh palm oil fruits	53
Plate	2.3	A cross section of overall single fruit palm oil showing the palm kernel	54
Plate	2.4	Scanning Electron Micrograph (SEM) Image of a palm kernel Testa Surface Image	56
Plate	2.5	Light Electron Micrograph (TEM) Image of the Outer Surface (Testa) of a Palm Kernel	56
Plate	2.6	Light Electron Micrograph (TEM) Image of a Thin Slice Palm Kernel showing the Honeycomb Cell Walls Embedded with Oil	57
Plate	2.7	Scanning Electron Micrograph (SEM) Image showing the Fibrous Palm Kernel Cell Wall Structure Without Oil	57
Plate	3.1	Picture showing two different sizes of overall single palm kernels	79
Plate	3.2	Picture showing the size of an internal diameter of an extractor cell	79
Plate	3.3	Picture showing the overall single palm kernels after sealed in a plastic bag of size (52 mm X 77 mm)	82
Plate	3.4	Picture of Supercritical Carbon Dioxide (SC-CO ₂) Extraction System	82
Plate	4.1	Light Electron Micrograph (TEM) of the Cross Section of a Single Palm Kernel before extraction with SC-CO ₂	136
Plate	4.2	Light Electron Micrograph (TEM) of a Cross Section of a Single Palm Kernel after extraction with SC-CO ₂ at 80 °C and 48.3 MPa	136

LIST OF ABBREVIATIONS

PKO	Palm Kernel Oil
CPKO	Crude Palm kernel Oil
RBDPKO	Refined Bleached Deodorized Palm Kernel oil
SCF	Supercritical Fluid
SC-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
v ₀	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-CO₂), 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-CO₂. Bagi pengekstrakan sebutir isirung sawit, keadaan lampau genting bagi komponen CO₂ 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-CO₂ 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-CO₂ 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 bergantung 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 pengestrakan minyak isirung sawit di dalam *lapisan terpadat isirung sawit* menunjukkan jumlah maksima 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 fungsi 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-CO₂) 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-CO₂) 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-CO₂ 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-CO₂ 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-CO₂ 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-CO₂) method. According to Bruno and Ely (1991), the SC-CO₂ 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-CO₂ 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-CO₂ 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-CO₂ 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-CO₂) 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-CO₂ 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 undergone 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-CO₂) 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-CO₂ method;

- (c) To investigate the effects of supercritical extraction parameters by using the laboratory scale supercritical (SC-CO₂) 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-CO₂) 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-CO₂) 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-CO₂) 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 Krukoni (1986).

2.3 Principles of Supercritical Fluids

Mc Hugh and Krukoni (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.

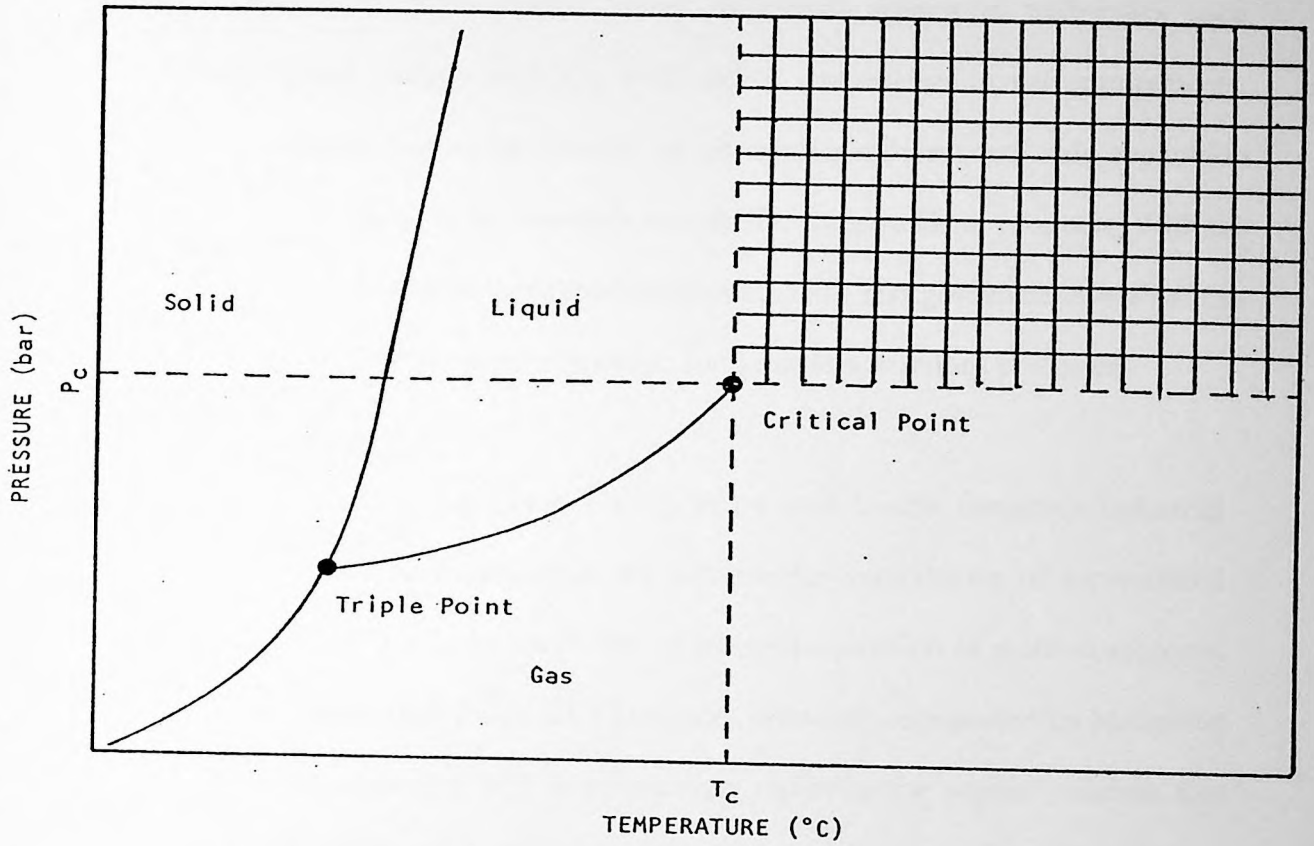


Figure 2.1 Typical pressure-temperature phase diagram for a pure component at a supercritical region denoted by the hatched area

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.

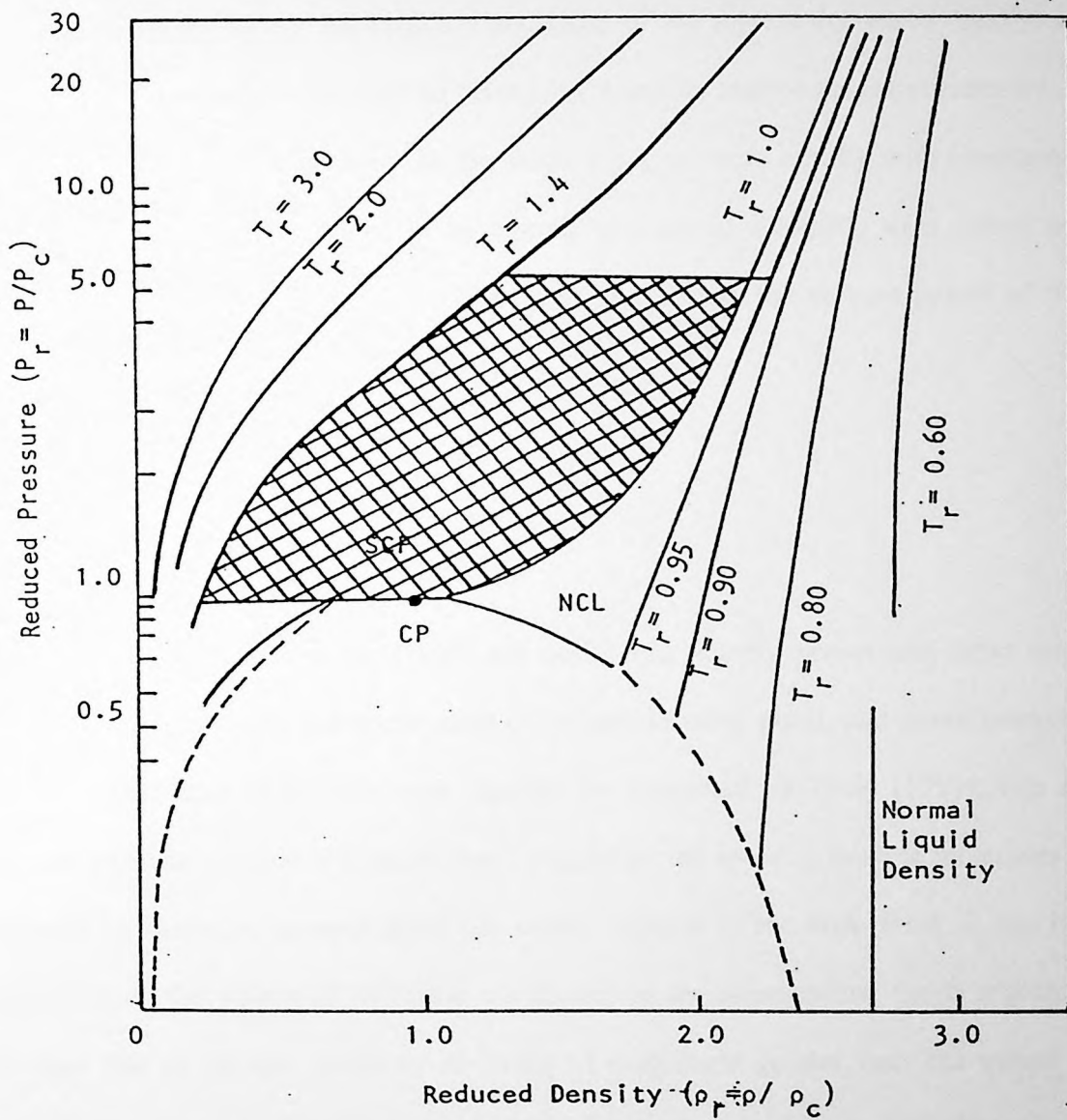


Figure 2.2 The reduced pressure-density diagram of SCF (Supercritical Fluid) and NCL (Near Critical Liquid)

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 (CO₂) and Nitrous Oxide (N₂O) 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-CO₂ 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 ² sec ⁻¹)
Gas 30 °C, 1 atmosphere	(0.6-2) X 10 ⁻³	(1-3) X 10 ⁻⁴	0.1-0.4
Supercritical fluid	0.2-0.9	(1-9) X 10 ⁻⁴	(0.2 – 0.7) X 10 ⁻³
Liquid 30 °C, 1 atmosphere	0.6-1.6	(0.2-3) X 10 ⁻⁵	(0.2-2) 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 chlorotrifluoromethane, 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 cyclohexanol 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
Cyclohexanol	356.0	38.0	0.273

Source: Yoshiaki Fukushima (1999)

2.3.3 Rationale of Supercritical Carbon Dioxide (CO₂)

As mentioned by Mohamed and Mansoori (2001), it appears that no material with critical parameters as mild as CO₂. Its solvating power is high. Therefore, Carbon Dioxide (CO₂) 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 CO₂ per mile of travel, the use of SC-CO₂ is unlikely to contribute significantly to the increase in CO₂ in the atmosphere since it may originate from other sources.

The important of using carbon dioxide (CO₂) 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 (CO₂) 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 (CO₂) is possible due to its low viscosities, high miscibility, and high diffusivities properties.