THE EXTRACTION OF ESSENTIAL OIL FROM *Quercus infectoria* (MANJAKANI) GALLS USING SUPERCRITICAL CARBON DIOXIDE PRESSURE SWING TECHNIQUE

STASHIA ELEANESS ROSLAND ABEL

UNIVERSITI TEKNOLOGI MALAYSIA

THE EXTRACTION OF ESSENTIAL OIL FROM *Quercus infectoria* (MANJAKANI) GALLS USING SUPERCRITICAL CARBON DIOXIDE PRESSURE SWING TECHNIQUE

STASHIA ELEANESS ROSLAND ABEL

A thesis submitted in fulfilment of the
requirements for the award of the degree of
Master of Engineering (Bioprocess)

Faculty of Chemical Engineering
Universiti Teknologi Malaysia

JUNE 2013

ACKNOWLEDGEMENT

In the name of Allah, the Most Gracious and the Most Merciful

Alhamdulillah, all praises to Allah for the strengths and His blessing in completing this thesis. This thesis would not have been possible without the guidance and the help of several individuals who in one way or another contributed and extended their valuable assistance in the preparation and completion of this study. First and foremost, I would like to express my sincere gratitude to my supervisor Dr. Liza Md. Salleh, with her enthusiasm, her inspiration and her great efforts to explain thing clearly and simply. Throughout my thesis writing, she provided encouragement, good teaching, good company and lots of good ideas, without her, this thesis would not have been completed or written.

I am obliged to many of my colleagues who supported me, their friendship and assistance has meant more to me than I could ever express. Their guidance has served me well and I owe them my heartfelt appreciation. Special thanks to Madam Siti Zalita for her friendly assistance in practical analysis of this thesis. Thank you very much.

Last but not least, I owe sincere and earnest thankfulness to my beloved family. To my father, Mr. Rosland Abel Richard Lee, my mother, Mrs. Jumatiah Sagulu, my dear husband, Mohd Azmi Pang Thien Soong, my dearest sisters, Sabrina, Stasha Eleanor, Synthia Attilah and Sylvia Viviena for helping me get through the difficult times and for all the emotional support, I owe them everything and wish I could show them how much I love and appreciate them. To them I dedicate this thesis.

ABSTRACT

The study of essential oil of*Quercus infectoria* (Manjakani) was carried out usingsupercritical carbon dioxide (SC-CO_2) extraction. Twotechniques were tested Soxhlet extraction and SC-CO_2extractionwith pressure swing technique.The experiments of SC-CO_2 extractioninvestigated the effect of pressure and temperature on extraction yields and solubility of galls oil. The extraction were performed at pressuresrange of 35 to 48 MPa, temperaturesbetween 40 and 60ºCwith extraction time of 30 to 60 minutes.The experiments were designed usingResponse Surface Methodology (RSM) to determine the optimum conditions. In this study,SC-CO_2 extractioncombined with the pressure swing technique produced higher oil extracted compared to the continuos SC-CO_2 extraction with 2.58 % and 1.12 % yield, respectively. The analysis ofRSM indicated that the extraction temperature has a major linear effect on the galls oil extractionwith 17.92 % yield. The optimum extraction process parameters were for pressure of 38 MPa, temperature of 75 °C and extraction time of 54 minutes with 1.12 % yield. The experimentalsolubility data was successfully correlated using Chrastil model with the coefficient of determination (R^2) value of 0.95.SC-CO_2 extraction combined with the pressure swing techniqueproved of potential to produce greater yield by usingmuch lower SC-CO_2compared to the continuos SC-CO_2 extraction. The identification of bioactive compounds from essential oil was analyzed using aHigh Performance Liquid Chromatography (HPLC) analysis, and it was observed that*Quercus infectoria* galls oil contained gallic acid as the major component at the retention time of 2.79 min.

ABSTRAK

Kajian pengekstrakan minyak galls dari *Quercus infectoria* (Manjakani) dijalankan menggunakan kaedah pengekstrakan karbon dioksida bendalir lampau genting (SC-CO_2). Pengekstrakan cecair ini diuji menggunakan pengekstrakan Soxhlet dan SC-CO_2 dengan teknik ayunan tekanan. Eksperimen melibatkan penyiasatan tentang kesan tekanan dan suhu pada hasil pengekstrakan dan kebolehlarutan minyak galls menggunakan pengekstrakan SC-CO_2. Keadaan proses pengekstrakan yang digunakan pada tekanan 35 hingga 48 MPa, suhu diantara 40 dan 60 ºC manakala masa pengekstrakan adalah diantara 30 dan 60 minit. Eksperimen telah direka menggunakan Kaedah Tindakbalas Permukaan (RSM) bagi menentukan keadaan proses yang optimum. Pengekstrakan menggunakan SC-CO_2 yang digabungkan dengan teknik ayunan tekanan menghasilkan produk ekstrak minyak yang lebih tinggi (2.58 % hasil ekstrak) berbanding pengekstrakan berterusan SC-CO_2 (1.12 % hasil ekstrak). Analisis menunjukkan bahawa suhu pengekstrakan mempunyai kesan utama pada ekstrak minyak galls dengan peratus hasil ekstrak 17.92 %. Keadaan proses yang optimum bagi proses perahan minyak galls adalah pada tekanan 48 MPa, suhu 75 °C dengan masa pengekstrakan 54 minit bagi menghasilkan ekstrak minyak galls 1.12 %. Data kelarutan dari eksperimen telah berjaya dikaitkan menggunakan model Chrastil dengan pekali penentuan, R^2 bernilai 0.95. Pengekstrakan SC-CO_2 yang digabungkan dengan teknik ayunan tekanan berpotensi tinggi mengeluarkan hasil ekstrak minyak galls yang lebih tinggi dengan penggunaan SC-CO_2 yang lebih rendah berbanding pengekstrakan berterusan SC-CO_2. Pengenalpastian sebatian bioaktif daripada minyak galls dianalisis menggunakan analisis Kromatografi Cecair Prestasi Tinggi (HPLC) dengan minyak *Quercus infectoria* galls mengandungi asid gallic sebagai komponen utama telah dikesan, manakala masa tahanan dikesan pada 2.79 minit.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AARD	-	Average absolute relative deviation
ACE	-	Angiotensin converting enzyme
BBD	-	Box-Behnken Design
CNSL	-	Cashew nut shell liquid
CO_2	-	Carbon dioxide
HPLC	-	High performance liquid chromatography
MOX	-	Malaysian Oxygen
P_c	-	Critical pressure
PT	-	Pressure-Temperature
RSM	-	Response Surface Methodology
SCF	-	Supercritical fluid
SC-CO_2	-	Supercritical carbon dioxide
SEM	-	Scanning electronic microscope
SFE	-	Supercritical fluid extraction
T_c	-	Critical Temperature

LIST OF SYMBOLS

α	-	Alpha
β	-	Beta
μ	-	Dipole moment
ρ	-	Density
ε	-	Porosity
ºC	-	Degree celcius
%	-	Percentage
µm	-	Micrometer
hr	-	Hour
K	-	Kelvin
k	-	Association number
kg	-	Kilogram
MPa	-	Mega pascal
min	-	Minute
ml	-	Mililiter
mm	-	Milimeter
Pa	-	Pascal
s	-	Second

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

Essential oils are aromatic liquids derived from various parts of different plants (Dorie, 2001). Depending on the plants, essential oils are located in the bark, leaves, flowers, seeds and roots. There are different methods of extracting essential oils, based on the plant parts from which the individual oils are derived. The extraction process, which separates oils from their sources, has been employed for more than 40 centuries. The extraction methods include cold press, steam distillation, microwave extraction and solvent extraction. Nevertheless, a fairly new modern technology supercritical fluid extraction (SFE) with carbon dioxide (CO_2) may increase the production efficiency and contributes to preservation of the environment by reducing the use of solvents and the generation of hazardous substances (Masayoshi, 2010).

Over the last decade, the extraction of essential oil by supercritical fluids technology has re-emerged, mainly due to the dramatic increased in the research and development activities focusing on innovative and new trends approaches. SFE technology is growing at rapid pace because it can overcomes many disadvantages associated with conventional technologies and meet the consumer demand for natural products. In addition, large amounts of organic solvents used, particularly in the pharmaceutical, food and chemical industries can cause toxicity and generate

hazardous wastes to the environment. Therefore, in the search for environmentally friendly solvents, supercritical fluid extraction has been given high attention in variety of applications (Jose *et al.,* 2007*)*.

Quercus infectoria or locally known as Manjakani in Malaysia is a small tree native of Greece and Asia Minor, with four to six feet in height. The stems are crooked, shrubby looking with smooth and bright-green leaves borne on short petioles of 1 to 1.5 inches long. The leaves is bluntly mucronate, rounded, smooth, unequal at the base and shiny on the upper side, as shown in Figure 1.1a. Meanwhile, *Quercus infectoria* (Figure 1.1b) galls are corrugated and can be used as a thickener in stews or mixed with cereals for making bread.

(a) (b)

Figure 1.1 (a) Oak gall tree leaves (b) *Quercus infectoria* galls

In India, it is known as Majuphal and is widely used as Indian traditional medicine for treatment of toothache and gingivitis. Compared with other plant seeds, Manjakani is relatively less known. This plant is also efficacious for women health. Manjakani is also known as "herbal magic" which are rich with tannins, calcium, protein, vitamins A and C (Rina *et al.,* 2011). Additionally, the galls contain elements of astringent which can help to inhibit bacterial growth in urinary tract of women. Galls are mainly imported from Syria and Turkey, with some high grades are brought in smaller quantity from other countries namely China and Japan. Galls

are purely effective astringent and scarcely stimulant. They can be used as an injection in bad leucorrhea where they arrest putrefactive tendencies, and can be combined with suitable stimulants (Hwang *et al.,* 2010).

1.1 Background of the Problem

In the past few years, a published article highlighted the potential of antioxidant activity from *Quercus infectoria* galls with an addition of ethno botanical that can act as a stimulant and also can be used in treating skin disorders (Umachigi *et. al.,* 2008). In addition to medicinal properties for all parts of plants, the galls can live for more than 10 years before undergo the seedling process. In Indonesia, few researches have been carried out in the extraction of *Quercus infectoria* galls by using solvent extraction. The most important components extracted from these techniques were gallotannin, gallic acid and ellagic acid (Ikram and Nowshad, 1977). Nevertheless, the study on extraction of essential oils from *Quercus infectoria* galls using SFE has never been reported before. Therefore, this research will be conducted to emphasize the investigation on the extraction of essential oils from *Quercus infectoria* by using supercritical carbon dioxide (SC-CO_2) method coupled with pressure swing technique.

Supercritical fluid extraction has been documented as an effective method for extraction of essential oils from plant materials (Modey *et al*., 1996). In Malaysia, the use of supercritical fluid extraction is still unpopular even though several local researchers have studied the feasibility of this technique especially in the herbs industry such as *Strobilanthes crispus* (Pecah Kaca) (Azizi *et al*., 2007, Norulaini *et al*., 2009 and Liza 2010). Therefore, the result from this research is important to be revealed and documented in order to evaluate the therapeutic properties of essential oils and their potentials in pharmaceutical or food industries.

1.2 Problem Statement

Generally, it is feasible to obtain quality results by using the SC-CO_2 extraction process, as well as selective extraction results. As the galls are usually coated by a hard shell, there is a limitation on the efficiency of the extraction system. The pressure swing technique approach is considered as an improvement of SC-CO_2 process, where the quantity and quality of extraction can be improved, particularly for hard grains, which is influenced the botanical structure of the material used. The pressure swing method of SC-CO_2 is considered as an economical process as it only consumes a small amount of CO_2 gas for the extraction process.

1.3 Research Objectives

The objectives of this research are to study the effects of process parameters on the yield of *Quercus infectoria* (Manjakani) galls oil and also the ability of SC-CO_2 with pressure swing technique for extraction of galls oil.

1.4 Scopes of Work

The extraction of *Quercus infectoria* galls was performed at selected range of conditions by using both conventional SC-CO_2 and SC-CO_2 pressure swing techniques. Therefore, the scopes of the work are as follows:

a) Conducting experiments to determine the effects of process parameters which include pressure, temperature and extraction time on the extraction yield at

selected range of conditions and analysis of crude yield composition was carried out using High Performance Liqiud Chromatography (HPLC) analysis.

b) Optimization of variable condition (pressure, temperature and extraction time) by using Response Surface Model, with Box-behnken design (BBD) was used in the design of the experiment.

c) Investigation on the correlation of the solubility behaviour by using Chrastil model.

d) Comparison of extraction yield between conventional SC-CO_2 and SC-CO_2 with pressure swing techniques.

1.5 Research Contributions

Supercritical fluid extraction techniques are widely investigated in many industrial areas, and most of the published materials are concerned with the extraction of analytes from solid or semi-solid materials matrices. Several extraction techniques available over the past decades such as steam distillation extraction, ultrasound-assisted extraction, Soxhlet extraction and water steam distillation have been used to extract various natural compounds and essential oils from plant materials (seed, galls or leaves). Unfortunately, the oldest methods of extractions are very time consuming and require large quantities of solvents. Recently, the industry comes out with new observations, where dissolution of solutes in supercritical fluid (SCF) media has introduced the possibility of a new solvent medium. Consequently, SFE using CO_2 as a solvent is known as an efficient extraction technique for solid materials and it is extensively studied for separation of active compounds from herbs and other plants. The findings of this study, together with the pressure swing technique, will be viewed as a new approach for comparison with the current SC-

CO_2 continuous extraction process. In addition, there is lack of information on pressure swing extraction reported on SFE study. Thus, the information obtained from this study may provide a new approach to disclose the essential oils obtained from *Quercus infectoria* galls extraction and also as a reference to the SFE industry involving extraction of essential oils from seed plants.

REFERENCES

Abbas, K.A., Mohamed, A.,Abdulamir, A.S. and Abas, H.A. (2008).A Review on Supercritical Fluid Extraction as New Analytical Method.*American Journal of Biochemistry and Biotechnology*.4: 345-353.

Adeib, I.S., Norhuda, I., Roslina, R.N. and Ruzitah, M.S. (2010). Mass Transfer and Solubility of *Hibiscus cannabinus* L. Seed Oil in Supercritical Carbon Dioxide.*Journal of Applied Sciences*. 10: 1140-1145.

Ali, G.M., George, T.F., Assoufid, L. and Zhang, G. (2007). Molecular Building Blocks for Nanotechnology: From Diamondoids to Nanoscale Materials and Applications. New York: Springer Publishers.

Amin, N.A.S. and Anggoro, D.D. (2004). Optimization of DirectConversion of Methane to Liquid Fuels over Cu Loaded W/ZSM-5 Catalyst.*Fuel*. 83: 487-494.

Amparo, C., Tiziana, F., Roumiana, P.S., Angel, B. and Jose, G.R. (2007). Solubility of the Natural Antioxidants Gallic Acid in Supercritical CO_2 + Ethanol as a Solvent.*Journal of Chemical and Engineering Data*. 52: 116-121.

Ana, R.C. D., Patricia, C., Herminio, C.S. and Catarina M.M.D. (2004). Solubility of Flurbiprofen in Supercritical Carbon Dioxide.*Journal of Chemical and Engineering Data*. 49: 449-452.

Ana, R.C.D., Susana, S., Herminio, C.S. and Catarina, M.M.D. (2005).Solubility of Acetazolamide in Supercritical Carbon Dioxide in the Presence of Ethanol as Cosolvent.*Journal of Chemical and Engineering Data*. 50: 216-220.

Ana NajwaMustapa (2008).Extraction of Palm Oil from Palm Mesocarp using Sub-Critical R134a.UniversitiTeknologi Malaysia: Master Thesis.

Azizi, C.Y.M.,Wahyu, B.S. and Zainudin, A.M. (2007).Advances in Separation Processes.*UTM Publishers*, Skudai Johor.

Baysal, T. andStarmens, D.A.J. (1999).Supercritical Carbon Dioxide Extraction of Carvoneand Limonene from Caraway Seed.*Journal of Supercritical Fluids*.14: 225–234.

Beckman, E.J. (2004). Supercritical and Near-Critical CO_2 in Green Chemical Synthesis and Processing.*The Journal of Supercritical Fluids*.22: 121-191.

Beis, S.H. and Dunford, N.T. (2006). Supercritical Fluid Extraction of Daphne (*Laurusnobilis L.*)Seed Oil. Journal of the American Oil and Chemists' Society. 83: 953-957.

Bianchi, F., Careri, M., Mangia, A. and Musci, M. (2007).Retention Indices in the Analysis of Food Aroma Volatile Compounds in Temperature-ProgrammedGas Chromatography: Database Creation and Evaluation of Precision and Robustness.*Journal of Separation Science*. 30: 563-572.

Bozan, B. and Temelli, F. (2003).Extraction of Poppy Seed Oil using Supercritical CO_2. *Journal of Food Science: Food Chemistry and Toxicology*. 68.

Brogle, H. (1982). CO2 as a solvent: Its Properties and Applications. *Chemistry andIndustry*. 385-390.

Brunner, G. (2005). Supercritical Fluids: Technology and Application to Food Processing. *Journal of Food Engineering*. 67: 21-33.

Brunner, G., Birthich, A. and Johannsen, M. (1995). Supercritical Fluid Extraction ofOil-Palm Components. *The Journal of Supercritical Fluids*. 8: 46-50.

Chen, R., Meng, F., Zhang, S. and Liu, Z. (2009). Effects of Ultrahigh Pressure Extraction Conditions on Yields and Antioxidant Activity Ginsenoside from Ginseng.*Separation and Purification Technology*. 66: 340-346.

D' Andrea, A., Ferri, D., Maccioni, O., Van der Esch, S.A. and Vitali, F. (1994). Application of SFE Technology to the extraction of Active Substances from *Azadirachtaindica (A. juss)* Seeds, Kleeburg, H. Editions, In: PracticeOriented Results on the Use and Production of Neem Ingredients andPheromones, Drug and Graphic, Giessen.

Dorie, B. (2001). Natural Beauty Basics: Create Your Own Cosmetics and Body Care Products. 1st edition.United States: Square One Publishers.

Eikani, M.H., Fereshteh, G. andSoosan, R. (2006).Subcritical Water Extraction of Essential Oils from Coriander Seeds(*Coriandrumsativum L.*).*Journal ofFood Engineering*. 80: 735-740.

Eliane, M.Z.M., Louisiane, F.V.B., Leandro, D., Rosendo, A.Y. and Sandra, R.S.F.(2005). Composition Profile of Horsetail (*Equisetum giganteum L.*) Oleoresin: Comparing SFE and Organic Solvents Extraction. *Journal of Supercritical Fluids*. 33: 131-138.

Erkucuk, A., Akgun, I.H. and Yesil-Celiktas, O. (2009).Supercritical CO_2Extraction of Glycosides from *Stevia rebaudiana* Leaves: Identification andOptimization. *The Journal of Supercritical Fluids*. 51: 29-35.

Fan, G.J., Han, Y.B., Gu, Z.X. and Chen, D.M. (2007). Optimizing Conditions for *Anthocyanins*Extraction from Purple Sweet Potato using Response SurfaceMethodology (RSM).*LWT-Food Science and Technology*. 41: 155-160.

Fattori, M., Bulley, N.R. and Meisen, A. (1988). Carbon Dioxide Extraction of Canola Seed: Oil Solubility and Effect of Seed Treatment. *Journal of the American Oil Chemists' Society*. 65: 968-974.

Ferreira, S.R.S. and Meireles, M.A.A. (2002).Modeling the Supercritical Fluid Extraction of Black Pepper (*Piper nigrumL.*)Essential Oil.*Journal of Food Engineering*.54: 263-269.

Ferreira, S.R.S., Nikolov, Z.L., Doraiswamy, L.K., Meireles, M.A.A. and Petenate,A.J. (1999).Supercritical Fluid Extraction of Black Pepper (*Piper nigrunL.)*Essential Oil.*The Journal of Supercritical Fluids*.14: 235-245.

Fiori, L. (2009). Supercritical Extraction of Sunflower Seed Oil: Experimental Data and Model Validation. *The Journal of Supercritical Fluids*. 50: 218-224.

Gabriela, B.G., Cristiano, O., Paulo, A., Rodrigues, M.F and Jose, M.E. (2001). Extraction of Lipids from Cherry Seed Oil using Supercritical Carbon Dioxide.*European Food Research Technology*.212: 170-174.

Geankoplis, C. (2003). Transport Processes and Separation Processes Principles(Includes Unit Operations). Fourth Edition. Upper Saddle River, N.J :Prentice Hall Press Publishers.

Gelmez, N.,Kincal., N.S. and Yener, M.E. (2009). Optimization of Supercritical Carbon Dioxide Extraction of Antioxidants from Roasted Wheat Germ Basedon Yield, Total Phenolic and Tocopherol Contents and Antioxidant Activitiesof Extracts. *TheJournal of Supercritical Fluids*. 48: 217-224.

George, W. (2001).Handbook of Solvents.ChemTec and William AndrewPublishing.

Gomez, A.M., Lopez, C.P. and De La Martinez, O.E. (1996). Recovery of GrapeSeed Oil by Liquid and Supercritical Carbon Dioxide Extraction:

AComparison with Conventional Solvent Extraction. *Chemical EngineeringJournal and the Biochemical Engineering Journal*. 61: 227-231.

Goto, M., Sato, M. and Hirose, T. (1993).Extraction of Peppermint Oil by Supercritical Carbon Dioxide.*Journal of Chemical Engineering Japan*.26:401-407.

Hannay, J.B. and Hogarth, J. (1879).On the Solubility of Solids in Gases.*Proceedings of the Royal Society of London 1880*.30: 484.

Hawthorne, S.B. (1990). Analytical-Scale Supercritical Fluid Extraction.American Chemical Society. 62: 633-642.

Ikram, M. and Nowshad, F. (1977).Constituents of *Quercusinfectoria*.*PlantaMed*. 31: 286-287.

Iwalewa, E.O., McGaw, L.J., Naidoo, V. and Eloff, J.N. (2007). Inflammation: The Foundation of Diseases and Disorders. A Review of Phytomedicines ofSouth African Origin Used to Treat Pain and Inflammatory Conditions.*African Journal of Biotechnology*. 6: 2868-2885.

Janet, M., Sue, B., Maggie, E., Beverly, M. and Angela, W. (2011).OxfordHandbook of Midwifery. New York: Oxford University Press.

Jarvis, A.P. and Morgan, E.D. (1997).Isolation of Plant Products by Supercritical-Fluid Extraction.*Phytochemical Analysis*.8: 217- 222.

Jia, L.L., Jun, S.J., Ze, T.Z. and Yu, B.W. (2011).Measurement and Correlation of Solubility of Benzamide in Supercritical Carbon Dioxide with and without Cosolvent.*Fluid Phase Equilibria*. 307: 11-15.

Jose, L. M. (2007). Supercritical Fluid Extraction of Nutraceuticalsand BioactiveCompounds.*Taylor and Francis Publishers*.

Kashif, G., Jiyong, P. and Yong-Hee, C. (2010). Optimization of Supercritical Fluid Extraction of Bioactive Compounds from Grape (*Vitislabrusca. B.*) Peel by using Response Surface Methodology. *Innovative Food Science andEmerging Technologies*. 11: 485-490.

King, M.B. and Bott, T.R. (1992).*Extraction of Natural Products Using Near-Critical Solvents.*1st edition.Chapman and Hall.Springer Publisher.

Kumoro, A.C. and Masitah, H. (2007).Supercritical Carbon Dioxide Extractionof Andrographolide from Andrographispaniculata: Effect of the Solvent Flow Rate, Pressure and Temperature.*Chinese Journal Chemical Engineering*. 15: 877-883.

Kurt, S. (1999). Medical Aromatheraphy: Healing with Essential Oils. Frog Publisher.

Kyung, T.K., Md, S.U., Go, W.J., Jeong, E.S., Seung, M.L., Hee, C.W. and Byung, S.C. (2011). Solubility of Red Pepper (*Capsicum annum*) Oil in near-and Supercritical Carbon Dioxide and Quantification of Capsaicin. 28:1433-1438.

Light, M. and Bryan, M. (1998). Ayurveda and Aromatheraphy: The Earth Essential Guide to Ancient Wisdom and Modern Healing. MotilalBanarsidass Publishers.

Li, G., Song, C., You, J., Sun, Z., Xia, L. and Suo, Y. (2011). Optimization of Supercritical Carbon Dioxide Extraction on Red Pepper Seed Oil using Response Surface Methodology. *International JournalofFood Science &Technology*. 46: 44-51.

Liu, S., Yang, F., Zhang, C., Ji, H., Hong, P. andDeng, C. (2009).Optimization ofProcess Parameters for Supercritical CarbonDioxide Extraction of*Passiflora*Seed oil by Response Surface Methodology.*The Journal ofSupercriticalFluids*. 48: 9-14.

Liu, X., Li, Z., Chen, S., Zhan, S., Xia, y. and Wei, Y. (2005).Experimental and Simulating Study of Supercritical Carbon DioxideExtraction of Ginger Essential Oil.*Chinese Journal Chemical Engineering*.13: 572-576.

Liu,W., Fu, Y.J., Zu, Y.G., Tong, M.H., Wu, N., Liu, X.L. and Zhang, S. (2009). Supercritical Carbon Dioxide Extraction of Seed Oil from *OpuntiadilleniiHaw.*and its Antioxidant Activity. *Journal of Food Chemistry*. 114: 334-339.

LizaMdSalleh(2010). *Extraction of Bioactive Flavonoid Compounds from PecahKaca(Strobilanthescrispus) by Supercritical Carbon Dioxide*.UniversitiPutra Malaysia: TesisDoktorFalsafah.

Liza, M.S., Russly, A.R.,Mandana, B., Jinap,S., Rahmat, A.,Zaidul I.S.M.and Hamid, A. (2010). Supercritical Carbon Dioxide Extraction of BioactiveFlavonoid from *Strobilanthescrispus* (PecahKaca). *Food and BioproductsProcessing*. 88: 319-326.

Lucas de, A., Ossa de la, E.M., Rincon, J., Blanco, M.A. and Gracia, I. (2002).Supercritical Fluid Extraction of Tocopherol Concentrates from Olive TreeLeaves.*TheJournal of Supercritical Fluids*. 22: 221-228.

Lucia, L., Lenardo, R., Loredana, C. and Giuseppe, Z. (2005).Supercritical Carbon Dioxide Extraction of Oil and α-tocopherol fromAlmond Seeds.*Journal ofthe Science of Food and Agriculture*. 85: 2167-2174.

Luque de Castro, M.D. and Garcia-Ayuso, L.E. (1998).Soxhlet Extraction of Solid Materials: An Outdated Technique with a Promising Innovative Future. *AnalyticaChimicaActa*. 369: 1–10.

Luque de Castro, M.D., Miguel, V.C. and Maria, T.T. (1994).AnalyticalSupercritical Fluid Extraction.Springer-Verlag Publishers.

Machmudah, S., Sulaswatty, A., Sasaki, M., Goto, M. and Hirose, T. (2006). Supercritical CO_2 Extraction of Nutmeg Oil: Experiments and Modeling. *The Journal of Supercritical Fluids*. 39: 30-39.

Machmudah, S., Kawahito, Y., Sasaki, M. and Goto, M. (2007).Supercritical CO_2Extraction of RoseshipSeed Oil: Fatty Acids Compositionand ProcessOptimization. *The Journal of Supercritical Fluids*. 41: 421-428.

Machmudah, S., Kawahito, Y., Sasaki, M. and Goto, M. (2008). Process Optimization and Extraction Rate Analysis of Carotenoids Extraction from Rosehip Fruit using Supercritical CO_2. *The Journal of SupercriticalFluids*. 44: 308-314.

Mandana B., Russly A.R., Farah S.T., Ali G., Liza M.S.,Jinap S., Azizah H.,Zaidul I.S.M.(2011).Comparison of Different Extraction Methods for theExtraction of Major Bioactive Flavonoid Compounds from Spearmint(*Menthaspicata L.*)Leaves.*Journal of Food and Bioproducts Processing*.89: 67-72.

Mandana, B., Russly, A.R., Farah, S.T., Ling, T.C., Ali G., Jinap, S. and Azizah, H.(2009). Supercritical Carbon Dioxide Extraction (SC-CO_2) of BioactiveFlavonoid Compounds from Spearmint (*Menthaspicata. L*.) Leaves.*European Journal of Scientific Research*. 33: 679-690.

Masayoshi, S. (2010).Citrus Essential Oils: Flavor and Fragrance.*Hoboken,N.J.Wiley Publishers*.

Mehr, C.B., Biswal, R.N and Collins, J.L. (1996).Supercritical Carbon DioxideExtraction of Caffeine from Guarana.*The Journal of Supercritical Fluids*.9: 185-191.

Mensor, L.L., Menezes, F.S., Leita, G.G., Reis, A. S., Dos Santos, T.C. andCoube,C.S. (2001).Screening of Brazilian Plant Extracts for AntioxidantActivityby the Use of DPPH free Radical Method.*Phytotherapy Research*. 15: 127–130.

Min, J., Li, S., Hao, J and Liu, N. (2010). Supercritical CO_2 Extraction of Jatropha Oil and Solubility Correlation.*Journal of Chemical andEngineering Data*. 55: 3755-3758.

Miguel, H., Alejandro, C., Elena, I. (2006). Optimzation of theExtraction ofAntioxidants from *Dunaliellasalina*Microalga by PressurizedLiquids.*Journal of Agricultural and FoodChemistry*.98: 136-148.

Miguel, H., Virginia, G.C., Carolina, S. and Alejandro, C. (2010). Recent Advancesin the Application of Capillary Electromigration Methods for Food Analysisand Foodomics. *Electrophoresis*. 31: 205-228.

Modey, W.K., Mulholland, D.A. and Raynor, M.W. (2006).AnalyticalSupercriticalFluid Extraction of Natural Products.*Pytochemical Analysis*.7: 1-15.

Mohd Faisal Sulong @ A Rashid (2006). *Extraction of Essential Oils from JasmineFlower using Solvent Extraction Method*. University College of Engineering& Technology Malaysia: TesisSarjanaMuda.

MohamedR.S. and G.A. Mansoori. (2002).TheUse of Supercritical FluidExtraction Technology in Food Processing.*Food Technology.*

Mostafa, K. (2011). Optimization of Process Variables for Essential OilComponents from *Saturejahortensis* by Supercritical Fluid Extraction usingBox-BehnkenExperimental Design. *The Journal of Supercritical Fluids*. 55:944-948.

Nagi, A.A., Mariana, N.S., Hana, F.Z. and Rasedee, A. (2008).Extraction ofEssential Oil from *Nigella sativa* using Supercritical Carbon Dioxide: Studyof

Antibacterial Activity.*American Journal of Pharmacology andToxicology*. 3: 225-228.

Nie, S.P., Li, J.E., Yang, C., Qiu, Z.H. and Xie, M.Y. (2010).Optimization of Supercritical Fluid Extraction of Essential Oil from*HerbaMoslae* by Response Surface Methodology and its Chemical Composition Analysis.*Food Science Technology Resources*. 16: 185-190.

Nik, N.N.A., Setianto, W.B., Zaidul, I.S.M, Nawi, A.H., Azizi, C.Y.M. and Mohd, O.A.K. (2009). Effects of Supercritical Carbon Dioxide ExtractionParameters on Virgin Coconut Oil Yield and Medium-Chain TriglycerideContent.*Journal of Food Chemistry*. 116: 193-197.

Norhuda, I. and Jusoff, K. (2009).Supercritical Carbon Dioxide ($SC\text{-}CO_2$) as aCleanTechnology for Palm Kernel Oil Extraction.*Journal of Biochemistry &Technology*. 1: 75-78.

Nyam, K.L., Tan, C.P., Lai, O.M., Long, K. and Che, M.Y.B. (2010).Optimizationof Supercritical Fluid Extraction of Phytosterol from Roselle Seeds with aCentral Composite Design Model.*Journal ofFood and BioproductsProcessing*. 88: 239-246.

Özkal S.G.,Yener, M.E. and Bayindirli, L. (2005). Response Surfaces of ApricotKernel Oil Yield in Supercritical Carbon Dioxide. *LWT-Journal of FoodScience Technology*. 38: 611-616.

Özkal, S.G., Yener, M.E. and Bayindirli, L. (2005).Mass Transfer Modeling of Apricot Kernel Oil Extraction Supercritical Carbon Dioxide.*Journal ofSupercriticalFluids.* 35: 119-127.

Özkal, S.G., Yener, M.E. and Bayindirli. (2006). The Solubility of Apricot KernelOil in Supercritical Carbon Dioxide. *International Journal of Food ScienceTechnology*. 41: 399-404.

Padayatchi, S. (2004).Artemisinin Content of SC-CO2 Derived Extracts from *Artemisia annua*. North-West University: Degree Thesis.

Patcharee, P. and Theeraphan, M. (2011).Fingerprint of Volatile Flavour Constituents and Antioxidant Activities of Teas from Thailand.*Food Chemistry*. 125: 797-802.

Pathumthip, T., Chuaprasert, S., Douglas, P. and Luewisutthichat, W. (2001).Supercritical CO_2Extraction of Nimbin from Neem Seeds-An ExperimentalStudy.*Journal of Food Engineering*. 47: 289-293.

Peng, J., Dong, F. and Xu, Q. (2006).Orthogonal Test Design for Optimization of Supercritical Fluid Extraction of Daphnoretin, 7-methoxy-daphnoretin and 1,5-diphenyl-1-pentanone from *Stellerachamaejasme* L. and Subsequent Isolation by High-speed Counter-current Chromatography. *Journal ofChromatography*. 1135: 151-157.

Ping, S., Sun, P., and Ying, Y. (2008).Response Surface Optimization of Wheat Germ Oil Yield by Supercritical Carbon Dioxide Extraction.*Journal ofFood and Bioproducts Processing.* 86: 227-231.

Pourmortazavi, S.M. and Hajimirsadeghi, S.S. (2007).Supercritical Fluid Extraction in Plant Essential and Volatile Oil Analysis.*Journal ofChromatography*. 1163: 2-24.

Rajesh, N.P., Santanu, B. and Anuradda, G. (2006).Extraction of Cashew(*Anacardiumoccidentale*) Nut Shell Liqiud using Supercritical CarbonDioxide.*Bioresource Technology*. 97: 847-853.

Renata, M.S.C., Janete, H.Y.V. and Fernando, M.L. (2001).Extraction and Quantitative HPLC Analysis of Coumarin in Hydroalcoholic Extracts of *Mikaniaglomerata*Spreng. (“guaco”) Leaves.*Journal of the Brazilian Chemical Society*. 12: 706-709.

Reverchon, E. and Marrone, C. (2001).Modelling and Simulation of theSupercriticalCO_2Extraction of Vegetable Oils.*The Journal ofSupercriticalFluids*. 19: 161-175.

Ribeiro, M.A. and Bernardo, G.M.G. (1995).Solubilities of Triolein inSupercriticalCO_2.*Journal of Chemical Engineering Data*. 40: 1188-1192.

Rina, R., Rafiquzzaman, M. and Hasmah, A. (2011). Spectrophotometric Determination of Total Phenol and Flavonoid Content in Manjakani (*Quercusinfectoria*) Extracts. *Health and the Environment Journal.* 2: 9-13.

RodolpheBalz. (1996). The Healing Power of Essential Oils. 1stedition.LotusLight Publications.

Schütz, E. (2007). Supercritical Fluids and Applications-A Patent Review.*ChemicalEngineering Technology*. 30: 685-688.

Setianto, W.B., Smith Jr, R.L. and Inomata, H. (2001).In proceedings of theJapan Oil Chemist's Society, 40th annual meeting, Sendai, Japan.

Shobha, S.V. and Ravindranath, B. (1991).Supercritical Carbon Dioxide and Solvent Extraction of the Phenolic Lipids of Cashew Nut (*Anacardiumoccidentale*) Shells.*Journal of Agriculture and Food Chemistry*.39: 2214–2217.

Silva, G.F., Gamarra, F.M.C., Oliveira, A.L. and Cabral, F.A. (2008).Extraction ofBixin from Annatto Seeds using Supercritical Carbon Dioxide.*BrazilianJournal of Chemical Engineering*. 25: 419-426.

Sivasankar, B. (2005). Bioseparations: Principles and Techniques. New Delhi: Prentice-Hall.

Slavčo, A., Helena, S., Beti, C. and Filimena, P. (1998). Supercritical of CO_2Extraction and Soxhlet Extraction of Grape Seeds Oil.*Bulletin of theChemists and Technologists of Macedonia*. 17: 129-134.

Smith Jr, R.L., Malaluan, R.M., Setianto, W.B., Inomata H. and Arai, K. (2003). Separation of Cashew (*Anacardiumoccidentale L.*)Nut Shell Liquid withSupercritical Carbon Dioxide.*Bioresource Technology*. 88: 1–7.

Soroush, Z., Kharrat, R. and Yazdi, A.V. (2010).Extraction of Oilfrom CanolaSeeds with Supercritical Carbon Dioxide: Experimental andModeling.*Journal of American Science*. 6: 368-373.

Sousa, E.M.B.D., Filho, O.C., Moreno, M.T., Silva, D.N., Marques, M.O.M. and Meireles, M.A.A. (2002). Experimental Results for the Extraction ofEssential Oil from *Lippiasidoides* Cham. using Pressurized CarbonDioxide.*Brazilian Journal of Chemical Engineering*. 19: 229-241.

Sovova, H., Zarevucka, M., Vacek, M. and Stransky, K. (2001).Solubility of TwoVegetable Oils in Supercritical CO_2.*The Journal of Supercritical Fluids*.20: 15-28.

Span, R. and Wagner, W. (1996). A New Equation of State Carbon DioxideCovering the Region from Triple-Point Temperature to 1100K at Pressureupto 800 MPa. *Journal of Physical and Chemical Reference Data*.25: 1509-1596.

Sue, C. (2009). Essential Chemistry for Aromatherapy.*2nd edition*.ElsevierHealth Sciences.

Turner, C., Whitehand, L.C., Nguyen, T. and McKeon, T. (2004).Optimization of a Supercritical Fluid Extraction/Reaction Methodology for the Analysis of Castor Oil using Experimental Design.*Journal ofAgricultural and Food*

Chemistry. 52: 26-32.

Ueno, H., Tanaka, M., Machmudah, S., Sasaki, M. and Goto, M. (2008). Supercritical Carbon Dioxide Extraction of Valuable Compounds from Citrus junos Seed. *Journal of Food and BioprocessTechnology*. 1: 357-363.

Ugur, S., Onur, D. and Ayla, C. (2006).Extraction of Sunflower Oil withSupercriticalCO_2: Experiments and Modeling. *TheJournal of SupercriticalFluids*. 38: 326-331.

Umachigi, S.P., Jayaveera, K.N., Ashok Kumar, C.K., Kumar, G.S., VrushabendraSwamy, B.M. and Kishore Kumar, D.V. (2008).Studies on Wound HealingProperties of *Quercusinfectoria*.*Tropical Journal of PharmaceuticalResearch*. 7: 913-919.

Vanessa, Y., Ixtaina, F.M., Cardarelli, D.A, Miguel, A.M., Susan, M.N. and MabelC.T. (2011).Supercritical Carbon DioxideExtraction and Characterizationof Argentinean Chia Seed Oil.*Journal ofTheAmerican Oil Chemists'Society*. 88: 289-298.

Wang, L. and Weller, C.L. (2006).Recent Advances in Extraction of Nutraceuticals from Plants.*Trends in Food Science and Technology*. 17: 300-312.

Wang, L.Z., Yang, B., Du, X. and Yi, C. (2008).Optimisation of SupercriticalFluidExtraction of Flavonoids from *Puerarialobata*.*Food Chemistry*.108:737-741.

Wellness, W. (2005). Technology Watch: Supercritical Fluid Extraction an upcoming "Green Technology".

Wen, H., Li, Z., Niu.H., Li, D. and Zhang, J. (2008).Optimization of Operating Parameters for Supercritical Carbon Dioxide Extraction of Lycopene by

Response Surface Methodology.*Journal of Food Engineering*. 89: 298-302.

Zaidul, I.S.M.,Nik, N.N.A., Mohd, O.A.K., Sato, Y. and Smith Jr,R.L. (2007).Separation of Palm Kernel Oil from Palm Kernel withSupercritical CarbonDioxide using Pressure Swing Technique.*Journal ofFood Engineering*. 81:419-428.