SOLUBILITY MODEL OF PALM OIL EXTRACTION FROM PALM FRUIT USING SUB-CRITICAL R134a

NUR SYUHADA BINTI ABD RAHMAN

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To my beloved husband and family

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ABSTRACT

The exploration of alternative solvents for supercritical fluid extraction (SFE) technology has been attributed to the high capital investment due to higher pressure required by using supercritical carbon dioxide (SC-CO_2) as a solvent. One of the potential alternative solvent is the sub-critical R134a, which can be operated at lower pressure than SC-CO_2. This research investigate the use of dense gas approach, density based approach and solubility parameter to predict the solubility model of palm oil extraction from palm fruit using sub-critical R134a in SFE systems. Firstly, the dense gas approach involves the estimation of pure component vapour pressures, critical properties and binary interaction was implemented. This is followed by the development of thermodynamic model by using the equation of states (EOS) which are Peng-Robinson (PR) and Soave-Redlich-Kwong (SRK) combined with four mixing rules that includes excess Gibbs energy model. The density-based as the second approach requires the information of density, pressure and temperature. The performance of seven density based models were analysed in this research. Lastly, the solvent and solute solubility parameters were calculated using regular solution theory. Solvent specific coefficient for R134a was then determined using experimental data published. The proposed solvent specific coefficient for R134a is 11.8138 and this coefficient can be used for universal calculation of solubility which involves R134a as a solvent. Based on comparison of all correlation method, dense gas approach using the combination of PR EOS and Solute-Solute Interaction (SSI) mixing rule shows the lowest Average Absolute Relative Deviation (AARD), 0.08% compared to other methods. Due to complex calculation involved, T-P model regressed by Design Expert software is suggested as the best method to model the solubility behaviour of palm oil extraction from palm fruit using sub-critical R134a in the SFE systems.

ABSTRAK

Penerokaan pelarut alternatif dalam teknologi pengekstrakan bendalir lampau genting (SFE) adalah disebabkan oleh pelaburan modal yang tinggi berpunca daripada penggunaan tekanan tinggi yang diperlukan oleh pelarut lampau genting karbon dioksida (SC-CO_2). Salah satu pelarut alternatif yang berpotensi adalah pelarut separa lampau genting R134a di mana ia boleh beroperasi pada tekanan yang lebih rendah daripada SC-CO_2. Penyelidikan ini mengkaji penggunaan pendekatan gas tumpat, pendekatan berdasarkan ketumpatan dan parameter keterlarutan bagi meramalkan model keterlarutan pengestrakan minyak kelapa sawit daripada buah sawit dengan menggunakan pelarut separa lampau genting R134a dalam sistem SFE. Pertama, pendekatan gas tumpat melibatkan anggaran tekanan wap komponen tulen, ciri-ciri kritikal dan parameter interaksi telah dilaksanakan. Prosedur ini diikuti oleh perkembangan model termodinamik dengan menggunakan persamaan keadaan (EOS); Peng-Robinson (PR) dan Soave-Redlich-Kwong (SRK) yang digabungkan dengan empat kaedah campuran termasuk model tenaga Gibbs lebihan. Teknik berdasarkan ketumpatan adalah pendekatan kedua yang memerlukan maklumat mengenai ketumpatan, tekanan dan suhu. Tujuh prestasi pendekatan berdasarkan ketumpatan telah dianalisa di dalam penyelidikan ini. Akhir sekali, parameter keterlarutan pelarut dan bahan larut dikira menggunakan teori penyelesaian tetap. Kemudian, pekali pelarut khusus bagi R134a diperolehi daripada data-data eksperimen. Pekali spesifik bagi pelarut yang dicadangkan adalah 11.8138 dan pekali ini boleh digunakan untuk semua pengiraan keterlarutan yang melibatkan pelarut R134a. Berdasarkan perbandingan semua kaedah korelasi, pendekatan gas tumpat yang menggabungkan persamaan PR EOS dan Interaksi Antara Bahan Larut (SSI) menunjukkan Purata Sisihan Relatif Mutlak (AARD) paling rendah, 0.08% berbanding dengan kaedah yang lain. Oleh kerana ia melibatkan pengiraan yang kompleks, model T-P yang didapati dari perisian '*Design Expert*' dicadangkan sebagai kaedah terbaik bagi memodelkan perilaku keterlarutan pengestrakan minyak kelapa sawit daripada buah sawit dengan menggunakan pelarut separa lampau genting R134a dalam sistem SFE.

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LIST OF ABBREVIATIONS

AARD	-	Average Absolute Relative Deviation
AL	-	Adachi-Lu
CO_2	-	Carbon Dioxide
CPO	-	Crude Palm Oil
CVD	-	Co-Volume Dependent
C12	-	Lauric Acid
C14	-	Myristic Acid
C16	-	Palmitic Acid
Dva	-	del Valle-Aguilera
EOS	-	Equation of State
EV	-	Ethyl-Vanillin
FFA	-	Free Fatty Acids
G^{ex}	-	Excess Gibbs Energy
GMP	-	Good Manufacturing Product
KJ	-	Kumar and Johnston
MHV1	-	Modified Huron- Vidal First Order
MHV2	-	Modified Huron- Vidal Second Order
MPOB	-	Malaysian Palm Oil Board
MPOC	-	Malaysian Palm Oil Council
MST	-	Mendez-Santiago and Teja
NRTL	-	Non-Random Two Liquid model
OS	-	Obey Sandler
O-EV	-	O-Ethyl-Vanillin
O-VA	-	O-Vanillin
PR	-	Peng-Robinson

PvT	-	Pressure-Volume-Temperature
RK	-	Redlich-Kwong
R134a	-	1,1,1,2-tetrafluoroethane
SC-CO_2	-	Supercritical Carbon Dioxide
SCF	-	Supercritical Fluid
SFE	-	Supercritical Fluid Extraction
SF_6	-	Sulfur Hexafluoride
SP	-	Solubility Parameter
SRK	-	Soave-Redlich-Kwong
SSI	-	Solute-Solute Interaction
UNIFAC	-	UNIversal Functional Activity Coefficient
UNIQUAC	-	UNIversal QUAsi Chemical
VA	-	Vanillin
VdW	-	Van der Waals Mixing Rules
VdW1	-	Van der Waals Mixing Rules with One Adjustable Parameter
VdW2	-	Van der Waals Mixing Rules with Two Adjustable Parameters
WS	-	Wong Sandler

LIST OF SYMBOLS

A,B,C,D,E,F - Fitted parameter

a - Cross-energy parameter

b - Co-volume parameter

c - Fluid specific constant

k, k_1, k_2 - Association parameter

k_{12} - EOS binary interaction parameter

k_{11} - Dimensionless binary interaction parameters for solvent–solvent interaction

k_{22} - Dimensionless binary interaction parameters for solute–solute interaction

l_{12} - EOS size binary interaction parameter

m, n - Polynomial function of the acentric factor, ω

N, n - Number of data

P_c - Critical pressure

P^L - Vapour pressure of sub-cooled liquid

P_{ref} - Reference pressure (1 bar)

P^S - Solid vapour pressure

P^{sat} - Vapour pressure

P_r^{sat} - Reduced vapour pressure

q - Pure component area parameter

r - Pure component volume

R - Universal gas constant (8.314 J mol^{-1} K^{-1})

R^2 - Regression coefficient

S - Solubility (g oil/kg solvent used)

T - Absolute temperature (K)

T_b - Normal boiling point temperature

T_c - Critical temperature

T_m - Melting point

T_r - Reduced temperature $\equiv T/T_c$

v - Molar volume

$V_{L,20}$ - Liquid molar volume at 20°C

V - Volume

U - Internal energy of the real fluid

U^{∞} - Internal energy of the gas at infinite volume

U^{*} - Internal energy ($P \approx 0$ MPa)

y - Solubility (mole fraction)

z - Coordination number

Z - Compressibility factor $\equiv PV / RT$

$\Delta G_{ij}, \alpha_{ij}$ - Binary interaction energy for NRTL

ΔH_{fus} - Enthalpy of fusion

ΔU - Change in internal energy

Δu_{ij} - Binary interaction energy for UNIQUAC

ρ - Density

ρ_{ref} - Reference density

ρ_r - Reduce density

δ - Solubility parameters

□ - Fugacity coefficient

α - Corrective function depending on the temperature

ω - Acentric factor

π^* - Polarity

Ω_a, Ω_b - EOS specific constants

Notation

Subscript

1 - Solvent

2 - Solute

exp - Experimental

calc - Calculated

i, j - i^{th}, j^{th} component

Superscript

S - Solid
L - Liquid
SCF - Supercritical Fluid

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CHAPTER 1

INTRODUCTION

1.1 Global Outlook on World Oil and Fats Industry

The world top five major fats and oils production in the year 2009 include palm oil and palm kernel oil, soybean oil, animal fats, sunflower oil and rapeseed oil as shown in Figure 1.1. As reported in the 1980's, palm oil has become the second most sought after vegetable oil, with soybean oil as the first. Increasingly since the past 20 years, palm oil has become the world's most important production of oils and fats, which forms about 30% of the world's production. The use of palm oil in the culinary world dated back over 5,000 years ago and it is presently consumed in more than 130 countries globally (MPOC, 2010).

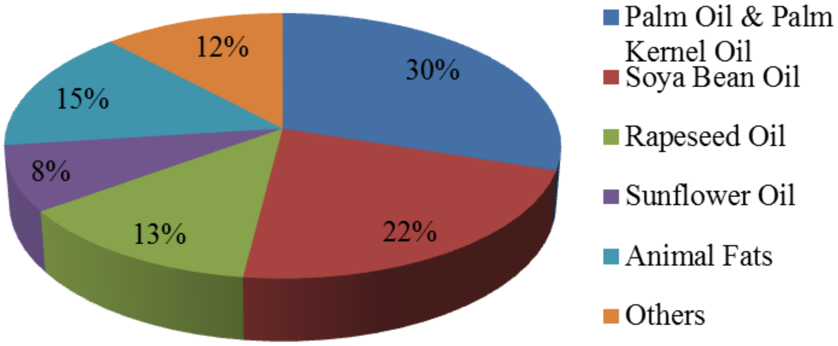

Figure 1.1: World’s oils and fats production in 2009 (MPOC, 2010)

Oil palm has been reported as the top yielding vegetable oil, producing 10 times more oil per hectare a year as compared to other oilseed products in the market. Table 1.1 shows a comparison of oil productions between the major oil yields of the world. As listed in Table 1.1, oil palm is grown on only 4.21% of the world’s agricultural land but produces 31.84% of global oil and fats. In comparison, in order to produce the same output, a soybean farm would need to cultivate up to 10 times more farming area (MPOB, 2008). Thus, palm oil is the best answer to the growing demand of the world’s increasing population while simultaneously serves as an option for optimized agricultural land usage.

Table 1.1: Oil productivity of major oil crops (MPOB, 2008)

Oil crops	**Oil production (million tonnes)**	**% of total production**	**Average oil yield (tonnes/ha/year)**	**Planted area (milllion ha)**	**% of total area**
Soybean	33.58	31.69	0.36	92.10	42.24
Sunflower	9.66	9.12	0.42	22.90	10.50
Rapeseed	16.21	15.30	0.59	27.30	12.52
Oil palm	33.73	31.84	3.68	9.17	4.21

1.1.1 World Palm Oil Industry

Over the last 20 years, palm oil demand has climbed exponentially due to its diverse usage in food, assorted merchandises as well as new preferred material for biofuel. However, about 80% of the world's palm oil production is intended to be used in the food industry. This is because the oil has excellent properties, making it the perfect candidate in cooking and frying. A steady increase in the world population has led to an increase in the demand for palm oil as a significant source of edible oils and fats.

At present, South-East Asia, particularly Malaysia and Indonesia, dominates the world's palm oil production. Figure 1.2 shows the market share in 2008, with the biggest palm oil producers which are Malaysia, Indonesia, Nigeria, Colombia and Thailand. The leading palm oil producer is Indonesia (46%), followed by Malaysia (41%). Currently, both countries are accountable for 87% of the world's oil palm production (MPOB, 2008).

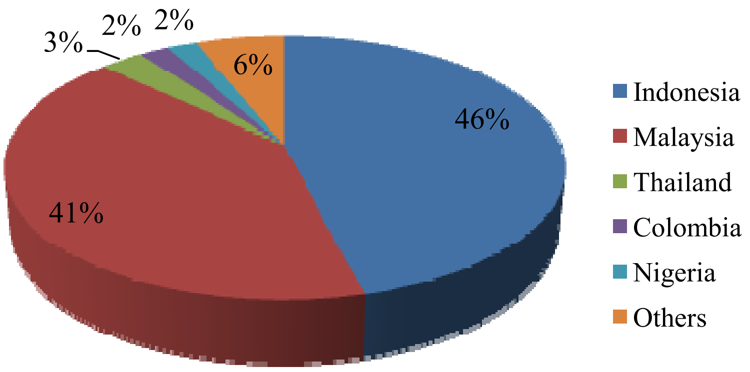

Figure 1.2: Market share of top 5 palm oil producers for 2008 (MPOB, 2008)

1.1.2 National Palm Oil Industry

There are 4.3 million hectares of palm oil plantations in Malaysia. This relatively small area produces about 41% of the world's palm oil production as well as contributing 12% to the world's oils and fats. The Malaysian palm oil production was observed to demonstrate an impressive performance from 1995 to 2010 (Figure 1.3). The country's production of crude palm oil (CPO) had increased from 7.5 million tonnes in 1995 to 18.3 million tonnes by 2010. Being one of the major palm oil producers and exporters, including its by-products, Malaysia plays a significant role in satisfying the growing demand for oils and fats across the world (MPOC, 2010).

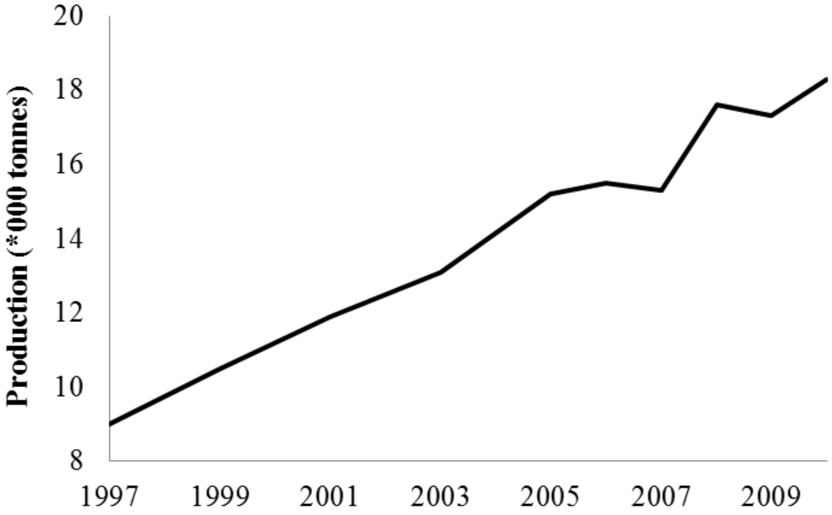

Figure 1.3: Malaysian palm oil production from1995 to 2010 (MPOC, 2010)

1.2 Development of Supercritical Fluid Extraction Technology

According to Tailor (1996), the discovery of critical point in a substance was first documented by Baron Cagniard de la Tour in 1822, while experimenting with his barrel. He observed critical temperature by listening to the gaps in the sound that a rolling flint ball made in sealed cannon that was filled with liquids at varying temperatures. He noticed that above the critical temperature, the distinction between the liquid and its gas phase disappears and the densities of the two phases become equal, leading to a single supercritical fluid (SCF) phase. About 27 years later, Hannay and Hogarth revealed the solvating power of supercritical fluids for solids. They established the fact that an increase in pressure will cause solutes to dissolve and that a decrease in pressure causes it to precipitate. The discovery of this behavior becomes fundamental to understanding the supercritical fluids extraction (SFE) technology.

SFE is a modern, safe and an environmentally friendly alternative among other available separation techniques; it can be used either to reduce or remove flammable and hazardous organic solvents (El-Aty et al., 2008). Over the recent years, there has been rapid development of SFE for the extraction of edible oil and natural products. SFE technology has been established to be efficient in the oil processing field (Fornari et al., 2008). Many of SFE applications have focused on the extraction of edible oil such as soybean (Lee et al., 1991), canola (Temelli, 1992), sunflower (Salgın et al., 2005), palm kernel (Hassan et al., 2000) and olive (Fornari et al., 2008) using supercritical carbon dioxide (SC-CO_2) to recover valuable minor components such as tocopherols and β-carotene.

SC-CO_2 is the most frequently used extraction agent due to its non-toxic property, it is chemically inert, has a low operating temperature and ease of solute-solvent separation as well as having high selectivity (El-Aty, 2008). SFE using carbon dioxide can be performed at a low temperature and it is a relatively pollution free operation. Its high selectivity permits the removal of free fatty acid (FFA) from the oil with minimum loss of neutral oil triglycerides and unsaponifiable matters (tocopherols, sterols and vitamins). Thus, when this technique is applied, the deacidification process can be carried out without significant loss in yield or the nutritional properties (Vazquez et al., 2009).

1.3 Problem Background

The application of SFE in various chemical processes has been researched extensively during the past thirty years. However, the commercialization of this technology is still inadequate. This is because of the high capital investment associated with plant start-up and intense operation due to the higher pressure as compared to conventional separation. SFE applications thus far are only focused on applying SC-CO_2 as a solvent in any separation processes. A satisfactory extraction or fractionation process using carbon dioxide as a solvent would require high pressure of up to 500 bar. Such a high pressure operation can contribute to high capital and operating cost.

SC-CO_2 (its polarity is effectively similar to hexane) is an exceptional solvent for non-polar solutes. However, its polarity is often too low for an efficient extraction. This could be due to the lack of sufficient solubility in the solutes. In order to rectify these problems, modifiers have been used to boost the SC-CO_2's ability to solvate polar organic compounds. The added of modifiers will also increase the cost of production (El-Aty, 2008). The discovery of a new or an alternative solvent having the same advantages as that of carbon dioxide is consequently essential in order to capitalize on the power of SFE technology over traditional technique. Sub-critical R134a is a possible option as it requires lower pressure compared to SC-CO_2. It has also been found to have comparable solvent properties to carbon dioxide in addition to being able to extract polar solutes at low temperature and pressure (Simoes and Catchpole, 2002).

The current status of research on the use of SFE technology has been focused on experiments using R134a as an alternative solvent in lab-scale environment (Najwa et al., 2008). In this work, a solubility model of palm oil extraction from palm fruit using sub-critical R134a is developed to apply for further design and operation of palm oil processes. The transformation of experimental solubility data into mathematical model could can be applied to predict the solubility at the operating condition (pressure and temperature) after measuring a minimum number of experimental data, which could accelerate the development of a sub-critical fluid process.

1.4 Problem Statement

Given a data set of temperature (T), pressure (P) and density (ρ), it is desired to develop a solubility model of palm oil extraction from palm fruit using sub-critical R134a solvent to ultimately achieve a simpler and efficient extraction processes.

1.5 Research Objectives

The research objectives are:

i. To develop solubility model of palm oil extraction from palm fruit using sub-critical R134a based on three different approaches; dense gas approach, density based approach and solubility parameter approach.
ii. To determine the best solubility model for palm oil solubility behavior prediction.
iii. To establish the solvent specific coefficient for sub-critical R134a.

1.6 Scope of Work

The key steps to be accomplished to achieve the objectives of this study consist of:

i. Estimation of the physical properties for the palm mesocarp fruit (solid phase) using prediction method.
ii. Correlation of palm oil solubility behavior based on dense gas approach using equation of state (EOS).
iii. Correlation of the palm oil solubility behavior based on density based approach.
iv. Correlation of the palm oil solubility behavior based on solubility parameter approach using regular solution theory and development of solvent specific coefficient for R134a.
v. Data validation of the three correlation approaches with other R134a application.
vi. Comparison of the best correlation approach for palm oil solubility behavior prediction.
vii. Comparison of solubility model between SC-CO_2 and sub-critical R134a.

1.7 Research Contribution

There are four key specific contributions predicted to emerge from this work which include:

i. The enhancement of the palm mesocarp fruit (solid phase) property database that is crucial for use in dense gas approach.

ii. The establishment of a thermodynamic model (dense gas approach) capable of demonstrating equilibrium solubility data for extraction of palm oil from palm fruit using sub-critical R134a system.
iii. The empirical model on the solubility behavior of palm oil extraction from palm fruit using sub-critical R134a provides a significant impetus for further SFE studies specific in sub-critical area.
iv. The introduction of solvent specific coefficient on the solubility parameter approach is envisioned to be a simpler method for further prediction of solute solubility in sub-critical R134a as an economical alternative solvent

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