OPTIMIZATION OF SUPERCRITICAL FLUID EXTRACTION OF ISOFLAVONE FROM SOYBEAN MEAL

MS. KANJANA LUMMAETEE

A SPECIAL RESEARCH PROJECT SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR
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Abstract

Supercritical fluid extraction technique is widely used in food industry because this technique is well known as a green separation process. The supercritical carbon dioxide is normally used as solvent because it is non-toxic, non-flammable and easy to remove. To extract isoflavone which consists of both polar and non-polar substances, adding methanol aqueous as co-solvent can increase the solubility of isoflavone. However, this technique has a high cost due to its high operating condition. Therefore, the study of optimization of supercritical fluid extraction of isoflavone from soybean meal can help find the optimum operating condition which provides the maximum profitability.

The objective of this study is to develop a mathematical model used to predict the yield of isoflavone from soybean meal in a supercritical extraction process using carbon dioxide and aqueous methanol as a co-solvent and to optimize the process using genetic algorithm (GA). To generate the mathematical model, a partial differential equation based on mass conservation was used to predict the yield of isoflavone extraction. The model parameters such as the density, the viscosity, the binary diffusion coefficient, the film mass transfer coefficient, the effective diffusivity, and the axial dispersion coefficient were estimated using available correlations, and the solubility was estimated using the Mohsen-Nia-Moddaress-Mansoori (MMM) equation of state. Moreover, finite difference was used to solve the partial differential equations in the model. The mathematical model was successfully validated with experimental data.

In the optimization, the operating conditions of isoflavone extraction process were identified as the decision variables and a profit function was maximized. Using GA, the optimum was found under the condition in which the carbon dioxide flow rate is 5.88 kg/h and the particle diameter is 0.68 mm, while the temperature is 323.15 K, the pressure is 59.45 MPa, and the extraction time is 283 minutes. The maximum profitability found under this optimal condition is 46.18 $ per batch.

Keywords: Isoflavone extraction/ Supercritical extraction/ Mathematical modeling/ Genetic algorithm/ Optimization

หัวข้อโครงการศึกษาวิจัย	ศึกษาหาสภาวะที่เหมาะสมในการสกัดไอโซฟลาโวนจากกากถั่วเหลืองด้วยวิธีการสกัดด้วยของไหลเหนือวิกฤต
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บทคัดย่อ

เทคนิคการสกัดด้วยของไหลเหนือวิกฤตนิยมนำมาใช้ในอุตสาหกรรมอาหาร เนื่องจากเป็นเทคนิคการสกัดที่ปลอดภัยต่อสิ่งแวดล้อม โดยทั่วไปคาร์บอนไดออกไซด์เหนือวิกฤตจะนิยมถูกนำมาใช้เป็นตัวทำละลายเนื่องจากไม่มีสารพิษ, ไม่ติดไฟ และ ง่ายต่อการกำจัด โดยในการสกัดสารไอโซฟลาโวนซึ่งมีองค์ประกอบของสารมีขั้วและไม่มีขั้วนั้น การใช้สารละลายเมทานอลร่วมในตัวทำละลายจะช่วยเพิ่มความสามารถในการสกัดสารไอโซฟลาโวนได้ แต่เทคนิคการสกัดนี้มีค่าใช้จ่ายสูงเนื่องด้วยสภาวะการดำเนินการที่สูงกว่าจุดวิกฤต ดังนั้นงานวิจัยนี้จึงมุ่งเน้นในการศึกษาหาสภาวะที่เหมาะสมในการดำเนินการที่ส่งผลให้ได้กำไรสูงสุด

วัตถุประสงค์ของงานวิจัยนี้คือสร้างแบบจำลองทางคณิตศาสตร์ที่สามารถทำนายผลที่ได้จากการสกัดไอโซฟลาโวนด้วยเทคนิคการสกัดด้วยของไหลเหนือวิกฤต และศึกษาหาสภาวะที่เหมาะสมในการสกัดไอโซฟลาโวนจากกากถั่วเหลืองโดยใช้ขั้นตอนวิธีเชิงพันธุกรรม สมการเชิงอนุพันธ์ย่อยที่ได้จากสมการอนุรักษ์มวลสารถูกนำมาใช้ในการสร้างแบบจำลองทางคณิตศาสตร์ในการทำนายผลที่ได้จากการสกัดไอโซฟลาโวน โดยพารามิเตอร์ที่เกี่ยวข้องในการสร้างแบบจำลองทางคณิตศาสตร์ได้แก่ ค่าความหนาแน่น (the density), ค่าความหนืด (the viscosity), ค่าสัมประสิทธ์การแพร่ระหว่างตัวทำละลายและตัวถูกละลาย (the binary diffusion coefficient), ค่าสัมประสิทธิ์การถ่ายเทมวลผ่านฟิล์ม

(the film mass transfer coefficient), ค่าสัมประสิทธิ์การแพร่ (the mass transfer coefficient), และค่าสัมประสิทธิ์การกระจายตัวตามแนวแกน (the axial dispersion coefficient) สามารถคำนวณได้จากสมการสหสัมพันธ์ และ ค่าการละลาย (the solubility) สามารถคำนวณได้จากสมการสภาวะของ มอห์เซนเนีย-มอดดาเรส-แมนซูริ (Mohsen Nia Moddaress Mansoori, MMM) วิธีการหาค่าเฉลยโดยประมาณได้ถูกนำมาใช้ในการคำนวณสมการเชิงอนุพันธ์ย่อย โดยแบบจำลองทางคณิตศาสตร์นี้ให้ผลสอดคล้องกับผลการทดลองได้เป็นอย่างดี

ในการศึกษาหาสภาวะที่เหมาะสมในการดำเนินการนั้น สภาวะในการดำเนินการได้ถูกพิจารณาให้เป็นตัวแปรในการตัดสินใจ และกำไรที่ได้จากการดำเนินการถูกพิจารณาเป็นฟังก์ชันในการตัดสินใจ ซึ่งหลังจากใช้ขั้นตอนวิธีเชิงพันธุกรรมในการศึกษาหาสภาวะที่เหมาะสมในการดำเนินการนี้ พบว่า สภาวะการดำการที่เหมาะสมภายใต้ ขนาดอนุภาคของกากถั่วเหลือง 0.68 มิลลิเมตร และ อัตราการไหลของคาร์บอนไดออกไซด์ 5.88 กิโลกรัมต่อชั่วโมง คือที่อุณหภูมิ 323.15 เคลวิน และ ความดัน 59.45 เมกะปาสคาล โดยใช้เวลาในการสกัดประมาณ 283นาที ซึ่งส่งผลให้ได้กำไรประมาณ 46.18 ดอลลาร์ ต่อ รอบการสกัด

คำสำคัญ : การสกัดไอโซฟลาโวน/การสกัดด้วยของไหลเหนือวิกฤต/ แบบจำลองทางคณิตศาสตร์/ ขั้นตอนวิธีเชิงพันธุกรรม/การหาสภาวะที่เหมาะสม

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NOMENCLATURES

ABBREVIATIONS

SYMBOLS		UNIT
a_{ii}	Attractive parameters of pure species	[-]
a_{ij}	Attractive parameters between species i and j	[-]
a_m	Attractive parameters of mixture system	[-]
AI	Aromaticity index	[-]
b_{ii}	Covolume parameters of pure species	[-]
b_{ij}	Covolume parameters between species i and j	[-]
b_m	Covolume parameters of mixture system	[-]
b_1	Constants in the LKP-EOS	[-]
b_2	Constants in the LKP-EOS	[-]
b_3	Constants in the LKP-EOS	[-]
b_4	Constants in the LKP-EOS	[-]
B	Dimensionless term in polynomial form in EOS (bmP/(RT))	[-]
Bi	Biot number (kfR/De)	[-]
c_1	Constants in the LKP-EOS	[-]
c_2	Constants in the LKP-EOS	[-]
c_3	Constants in the LKP-EOS	[-]
c_4	Constants in the LKP-EOS	[-]
C	The number of atoms of carbon in the solute molecule	[atom]
Cb	Solute concentration in the bulk of supercritical phase	[mol/m^3]
Cp	Solute concentration in the pore volume	[mol/m^3]
Csat	Saturated solute concentration in SCCO2	[mol/m^3]
CS	Cosolvent concentration	[wt.%]
d_1	Constants in the LKP-EOS	[-]
d_2	Constants in the LKP-EOS	[-]
d_p	Particle size	[mm]
D	Inner extractor diameter	[m]
D_{AB}	Binary diffusion coefficient of solutes (A) in supercritical solvents (B)	[m^2/s]
D_e	Effective diffusivity	[m^2/s]
D_L	Axial dispersion coefficient	[m^2/s]
EOS	Equation of state	[-]
f_i	Fugacity of component i	[-]
f_i^s	Fugacity of component *i* as a pure solid phase	[-]
f_i^{scf}	Fugacity of component *i* in supercritical fluid phase	[-]
k_f	Film mass transfer coefficient	[m/s]
k_{ij}	Binary interaction parameter between component i and j for a_{ij}	[-]
K	Distribution coefficient	[-]
l_{ij}	Binary interaction parameter between component i and j for b_{ij}	[-]
L	Bed length	[m]
n_i	Mole number of component i	[mole]
n_j	Mole number of component j	[mole]
P_c	Critical pressure	[MPa]

P_e	Peclet number	[-]
P_i^{sub}	Sublimation pressure of the pure solid	[MPa]
P_r	Reduced pressure (P/Pc)	[-]
q	Solid phase concentration	[mol/m^3]
q_o	Initial solid phase concentration	[mol/m^3]
Q	Solvent mass flow rate	[kg/h]
R	Initial radial coordinate of the solid phase (*dp*/2)	[m]
Re	Reynolds number	[-]
Sc	Schmidt number	[-]
SCF	Supercritical fluid	[-]
Sh	Sherwood number	[-]
t	Time	[min]
T	Temperature	[K]
T_c	Critical temperature	[K]
T_r	Reduced temperature (T/Tc)	[-]
v	Interstitial fluid velocity	[m/s]
V_c	Critical volume	[m^3/ mol]
V_r	Reduced volume (vPc/(RTc))	[-]
w	Weight of solid packed in an extractor	[g]
x_0	Initial mass fraction of solute in solid phase	[-]
yield	Mass of extract per mass of raw material	[-]
z	Dimensionless axial	[-]
$z^{(o)}$	Compressibility factor of the simple fluid	[-]
$z^{(r)}$	Compressibility factor of the reference fluid	[-]
Z	Compressibility factor (PV/RT)	[-]

GREEK SYMBOLS		**UNIT**
Δz	Dimensionless length of axial coordinate increment, 1/h^{-1}	
ε	Void fraction in bed	[-]
ε_p	Porosity of the solid	[-]
μ_m	Mixture viscosity	[kg/m·s]
ρ_m	Mixture density	[kg/m^3]
ρ_s	Solid density	[kg/m^3]
τ	Time of process	[min]
τ_r	Time of process, reference value	[min]
v	Total system volume per mol in vapour phase	[m^3/mol]
v_f	Interstitial velocity of SCCO2 through the process vessel	[m/s]
v_s	Solid molar volume	[m^3/mol]
θ	Dimensionless time (tDe/R2)	[-]
ϕ	Fugacity coefficient	[-]
ω	Acentric factor	[-]
β	Constants in the LKP-EOS	[-]
γ	Constants in the LKP-EOS	[-]

NOMENCLATURES

SUBSCRIPTS

a	Apparent
c	Critical
exp	Experimental
f	Fluid phase
g	Gas phase
p	Particle
s	Surface of particle, solid
o	At time zero

SUPERSCRIPTS

v	Vapor phase
l	Liquid phase
sat	Saturation condition

CHAPTER 1 INTRODUCTION

1.1 Introduction

Industrial extraction of isoflavone from soybeans has increased in demand because of the many health benefits associated with isoflavone consumption. The health benefits of isoflavone are derived from the fact that isoflavone behaves like estrogen (Nakada et al., 2009). Moreover, this isoflavone can prevent cancer and osteoporosis by increasing the bone mineral density and decreasing the bone resorption marker (Siwarasak et al., 2001; Wei et al., 2012).

Although there are many methods available for extracting isoflavone from soybeans, supercritical fluid extraction (SFE) is currently the most popular. Examples of methods used to extract soy isoflavone are extraction using an organic solvent (Murphy et al., 2002), pressurized liquid extraction (PLE) with mixed solvents (Luthria et al.,2007), ultrasound (Rostagno et al., 2007), and supercritical carbon dioxide ($SCCO_2$) (Zuo et al., 2008). $SCCO_2$ is the most popular method used to extract isoflavone in industry because this method can be considered a green separation process. Specifically, $SCCO_2$ can be used as a “green” solvent for isoflavone extraction because it is easy to remove, non-toxic, and non-flammable, which means that the extracted products are clean and the process operation is safe (Mongkholkhajornsilp et al., 2005).

Over time, the SFE process has been improved to increase targeted isoflavone extraction by adding aqueous methanol as a co-solvent. Soy isoflavone can be divided into 2 types, namely glycoside and its aglygon counterpart. The isoflavone targeted for industrial extraction are the glycosides, which make up 93% of the isoflavone extraction industry (Nakada et al., 2009). The preference for glycoside is significant because these molecules are structurally identical to their aglygon counterpart, except that they are bonded with a glucose chain. Thus, glycosides have a polar structure because of their glucose chain (for example, diadzin and genistin), whereas their aglycon counterparts are non-polar (for example, diadzein and genistein). $SCCO_2$ is non-polar, thus impeding the direct extraction of glycosides when it is used as the only solvent. As a result, it is necessary to add aqueous methanol, which is polar, to the $SCCO_2$ to increase the solubility of glycoside. This process uses a packed bed extractor as the isoflavone extraction unit, where soy bean meal makes up the solid bed, and $SCCO_2$ and aqueous methanol are used as solvents.

The supercritical extraction process contains 5 main units, namely a solvent storage vessel, a pump, a heater, an extractor, and a separator. First, fresh solvent from the solvent storage vessel is heated and pressurized to the operating conditions by passing through the heater and pump. Second, the supercritical solvents will extract the target solute from the packed solid inside the extractor via mass transfer. Third, the solution of solute and solvents will be separated inside the separator by depressurizing it.

The solute will be present at the bottom of the separator, while the solvent will go to the top of the vessel due to its lower boiling point and will be collected inside a solvent storage vessel later.

Because supercritical fluid extraction is operated at high temperature and pressure, the performance of the solute solubility increases. Phase equilibrium is used to describe the relationship of the fugacity between solid and supercritical fluid phase (Poling et al., 2001) in which an equation of state is used to estimate the fugacity coefficient of supercritical fluid phase (Ajchariyapagorn et al., 2009).

Supercritical fluid extraction incurs a high cost due to its high operating condition. Therefore, it is desirable to determine the most economical condition for this operation. Genetic algorithm has been used as a search or optimization technique to determine the optimum operating condition that gives the maximum profit. This method is widely used because it is capable of finding the global optimal solution instead of being stuck in a local minimum, even though it does not guarantee global optimality.

Genetic algorithm (GA) has been inspired from natural selection in nature which was discovered by Charles Darwin. In GA, a parent chromosome is operated on by crossover with another parent chromosome or mutation in order to generate a new generation. GA uses this principle to successively create stronger offspring which is equivalent to maximizing a given objective function until the optimum is found. The objective function and the constraint are required as input data. Generally, GA will begin by using an initial population created randomly. After that, the next generation of solution is produced by using the crossover and mutation operations to create stronger and more diverse offspring. At any given time in the GA iterations or generations, the best solution is always tracked and retained. After a fixed number of generations are reached or when no more improvement can be found after a certain number of generations, GA will terminate and the best solution is assumed to be the optimum solution.

In this study, a mathematical model is proposed to solve the optimization of a supercritical isoflavone extraction process. This optimization problem involves varying operation parameters, namely the temperature and the pressure, while the remaining variables in the model will be held constant. The constants in the model are the size of solid particles, and the solvent flow rate, the size of the vessel, the packed solid mass, the co-solvent type, and the residence time.

1.2 Objective

This research proposes a mathematical model that can predict the yield of isoflavone from soybean meal in a supercritical extraction process and can optimize the process to achieve maximum profitability by using genetic algorithm (GA).

1.3 Scopes of work

1. The operation parameters of the extractor, namely the temperature and the pressure will be varied with extraction time, whereas the remaining variables in the extractor will be held constant.
2. A mathematical model will be developed using MATLAB program.

1.4 Expected results

1. Obtain a mathematical model which can predict the performance of the soy bean extraction process using supercritical carbon dioxide.
2. Obtain the optimum operating condition of the extractor which provides maximum profitability.

CHAPTER 2 THEORY AND LITERATURE REVIEW

This chapter contains the basic principles of supercritical fluid extraction and a mathematical model used to estimate soy-isoflavone yield. In addition, the basic principles of genetic algorithm (GA) used to solve the optimization in this extraction process are explained in this chapter.

2.1 Supercritical fluid

Supercritical fluid is a substance that has properties above its critical points, where distinct liquid and gas phases do not exist. Therefore, the properties of supercritical fluid can exhibit both gas and liquid, and they can be adjusted to behave more like gas or liquid by changing the temperature or the pressure. A three dimensional pressure–volume–temperature (PVT) diagram and the pressure-temperature (P-T) projections (as shown in Figure 2.1) shows the different physical states of a pure substance. When both temperature and pressure are above the critical point, the system is considered to be a supercritical state, and under critical point, phase equilibrium is used to describe its relationship.

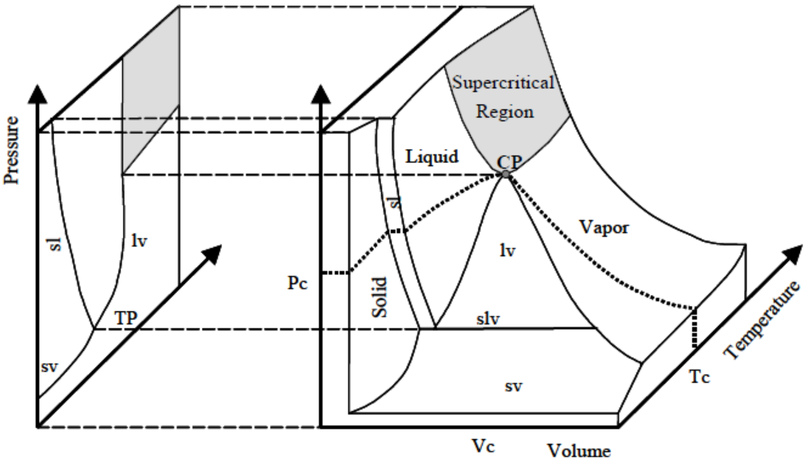

Figure 2.1 PVT diagram of a pure substance and its projection on the PT plane (Martinez, 2008).

A list of fluids that have been proposed as supercritical fluid solvents is shown in Table 2.1. These fluids can be classified as low-critical temperature (low-Tc) and high-critical temperature (high-Tc) solvents. Some condensable gases like CO_2, ethane, and propane are considered low-Tc solvents, while the higher alkanes, methanol, and water can be considered high-Tc solvents.

High-critical temperature solvents have more efficiency to extract solutes from high molecular weight of solvents, but the material will be damaged because of its operating conditions and hard to separate from its solution. On the other hand, the low-critical temperature solvents have lower efficiency to extract solutes than high-critical temperature solvents, but it has a lower operating condition and is easy to separate from its solution which makes the process easy to control and saves cost due to the operating conditions.

Table 2.1 Critical properties of fluids of interest in supercritical processes (Francis, 1954).

Fluid	Critical Temperature Tc (K)	Critical Pressure Pc (bar)	Critical Volume Vc (cm^3/mol)
CO_2	304.12	73.7	94.07
Ethane	305.3	48.7	145.5
Propane	369.8	42.5	200
Water	647.1	220.6	55.95
Ammonia	405.4	113.5	72.47
n-Hexane	507.5	30.2	368.0
Methanol	512.6	80.9	118.0

2.1.1 Physical properties of supercritical fluids

The physical properties of supercritical fluids are between those of the gas phase and the liquid phase. The physical properties of gas, supercritical fluids, and liquid are shown in Table 2.2

Table 2.2 Comparison of the physical properties of gas, liquid and supercritical fluids (Martinez, 2008).

Physical Property	Gas ($T_{ambient}$)	SCF (Tc,Pc)	Liquid ($T_{ambient}$)
Density (kg/m^3)	0.6 - 2	200 - 500	600 - 1600
Dynamic viscosity (mPa.s)	0.01 – 0.3	0.01 – 0.03	0.2 – 3
Kinematic viscosity (10^6 m^2/s)	5 - 500	0.02 – 0.1	0.1 - 5
Thermal conductivity (W/mK)	0.01 – 0.025	Maximum[a]	0.1 – 0.2
Diffusion coefficient (10^6 m^2/s)	10 - 40	0.07	0.0002 – 0.002
Surface tension (dyn/cm^2)	-	-	20 - 40

[a] Thermal conductivity presents maximum values in the near-critical region, highly dependent with temperature

Density, dynamic, and kinematic viscosity of supercritical fluids are lower than those of liquid, while the diffusion coefficient is higher. Thermal conductivity of supercritical fluids is higher than that of both the gas phase and the liquid phase, which has maximum values near the critical point, because in principle the heat capacity of a fluid tends to go to infinity at the critical point. Interfacial tension is close to zero in the critical region.

2.1.2 Supercritical carbon dioxide

Carbon dioxide is commonly used as a supercritical solvent for non-polar extraction because it is non-flammable, is non-toxic, has good solvent power, is easy to remove, and has low cost (Mongkholkhajornsilp et al., 2005). The critical temperature and pressure of carbon dioxide are 304.12 K and 73.7 bar, respectively. However; carbon dioxide is non-polar solvent; therefore, the polar solvent should be required as a modifier in order to increase the solubility of isoflavone.

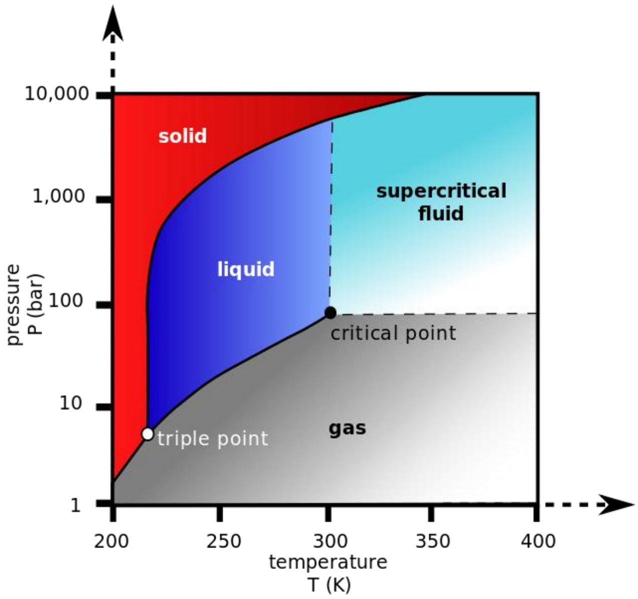

Figure 2.2 The phase diagram of carbon dioxide (Martinez, 2008).

2.1.3 Co-solvents

Co-solvents can be used to increase the solute solubility. Isoflavone consists of glycoside and aglycon which are polar and non-polar compounds, respectively; therefore, adding a polar solvent as a modifier will increase its solubility. Aqueous methanol is normally used as a co-solvent in food industry because of its safety (Nakada et al., 2009). The critical properties of methanol are 512.6 K, 80.9 bar, and 118.0 cm^3/mol, while the critical properties of water are 647.1 K, 220.6 bar and 55.95 cm^3/mol.

2.1.4 Supercritical extraction process

Basically, the supercritical extraction process consists of 5 main parts which are: a heater, pumps, an extractor, a valve to depressurize, and a separator. First, fresh solvents will pass through the pumps and the heater to increase the temperature and the pressure to its operating condition. Second, the solvents will extract the solute in the extractor which contains packed solids. Third, the solvents will be depressurized by passing through the valve and they will be removed at the top of the separator. Figure 2.3 shows the basic schematic of the supercritical extraction process.

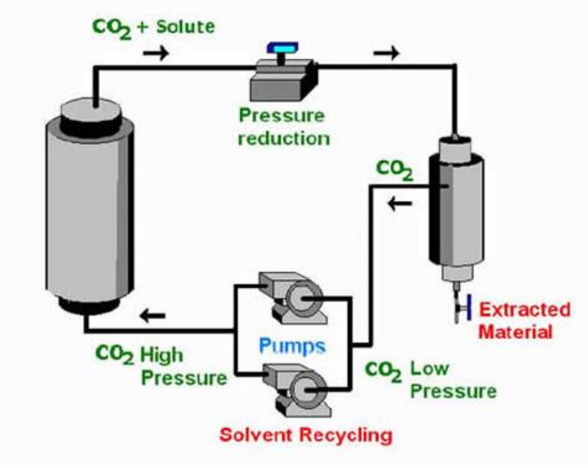

Figure 2.3 The basic schematic of supercritical extraction process (Rahoma et al., 2002).

2.2 Calculation of solid solubility in supercritical fluids

The solubility of solid in supercritical fluids can be estimated using phase equilibrium between the solid phase and the supercritical fluids phase in terms of fugacity (Poling et al., 2001).

$$f_i^s = f_i^{scf} \qquad (2.1)$$

Where f_i^s and f_i^{scf} are the fugacity of component *i* in solid and supercritical fluid, respectively.

The fugacity of solid (f_i^s) can be estimated from the following equation;

$$f_i^s = P_i^{sub} \phi_i^s exp\left(\int_{P_i^{sub}}^{P} \frac{v_i^s}{RT} dP\right) \qquad (2.2)$$

Where P_i^{sub} is sublimation pressure of a pure solid at system temperature (MPa),
P is system pressure or total pressure (MPa),
R is a gas constant (8.314 x 10^{-6} MPa·m^3/ (gmol·K)),
T is system temperature (K),
v_i^s is a pure solid molar volume (m^3/ gmol), and
ϕ_i^s is a fugacity coefficient of component *i* in solid solute.

The fugacity of supercritical fluid (f_i^{scf}) can be estimated from the following equation:

$$f_i^{scf} = y_i \phi_i^{scf} P \qquad (2.3)$$

Where y_i is mole fraction of component *i* in supercritical phase, and ϕ_i^{scf} is a fugacity coefficient of component *i* in the supercritical fluid phase.

Substitute the fugacity (f_i^s, f_i^{scf}) from equations 2.2 and 2.3 into equation 2.1;

$$P_i^{sub}\phi_i^s exp\left(\int_{P_i^{sub}}^{P}\frac{v_i^s}{RT}dP\right) = y_i\phi_i^{scf}P \tag{2.4}$$

Rearrangement;

$$y_i = \frac{P_i^{sub}\phi_i^s}{P\phi_i^{scf}} exp\left(\int_{P_i^{sub}}^{P}\frac{v_i^s}{RT}dP\right) \tag{2.5}$$

In general, it can be assumed that the solid is pure because the supercritical fluids cannot dissolve in the solid phase; therefore, v_i^s does not depend on the system pressure. Moreover, ϕ_i^s can be assumed to be unity ($\phi_i^s \sim 1$) because P_i^{sub} is very low; thus equation 2.5 can be written as shown below;

$$y_i^* = \frac{P_i^{sub}}{P\phi_i^{scf}} exp\left(\frac{v_i^s(P-P_i^{sub})}{RT}\right) \tag{2.6}$$

In order to estimate the solid solubility (y_i^*) in equation 2.6, the solid molar volume (v_i^s), the sublimation pressure (P_i^{sub}), and the fugacity coefficient in the supercritical fluids phase (ϕ_i^{scf}) are needed for the estimation.

2.2.1 Estimation of properties

2.2.1.1 Solid molar volume

Solid molar volume (v_i^s) is the volume of substance in the crystal state which can be estimated from the following equations. (Immari and Perini, 1977);

$$\bar{v}_s = \textstyle\sum_i m_i v_i \tag{2.7}$$

$$v_i^s = \frac{\bar{v}_s}{1.66} x \frac{1}{(100\%-0.9\%)} = \frac{\bar{v}_s}{1.645} \tag{2.8}$$

Where $\bar{v}_s$ is the calculated crystal volume for single molecule (angstrom^3/molecule), v_i is the unit volume of an atomic element (angstrom^3), and m_i is the relative stoichiometric multiplicities which are presented in Appendix A.

2.2.1.2 Sublimation pressure

Sublimation pressure is the vapor pressure used to directly convert solid into gas. Watson correlation is used to estimate the sublimation pressure shown in equation 2.9 (Lyman, Reehl and Rosenblatt, 1982).

$$\ln P_i^{sub} \approx \frac{\Delta H_{vb}}{\Delta Z_b R T_b}\left[1 - \frac{(3-2T_{\rho b})^m}{T_{\rho b}} - 2m(3-2T_{\rho b})^{m-1}\ln T_{\rho b}\right] \tag{2.9}$$

Where R is a gas constant, ΔZ_b is assumed to be 0.97, and K_F is Fishtine constant which depends on the dipole moments of polar and nonpolar molecules. K_F can be estimated from Table A.6-A.7 (Fishtine, 1963)

Furthermore, $T_{\rho b}$ can be estimated as a fraction of temperature and normal boiling point ($T_{\rho b} = \frac{T}{T_b}$).

m can be estimated from $T_{\rho b}$: If $T_{\rho b} < 0.5$; m = 1.9

$0.6 > T_{\rho b} > 0.5$; m = 0.8

$T_{\rho b} > 0.6$ ‘ m=0.36

ΔH_{vb} is the enthalpy at the boiling temperature which can be estimated from T_b and K_F

$$\frac{\Delta H_{vb}}{T_b} = K_F(8.75 + R \ln T_b) \qquad (2.10)$$

2.2.1.3 Normal boiling point and Critical properties

The normal boiling point (T_b) is the temperature at which make a liquid boils at 1 atmosphere of pressure, while the critical properties such as critical temperature (T_c), critical pressure (P_c) and critical volume (V_c) show the properties at the end of the phase boundaries which the properties of liquid and vapor are the same. Joback GCM and Consatantinou and Gani GCM equations have been proposed to estimate these parameters as shown in Table 2.3.

Table 2.3 Joback and Gani equations for estimating boiling point and critical properties (Joback and Reid, 1987; Constantinou and Gani, 1994).

Joback GCM	Constantinou and Gani GCM
$T_b = 198 + \sum_k N_k \Delta_{BJ}$	$T_b = 204.359 \ln \left[\sum_k N_k t_{b1k} + W \sum_j M_j t_{b2j} \right]$
$T_c = \frac{T_b}{0.584 + 0.965 \sum_k N_k (tck) - (\sum_k N_k (tck))^2}$	$T_c = 181.128 \ln \left[\sum_k N_k t_{c1k} + W \sum_j M_j t_{c2j} \right]$
$P_c = \frac{1}{1.01325[0.133 + 0.0032 n_A - \sum_k N_k (pck)]^2}$	$P_c = \left(1.3705 + \left[p_{c2}t + \sum_k N_k t_{m1k} + W \sum_j M_j t_{m2j} \right]^{0.5} \right) 10^{-5}$
$V_c = 17.5 + \sum_k N_k (vck)$	$V_c = \left(-0.00435 + \sum_k N_k v_{c1k} + W \sum_j M_j v_{c2j} \right) 10^{-3}$
Where Δ_{BJ} represents group increments obtained in Table A-4. *tck*, *pck* and *vck* are contributions obtained in Table A-5.	Where N_k is number of groups of type *k* in a molecule for first-order groups. M_j is number of groups of type *j* for second-order groups. t_{b1k}, t_{c1k}, t_{m1k}, and v_{c1k} are first-order group contributions given in Table A-2. t_{b2k}, t_{c2k}, t_{m1k}, and v_{c2k} are second-order group contributions given in Table A-3. W is weight for second-order groups. (W=0 for first-order estimation only and W=1 for full estimation or second-order estimation).

Joback GCM method is used to estimate the properties of a functional group. The estimation result of large molecules is not accurate, whereas Constatinou and Gani GCM method is used to estimate the advanced group based on UNIFAC groups. The estimation result is not accurate for very small and large molecules, especially fluorinated and larger ring compounds.

2.2.1.4 Pitzer's Acentric factor

Pitzer's acentric factor (ω) is obtained from the deviation of the experimental vapor pressure-temperature function from that which might be expected for a similar substance. ω for all molecules were estimated using a correlation based on Lee-Kesler equation as shown in the following equation:

$$\omega = \frac{3}{7}\frac{\theta}{1-\theta}\log_{10} P_c - 1.0 \qquad ; \theta = \frac{T_b}{T_c} \qquad (2.11)$$

2.2.1.5 Aromaticity Index

Aromaticity index (AI) is used to classify the equation of state to calculate the solid solubility. AI is explained in term of the potential formation of contribution of heteroatom to the 'double-bond equivalent' or DBE by calculating from an alternative DBE_{AI}/ C_{AI} ratio following the Equation 2.11:

$$AI = \frac{DBE_{AI}}{C_{AI}} = \frac{1+C-O-S-0.5H}{C-O-S-N-P} \qquad (2.12)$$

Where C, O, S, H, N and P are the number of atoms of carbon, oxygen, sulphur, hydrogen, nitrogen, and phosphorous, respectively, in the molecule that affects the degree of unsaturation or double atoms and not the number of total atoms in the molecule (Koch and Dittmar, 2006).

2.2.2 Equation of state

Equation of state (EOS) is used to describe the relationship of intensive parameters which are pressure, temperature, and volume, including the compressibility factor (Z) and fugacity coefficient.

2.2.2.1 Mohsennia-Modarres-Mansoori equation of state

The MMM-EOS is based on a statistical mechanics model of repulsive and attractive forces (Mohsen-Nia et al., 2003). This EOS is suitable for AI≤ 0.3 (Ajchariyapagorn et. al, 2008).

$$P = \frac{RT(v+1.3191b_m)}{v-b_m} - \frac{a_m}{T^{0.5}v(v+\sum_i y_i b_{ii})} \qquad (2.13)$$

$$a_i = 0.48748\frac{R^2 T_{c_i}^{2.5}}{P_{c_i}} \qquad (2.14)$$

$$b_i = \frac{0.064662RT_{c_i}}{P_{c_i}} \qquad (2.15)$$

$$\phi_i = exp\left[2.3191\left[\frac{3\left(2\sum_j y_j b_{ij} - \sum_i\sum_j y_i y_j b_{ij}\right)+b_{ii}}{4(v-b_m)} - \ln\left(1-\frac{b_m}{v}\right)\right] - \ln Z + \frac{a_m}{RT^{1.5}\sum_i y_i b_i}\left[\left(\frac{b_i}{\sum_i y_i b_i} - \frac{2\sum_j y_j a_{ij}}{a_m}\right)\ln\left(1+\frac{\sum_i y_i b_i}{v}\right) - \frac{b_i}{v+\sum_i y_i b_i}\right]\right] \qquad (2.16)$$

2.2.2.2 Peng-Robinson equation of state

The PR-EOS was developed from Redlich-Kwong equation of state. This equation is usually used to predict the density of non-polar and slightly polar components at high pressure (Peng and Robinson, 1976).

$$P = \frac{RT}{v-b_m} - \frac{a_m(T)}{v(v+b_m)+b_m(v-b_m)} \tag{2.17}$$

$$a_i = \frac{0.45724R^2T_{ci}^2}{P_{ci}}\alpha(T_{ri},\omega_i) \tag{2.18}$$

$$b_i = \frac{0.07780RT_{cii}}{P_{cii}} \tag{2.19}$$

$$\alpha(T_{ri},\omega_i) = \left[1 + K_i(1 - T_{ri}^{0.5}\right]^2 \tag{2.20}$$

$$K_i = 0.37464 + 1.5422\omega_i - 0.26922\omega_i^2 \tag{2.21}$$

2.2.2.3 Lee-Kesler-Plöcker equation of state

The LKP-EOS is an accurate method for describing PVT properties of non-polar components and mixtures (Plöcker et al., 1978). The compressibility (Z) from LKP-EOS was developed by starting from a polynomial form in the acentric factor (ω), but it is a reduced form of two terms of the compressibility factors of the simple fluid, z $^{(0)}$ and the reference fluid, z$^{(r)}$.

$$\begin{aligned} \ln\phi_i^{scf} = {} & \\ & \ln\phi_M - \frac{1}{T}\frac{\Delta h_M}{RT_{cM}}\sum_{j\neq i} Z_j\left(\frac{dT_{cM}}{dZ_j}\right)_{Z_k} + \frac{Z_M-1}{P_{cM}}\sum_{j\neq i} Z_j\left(\frac{dP_{cM}}{dZ_j}\right)_{Z_k} - \\ & \left(\frac{\partial\ln\phi_M}{\partial\omega_M}\right)_{T_r,P_r}\sum_{j\neq i} Z_j\left(\frac{d\omega_M}{dZ_j}\right)_{Z_k} \end{aligned}$$

$$; k\neq i,j \tag{2.22}$$

$$\left(\frac{\partial\ln\phi_M}{\partial\omega_M}\right)_{T_r,P_r} = \frac{1}{\omega^{(r)}}\left[(\ln\phi_M)^{(r)} - (\ln\phi_M)^{(0)}\right] \tag{2.23}$$

$$\left(\frac{dT_{cM}}{dZ_j}\right)_{Z_k} = \frac{\left[2\sum_l Z_l\left(V_{clj}^n T_{clj} - V_{cli}^n T_{cli}\right) - \eta V_{cM}^{\eta-1}\left(\frac{dV_{cM}}{dZ_j}\right)_{Z_k} T_{cM}\right]}{V_{cM}^{\eta}}, \eta = 0.25 \tag{2.24}$$

$$\left(\frac{dV_{cM}}{dZ_j}\right)_{Z_k} = 2\sum_l Z_l\left(V_{clj} - V_{cli}\right) \tag{2.25}$$

$$\left(\frac{dP_{cM}}{dZ_j}\right)_{Z_k} = P_{cM}\left[\frac{\left(\frac{dZ_{cM}}{dZ_j}\right)}{Z_{cM}} + \frac{\left(\frac{dT_{cM}}{dZ_j}\right)_{Z_k}}{T_{cM}} - \frac{\left(\frac{dV_{cM}}{dZ_j}\right)_{Z_k}}{V_{cM}}\right] \tag{2.26}$$

$$\left(\frac{dZ_{cM}}{dZ_j}\right)_{Z_k} = -0.085\left(\frac{d\omega_M}{dZ_j}\right)_{Z_k} \tag{2.27}$$

$$\left(\frac{d\omega_M}{dZ_j}\right)_{Z_k} = \omega_j - \omega_i \tag{2.28}$$

Where subscripts i and j refer to the solute and the supercritical fluid, respectively. Mixing rules for pseudo critical properties used in LKP-EOS are as follows:

$$T_{cM} = \left(\frac{1}{V_{cM}^{\eta}}\right)\sum_i \sum_j y_i y_j \, V_{cij}^{\eta} T_{cij} \tag{2.29}$$

$$T_{cij} = \sqrt{T_{ci}T_{cj}} \tag{2.30}$$

$$T_{cii} = T_{ci} \; ; \; T_{cjj} = T_{cj} \tag{2.31}$$

$$V_{cM} = \sum_i \sum_j y_i y_j V_{cij} \tag{2.32}$$

$$V_{cij} = \frac{1}{8}\left(V_{ci}^{\frac{1}{3}} - V_{cj}^{\frac{1}{3}}\right) \tag{2.33}$$

$$V_{ci} = \frac{Z_{ci}RT_{ci}}{P_{ci}} \tag{2.34}$$

$$Z_{ci} = 0.2905 - 0.085\omega_i \tag{2.35}$$

$$P_{cM} = \frac{Z_{cM}RT_{cM}}{V_{cM}} \tag{2.36}$$

$$Z_{cM} = 0.2905 - 0.085\omega_M \tag{2.37}$$

$$\omega_M = \sum_i y_i \omega_i \tag{2.38}$$

The fugacity coefficient of a pure component (ϕ) is estimated as follows:

$$\ln \phi = Z - 1 - \ln Z + \frac{B}{V_r} + \frac{C}{2V_r^2} + \frac{D}{5V_r^5} + E \tag{2.39}$$

$$Z = Z^{(0)} + \frac{\omega}{\omega^{(r)}}\left(Z^{(r)} - Z^{(0)}\right) \tag{2.40}$$

$$Z = \frac{P_r V_r}{T_r} = 1 + \frac{B}{V_r} + \frac{C}{V_r^2} + \frac{D}{V_r^5} + \frac{c_4}{T_r^3 V_r^2}\left(\beta + \frac{\gamma}{V_r^2}\right) exp\left(-\frac{\gamma}{V_r^2}\right) \tag{2.41}$$

Where B, C, D, and E are expressed as functions of the reduced temperature, which can be calculated from the equation below. There are two sets of constants of b_1, b_2, b_3, b_4, c_1, c_2 c_3, c_4, d_1, d_2, β, and γ. One set is used for the simple fluid (superscript “o”) and the other set is used for the reference fluid (superscript “r”) as shown in Table 2.4.

$$B = b_1 - \frac{b_2}{T_r} - \frac{b_3}{T_r^2} - \frac{b_4}{T_r^3} \tag{2.42}$$

$$C = c_1 - \frac{c_2}{T_r} + \frac{c_3}{T_r^3} \tag{2.43}$$

$$D = d_1 + \frac{d_2}{T_r} \tag{2.44}$$

$$E = \frac{c_4}{2T_r^3\gamma}\left[\beta + 1 - (\beta + 1 + \frac{\gamma}{V_r^2}) exp\left(-\frac{\gamma}{V_r^2}\right)\right] \tag{2.45}$$

Table 2.4 Two sets of constants of simple fluid (o) and reference fluid (r) (Plöcker et al., 1978).

Constants	**Simple fluids (o)**	**Reference fluid (r)**
b_1	0.118	0.203
b_2	0.266	0.332
b_3	0.155	0.028
b_4	0.030	0.203
c_1	0.024	0.031
c_2	0.019	0.050
c_3	0	0.017
c_4	0.043	0.042
d_1	1.55×10^{-5}	4.87×10^{-5}
d_2	6.24×10^{-5}	0.74×10^{-5}
β	0.054	1.226
γ	0.06	0.038

2.2.3 Conventional van der Waals Mixing rule

The conventional van der Waals mixing rule (Kwak and Mansoori, 1986) is used to estimate the mixing parameters for PR-EOS and LKP-EOS, a_m and b_m are defined as following

$$a_m = \sum_{i=1}^{nc} \sum_{j=1}^{nc} y_i y_j a_{ij} \tag{2.46}$$

$$b_m = \sum_{i=1}^{nc} \sum_{j=1}^{nc} y_i y_j b_{ij} \tag{2.47}$$

For MMM-EOS, b_m is defined as follows:

$$b_m = \frac{1}{4}\left(3\sum_{i=1}^{nc}\sum_{j=1}^{nc} y_i y_j b_{ij} + \sum_{i=1}^{nc} y_i b_{ii}\right) \tag{2.48}$$

Where nc is the number of components in the mixture and a_{ij} and b_{ij} are the cross parameters which can be obtained from a set of combining rules, as the follows:

$$a_{ij} = \left(1 - k_{ij}\right)\sqrt{a_{ii}a_{jj}} \tag{2.49}$$

$$b_{ij} = \frac{(b_i + b_j)}{2}\left(1 - l_{ij}\right) \tag{2.50}$$

2.3 Mathematical modeling of supercritical fluid extraction

In this study, a mathematical model is developed to predict the isoflavone extraction process. The model is based on differential mass balance equations with mass transfer between the solid particles in a packed bed and the supercritical solvents. In addition, the parameters involved in this model are presented in this topic as well.

2.3.1 Model equation

The isoflavone extraction process was set as a fixed bed extractor. Soybean meal is present as a pack of solids, while $SCCO_2$ and aqueous methanol present as solvents pass through the packed bed axially. The assumptions of this model (Hatami et al., 2010) are:

(1) Axial dispersion is significant;
(2) Radial concentration gradients are neglected in the fluid phase;
(3) The system is isothermal and isobaric;
(4) The physical properties of the supercritical fluid are constant along the bed;
(5) There is local equilibrium at interface of fluid and solid phase;
(6) The bed void fraction and particle porosity do not change during extraction;
(7) For small particles, it was assumed that the particle solute concentration is independent of radius and is a function of time only (lumped system);
(8) The solute concentration in particles is independent of coordinates Φ and θ.

Because the solute is a multi-component mixture, ‘pseudo-component’ will be used to estimate the single component to describe the global behavior.

The mass balance equations are:
Bulk phase:

$$\frac{\partial C_i}{\partial \tau} - \frac{1}{P_e}\frac{\partial^2 C_i}{\partial Z^2} + \frac{\partial C_i}{\partial Z} - \frac{(1-\varepsilon)}{\varepsilon} 3 \frac{k_f}{v}\frac{L}{R_p}\left[C_i - C_{i,s}\right] = 0 \tag{2.51}$$

Where the boundary and initial conditions are:

IC: at $\tau = 0$ → $C_i = 0$ (2.52)

BC1: at $Z = 0^-$ → $C_i = 0$ (2.53)

at $Z = 0+$ → $\frac{\partial C_i}{\partial Z} = P_e(C_i - 0)$ (2.54)

BC2: at $\tau = 0$ → $\frac{\partial C_i}{\partial Z} = 0$ (2.55)

Solid Phase:

$$\frac{dq_i}{d\tau} = -3\frac{k_f}{v}\frac{L}{R_p}\left[C_{i,s} - C_i\right] \qquad (2.56)$$

Where the initial condition is:

IC: at $\tau = 0$ → $q_i = q_{i,0}$ (2.57)

Where q and Cs are related by assuming equilibrium condition as:

$$q_i = KC_{i,s} \qquad (2.58)$$

Where K stands for the distribution coefficient.

By applying the conservative of mass law for the whole extractor system, the extraction yield (F) can be described as follows:

$$\frac{dF}{d\tau} = \frac{LA\varepsilon}{n_0}C_{z=1} \qquad (2.59)$$

Where the initial condition is:

IC: at $\tau = 0$ → $F = 0$ (2.60)

2.3.2 Model parameters

The isoflavone extraction model requires 5 parameters to complete the mathematical model which are: mixture density (ρ_m), mixture viscosity (μ_m), film mass transfer coefficient (k_f), axial dispersion coefficient in fluid phase (D_L), the binary diffusion coefficient (D_{AB}), and the effective pore diffusivity in the particles (D_e). These parameters can be estimated using correlations and existing data.

2.3.2.1 Mixture density

Under the assumption that co-solvents are incompressible fluid, LKP-EOS and PR-EOS are used to estimate the density of carbon dioxide (non-polar) and aqueous methanol (polar), respectively. The molar fractions of carbon dioxide and co-solvents ($y_{CO_2}$and y_{CS}) are required to estimate the mixture density.

$$\rho_m = y_{CO_2}\rho_{CO_2} + y_{CS}\rho_{CS} \qquad (2.61)$$

2.3.2.2 Mixture viscosity

Because this system operates at the supercritical state, American Petroleum Institute-Technical Data Book (API-TDB) recommends the following equations to estimate the viscosity of gas at high pressure.

For non-polar gas

$$(\mu - \mu_a)\xi = 1.08x10^{-4}[exp(1.439\rho_r) - exp(-1.11{\rho_r}^{1.858})] \qquad (2.62)$$

For polar gas

$$(\mu - \mu_a)\xi = 1.656x10^{-4}{\rho_r}^{1.111} \quad \text{for} \quad \rho_r \leq 0.1 \qquad (2.63)$$

$$(\mu - \mu_a)\xi = 6.07x10^{-4}(9.045\rho_r + 0.63)^{1.739} \quad \text{for} \ 0.1 \leq \rho_r \leq 0.9 \qquad (2.64)$$

$$\log_{10}\{4 - \log_{10}[(\mu - \mu_a)x10^{-4}\xi]\} = 0.6439 - 0.1005\rho_r \quad \text{for} \ 0.9 \leq \rho_r \leq 2.2 \qquad (2.65)$$

Where ξ is a viscosity parameter which is a function of M, T_c, and P_c:

$$\xi = T_c^{1/6}M^{-1/2}(0.987P_c)^{-2/3} \qquad (2.66)$$

Where μ and μ_a are the viscosity at the desired condition and viscosity at 1 atm. Also ρ, ρ_c and ρ_r are the density at the desired condition, critical density, and critical reduced density (ρ/ρ_c), respectively. μ_a can be estimated based on nonpolar and polar gas.

For nonpolar gas, $\mu_a\xi$ is a function of T_r:

For $T_r \leq 1.50$, $$\mu_a\xi = 34.0x10^{-5}T_r^{0.94} \qquad (2.67)$$

For $T_r > 1.50$, $$\mu_a\xi = 17.78x10^{-5}[4.58T_r - 1.67]^{5/8} \qquad (2.68)$$

For polar gases, $\mu^*\xi$ is a function of T_r and Z_c, where Z_c is the compressibility factor at the critical point ($Z_c = P_cV_c/RT_c$). In order to estimate $\mu_a\xi$ for polar gases, hydrogen bonding is effective in determining $\mu_a\xi$. For polar gases in which the hydrogen bonding is present:

$$(\mu_a \xi) Z_c^{5/4} = [7.55 T_r - 0.55] x 10^{-5} \tag{2.69}$$

For polar gases in which the hydrogen bonding is not present:

$$(\mu^* \xi) Z_c^{2/3} = [1.90 T_r - 0.29]^{4/5} x 10^{-4} \tag{2.70}$$

2.3.2.3 Film mass transfer coefficient

The film mass transfer coefficient describes the mass transfer resistance from the particle surface to the solute. The mass transfer coefficient can be estimated from the correlation of the dimensionless. Under the assumption that the mass transfer coefficient does not depend on the concentration or bed co-ordinates, the local mass transfer coefficient will be the average mass transfer coefficient.

In order to estimate the mass transfer coefficient of a supercritical system, the correlations from Wakao and Funazkri (1978), Tan et al. (1988), and Mongkholkhajornsilp et al. (2005) given in Equation 2.71 - 2.73 are used to increase the accuracy of the mass transfer coefficient. These correlations are present as a Sherwood number (*Sh*) which depends on Reynolds number (*Re*) and Schmidt number (*Sc*). The dimensionless quantities can be determined from the following relation: $Sh = \frac{d_p k_f}{D_{AB}}$, $Re = \frac{d_p v_f \rho_m}{\mu_m}$ and $Sc = \frac{\mu_m}{\rho_m D_{AB}}$, where v_f is the interstitial velocity of $SCCO_2$ through the process vessel and D_{AB} is the binary diffusion coefficient.

The Wakao and Funazkri correlation:

$Sh = 0.38Re^{0.83}Sc^{0.33}$ When $0.5 < Sc < 10{,}000$ and $3 < Re < 3{,}000$ (2.71)

The Tan et al. correlation:

$Sh = 0.38Re^{0.83}Sc^{0.33}$ When $2 < Sc < 40$ and $2 < Re < 40$ (2.72)

The Mongkholkhajornsilp et al. correlation:

$Sh = 0.135Re^{0.5}Sc^{0.33}$ When $6 < Sc < 25$ and $0.1689 < Re < 1.2918$ (2.73)

2.3.2.4 Axial dispersion coefficient

The axial dispersion coefficient (D_L) can be measured from back-mixing in the extraction vessel during fluid flow. The available values of axial dispersion is in the range between zero and infinity ($0 < D_L < \infty$), where zero represents no back-mixing of extraction vessel whereas infinity represents perfect mixing. Funazukuri et al. correlation (1998) was used to estimate the dispersion coefficients as shown below.

$$D_L = 1.317 \frac{D_{AB}}{\varepsilon_b} (\varepsilon_b R_e S_c)^{1.392} \qquad where\ \ \varepsilon_b ReSc > 0.3 \tag{2.74}$$

Normally, the axial dispersion of solutes is avoided in the process to maintain maximum level of their driving forces. Axial dispersion can be neglected in the modeling by maintaining a larger interstitial solvent velocity in the bed and by using sintered metal plates to cause pressure loss ≥ 1 MPa of the solvent inlet. Moreover, the gradients in the solvent viscosity due to radial gradients in the temperature can be avoided by operating near the ambient temperature and/or using a smaller diameter extraction vessel and maintaining a small enough particle diameters to extractor diameter ratio ($d_p/D < 0.1$).

2.3.2.5 Effective diffusivity coefficient

The effective diffusivity coefficient (D_e) describes the influence of the porous network on the diffusion inside the particle. D_e can be estimated from the correlation of Wakao and Smith (1962) which is a function of particle porosity (ε_p) and binary diffusion coefficient (D_{AB}).

$$D_e = \varepsilon_p^2 D_{AB} \tag{2.75}$$

Where ε_p depends on the pore size and the pore structure, and D_{AB} can be estimated from the correlation proposed by He et al. (He, 1997).

$$D_{21} = \left(V_1^k - 23\right)\sqrt{\frac{T}{M_2}}10^{-10}\left[0.61614 + 3.0902exp\left(\frac{-0.87756\sqrt{M_1 V_{C,1}}}{P_{C,1}}\right)\right] \tag{2.76}$$

$$k = 1 \text{ for } \rho_r \geq 1.2 \tag{2.77}$$

$$k = 1 + (\rho_r - 1.2)/\sqrt{M_A} \text{ for } \rho_r \leq 1.2 \tag{2.78}$$

Where 1 and 2 are solvents and solute, respectively. $P_{C,1}$ is the critical pressure of solvents (bar), $V_{C,1}$ is the critical volume of solvents (cm^3/ mol), V_1 is the volume of solvents (cm^3/ mol),, and M_1 and M_2 are the molecular weight of solvents and solute, respectively.

2.4 Genetic algorithm

Genetic algorithm (GA) was invented by John Holland in 1960s and developed by Holland and colleagues at the University of Michigan in the 1970s. Genetic algorithm is a search method that uses the principle of natural selection in organisms together with the evolutionary operators of selection, crossover, and mutation (Younes et al., 2008).

The starting fitness chromosomes are estimated by first generating a population of chromosomes randomly, and then calculating the fitness function of each chromosome. Next, a pair of parent chromosomes is selected from the current population and they are crossed over to obtain a new pair of offspring chromosomes. Finally, the fitness function of each chromosome is calculated again and compared with those of the parent generation. This procedure is repeated until no further improvement in the offspring fitness is possible. Figure 2.4 shows the diagram of the GA.

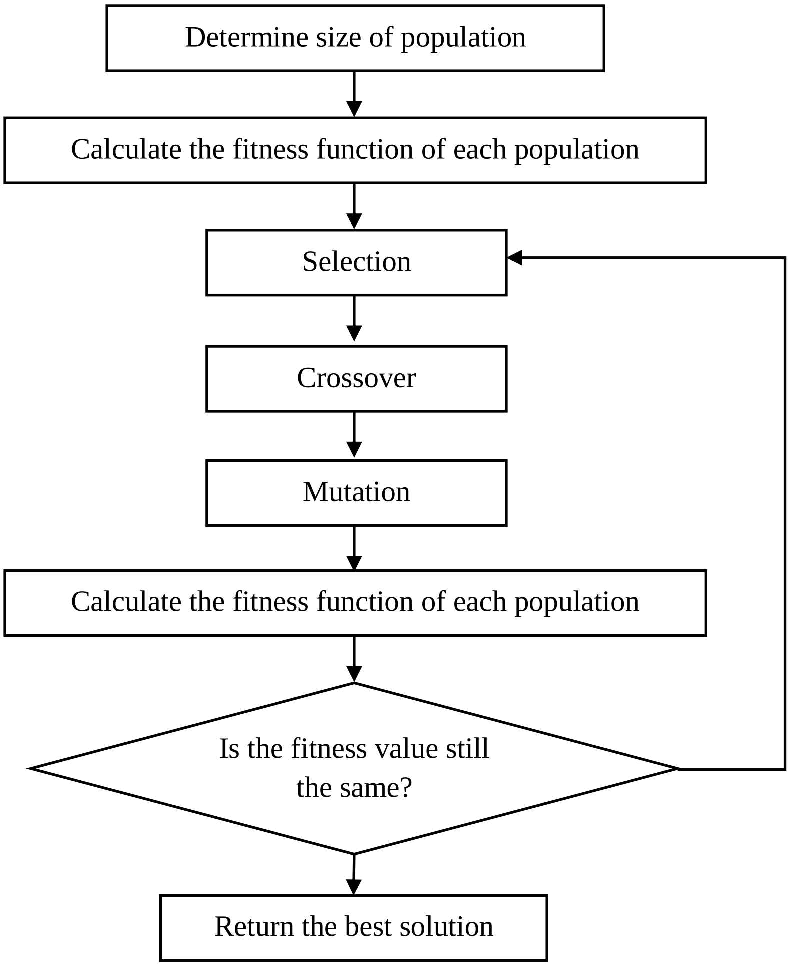

Figure 2.4 Genetic algorithm diagrams (Younes et al., 2008).

2.4.1 Initial population

The GA always starts with an initial population, which in the case of optimization represents feasible solutions in the problem. An initial population can be generated by selecting some of chromosomes from the entire search space. There are several approaches used to generate the initial population such as random, uniform, and biased methods as shown in Figure 2.5.

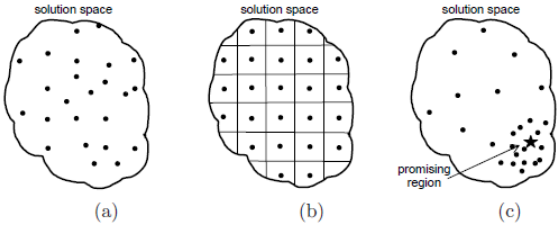

Figure 2.5 Population initiation. (a) random. (b) uniform. (c) biased.

2.4.1.1 Random

In generating the initial population using the random method, the population chromosomes are picked up randomly in order to avoid biasing the population around particular regions in the search space. If binary representation is used, complementary sampling can be used to create the initial population. In this method, half the bits in the chromosome are created randomly and the other halves are the complements of those of the first half.

2.4.1.2 Uniform

Although the random method can easily generate an initial population, it does not ensure that the sample of search space is fair, especially when the population is small. Therefore, the uniform method will be used if the population is distributed uniformly over the search space, for example, dividing the search space into sub-regions and ensuring that each sub-region represents one of the initial populations.

2.4.1.3 Biased

The biased method is useful for picking up the initial population if the user has prior knowledge of what region in the solution space most likely contains good solutions. This method will save time in the search. However, the biased method still does not guarantee that the search region will contain the best solution.

2.4.2 Selection

This operator selects suitable chromosomes from the population for reproduction. There are many methods used in the selection, such as roulette wheel selection (RWS), fitness scaling, ranking selection, and tournament selection. Figure 2.6 shows how solutions in the initial population are selected for reproduction to produce the next generation of solutions.

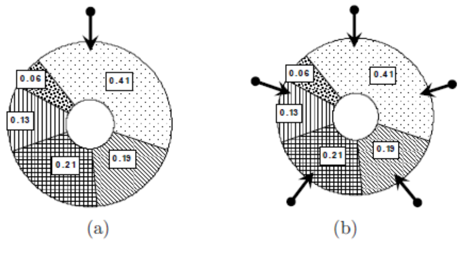

Figure 2.6 Fitness Proportionate Selections.
(a) Roulette Wheel Sampling. (b) Stochastic Universal Sampling.

2.4.3 Crossover

Crossover or recombination is an operator that chooses a locus of a pair of parent chromosomes randomly and exchanges the sequences before and after that locus between two chromosomes to create two offspring. For example, a pair of parent chromosomes 100110 and 011100 could be crossed over after the second locus in each to produce the new two offspring, namely 101100 and 010110 as shown in the Figure 2.7 below.

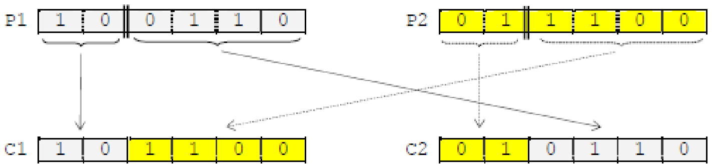

Figure 2.7 Single point crossover.

2.4.4 Mutation

The mutation operator randomly flips some of the bits in a chromosome which is akin to producing an offspring through mutation. For example, the string 101110 might be mutated in the fourth position to get 101010. Mutation can occur at each bit position in a string with some probability, usually very small such as 0.001. The mutation operation is demonstrated in Figure 2.8.

Figure 2.8 Mutation.

2.4.5 Advantages and disadvantages of genetic algorithm

2.4.5.1Advantages

Genetic algorithm has several advantages to be used as a search method in optimization. For example, GA uses various transformation operators to create diverse populations; therefore, the effective sample has more probability to pick up the global optimum and less chance to obtain a local optimum when compared with a point-based search method as shown in Figure 2.9. Moreover, GA is able to solve for a variety of decision variables such as binary, integer, or continuous variables because genetic operators use coding of the parameter space rather than the parameters themselves (only objective function information is used).

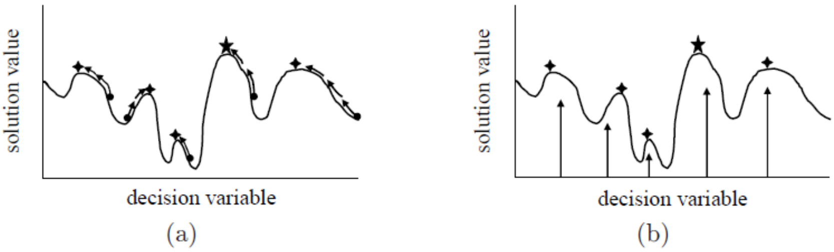

Figure 2.9 A point-based search versus a population heuristic.

(a) A local search method that inspects a single point at a time ends at a local optimum that depends on the starting point.

(b) Population-based heuristics sample several regions of the search space simultaneously.

2.3.5.2 Disadvantages

Because GA is a kind of meta-heuristic approach, the global optimum is not guaranteed. For this reason, if there is an exact method or a simple heuristic that can solve the problem at hand in reasonable and acceptable time, then we should not use GA or any other meta-heuristic approach to solve that problem. However, most real-world problems are too complex to be solved exactly and in short time; therefore, GA will be a good choice to provide an acceptable solution in an acceptable time.

2.5 Literature review

Nakada et al. (2009) presented a review of the soy isoflavone extraction process technology. The supercritical carbon dioxide extraction ($SCCO_2$) is widely used for food functional components such as caffeine, capsaicin, carotenoids, aspirin and coenzyme Q_{10}. In general, $SCCO_2$ has low solubility for polar components; therefore, Nakada et al. (2009) tried to develop the ability of solubility by studying the impact of ethanol addition as a co-solvent on the solubility of soy isoflavone. Adding ethanol in $SCCO_2$ can increase the solubility of isoflavone by enhancing the hydrophobicity of hydrophilic isoflavone (daidzin, genistin and glycitin). As a result, the supercritical carbon dioxide using ethanol as co-solvents was considered to produce soy isoflavone extraction because of increased solubility of soy isoflavone.

Zuo et al. (2008) presented experimental data of soy isoflavone extraction using supercritical carbon dioxide and aqueous methanol as co-solvents. In this experiment, 100 grams of soybean meal is packed in 1 liter of the packed bed extractor size. The effects of the modifier composition in terms of methanol content in water, modifier concentration, particle size of soy bean meal, and extraction conditions (temperate, pressure and flow rate of carbon dioxide) on isoflavone recovery were investigated. From the experimental data, 80% (v/v) of aqueous methanol, 7.8% of modifier concentration, 20-30 mesh of particle size, 9.8 kg/h of carbon dioxide flow rate, 40 ^{o}C, and 50 MPa provides the highest isoflavone recovery which is 87.3%.

Hatami et al., (2010) presented a mathematical model of clove oil extraction with supercritical carbon dioxide. This model is a function of pressure, temperature, solvents flow rate, solid particle size, co-solvents concentration, extraction time, solubility, diffusion coefficient, density, and viscosity. The critical properties were estimated from Joback and Gani correlations using the group contribution method. The other model parameters were estimated from correlations, e.g. film mass transfer coefficient (k_f) was estimated from Tan et al. correlation (Tan et al, 1988), the effective diffusivity coefficient (D_e) was approximated by Wakao and Smith correlation, the binary diffusion coefficients (D_{AB}) was estimated from He correlation (He, 1997), the axial dispersion coefficient in the supercritical phase (D_L) was estimated from Funazukuri et al. correlation, and the solubility was estimated from the equations of state. MMM-EOS and LKP-EOS were used to determine the solubility, where MMM-EOS is suitable for polar compounds and LKP-EOS is suitable for non-polar compounds.

Rahimi et al. (2011) and Hatami et al. (2010) presented a mathematical model of supercritical fluid extraction and optimization using genetic algorithm. The objective of their study is to develop a mathematical model to identify the optimum operating condition (temperature and pressure). They use the numerical method of Meireles et al. (2009) to convert PDEs to ODEs and then solved them using MATLAB software. Moreover, Hatami et al. (2010) proposed a relationship between solid particle size and solvents flow rate and found out that the optimal particle size should be as small as possible and the optimal solvent flow rate should be as large as possible. However, the channeling problem must be considered as well. Rahimi et al. (2011) and Hatami et al. (2010) also used the genetic algorithm as a search method to identify the optimum operating condition. Genetic algorithm is a kind of natural selection which consists of eight main steps in this study: 1) Definition of the fitness function (objective function), 2) Characterization of GA parameters such as the population size, the crossover rate, the mutation rate etc., 3) Production of the initial generation in a random way, 4) Fitness evaluation, 5) Reproduction of a new generation using GA selection operator, 6) Obtaining crossover, 7) Performing mutation, and 8) Step 4-7 should be repeated until the number of generations reaches the prescribed value.

CHAPTER 3 METHODOLOGY

This chapter covers the methodology used to develop a mathematic model and the optimization algorithm of isoflavone extraction process. MATLAB program, a mathematical solver software, is used to solve this problem. The methodology of this study consists of five main steps as shown in Figure 3.1.

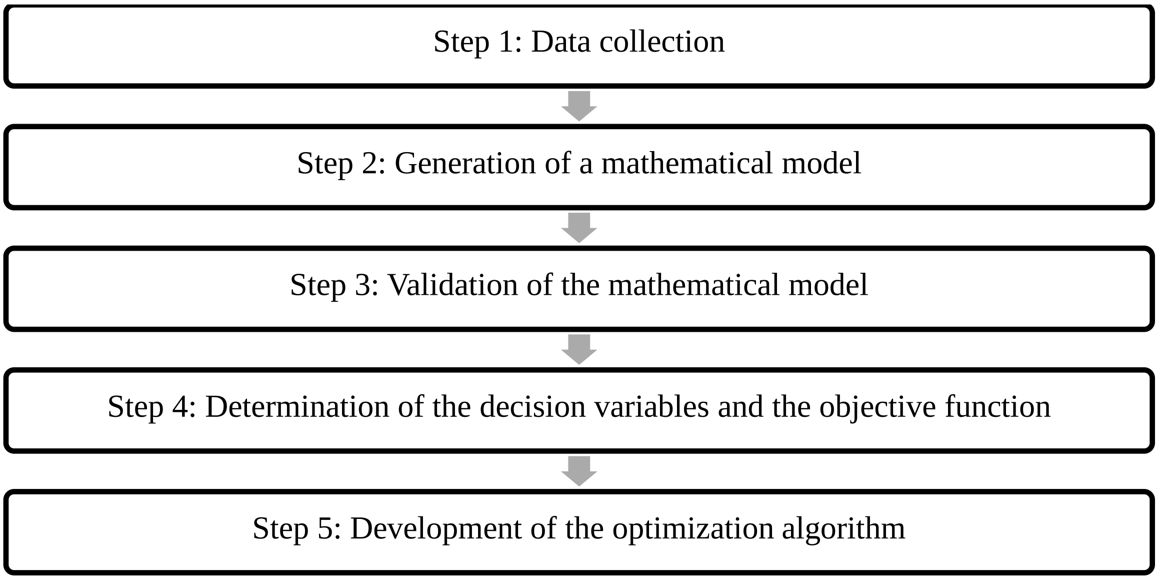

Figure 3.1 Methodology.

3.1 Data collection

The necessary data of isoflavone extraction process was collected in this step such as critical properties of carbon dioxide and methanol aqueous, isoflavone composition, modifier content, solid particle size, and solvents flow rate. Table 3.1 shows the critical properties of the chemical species present in the extraction process, and Table 3.2 shows the parameters and characteristics of isoflavone extraction process.

Table 3.1 Critical properties (Francis, 1954).

Fluid	Critical Temperature Tc (K)	Critical Pressure Pc (bar)	Critical Volume Vc (cm^3/mol)
CO_2	304.12	73.7	94.07
Water	647.1	220.6	55.95
Methanol	512.6	80.9	118.0
Isoflavone	1496.91	40.356	778.0

Table 3.2 Parameters and characteristics of isoflavone extraction process (Zuo et al, 2008).

Characteristics of the raw material	**Value**
Total isoflavone	2628.4 ± 51.6 µg/g
Daidzin	1445.9 ± 48.4 µg/g
Daidzein	459.8 ± 39.9 µg/g
Genistin	326.5 ± 25.8 µg/g
Genistein	396.1 ± 10.2 µg/g
Solvent-cosolvent concentration	
Carbon dioxide	92.2 wt%
Methanol and water (80:20, v/v)	7.8 wt%
Operating condition	
Soybean meal weight	100 g
SCCO$_2$ flow rate	5.88 kg/h
Modifier flow rate	0.6 L/h
Extraction time	210 min
Characteristics of the extractor	
Length	0.725 m
Diameter	0.042 m
Volume	1 L

3.2 Generation of a mathematical model

In order to solve the partial differential equations (PDEs) and the boundary conditions of the mass balance equation, the finite difference is applied to expand the PDEs as follows:

For mass balance in fluid phase (Equation 2.51)

$$\frac{dy(i)}{d\tau} - \frac{1}{Pe_b}\frac{y(i+1)-2y(i)+y(i-1)}{(\Delta z)^2} + \frac{y(i)-y(i-1)}{\Delta z} + \frac{1-\varepsilon}{\varepsilon}3\frac{k_f}{v}\frac{L}{R_p}\left(y(i) - \frac{y(h+i)}{k}\right) = 0 \qquad (3.1)$$

Or

$$\frac{dy(i)}{dt} = \frac{u}{L}\left(\frac{1}{Pe_b}\frac{y(i+1)-2y(i)+y(i-1)}{(\Delta z)^2} - \frac{y(i)-y(i-1)}{\Delta z} - \frac{1-\varepsilon}{\varepsilon}3\frac{k_f}{v}\frac{L}{R_p}\left(y(i) - \frac{y(h+i)}{k}\right)\right) \qquad (3.2)$$

For i = 2, 3, … ,h-1

The boundary conditions for this equation are (Equation 2.52 - 2.55):

At $z = 0^-$; $C = 0$; $(y(1))^- = 0$ (3.3)

At $z = 0^+$; $\frac{\partial C}{\partial z} = Pe_b(C - 0)$; $\frac{y(2)-y(1)}{\Delta z} = Pe_b y(1)$ (3.4)

; $(y(1))^+ = \frac{1}{1+\Delta z Pe_b} y(2)$

At z = 1 ; $\frac{\partial C}{\partial z} = 0$; $\frac{y(h)-y(h-1)}{\Delta z} = 0$ (3.5)

; $y(h) = y(h-1)$

At τ = 0 ; C = 0 ; $y(i) = 0$ For i = 1, 2, … , h (3.6)

For mass balance in solid phase (Equation 2.56)

$$\frac{\mathrm{dy(i+h)}}{\mathrm{d\tau}} = -3\frac{\mathrm{k_f}}{\mathrm{v}}\frac{\mathrm{L}}{\mathrm{R_p}}\left(\frac{\mathrm{y(i+h)}}{\mathrm{k}} - \mathrm{y(i)}\right) \quad (3.7)$$

Or

$$\frac{\mathrm{dy(i+h)}}{\mathrm{dt}} = \frac{\mathrm{u}}{\mathrm{L}}\left(-3\frac{\mathrm{k_f}}{\mathrm{v}}\frac{\mathrm{L}}{\mathrm{R_p}}\left(\frac{\mathrm{y(i+h)}}{\mathrm{k}} - \mathrm{y(i)}\right)\right) \quad (3.8)$$

For i = 1, 2,…, h

The initial condition for this equation is (Equation 2.57):

At τ = 0 → $q = q_0$; $(y(i+h)) = q_0$ For i = 1, 2,3 … h (3.9)

For yield calculation (Equation 2.59)

$$\frac{\mathrm{dy(h+h\times m+1)}}{\mathrm{d\tau}} = \frac{\mathrm{LA\varepsilon}}{\mathrm{m_0}}\mathrm{y(h)} \times 100 \quad (3.10)$$

Or

$$\frac{\mathrm{dy(h+h\times m+1)}}{\mathrm{dt}} = \frac{\mathrm{uA\varepsilon y(h)}}{\mathrm{m_0}} \times 100 \quad (3.11)$$

The initial condition for this equation is (Equation 2.60):

At τ = 0 → y(h + h x m + 1) = 0 (3.12)

The length of the extractor was divided into ‘h’ sections as shown in Figure 3.2.

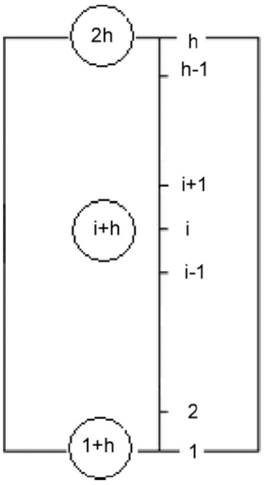

Figure 3.2 Schematic of increments in both fluid and solid phases for small particles (Melerles et al., 2009).

From the Figure 3.2, y(i) and y(i+h) denoted the solute concentration of a point in fluid phase and in a small particle, respectively where the distance of this points from inlet place of fluid is (i-1)LΔz.

3.3 Validation of the mathematical model

In this step, the proposed mathematical model is compared with experimental data from Zuo et al. (2008) in order to ensure that the mathematical model can predict the performance of the isoflavone extraction process accurately.

One of the parameters used for tuning the results from mathematical model to fit the experimental data is the distribution coefficient (K). The value of K can be determined by minimizing the sum of the squares of the difference between the experimental extraction yield and the predicted extraction yield. The criterion is described in the following equation:

$$Objective = \sum(F_{model} - F_{exp})^2 \tag{3.13}$$

The algorithm for the distribution coefficient calculations is shown in Figure 3.3. In this case a value for K was guessed, then solved in the mathematical model, and was used to calculate the objective function in the minimization. The optimization will stop when the objective function reaches to a minimum value; otherwise the procedure continues.

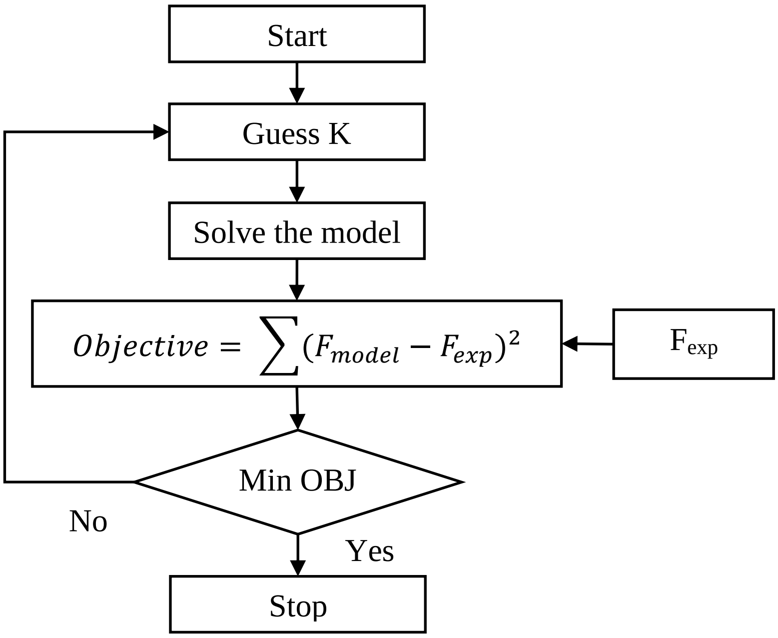

Figure 3.3 Procedure of the distribution coefficient estimation (Melreles et al., 2009).

3.4 Determination of decision variables and the objective function

The decision variables of this process are temperature, pressure and extraction time. Because this process involves supercritical extraction, the minimum temperature and pressure for the process to operate in should be the critical point of the solvents, namely carbon dioxide and aqueous methanol. As the results, the range of temperature and pressure is 40-70 ^{o}C and 30-60 MPa, respectively based on the experimental data.

The objective function of this study is profitability which is more comprehensive than the cumulative isoflavone production rate. The profitability of the extraction process consists of four parts as shown in the following equations (Zahedi et al., 2010):

$$\text{Profit} = C_1 - C_2 - C_3 - C_4 \tag{3.14}$$

$$C_1 = \text{yield x total isoflavone x Cost1} \tag{3.15}$$

$$C_2 = P_{wc} \text{ x time x Cost2} \tag{3.16}$$

$$C_3 = \text{Cost3 x } Q_m \text{ x time} \tag{3.17}$$

$$C_4 = \text{Cost4 x wt.} \tag{3.18}$$

Where Cost1 is the isoflavone price which was found to be 228.3 \$/g. P_{wc} is the real compressor work that provides the supercritical fluid and circulates it.

$$P_{WC} = \frac{1}{440}\frac{\Upsilon}{\Upsilon-1}\sqrt{z_1 z_2} N_s P_1 V_1 \left[\left[\frac{P_2}{P_1}\right]^{\frac{\Upsilon-1}{\Upsilon N_s}} - 1\right] \qquad (3.19)$$

Cost2 is the electricity price, (i.e. in Ontario, Canada) which is 11.9 cent/kWh. Cost3 is the price of solvents; the price of liquid CO_2 was found to be 0.3 $/kg. Cost4 is the price of soybean meal at 0.512 $/kg (USDA Market News, 2013).

3.5 Development of an optimization algorithm

After the decision variables and the objective function have been identified, an optimization algorithm was developed to determine the optimum operating condition that provides maximum profitability.

A GA program was used in this study. This method starts with a randomly generated initial population whose individual fitness (in this case, the fitness is the objective function that gives the profit) is calculated. Solutions in the population with smaller fitness are removed from the population. This elimination process is used to ensure that the general fitness of the population keeps increasing. Reproduction is used to make a new generation or “offspring” in which two individuals selected from parent population are made to crossover, and one individual is selected for mutation. The reproductive method is used to ensure that it can produce diverse solutions. The process is repeated until the termination condition is satisfied as shown in Figure 3.4

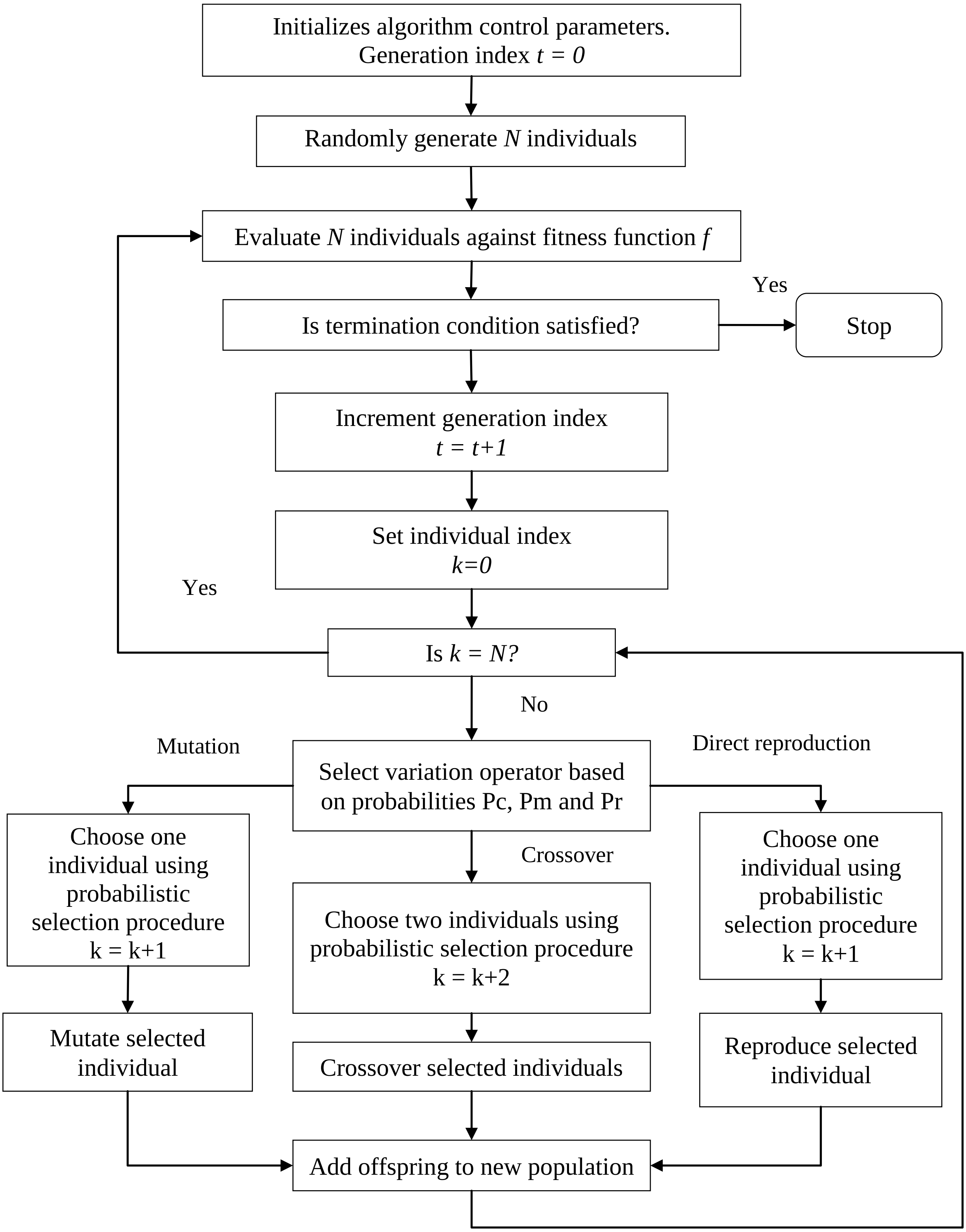

Figure 3.4 Flow chart of GA optimization (Zahedi et al., 2010).

CHAPTER 4 RESULTS AND DISCUSSION

This chapter shows the mathematical model used to predict the supercritical extraction process of isoflavone. The simulation results from the mathematical model which are the isoflavone solubility and the model parameters will be presented in this chapter. In addition, the effect of the operating conditions on the isoflavone extraction yield will be validated by comparing the calculated results with the experimental results (Zuo et al., 2008). Moreover, the optimization result from the genetic algorithm will be presented in this chapter as well.

4.1 Mathematical model

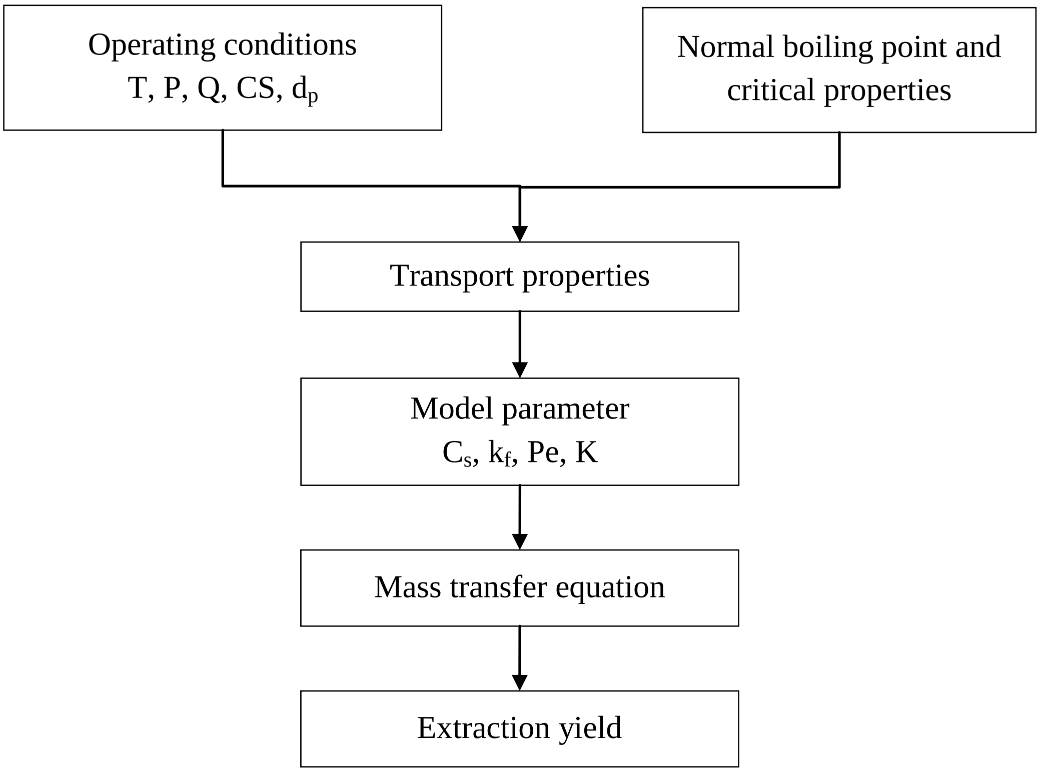

Figure 4.1 Summary of the mathematical model.

The proposed mathematical model is shown in Figure 4.1. The mathematical model begins with gathering information regarding the operating condition of isoflavone extraction process such as the operating temperature (T), the operating pressure (P), the solvent flow rate (Q), the ratio of solvent and co-solvent concentration (CS), and the particle diameter (d_p), including the normal boiling point and critical properties of isoflavone and solvents.

Next, transport properties, such as the density, the viscosity, the binary diffusion coefficient (D_{AB}), the axial dispersion coefficient (D_L) the Reynolds number (Re), the Schmidt number (Sc) and the Sherwood number (Sh), were estimated from the auxiliary equations. The density of solvents was estimated by the equation of state which was divided into polar and non-polar solvent. The density of polar solvent (aqueous ethanol) was estimated from Peng-Robinson equation of state, while the density of non-polar solvent (carbon dioxide) was estimated from Lee-Kesler-Plocker equation of state. Similarly, the viscosity of the solvents was also estimated based on their polarity by using the correlations from American Petroleum Institute-Technical Data Book (API-TDB). Then, the Kay's mixing rules were used to estimate the mixed property of polar and non-polar properties. The other transport properties, namely the binary diffusion coefficient (D_{AB}), the Reynolds number (Re), the Sherwood number (Sh), the Schmidt number (Sc), and the axial dispersion coefficient (D_L), were estimated using existing correlations as presented in Chapter 2.

After the transport properties are obtained, the model parameters, namely the solubility (C_s), the Peclet number (Pe), the film mass transfer coefficient (k_f), and the distribution coefficient (K), were estimated from existing correlations. The solubility of isoflavone was estimated by the Mohsen-Nia-Moddaress-Mansoori equation of state (MMM-EOS) based on the method of the equilibrium fugacity. The solubility calculation was shown in Figure 4.2. The Peclect number and the film mass transfer coefficient were estimated from the available correlations as mentioned in Chapter 2. However, the distribution coefficient is a constant value which is unique to a specific extraction condition and has no correlation. Therefore, this parameter was estimated via optimization by minimizing the sum of the squares of the difference between the experimental extraction yield and the predicted extraction yield from the mathematical model.

Finally, a partial differential equation based on mass conservation was used to estimate the yield of isoflavone. To simplify this equation, finite difference was applied to this partial differential equation. The yield of isoflavone was estimated from the cumulative amount of isoflavone in the solvent at the time.

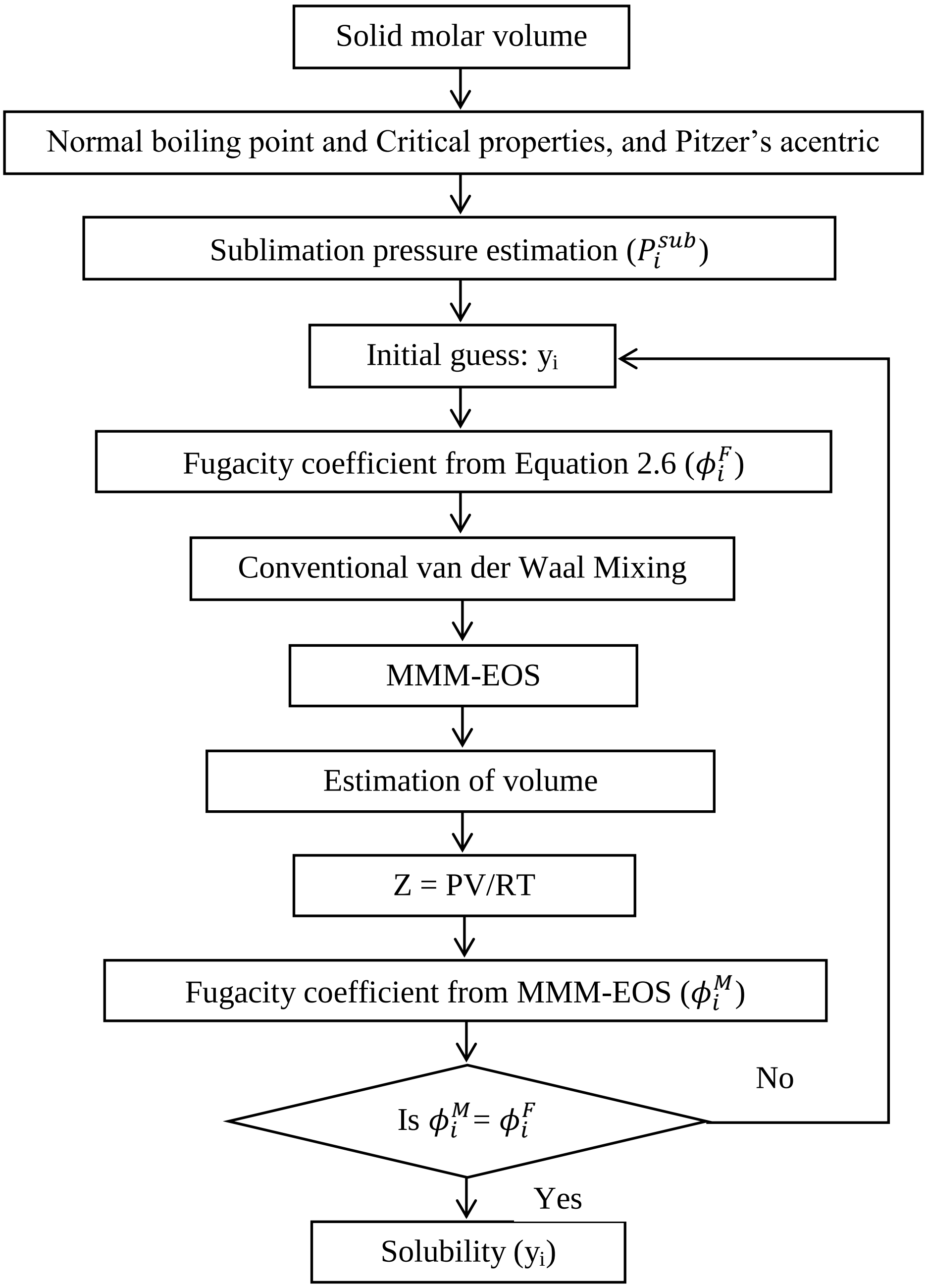

Figure 4.2 Solubility calculation flow chart.

4.2 Model parameters

The mathematical model requires four parameters, namely the solubility (C_s), the Peclet number (Pe), the film mass transfer coefficient (k_f), and the distribution coefficient, which were estimated from its transport properties. The model used 100 g. of soybean meal with 1 liter of extractor. The ratio of carbon dioxide and aqueous methanol (80 %v/v) is 92.2:7.8 wt.%. The transport properties and the model parameters as a function of the operating condition are shown in Table 4.1.

Table 4.1 Model parameters.

P (MPa)	**T (K)**	**Q (kg/h)**	**d_p (mm)**	**Density (kg/m^3)**	**Viscosity (x10^4) (kg/ms)**	**D_{AB} (x10^9) (m^2/s)**	**D_L (x10^5) (m^2/s)**	**Re**	**Sc**	**Sh**	**Pe**	**Solubility (g/g)**	**k_f (x10^5) (m/s)**	**K**
30	313.15	5.88	0.68	884.45	2.02	8.223	1.18	5.87	27.707	4.943	136	0.0689	5.977	250.15
40	313.15	5.88	0.68	922.64	2.23	7.570	1.15	5.31	31.921	4.763	134	0.0777	5.302	231.12
50	313.15	5.88	0.68	951.54	2.41	7.110	1.13	4.91	35.596	4.628	132	0.0852	4.839	186.24
60	313.15	5.88	0.68	975.08	2.57	6.756	1.11	4.60	39.056	4.520	131	0.0917	4.491	177.34
50	323.15	5.88	0.68	926.66	2.26	7.623	1.14	5.02	32.029	4.710	135	0.0857	5.280	201.36
50	333.15	5.88	0.68	901.51	2.12	8.174	1.15	5.57	28.832	4.793	137	0.0864	5.762	246.03
50	343.15	5.88	0.68	876.08	2.00	8.766	1.16	5.93	25.999	4.878	139	0.0873	6.288	270.03
50	313.15	3.92	0.68	951.54	2.41	7.110	7.83	3.97	35.596	3.657	147	0.0852	3.854	152.39
50	313.15	7.84	0.68	951.54	2.41	7.110	2.06	7.40	35.596	6.502	112	0.0852	6.798	187.19
50	313.15	9.80	0.68	951.54	2.41	7.110	2.81	9.25	35.596	7.824	102	0.0852	8.182	207.91
50	313.15	5.88	0.48	951.54	2.41	7.110	8.48	3.92	35.596	3.835	203	0.0852	5.681	215.27
50	313.15	5.88	1.19	951.54	2.41	7.110	3.00	9.71	35.596	8.148	57	0.0852	4.868	241.94

4.3 Model validation: Comparison of isoflavone yield

The mathematical model was validated by comparing the yield of isoflavone with the experimental data from Zuo et al. in 2008. The temperature, the pressure, the solvent flow rate, and the solid particle size of soybean meal were varied at different operating conditions. The pilot plant scale of the isoflavone extractor is 1 liter. The soybean meal used for the extraction is 100 gram. The yield of isoflavone from the experimental data was collected every 30 minutes, and the total extraction time of the experimental data is 210 minutes. The results of cumulative yield of isoflavone from the mathematical model and experimental results within 210 minutes are shown in Figures 4.3-4.6.

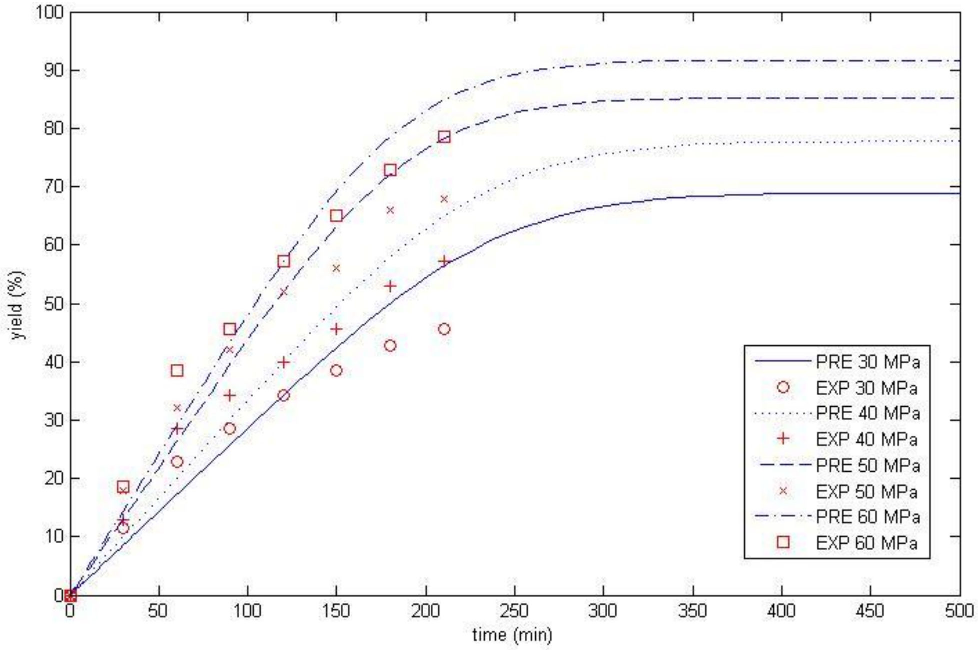

Figure 4.3 Comparison of model results with experimental data at T = 40 °C, Q = 5.88 kg/h, CS = 7.8 wt%, and dp = 0.68 mm.

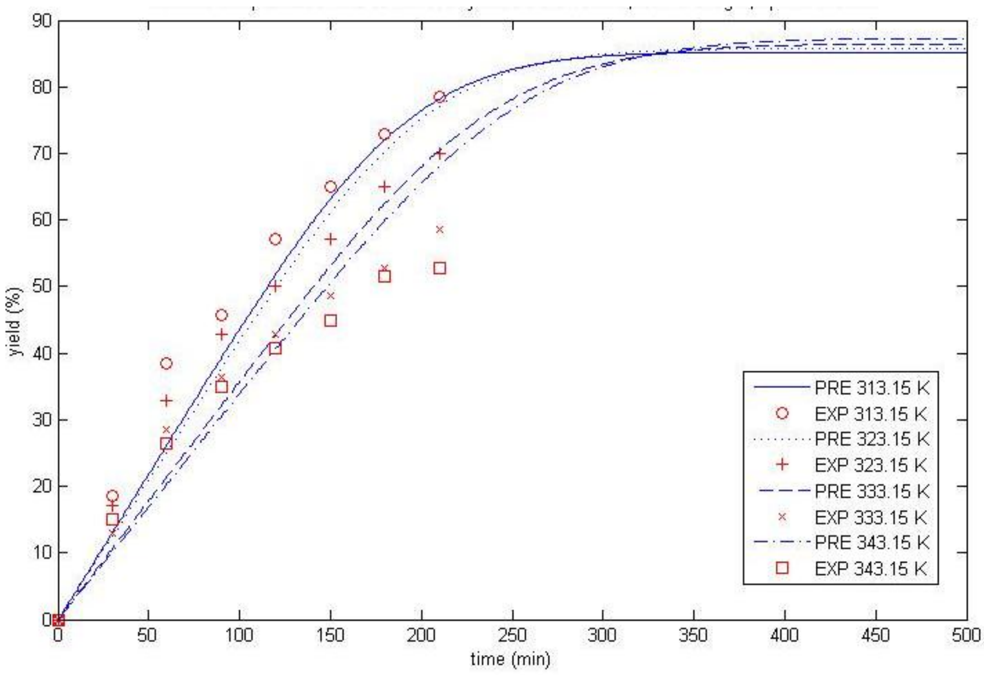

Figure 4.4 Comparison of model results with experimental data at P = 50 MPa, Q = 5.88 kg/h, CS = 7.8 wt%, and dp = 0.68 mm.

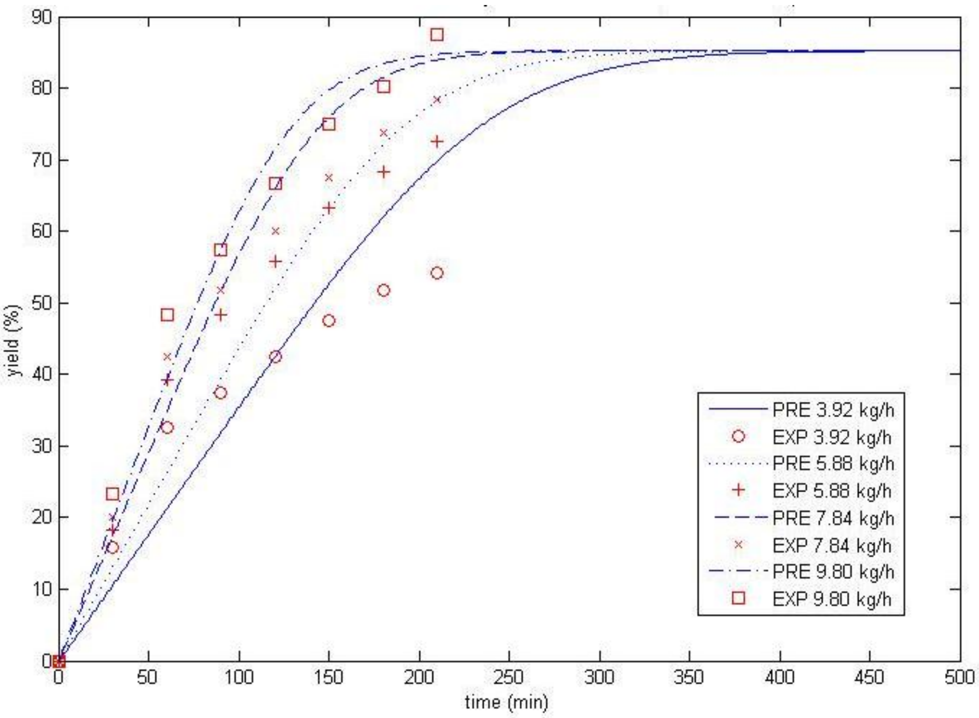

Figure 4.5 Comparison of model results with experimental data at P = 50 MPa, T = 40 °C, CS = 7.8 wt%, and dp = 0.68 mm.

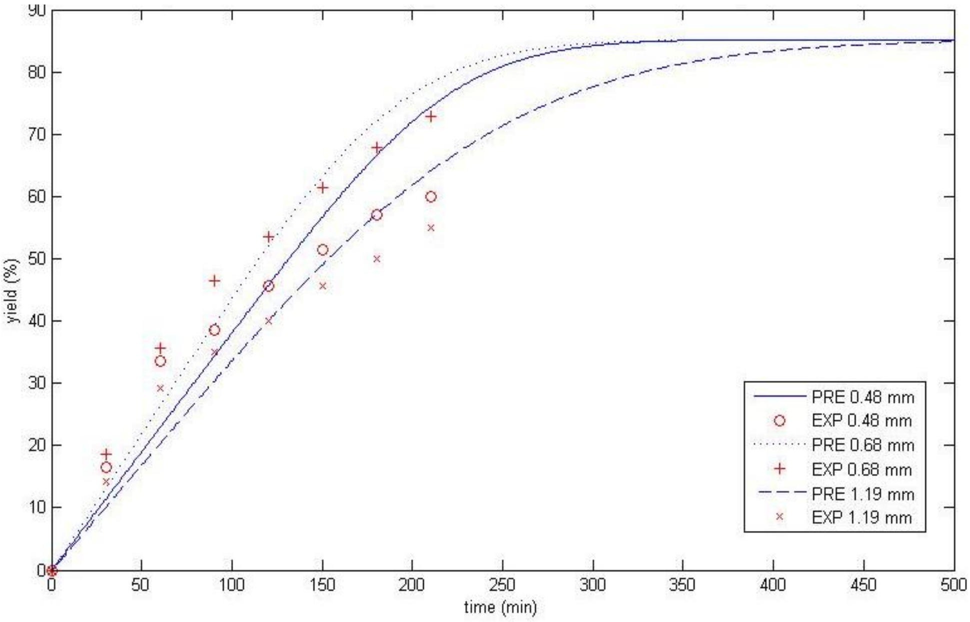

Figure 4.6 Comparison of model results with experimental data at P = 50 MPa, T = 40 °C, CS = 7.8 wt%, and Q = 5.88 kg/h.

The average absolute relative deviation (AARD) was used to present the different values of the cumulative yield between the mathematical model and the experimental data. This mathematical model can be used to predict the yield of isoflavone with a maximum AARD of 17.79. The AARD of each operating condition is shown in Table 4.2.

Table 4.2 The error between experimental data and mathematical model results.

Pressure (MPa)	Temperature (K)	Solvent flow rate (kg/h)	Particle diameter (mm)	AARD
30	313.15	5.88	0.68	13.74
40	313.15	5.88	0.68	11.94
50	313.15	5.88	0.68	11.03
60	313.15	5.88	0.68	9.28
50	323.15	5.88	0.68	10.95
50	333.15	5.88	0.68	12.66
50	343.15	5.88	0.68	15.73
50	313.15	3.92	0.68	17.79
50	313.15	7.84	0.68	8.89
50	313.15	9.80	0.68	6.87
50	313.15	5.88	0.48	15.51
50	313.15	5.88	1.19	13.90

4.4 Effect of operating parameter on isoflavone yield

In order to study the effect of the operating condition on the yield of isoflavone, the temperature, the pressure, the solvent flow rate, and the solid particle size of soybean meal were varied. The pilot plant scale of the isoflavone extractor is 1 liter and the amount of soybean meal used for the extraction is 100 gram. The effect of the operating parameters on the isoflavone yield was presented below.

4.4.1 Effect of pressure

Figure 4.7 shows the effect of pressure on the cumulative yield. The pressure has a direct effect on the cumulative yield. After 300 minutes of extraction time, the cumulative yield of isoflavone reaches a plateau.

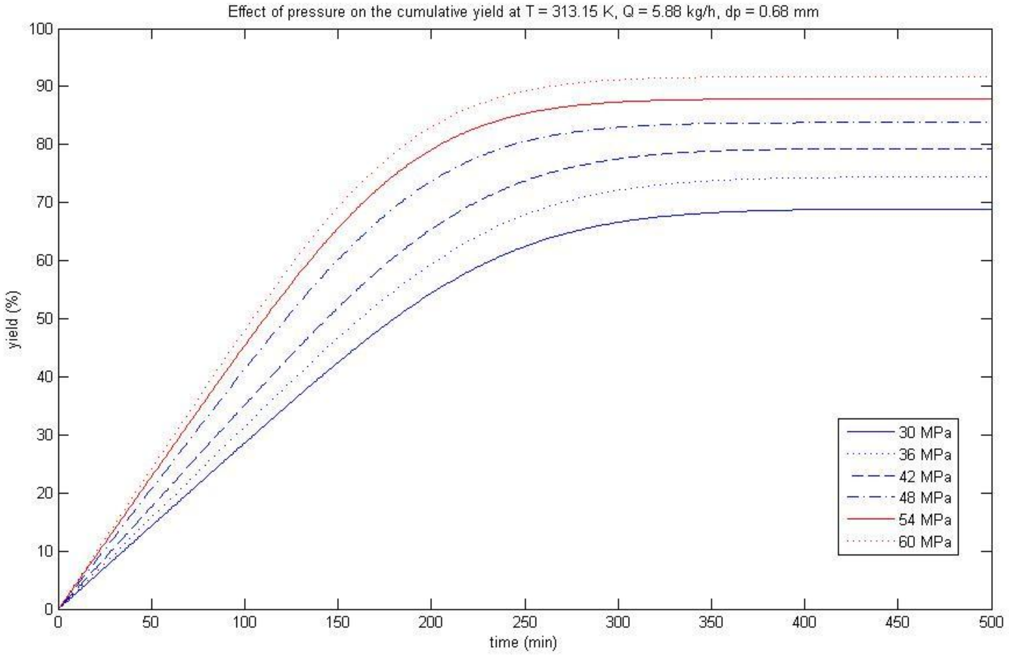

Figure 4.7 Effect of pressure on the cumulative yield at T = 40 ^{o}C, Q = 5.88 kg/h, CS = 7.8 wt%, and dp = 0.68 mm.

The effect of pressure on the solubility and transport properties is presented in Figures 4.8-4.9. The increase of pressure contributes to the decrease of the diffusion coefficient and mass transfer coefficient which gives a reverse effect on the cumulative yield. On the other hand, the pressure has a direct effect on the fluid density, resulting in higher solubility of isoflavone. The effect of the solubility was significant to the cumulative yield when compared with the internal and external mass transfer resistance from the diffusion coefficient and mass transfer coefficient. Therefore, the pressure has an overall positive effect on the cumulative yield.

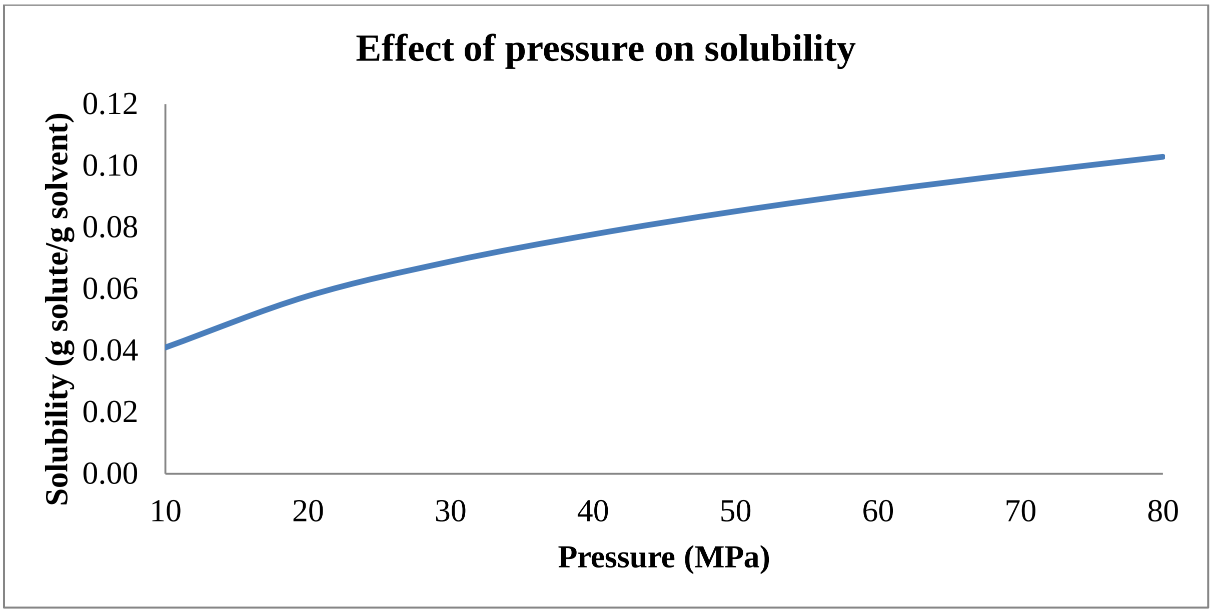

Figure 4.8 Effect of pressure on solubility of isoflavone in soybean at T = 313.15 K, and CS = 7.8 wt.%.

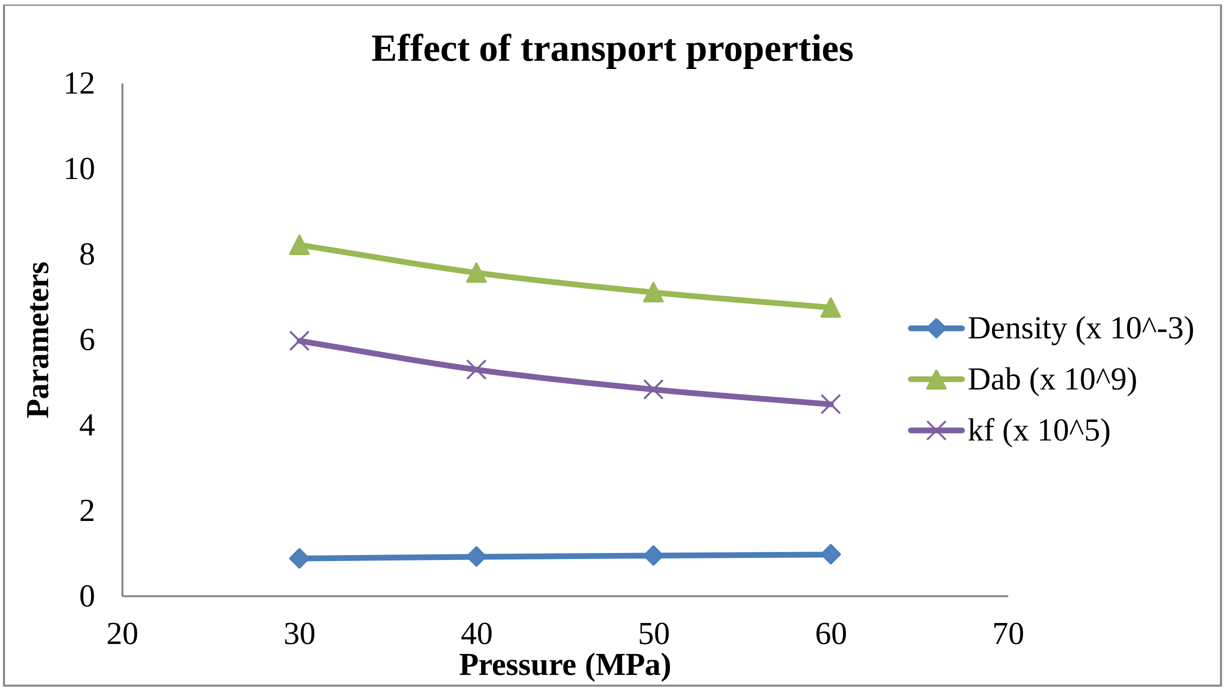

Figure 4.9 Effect of pressure on the transport properties of isoflavone in soybean at T = 313.15 K, Q = 5.88 kg/h, CS = 7.8 wt.%, and dp = 0.68 mm.

4.4.2 Effect of temperature

Figure 4.10 shows the effect of temperature on the cumulative yield of isoflavone. It is interesting to note that the temperature has a reverse effect on the cumulative of isoflavone. When the extraction time was over 325 minutes, the cumulative yield of isoflavone becomes constant.

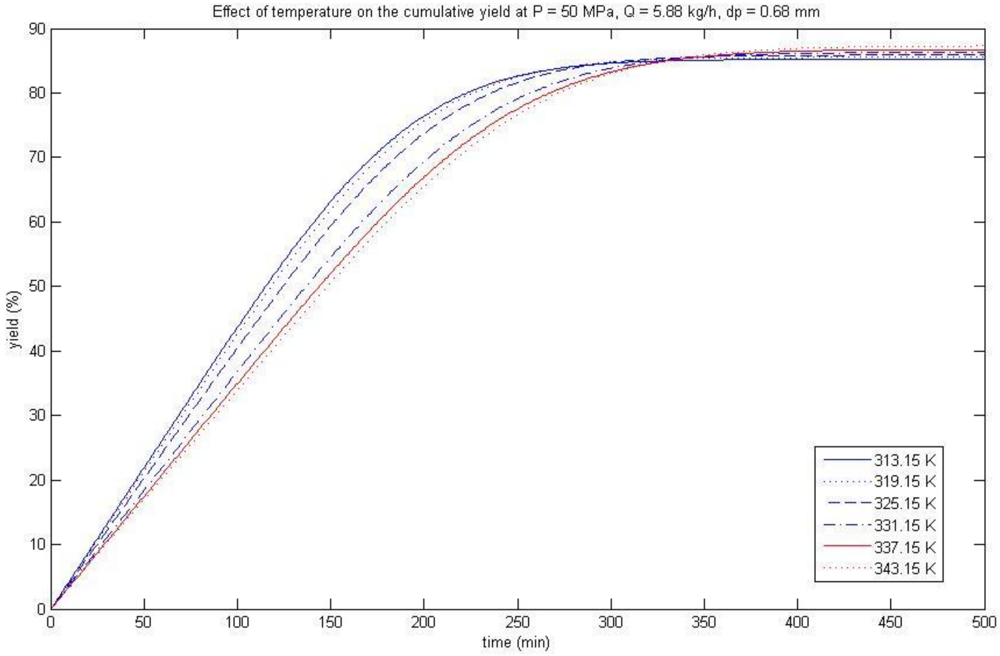

Figure 4.10 Effect of temperature on the cumulative yield at P = 50 MPa, Q = 5.88 kg/h, CS = 7.8 wt%, and dp = 0.68 mm.

The effect of temperature on the solubility and transport properties is shown in Figures 4.11-4.12. The increase of temperature tends to decrease the fluid density which results in the reduction in the extraction yield. On the other hand, the increase in temperature enhances the increase of isoflavone solubility. Moreover, the temperature has a direct effect on the binary diffusion coefficient and the mass transfer coefficient which means that the internal and external mass transfer resistances are decreased. However, the effect of density is more significant than the mass transfer resistance and solubility; therefore, the temperature has an overall reverse effect on the isoflavone yield.

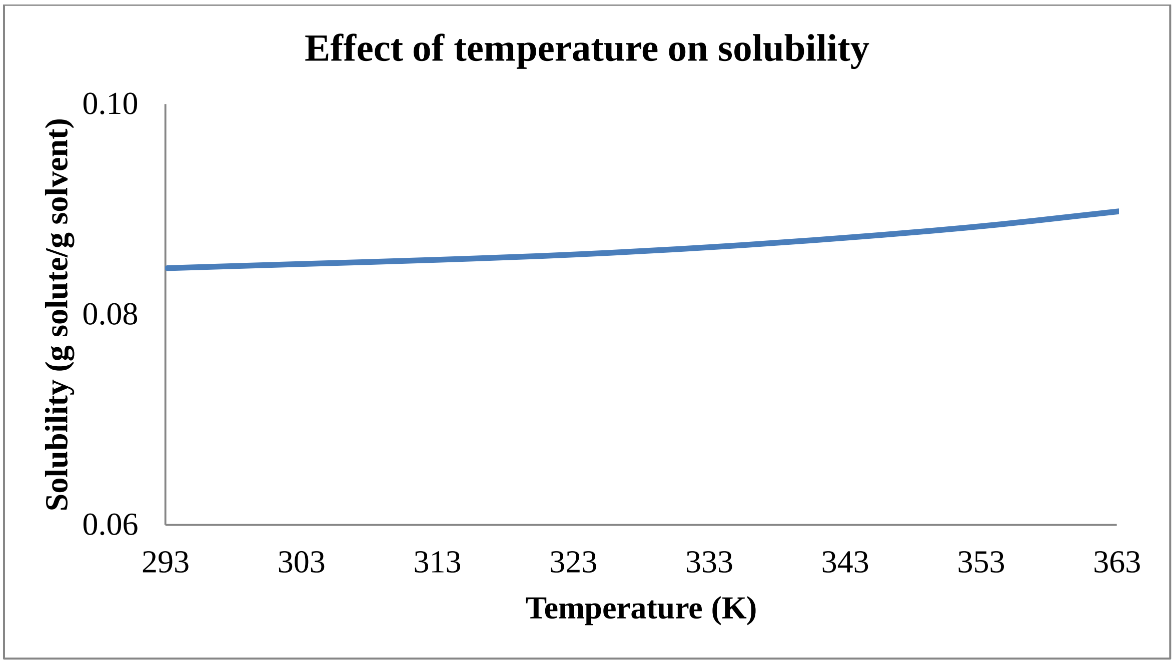

Figure 4.11 Effect of temperature on solubility of isoflavone in soybean at P = 50 MPa, and CS = 7.8 wt.%.

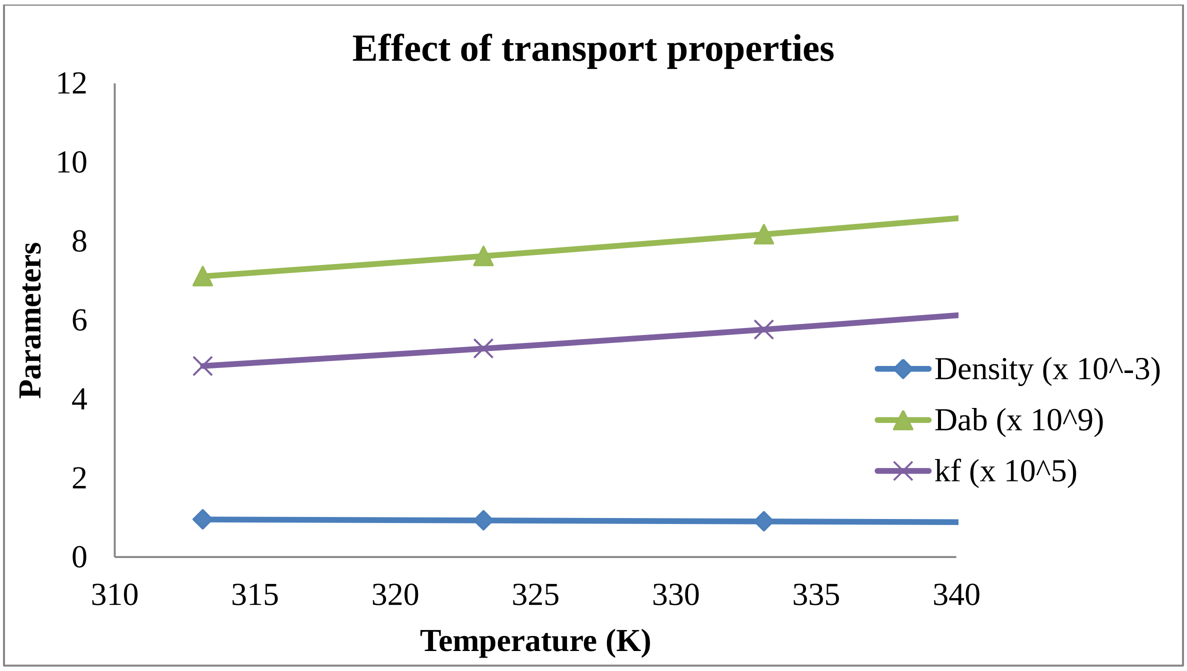

Figure 4.12 Effect of temperature on the transport properties of isoflavone in soybean at T = 313.15 K, Q = 5.88 kg/h, CS = 7.8 wt.%, and dp = 0.68 mm.

4.4.3 Effect of carbon dioxide flow rate

Figure 4.13 shows the effect of carbon dioxide flow rate on the cumulative yield of isoflavone. The flow rate of carbon dioxide has a direct effect on the cumulative yield of isoflavone. The cumulative yield of isoflavone becomes constant after 350 minutes of extraction time.

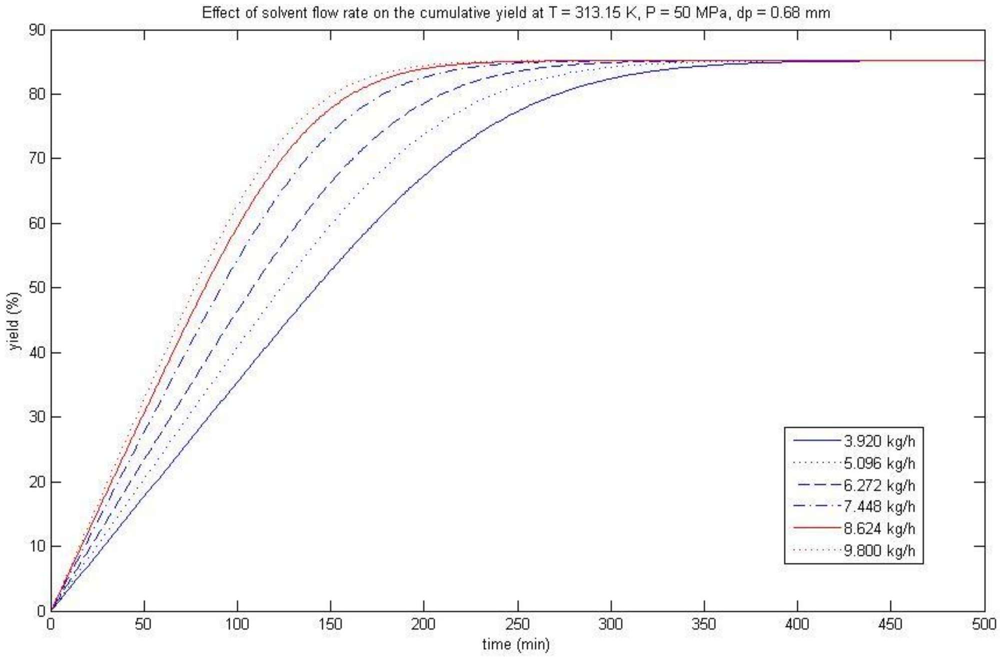

Figure 4.13 Effect of carbon dioxide flow rate on the cumulative yield at P = 50 MPa, T = 40 ^{o}C, CS = 7.8 wt%, and dp = 0.68 mm.

The effect of carbon dioxide flow rate on the transport properties is shown in Figure 4.14. The increase of carbon dioxide flow rate results in an increase of the mass transfer coefficient, the Reynolds number, and the axial dispersion coefficient, while the other parameters remain constant. From this viewpoint, the increase of carbon dioxide flow rate has an overall direct effect on the isoflavone yield due to the decrease of mass transfer resistance and the increase of mass transfer rate from axial dispersion.

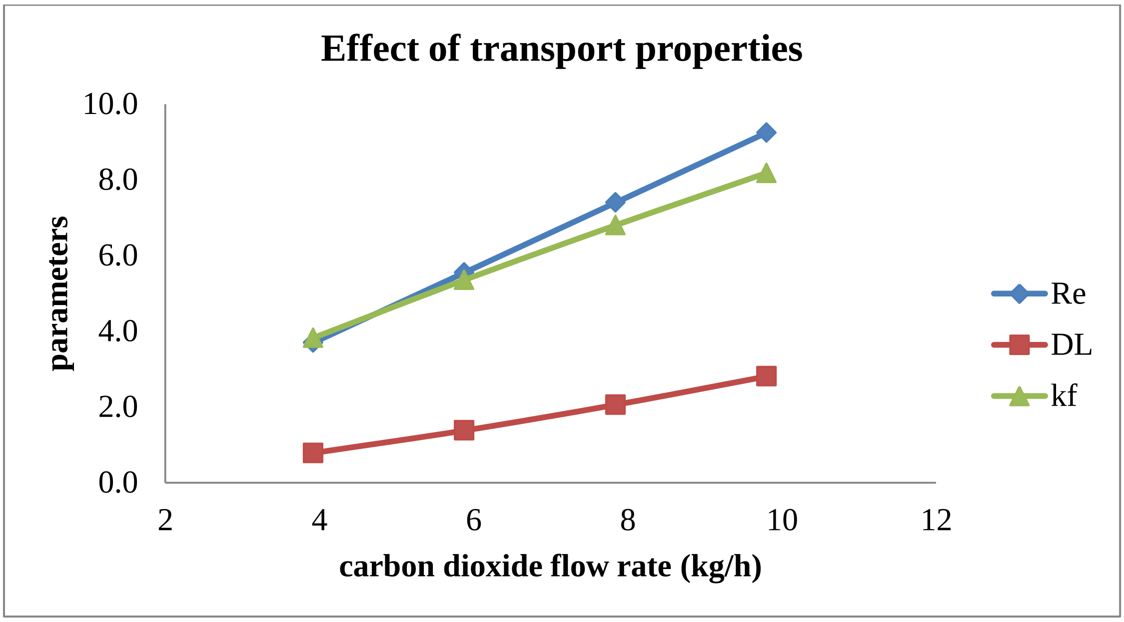

Figure 4.14 Effect of carbon dioxide flow rate on the transport properties of isoflavone in soybean at P = 50 MPa, T = 313.15 K, CS = 7.8 wt.%, and dp = 0.68 mm.

4.4.4 Effect of particle diameter

Figure 4.15 shows the effect of particle diameter on the cumulative yield of isoflavone. The decrease of solid particle size results in an increase of the surface area, resulting in a decrease of mass transfer resistance. However, the very small particle causes a channeling problem in the extractor. Therefore, the suitable particle size with the solvent flow rate should be considered. From this viewpoint, the suitable particle size at the solvent flow rate of 5.88 kg/h is 0.68 mm because of maximum isoflavone extraction.

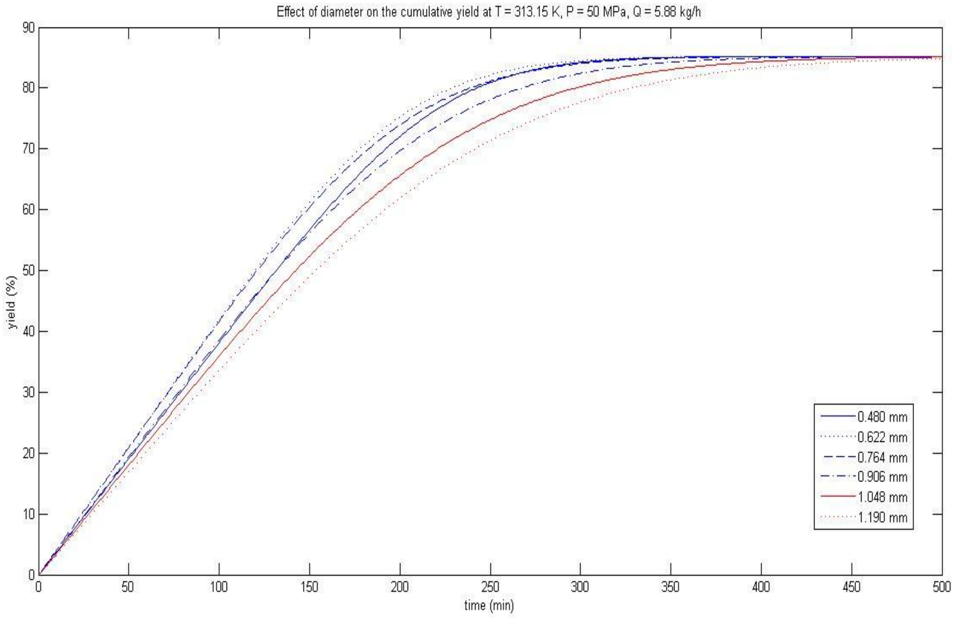

Figure 4.15 Effect of particle diameter on the cumulative yield at P = 50 MPa, T = 40 ^{o}C, CS = 7.8 wt%, and Q = 5.88 kg/h.

4.5 Effect of operating parameter on the profitability

The profitability of this process was calculated using Equation 3.1, which consists of the price of isoflavone, the cost of the electricity from the compressor, and the cost from the solvent and the soybean meal. The operating parameters, namely the pressure, the temperature, the solvent flow rate, and the size of solid particle diameter, were varied at six different values. The size of the extractor in this process is 1 liter. The soybean meal used in this process is 100 grams.

4.5.1 Effect of pressure on the profitability

The effect of pressure on the profitability provides the same trend as the effect of pressure on the isoflavone yield. The increase of pressure resulted in an increase of isoflavone extracts which caused higher isoflavone product cost, while the solvent cost and raw material cost were fixed at constant values. However, after 250 minutes of extraction time, the increase of profitability started to decrease because of the isoflavone extraction yield was decreasing. Therefore, the maximum profit should be obtained at the highest pressure and 250 minutes of extraction time. The effect of pressure on the profitability is shown in Figure 4.16.

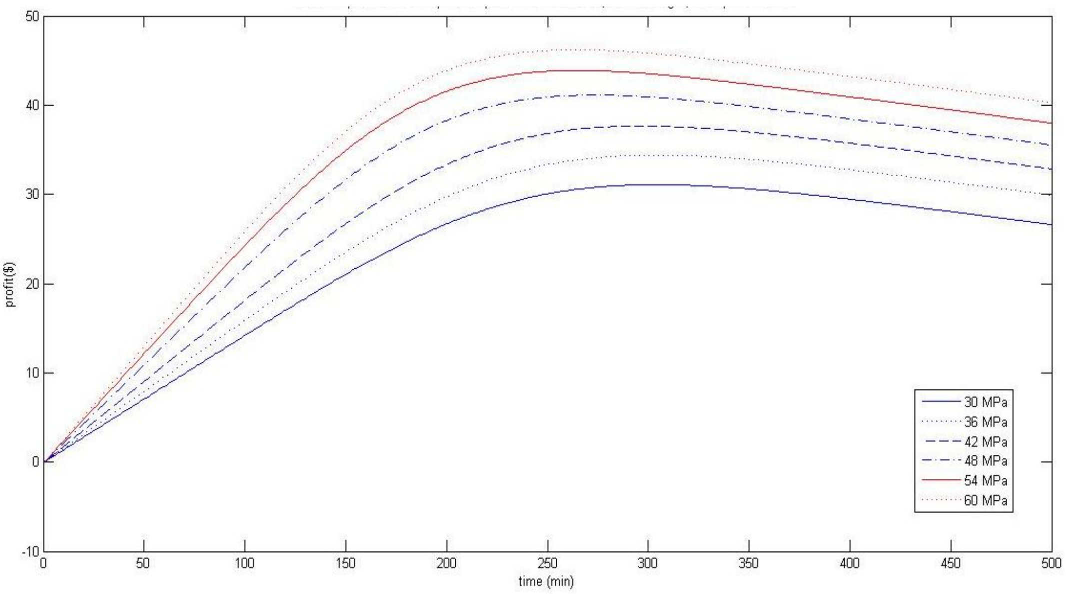

Figure 4.16 Effect of pressure on the profitability at T = 40 °C, Q = 5.88 kg/h, CS = 7.8 wt%, and dp = 0.68 mm.

4.5.2 Effect of temperature on the profitability

The effect of temperature on the profitability provides the same trend as the effect of temperature on the isoflavone yield. The decrease of temperature caused an increase of isoflavone extracts which resulted in higher isoflavone product cost, while the solvent cost and raw material cost were set as constant value. Thus, a lower temperature should be used to obtain the maximum profitability. However, after 300 minutes of extraction time, the effect of temperature was reversed; therefore, the higher temperature should be used to improve the profit. The effect of temperature on the profitability is shown in Figure 4.17.

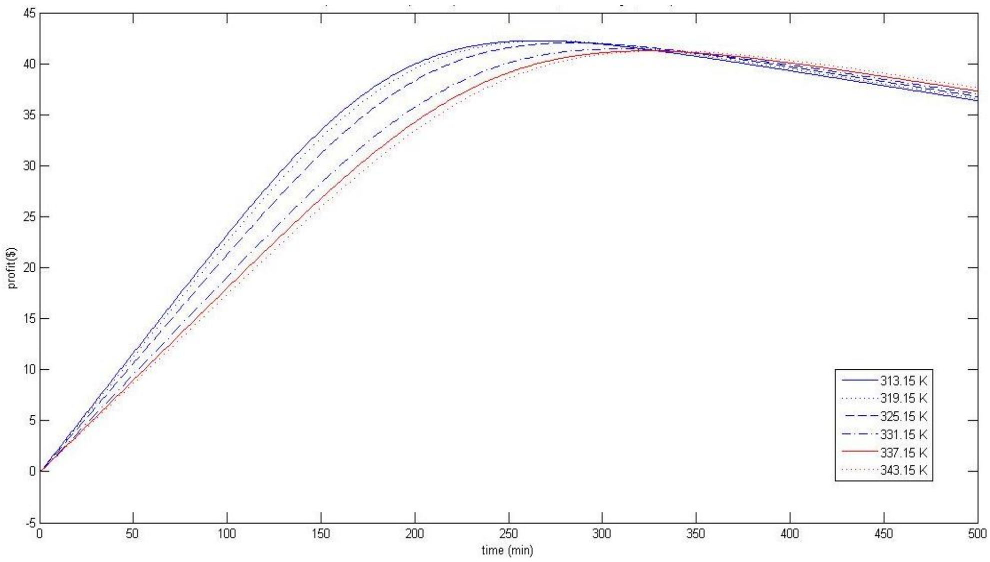

Figure 4.17 Effect of temperature on the profitability at P = 50 MPa, Q = 5.88 kg/h, CS = 7.8 wt%, and dp = 0.68 mm.

4.5.3 Effect of carbon dioxide flow rate on the profitability

The effect of carbon dioxide flow rate on the profitability is interesting. Before 200 minutes of the extraction time, the effect of carbon dioxide flow rate provides the same trend as the effect of carbon dioxide flow rate on the isoflavone yield. Therefore, a higher carbon dioxide flow rate should be used to obtain the maximum profitability. However, after 200 minutes of the extraction time, the effect of carbon dioxide flow rate was reversed due to the decrease of isoflavone yield with time. Therefore, a lower carbon dioxide flow rate should be used to obtain the maximum profitability. The effect of carbon dioxide flow rate on the profitability is shown in Figure 4.18.

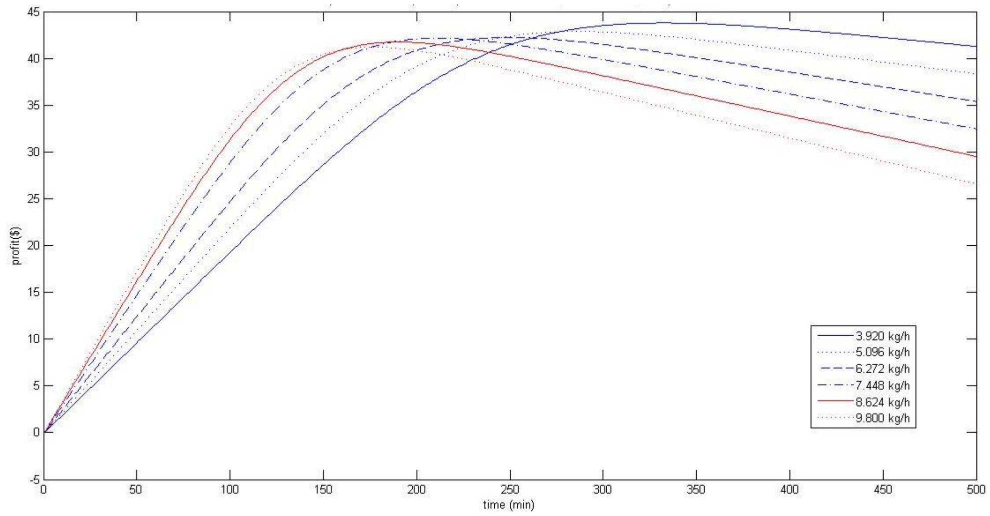

Figure 4.18 Effect of carbon dioxide flow rate on the profitability at P = 50 MPa, T = 40 ^{o}C, CS = 7.8 wt%, and dp = 0.68 mm.

4.5.4 Effect of particle diameter on the profitability

The effect of particle diameter on the profitability provides the same trend as the effect of particle diameter on the isoflavone yield. Normally, a smaller particle diameter provides higher profitability. However, a very small particle diameter causes a channeling problem. Therefore, the optimum particle diameter within the solvent flow rate of 5.88 kg/h is 0.68 mm which agrees with the experimental data. The effect of particle diameter on the profitability is shown in Figure 4.19.

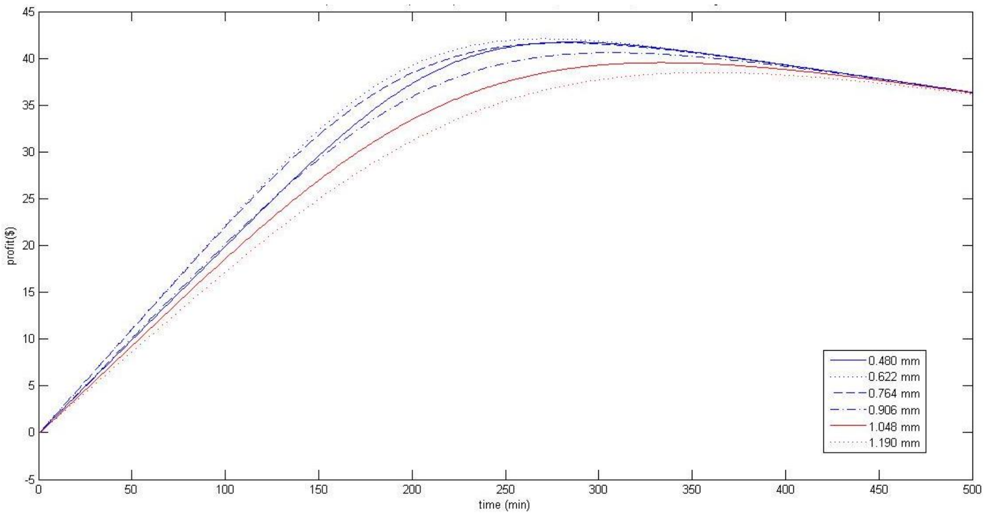

Figure 4.19 Effect of particle diameter on the profitability at P = 50 MPa, T = 40 ^{o}C, Q = 5.88 kg/h, and CS = 7.8 wt%.

4.6 Optimization results

The optimum operating condition which provides the maximum profitability of this extraction process was determined using the genetic algorithm. The carbon dioxide flow rate and the size of the solid particle were kept constant because of the limits of the experimental data. In addition, the fixed values of these parameters are reasonable and safe to operate because the channeling problem does not occur at the given fixed flow rate and particle size. The bounding of the operating variables is shown in Table 4.3.

Table 4.3 Operating variables and their bounding in maximum extraction yield

Independent variables	Lower – upper bounded variable
Pressure (MPa)	30 – 60
Temperature (K)	313.15 – 343.15
CO_2 flow rate (kg/h)	5.88
Particle size (mm)	0.68
Extraction time (min)	200 - 320

The profitability at the bounding operating temperature and operating pressure under 250 minute of extraction time is shown in Figure 4.20. The optimization result from GA is shown in Table 4.4. The optimum operating condition which gives the maximum profitability is 323.13 K, 59.45 MPa, and 283 minutes, respectively. About 90.1 wt.% of isoflavone from soybean meal was obtained at this condition, which yields 46.48 $/batch of profit.

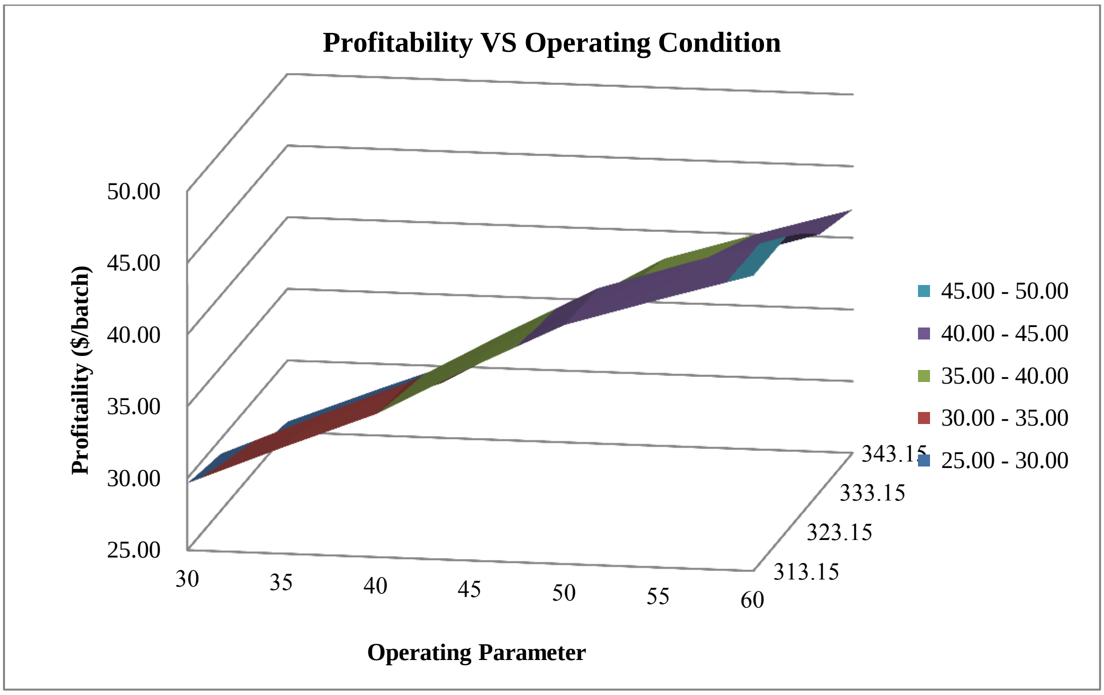

Figure 4.20 The profitability at operating temperature 313.15 – 343.15 and operating pressure 30-60 MPa under 250 minutes of extraction time.

Table 4.4 GA optimum values for isoflavone extraction

Quantity	T, P and time
The optimum temperature (K)	323.13
The optimum pressure (MPa)	59.45
The optimum time for extraction (min)	283.00
The maximum yield (wt.%)	90.926
The maximum profit ($/batch)	46.18
The number of generations	51
The number of function evaluations	1040
The optimization terminated	average change in the fitness value less than options

CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

A mathematical model used to predict the yield of isoflavone extraction from soybean meal using the supercritical carbon dioxide with aqueous methanol as co-solvent was proposed in this study. This model requires four parameters, namely the solubility, the film mass transfer coefficient, the Peclet number, and the distribution coefficient. To estimate these model parameters, the transport properties including the density, the viscosity, the binary diffusion coefficient, the axial dispersion coefficient, the Reynolds number, the Schmidt number, and the Sherwood number were estimated from existing correlations. The equation of state from Mohsen-Nia-Moddaress-Mansoori (MMM) was used to estimate the solubility of isoflavone based on the equilibrium of fugacity. The distribution coefficient was estimated by using an optimization technique to minimize the sum of the squares of the difference between the experimental extraction yield and the predicted extraction yield from the mathematical model. The average absolute relative deviation (AARD) was used to show the difference in the isoflavone extraction yield between the experimental data from Zuo et al. in 2008 and results from the mathematical model. This model can predict the isoflavone concentration as a function of time with the maximum AARD is 17.79.

The study on the effect of the operating conditions (the temperature, the pressure, the carbon dioxide flow rate, and the particle diameter) on the cumulative yield shows that the yield of isoflavone increases along with the pressure and the carbon dioxide flow rate. On the other hand, the yield of isoflavone decreases when the temperature increases. In addition, the same study shows that profitability increases when the pressure and the carbon dioxide flow rate increase. On the other hand, the profitability decreases when the temperature increases, but after a certain point in time, the profitability starts to decrease.

Genetic algorithm was used to determine the optimum operating condition that provides maximum profitability. The maximum profitability of this process was found at the carbon dioxide flow rate of 5.88 kg/h and the particle diameter of 0.68 mm with the temperature of 323.15 K and the pressure of 59.5 MPa. The optimum extraction time was approximately 283 min.

5.2 Recommendations

1. The equilibrium constant should be modified to make this model more realistic.
2. The other parameters such as the particle diameter and the solvent flow rate should also be included in the optimization as decision variables.
3. The configuration of the extractors should be considered in order to make the simulation model reflect more closely what really takes place in industry.

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Appendix A

Group contribution for properties estimation

Table A.1 Volume increments (υ_i) for common elements and ions (Lyman et al., 1982).

Element or Ion	υ_i(Å3)
-H	6.9
=C=	15.3
-C≡	15.3
>C=	13.7
>C<	11
=O	14
-O-	9.2
N≡	16
-N=	12.8
-N<	7.2
S	23.8
-F	12.8
-Cl	26.7
-Br	33
-I	45
Cl-	28.9
Br-	39.3
I-	56.6
Na+	13.6
K+	27.3
H2O	21.5
Benzene frame (carbons only)	75.2
O-H…O hydrogen-bond	-2.6
N-H…O hydrogen-bond	-2.8
N-H…N hydrogen-bond	-0.3
Non-aromatic rings (rough estimate)	-3
Naphthalene frame (carbons only)	123.7

Table A.2 First-order groups and their contributions for the physical properties (Gani method) (Constantinou and Gani, 1994).

Group	t_{c1i}	p_{c1i} (bar$^{-0.5}$)	v_{c1i} (m^3/kmol)	t_{b1i}
CH_3	1.6781	0.00199	0.07504	0.8894
CH_2	3.492	0.010558	0.05576	0.9225
CH	4.033	0.001315	0.03153	0.6033
C	4.8823	-0.0104	-0.00034	0.2878
CH_2 = CH	5.0146	0.025014	0.11648	1.7827
CH = CH	7.3691	0.017865	0.09541	1.8433
CH_2=C	6.5081	0.022319	0.09183	1.7117
CH=C	8.9582	0.01259	0.07 3 27	1.7957
C = C	11.3764	0.002044	0.07618	1.8881
CH_2 = C = CH	9.9318	0.03127	0.14831	3.1243
ACH	3.7337	0.007542	0.04215	0.9297
AC	14.6409	0.002136	0.03985	1.6254
$ACCH_3$	8.213	0.01936	0.10364	1.9669
$ACCH_2$	10.3239	0.0122	0.10099	1.9478
ACCH	10.4664	0.002769	0.0712	1.7444
OH	9.7292	0.005148	0.03897	3.2152
ACOH	25.9145	-0.00744	0.03162	4.4014
CH_3CO	13.2896	0.025073	0.13396	3.5668
CH_2CO	14.6273	0.017841	0.11195	3.8967
CHO	10.1986	0.014091	0.08635	2.8526
CH_3COO	12.5965	0.02902	0.1589	3.636
CH_2COO	3.8116	0.021836	0.13649	3.3953
HCOO	11.6057	0.013797	0.10565	3.1459
CH_3O	6.4737	0.02044	0.08746	2.2536
CH_2O	6.0723	0.015135	0.07286	1.6249
CH-O	5.0663	0.009857	0.05865	1.1557
FCH_2O	9.5059	0.009011	0.06858	2.5892
$CH2NH_2$	12.1726	0.012558	0.13128	3.1656
$CHNH_2$	10.2075	0.010694	0.07527	2.5983
CH_3NH	9.8544	0.0 12589	0.12152	3.1376
CH_2NH	10.4677	0.01039	0.09956	2.6127
CHNH	7.2121	-0.00046	0.09165	1.578
CH_3N	7.6924	0.015874	0.12598	2.1647
CH_2N	5.5172	0.004917	0.06705	1.2171
$ACNH_2$	28.757	0.00112	0.06358	5.4736
$C5H_4N$	29.1528	0.029565	0.24831	6.28
$C5H_3N$	27.9464	0.025653	0.17027	5.9234
CH_2CN	20.3781	0.036133	0.15831	5.0525
COOH	23.7593	0.011507	0.10188	5.8337
CH_2CL	11.0752	0.019789	0.11564	2.9637
CHCL	10.8632	0.01136	0.1035	2.6948
CCL	11.3959	0.003086	0.07922	2.2073
$CHCL_2$	16.3945	0.026808	0.16951	3.93
CCL_2	****	****	****	3.56
CCL_3	18.5875	0.034935	0.21031	4.5797
ACCL	14.1565	0.013135	0.10158	2.6293
$ACNO_2$	34.587	0.01505	0.14258	6.0837

Table A.2 First-order groups and their contributions for the physical properties (Gani method) (Constantinou and Gani, 1994) (Cont').

Group	t_{c1i}	p_{c1i} (bar$^{-0.5}$)	v_{c1i} (m^3/kmol)	t_{b1i}
CH_2SH	13.8058	0.013572	0.10252	3.2914
I	17.3947	0.002753	0.10814	3.665
BR	10.5371	-0.00177	0.08281	2.6495
CH ≡ C	7.5433	0.014827	0.09331	2.3678
C≡C	11.4501	0.004115	0.07627	2.5645
CL-(C=C)	5.4334	0.016004	0.05687	1.7824
ACF	2.8977	0.013027	0.05672	0.9442
$HCON(CH_2)_2$	* * * *	****	* * * *	7.2644
CF_3	2.4778	0.044232	0.1148	1.288
CF_2	1.7399	0.012884	0.09519	0.6115
CF	3.5192	0.004673	****	1.1739
COO	12.1084	0.011294	0.08588	2.6446
CCL_2F	9.8408	0.035446	0.18212	2.8881
HCCLF	****	****	****	2.3086
$CCLF_2$	4.8923	0.039004	0.14753	1.9163
F (except as above)*	1.5974	0.014434	0.03783	1.0081
$CONH_2$	65.1053	0.004266	1.4431	10.3428
$CONCHCH_3$	****	****	****	****
$CONCHCH_2$	****	****	****	****
$CON(CH_3)_2$	36.1403	0.040149	2.5031	7.6904
$CONCH_3CH_2$	****	****	****	****
$CON(CH_2)_2$	****	****	****	6.7822
$C2H_5O_2$	17.9668	0.025435	0.16754	5.5566
$C2H_4O_2$	****	****	****	5.4248
CH_3S	14.3969	0.016048	0.13021	3.6796
GH_2S	17.7916	0.011105	0.1165	3.6763
CHS	****	****	****	2.6812
C_4H_3S	****	****	****	5.7093
C_4H_2S	****	****	****	5.826
$CH2NO_2$	24.7369	0.020974	0.16531	5.7619
$CHNO_2$	23.205	0.012241	0.14227	5.0767

Table A.3 Second-order oroups and their contributions for the physical properties (Gani method) (Constantinou and Gani, 1994).

Group	t_{c2i}	p_{c2i} (bar$^{-0.5}$)	ν_{c2i} (m^3/kmol)	t_{b2i}
$(CH_3)_2CH$	-0.5334	0.000488	0.004	-0.1157
$(CH_3)_3C$	-0.5143	0.00141	0.00572	-0.0489
$CH(CH_3)CH(CH_3)$	1.0699	-0.001849	-0.00398	0.1798
$CH(CH_3)C(CH_3)_2$	1.9886	-0.005198	-0.01081	0.3189
$CH(CH_3)_2C(CH_3)_2$	5.8254	-0.01323	-0.023	0.7273
3 membered ring*	-2.3305	0.003714	-0.00014	0.4745
4 membered ring*	-1.2978	0.001171	-0.00851	0.3563
5 membered ring*	-0.6785	0.000424	-0.00866	0.1919
6 membered ring'	0.8479	0.002257	0.01636	0.1957
7 membered ring'	3.6714	-0.009799	-0.027	0.3489
$CH_n=CH_m-CH_p=CH_k$;k,n,m,p Є (0,2)	0.4402	0.004186	-0.00781	0.1589
$CH_3=CH_m=CH_n$;m,n Є (0,2)	0.0167	-0.000183	-0.00098	0.0668
$CH_2=CH_m=CH_n$;m,n Є (0,2)	-0.5231	0.003538	0.00281	-0.1406
CH-$CH_m=CH_n$ or C-$CH_m=CH_n$;m,n Є (0,2)	-0.385	0.005675	0.00826	-0.09
Alicyclic side chain $C_{cyclic}C_m$;m>1	2.116	-0.002546	-0.01755	0.0511
$CH_3=CH_3$	2.0427	0.005175	0.00227	0.6884
CHCHO or CCHO	-1.5826	0.003659	-0.00664	-0.1074
CH_3COCH_2	0.2996	0.001474	-0.0051	0.0224
CH_3COCH or CH_3COC	0.5018	-0.002303	-0.00122	0.092
C_{cyclic} (=O)	2.9571	0.003818	-0.01966	0.558
ACCHO	1.1696	-0.002481	0.00664	0.0735
CHCHOOH or CCOOH	-1.7493	0.00492	0.00559	-0.1552
ACCOOH	6.1279	0.000344	-0.00415	0.7801
CH_3COOCH or CH_3COOC	-1.3406	0.000659	-0.00293	-0.2383
$COCH_2COO$ or COCHCOO or COCCOO	2.5413	0.001067	-0.00591	0.4456
CO-O-CO	-2.7617	-0.004877	-0.00144	-0.1977
ACCOO	-3.4235	-0.000541	0.02605	0.0835
CHOH	-2.8035	-0.004393	-0.00777	-0.5385
COH	-3.5442	0.000178	0.01511	-0.6331
$CH_m(OH)CH_n(OH)$;m,n Є (0,2)	5.4941	0.005052	0.00397	1.4108
$CH_{m\ cyclic}$-OH m Є (0,1)	0.3233	0.006917	-0.00297	-0.069
$CH_m(OH)CH_n(NH_p)$ m,n,p Є (0,3)	5.4864	0.001408	0.00433	1.0682
$CH_m(NH_2)CH_n(NH_2)$;m,n Є (0,2)	2.0699	0.002148	0.0058	0.4247
$CH_{m\ cyclic}$-NH_p-$CH_{n\ cyclic}$;m,n,p Є (0,2)	2.1345	-0.005947	-0.0138	0.2499
CH_m-O-$CH_n=CH_p$ m,n,p Є (0,2)	1.0159	-0.000878	0.00297	0.1134
AC-O-CH_m;m Є (0,3)	-5.3307	-0.002249	-0.00045	-0.2596
$CH_{m\ cyclic}$-S-$CH_{n\ cyclic}$ m,n Є (0,2)	4.4847	* * * *	* * * *	0.4408
$CH_m=CH_n$-F;$_m$,n Є (0,2)	--0.4996	0.000319	-0.00596	-0.1168
$CH_m=CH_n$-Br;m,n Є (0,2)	-1.9334	-0.004305	0.00507	-0.3201
$CH_m=CH_n$-I;m,n Є (0,2)	****	****	* * * *	-0.4453
ACBr	-2.2974	-0.009027	-0.00832	-0.6776
ACI	2.8907	0.008247	-0.00341	-0.3678
$CH_m(NH_2)$-COOH;m Є (0,2)	****	****	****	****

Table A.4 Groups and their contributions for the boiling point properties (Joback method) (Reid et al., 1987).

Group	ΔBJ	Group	ΔBJ
-CH$_3$ (non-ring)	23.58	-OH (phenols)	76.34
>CH$_2$ (non-ring)	22.88	-O- (non-ring)	22.42
>CH- (non-ring)	21.74	-O- (ring)	31.22
>C< (non-ring)	18.25	>C=O (non-ring)	76.75
=CH$_2$ (non-ring)	18.18	>C=O (ring)	94.97
=CH- (non-ring)	24.96	-HC=O (aldehyde)	72.24
>C= (non-ring)	24.14	-COOH (acid)	169.09
=C= (non-ring)	26.15	-COO- (ester)	81.1
-CH (non-ring)	9.2	=O (any other)	-10.5
-C- (non-ring)	27.38	-NH$_2$	73.23
>CH$_2$ (ring)	27.15	>NH (non-ring)	50.17
>CH- (ring)	21.78	>NH (ring)	52.82
>C< (ring)	21.32	>N- (non-ring)	11.74
=CH- (ring)	26.73	-N=, HN= (non-ring)	74.6
>C= (ring)	31.01	-N= (ring)	57.55
-F	-0.03	-CN	125.66
-Cl	38.13	-NO$_2$	152.54
-Br	66.86	-SH	63.56
-I	93.84	-S- (non-ring)	68.78
-OH (alcohol)	92.88	-S- (ring)	52.1

Table A.5 Groups and their contributions for the critical point properties (Joback method) (Reid et al., 1987).

Group	*tck*	*pck*	*vck*	n_A	Group	*tck*	*pck*	*vck*	n_A
-CH3 (non-ring)	0.0141	-0.0012	65	4	-OH (phenols)	0.024	0.0184	-25	2
>CH2 (non-ring)	0.0189	0	56	3	-O- (non-ring)	0.0168	0.0015	18	1
>CH- (non-ring)	0.0164	0.002	41	2	-O- (ring)	0.0098	0.0048	13	1
>C< (non-ring)	0.0067	0.0043	27	1	>C=O (non-ring)	0.038	0.0031	62	2
=CH2 (non-ring)	0.0113	-0.0028	56	3	>C=O (ring)	0.0284	0.0028	55	2
=CH- (non-ring)	0.0129	-0.0006	46	2	-HC=O (aldehyde)	0.0379	0.003	82	3
>C= (non-ring)	0.0117	0.0011	38	1	-COOH (acid)	0.0791	0.0077	89	4
=C= (non-ring)	0.0026	0.0028	36	1	-COO- (ester)	0.0481	0.0005	82	3
บCH (non-ring)	0.0027	-0.0008	46	2	=O (any other)	0.0143	0.0101	36	1
บC- (non-ring)	0.002	0.0016	37	1	-NH2	0.0243	0.0109	38	3
>CH2 (ring)	0.01	0.0025	48	3	>NH (non-ring)	0.0295	0.0077	35	2
>CH- (ring)	0.0122	0.0004	38	2	>NH (ring)	0.013	0.0114	29	2
>C< (ring)	0.0042	0.0061	27	1	>N- (non-ring)	0.0169	0.0074	9	1
=CH- (ring)	0.0082	0.0011	41	2	-N=, HN= (non-ring)	0.0225	-0.01	0	1
>C= (ring)	0.0143	0.0008	32	1	-N= (ring)	0.0085	0.0076	34	1
-F	0.0111	-0.0057	27	1	-CN	0.0496	0.0101	91	2
-Cl	0.0105	-0.0049	58	1	-NO2	0.0437	0.0064	91	3
-Br	0.0133	0.0057	71	1	-SH	0.0031	0.0084	63	2
-I	0.0068	-0.0034	97	1	-S- (non-ring)	0.0119	0.0049	54	1
-OH (alcohol)	0.0741	0.0112	28	2	-S- (ring)	0.0019	0.0051	38	1

Table A.6 K_F Factors for alicyclica organic compounds (Constantinou and Gani, 1994).

Compound Type	Number of carbon atoms (N) in compound, including carbon atoms of functional group											
	1	2	3	4	5	6	7	8	9	10	11	12-20
Hydrocarbon												
n-Alkanes	0.97	1	1	1	1	1	1	1	1	1	1	1
Alkane isomers				0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99
Mono-and dipolefins and isomers		1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1
Cyclic saturated hydrocarbons			1	1	1	1	1	1	1	1	1	1
Alkyl derivatives of cyclic saturated hydrocarbons				0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99
Halides (saturated or unsaturated)												
Monocylorides	1.05	1.04	1.03	1.03	1.03	1.03	1.03	1.03	1.02	1.02	1.02	1.01
Monobromides	1.04	1.03	1.03	1.03	1.03	1.03	1.02	1.02	1.02	1.01	1.01	1.01
Monoiodides	1.03	1.02	1.02	1.02	1.02	1.02	1.01	1.01	1.01	1.01	1.01	1.01
Polyhalides (not entirely halogenated)	1.05	1.05	1.05	1.04	1.04	1.04	1.03	1.03	1.03	1.02	1.02	1.02
Mixed halides (completely halogenated)	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01
Perfluorocarbons	1	1	1	1	1	1	1	1	1	1	1	1
Compounds Containing the Ketone Group												
Esters		1.14	1.09	1.08	1.07	1.06	1.05	1.04	1.04	1.03	1.02	1.01
Ketones			1.08	1.07	1.06	1.06	1.05	1.04	1.04	1.03	1.02	1.01
Aldehides		1.09	1.08	1.08	1.07	1.06	1.05	1.04	1.04	1.03	1.02	1.01
Nitrogen Compounds												
Primary amines	1.16	1.13	1.12	1.11	1.1	1.1	1.09	1.09	1.08	1.07	1.06	1.05b
Secondary amines		1.09	1.08	1.08	1.07	1.07	1.06	1.05	1.05	1.04	1.04	1.03b
Tertiary amines			1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01
Nitriles		1.05	1.07	1.06	1.06	1.05	1.05	1.04	1.04	1.03	1.02	1.01
Nitro compounds	1.07	1.07	1.07	1.06	1.06	1.05	1.05	1.04	1.04	1.03	1.02	1.01
Sulfur compounds												
Mercaptans	1.05	1.03	1.02	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01
Sulfides		1.03	1.02	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01
Alcohols												
Alcohols (single-OH group)	1.22	1.31	1.31	1.31	1.31	1.3	1.29	1.28	1.27	1.26	1.24	1.24b
Diols (glycols or condensed glycols)		1.33	1.33	1.33	1.33	1.33	1.33	1.33				
Triols (glycerol, etc.)			1.38	1.38	1.38							
Cyclohexanol, cycloheyl methyl alcohol, etc.						1.2	1.2	1.21	1.24	1.26		
Miscellaneous Compounds												
Ethers (aliphatic only)		1.03	1.03	1.02	1.02	1.02	1.01	1.01	1.01	1.01	1.01	1.01
Oxides (cyclic ethers)		1.08	1.0	1.06	1.05	1.05	1.04	1.03	1.02	1.01	1.01	1.01

Carbocyclic or heterocyclic compounds having aliphatic properties. For $N = 12$ only; no prediction is made for K_F where $N > 12$ Notes:

1. Consider any phenyl group as a single carbon atom.
2. K_F factors are the same for all aliphatic isomers of a given compound. For example, $K_F = 1.31$ for n-butyl alcohol, i-butyl alcohol, t-butyl alcohol, and s-butyl alcohol.
3. In organometallic compounds, consider any metallic atom as a carbon atom.
4. For compounds not included in this table, assume $K_F = 1.06$.

Table A.7 Values of K_F for aromatic hydrogen bonded system (Constantinou and Gani, 1994).

Compound Type	**K_F**
Phenols (single-OH)	1.15
Phenols (more than one-OH)	1.23
Anilines (single-NH_2)	1.09
Anilines (more than one - NH2)	1.14
N-substituted anilines (C_6H_5NHR)	1.06
Naphthols (single-OH)	1.09
Naphthylamines (single-NH2)	1.06
N-substituted naphthylamines	1.03

Note: For mixed systems, K_F for OH group takes precedence. Thus, K_F for p-aminophenol is 1.15.

APPENDIX B

Mathematical model

Appendix B.1: Matlab command for optimization

```
%File name: isomodel.m

%function fun = isomodel
global T P CS h peb rp l eps u area k ke mtotal Z x

T = 313.15;
P = 30*10^6;
CS = 7.8;
flow = 5.88; %kg/h
dp = 0.68*10^-3; %m


%k estimation of temperature and pressure
press = 30*10^6:10*10^6:60*10^6;
temp = 313.15:10:343.15;

kval = [250.1503 231.1186 186.2388 177.3367
    265.2699 246.2382 201.3584 192.4563
    309.9508 290.9191 246.0393 237.1372
    333.9463 314.9146 270.0348 261.1327];
k = interp2(press,temp,kval,P,T);

%k estimation of diameter and solvent flow rate
% flowr = [3.92 5.88 7.84 9.8];
% diamt= [0.48*10^-3 0.68*10^-3 1.19*0^-3];
%
% kval = [181.42 215.27 216.22 236.94
%     152.39 186.24 187.19 207.91
%     208.09 241.94 242.89 263.61];
% k = interp2(flowr,diamt,kval,flow,dp);
%-----------------------------------------------------------------
% fluid properties vector by correlation.m
param = correlation;
rhom = param(1);  %kg/m3
mu   = param(2);  %kg/ms
DAB  = param(3);  %m2/s
rhoco2 = param(4); %kg/m3
rhome = param(5); %kg/m3
%Q = flow/(3600*rhom); %m3/s
Q = flow/(3600*rhoco2)+0.078*flow/(0.922*3600*rhome);

%-----------------------------------------------------------------
%isoflavone
Dtank = 0.0339;  %m
L = 0.834293;    %m
e = 0.850115;    % [porosity]

Rp = dp/2;         %m
Rtank= Dtank/2;    %m
A = pi*(Rtank^2); %m2
vf = Q/A;          %m/s
ep = 1.1766;        % [solid porosity]

%Dimensionless Correlations
Re = dp*vf*rhom/mu;            % [Renold number]
Sc = mu/(rhom*DAB);             % [Schmidt number]
Sh = 0.38*(Re^0.83)*(Sc^0.33); % [Sherwood number]
if  Re < 1.2918
     Sh=0.135*(Re^0.5*Sc^0.33);% shervood number
```

```
else
    Sh=0.38*(Re^0.83*Sc^0.33); % shervood number
end

%Correlations
DL = (1.317*DAB/e)*(e*Re*Sc)^1.392; %m2/s [Axial dispersion
coefficient]
kf = Sh*DAB/dp;  %m/s [Film mass transfer coefficient]
De = DAB*ep^2;   %m2/s [Effective Diffusivity Coefficient]
Bi = kf*Rp/De;   % [Biot Number]
Pe = L*vf/DL;    % [Peclect Number]

h=200;      % [axial increment number]

%Isoflavone process
Csat = solubility;
factor = 78.56879;
miso = Csat(1)*factor; %g/g   [initial mass fraction of extracable
isoflavone]
rop = 0.836116; %g/cm3 [density of isoflavone]
q0 = miso*rop;      %g/cm3 [initial concentration of solute in
particle]

%gas constant
R = 8.314;  %m3*Pa/K Mol

%unit converter
rp = (dp/2)*100; %cm     [particle radius]
l=L*100;         %m      [length of the extractor]
eps = e; % [extractor void fraction]
u = vf*100*60/eps;   %cm/min [fluid velocity inside the extractor]
area = A*10000;  %cm2    [area of the extractor]
ke = kf*100*60;  %cm/min [external mass transfer coefficient]
peb=Pe;  % [bed peclet number]

volume = ((pi()*L*Dtank^2)/4)*10^6; %cm3
rob = rop*(1-eps);
mtotal = rob*volume; %g [total mass of soybean]
cf0=0;           %g/cm3  [initial solute concentration in fluid]
bc=[];
%---------------------------------------------------------------------
-----
tspan=[0:1:500]; % [total extraction time]
%---------------------------------------------------------------------
-----
% initial boundary condition
%---------------------------------------------------------------------
-----
for i=1:h
    bc(i)=cf0;  %g/cm3 [initial solute conc. at different high of
fluid]
end

for i=h+1:2*h
    bc(i)=q0; %g/cm3 [initial solute conc.at different high of solid]
end

bc(2*h+1)=0; % [extraction yield at time zero]
%---------------------------------------------------------------------
-----
y0=bc'; % [the vector of initial conditions]
```

```
[t,y]=ode15s(@equation,tspan,y0);

yield = y(length(tspan),2*h+1);
P1 = 6*10^6;        %Pa
V1 = 5.8846*10^-5; %m3
r = 1.2;
Power =  (r/(400*(r-1)))*sqrt(0.135614*Z)*P1*V1*((P/P1)^((r-1)/r)-1);

cost1 = 228; %$/g %Isoflavone price
cost2 = 11.9/(100*1000); %$/Wh %electricity price 11.9 cent/kWh
cost3 = 0.3; %$/kg %carbon dioxide price
cost4 = 511.58/(1000*1000); %$/g %soybean meal cost (511.58 $/tonm)

C1 = (y(:,2*h+1)/100)*100*2628*10^-6*cost1;
C2 = Power*(t(:,1)/60)*cost2;
C3 = flow*(t(:,1)/60)*cost3;
C4 = 100*cost4;

fun = (C1-C2-C3-C4); %operating cost ($/g)

hold on
box on
plot(t(:,1),fun,'b','LineStyle',':')
xlabel('time (min)');
ylabel('Profitability ($/g)');
% title('Effect of pressure on the operating cost at P = 50 MPa, T =
313.15 K, and Q = 5.88 kg/h')

%
hold on
```

Appendix B2: Matlab command for obtaining the model parameters

```
%File name: correlation.m
%Estimated density, viscosity, binary diffusion coefficient
%prop=[rhom mu DAB rho_CO2 rho_MeOHco]
function prop = correlation
global T P CS h peb rp l eps u area k ke mtotal Z
%Isoflavone
Mw_A = 130.37646; %kg/kmol
%MeOH:water = 80:20
y_MeOH = 0.8;
y_H2O = 1-y_MeOH;
%solvent-cosolvent concentration (CO2:methanol+water = 92.2:7.8)
MeOHco_percent = CS;
CO2_percent = 100-MeOHco_percent;
%Gas constant
R = 8.314; %m3*Pa/K.mol
%-----------------------------------------------------------------------
--
%Co-solvent's critical temperature and pressure and acentric factor
%1 bar = 10^5 Pa
%Critical properties of methanol
Tc_MeOH = 512.6;     %K
Pc_MeOH = 80.9*10^5; %Pa
Vc_MeOH = 118*10^-6; %m3/mol
Mw_MeOH = 32.05;     %kg/kmol
w_MeOH  = 0.50547735;
%Critical properties of water
Tc_H2O = 647.1;       %K
Pc_H2O = 220.6*10^5;  %Pa
Vc_H2O = 55.95*10^-6; %m3/mol
Mw_H2O = 18.015;      %kg/kmol
w_H2O = 0.344861;

%Properties of Co-solvents
Tc_MeOHco = Tc_MeOH*y_MeOH+Tc_H2O*y_H2O; %K
Pc_MeOHco = Pc_MeOH*y_MeOH+Pc_H2O*y_H2O; %Pa
Vc_MeOHco = Vc_MeOH*y_MeOH+Vc_H2O*y_H2O; %m3/mol
Mw_MeOHco = y_MeOH*Mw_MeOH+y_H2O*Mw_H2O; %kg/kmol
w_MeOHco = w_MeOH*y_MeOH+w_H2O*y_H2O;
%-----------------------------------------------------------------------
--
%Critical properties of carbon dioxide
Tc_CO2 = 304.12;      %K
Pc_CO2 = 73.7*10^5;   %Pa
Vc_CO2 = 94.07*10^-6; %m3/mol
Mw_CO2 = 44.01;       %kg/kmol
w_CO2  = 0.22;

MeOHco_ratio = MeOHco_percent/Mw_MeOH;
CO2_ratio = CO2_percent/Mw_CO2;
y_MeOHco = MeOHco_ratio/(MeOHco_ratio+CO2_ratio);
y_CO2 = 1-y_MeOHco;
%-----------------------------------------------------------------------
--
%PR-EOS is used to estimate the density of aqueous methaol (Polar
solvent)
%subscript 1 = MeOH
%subscript 2 = H2O
%Critical properties of methanol
```

```
Tc_cs(1) = Tc_MeOH; %K
Pc_cs(1) = Pc_MeOH; %Pa
Vc_cs(1) = Vc_MeOH; %m3/mol
w_cs(1)  = w_MeOH;
%Critical properties of water
Tc_cs(2) = Tc_H2O; %K
Pc_cs(2) = Pc_H2O; %Pa
Vc_cs(2) = Vc_H2O; %m3/mol
w_cs(2)  = w_H2O;
%MeOH:water = 80:20
y_cs(1) = y_MeOH;
y_cs(2) = y_H2O;

% Define some parameters
a = zeros(2,2);
b = zeros(2,2);
kappa = zeros(2,1);
alfa = zeros(2,1);
A = zeros(2,2);
B = zeros(2,2);
% Reduced variables and Parameters of the EOS for a pure component
for i=1:2
    kappa(i) = 0.37464 + 1.54226*w_cs(i) - 0.26992*w_cs(i)^2;
    alfa(i) = (1 + kappa(i)*(1 - sqrt(T/Tc_cs(i))))^2;
end
for i=1:2
    a(i,i) = alfa(i)*0.45724*(R*Tc_cs(i))^2/Pc_cs(i);
    b(i,i) = 0.0778*R*Tc_cs(i)/Pc_cs(i);
end
a(1,2) = sqrt(a(1,1)*a(2,2));
b(1,2) = (b(1,1)+b(2,2))/2;
a(2,1) = a(1,2);
b(2,1) = b(1,2);

am = 0;
bm = 0;
am1 = 0;
for i=1:2
    for j=1:2
        am = am+y_cs(i)*y_cs(j)*a(i,j);
        bm = bm+y_cs(i)*y_cs(j)*b(i,j);
    end
    am1 = am1+y_cs(i)*a(2,i);
end
A = am*P/((R*T)^2);
B = bm*P/(R*T);

c1 = 1;
c2 = B-1;
c3 =(A-2*B-3*B^2);
c4 =(B^3+B^2-A*B);
% Compressibility factor
GG = roots([c1 c2 c3 c4]);
j = 1;
zee=[];
for i =1:3
    if imag(GG(i))==0;
        zee(j)=GG(i);
        j = j+1;
    end
end
```

```
z_MeOHco   = min(zee);
rho_MeOHco = P*Mw_MeOHco /(z_MeOHco *R*T*1000); %kg/m3
%-----------------------------------------------------------------------
--
%LKP-EOS is used to estimate the density of carbon dioxide (non-polar)
%Critical properties of carbon dioxide
% define two universal sets of constants for the LK EOS
bo1 = 0.1181193;
br1 = 0.2026579;
bo2 = 0.265728;
br2 = 0.331511;
bo3 = 0.154790;
br3 = 0.027655;
bo4 = 0.030323;
br4 = 0.203488;
co1 = 0.0236744;
cr1 = 0.0313385;
co2 = 0.0186984;
cr2 = 0.0503618;
co3 = 0.0;
cr3 = 0.016901;
co4 = 0.042724;
cr4 = 0.041577;
do1 = 0.155428*(10^-4);
dr1 = 0.48736*(10^-4);
do2 = 0.623689*(10^-4);
dr2 = 0.0740336*(10^-4);
beo = 0.65392;
ber = 1.226;
gao = 0.060167;
gar = 0.03754;
wr = 0.3978;

Tcm = Tc_CO2; %K
Pcm = Pc_CO2; %Pa
Vcm = Vc_CO2; %m3/mol
wm = w_CO2;

Zcm = (0.2905-0.085*wm);
V0 = Zcm*R*T/(P*Vcm);
Trm = T/Tcm;
Prm = P/Pcm;

%for simple fluid cal. specific volume, Z, fugacity coeff. and...
%Isothermal Enthalpy Departure.
B = bo1 - bo2/Trm - bo3/Trm^2 - bo4/Trm^3;
C = co1 - co2/Trm + co3/Trm^3;
D = do1 + do2/Trm;
cc = co4;
bbe = beo;
gga = gao;
options = optimset( ... %%% defaults %%%
    'MaxFunEvals' , 1000000,...
    'MaxIter' , 1000000,...
    'TolCon' , 1e-1000000,...
    'TolFun' , 1e-1000000, ... % 1e-6
    'TolX' , 1e-1000000); % 1e-6
% 'Diagnostics' , 'on' , ... % 'off'
% 'Display' , 'iter' , ... % 'final'
% 'LargeScale' , 'on' , ... % 'off'
% 'MaxPCGIter' , 200 , ... % n/2
```

```
% 'PrecondBandWidth', inf , ... % 0
F1= @(Vrm)Vrm-Trm/Prm-B*Trm/Prm/Vrm-C*Trm/Prm/(Vrm^2)-
D*Trm/Prm/(Vrm^5)-...
    Trm/Prm*cc/((Trm^3)*(Vrm^2))*(bbe+gga/(Vrm^2))*exp(-gga/(Vrm^2));
Vorm = fsolve(F1,V0,options);
Zorm = Prm*Vorm/Trm;

%for reference fluid cal. specific volume, Z, fugacity coeff. and...
%Isothermal Enthalpy Departure.
B = br1 - br2/Trm - br3/Trm^2 - br4/Trm^3;
C = cr1 - cr2/Trm + cr3/Trm^3;
D = dr1 + dr2/Trm;
cc = cr4;
bbe = ber;
gga = gar;
F2= @(Vrm)Vrm-Trm/Prm-B*Trm/Prm/Vrm-C*Trm/Prm/(Vrm^2)-
D*Trm/Prm/(Vrm^5)-...
    Trm/Prm*cc/((Trm^3)*(Vrm^2))*(bbe + gga/(Vrm^2))*exp(-
gga/(Vrm^2));
Vrrm = fsolve(F2,V0,options);
Zrrm = Prm*Vrrm/Trm;

%total
Zm = (Zrrm-Zorm)*wm/wr+Zorm;
Vm = (Vrrm-Vorm)*wm/wr+Vorm;

z_CO2 = (Zrrm-Zorm)*wm/wr+Zorm;
rho_CO2= P*Mw_CO2/(z_CO2*R*T*1000); %kg/m3
%-----------------------------------------------------------------
%Mixed density
rhom = y_CO2*rho_CO2+y_MeOHco*rho_MeOHco;  %kg/m3
%-----------------------------------------------------------------
%Critical density of co2
zc_CO2 = Pc_CO2*Vc_CO2/(R*Tc_CO2);
rhoc_CO2 = Pc_CO2*Mw_CO2/(zc_CO2*R*Tc_CO2*1000);
%Critical density of MeOHco
zc_MeOHco= Pc_MeOHco*Vc_MeOHco/(R*Tc_MeOHco);
rhoc_MeOHco= Pc_MeOHco*Mw_MeOHco/(zc_MeOHco*R*Tc_MeOHco*1000);

%Critical density
rhoc = y_CO2*rhoc_CO2+y_MeOHco*rhoc_MeOHco;
%Residue density
rhor = rhom/rhoc;
%---------------------------------------------------------------------
%viscosity estimaiton
%Non-polar (co2)
%low pressure - Stiel&Thodos
Tr_CO2 = T/Tc_CO2;
%1 bar = 10^5 Pa

%Zahadi
%e_CO2 = (Tc_CO2^(1/6))*(Mw_CO2^(-0.5))*(0.987*Pc_CO2*10^-5)^(-2/3);

%isoflavone
e_CO2 = (Tc_CO2^(1/6))*(Mw_CO2^(-0.5))*(0.987*Pc_CO2)^(-2/3);

if Tr_CO2<=1.50
    muo_CO2=(3.4*10^-4)*(Tr_CO2^0.94)/(e_CO2);
else
    muo_CO2=(1.778*10^-4)*(4.58*Tr_CO2-1.67)^(0.625)/(e_CO2);
end
```

```
%API-TDB
%High pressure - Jossi et al.
rhor_CO2 = rho_CO2/rhoc_CO2;
group_CO2 = 0.10230+0.023364*rhor_CO2+0.058533*rhor_CO2^2-0.040758*...
    rhor_CO2^3+0.0093324*rhor_CO2^4;
mu_CO2 = ((group_CO2^4-10^-4)/e_CO2)+muo_CO2; %cp
mu_CO2 = mu_CO2*0.001;  %kg/ms
%----------------------------------------
%Polar (MeOHco)
%low pressure - Stiel&Thodos
Tr_MeOHco = T/Tc_MeOHco;

%Zahadi
%e_MeOHco =  (Tc_MeOHco^(1/6))*(Mw_MeOHco^(-
0.5))*(0.987*Pc_MeOHco*10^-5)^(-2/3);

%isoflavone
e_MeOHco =  (Tc_MeOHco^(1/6))*(Mw_MeOHco^(-0.5))*(0.987*Pc_MeOHco)^(-
2/3);

muo_MeOHco=((7.55*Tr_MeOHco-0.55)*10^-5)*zc_MeOHco^(-5/4)/e_MeOHco;
rhor_MeOHco = rho_MeOHco/rhoc_MeOHco;

%API-TDB
if rhor_MeOHco<=0.1
    mu_CS = (1.656*10^-4*rhor_MeOHco^1.111)/e_MeOHco+muo_MeOHco;
else if rhor_MeOHco<=0.9
        mu_CS  = (6.07*10^-
6*(9.045*rhor_MeOHco+0.63)^1.739)/e_MeOHco+muo_MeOHco;
    else if rhor_MeOHco<=2.2
        mu_CS = (10^(4-10^(0.6439-
0.1005*rhor_MeOHco)))/(e_MeOHco*10^4)+muo_MeOHco;
        else if rhor_MeOHco<=3
           group_CS = 0.10230+0.023364*rhor_MeOHco
+0.058533*rhor_MeOHco^2 ...
                      -0.040758*rhor_MeOHco^3+0.0093324*rhor_MeOHco^4;
           mu_CS = ((group_CS^4-10^-4)/e_MeOHco)+muo_MeOHco;
            else
           mu_CS =((1.08*10^-4)*(exp(1.439*rhor_MeOHco)-exp(-
1.11*rhor_MeOHco^1.858)))/e_MeOHco+muo_MeOHco;
            end
        end
    end
end
mu_CS = mu_CS*0.001;  %kg/ms
%1 cP = 0.001 kg/ms

%Zahedi
%mu = (y_CO2*mu_CO2+y_MeOHco*mu_CS);  %kg/ms

%isoflavone
mu = (y_CO2*mu_CO2+y_MeOHco*mu_CS)/1000;  %kg/ms

%------------------------------------------------------------------
%Binary diffusion coefficient
%A : solute (isoflavone component 2)
%B : solvent (supercritical fluid 1)
%Isoflavone
%10^5 Pa = 1bar
%solvent
```

```
Mw_B = (y_CO2*Mw_CO2+y_MeOHco*Mw_MeOHco); %kg/kmol
V_B = 1000*Mw_B/rhom; %cm3/mol
Vc_B = 1000*Mw_B/rhoc; %cm3/mol
Pc_B = (y_MeOHco*Pc_MeOHco+y_CO2*Pc_CO2)*10^-5; %bar
if rhor < 1.2
    K = 1+(rhor-1.2)/sqrt(Mw_B);
else
    K = 1;
end
group_A = 0.61614+3.0902*exp(-0.87756*sqrt(Mw_B*Vc_B)/Pc_B);
DAB = (group_A*10^-10)*((V_B^K)-23)*sqrt(T/Mw_A);  %m2/s
prop=[rhom mu DAB rho_CO2 rho_MeOHco];
```

Appendix B.3 : Matlab command for partial differential equation

```
function dy=equation(t,y)

global T P CS h peb rp l eps u area k ke mtotal Z
dy=zeros(2*h+1,1);
%-------------------------------------------
% the PDE for solute concentration in fluid phase (equation (6) in
word file)
%-------------------------------------------
delz=1/(h-1);
dy(1)=0;
for i=2:h-1
    dy(i)=u/l*(1/peb*(y(i+1)-2*y(i)+y(i-1))/delz^2-(y(i)-y(i-1))/delz-
(1-eps)/eps*3*ke/u*l/rp*(y(i)-y(h+i)/k));
end
    dy(h)=u/l*(1/peb*(y(h)-2*y(h-1)+y(h-2))/delz^2-(y(h)-y(h-1))/delz-
(1-eps)/eps*3*ke/u*l/rp*(y(h-1)-y(2*h-1)/k));
%-------------------------------------------
% the PDE for solute concentration in solid phase  (equation (8) in
word file)
%-------------------------------------------
    for j=1:h
        dy(j+h)=-3*ke/rp*(y(j+h)/k-y(j));
    end
%-------------------------------------------
% The PDE for yield  (equation (10) in word file)
%-------------------------------------------
dy(2*h+1)=u*area*eps*y(h)/mtotal*100;
```

Appendix B.4 : Matlab command for MMM equation of state

```
% MMM.m: calculate fugacity coefficient with MMM-EOS
%Parameters:
%T: Temperature K
%P: Pressure Pa
%Tc: critical temperature K
%Pc: critical pressure Pa
%w: acentric factor
%Psub: sublimation pressure Pa
% i = solute
% j = supercritical fluid

function F = MMM(y,T,vs,Tc,Pc,P,Psub);
global T P CS h peb rp l eps u area k ke mtotal Z
R = 8.314;
a = zeros(2,2);
b = zeros(2,2);

a(1,1) = 0.48748*(R^2)*(Tc(1)^2.5)/Pc(1);
b(1,1) = 0.064662*R*Tc(1)/Pc(1);
a(2,2) = 0.48748*(R^2)*(Tc(2)^2.5)/Pc(2);
b(2,2) = 0.064662*R*Tc(2)/Pc(2);

a(1,2) = (a(1,1)*a(2,2))^0.5;
b(1,2) = 1/8*(((b(1,1)^(1/3))+(b(2,2)^(1/3)))^3);
a(2,1) = a(1,2);
b(2,1) = b(1,2);
%----------------------------------------------------------------------
--
%y(1) is the mole fraction of isoflavone
%x(2) is the mole fraction of isoflavone
%x(1) is the mole fraction of solvent
x(2) = y(1);
x(1) = 1-x(2);

am  = 0;
bmi = 0;
bmj = 0;
b1  = 0;
b2  = 0;
a1  = 0;

for i = 1:2
    for j = 1:2
        am = am+x(i)*x(j)*a(i,j);
        bmi = bmi+3*x(i)*x(j)*b(i,j);
        b2 = b2+x(i)*x(j)*b(i,j);
    end
    bmj = bmj+x(i)*b(i,i);
    b1 = b1+x(i)*b(2,i);
    a1 = a1+x(i)*a(2,i);
```

```
end
bm = 1/4*(bmi+bmj);
%-----------------------------------------------------------------------
--
%syms V
%G1 = R*T*(V+1.319*bm)/(V*(V-bm));
%G2 = am/((T^0.5)*V*(V+bmj));
%G = G1-G2;
%v = double(solve(P-G));
%zee=[];
%for i =1:3
   % if imag(v(i))==0
   %     zee(i)=v(i);
   % end
%end
%V=min(zee);
%z=P*V/(R*T);
%s1 = 2.3191*((3*(2*b1-b2)+b(2,2))/(4*(V-bm))-(log(1-bm/V)))-log(z);
%s2 = am/(R*(T^1.5)*bmj);
%s3 = (b(2,2)/bmj-2*a1/am)*(log(1+bmj/V))-b(2,2)/(V+bmj);
%-----------------------------------------------
bmc = 1.3191*bm;
amc = am/(R*(T^1.5));
rtc = R*T/P;

c1 = (rtc^2);
c2 = rtc*(bmj-bm)-(rtc^2);
c3 = -bm*bmj-rtc*(bmj+bmc-amc);
c4 = -(bmc*bmj+amc*bm);

GG = roots([c1 c2 c3 c4]);

j = 1;
zee = [];
for i = 1:3
    if imag(GG(i))==0;
        zee(j) = GG(i);
        j = j+1;
    end
end

Z = min(zee);
v = R*T*Z/P; % m3/gmol

s1 = 2.3191*((3*(2*b1-b2)+b(2,2))/(4*(v-bm))-(log(1-bm/v)))-log(Z);
s2 = am/(R*(T^1.5)*bmj);
s3 = (b(2,2)/bmj-2*a1/am)*(log(1+bmj/v))-b(2,2)/(v+bmj);
phim = exp(s1+s2*s3);
%solubility eq
phif = (Psub/(y(1)*P))*(exp(vs*(P-Psub)/(R*T)));
%phif = (Psub/P)*(exp(vs*(P-Psub)/(R*T)));
%F = [phim-phif/y(1) y(2)-phim];
F = [phim-phif];
```

Appendix B.5 : Matlab command for obtaining the solubility

```
%File name: solubility.m
function solub = solubility
global T P CS h peb rp l eps u area k ke mtotal Z
vs = 0.000399; %m3/mol
Tb = 1173.33;  %K
%----------------------------------------------------------------------
--
%Solute's critical temperature and pressure and acentric factor
%Isoflavone
Tc_iso = 1496.907; %K
Pc_iso = 4035882;  %Pa
Vc_iso = 0.778*(10^-3); %m3/mol
w_iso = 1.594;

%Critical properties of carbon dioxide
Tc_CO2 = 304.12;      %K
Pc_CO2 = 73.7*10^5;   %Pa
Vc_CO2 = 94.07*10^-6; %m3/mol
Mw_CO2 = 44.01;       %kg/kmol
w_CO2  = 0.22;
%Co-solvent's critical temperature and pressure and acentric factor
%Critical properties of methanol
Tc_MeOH = 512.6;     %K
Pc_MeOH = 80.9*10^5; %Pa
Vc_MeOH = 118*10^-6; %m3/mol
Mw_MeOH = 32.05;     %kg/kmol
w_MeOH  = 0.50547735;

%Critical properties of water
Tc_H2O = 647.1;       %K
Pc_H2O = 220.6*10^5;  %Pa
Vc_H2O = 55.95*10^-6; %m3/mol
Mw_H2O = 18.015;      %kg/kmol
w_H2O  = 0.344861;
%MeOH:water = 80:20
y_MeOH = 0.8;
y_H2O = 1-y_MeOH;
%Properties of Co-solvents
Tc_MeOHco = Tc_MeOH*y_MeOH+Tc_H2O*y_H2O;
Pc_MeOHco = Pc_MeOH*y_MeOH+Pc_H2O*y_H2O;
Vc_MeOHco = Vc_MeOH*y_MeOH+Vc_H2O*y_H2O;
w_MeOHco  = w_MeOH*y_MeOH+w_H2O*y_H2O;
%----------------------------------------------------------------------
--
%solvent-cosolvent concentration (CO2:methanol+water = 92.2:7.8)
MeOHco_percent = CS;
CO2_percent = 100-MeOHco_percent;
MeOHco_ratio = MeOHco_percent/Mw_MeOH;
CO2_ratio = CO2_percent/Mw_CO2;
y_MeOHco = MeOHco_ratio/(MeOHco_ratio+CO2_ratio);
y_CO2 = 1-y_MeOHco;
%----------------------------------------------------------------------
--
Tc = zeros(2,1);
Pc = zeros(2,1);
Vc = zeros(2,1);
w  = zeros(2,1);
%Solvents
```

```
Tc(1) = Tc_CO2*y_CO2+Tc_MeOHco*y_MeOHco; %K
Pc(1) = Pc_CO2*y_CO2+Pc_MeOHco*y_MeOHco; %Pa
Vc(1) = Vc_CO2*y_CO2+Vc_MeOHco*y_MeOHco; %m3/mol
w(1)  = w_CO2*y_CO2+w_MeOHco*y_MeOHco;
%Isoflavone
Tc(2) = Tc_iso; %K
Pc(2) = Pc_iso;  %Pa
Vc(2) = Vc_iso; %m3/mol
w(2)  = w_iso;
%-------------------------------------------------------------------
--
%Define Psub - the sublimation pressure of the condensed phase (Pa)
delZb = 0.97;
Kf = 1.3;
delSb = Kf*(8.75+1.987*log(Tb));
%above eq use R = 1.987 cal/mol-K (only for Psub estimation)
Trb = T/Tb;
if Trb > 0.5
    if Trb < 0.6
        m = 0.8;
    else
        m = 0.36;
    end
else
    m=1.19;
end
group_Psub = 1-((3-2*Trb)^m)/Trb-2*m*((3-2*Trb)^(m-1))*log(Trb);
Psub = (exp(delSb*group_Psub/(1.987*delZb)))*760*0.00133322*100000;
%-------------------------------------------------------------------
--
%Esitimaiton of solubility
%P = 0;
%Pc1 = Pc(1);
%i = 0;
%for m = 1:1:7
    %P = m*10000000
    %i = round(1*m);
    %Pr(i) = P/1000000;

    options = optimset(...
        'MaxFunEvals'     , 100000000,...
        'MaxIter'         , 100000000,...
        'TolCon'          , 1e-100,...
        'TolFun'          , 1e-100,...
        'TolX'            , 1e-100);
format long
%Make a starting guess at the solution
%y(2)
%y0 = [10^-3; 10^-8];
y0 = [10^-3];
%Mohsennia Modarres Mansoori Equation of state (MMM-EOS)
[ym] = fsolve(@MMM,y0,options,T,vs,Tc,Pc,P,Psub);
%ymmm(i) = log10(ym(1));
solub = [ym(1)];
%end
%cftool(Pr,ymmm)
%R = 8.314;
%phif = (Psub/(ym*P))*(exp(vs*(P-Psub)/(R*T)));
%-------------------------------------------------------------------
--
```

CURRICULUM VITAE

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