

Solubility of *Swietenia Macrophylla* Seeds In Supercritical Carbon Dioxide Extraction

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Abstract. *Swietenia macrophylla* seeds oil has been claimed to possess anti-diabetic, antioxidant and other health benefit properties which have garnered the interest from food and pharmaceutical industries. This study aimed to determine solubility data of *S. macrophylla* seeds oil in order to understand the behaviour of the separation process which is fundamental in the designing process. Solubility of *S. macrophylla* seeds oil in supercritical carbon dioxide (SC-CO₂) was determined by using dynamic method at 20-30 MPa and 40-60°C at fixed CO₂ flowrate, 2 mL/min. The solubility of *S. macrophylla* seeds oil obtained were 1.93 to 4.77 mg (g CO₂)⁻¹ and was increased with pressure and temperature. In this study, the Chrastil, Adachi-Lu, del Valle-Aguilera, Gordillo and Sparks as semi-empirical models were tested to fit the experimental data. The Sparks model showed the best-fitted model for *S. macrophylla* seeds oil solubility data with an average absolute relative deviation (AARD) of 7.76% and a high coefficient of determination (R²) of 0.992. It can be concluded that the semi-empirical model give good correlation between observed value and predicted value.

1. Introduction

Swietenia macrophylla is one of the members of the family Meliaceae. *S. macrophylla* is popularly known as *S. mahagoni* in Indonesia due to local language. The characteristic of *S. macrophylla* fruit is pointing upwards to the sky from the tree and thus commonly called as "sky fruit" or in Malaysia, "Tunjuk Langit". *S. macrophylla* is one of the plants that are commonly used in the community far and wide particularly in a few nations which have high dissemination of this species. Over the years, traditional medicines extracted from the plant have been practiced by local neighborhood networks since a long time prior to treating diverse sorts of ailment, for example, diabetes without adverse effect. It is very popular for various treatments and has an example of properties that are very useful in pharmaceutical such as antibacterial, antioxidant, anti-inflammatory and antidiabetic activity[1].

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Conventional method consist of Soxhlet, sonification and maceration have a few drawbacks on the quality of extract which contain low concentration of extract and antioxidant activity. Thus, much better efficiency method extraction for solid materials was introduced and extensively studied for better separation of active compounds from herbs and other plants. One of the greatest enthusiasm since the most recent decade has been the use of supercritical carbon dioxide (SC-CO₂), as it has a close to ambient critical temperature. CO₂ supercritical properties above 31.1 °C and 7.38 MPa, which makes it a perfect solvent for extracting thermally delicate materials[2]. SC-CO₂ offers advantages such nontoxic, inexpensive, high selectivity and environmental.

To-date, there are limited existing reports on the solubility of *S.macrophylla* seeds oil in SC-CO₂ but solubility data is important as it gives valuable indication about the biological activity and behavior of the separation process which is fundamental in the designing process. In this paper, five semi-empirical density based models were used namely, Chrastil model, Adachi-Lu model, del Valle-Aguilera model, Gordillo model and Sparks model. The objective of this study is to apply semi-empirical modelling of extraction of *S.macrophylla* seeds oil and determined the best suited model based on solubility correlation between experimental data and model data.

2. Materials And Methods

2.1. Materials

S.macrophylla dry seeds were bought from local suppliers in Johor, Malaysia. The solvent used for supercritical fluid extraction is 99.9% purity of carbon dioxide (CO₂) supplied by Mega Mount Industrial Gases Sdn. Bhd, Johor, Malaysia. The seeds were carefully rinsed with tap water to remove undesired particles and dirt prior to drying. Then, the cleaned seeds were cut into small pieces and dried by using an oven at temperature 50°C for 7 days to reduce moisture content. After that, the seeds were ground by using a blender and sieved to approximately 0.50 mm of particle size. Prior to the experimental work, the dried sample was stored in -30oC freezer using a sealed container in order to maintain the quality of the sample.

2.2. Supercritical carbon dioxide (SC-CO₂) extraction

The experiment of SC-CO₂ was performed by using supercritical fluid extraction machine in the Center of Lipids Engineering and Applied Research (CLEAR), Universiti Teknologi Malaysia (UTM). The machine consists of CO₂ gas cylinder, CO₂ controller pump (Lab Alliance), 10 ml stainless steel extraction vessel, pressure gauge Swagelockk, Germany), automatic back pressure regulator (Jasco BP-2080 Plus) and a restrictor valve. The extraction was done for 120 minutes and the total yield of extracted oil was recorded every 15 min. Approximately 3 g of *S.macrophylla* seeds were placed into a 10 ml extraction vessel for a typical run. Solubility data of *S.macrophylla* seeds oil was determined using SC-CO₂ at flow rate 2 ml/min for 120 min with temperature (40-60°C) and pressure (20-30 MPa). Pressure was limited until 30 MPa due to constraints of equipment used whereas for extraction temperature was at 60°C for maximum as above that denatured bioactive compound in seeds oil.

2.3. Experimental Data of Solubility

As per future reference, solubility data is important in research field due to its value that represent the maximum solute concentration in the solvent phase at various parameter. The solubility of *S.macrophylla* seeds oil was determined at pressure of 20 MPa, 25 MPa and 30 MPa meanwhile temperature of 40°C, 50°C and 60°C. At each condition, the value of solubility was calculated at the initial slope of overall extraction curve by plotting mass of oil extracted (mg) vs mass of CO₂ used (g). The obtained solubility data are shown in Table 1 in (mg_{oil}/g_{CO2}).

3. Main Results

Table 1 shows the result on solubilities for *S. macrophylla* seeds oil ranged from 1.9343 to 4.7788 ($\text{mg}_{\text{oil}}/\text{g}_{\text{CO}_2}$). In this study, the increasing of pressure increased the solubility of extracts due to density effect. This finding correspond to the fundamental knowledge of SC-CO₂ where solubility becomes favorable at high pressure because of increasing CO₂ density. In addition to that, the intermolecular interaction between solute-solvent molecules getting higher as the density CO₂ increased which enhanced the solvent strength to dissolve solute. The result on the effect of pressure on solubility of *S. macrophylla* seeds oil through SC-CO₂ extraction is in agreement with studies conducted by other authors[2,3]. Temperature has complex effect on solubility where it can have two opposing effects due to the combination of variables, density and vapor pressure. The vapor pressure of solute increases with temperature resulting higher solubility, however at the same time, density of CO₂ decreases hence lower the solvating power. In this study, it also can be observed that the solubility of *S. macrophylla* seeds oil increases with temperature. As the temperature increases, the vapor pressure and diffusivity of solute also increases thus increasing the solubility of solute. Similar results were reported by several authors in their extraction of plant materials using the SC-CO₂ method[4,5]. There is no crossover effects in the extraction of oil from *S. macrophylla* seeds. Crossover pressure or retrograde vaporization is a point where the plot intercept with each other indicated the boundary between effect of solvent density (pressure) and solute volatility (temperature). The crossover phenomena happened due to difference in composition of extracts such as free fatty acid, mono-, di-, and triglycerides[6]. Difference components of extract have different volatilities and solubilities in the solvents.

3.1. Mathematical Modelling with Semi-Empirical Models

The optimum fitting parameters for the correlation were obtained using the least AARD% and coefficient of determination (R^2) between model and experimental data. Figure 1 shows logarithmic relationship between solubility of *S. macrophylla* seeds oil in SC-CO₂ and density of pure SC-CO₂ of the semi-empirical models used i.e. Chrastil, Adachi-Lu, del Valle-Aguilera, Gordillo and Sparks et al. models while the fitted parameters were shown in Table 2 for each correlation. In this table, correlating solubility of *S. macrophylla* seeds oil with semi-empirical density based model of Chrastil

Table 1. Measured solubilities of *S. macrophylla* seeds oil in SC-CO₂

Run	T (°C)	P (MPa)	Solubility($\text{mg}_{\text{oil}}/\text{g}_{\text{CO}_2}$)			Av. Solubility	Std. Dev	Std. Error
			1	2	3			
1	40	20	1.9048	1.8501	2.048	1.9343	0.1021	0.0589
2	40	25	2.9487	2.5031	3.0659	2.8393	0.2969	0.1714
3	40	30	3.7778	3.3914	3.8638	3.6776	0.2516	0.1453
4	50	20	2.7027	2.7282	2.5818	2.6709	0.0782	0.0451
5	50	25	3.3333	3.0427	3.6674	3.3478	0.3126	0.1805
6	50	30	3.9683	3.9545	3.9846	3.9691	0.1507	0.0870
7	60	20	3.0679	2.9559	3.1070	3.0466	0.0784	0.0453
8	60	25	3.5294	3.5532	3.6400	3.5742	0.0582	0.0336
9	60	30	4.8000	4.5709	4.9655	4.7788	0.1982	0.1144

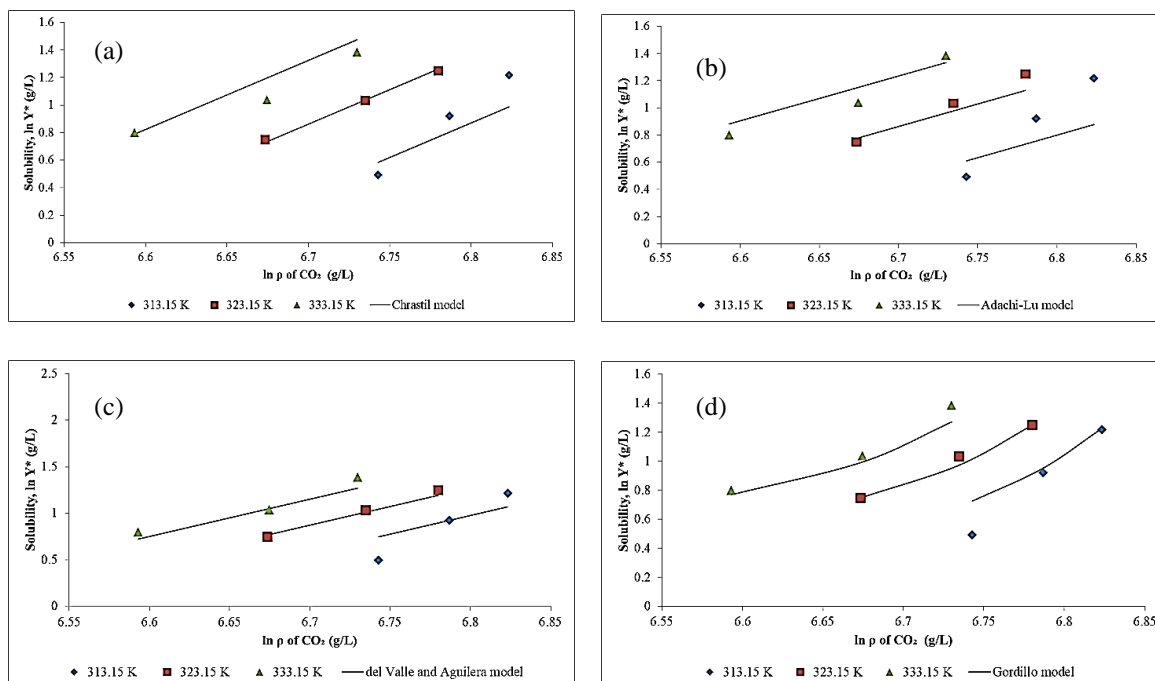
model, Adachi-Lu model, del Valle-Aguilera model, Gordillo model and Sparks model with average AARD (8.47%, 12.56%, 10.15%, 8.16% and 7.76%) and average coefficient of determination (0.992, 0.992, 0.992 and 0.992). All 5 semiempirical models used showed approximately the same value of average R^2 , 0.992 which can be claimed that those models have high correlation between model data and experimental data, only AARD value were different between these models.

In general, the more parameters the model has, the more accurate the correlations are. Sparks equation had successfully correlated the solubility of *S.macrophylla* seeds oil data with lowest AARD and coefficient of determination. The reason was that Sparks combined both parameters by Adachi-Lu and del Valle Aguilera while considered the impact of both density and temperature. A comparison between Gordillo model and Sparks model demonstrates slight difference of AARD value between them. This is because Gordillo had 6 parameters in his equation which agree with statement before which stated that more parameters, more accurate. Similarly, in the solubility of 27 different pharmaceutical solutes in supercritical carbon dioxide, Sparks equation provides the best fit to the solubility data for those kind of solutes in SC-CO₂[7].

Table 2. Solubility fitting constant for five semi-empirical density based correlations

Parameters	Chrastil model	Adachi-Lu model	del Valle-Aguilera model	Gordillo model	Sparks model
k	5.015457	3.15	4.002574	-	3
a	-4987.45	-4000	-3000	1.47E-11	-4000
b	-17.3081	-8	-10	3.51E-09	-8
c	-	-	-16.6616	1E-05	-8.2
d	-	0.000025	-	1.00E-18	0.00025
e	-	1E-10	-	4.73E-09	1.00E-18
f	-	-	-	3.33E-06	-
AARD (%)	8.471273	12.56246	10.15365	8.161415	7.760097
R ²	0.992011	0.992068	0.992011	0.992	0.992418

The parameters of k , a and b in equations represent average number of molecules that form the solvate complex, enthalpy of extraction process which are solvation and enthalpy of vaporization and molecular weight and melting point of the solute. However, Adachi-Lu had inserted constant d and e in equation indicating high influence of density in extraction process whereas del Valle-Aguilera had additional of constant c in equation with assumption that temperature was the biggest influence in the extraction process[8–10]. Other than that, Sparks combined both additional constant from Adachi-Lu and del Valle-Aguilera into one equation with consideration that temperature and density have influence in extraction process[11]. Besides that, Gordillo equation was difference in term of structure compared to those four models with assumption pressure and temperature has big influence in the semiempirical modelling with additional constant f [12].



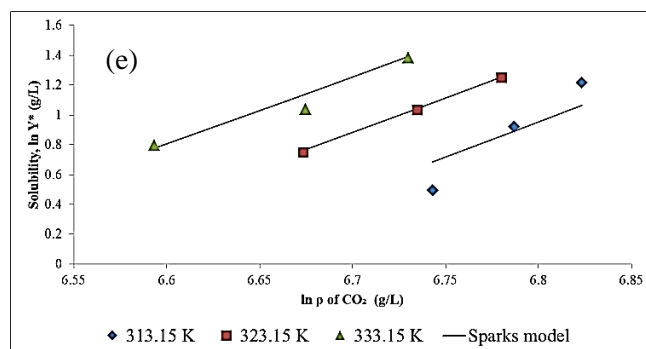


Figure 1. Modelling of semi-empirical models using (a) Chrastil model (b) Adachi-Lu model (c) del Valle-Aguilera model (d) Gordillo model (e) Sparks model

If the AARD value below 12%, it can be concluded that the model give good agreement with the experimental data[13]. Adachi-Lu gave the highest AARD value which was 12.56%, indicated that this model was unsuccessful to correlate the solubility of *S.macrophylla* seeds oil compared with another semiempirical model. This finding contradicted to finding in kernel lipid study where Adachi-Lu had successfully correlated with solubility from experimental data compared with Chrastil and del Valle-Aguilera models.

Chrastil and del Valle-Aguilera model were given in Figures 1(a) and 1(c), while the coefficients of the model were shown in Table 2. The equations were related to high temperature effects which were exothermic or endothermic. In short, high value of k show better efficiency of SC-CO₂ in extracting the solute. Furthermore, parameter b indicates that the solute was extracted[14]. In addition to that, value of d and e parameter showed the effect of density in extracted the solute from *S.macrophylla* seeds oil. It also can be observed that effect of adding parameter does not too significant between modified equation and original equation for AARD and R² value.

4. Conclusion

Under isotherm conditions, increasing of pressure increased the solubility of *S.macrophylla* seeds oil and no cross-over was observed on the solubility of *S.macrophylla* seeds oil. In addition to that, at constant pressure, the solubility of *S.macrophylla* seeds oil increased at elevated temperature although the extracts density was reduced. To correlate the experimental solubility data in mathematical term, five density-based semi-empirical models were proposed; Chrastil, Adachi-Lu, del Valle-Aguilera, Gordillo and Sparks models. The resulting average values of AARD% were Chrastil model (8.47%), Adachi-Lu model (12.56%), del Valle-Aguilera model (10.15%), Gordillo model (8.16%) and Sparks model (7.76%). Based on the lowest deviation, AARD value between experimental and calculated solubility (7.76%) and high coefficient of determination, R² (0.992) produced by Sparks model, this shows that Sparks model represent the experimental solubility behavior better than the other models. The text of your paper should be formatted as follows:

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