Correlating Solubility of Piperine Extraction Using Empirical Models

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***Abstract*— Bioactive compound, which known as piperine was extracted from Malabar black pepper at temperature of 313, 323 and 333 K and operating pressure of 200, 250 and 300 bar in supercritical carbon dioxide ($SCCO_2$). The experimental data was obtained from literature to be analyzed with the application of four empirical correlation models which are Chrastil's model (CH), Del Valle and Aguilera's model (DVA), Kumar and Johnston model (K-J) and Sung and Shim model (S-S) to estimate the solubility data. The comparison of the data was discussed and based on the correlated results, S-S model performed better among the four models and proved the effect of temperature and pressure on the solubility of piperine in $SCCO_2$. The thermodynamic properties, total enthalpy, ΔH of the solid solute was obtained.**

Keywords*— Empirical correlation, piperine, solubility, supercritical carbon dioxide

I. INTRODUCTION

Black pepper is also known as Piper nigrum L. is an aromatic plant that belongs to Piperaceae family which widely known as a valuable spice and prized for its content in alkaloids, essential oil and terpenes respectively. Derived from the dried unripe berries and it gives peppercorn or well known as black pepper [1]. The processing into black pepper is depending on the harvest time and the processing. Two main components exist in black pepper are volatile oil and pungent compounds. The volatile oil content is equivalent to 2.0-2.6% and black pepper also contain as much as 6% to 13% of oleoresin. The study of the pungency of the oil has been investigated since the early nineteenth century. The pungency of black pepper was caused by the presence of piperine [2]. Black pepper is universally used as a taste and flavor enhancing food agent and effectively used in medical field worldwide and act as one of the most important constituents due to its beneficial influence in antioxidant, anticancer, gastrointestinal, anti-inflammatory, antidiabetic, antipyretic, and antihypertensive, improves digestion and promotes intestinal health [3].

Recovery process of black pepper oil is traditionally obtained by steam distillation, solvent extraction and hydro-distillation which have a number of disadvantages such as thermolabile components can be broken down during the extraction process, hydration reaction of certain chemical components, and requirement of long distillation time and the need of post-extraction in order to eliminate the water content. Chemical alteration of these heat-sensitive compounds may occur as it involves high temperature. Thus, this may degrade the quality of the extracted oil [4,5]. Solvent extraction or known as soxhlet is viewed as serious threat to the environment as it is toxic and pollutant organic solvents. On the other hand, hydro-distillation is a very simple extraction process, it has many drawbacks such as thermal degradation, hydrolysis and solubilization in water of some contents that can alter the flavor and fragrances profile [6].

In order to overcome the disadvantages in extraction process, researchers adopt a new sustainable process which environmentally safe and rapid extraction. Hence, the supercritical fluid technology (SFT) is an attractive technology which effective, non-toxic and require shorter time of extraction. Extraction process by using supercritical fluids (SCFs) has been widely used because of the ease of separation of the simple expansion between the solvent and extracted solute [7]. The densities are liquid-like and yet the characteristics of the superior mass transfer is higher if compared to liquid solvents and the surface tension is very low, hence enable easy penetration into the porous of the solid matrix in order to extract the solute. The properties of rapid expansion of supercritical carbon dioxide ($SCCO_2$) causes the removal process become easier by simply reducing the pressure, and it leaves no trace and also environmentally benign which the CO_2 used is a by-product from industrial processes or brewing and cause no extra emissions [8].

With the purpose of scale up design, thermodynamic data are needed in designing of equipment and equipment sizing. There are two most widely used method which is known as equations of state (EOS) and empirical correlations. However, in some cases, EOS application is not recommended due to the needs of several properties such as critical pressure and temperature, and also acentric factor which cannot be easily measured through experimental work [9]. Hence, the necessity of estimated parameters is needed in obtaining predicted solubility which introduce along the errors. Furthermore, EOS based model needs large and complicated computational method and the properties of the solid and the lack of data on complex structural compound, produced and error in the estimation. Hence, correlation of solubility data in the determination of the most efficiency empirical correlation in extraction by using $SCCO_2$ can be applied in order to overcome the complexities.

A reliable correlation can be utilized to estimate the solubility of the piperine in $SCCO_2$ since the experimental measurement of solubility is tedious and also time consuming at different conditions. Most common empirical models are density-based models which providing a correlation between solubility of solute and density of $SCCO_2$ and only need independent variables such as temperature pressure and density of $SCCO_2$ [10]. Each type of model can be represented by experimental extraction curves by fitting the kinetic coefficient to the fluid, the effectiveness of coefficient transport in the solid and axial dispersion coefficient obtained from the laboratory experiments [11]. The goal of the model fitting for the extraction process is to obtain a quantitative

representation of the process with a simple system of equations with few parameters affecting the extraction process. With the parameters chose for the process in such model, it is sufficient to calculate the result of an extraction which are distribution of equilibrium between solute and SCFs solvent, diffusion in the solid and mass transfer from the surface of the solid to the bulk of the fluid phase [12].

In this work, solubility of piperine was obtained from literature were then correlated by four empirical models. Comparison between these four models were also investigated to provide fundamental knowledge for the extraction process of piperine in $SCCO_2$.

II. METHODOLOGY

A. Method

Selected models in correlating piperine solubility experimental data, Chrastil's, Del Valle and Aguilera's, Kumar and Johnston and Sung and Shim models, were applied. These four models were described to be appropriate for the range of temperature of the desired extraction process in this experiment. These models were mathematically simple and easy to apply as all the models represent a linear relation between solubility and solvent density and to show good adjustment to experimental values.

Chrastil's model (CH)

Chrastil's model shows linear relation of solubility, solvent density and temperature of the process which considers the formation of a solvation complex between solvent and also solute molecules in the equilibrium. It described the solubility which solely density-dependent, disregarding the variations with the extraction temperature condition [13].

$$\ln y = k \ln \rho + \frac{a}{T} + b \tag{1}$$

The y represents the solubility of solute, T is the temperature of the system (K) and ρ is the solvent density. a, b and k in the equation represent the adjustable constants of the model that are specific for each solute-supercritical solvent pair and not dependent on temperature and pressure. Determination of these parameters can be done by performing nonlinear regression fitting of the model toward actual solubility data. The k constant represents the number of CO_2 molecules present in the complex solute-solvent while a= ΔH/R and b parameters indicate the vaporizing enthalpy and molecular weight dependents.

Del Valle and Aguilera's model (DVA)

This Del Valle and Aguilera model, in equation (2.3), proposed adequate for temperature in a range of 293 K to 353 K and pressure varying from 150 bar to 880 bar. It is also the modification of the Chrastil's model and the changes were based on the behavior of the adjustment of several vegetable oils solubility data such as corn, soy and sunflower However, it did not improve the accuracy but it did successfully predict the solubility of vegetable oil [14].

$$\ln y = k \ln \rho + \frac{a}{T} + \frac{b}{T^2} + c \tag{2}$$

Where a, b c and k are Del Valle and Aguilera model constants.

Kumar and Johnston model (K-J)

The model presented by Kumar and Johnston is a thermodynamic model which to correlate between nonvolatile solute in SCFs and the density of the solvent. In order to obtain linear relationship with ln y, Kumar and Johnston pointed out that, density (ρ) or ln ρ must be used as the independent variables. It was also stated that, in some cases, ln y was a system-dependant choice and cannot be validly generalized. Furthermore, slopes of the plots obtained depended on the isothermal compressibility and partial molar volume of solvent present in SCFs. The K-J model assumes that the solubility varies approximately according to solvent density in a linear fashion [15].

$$\ln y = k \rho + a + \frac{b}{T} \tag{3}$$

Where y is the solubility (mole fraction) of the solute present in SCFs while, a, b and k are the adjustable parameters which can be correlated from the experimental data. The parameter of b in K-J model is the same as the a parameter in the Chrastil's model which is defined as ΔHtotal/R

Sung and Shim model (S-S)

Sung and Shim (S-S) model is modified from the K-J model by considering the temperature influence on the solubility and changing the linear relationship into ln y-ln ρ plot and introduced a function of temperature for constant c in K-J model as c=c+d/T in S-S model. Sung and Shim pointed out that the ln y-ln ρ plot solubility isotherm is linear, however the slopes of the slopes were decreasing with temperature [16].

$$\ln y = a + \frac{b}{T} + c \ln \rho + \frac{d \ln \rho}{T} \tag{4}$$

Where a, b c and d are the adjustable parameters

Average Absolute Relative Deviations (AARD)

Next, the average absolute relative deviations (AARD) was calculated as an accuracy criteria for the comparison between both experimental and modeled values [17].

$$AARD = \frac{100}{n} \sum \frac{y^{experimental} - y^{calculated}}{y^{experimental}} \tag{5}$$

Where,

n = number of data

$y^{experimental}$ = solubility data obtained from experimental respectively at i^{th} condition.

$y^{calculated}$ = solubility data obtained from model respectively at i^{th} condition.

Standard Deviation (SD)

The standard deviation was calculated which to represent the discrete degrees of the AARD value for each model correlated.

$$SD = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}(x_i - \bar{x})^2} \quad (6)$$

Where the x_i is the value of AARD (%) of each model, $\bar{x}$ is the average of AARD (%) of each model and n is the number of data [18].

III. RESULTS AND DISCUSSION

A. CORRELATION WITH EMPIRICAL MODELS

Table 1: Correlated results of Empirical models for the solubility of piperine in $SCCO_2$

Model	a	b	c	d	k
Chrastil	-684.67	0.52367	-	-	0.22332
Del Valle	-683.33	0.5000	0.52893	-	0.22180
Kumar and Johnston	-0.09997	-46.23	0.00010	-	-
Sung and Shim	-0.23224	10.16	0.00554	0.00100	-

The correlated results from using four different empirical models which were applicable to the experimental conditions for the data obtained from literature were listed in Table 1. The correlation constants in empirical models were calculated by using Microsoft Excel 2013 software which provide the best linear fitting for the empirical models and calculated the values for each parameters in the fitting line. Based on results obtained, the application of these models in order to correlate the solubility data was proved to be successful. For comparison of the accuracy between the empirical models, the AARD (%) values calculated based on the equation 5 are presented in Table 1.

The higher the number of parameters present in each model, the higher the accuracy of the correlation models, hence, this is one of the important factors of the precision of the correlation [19]. Usually, the more parameters, the calculated results will have high precision and the better the results calculated. The values of constant parameter, k in CH and K-J models representing the number of $SCCO_2$ associates with one solute molecule in the solvated complex to the total heat ΔH_{total} of the solute [20]. Based on the results in Table 1, the k value in CH and DVA model shows that the interaction between piperine and $SCCO_2$ molecule. There were about 0.2 about CO_2 molecules clustered around the one molecule of piperine in the solvated complex. While the b value in CH model depends on the molecular weights of the piperine and $SCCO_2$.

The thermodynamic properties can be obtained through calculation of the parameter of a in CH model and b in K-J model. The total enthalpy, ΔH can be calculated from equation of a is equivalent to $\Delta H_1/R$ and b equals to $\Delta H_2/R$. ΔH_1 equals to -5692.35 J/mol whereas, ΔH_2 equals to -41.99 J/mol. Both ΔH_1 and ΔH_2 are total enthalphy. The average of ΔH is expressed as summation of ΔH_1 and ΔH_2 divided into two. Therefore, the ΔH is equivalent to -2867.27 J/mol. The thermodynamic properties are useful in scaling up and designing extractor. Furthermore, the data can be used to calculate the enthalpy of sublimation, enthalpy of solvation of piperine and to determine the diffusion rate of piperine in other SCFs [18].

The advantage of using empirical models in correlating the solubility of piperine was all the parameters required can fit all experimental data regardless of the operating extraction temperature without the need of critical properties estimation of the solute. Furthermore, it speeds up the development of $SCCO_2$ technology by proposing the most suitable empirical model and provide a better understanding about the dissolution phenomenon and also to predict solubility of piperine at interested pressure and temperature. According to plots of each model, it clearly shows the linear correlation between the piperine solubility and $SCCO_2$ density at all conditions in extraction process. Density of $SCCO_2$ is higher at low temperature as seen from Fig. 1, 2, 3 and 4. Thus, density was a measure of solvating power of the $SCCO_2$ whilst varies of temperature and pressure controlled the solubility and separation of the piperine.

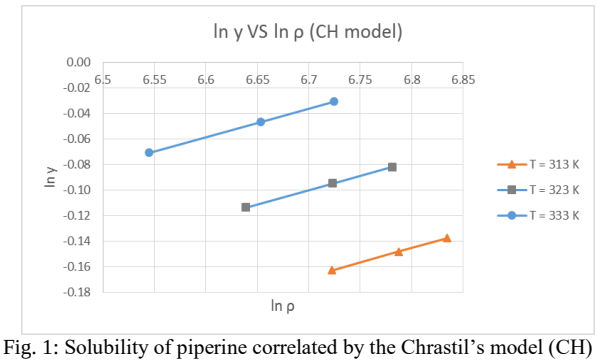

Fig. 1: Solubility of piperine correlated by the Chrastil's model (CH) at temperature of 313 K, 323 K, and 333 K

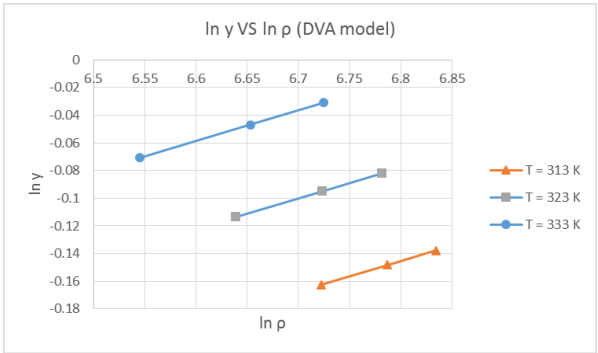

Fig. 2: Solubility of piperine correlated by the Del Valle and Aguilera's model (DVA) at temperature of 313 K, 323 K, and 333 K

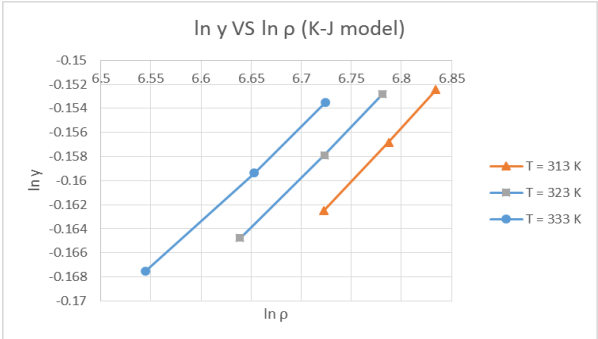

Fig. 3: Solubility of piperine correlated by the Kumar and Johnston model (K-J) at temperature of 313 K, 323 K, and 333 K

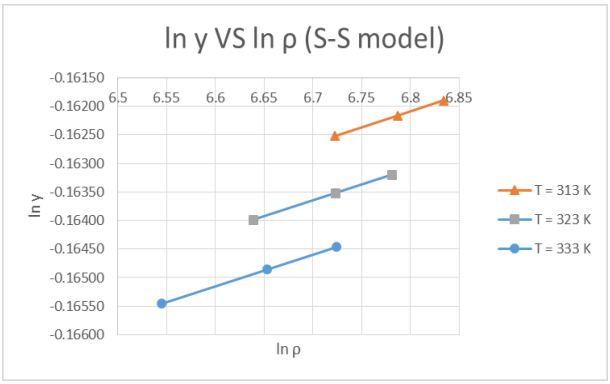

Fig. 4: Solubility of piperine correlated by the Sung and Shim model (S-S) at temperature of 313 K, 323 K, and 333 K

In Figure 1, 2, 3, and 4 shows the relationship between piperine solubility and the $SCCO_2$ density according to model expression. Both solute solubility and density of solvent are closely related to the precision of all four models. All the four models plots show good agreement between the experimental and the correlated solubility values. The plots proved that the solubility of piperine increased with the increasing of density of $SCCO_2$. However, as shown in Figure 1, 2 and 3, the CH, DVA and K-J log-log plots were decreasing with temperature. On the other hand, S-S slopes shows the relationship between the temperature and the solubility of piperine was not linear to each other. The log-log plots increase while the temperature decreased which was shown in Figure 4. Sung and Shim pointed out that the linear solubility isotherm and discussed about the effects of temperature on solubility hence, modified the K-J empirical correlation which containing temperature effects.

The solubility of piperine increased with the increasing of temperature which was shown in Figure 1, 2 and 3. Pressure and temperature were used as indicators to determine the solubility of piperine due to the immeasurability of the probability of collision between the piperine and $SCCO_2$ molecules. Hence, the differences between these 4 models (CH, DVA, K-J and S-S) are the complexity between the solubility of piperine and the density of $SCCO_2$. The experimental data from literature were better correlated by using the latest model, which is the S-S model than the CH, DVA and K-J models. The CH, DVA and K-J models correlated the solubility experimental data according to the relationship between the logarithm of piperine solubility (ln y) and the $SCCO_2$ density (ln ρ) and the results of these expressions was proven to be linear. While S-S model considered the temperature and pressure changes, the relationship between the logarithm of piperine solubility (ln y) and the density of $SCCO_2$ (ln ρ) which is more complex than linear. As shown in Figure 4, the slopes of the solubility correlated values were not parallel towards each other and also decreasing with the increasing of temperature.

Table 2: AARD (%) and SD values for each model

Model	AARD (%)	SD
Chrastil	6.9928	2.448
Del Valle	6.9897	2.447
Kumar and Johnston	5.7786	2.023
Sung and Shim	5.6075	1.963

According to the value The AARD (%) values calculated from the empirical models of S-S, K-J, DVA and CH show the increasing value from 5.6075, 5.7786, 6.9897 and 6.9928. The AARD value indicates that the satisfactory correlation results which have been achieved for each empirical models. However, it shows that the CH model has the highest value of AARD (%) which was equivalent to 6.9928 and this shows that this correlation model was the least suitable to correlate the piperine solubility in $SCCO_2$. However, the modified of K-J equation, S-S scores 5.6075% of AARD and the lowest value among all the four empirical models which shows it has the most better performance and agreement with the experimental solubility data. When the S-S model provides the minimum value of AARD (%) respectively, the S-S model can be used to predict other operational condition.

From the four models applied to the experimental data obtained from literature, CH model is the most common empirical model used which was based on three adjustable parameters. As stated in Table 2, the SD calculated for CH model was equivalent to 2.448% respectively. However, the modified model from CH model, which is DVA model, scored 2.447% of SD value. K-J model which has three parameters, similar to CH model scored 2.023%. Compared to S-S models which has four adjustable parameters, and also the modified model from K-J improved from 2.023% to 1.963%. The four parameters of both DVA and S-S improved the accuracy of the empirical models expression. Moreover, the S-S model provides better correlated result and predictive capability with more adjustable parameters and included temperature effects on solubility which differed from the other three models (CH, DVA and K-J). From the results tabulated in Table 2, in general, the models that have more adjustable parameter have lower values of SD which proved that the accuracy of the models is depending on the expression of the empirical models and the relation between piperine solubility and $SCCO_2$ density. The complexity of the empirical models and the increase of number of adjustable parameter enhanced the accuracy of the models. The original models, CH and K-J if compared to the modified models, DVA and S-S give better fit than the original models. Furthermore, the models that was developed earlier (CH (1982), DVA (1988), and K-J (1988)) did not consider the complexity correlation which includes the effect of operating temperature and pressure until the S-S model was developed in 1999.

IV. Conclusion

The experimental solubility data range of piperine extracted from 0.78 to 0.99 mg/kg in $SCCO_2$ at temperature of 313 K, 323 K and 333 K at operating pressure of 200 bar, 250 bar and 300 bar obtained from literature was correlated by applying four density-based empirical correlations, which are Chrastil's (CH), Del Valle and Aguilera's (DVA), Kumar and Johnston (K-J) and Sung and Shim (S-S) models. From the correlated results, the AARD (%) values of CH, DVA K-J and S-S are 6.9928%, 6.9897 %, 5.7786 % and 5.6075 % with SD of 2.448, 2.447, 2.023 and 1.963. The latest model, S-S model with the minimum AARD (%) value that indicates the satisfactory correlation results which have been achieved for each empirical models which has the highest number of parameters present and containing temperature effects, thus, increased the accuracy of the correlation models was employed to predict the solubility of piperine in $SCCO_2$. This matched with the objective of the study to determine the most suitable correlation to predict the solubility of piperine in $SCCO_2$. S-S models that have more adjustable parameter have lower values of SD has proven that the accuracy of the models is depending on the expression of the empirical models and the relation between piperine solubility and $SCCO_2$ density The thermodynamic properties of solid solute were obtained, which was equivalent to -2867.27 J/mol which can be applied in designing extractor and comparison between SCFs based on diffusion rate of piperine. All the correlated results obtained in this study can be used to scale up the SFT equipment from laboratory scale to larger scale and to determine the solubility at a wide range of operating pressure and temperatire without experimentally determination.

ACKNOWLEDGMENT

I would like to express the deepest appreciation to Faculty of Chemical Engineering and Universiti Teknologi MARA (UiTM) for the support of this research.

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