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Evaluation of Density-Based Models for the Solubility of *Sclerocarya Birrea* Kernel Oil in Supercritical Carbon Dioxide and the Formulation of a New Model

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Solubility data obtained from literature for *Sclerocarya birrea* kernel oil in supercritical carbon dioxide (CO_2) were correlated using six semi-empirical density-based models viz. Chastril, del Valle and Aguilera (DVA), Adachi and Lu (AL), Sparks et al., Kumar and Johnston (KJ), and Mendez-Santiago and Teja (MST). The determination coefficient values (R^2) ranged from 0.72 to 0.95. The average absolute relative deviations (AARD%) ranged from 15.53 to 0.049. A comparison was made between all six semi-empirical density-based models, and it was concluded that the MST model provided an improved and better fit than the other models investigated. After examining each of the six models under investigation, an improved model is proposed, which can characterize most of the findings taken into account about *Sclerocarya birrea* kernel oil yield.

1. Introduction

Addressing what we consume and how it is produced is essential to eradicate the adverse effects of climate change and pollution (Ritchie et al., 2017). The deterioration of the environment has become a major cause of concern. Consumers are becoming aware of the dying planet and thus not only desiring nutritious and healthy food-based products but also making sure that it is produced with high levels of food safety and the use of green technologies (Barba et al., 2016; Lavenburg et al., 2021). The current energy crisis and environmental restrictions have also sparked an interest in the expansion of renewable fossil fuels that are not derived from petroleum matrices (Sinha et al., 2012). It is, therefore, imperative to investigate alternative sources of fossil fuels, such as the creation of biofuels from vegetable oils to overcome the challenge mentioned above (Ntalikwa, 2021). Marula (*Sclerocarya birrea*) oil is one of the available alternatives that can help alleviate the burden placed on fossil fuels (Ramanujan, 2008). The marula tree belongs to the Anacardiaceae family and is endemic to South Africa and neighboring countries (Mokgolodi et al., 2011). Traditional knowledge holders in South Africa and other neighboring African countries utilize almost all the major constituents of the marula tree for various applications (Vermaak et al., 2011). In addition, Marula oil is extracted from the plant's kernels and contains a high concentration of fatty acids viz. oleic, myristic, palmitic, and stearic acid. The extracted oil can therefore be utilised as an ingredient in cosmetic products because of its moisturizing, hydrating, and occlusive qualities (Komane et al., 2015). Marula oil can also be used instead of sunflower oil in cooking because of its high mono-unsaturated oleic acid content (Mashau et al., 2022).

These oilseeds can be processed by mechanical, enzymatic, and chemical extraction methods; however, supercritical fluid extraction (SFE) has emerged as one of the most attractive alternatives to natural product extraction due to its efficiency and environmental friendliness. It is also regarded as a mature technology because it has been around for a long time and most of the early flaws and inherent problems have been eliminated and mitigated (Valverde et al., 2020). The global rise of industrial SFE plants and patents is evidence of this fact (Ahmad et al., 2019). This is because, in contrast to conventional extraction procedures, the technique typically involves moderate temperatures, quick extraction times, and minimal solvent quantities (Mohamed Zahari and Salleh, 2017).

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Thus, the numerous limitations associated with traditional extraction techniques, such as the need for significant volumes of solvent, time consumption and waste treatment, can be overcome with SFE (Sunarso and Ismadji, 2009). As a result, SFE has the potential to enhance functional and/or nutritional qualities, which can be applied to novel food recipes.

2. Review of density-based models

The earliest known density-based empirical model was developed by Chrastil (Kostrzewa et al., 2019). Chrastil's model is a density-based model that considers the solvent's temperature and density; it is widely utilised to determine the solubility of substances in the solvent (Martinez, 2007). The empirical model is given by equation 1 below (Chrastil, 1982).

$$S = \rho^k e^{\frac{A}{T}+B} \quad (1)$$

Where S is the concentration of the solute in the solvent in $g.L^{-1}$, ρ is the density of the solvent in $g.L^{-1}$, T is the temperature of the solvent in Kelvin, k is a constant which is based on the molecular bonding at equilibrium conditions, A is an extension of the enthalpy and B is an extension of the molecular weights of the solute, solvent and constant k.

Del Valle and Aguilera (1988) developed an improved model to accurately determine the solubility of substances with greater precision due to the shortcomings of the Chastril model. The model by del Valle and Aguilera can produce more accurate results since it accounts for variations in the solute's heat of vaporization. The model is given in equation 2 below, where C is the model parameter that can be determined by manipulating the experimental data.

$$S = \rho^k e^{\frac{A}{T}+B+\frac{C}{T^2}} \quad (2)$$

It should be noted that the temperature and solvent density are not considered by parameter k in the models of Chastril and DVA. Due to this, Adachi and Lu (1983) modified the model by changing the exponential density term into a quadratic function that considers both the temperature and solvent density. The model is provided in equation 3 below, where D and E are the model constants.

$$S = \rho^{(k+D\rho+E\rho^2)} e^{\frac{A}{T}+B} \quad (3)$$

The solvent's density was considered in the Adachi and Lu model. However, DVA's model modified Chastril's model to account for the solvent's temperature, indicating that density and temperature were not considered in one model. As a result, Sparks et al. (2008) devised a model that considered these two conditions and is provided in equation 4 below.

$$S = \rho^{(k+D\rho+E\rho^2)} e^{\frac{A}{T}+B+\frac{C}{T^2}} \quad (4)$$

A new model was developed by Kumar and Johnston (1988); however, the solubility is expressed as a mole fraction (y_2) of the solute in the solvent. Plotting the natural logarithm of the mole fraction versus the solvent density will result in a straight-line graph. The link between the partial molar volume of the solute and the solvent's compressibility coefficient is explained by the slope of the straight line.

$$ln(y_2) = \frac{A}{T} + B + C\rho \quad (5)$$

The model proposed by Mendez-Santiago and Teja is also popular and has been widely adopted (Bian and Tang, 2011). Mendez-Santiago and Teja (1999) included the sublimation pressure in the model, which is elicited from the theory of dilute solutions by van't Hoff. According to van't Hoff, a gas's pressure is equivalent to the solution's osmotic pressure (Huang and Xie, 2012). However, if the sublimation pressure of the solute is unknown, then the two-constant Antoine equation replaces the sublimation pressure (Sparks et al., 2008). The MST model is given in equation 6 below, where P represents the pressure in mPa.

$$\ln(Py_2) = \frac{A}{T} + B + C\frac{\rho}{T} \quad (6)$$

3. Computational methods: Semi-empirical density modeling experimental design

The semi-empirical density-based models were correlated from literature data on *Sclerocarya birrea* kernel oil yield in supercritical CO_2. From the literature data obtained, experimental work was conducted in which the extraction pressure was adjusted between 250, 350, and 450 bar while the extraction temperature was adjusted between 40, 60, and 75 °C.

The particle size was constant at 850 µm across all experimental runs, while the extraction time remained at 270 minutes. The carbon dioxide flow rate was steady at 30 kg CO_2.hour^{-1} for all experimental runs. Each set of extraction conditions was repeated three times and the average oil yield at each set of extraction conditions was then used for optimization purposes (Taseski, 2015). Using the models of Chastril, DVA, AL, Sparks et al., KJ, and lastly MST; six empirical models have been correlated for the solubility of marula oil in supercritical CO_2. The model constants were determined by using the solver feature on Microsoft Excel 2016. The least squares regression approach was combined with the solver function by selecting the squared difference between the experimental and predicted solubility for each run. A cumulative summation for all of the experimental runs was then performed. When the squared sums for each iteration were minimized, the solver function was then used to determine the values of the constants. The accuracy of the models was assessed by calculating the determination coefficient value (R^2) for each model as depicted in equation 7 below. Additionally, the AARD% was computed by taking into account for both the experimental and model-predicted solubility as shown in equation 8 below, where N represents the number of experimental runs, yi^{calc} and yi^{exp} represents the calculated and experimental values.

$$R^2 = 1 - \frac{sum\ of\ squares\ of\ residuals}{total\ sum\ of\ squares} \tag{7}$$

$$AARD\% = \frac{100}{N}\sum_i^N \left|\frac{y_i^{calc} - y_i^{exp}}{y_i^{exp}}\right| \tag{8}$$

4. Results and Discussion

Semi-empirical density models viz. Chrastil (1982), del Valle and Aguilera (1988), Adachi and Lu (1983), Sparks et al. (2008), Kumar and Johnston (1988), and finally Mendez-Santiago and Teja (1999) were modeled to determine the accuracy of the calculated solubilities to that of the experimental data. The models' most optimum constants were determined using the least squares regression method. In the case of Chrastil's model, a log-log plot of solubility versus density was graphically represented and the constants were extracted from the graph. Finally, the R^2 and AARD% were calculated for each model to determine accuracy. Refer to Table 1 below which depicts the results.

Table 1: The correlated parameters obtained for the six semi-empirical density models.

	Chrastil, 1982	Del Valle and Aguilera, 1988	Adachi and Lu, 1983	Sparks et al., 2008	Kumar and Johnston, 1988	Méndez-Santiago and Teja, 1999
k	5.33	5.33	5.33	5.33	-	-
A	-1960	-1967.57	-2013	-2023	-1587.63	-6652.35
B	-28.18	-28.20	-27.90	-27.59	-7.57	6.80
C	–	0.00008.13	–	-2516	0.0051	3.37
D	–	–	0.00025	-0.0005	–	–
E	–	–	-0.00000031	0.000000450	–	–
R^2	0.87	0.87	0.75	0.72	0.94	0.95
AARD %	7.94	7.92	14.90	15.53	5.12	0.049

The results demonstrate that all the models under investigation performed well as depicted in figures 1 to 3. However, The MST model proved to represent the experimental data best when compared to the five models in the pressure and temperature ranges studied. According to Kostrzewa et al. (2019), larger R^2 values approaching 1 and lower AARD percentages is an indication that the model correlates well with the experimental data. With the above-mentioned statement, the R^2 and the AARD% was calculated to be 0.95 and 0.049 for the model of MST respectively. Conversely, the model presented by Adachai and Lu (1983) followed by Sparks et al. (2008) fared the worst when compared to the actual experimental results. The model presented by Chrastil and DVA performed similarly given that the parameters of the two models are just slightly different whilst the KJ model performed the second best. The R^2 and the AARD % was almost identical for both models of DVA and Chrastil. The parameters of the two models are almost identical since the DVA model is a modified version of Chrastil's model. The value for parameter k was calculated to be 5.33 for the model of Chrastil, DVA, AL, and Sparks et al., which indicates that 5.33 molecules of carbon dioxide attach to one molecule of marula oil in the supercritical region by the process of solvation.

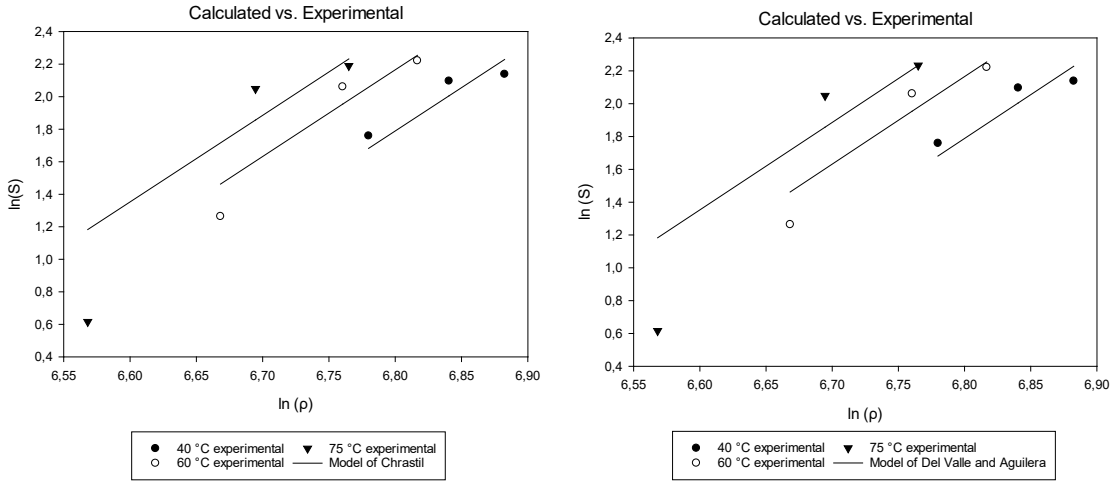

Figure 1: a) Model of Chrastil (1982) b) Model of Del Valle and Aguilera (1988).

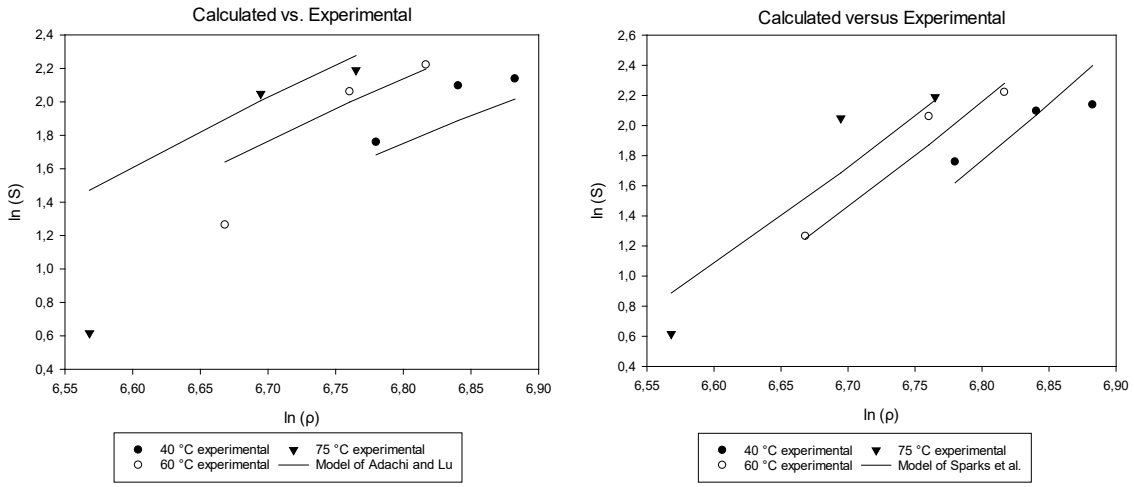

Figure 2: a) Model of Adachi and Lu (1983) b) Model of Sparks et al. (2008).

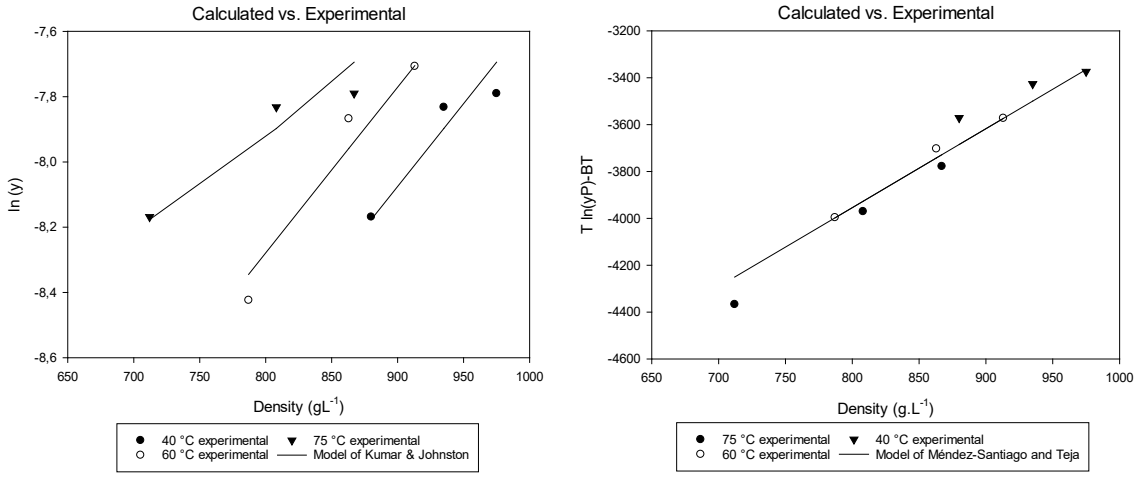

Figure 3: a) Model of Kumar and Johnston (1988) b) Model of Méndez-Santiago and Teja (1999).

Parameter A in both the models of Chrastil and del Valle and Aguilera regressed to be a negative integer thus indicating that the process which has taken place is endothermic (Dwi et al., 2016). This suggests that an endothermic reaction is the most suitable reaction for optimum solubility yield to take place. The total heat (ΔH) can be approximated to be -16.39 kJ.mol^{-1} for the model of Chrastil and -16.36 kJ.mol^{-1} for the model of del Valle and Aguilera in which ΔH is the product of the universal gas constant (8.3145 J.mol^{-1}.K^{-1}) and parameter A, as proposed by Chrastil (1982). This is evident that temperature is an important parameter influencing marula oil yield. Similar trends were noted by Reddy et al. (2022) in which the authors concluded that temperature had a significant effect on marula oil yield.

To summarise all the findings considered in the study, the following equation (equation 9 below) is suggested, a modified version of the MST model. Including one additional parameter resulted in a modest reduction in the AARD%. Similarly, when comparing the DVA model to the model of Chrastil, the additional parameter reduced the AARD% slightly thus proving to be more accurate in solubility prediction.

$$T\ln(Py_2) = A + BT + C\rho + \frac{D}{T} \tag{9}$$

Table 2: The fitting constants obtained for the novel model

Parameter	Value
A	-6660.26
B	6.80
C	3.37
D	1980
R^2	0.95
AARD %	0.00065
Equation	$\ln(Py_2) = \frac{-6660.26}{T} + 6.80 + 3.37\frac{\rho}{T} + \frac{1980}{T^2}$

Table 2 shows the values of the constants as well as the AARD% and R^2 value obtained for marula kernel oil using the proposed model, which is applicable for a temperature range of 40 – 75 °C and pressure range of 25 – 45 mPa. The resulting values for parameters A, B, and C were very similar to that of the MST model. The fact that parameter D has a high value suggests that the new parameter is important and relevant to the model. Additionally, the new parameter drastically decreased the AARD% from 0.049 obtained for the MST model to 0.00065, thus demonstrating that the modified model is considerably more accurate.

5. Conclusions

The study assessed the accuracy of solid solubility in supercritical CO_2 using semi-empirical approaches. The MST model was found to be the most accurate, and further modifications were made for improved accuracy. Further testing on different seed oils and marula plant species is recommended.

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