Experimental Measurements and Solubility Correlation of *Swietenia macrophylla* Seeds Oil in Supercritical CO₂

Nur Salsabila Md Norodin¹², Ahmad Ramdan Ismail¹², Ahmad Syahmi Zaini¹², Nor Faadila Idrus¹², Hartati³, Mohammad Lokman Hilmi¹², Liza Md Salleh¹²

¹School of Chemical and Energy Engineering, Faculty of Engineering, Universiti Teknologi, Malaysia.
²Centre of Lipid Engineering and Applied Research (CLEAR), Ibnu Sina Institute for Scientific and Industrial Research (ISI-SIR), Universiti Teknologi Malaysia.
³Department of Biology, Faculty of Mathematics and Natural Sciences, Universitas Negeri Makassar, Indonesia.

Email: r-liza@utm.my

**Abstract.** The aim of this study was to determine the oil recovery from *Swietenia macrophylla* seeds and its solubility in Supercritical CO₂ extraction process. Experimentally, the oil recovery from the seeds were conducted at 15-35 MPa and 40-60°C by Supercritical CO₂ extraction process. Density-based models such as Chrastil and del Valle and Aguilera models were used to correlate the solubility data of *Swietenia macrophylla* seeds oil. The high oil recovery obtained at 35 MPa and 60°C was 6.609 mg oil/g CO₂ while the lowest oil recovery was at 15 MPa and 40°C (0.810 mg oil/g CO₂). Chrastil model provide the best correlation between experimental and calculated solubility data for oil recovery from *Swietenia macrophylla* seeds with lowest value of average absolute percent deviation (AAPD) which is 0.33% compared to del Valle and Aguilera model (0.39%).

1. Introduction

*Swietenia macrophylla*, also known as ‘tunjuk langit’ in Malaysia is used traditionally to treat various diseases such as diabetes and high blood pressure [1]. *Swietenia macrophylla* seeds have been reported to have various biological activities such as anti-inflammatory, anticancer and antitumor [2], wound healing properties [3,4] as well as antidiabetic activities [5]. The main component in *Swietenia macrophylla* seeds oil is fatty acid which cannot be synthesized by the human body, but it is essential for normal metabolism. The example of these fatty acids is linoleic acid. Linoleic acid extracted from *Swietenia macrophylla* seeds was 37.58% [6], contributed to antidiabetic [5] and wound healing properties [3,4].

The definition of extraction is a mass transfer process between two components from one phase to another where the extracting solvent can be in the form of liquid, solid or supercritical fluid [7]. Supercritical fluids (SF) describe as a single substance at above its critical point (pressure and temperature) with physicochemical properties indistinguishable between gases and liquid [8].

---

¹ To whom any correspondence should be addressed.
The advantage of SF, supercritical carbon dioxide (CO$_2$) is the transport phenomena that can be altered accordance to its supercritical region. The disadvantage of SF accounted to its high operating cost, handling with high pressure and temperature in its processing. Adaption of SF in various technologies such as extraction is a greener and effective approach on both industrial and analytical scale.

The utilization of supercritical fluid extraction process in the industry for separation process included the needs of correlation or prediction of the solubility solutes in supercritical solvents. Solubility refer to the solvating capability of supercritical solvent where the maximum amount of solute that can be extracted at saturation equilibrium [9]. Density-based approach able to correlate the pressure, temperature and density of solvent in order to predict the solute solubility in supercritical fluid. [10]. To the best of our knowledge, there is no information in the available literature on evaluation of *Swietenia macrophylla* seeds oil solubility in supercritical CO$_2$. In the present study, supercritical CO$_2$ extraction process was used for the recovery of oil from *Swietenia macrophylla* seeds. The aim was to correlate the solubility and its influence toward recovery of oil.

2. Experimental Details

2.1. Chemicals
Commercial grade liquid carbon dioxide (purity 99.99%) used in supercritical carbon dioxide extraction was purchased from Kras, Instrument and Services, Johor, Malaysia.

2.2. Plant Material
The Authentication of the *Swietenia macrophylla* seeds was performed by Forest Research Institute Malaysia (FRIM) (Sample No.: PID 270818-25). The seeds were oven dried for a whole day using an oven (Memmert, Germany). Then, the seeds were grinded into 500 µm mean particle size using commercial blender (Waring, US) and sieved using Endecotts Octagon 200 Digital Sieve Shaker. Lastly, the samples were kept in a tight sealed storage plastic stored in freezer at -20 °C for further analysis.

2.3. Extraction Procedure
Supercritical fluid extraction (SFE) unit in Center of Lipids Engineering and Applied Research (CLEAR), Universiti Teknologi Malaysia consisted of CO$_2$ gas cylinder, CO$_2$ controller pump (Lab Alliance), co-solvent pump (Lab Alliance), oven (Memmert, Germany), 10 ml stainless steel extraction vessel, pressure gauge (Swagelockk, Germany), automatic back pressure regulator (Jasco BP 2080- Plus) and restrictor valve. A schematic diagram of SFE apparatus is illustrated in Figure 1.

![Figure 1. Schematic Diagram of SFE](image-url)
2.4. For each experiment, 3 grams of sample matrix was placed in 10 ml stainless steel extraction vessel and sealed tightly in the oven. The flow rate of supercritical CO$_2$ was maintained at 1.82 g/min. The extraction process was conducted at 15-35 MPa and 40-60°C. The oil yields were collected after 120 minutes in a vial and refrigerated at -4°C until further analysis. The expression of the extracted oil yield of *Swietenia macrophylla* can be expressed as:

$$W_{oil} = W_i - W_f$$

Where $W_{oil}$ is the mass of the extracted oil yield (mg), $W_i$ is the mass of the sample after the extraction (mg) and $W_f$ is the mass of the sample before the extraction (mg).

2.5. Solubility Modelling
The experimental solubility ($Y_s$) data were calculated from the initial slope of the first period of extraction curve at 15-35 MPa and 40-60°C. Chrastil and del Valle and Aguilera models were modelled based on the equations.

Chrastil equation was formed for the solubility in dense gas considering the interaction of solvato complex [11] is given as follows:

$$\ln Y_s = k \ln p_{CO_2} + \frac{a}{T} + b$$

Where $Y_s$ is the solubility of solute in dense gas (g/L), $k$ is the association, $p_{CO_2}$ is the CO$_2$ density (g/L), $a$ and $b$ are constants.

del Valle and Aguilera equation is a modification of Chrastil equation to compensate the variations of the solute’s heat of vaporization with temperature [12] is given as follows:

$$\ln Y_s = k \ln p_{CO_2} + \frac{a}{T} + b + \frac{c}{T^2}$$

2.6. Statistical analysis
Analysis of average absolute percent deviation (AAPD) was used to determine the accuracy of these models, as shown in equation below:

$$AAPD (%) = \frac{1}{n} \sum_{i=1}^{n} \left| \frac{Y_{exp} - Y_{calc}}{Y_{exp}} \right| \times 100$$

Where where $n$ is is the total experimental data and $Y_{exp}$ and $Y_{calc}$ are the data obtained from experiment and model equations, respectively, at i condition. Aside to AAPD, $R^2$, analysis of determination coefficient value was also used in evaluating the consistency of the solubility curves.

3. Results and Discussion
The density of CO$_2$ and the solubility of *Swietenia macrophylla* seed oil in Supercritical CO$_2$ at various conditions are presented in Table 1. The correlation of solubility data was further studied based on density-based models which are Chrastil and del Valle and Aguilera models.
Table 1. Solubility of *Swietenia macrophylla* seed oil in Supercritical CO₂

| Pressure (MPa) | Temperature (°C) | Density of CO₂ (g/mL) | Solubility (mg oil/g CO₂) | Solubility (g oil/L CO₂) |
|---------------|------------------|-----------------------|--------------------------|--------------------------|
| 15            | 40               | 0.790                 | 0.810                    | 0.640                    |
| 20            | 50               | 0.708                 | 1.032                    | 0.731                    |
| 25            | 60               | 0.606                 | 1.800                    | 1.091                    |
| 30            | 50               | 0.791                 | 2.703                    | 2.138                    |
| 35            | 60               | 0.730                 | 3.077                    | 2.246                    |
| 40            | 50               | 0.848                 | 1.905                    | 1.615                    |
| 40            | 60               | 0.708                 | 3.148                    | 2.789                    |
| 40            | 50               | 0.841                 | 3.333                    | 2.803                    |
| 40            | 60               | 0.792                 | 3.529                    | 2.795                    |
| 40            | 50               | 0.919                 | 3.778                    | 3.472                    |
| 40            | 60               | 0.880                 | 3.968                    | 3.492                    |
| 40            | 50               | 0.837                 | 4.800                    | 4.018                    |
| 40            | 60               | 0.942                 | 5.185                    | 4.884                    |
| 40            | 50               | 0.906                 | 5.376                    | 4.871                    |
| 40            | 60               | 0.869                 | 6.609                    | 5.743                    |

Figure 2 represents the solubility of *Swietenia macrophylla* seed oil in Supercritical CO₂ as a function of pressure at each constant temperature of 40°C, 50°C and 60°C. The pattern from the graph shows that the solubility of oil is increased proportionally as the pressure is increased at constant temperature. The highest solubility of oil is observed at highest temperature of 60 °C and pressure of 35 MPa, which is 6.609 mg oil per g CO₂. Meanwhile at lowest temperature of 40 °C and pressure of 15 MPa, the lowest solubility of 0.81 mg oil per g CO₂ oil is obtained.

The solubility of *Pithecellobium jiringan* (Jack) prain seeds was evaluated at 40-70°C and 27.58-44.81 MPa [13]. It showed that the solubility of oil yield is slightly increased with the increases of CO₂ density when the pressure is increased. Figure 3 shows the effect of temperature on solubility of *Swietenia macrophylla* oil yield in supercritical CO₂ extraction at constant pressure. It is observed that the solubility of *Swietenia macrophylla* oil is increased with the increases of temperature, even though the solvent density was decreased. The solubility of palm oil at 40-60°C and 4-10 MPa shows
the increment of the extraction yield with the temperature [14]. It is also stated that increasing of solubility as a function of temperature was much faster than the increment of solubility as a function of pressure.

![Figure 3. Solubility of *Swietenia macrophylla* seed oil as a function of temperature at different pressure](image)

The solubility parameters for both Chrastil and del Valle and Aguilera equations are presented in Table 2. The parameters of $k$, $a$ and $b$ in Chrastil equation represents average number of molecules that form the solvate-complex, the heat of salvation and vaporization of the solute, and the molecular weight and melting point of solute respectively. Meanwhile the parameters of $k$, $a$, $b$ and $c$ in del Valle and Aguilera equation represents the same function as in Chrastil equation with additional of constant $c$ in the equation. The correlation of solubility data of *Pithecellobium Jiringan* (Jack) prain seeds at 40-70°C and 27.58-44.82 MPa shows that Chrastil model as the best model that fit the experimental data due to its lower AAPD (0.206%) value compared to del Valle and Aguilera model (0.582%) [13]. But since the $R^2$ values for the both models were similar. Hence, the modification in de Valle and Aguilera model has no significant changes in the experimental data compared to Chrastil model [16].

| Equations                  | Constants  | AAPD (%) | $R^2$  |
|----------------------------|------------|----------|--------|
| Chrastil                   | $k$ = 4.70401, $a$ = -6368.44, $b$ = -10.9353 | 0.33     | 0.9764 |
| Del Valle and Aguilera     | $k$ = 5.66111, $a$ = -9811.87, $b$ = -35.8699, $c$ = -6.73102 | 0.39     | 0.9764 |

Figure 4 shows the correlation of *Swietenia macrophylla* oil solubility experimental data with Chrastil and del Valle and Aguilera model. From the graph, both models are closed to the experimental data, but it was observed that the correlation using Chrastil model is more precise and fitted with the experimental data compared to del Valle and Aguilera model but the comparison between both models itself does not shows any significant difference in statistical evaluation.
4. Conclusion
The highest solubility of *Swietenia macrophylla* oil was obtained at 35 MPa and 60°C which is 6.609 mg oil/g CO$_2$ while the lowest solubility of *Swietenia macrophylla* oil was obtained at 15 MPa and 40°C which is 0.810 mg oil/g CO$_2$. The solubility of *Swietenia macrophylla* oil is increased with increasing pressure and CO$_2$ density at constant temperature. On the other hand, the solubility of *Swietenia macrophylla* oil is increased with increasing temperature at constant pressure, even though the CO$_2$ density is decreased. The correlation of solubility experimental data with density-based model was conducted using Chrastil and del Valle and Aguilera models. From the result, the best model that fitted to the experimental data was Chrastil model due to the lowest value of average absolute percent deviation (AAPD) which is 0.33% compared to del Valle and Aguilera model (0.39%) but the R$^2$ for both models were similar (0.9764).

References
[1] Moghadamtousi S Z, Goh B H, Chan C K, Shabab T and Kadir H A 2013 *Molecules* **18**(9) 10465-83.
[2] Sayyad M, Tiang N, Kumari Y, Goh B H 2017 *Saudi Pharm. J.* **25**(2) 196-205.
[3] Hartati H, Mohd-Nasir H, Md Salleh L, Idris I S and Abd Aziz A 2018 *Mal. J. Fund. Appl. Sci.* **14**(4) 432-436
[4] Hartati, Liza M S, Irma S I and Azis A A 2019 *J. Teknol.* **81** 119–123.
[5] Md Norodin N S, Md Salleh L, Yusof N, Mustapha N M 2018 *Int. J. Eng. Trans. B Appl.* **31**(8) 1308-1317.
[6] Hartati, Salleh L M, Pagarra H and Rachmawaty 2018 *IOP J. of Physics: Conf. Series* 1028 012011 doi:10.1088/1742-6596/1028/1/012011

[7] Hartati, Salleh L M, Idris I S, and Azis A A 2019 *J. Teknol.* 81 119–123.

[8] Reverchon E, and De Marco I 2006 *J. Supercrit. Fluids* 38(2) 146-166.

[9] da Silva R P F F, Rocha-Santos T A P, and Duarte A C 2016 *TrAC - Trends Anal. Chem.* 76 40-51.

[10] Soetaredjo F E, Ismadji S, Yuliana Liauw M, Angkawijaya A E and Ju Y H 2013 *Fluid Phase Equilib.* 358 220-225.

[11] Bruno T J and Ely J F 2017 Supercritical fluid technology: Reviews in modern theory and applications. Boca Raton Publisher CRC Press.

[12] Chrastil J 1982. *J. Phys. Chem.* 3016–3021.

[13] del Valle J M, and Aguilera J M 1988 *Ind. Eng. Chem. Res.* 1551–1553.

[14] Yunus M A C, Arsal N H, Zhari S and Idham Z 2013 *J. Teknol. (Sciences Eng).* 45–50.

[15] Md Norodin N S, Md Salleh L, Machmudah S and Mustafa N M 2018 *Malay. J. Fundam. Appl. Sci.* 14 411–417.

[16] Kostrzewa D, Dobrzyńska-Inger A, and Turczyn A 2019 *Molecules* 24 1–13.

[17] Mustapa A N, Manan Z A, Mohd Azizi C Y, Nik Norulaini N A and Omar A K M 2009 *J. Food Eng.* 606–616.

**Acknowledgments**

The authors gratefully acknowledge the financial support by the Zamalah, Universiti Teknologi Malaysia (UTM). Acknowledgement also extended to UTM Research University Grants 16H97, 04G03, 01M65 and 4C242 for funding this study.