

# Mass Transfer Modelling of *Sclerocarya Birrea* Kernels in Supercritical Carbon Dioxide

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Experimental data was obtained from literature for the supercritical fluid extraction (SFE) process of *Sclerocarya birrea* kernel oil in supercritical carbon dioxide (CO<sub>2</sub>). The external mass transfer, diffusion, and axial dispersion coefficients were determined from the experimental values as well as the Sherwood, Reynolds, and Schmidt dimensionless consortiums. The Reynolds number ranged between 8 to 15, indicating that natural convection occurred. The Sherwood and Schmidt numbers were between 2 to 3.4 and 1.6 to 4. Although the solubility of marula oil decreased with an increase in temperature, its effective diffusivity and external mass transfer coefficient increased. However, the external mass transfer coefficient, diffusion coefficient and axial dispersion coefficient decreased with an increase in pressure due to a decrease in binary diffusivity. Even though the density of the solvent increases with pressure, which results in an increase in the diffusivity of the solute in supercritical CO<sub>2</sub>, the coefficients however decrease. The amount of extract is also amplified by the increase in solvent power.

## 1. Introduction

*Sclerocarya birrea* is commonly referred to as Marula and is claimed to be the “tree of life” (Welford, Abad & Gericke, 2008). Despite these prerogatives, it is startling that no modelling has been conducted on extracting marula oil from SFE processes. Aside from the extraction process, modelling the process is crucial for design purposes (Louli et al., 2004; Wynn and Clarkson, 2018). The main goal of subjecting experimental data to mathematical modelling is to establish specifications for process design viz., equipment sizing, solvent flow rates, particle size, optimization, process control, troubleshooting and diagnostics. These specifications can provide insight on the practicality of SFE processes on a commercial scale (Melreles et al., 2009; Rasmuson et al., 2014). Honarvar et al. (2013) and Hassim et al. (2021) stress that mathematical modelling is essential for the costing of SFE processes from laboratory to pilot and industrial scale. In addition, applying models that enable experimental data correlation and extrapolation for potential industrial SFE process applications is crucial (Martín et al., 2011).

According to Attard et al. (2018), SFE has been used recently to study the extracts of a large number of plant species. Even though a large variety of these plant species have already been used to supplement sustenance and create products with health benefits, many of these species have not yet been explored scientifically and may exhibit novel applications. Therefore, mathematical models must be developed to determine the most viable operating conditions to increase oil output, which can impact the agricultural sector largely.

It is important to understand the three fundamental properties viz. the diffusion coefficient of the solute, the viscosity and the density of the supercritical fluid phase to develop mass transfer models (Lim et al., 1989). These properties frequently connect to the pertinent Sherwood, Reynolds and Schmidt dimensionless consortiums (Bernardo-Gil and Casquilho, 2007). The equations are depicted below (refer to equations 1, 2 and 3).

$$Sh = \frac{d_p k_f}{D_{12}} \quad (1)$$

$$Sc = \frac{\mu_f}{\rho_f D_{12}} \quad (2)$$

$$Re = \frac{d_p \rho_f u}{\mu_f} \quad (3)$$

Where Sh is the Sherwood number, Sc is the Schmidt number, Re is the Reynolds number,  $\mu_f$  is the viscosity of the fluid in Pa.s, u superficial velocity of the supercritical fluid in  $m.s^{-1}$ ,  $d_p$  is the particle diameter in m,  $\rho_f$  is the fluid density in  $kg.m^{-3}$ ,  $\rho_s$  is the solid density  $kg.m^{-3}$  and  $D_{12}$  is the diffusion coefficient in  $m^2.s^{-1}$

Dwivedi and Upadhyay (1977) developed the generalized correlation for the Sherwood number and is given by equation 4 below, where  $C_1$  and  $C_2$  are constants, which can be determined by manipulating the experimental data.

$$Sh = C_1 Re^{C_2} Sc^{1/3} \quad (4)$$

The diffusion coefficient can be obtained using equation 5 below proposed by Wilke and Chang (1955) where  $K_B$  is the Boltzman constant, T is temperature of the supercritical fluid in Kelvin and r is the molecular radius of the spherical solute.

$$D_{12} = \frac{K_B T}{6\pi r \mu} \quad (5)$$

The axial dispersion coefficient can be calculated using the correlation proposed by Funazukuri et al. (1998) as depicted in equation 6 below where  $D_{ax}$  is the dispersion coefficient in  $m^2.s^{-1}$  and  $\epsilon$  is the void fraction.

$$D_{ax} = 1.317 (\epsilon Re Sc)^{1.392} \left( \frac{D_{12}}{\epsilon} \right) \quad (6)$$

## 2. Methodology: Mass transfer modelling experimental design

The external mass transfer coefficient ( $K_f$ ), axial dispersion coefficient ( $D_{ax}$ ) and diffusion coefficient ( $D_{12}$ ) for marula kernel oil was determined on the solubility of marula oil in supercritical  $CO_2$  for the experimental conditions obtained from literature data conducted by Taseski (2015) on marula kernels conducted at 40 to 80 °C and 250 to 450 bar. The density and viscosity of supercritical  $CO_2$  were also required in order to compute the external mass transfer coefficient. Chemcad version 8.1.0 was utilised to determine the properties of supercritical  $CO_2$  utilising the Benedict-Webb-Rubin-Starling (BWRS) equation of state (EOS). The BWRS EOS is a modified version of the Beattie Bridgeman equation, which better captures the critical properties of pure hydrocarbons in the gaseous or liquid phase (Benedict et al., 1940). A very straightforward unit operation was generated with an inlet feed of  $100 kg.hour^{-1}$  comprising of pure  $CO_2$ . The properties of supercritical  $CO_2$  were determined using a pipe with a length of 10 meters, an inside diameter of 0.9 meters, and a roughness factor of  $4.572 \times 10^{-5}$  that was installed under minimal pressure drop.

## 3. Assumptions made during the calculations

The following assumptions were made to enable model calculations

- The void fraction could not be calculated because the apparent (bulk) density of marula is unknown and unavailable in literature. It is therefore assumed that the particles are spherical in nature thus having a void fraction within the range of 0.35 to 0.45 (Rolland et al., 2019).
- The molecular radius of olive oil was utilised to calculate the dispersion coefficient since the radius of marula (solute) could not be found in literature. Olive oil was utilised since the fatty acid structure of olive oil is similar to that of marula oil.
- The void fraction does not change.
- The Boltzman constant of  $1.380649 \times 10^{-23} m^2kg.s^{-2}.K^{-1}$  was utilised to calculate the axial dispersion coefficient.
- The fluid velocity is uniform during the extraction process.

- The superficial velocity was calculated using the dimensions of the extractor that was utilised by Taseski (2015) in which the experimental work was conducted. The area of the extractor was therefore calculated using a diameter of 0.1 meters.
- The Sherwood number was calculated using 0.38 and 0.83 for constants  $C_1$  and  $C_2$  since the Reynolds number was between  $2 < Re < 40$  and the Schmidt number was between  $2 < Sc < 40$  (Tan et al., 1988).
- A constant  $CO_2$  flowrate of  $30 \text{ kg}\cdot\text{hour}^{-1}$  was utilised for all experimental runs by Taseski (2015). Therefore, the very same flow rate was utilised to calculate the superficial velocity.
- The average particle size of the marula kernels of  $850\mu\text{m}$  was utilised as the particle diameter.
- A single  $CO_2$  property estimate obtained from the simulation data from Chemcad was utilised at the corresponding temperature and pressure calculations, thus overlooking any fluctuations in these parameters.

#### 4. Results and Discussion

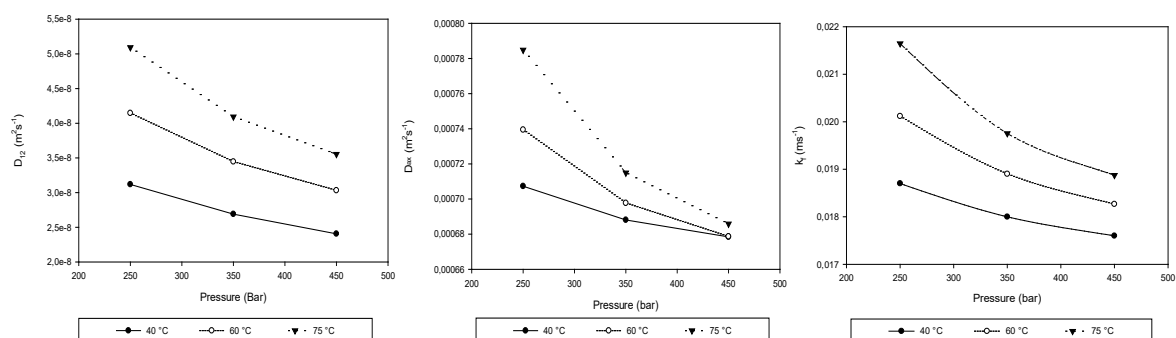
The  $K_f$ ,  $D_{ax}$  and  $D_{12}$  values for marula kernel oil was determined from the SFE experimental values, together with the Sherwood, Reynolds and Schmidt dimensionless consortiums presented in Table 1 below.

*Table 1: The correlated parameters obtained for the mass transfer model for marula kernel oil.*

Experiment	Pressure (bar)	Temperature (°C)	Density ( $\text{kg}\cdot\text{m}^{-3}$ )	Viscosity (Pa.s)	Superficial velocity ( $\text{m}\cdot\text{s}^{-1}$ )	$D_{12}$ ( $10^{-8} \text{ m}^2\cdot\text{s}^{-1}$ )	Sc	Sh	$k_f$ ( $\text{m}\cdot\text{s}^{-1}$ )	$D_{ax}$ ( $\text{m}^2\cdot\text{s}^{-1}$ )
1	250	40	880	0.00008660	0.00121	3.12	3.159	2.799	0.0187	0.00071
2	250	60	787	0.00006928	0.00135	4.15	2.127	2.267	0.0201	0.00074
3	250	75	712	0.00005896	0.00149	5.09	1.630	1.987	0.0216	0.00078
4	350	40	935	0.00010039	0.00114	2.69	3.993	3.129	0.0180	0.00069
5	350	60	863	0.00008338	0.00123	3.44	2.804	2.564	0.0189	0.0007
6	350	75	808	0.00007334	0.00131	4.09	2.217	2.255	0.0198	0.00071
7	450	40	975	0.00011223	0.00109	2.41	4.787	3.42	0.0176	0.00068
8	450	60	913	0.00009477	0.00116	3.03	3.425	2.816	0.0183	0.00068
9	450	75	867	0.00008448	0.00123	3.55	2.744	2.482	0.0189	0.00069

##### 4.1. The effect of pressure on the mass transfer coefficient at constant temperature

The mass transfer coefficients of marula kernel oil in supercritical  $CO_2$  were determined as a function of pressure at a constant temperature of 40, 60 and 75 °C. It should be emphasized that the experiments were not carried out isothermally and that the values in figures 1a, b and c were extrapolated from the experimental results.



*Figure 1: The effect of pressure on a) Diffusion coefficient b) Axial Dispersion coefficient c) External mass transfer coefficient*

Figure 1a, b and c show that at higher pressures, the effect of pressure on the coefficients was less significant. Given that these parameters change more quickly at lower pressures, the sudden diffusivity shift at low pressures suggests that solvent density and viscosity are crucial parameters affecting the mass transfer coefficients (Liong et al., 1992). It can also be seen from figure 1b that the values of the axial dispersion coefficient at the highest pressure of 450 bar differed marginally at the various isotherms. In contrast, the diffusion and external mass transfer coefficients were at their lowest at 450 bar; however, they differed largely.

The relationship between pressure and the coefficients are therefore inversely proportional. similar trends were observed by many studies correlating to the findings observed for marula oil. For example, Raspo et al. (2008) noticed the same trends in a study on the diffusion coefficients of solids in supercritical CO<sub>2</sub>. The external mass transfer coefficient was also noted to be lower at higher pressures on a study conducted by Lin et al. (2013) on the mass transfer coefficients and correlation of supercritical CO<sub>2</sub> extraction of Sarawak black pepper. Honarvar et al. (2013) noted that the axial dispersion coefficient and mass transfer coefficient decreased with increased pressure. The authors explain that at higher pressures, there is a decrease in binary diffusivity. Leila et al. (2022) conducted experimental and mathematical modelling data of green process of essential oil extraction in supercritical CO<sub>2</sub>. The authors found the very same trends to that of marula oil in relation to the mass transfer coefficient. They explain why the mass transfer coefficient decreases with an increase in pressure by stating that the density increases with pressure, thus increasing the solute's diffusivity in the supercritical CO<sub>2</sub>. The coefficient  $K_f$  drops as a result, but the amount of extract is amplified by the increase in solvent power. This may suggest that while pressure itself has a negative impact on the coefficient  $K_f$ , the external mass transfer's resistance has a minimal impact on the total amount of mass transfer.

#### 4.2. The effect of temperature on the mass transfer coefficient at constant pressure

The mass transfer coefficients of marula kernel oil in supercritical CO<sub>2</sub> were determined as a function of temperature at a constant pressure of 250, 350 and 450 bar. Notably, the experiments were not carried out isobarically and that the values in figures 2a, b and c were extrapolated from the experimental results. The effect of temperature on the coefficients will be discussed in conjunction with density and pressure.

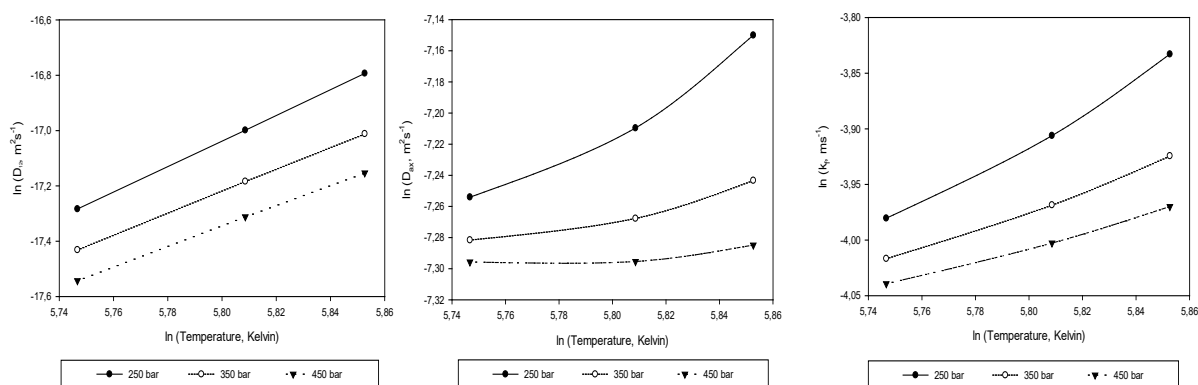


Figure 2: The effect of temperature on a) Diffusion coefficient b) Axial Dispersion coefficient c) External mass transfer coefficient

According to Reddy et al. (2022), the solubility of marula oil decreases with an increasing temperature, however from figures 2a, b and c, one can observe that temperature had an opposing effect on the diffusion, axial and mass transfer coefficient which had increased when the temperature was elevated. The findings also show that as the pressure increased, the reliance of the diffusion coefficient on temperature reduced which is also indicated by the decrease in the slopes for the diffusion, dispersion, and mass transfer coefficients when the pressure was elevated. The rising temperature dependency of the fluid density as the pressure approaches the critical pressure may be related to the increased temperature dependence of the diffusion coefficient at lower pressures (Liong et al., 1992). Ahmed et al. (2012) conducted extraction and modelling of Algerian rosemary essential oil using supercritical CO<sub>2</sub> and studied the extraction temperature and pressure effect on oil yield. The authors found that an increasing temperature increased the external mass transfer coefficient. The effects of temperature is therefore an important parameter affecting both the yield of marula oil as well as mass transfer (Reddy et al., 2023). Ahmed et al. (2012) go on to explain the importance of mass transfer on the yield of oil and state that the external mass transfer resistance controls the extraction dynamics during the early stages of the extraction process. However, Leila et al. (2022) argue that the resistance of the external mass transfer has an insignificant effect on the total mass transfer. The findings also agree with Rai et al. (2014) who found that mass transfer coefficient increased with temperature due to the greater diffusivity in supercritical CO<sub>2</sub> at higher temperatures. Therefore, when the temperature rises, the rate of mass transfer of the solute to the bulk liquid phase also increases.

### 4.3. Dimensionless numbers

The values for the dimensionless numbers for extracting marula kernel oil are presented in Table 2 below. The table also includes additional ratios and interaction calculations of the terms.

Table 2: Values of dimensionless numbers for the extraction of marula kernel oil.

Experiment	Pressure (bar)	Temperature (°C)	Re	Sc	Sh	$\epsilon\text{ReSc}$	$\epsilon\text{D}_{\text{ax}}\text{D}_{12}^{-1}$	$(\text{Sh}/\text{Sc})^{1/3}$
1	250	40	10.419	3.159	2.799	14.813	56.122	0.295
2	250	60	13.024	2.127	2.267	12.462	44.123	0.355
3	250	75	15.305	1.630	1.987	11.223	38.135	0.406
4	350	40	8.988	3.993	3.129	16.149	63.289	0.261
5	350	60	10.822	2.804	2.564	13.654	50.101	0.305
6	350	75	12.303	2.217	2.255	12.276	43.209	0.339
7	450	40	8.0404	4.787	3.42	17.319	69.760	0.238
8	450	60	9.521	3.425	2.816	14.675	55.393	0.274
9	450	75	10.681	2.744	2.482	13.190	47.749	0.302

The Reynolds number ranged between 8 to 15. Grosso et al. (2010) state that natural convection occurs at low Reynolds numbers for high soluble solutes fed in extractors with an upward configuration. Puiggené, Larrayoz and Recasens (1997) state that a low Reynolds numbers fall between 10 and 100, and that the liquid side exhibits a strong resistance in relation to the mass transfer coefficient, which becomes smaller when the Velocity is elevated. del Valle et al. (2006) found that the Reynolds number was within the range of  $4.74 < \text{Re} < 13$ . The Sherwood number was calculated using 0.38 and 0.83 for constants  $C_1$  and  $C_2$  since the Reynolds number was between  $2 < \text{Re} < 40$  and the Schmidt number was between  $2 < \text{Sc} < 40$  (Tan et al., 1988). Funazukuri et al. (1998) state that the value of  $\epsilon\text{ReSc}$  should be greater than 0.3 to utilise the equation;  $\text{D}_{\text{ax}} = 1.317(\epsilon\text{ReSc})^{1.392}(\text{D}_{12}\epsilon^{-1})$ . The equation is also valid for Reynolds numbers between 2–80 (Catchpole et al., 1996). Thus, the axial dispersion coefficient equation stated above could be utilised since the values of  $\epsilon\text{ReSc}$  were all greater than 0.3. Funazukuri et al. (1998) plotted  $\epsilon\text{D}_{\text{ax}}\text{D}_{12}^{-1}$  versus Re to study the effects of pressure and found that slope of the plots at the various pressures decreased when the pressure was increased.

### 5. Conclusions

Pressure had a less effect on the diffusion, axial dispersion, and external mass transfer coefficient at higher pressures. The abrupt shift in diffusivities at lower pressures implied that solvent density and viscosity are important characteristics influencing the effects on the coefficients. The coefficients also increased with an increase in temperature. The findings also revealed that the diffusion coefficient's reliance on temperature decreased when the pressure was elevated. The external mass transfer coefficient increased with temperature because supercritical CO<sub>2</sub> has higher diffusivity at higher temperatures. As a result, as temperature rises, the rate of mass transfer of the solute to the bulk liquid phase also rises.

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