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Response Surface Analysis and Modeling of *Sclerocarya Birrea* kernel Oil Yield in Supercritical Carbon Dioxide

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The response surface methodology (RSM) was used to evaluate the influence of two independent variables namely extraction temperature and extraction pressure via literature data obtained from supercritical fluid extraction (SFE) process of *Sclerocarya birrea* kernel oil. The optimal (custom) option was utilised on Design Expert Version 13 to optimise the variables taken into consideration. The raw experimental data comprised of 9 experimental runs of which the temperature was varied between 40, 60 and 75 °C and the pressure was varied between 250, 350 and 450 bar. The reaction time, particle size and carbon dioxide (CO_2) flowrate was kept constant at 30 kg CO_2/hour for all experimental runs. Each extraction lasted for 270 minutes and each set of extraction conditions was repeated in triplicate. The determination coefficient value (R^2), adjusted R^2 value, p-values and F-values were considered in determining the effectiveness of the response surface methodology model. The results from the analysis of variance indicated that the all model terms excluding the quadratic temperature term are all highly significant with p values less than 0.01. The quadratic term of temperature has no significant effect on *Sclerocarya birrea* kernel oil yield. The optimal conditions to obtain the maximum oil yield from *Sclerocarya birrea* kernels were at a pressure of 450 bar and temperature of 60 °C. Under these optimal conditions, the yield of *Sclerocarya birrea* kernel oil was predicted to be 9.22 g oil/L CO_2. The experiment results obtained from literature agreed with the predicted values as indicated by the R^2 and adjusted R^2 values which were 0.98 and 0.97 respectively.

1. Introduction

Sclerocarya birrea is commonly known as marula (English); maroela (Afrikaans); morula (Tswana); and umGanu (isiZulu). The plant is widely distributed in South Africa, Botswana, Congo, Eritrea, Ethiopia, Gambia, Kenya, Malawi, Mozambique, Namibia, Niger, Senegal, Somalia, South Africa, Sudan, Swaziland, Tanzania, Uganda, Zambia and Zimbabwe (Orwa et al., 2009). It is a popular plant species because it provides nutritional sustenance to the population throughout the year (Mojeremane & Tshwenyane, 2004). For this reason, it is often referred to as the "tree of life" (Welford, Abad & Gericke, 2008). Almost all of the major constituents of the marula tree can be utilised (Orwa et al., 2009). The wood of the plant is utilised to produce fencing, erecting housing, roofing and poles (Mojeremane & Tshwenyane, 2004). The bark of the tree is also utilised by the locals to treat many ailments viz. fevers, diarrhea, boils, syphilis, leprosy, dysentery, hepatitis, rheumatism, gonorrhoea, diabetes, dysentery and malaria (Mutshinyalo & Tshisevhe, 2003). The fruits of the plant are consumed as is or can be processed to manufacture juices and a fermented alcohol beverage whilst the nut of the marula tree has a diameter of 2-3 cm of which holds 3-4 kernels that are utilised to produce porridges (Mojeremane & Tshwenyane, 2004). The kernels have a composition that is made up of 5.2 % moisture and 55.9 % oil (Zharare & Dhlamini, 2000). South African marula kernels are rich in fatty acids namely oleic, palmitic and stearic acid (Mthiyane & Hugo, 2019). Oleic, palmitic, and stearic acid are fatty acids that the human body naturally produces. (Vermaak et al., 2011). Oilseeds can be processed by mechanical means however the process is time consuming and labour intensive (Jahirul et al.,2013). Solvent extraction is also utilised in oil extraction as it is more effective than mechanical processing methods; but the process is hazardous and the quality of the oil is compromised (Ajila et al., 2011).

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For this reason, supercritical fluid extraction has gained popularity recently (Sovova & Stateva, 2011). It is also a process that is environmentally friendly (Hashemi, Khaneghah & de Souza Sant'Ana, 2017). It is claimed to be environmentally friendly because the most common solvent that is utilised in SFE is carbon dioxide which is safe and non-flammable (Chemat, 2017). Carbon dioxide can also be reutilised in the process and hence, it is a cost effective process (Lavenburg, Rosentrater & Jung, 2021). A maximum recovery of 55 % *Sclerocarya birrea* kernel oil under supercritical fluid conditions at 450 bars and 60 °C has been reported (Taseki, 2015).

2. Materials and Methods

2.1. Computational methods: Response surface experimental design

In this study, RSM was utilised to optimise the operating conditions of supercritical carbon dioxide via literature data obtained from (SFE) process of *Sclerocarya birrea* kernel oil. Taseski (2015), conducted supercritical fluid extraction of *Sclerocarya birrea* kernel oil which comprised of 9 experimental runs for the determination of the solubility of Sclerocarya birrea kernel oil in supercritical carbon dioxide. The extraction temperature was varied between 40, 60 and 75 °C and the extraction pressure was varied between 250, 350 and 450 bar. The reaction time remained constant at 270 minutes for all experimental runs whilst the particle size was kept constant at 850 µm. The carbon dioxide flowrate was maintained at 30 kg CO_2/hour for all experimental runs. Each set of extraction conditions was repeated in triplicate and the average oil yield at each extraction condition was then utilised for optmisation purposes. The two independent variables were studied namely extraction temperature (X_1) and extraction pressure (X_2). The independent variables were coded at three levels to ensure that there is an equal and even distribution of the intervals and levels (Baş & Boyacı., 2007). The independent variables are typically coded as it makes it easier to observe their influence on the response (Tirado-Kulieva et al., 2021). The independent variables were therefore coded using equation 1 below (Nandiwale & Bokade, 2014). The coded levels and intervals were therefore dispersed between 1-low, 0-medium and 1-high (Tharazi, Sulong & Mohd Salleh, 2020).

$$X_i = \frac{x_i - x_o}{\left(\frac{x_{maximum} - x_{minimum}}{2}\right)} \tag{1}$$

Where x_i represents the actual value for temperature and pressure), x_o represents the real variable value at centre point, X_i denotes the variable that has been coded, $x_{maximum}$ and $x_{minimum}$ are the maximum and minimum values of the real independent variables. Using equation 1 resulted in the following coded levels as depicted in table 1.

Table 1: Independent variables and their levels for RSM design.

Factor	Description	Unit of measure	Type	Level -1 Low	Level 0 Medium	Level 1 High
X_1	Temperature	°C	Numerical	40	60	75
X_2	Pressure	Bar	Numerical	250	350	450

The response surface methodology was conducted to study the effect of the operating parameters on the solubility of *Sclerocarya birrea* kernel oil in supercritical carbon dioxide. The optimal (custom) design was utilised on Design Expert Version 13 to develop a second order polynomial equation as shown in equation 2 was utilised to express the oil yield (Y) of *Sclerocarya birrea* kernel oil.

$$Y = B_O + \sum_{i=1}^{n} B_i x_i + \sum_{i=1}^{n} B_{ii} x_i^{\ 2} + \sum_{i=1}^{n} \sum_{j=i+1}^{n} B x_i x_j \tag{2}$$

Where, Y is the predicted response; B_0 is a constant; B_i is the coefficient of the linear terms, B_{ii} is the coefficient of the quadratic terms, x_i and x_j is the independent variables.
The coefficients of the second order model was obtained via Design Expert version 13. The goodness of fit was determined using the analysis of variance and the efficacy of the models was tested by calculating the R^2 for each model and also the average absolute relative deviation.

3. Results and Discussion

3.1. Model Fitting

Sclerocarya birrea kernel oil yield obtained from literature is presented in table 2. The experimental data was utilised to determine the coefficients of the second order polynomial equation. For each of the responses under investigation, a second-order polynomial equation was obtained using the multiple regression analysis and the partial sum of squares. The Fisher's test was used to determine the model coefficients' significance. The Fisher test considers the residual error and the F-value, which is a portion of the average square of the model (Rassem et al., 2019). As a function of the independent variables in terms of coded components, the second-order polynomial equation was used to express the solubility of *Sclerocarya birrea* kernel oil in supercritical carbon dioxide and is provided in equation 3.

$$Y\left(\frac{g\ oil}{L\ CO_2}\right) = 8.05 - 0.6058X_1 + 2.58X_2 + 1.15X_1X_2 - 0.0704{X_1}^2 - 1.66{X_2}^2 \quad (3)$$

Equation 3 can also be expressed in terms of uncoded factors and is given in equation 4.

$$Y\left(\frac{g\ oil}{L\ CO_2}\right) = -6.89065 - 0.238031x_1 + 0.104401x_2 + 0.000657x_1x_2 - 0.000230{x_1}^2 - 0.000166{x_2}^2 \quad (4)$$

3.2. Response surface analysis

The overall F value of 208.6 indicates that the model is significant. The linear model terms of temperature and pressure, as well as the interaction model term and quadratic pressure term all have p-values that are less 0.01; which is an indication that these model terms are very significant. The quadratic term of temperature however had no significant effect on *Sclerocarya birrea* kernel oil yield as indicated by the p value of 0.6753. Figures. 1a and figure 1b show how the independent factors and oil yield relate to one another as shown in figure 1a and figure 1b depicting the response surface curve and its contour plot. From figure 1a and figure 1b, it can be seen that the extraction pressure showed a quadratic effect on the response. The higher solvent-solute interaction is a result of the high concentrations of CO_2 at the elevated pressure levels which can be attributed to the high negative yet substantial quadratic pressure term (Bala et al., 2016). Similar patterns were seen in the extraction of mango seed kernel oil using SFE, according to Cerón-Martnez et al. (2021). The quadratic pressure term was observed by the authors to be both negative and extremely significant. According to Nandiwale and Bokade (2014), positive values for the linear variables show that the yield increases immediately as the positive variable rises. The fact that the coefficient of pressure is greater than both the coefficient of temperature and the interaction term suggests that pressure controls how much oil is produced. The similar patterns were seen by Peng, Setapar, and Nasir (2020) when they optimized the supercritical CO_2 extraction of roselle oil using RSM. From figure 1b, it can be seen that the yield for the concentration can be optimised, as there is a continual linear increase on oil yield pertaining to the lower extraction pressure range corresponding to a decrease in extraction temperature. It can also be observed that as the extraction pressure increases, the yield also increases with an increasing temperature. The yield however reaches a maximum with an increase in pressure and thereafter decreases in a parabolic manner. The maximum/minimum oil yield can therefore be located using a partial derivative of equation 4 with respect to pressure.

$$\frac{\partial Y}{\partial X_2} = 0.10440057568066 + 0.00065669012459622x_1 - 0.000332582x_2 = 0 \quad (5)$$

The plot of the optimised concentration is depicted in figure 2a. The variance inflation factors for each model term are all relatively close to 1, which shows that the components are orthogonal. The robust agreement between the projected R^2 value and the adjusted R^2 value demonstrates the model's appropriateness. The parity plot as shown in figure 2b demonstrates that the predicted values and experimental values are on par. The oil yield is dependent on both temperature and pressure, according to the response surface plot, but pressure has a far greater impact than temperature. This is demonstrated by the unimportant temperature quadratic model term, which had a p-value of 0.6753. The results are in line with Rassem et al. (2019) in which the authors emphasize that pressure was the most significant factor influencing the output of essential oil from jasmine flowers. The authors go on to explain that pressure can interact with temperature indefinitely because of its polarity. The response surface plot shows that the maximum oil yield was attained at 60 °C for the midpoint temperature and 450 bar for the maximum pressure. As a result, pressure has a significant impact on the oil yield, and the two variables are directly related. dos Santos Garcia, da Silva, and Cardozo Filho (2013) also noted that the corresponding temperature and pressure that produced the best oil yield were 40 °C and 60 °C, respectively. According to Louaer et al. (2018), operating at lower pressures and at an elevated temperature simultaneously reduced the solvent power, which in turn decreased the oil output. This is clear when the oil output is at its lowest, 1.85 g.L-1, at the lowest pressure of 250 bar and the maximum temperature of 75 °C. Montesantos et al. (2019) state that an increase in the solvents density results in an increase in the oil extraction. Lachos-Perez et al. (2020) also agrees in which the authors found that the highest yield was obtained at higher CO_2 density on the SFE process using CO_2 of lipophilic molecules from sugarcane straw.

Table 2: Optimal (custom) design and response for the oil yield of Sclerocarya birrea kernels.

Run	X_1 (°C)	X_2 (bar)	Coded Temperature variable	Coded Pressure variable	Observed response (g oil/L CO_2)	Predicted response (g oil/L CO_2)
1	40	250	-1	-1	5.808	5.515
2	60	250	0	-1	3.5415	3.580
3	75	250	1	-1	1.8512	2.007
4	40	350	-1	0	8.1345	8.623
5	60	350	0	0	7.8533	8.002
6	75	350	1	0	7.7568	7.415
7	40	450	-1	1	8.4825	8.412
8	60	450	0	1	9.2213	9.104
9	75	450	1	1	8.9301	9.502

Table 3: Analysis of variance for the fitted quadratic polynomial model.

Source	Sum of Squares	Degree of freedom	Mean Square	F-value	p-value	
Model	104.88	5	20.98	208.36	< 0.0001	significant
X_1-Temperature	2.69	1	2.69	26.71	0.0004	
X_2-Pressure	60.43	1	60.43	600.2	< 0.0001	
X_1X_2	6.13	1	6.13	60.84	< 0.0001	
X_1^2	0.0187	1	0.0187	0.1862	0.6753	
X_2^2	10.11	1	10.11	100.41	< 0.0001	
Residual	1.01	10	0.1007			
Lack of Fit	1.01	3	0.3356			
Pure Error	0	7	0			
Total	105.89	15				
Standard deviation	0.3173		R^2	0.9905		
Mean	6.45		Adj R^2	0.9857		
C.V %	4.92		Adeq precision	38.3409		

Table 4: Regression coefficient of polynomial function of response surface oil yield.

Factor	Coefficient Estimate	Degree of freedom	Standard Error	95% CI Low	95% CI High	Variance inflation factor
Intercept	8.05	1	0.1555	7.7	8.39	
X_1-Temperature	-0.6058	1	0.1172	-0.867	-0.3446	1.03
X_2-Pressure	2.58	1	0.1051	2.34	2.81	1.07
X_1X_2	1.15	1	0.1473	0.8209	1.48	1.08
X_1^2	-0.0704	1	0.1631	-0.4338	0.2931	1.01
X_2^2	-1.66	1	0.1659	-2.03	-1.29	1.03

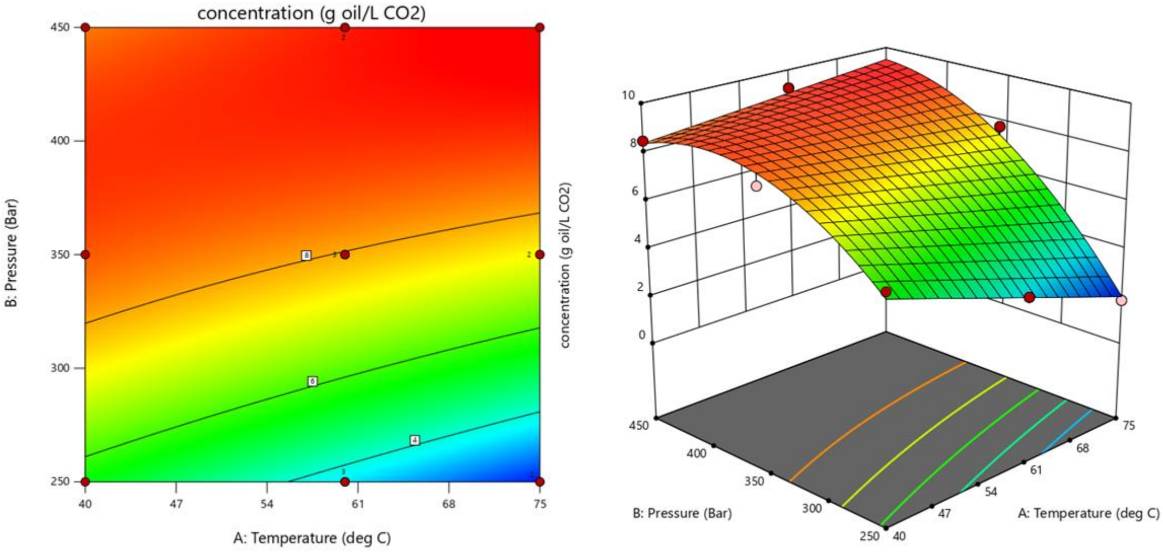

Figure 1: a) Contour plot for the effects of temperature and pressure on oil yield b) Response surface for the effects of temperature and pressure on oil yield.

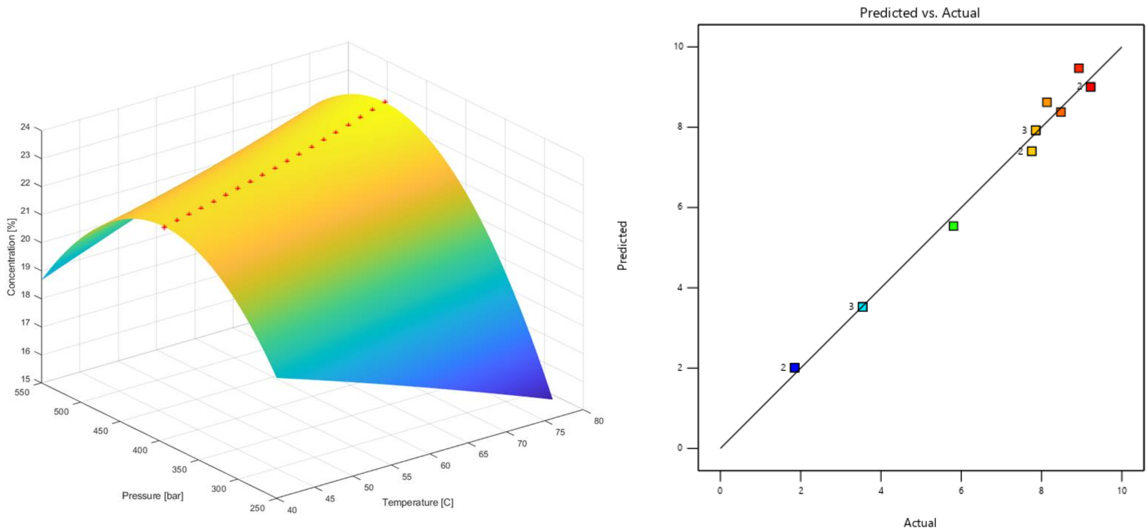

Figure 2: a) Optimisation of pressure and temperature b) Predicted values versus actual response.

4. Conclusions

RSM was successfully used to optimize the supercritical fluid extraction parameters to increase the production of *Sclerocarya birrea* kernel oil. The two variables namely extraction pressure and extraction temperature both had a significant effect on the oil yield, both alone and in conjunction, according to the response surface plots. A higher fluid density results from an increase in pressure, which raises the solubility. When it comes to temperature, the opposite is observed because an increase in temperature at a fixed pressure reduces the density of the CO_2 in the supercritical state, thus reducing the solubility. The quadratic temperature term however had no significant effect on *Sclerocarya birrea* kernel oil yield. The coefficient of pressure is also much larger in comparison to the coefficient of temperature and the interaction term which is an indication that pressure is an indispensable variable on the yield of *Sclerocarya birrea* kernel oil.

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