International Journal of Scientific Research in Biological Sciences
Vol.9, Issue.3, pp.34-38, June (2022)

Research Paper

E-ISSN: 2347-7520

Comparative Study of the Supercritical Extraction on Extracts of Palm Kernel Cake and Candlenut Samples After being used

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Available online at: www.isroset.org

Received: 21/Apr/2022, Accepted: 20/May/2022, Online: 30/Jun/2022

Abstract— In this paper, the extraction of palm kernel oil from palm kernel cake and candlenut samples after being used was studied. Supercritical fluid (SC-CO_2) at pressure of 7.28 MPa and temperature 31°C was examined and tested. The obtained results indicated that the increase in particle size, pressure and temperature enhanced the oil solubility. The supercritical carbon dioxide extraction at optimized parameters resulted in oil yield extraction of 46.4% at solubility of 9.6 g oil/kg CO_2. The obtained candlenut oil from supercritical carbon dioxide extraction has better oil quality than oil which was extracted by Soxhlet extraction using n-hexane solvent. The oil contains high unsaturated oil (linoleic acid and linolenic acid), which have many beneficial effects on human health.

Keywords—Palm kernel oil, Extraction, kernel cake, (SC-CO_2).

I. INTRODUCTION

Supercritical fluid extraction is a powerful alternative extraction process in modern days. It already has taken over the conventional solvent extraction process in terms of food grade use. It is effective, safe, non-toxic and cheap on commercial scale usage. When CO_2 is used as supercritical fluid, owing to its low critical temperature (31.1 °C) and pressure (7.28 MPa), it is the better choice for thermally labile compounds. Thermal and hydrolytic degradation of heat-labile compounds can be eluded using SC-CO_2.[1] Supercritical CO^{-2} (SC-CO_2), being a lipophilic solvent, has adaptable selectivity and solvent power. Hence, the process selectivity is easy to control, which is an significant factor for food and pharmaceutical industries.[2] Due to its low critical pressure and 'evaporation temperature', the yield becomes free from solvent at room temperature while yields from solvent extraction process need to be desolventized to make them suitable for consumption.[3] Moreover, yields or substances extracted by SC-CO_2 extraction are easy to refine and contain lower impurities.[4]

Palm kernel cake is produced as a by-product from palm oil industry. Palm kernel is pressed and extracted oil from it. Commercially palm fruit is pressed twice for this purpose using mechanical pressure. On a wet basis, the oil content in palm kernel is about 45–50%.[5] Although from the same source, palm kernel oil (PKO) and palm oil differ significantly in their characteristics and properties. PKO is rich in lauric acid, C12 (48.3%) and other major fatty acids are myristic, C14 (15.6%) and oleic acids, C18:1 (15.1%).[6,7] However, candlenut is a native seed in Malaysia. Although it has not been studied extensively, it is a rich source of great quality oil containing almost 39.6% of unsaturated oil.[8] It also has antioxidant property . The candlenut oil is a strong candidate to compete with other available culinary oils.[9]

There are 3 conventional approaches that are being used in Malaysia to extract palm oil. Those are i) high pressure screw press ii) direct solvent extraction iii) mechanical press (screw press) followed by solvent extraction.[10] Mechanical pressing is good method to extract oil keeping its nutritional value high, though it does not extract all oil from the cells and it is not as much efficient as solvent extraction process.[11,12] However, solvent extraction of oil by using hexane or other organic solvent can result in the deterioration of the heat-labile poly-unsaturated fatty acids (PUFA) in the oil since higher temperature is used which also can rise its oxidative rancidity.[13] On the other hand, SC-CO_2 extracted oil is nearly odourless and the heat-labile fatty acids are recollected.[14]

Three types of samples were analysed among them two are from the same source. Two similar samples were first time extracted palm kernel cake and that of second time extracted in the same factory under same condition. Whereas, another sample i.e. candlenut was used after being extracted at lab at 40°C, 4000psi and for 40 mins.

These samples were used for this study to compare the extractability of SC-CO_2 extraction method on the trace oil content and to evaluate the best condition of extraction by developing a model by using response surface methodology (RSM).

II. METHODOLOGY

The dried and de-hulled candlenut was obtained from a local market in Pulau Pinang, Malaysia. ground to powder using a laboratory blender, sieved to collect sample of particle size of 1–2 mm in diameter. It was used for SC-CO_2 extraction at varying extracting time, pressure and temperature while palm kernel cake was obtained from "Palmolis" palm oil factory, Penang, Malaysia. All reagents and chemicals used were of an analytical grade. CO_2 with a purity of 99.9% was obtained (MOX) (Pulau Pinang, Malaysia). SC-CO_2 extraction was used to extract the oil, which then compared to the oil extracted by the Soxhlet extraction method, where the solvent was hexane.

Soxhlet extraction of candlenut oil: Oil from all three types of samples was extracted by Soxhlet extraction, using n-hexane (Merck) for 7 h. The extracted oil was considered as the total oil content of the samples. A sample size of 5 g was used for all types of extraction, and the resultant oil was compared with that extracted by SC-CO_2 total oil content across the samples.

Supercritical CO_2 extraction: A supercritical CO_2 extractor (ISCO, Inc., Lincoln, NE; model SFX 220) was used to perform the extraction. The extractor was connected to a CO_2 cylinder along with a chiller (B/L-730, YIH DER, Taipei), for liquefaction of the CO_2, and a high-pressure syringe pump (ISCO, Inc; Model 100DX) with a maximum operating pressure of 69 MPa to deliver the CO_2. The volume of the extraction vessel was 2.5 mL. The extractor was equipped with a heated capillary restrictor (ISCO, Inc.) that had an outer diameter of 50 µm and a maximum operating temperature of 150˚C. The temperature, pressure, and time of extraction were controlled using the software (ISCO, Inc.; Model 220) that was integrated with the system.

Extractions were performed in the temperature range of 40 to 80˚C, pressure range of 27.58 MPa to 48.26 MPa, and for different time durations ranging from 40 to 70 min. The average flow rate of CO_2 was maintained at 2 mL/min. Approximately 1.6g of sample was poured into the extraction cell. The cell was placed in the extraction chamber and was allowed to equilibrate to the preset temperature, after which the chamber was pressurized. The oil from the CO_2 was collected in a weighed vial at the fluid outlet. At room temperature, the triglycerides that constitute the oil are liquid and are readily separated from the CO_2 gas phase. Collection vials were weighed, and the weight of the empty vial was deducted to obtain the weight of the oil. The extraction yield was determined in comparison to the total oil content, the amount of sample, and the amount of oil extracted by supercritical fluid extraction (SFE). The present yield (Y) was determined using the following equation:

$$Y = \frac{m_{SCF}}{m_{Sox}} \times 100 \qquad (1)$$

where m_{SCF} is the mass of oil extracted by the SFE process, and m_{Sox} is the mass of total oil extracted by Soxhlet extraction.
The volume of CO_2 consumed was recorded for each run by the flow meter integrated into the SC-CO_2 extractor. The volume was displayed on the monitor of the meter. Later, the mass of CO_2 was further calculated using the CO_2 density for each condition.

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Scanning Electron Microscope (SEM)
Morphological properties of the samples were analyzed by Scanning Electron Microscope (LeoSupra 50 VP Field Emission SEM, Germany) equipped with Oxford INCA 400 energy dispersive X-Ray microanalysis system. Samples after and before of extraction were studied. Sample specimen was coated with 100-120 A˚ thickness of gold and put on a specimen holder; images were recorded on Kodak Plus-X pan.

Statistical analysis
To study the influential factors and their combination among the three factors of Pressure, temperature and time, The Box-Benhken design was used on the yield of oil extracted from candlenut, PKC 1st time extracted as well as PKC 2nd time extracted samples. The high and low levels of these factors were set at 31 and 34.50 MPa, 60 and 70 ºC, 40 and 50 min for the pressure, temperature, and extraction time, respectively. The total number of experiments was 15 runs for each sample. A model was developed to optimize the process by finding the best operating conditions from among these factors so as to maximize the yield of extracted oil.

III. RESULTS AND DISCUSSION

The results obtained from the above mentioned design were analysed by ANOVA to evaluate the relationship between the yield and the parameters (temperature, pressure and time). The first and second order models were developed to optimize yield through the optimal settings of the parameters used. In terms of the coded values of factors, the model obtained as follows:

Y_C = -2220.58 - 4.09X_1 + 131.52X_2 +1.99 X_3 - 0.02 X_1^2- 2.17 X_2^2 + 0.01 X_3^2+ 0.28 X_1X_2- 0.06 X_1X_3+ 0.06 X_2X_3 ……………………………………………………..… (2)

Y_{P1}= 172.81- 15.84 X_1+ 13.79 X_2+10.55 X_3+ 0.056 X_1^2- 0.083 X_2^2+ 0.087 X_3^2+ 0.259 X_1X_2+ 0.005 X_1X_3- 0.589 X_1X_3 ……………………………………………….. (3)

Y_{p2}= -2046.66 – 9.83 X_1 + 118.04 X_2 +23.01 X_3 + 0.11 X_1^2 – 1.63 X_2^2– 0.09 X_3^2 + 0.01 X_1X_2 – 0.10 X_1X_3– 0. 25 X_2X_3 …………………………………………………… (4)

The subscripts of Y indicate the sample type, that is, C, P1 and P2 which refer to Candlenut, PKC 1st time pressed and PKC 2nd time pressed samples, respectively. The coefficient of determination for the yields and p value for equation 1 and 2 (0.052 and 0.078 respectively) of Y_C and Y_{P1} showed that the second order model fit the data adequately. The R^2 values for Y_C and Y_{P1} were found to be 97.5 and 78.8% respectively. The R^2 value explained that almost 98% and 79% of the total variation was explained for the Y_C and Y_{P1}.

The relative contribution of each factors to yield (Y) were directly measured by the regression coefficient in the above equations (2, 3 and 4). A positive sign in the fitted regression model indicates the ability of the factors to increase the response while negative signs refer to the decreasing capability of the factors to the yield.

For Candlenut extraction

Table 1. Estimated Regression Coefficients for Yield %

Term	Coef.	SE Coef.	T	P
Constant	-2220.58	1071.65	-2.072	0.093
Temp	-4.09	13.61	-0.300	0.776
Press	131.52	47.94	2.744	0.041
Time	1.99	11.77	0.169	0.873
Temp x Temp	-0.02	0.08	-0.231	0.826
Press x Press	-2.17	0.68	-3.203	0.024
Time x Time	0.01	0.08	0.137	0.896
Temp x press	0.28	0.23	1.246	0.268
Temp x Time	-0.06	0.08	-0.739	0.493
Press x Time	0.06	0,23	0.256	0.808

R^2 value = 97.5%

Table 2. Analysis of Variance for Yield %

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	9	3072.98	3072.983	341.44	31.4	0.002
Linear	3	2872.90	134.842	44.947	2.82	0.146
Square	3	165.64	165.642	55.214	3.47	0.107
Interaction	3	34.44	34.444	11.481	0.72	0.581
Residual Error	5	79.60	79.601	15.920	-	-
Lack-of-Fit	3	76.90	76.899	25.633	18.98	0.052
Pure Error	2	2.70	2.701	1.351	-	-
Total	14	3152.58	-	-	-	-

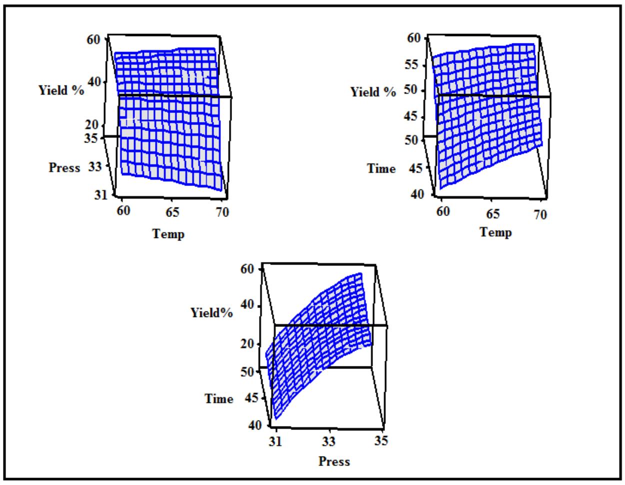

Figure 1. %Yield as response for the combination of variation of binary factors of temperature, time and pressure.

For PKC (1st time extracted):

Table 3. Estimated Regression Coefficients for Yield %.

Term	Coef.	SE Coef.	T	P
Constant	172.81	1024.30	0.169	0.873
Temp	-15.84	13.01	-1.218	0.278
Press	13.79	45.82	-0.301	0.776
Time	10.55	11.25	0.938	0.391
Temp x Temp	0.056	0.08	0.708	0.511
Press x Press	-0.083	0.65	-0.128	0.903
Time x Time	0.087	0.08	1.100	0.322
Temp x press	0.259	0.22	1.187	0.289
Temp x Time	0.005	0.08	0.060	0.954
Press x Time	-0.589	0.22	-2.701	0.043

R-Sq = 78.8%

Table 4. Analysis of Variance for Yield %.

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	9	289.560	289.560	32.1733	2.19	0.201
Linear	3	124.275	40.016	13.3387	0.91	0.500
Square	3	35.257	35.257	11.7522	0.80	0.545
Interactions	3	130.029	130.029	43.3428	2.95	0.137
Residual Error	5	73.482	73.482	14.6965	-	-
Lack-of-Fit	3	71.751	71.751	23.9171	27.64	0.035
Pure Error	2	1.731	1.731	0.8654	-	-
Total	14	363.042	-	-	-	-

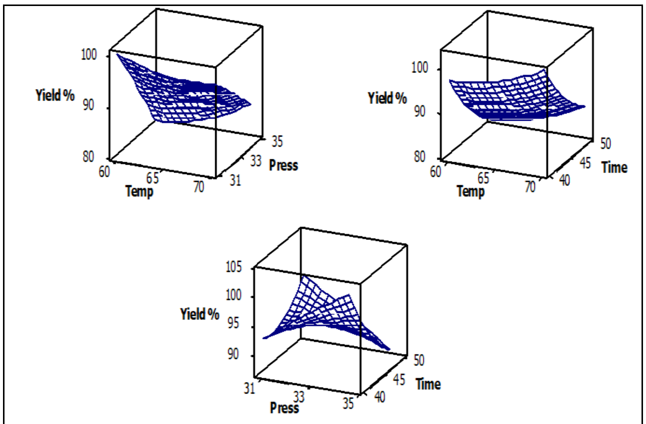

Figure 2. %Yield as response for the binary combination of temperature, pressure and time for palm kernel cake after first time extraction.

For PKC 2nd (time extracted)

Table 5.Estimated Regression Coefficient for Yield %.

Term	Coef.	SE Coef.	T	P
Constant	-2046.66	1835.68	-1.115	0.316
Temp	-9.83	23.32	-0.422	0.691
Press	118.04	82.11	1.437	0.210
Time	23.01	20.17	1.141	0.305
Temp x Temp	0.11	0.14	0.778	0.472
Press x Press	-1.63	0.16	-1.406	0.219
Time x Time	-0.09	0.14	-0.605	0.544
Temp x press	0.01	0.39	0.026	0.981
Temp x Time	-0.10	0.14	-0.759	0.482
Press x Time	-0.25	0.39	-0.647	0.546

S=6.835 R^2= 49.6

Table 6. Analysis of variance for yield %.

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	9	230.08	230.08	25.56	0.55	0.796
Linear	3	36.90	170.13	56.71	1.21	0.395
Square	3	146.68	146.68	48.89	1.05	0.448
Interactions	3	46.50	46.50	15.50	0.33	0.804
Residual Error	5	233.56	233.56	46.71	-	-
Lack-of-Fit	3	75.08	75.08	25.03	0.32	0.818
Pure Error	2	158.48	158.48	79.24	-	-
Total	14	463.64	-	-	-	-

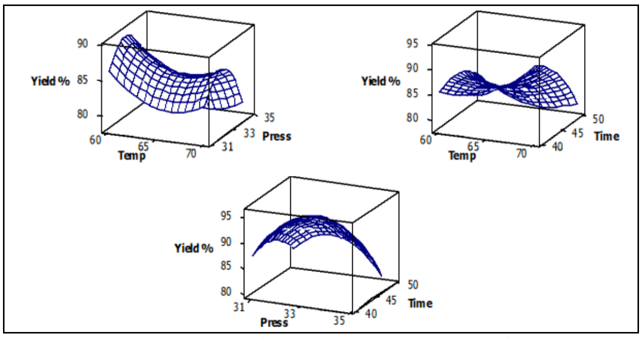

Figure 3. *Yield as response for the binary combination of temperature, pressure and time for palm kernel cake after second time extraction.*

IV. CONCLUSION

Supercritical fluid technology has made significant advances for the extraction of oil from natural sources over the past 20 years. The oil industry is a prospective field for the application of SFE method using SC-CO_2 as a solvent that can minimize wastewater compared to conventional mechanical extraction. It is a cost effective technique at both the laboratory- and industrial-scale for the extraction of oil Supercritical extraction is a powerful environmentally technique to enhance the production of the separation of oil without affecting its nutrient composition. Furthermore, defatted palm kernel cake and Candlenut extracted using SFE, were superior compared to defatted palm kernel cake PKC sample from the palm oil mill. The defatted cake composition after the supercritical extraction has enhanced and become higher in oil. Yet, there are more tests and experiments are needed to approve its safety and acceptance for human consumption that is in progress in our laboratory and among our research group. concluded that supercritical fluid extraction is the best method for exploitation in the extraction of palm oil on an industrial scale.

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