Oil extraction from sheanut (*Vitellaria paradoxa* Gaertn C.F.) kernels assisted by microwaves

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Abstract Shea butter, is highly solicited in cosmetics, pharmaceuticals, chocolates and biodiesel formulations. Microwave assisted extraction (MAE) of butter from sheanut kernels was carried using the Doehlert's experimental design. Factors studied were microwave heating time, temperature and solvent/solute ratio while the responses were the quantity of oil extracted and the acid number. Second order models were established to describe the influence of experimental parameters on the responses studied. Under optimum MAE conditions of heating time 23 min, temperature 75 °C and solvent/solute ratio 4:1 more than 88 % of the oil with a free fatty acid (FFA) value less than 2, was extracted compared to the 10 h and solvent/solute ratio of 10:1 required for soxhlet extraction. Scanning electron microscopy was used to elucidate the effect of microwave heating on the kernels' microstructure. Substantial reduction in extraction time and volumes of solvent used and oil of suitable quality are the main benefits derived from the MAE process.

Keywords Shea butter · Microwave assisted extraction · Optimization · Doehlert design · Biodiesel

Introduction

For more than 10 years now, shea nut (*Vitellaria paradoxa*) has been projected as a potential oil tree capable of significantly increasing the income levels of local women processors in Sub-Saharan Africa. This is because women are the main processors of the shea fruit whose kernels contain up to 50 % oil. This oil is cherished in cosmetics, pharmaceutical formulations and in food. Although the she tree is indigenous to Sub Saharan Africa, its oil and/or products are used worldwide. While shea butter is mostly used in cosmetic formulations in the United States, in the European Union and some Asian countries such as Japan and India, it is used both in cosmetics and chocolate formulations. Shea butter has a high content of essential fatty acids (oleic, stearic, linoleic and palmitic acid), more than most vegetable butters (Nde Bup et al. 2011) which play a very important moisturizing, softening, and anti-inflammatory role. Shea butter also contains vitamins A & E, which have a recognized effect against skin aging due to its rich mineral content with skin protecting and regenerating benefits.

Most of the companies (Aarhus United in Denmark, Fuji Oil in Japan, Karlsham AB in Sweden and Loders Croklaan in Holland) that process shea nut use organic solvents such as hexane (Addaquay 2004). Organic solvents are known for their high extraction efficiency and adaptability to most oil-seeds though they have been highly criticized for being toxic to the environment. Other extraction methods such as supercritical solvent extraction, press extraction and the use of ultrasound, have their various advantages and disadvantages. The setting up of an extraction plant therefore requires a judicious and meticulous choice of the extraction method in order to limit the disadvantages as much as possible. For example, shea butter producers in Africa are constrained to use mostly traditional methods for butter extraction because of the lack of

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financial means to install most of the modern production methods mentioned above. On the other hand, in Europe and America most of the processors are ‘comfortable’ with the use of solvent extraction methods which produce large volumes of oil of good quality.

Generally speaking, no ‘ideal’ method for vegetable oil extraction exists that can be used without concerns due to one or more of the following problems: low yields, long time, solvent consumption and toxicity, high energy consumption, high cost, environmental pollution etc. The development and/or modification of new extraction methods that may limit the disadvantages of the extraction methods earlier cited is a step in the right direction. A case in point is the use of Microwave Assisted Extraction (MAE) technology to recover oil from oilseeds. The major advantages of MAE method include drastic reduction in extraction times from about 10 h in solvent extraction to about 20 min with a corresponding increase in energy savings and reduction of the quantities of solvent used. This method has been used successfully for the extraction of oils from algae (Balasubramanian et al. 2011; Suganya and Renganathan 2012; McMillan et al. 2013), rice bran and soybeans (Boldor et al. 2010; Kanitkar et al. 2011; Terigar et al. 2011), tallow seeds (Boldor et al. 2010; Terigar et al. 2010b), phenolic compounds from rice bran oil (Wataniyakul et al. 2012), bioactive alkaloid compounds from *Rhizoma Coptidis* (Teng and Choi 2013), isoflavones from soybeans (Terigar et al. 2010c) and in the in-situ trans esterification of algae oil into biodiesel (Patil et al. 2011).

The use of microwave heating either as a pre-treatment or process enhancement is appealing because, it has been demonstrated that it is possible to scale up both batch and continuous microwave assisted extraction systems for vegetable oil (Terigar et al. 2011). Microwave pre-treatment has the potential to induce stress reactions in biological systems. The use of microwave radiation in oil extraction may therefore lead to increase in mass transfer coefficients and as a consequence to higher extraction yield because of cell membrane rupture resulting from localized heating of microwaves (Balasubramanian et al. 2011; Boldor et al. 2010; Chen et al. 2012; Terigar et al. 2010b). This effect results in formation of permanent pores, enabling the oil to move easily through the permeable cell walls (Uquiche et al. 2008).

Over the past decades, trade in shea butter has been on the rise because of increased demands in the European Union, Japan, India, Canada and the United States (Carette et al. 2009). Given the importance of the shea butter cited above, coupled with the fact that it is one of the most consumed sources of oil in the producing areas, it can be conjured that the demand for shea butter will continue to rise in the future (Nde Bup et al. 2014). A rise in the demand for this product has some advantages on the countries that produce this fruit

because of the positive observations observed lately related to shea butter processing and marketing. For example, shea is fast becoming an export crop in many West African countries and its products are listed among the top ten non-traditional exports of Ghana (Hatskevich et al. 2011). In Burkina Faso it is the fourth most important export crop after gold, cotton and livestock and makes a contribution of about 6 million USD to the national economy (Konaté 2012). Today the shea tree is the second most important oil crop in Africa after the palm nut tree but its potentials is not fully exploited. The use of microwave extraction technology has the potential of producing volumes good quality oil within short production cycles and therefore should be evaluated for each oilseed to determine optimum processing conditions. The microwave extraction process is influenced by factors such as time, temperature, solvent type, dielectric properties of the solute solvent mixture (Terigar et al. 2010a), among others. Several works have been reported in the literature on extraction of oil from sheanut kernels using super critical carbon dioxide (Nkouam et al. 2012), soxhlet method (Maranz et al. 2003; Nde Bup et al. 2012) but to the best of our knowledge, this is the first time microwave heating technology is being used for the extraction of butter from sheanut kernels. The aim of this work is to evaluate the combined influence of microwave extraction time, temperature and oil/solvent ratio on the quantity and quality of shea butter.

Material and methods

Response surface methodology and the Doehlert’s experimental design was used in this study (Doehlert 1970). The benefits of the Doehlert’s experimental over other designs are elaborated in (Mathieu and Phan-Tan-Luu 1995) and have been emphasized by Imandi et al. (2007) and Nde Bup et al. (2012). These include, amongst others, a reduction in the number of experiments, increased efficiency and possibility of increasing experimental domains or adding new factors to the design without necessarily repeating the experiments that have already been carried out.

Coded variables, x_{ij} , from the Doehlert experimental design (Table 1) were used as the independent variables in the regression analysis (Doehlert 1970). These values were then transformed to natural values using the relation

$$U_i = U_i^0 + x_i \Delta u \quad (1)$$

Where U_i is the value of natural variable (or real value), U_i^0 is the central value of natural variable i , Δu is the increment that can be calculated from Eq. 2, max denotes maximum value.

$$\Delta u = \frac{U_{i\max} - U_i^0}{x_{i\max}} \quad (2)$$

Table 1 Doehlert experimental design used in the MAE of sheanut butter

S/No	Coded values			Real values			Responses	
	x_1	x_2	x_3	X_1	X_2	X_3	Quantity of oil extracted (%)	Acid value (mg KOH/g oil)
1	1.000	0.000	0.000	45.00	75.00	4.50	32.45 ± 1.47	11.58 ± 0.43
2	−1.000	0.000	0.000	1.00	75.00	4.50	27.19 ± 0.88	11.98 ± 0.00
3	0.500	0.866	0.000	34.00	100.00	4.50	31.25 ± 0.64	10.14 ± 0.02
4	−0.500	−0.866	0.000	12.00	50.00	4.50	28.19 ± 2.15	11.71 ± 0.09
5	0.500	−0.866	0.000	34.00	50.00	4.50	31.26 ± 1.08	8.51 ± 0.09
6	−0.500	0.866	0.000	12.00	100.00	4.50	34.67 ± 0.66	8.24 ± 0.17
7	0.500	0.289	0.816	34.00	83.34	6.00	34.10 ± 0.23	9.06 ± 0.16
8	−0.500	−0.289	−0.816	12.00	66.66	3.00	25.47 ± 0.83	2.54 ± 0.12
9	0.500	−0.289	−0.816	34.00	66.66	3.00	36.76 ± 1.08	3.72 ± 0.23
10	0.000	0.577	−0.816	23.00	91.66	3.00	19.23 ± 0.00	11.53 ± 0.20
11	−0.500	0.289	0.816	12.00	83.34	6.00	28.27 ± 1.80	1.43 ± 0.02
12	0.000	−0.577	0.816	23.00	58.34	6.00	29.38 ± 0.22	3.95 ± 0.11
13	0.000	0.000	0.000	23.00	75.00	4.50	31.35 ± 2.06	4.0 ± 0.21

Experimental domains

The factors studied were heating time (1–45 min), heating temperature (50–100 °C) and solvent/solute ratio (3:1–6:1). The choice of these domains were based on preliminary experiments and on previous work carried out in the literature (Boldor et al. 2010).

Modelling of the MAE process

The chosen model was a second degree polynomial with interaction represented by Eq. 3. b_0 , b_i , b_{ii} and b_{ij} are model coefficients for intercept, linear, quadratic and interaction terms, respectively. Coefficients of the model were determined through multiple linear regression analysis using Sigmaplot 12.5 version.

$$y = b_0 + \sum_{i=1}^3 b_i x_i + \sum_{i=1}^3 b_{ii} x_i^2 + \sum_{i=1}^2 \sum_{j=i+1}^3 b_{ij} x_i x_j \quad (3)$$

Microwave extraction process

Mature shea nuts used in this work were picked from Ngaoundere Cameroon, cooked at 85 °C for 2 h (Nde Bup et al. 2012). They were then de-corked, cut into about 5 mm thick slice and dried in an electric oven at 50 °C for 24 h to a moisture content of 3.97 ± 0.5 % d.b. The seeds were stored in a refrigerator at 4 °C until analyses. Samples were withdrawn from the refrigerator and allowed to rest on a laboratory bench to equilibrate the moisture content within the product. They were then ground in a kitchen type electrical grinder for 2 min. Experiments were carried out in an Ethos E batch microwave

system (Milestone Inc., Monroe, CT) with maximum power output of 1000 W. Thirty grams of ground kernels were measured into 250 ml Teflon® (polyfluorotetraethylene) holders equipped with magnetic stirrers and a built-in optical fiber temperature sensor for process monitoring and control. The holders were then firmly corked inserted into the working chamber of the microwave extraction apparatus according to previously established procedures (Boldor et al. 2010; Kanitkar et al. 2011; Terigar et al. 2010b). Programming of temperature and time was done through an external data logger equipped with EasyDoc software which was connected to the equipment. In all, 26 (13 experiments in duplicates) runs were carried out and the average values recorded as shown in Table 1. Heating ramp-up time was 3 min with a chamber vent time of 10 min. After extraction, the mixture was allowed to cool and then vacuum filtered through a No 42 Whatman filter paper. The hexane solvent used was evaporated on a rota-vapor and the residual solvent was dried overnight in a vacuum. The quantity of oil extracted was computed as mass of oil over the sample mass. Control extraction experiments were carried out in duplicates using hexane in a soxhlet apparatus for 10 h.

Fatty acid profiles of the oil by gas chromatography

To determine the fatty acid composition of the oils, 0.02–0.03 g of the oil sample was mixed with heptadecanoic acid (C17:0) (0.1 mg/ml in hexane), as an internal standard and vortexed for about 30–45 s to dissolve the sample. The solvent was then evaporated in a vacuum centrifuge for 15–20 min. Two milliliters BC13-methanol and 1 ml 2, 2-dimethoxypropane were added to the test tubes. The test tubes were then corked and incubated at 60 °C in a water bath for

30 min to perform the derivatisation of fatty acid methyl esters. Then, 1 ml hexane and 1 ml water were added to the tubes and vortexed for 30 s. The upper hexane layer was transferred to another tube, dried with anhydrous sodium sulfate, and transferred to a GC vial. A gas chromatograph (Hewlett Packard 5890, Agilent Technologies, Palo Alto, Calif., U.S.A.) with an FID detector was used for the analysis. Helium was used as a carrier gas with a column flow rate of 1.2 ml/min. The injection volume was 5 µL and the split ratio was 1:100. The injector and detector temperatures were 250 and 270 °C, respectively. The oven temperature program was set to hold at 50 °C for 3 min and then increased at 4.0 °C/min to 250 °C. The column used was a Supelco SP2380 (30 m×0.25 mm). Fatty acid profiles of the oils extracted traditionally were also determined and compared to those obtained by microwave and solvent extractions. Traditional extraction was done by boiling ground kernels of the seeds in water and ladling off the extracted oil. The extracted oil was then filtered and dried at 105 °C to remove residual water.

Scanning electron microscopy of the shea kernel samples

The untreated samples and the defatted shea cake obtained under optimum MAE condition and after soxhlet extraction were analysed by SEM to determine the effect of the extraction method used on the microstructure of the kernels. The samples were dried in vacuum at 40–50 °C for 72 h and sputter coated and then observed under a Scanning electron microscope, (JEOL JSM-6610LV, Tokyo, Japan).

Optimization of the extraction process

To optimize the cooking process, the optimum point for each response (minimum or maximum point) of Eq. 3 was defined as the point where the first partial derivative of the function equals zero: That is

$$\left. \begin{aligned} \frac{\partial Y}{\partial x_1} &= b_1 + 2b_{11}x_1 + b_{12}x_2 + b_{13}x_3 \\ \frac{\partial Y}{\partial x_2} &= b_2 + 2b_{12}x_1 + b_{22}x_2 + b_{23}x_3 \\ \frac{\partial Y}{\partial x_3} &= b_3 + 2b_{13}x_1 + b_{23}x_2 + b_{33}x_3 \end{aligned} \right\} = 0 \quad (4)$$

The system of equations for each response was then solved using the matrix method on Microsoft excel to find the coded values of x_1 , x_2 and x_3 which were then transformed to real values using Eq. 1.

Validation of models

Two criteria: the regression coefficient (R^2) and the percentage Absolute Error of Deviation (AED) between experimental and calculated results were used to evaluate the validity of the models. A model was considered valid if $R^2 > 0.7$ and/or $AED < 10\%$. Regression coefficient were obtained from

multiple linear regression analysis carried out on the results using SigmaPlot 12.5 software while AED was calculated from Eq. 4.

$$AED (\%) = \frac{100}{P} \sum_{i=1}^P \left| \frac{Y_{\text{exp}} - Y_{\text{mod}}}{Y_{\text{exp}}} \right| \quad (5)$$

where Y_{exp} and Y_{mod} are the values obtained from experiments and from the model respectively. P is the number of points at which measurements were carried out.

Results and discussion

Modelling of the microwave assisted oil extraction process

In this process, the quantity oil extracted was used to measure the efficiency of the MAE process, while acid value was used as an indicator to evaluate the effect of microwave heating on the quality of the extracted oil. Table 1 presents the model constants and the associated p-values, R^2 values and AED for the quantity of oil extracted and acid value. At least one of the conditions $R^2 > 0.7$ and/or $AED < 10\%$ was satisfied for both responses so the proposed second order models could be used to describe the effect of the studied parameters on the responses and optimize the MAE process. However it should be noted that $R^2 < 0.7$ or $AED > 10\%$ suggest that some factors which are likely to influence the efficiency of the extraction process and /or quality of the extracted oil such as agitation speed, particle size, power output and residual water in the oilseed which were not evaluated in this work, could be taken into account in future experiments (Suganya and Renganathan 2012).

To better appreciate the influence of the variables on the responses, the validated models were used in three different ways: First the probability (p) values given by multiple linear regression analysis for each model coefficient were considered. A factor associated to a model constant with $p < 0.05$ has a significant effect on the response of interest. Secondly, the effect of each independent factor on the responses was considered by maintaining one of the factors constant at the central point (heating time 23 min, heating temperature 75 °C, and solvent/solute ratio 4.5:1) and plotting the other as a function of the response. Lastly the combined effect of the two factors was evaluated using surface response plots. The following sections describe the effect of the independent variables on the responses using these three approaches.

Effect of experimental parameters on quantity of oil extracted

The quantity of oil extracted varied from 19 to 35 %. Analysis of variance showed that the entire MAE process had a

significant effect ($p < 0.05$) on the quantity of oil extracted. Extraction time and solvent/solute ratio had positive coefficients indicating that the quantity of oil extracted increased with these parameters Table 2. Figure 1 confirms the increase of the quantity of oil extracted with either extraction time or solvent/solute ratio to stable values of 32–33 % when the other parameters were kept constant. The linear effect of extraction time and the interaction effect of temperature and solvent/solute ratio all had significant effects on the quantity of oil extracted ($p < 0.05$). The individual effect of temperature at constant temperature and solvent/solute ratio was negative but insignificant on the value of the quantity of oil extracted varying only between 31 and 32 % when the other parameters were kept constant at the central point (heating time 23 min and solvent/solute ratio 4.5:1).

To better visualize the interaction effects of the independent variables on the responses, one factor was kept constant at the central point and the others plotted as a function of the quantity of oil extracted. Figure 2a shows the combined effect of extraction time and temperature at constant solvent/solute ratio (4.5). As both heating time and temperature increased, the quantity of oil extracted increased and was highest for a processing time of 45 min. Microwave energy has the ability of disrupting the cell walls of plant materials thereby by leading to the fast and complete extraction of components such as lipids, and antioxidants within very short times compared to soxhlet extraction methods. It is possible that this cell disruption increases with heating temperature as the reaction progresses thereby facilitating oil flow. Nde Bup et al. (2012) demonstrated the increase in extraction yields from sheanut kernels with cooking temperature and this was attributed to cell wall disruption brought about by conventional

heating, though heating time in their study was longer (120 min) compared to the 45 min or less used in the present study. In addition, increase in temperature can increase the solubility of the oil and enhance the capacity of solvents to dissolve the oil because thermal energy can overcome cohesive and adhesive interactions between molecules (Karlovic et al. 1992; Suganya and Renganathan 2012).

Figure 2b shows the interaction effect of heating time and solvent/solute ratio at constant temperature (75 °C). The quantity of oil extracted increases as both parameters increase as expected, since as the solvent/solute ratio increases, the volume of the head space reduces and more liquid hexane is available for extraction.

In Figure 2c, at higher solvent/solute ratios there was a remarkable increase in the quantity of oil extracted even at higher temperatures. At higher ratios more of the hexane is available in the liquid phase while solubility increases due to mass fraction considerations (the gradients driving mass diffusion and solubility are higher) so that the effect of temperature on evaporation is greatly diminished due the reduction in the volume of the head space. Recall that the volumes of the extraction flask and the solute remained constant so only the volume of the head space changed in relation to the amount of solvent used. It is possible that under these conditions the effects of cell wall disruption by microwave heating and the availability of hexane in the liquid phase for extraction were more pronounced than the effect of evaporation of the solvent into the vapor phase due to high temperatures, on the quantity of oil extracted.

Fatty acid composition by GC

GC analysis showed that the major fatty acids present in shea butter are palmitic (6.93 ± 1.68), stearic (38.83 ± 1.86), oleic (46.76 ± 0.82) and linoleic acids (7.48 ± 0.35) (Table 3). Akihisa et al. 2010; Davrieux et al. 2010; Nde Bup et al. 2011, evaluated fatty acid composition of shea butter from different African countries and reported that major fatty acids were palmitic, stearic, oleic and linoleic acids in proportions similar to those obtained in this work. In each case the ratio of unsaturated to saturated fatty acids ranged from 1.09 to 1.9 compared to 1.19 obtained in this work. Analysis of variance showed that the entire microwave heating process did not have a significant effect ($p < 0.05$) on any of the major fatty acids present in shea butter (Table 3). Fatty acid profiles extracted under optimum MAE process were not significantly different from those obtained from the soxhlet and traditional methods. These results go a long way to confirm that the MAE process can be conveniently adopted for oil extraction from these kernels without fear of alteration of the composition of the major fatty acids present in the oil.

Table 2 Model constants p-values R² and SEE values for the responses studied

	Oil content		Acid value	
	MC	p-value	MC	p-value
b ₀	31.346	0.001	3.998	0.031
b ₁	3.415	0.013	0.837	0.335
b ₂	−0.054	0.965	1.003	0.251
b ₃	2.101	0.103	−0.687	0.427
b ₁₁	−1.527	0.615	7.784	0.002
b ₂₂	0.504	0.868	4.94	0.029
b ₃₃	−3.47	0.248	−1.121	0.585
b ₁₂	−3.748	0.200	2.943	0.15
b ₁₃	−2.021	0.529	2.904	0.201
b ₂₃	10.409	0.004	−6.039	0.014
R ²	0.631		0.751	
SEE	7.71		28.06	

MC Model coefficient, VMC Value of model coefficient absolute values

Fig. 1 Effect of individual factors (constant heating time 23 min constant temperature 75 °C) and solvent/solute ration 4.5:1) on the quantity of oil extracted

Effect of experimental parameters on acid value (FFA)

Acid value is an important parameter that is used among others to define the quality of an oil. It is double the free fatty acid (FFA) value. Analysis of variance shows, that the entire process had a significant influence on acid value ($P < 0.05$). The second order terms of time and temperature as well as the interaction effect of heating temperature and solute/solvent ratio all had significant effects on the acid value. The linear terms of microwave heating time and temperature were positive indicating that acid value increases with these parameters. It was observed that acid value increased non-linearly with temperature throughout the entire process. Increase in acid value is linked to hydrolysis of the oil which is favoured by heating thus the increase in acid value with increasing temperature (Gunstone 2004). Solvent ratio had no significant effect on acid value at constant reaction time and temperature. This points to the fact that lower solvent/solute ratios could be employed without losing much on the quality of the oil and a resultant economy of the amount of solvent used in the extraction process.

The interaction effects of the parameters studied on acid value are present in Fig. 3a–c. Figure 3a shows the combined effect of heating temperature and time at constant solvent/solute ratio on acid value. At constant solvent/solute ratio (4.5:1), acid value decreased with time to a minimum value then increased to high values of about 18 mg KOH/g oil at

high temperatures as heating is prolonged. Table 2 gives high positive coefficients of heating time and temperature which indicate their ability to increase acid value.

The variation of acid value as a function of heating time and solvent/solute ratio at constant temperature (75 °C) is presented in Fig. 3b. Again acid value decreased to a minimum value and then increased as reaction time increased but remained virtually constant with solvent/solute mole ratio. At constant heating time (23 min), acid value increased with temperature at lower solvent/solid ratios from less than 2 to about 12 mg KOH/g oil. At solvent/solid ratios greater than 4, acid values decreased as heating temperature is increased. It seems that in the presence of higher quantities of the solvent, the effect of hydrolysis brought about by higher temperatures is minimized.

Optimization of MAE parameters

Optimization of the MAE parameters as described in Modelling of the MAE process section gave the following results for the quantity of oil extracted: Heating time 40.47 min, heating temperature 78.60 °C and solvent solid ratio 4.98:1. The corresponding values for acid value were 22.42 min, 71.71 °C and 4.43:1. However, as Table 1 showed that the quantity of oil extracted at 75 °C for 23 min (32.45 ± 2.01 %) was not significantly different from that obtained after 45 min at 75 °C (31.43 ± 1.47 %). Therefore taking into consideration the two responses measured, optimum ranges of

Fig. 2 Surface plots of quantity of oil extracted as affected by experimental parameters **(a)** Heating time and temperature (Solvent/solute ratio 4.5:1) **(b)** cooking time and nut size (temperature 75 °C) **(c)** temperature and solvent/solute ratio (time 23 min)

the parameters were defined as: Heating time 23 min, heating temperature 70–80 °C and solvent/solid ratio 4:1–5:1. To confirm these optimum domains, contour plots of quantity of oil

Table 3 Fatty acid compositions (%) of shea butter obtained from MAE Soxhlet and Traditional Extraction (TE) method

Exp't No	C16:0	C18:0	C18:1	C18:2
1	9.35	39.37	44.11	7.17
2	4.98	39.19	48.70	7.13
3	5.97	37.57	48.27	8.19
4	5.91	38.40	47.98	7.71
5	6.50	39.07	46.76	7.67
6	7.19	37.09	47.40	8.33
7	7.89	37.42	47.35	7.34
8	6.04	39.27	46.84	7.84
9	8.19	38.12	46.21	7.48
10	nd	nd	nd	nd
11	6.58	39.24	46.78	7.41
12	6.54	38.26	47.65	7.55
13	10.29	36.10	46.00	7.61
MAE	6.18	39.19	47.21	7.42
Soxhlet	6.31	38.36	47.34	7.99
TE	5.67	41.83	45.57	6.93
Mean	6.93 ± 1.68	38.83 ± 1.86	46.76 ± 0.82	7.48 ± 0.35

extracted and acid value were superimposed and the optimum region (shaded area) was define as the intersection zone which corresponded to maximum oil yield and minimum acid value. From Fig. 4a–c, it is seen that the optimum points for the studied parameters fell within the range given by mathematical calculations. The following optimum conditions were therefore retained for the MAE of oil from sheanut kernel: Reaction time 23 min, temperature 75 °C for and a solvent/solute ratio of 4. These gave calculated optimum responses of quantity of oil extracted and acid value of 31.66 % and 3.72 mg KOH/ g oil respectively. Experiments were conducted to verify the established optimum conditions. Quantity of oil extracted and acid value obtained from verification experiments under optimum conditions were 31.58 ± 2.22 % and 3.45 ± 0.23 % mg KOH/ g oil which compared well with calculated results and confirmed that the models developed were adequate. Corresponding results obtained from soxhlet method after 10 h of extraction were 35.71 ± 0.37 % and 4.39 ± 0.12 mg KOH/ g oil.

This represents an extraction efficiency of 88.76 %. The extraction efficiency obtained under optimum conditions is very appealing when compared to the 10 h used in soxhlet extraction. Note from Table 1 that, if the acid value is not taken into consideration during optimization, conditions can be selected such that more oil is extracted compared to that obtained from the conventional soxhlet method. For example, extraction efficiency from experiment 9 is 102.87 %. This effect was observed in extraction of lipids from other feed-stock such as soybeans and rice bran using microwave (Boldor et al. 2010; Kanitkar et al. 2011; Terigar et al. 2010b).

Fig. 3 Surface plots of acid value as affected by experimental parameters (a) Heating time and temperature (Solvent/solute ratio 4.5:1) (b) cooking time and nut size (temperature 75 °C) (c) temperature and nut size (time 23 min)

Acid value obtained under optimum MAE conditions was 15 % less than that obtained from soxhlet extraction indicating that the process does not negatively impact the quality of the oil. Optimum acid value of 3.73 (FFA of 1.87 %) permits the classification of the oil as Category 2 butter which is recommended in food industry (confectionaries, chocolates, edible oil, margarines) (Masters 2007). This low FFA value can also enable the one step (using basic catalysis only) rather the two step (acid followed by basic catalysis) transesterification of oils with high FFA values into biodiesel.

Many researchers have reported that microwave heating technology is effective either as a pretreatment or enhancement method for the extraction of lipids and other substances from biological materials. Microwave heating causes direct generation of heat within the material (volumetric heating), which lead to immediate temperature rise within the matrix and pressure effects on the cell wall membrane structure (Balasubramanian et al. 2011). This facilitates oil flow from the matrix to the solvent. Lee et al. (2010) tested six methods for effective lipid extraction and including autoclaving, bead-beating, microwaves, sonication, and a 10 % NaCl solution and concluded that microwave oven method was the most simple, easy, and effective for lipid extraction from microalgae. Balasubramanian et al. (2011) reported that a continuous microwave system extracted 76–77 % of total recoverable oil at 20–30 min and 95 °C from *Scenedesmus obliquus*. McMillan et al. (2013) equally, reported a 94.97 % extraction efficiency of lipids from algal cells after cell disruption by microwave treatment. Similar results highlighting the effectiveness of microwave technology in lipid extraction have been reported by other researchers (Boldor et al. 2010; Balasubramanian et al. 2011; Kanitkar et al. 2011; Terigar et al. 2010a, b, c; Momeny et al. 2012). Optimum solvent/solid ratio obtained in this work was 4:1 while that for soxhlet extraction is more than 10:1. This represents substantial gains with respect to the quantity of solvent required for MAE compared to the conventional soxhlet extraction.

Effect on microstructure

The various extraction methods produced distinguishable physical changes in the shea nut kernels. For example, the samples after extraction were powdery in nature compared to the untreated samples while the MAE sample produced a visually finer powder compared to that obtained from the soxhlet method. SEM micrographs of the untreated sample and the defatted cake obtained after MAE and soxhlet extractions are presented in Fig. 5a–c. The untreated sample shows a more intact structure due to the absence of heat treatment. However the soxhlet sample shows that the cells have been ruptured and agglomerated creating space for oil flow. This cell rupture and agglomeration was more pronounced in the MAE sample which explains the efficient and rapid extraction

Fig. 4 Superimposed contour plots of quantity of oil and acid showing the optimum zones (shaded regions) of the parameters studied (a) Heating time and temperature (Solvent/solute ratio 4.5:1) (b) cooking time and nut size (temperature 75 °C) (c) temperature and nut size (time 23 min)

Fig. 5 Effect of extraction method on the microstructure of sheanut kernels (a) Untreated sample (b) Sample after soxhlet extraction (c) Sample after MAE

of oil in MAE method compared to the soxhlet method. These results confirm those of Lucchesi et al. (2007), Terigar et al. (2010a) and Pasquet et al. (2011) who used SEM to elucidate the positive effects of microwave heating on cell membrane rupture for rapid and efficient extraction of components from

biological materials. Nde Bup et al. (2012) demonstrated that conventional heating of whole shea nuts in water at 85 °C before soxhlet extraction promoted cell membrane rupture and improved extraction yields. However the cooking and the soxhlet extraction processes used in their study took a total of 12 h compared to the 23 min in MAE process to obtain similar results.

Conclusion

MAE extraction is an effective method for the extraction of lipids from sheanut kernel with substantial gains in reaction time and quantities of solvent used. Optimum conditions for the MAE of oil from sheanut kernels were established as heating time 23 min, temperature 75 °C and solvent/solute ratio of 4:1. Under these conditions more than 88 % of the oil of good quality is extracted. This work presents for the first time the MAE extraction of shea butter a technology which if well harnessed can promote shea trade because in most shea producing countries extraction methods are mostly traditional with attendant consequences of low yields and poor quality.

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