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Influence of Fractionation on the Oxidative Stability, Thermal Stability, and Fatty Acid Profile of Shea Olein Fractions

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ABSTRACT

Oxidative stability can directly affect oil quality and shelf life, especially in fat and oil-containing products such as shea olein. Shea butter is becoming increasingly popular in foods, cosmetics and pharmaceutical products, but is generally unstable. The fractionation of shea butter affects the stability of shea olein. Therefore, this study investigated the effect of fractionalization on oxidative and thermal stability with fatty acid composition of shea olein. Shea butter was fractionalized using a cold centrifuge at 5 °C and -5 °C to obtain two fractions of shea olein. The stability of the shea olein fractions was evaluated with peroxide values (PV), p-anisidine value (p-AV), conjugated dienes (CD), and Thiobarbituric Acid Reactive Substances (TBARS). The thermal stability and fatty acid composition were determined using the differential scanning calorimetry method and the Gas Chromatographic method. The percentage yield for crude shea butter, shea olein (DSOA), and super shea olein (DSOB) were 37.5%, 75.59% and 50.94%, respectively. The PV, p-AV, CD and TBARS were in the ranges 0.32-1.59 meq O/kg, 7.28 - 11.51, 0.59 - 5.00 mmol/g and 0.10 to 0.14 mmol/g. The thermal stability reflects an endothermic transition of CSB, DSOA, and DSOB as -17.35 mW, -12.93 mW, and -3.85 mW, while their fatty acid profile revealed two prominent acids, arachidic acid (39.87, 40.04, and 29.26%), oleic acid (47.83%, 48.30%, and 56.23%), respectively. The study demonstrated that the oxidative and thermal stability of shea olein is achievable during fractionation, leading to a more stable oil for food formulations.

INTRODUCTION

Fractionation is a method of fat modification employed to extend the usefulness of fat in the vegetable oil industry. Fats are limited in use in their natural state due to a fixed profile of fatty acids, which render them limited in applications (Azad *et al*., 2021). To maximize vegetable fats/oils, they are separated into different fractions via fractionation to extend their use via dry process, solvent, and detergent process. Some vegetable fats and oils that have gone through fractionation include shea butter, sunflower oil, palm oil, coconut oil, sal butter, palm kernel oil, and illipe butter (Hwang *et al.,* 2021).

Shea butter originates from the nuts of the shea (butter) tree (*Vitellaria paradoxa*), which is an indigenous fruit tree belonging to the Sapotaceae family (Choungo Nguekeng *et al*., 2021). Shea butter holds its importance in both local and international trade due to its unique composition of triacylglycerol of stearic-oleic-stearic (St-O-St) and high content of unsaponifiables (7-11%) (Lovett, 2015; Hwang *et al*., 2021). These properties make them relevant raw materials in cosmetic and food

industry. Due to its triacylglycerol of stearic-oleic-stearic (St-O-St), shea butter is fractionated into stearin (hard fraction) and olein (soft fraction). The stearin fraction is widely used in the chocolate industry as a substitute for cocoa butter due to its similar melting point, while olein is often regarded as waste (Declerck *et al.,* 2021).

Shea olein is the liquid fraction of shea butter, which is grossly underutilized in the food industry. It is the golden yellow-coloured oil obtained from the fractionation of shea butter, which is considered a less valuable product of shea butter fractionation. However, shea olein is rich in bioactive compounds, possesses similar chemical properties to palm olein, and has a higher content of alpha-tocopherol, which is a natural antioxidant (Abdel-Razek *et al*., 2023; Korede *et al.,* 2024). Shea olein has also been reported to have a high content of unsaturated fatty acids, ranging from 44.47 to 56% monounsaturated fatty acids and 8.06% polyunsaturated fatty acids (Abdel-Razek *et al.,* 2023; Korede *et al*., 2024). To promote the utilization of shea olein in the food industry, its stability is essential, as stability is one of the major factors that drive the applications of fats/oils in the food industry. There is, however, a paucity of information reported in the literature on shea olein regarding its stability during the fractionation process, specifically on its compliance with the desired end-use requirements (Pattnaik and Mishra, 2021).

Several studies have investigated the preparation, quality attributes, and applications of shea olein in various food formulations (Hwang *et al*., 2021; Korede *et al*., 2024; Zhang *et al.*, 2017; Gao *et al.*, 2022). Regarding preparation methods, Korede *et al*. (2024) described the dry fractionation technique for producing shea olein, while Zhang *et al.* (2017) and Hwang *et al*. (2021) explored single- and double-solvent fractionation approaches. In the present study, the solvent fractionation method was adopted because it yields a more liquid olein fraction at lower temperatures compared to dry fractionation.

The quality of shea olein has been assessed primarily through physicochemical properties, as well as its antioxidant and antimicrobial activities (Korede *et al*., 2024; Abdel-Razek *et al.*, 2023). Additionally, shea olein has been successfully incorporated into various formulations as a partial or complete replacement for palm olein in palm-based products. Its incorporation enhances beta-crystal formation during crystallization, thereby improving melting profiles, polymorphic behaviour, and overall functional properties (Gao *et al.,* 2022; Zhang *et al*., 2017).

Despite these advances, no previous research has systematically evaluated the oxidative stability indices of shea olein during the fractionation process itself. Furthermore, there is a notable lack of data on the changes in fatty acid composition and thermal behaviour under heat stress throughout fractionation. This study addresses these critical gaps by examining the effects of the fractionation process on the oxidative stability, fatty acid profile, and thermal characteristics of shea olein.

METHODOLOGY

Shea butter extraction

Shea kernels were procured from a local market in *Kishi*, *Irepodun* Local Government Area, Oyo State. Shea butter was traditionally extracted. All chemicals used were of analytical grade. Well-cleaned, sorted, and dried kernels (4.4 kg) were used for the traditional extraction of shea butter. The kernels were initially pounded with a pestle and mortar to break them into grits. Next, the grits were roasted to facilitate the extraction of butter or fat, and then the roasted grits were ground into a smooth paste. The extraction process involved kneading the paste in water to form an emulsion, which helped capture the fat. The resulting emulsion was then boiled for approximately 120 min to promote

separation of the fat, after which the fat was skimmed off, filtered, and allowed to cool into the final product, shea butter (Korede *et al*., 2024). The yield was determined using Equation 1.

$$\%yield = \frac{Weight\ of\ extracted\ shea\ butter}{Weight\ of\ shea\ kernels}\ x100 \quad (1)$$

Fractionation of shea butter

As shown in Figure 1, crude shea butter was degummed following a method previously described by Addaquay (2004) with minor modifications. Shea butter (1500 g) was melted at 50 °C and dosed with 0.4% by volume 85% phosphoric acid in a mixer for 5 min. The gums were removed from shea butter using an Eppendorf 5430R refrigerated centrifuge at 20 ℃ for 20 min at 15,000 revolutions per min. The resultant shea butter recovered was designated degummed shea butter (1368.08 g). This served as the starting material for the fractionation process.

The oleic acid-rich oil was prepared by performing a two-step hexane fractionation of shea butter described by Hwang *et al*. (2021) with slight modification. For the first fractionation step, degummed shea butter and the specified volume of hexane (2500–2800 mL) were introduced into the vessel, which was then heated to 45 °C using a water bath (WBE601, LAB CON, Maraisburg) to melt the degummed shea butter in hexane. The mixture obtained was centrifuged at 5 °C using a cold centrifuge (5430R, Eppendorf, Germany) for 3 h. The liquid fraction was decanted from the centrifuge tubes and evaporated using a rotary vacuum evaporator (EV311 PLUS, Lab Tech, Italy) at 30 ℃. The liquid fraction obtained under these conditions during the first fractionation step was labelled as shea olein (DSOA). The second fractionation step was conducted in the same manner as the first. Approximately 1,000 g of shea olein was further crystallized in 4,000 mL of hexane using a cold centrifuge at -5 ℃ for 4 h.

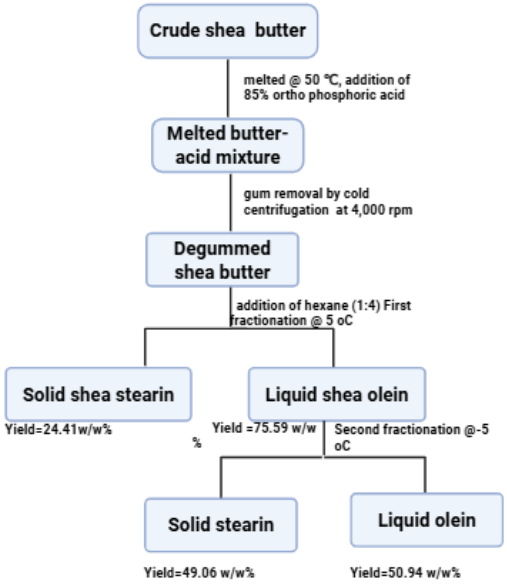

Figure 1: Flow chart of solvent fractionation of crude shea butter

The liquid fraction obtained under these conditions was labelled super shea olein (DSOB). The percentage olein fraction was calculated as follows:

$$\%\ olein\ fraction = \frac{wt\ olein}{wt\ shea\ butter}\ x\ 100 \quad (2)$$

Determination of peroxide value

About five (5) g of oil sample was weighed into a conical flask. The content of the flask was dissolved in a 30 mL mixture of acetic acid and chloroform (2:1), and 0.5 mL of a saturated potassium iodide solution was added. The mixture was then shaken and allowed to stand for 1 min. After which, 30 mL of distilled water and 0.5 mL starch indicator were added, and the content was titrated against 0.01 N sodium thiosulphate. The blank test was conducted (AOAC, 2012). Peroxide value was calculated as ml equivalent of active oxygen /kg of sample as indicated in Eqn. 3.

$$\text{Peroxide value} = \frac{S \times N \times 1000}{Sample\ weight} \quad (3)$$

S = Titre value of sample – Titre value of blank,

N = Molarity of the thiosulphate

Determination of ρ-anisidine value

The p-anisidine value (AV) was determined according to the AOCS Official Method Cd 18-90, with modification using a UV-visible microplate reader (PowerWave HT microplate reader, BioTek) at a wavelength of 350 nm. The 0.25% p-anisidine reagent was prepared every working day. 0.25 grams of p-anisidine was dissolved in 100 mL of 100 % acetic acid, and the absorbance was measured to ensure a value below Abs = 0.2. To analyze the samples, 0.1 g (100 mg) of oil was weighed directly in test tubes and dissolved in 5 mL of iso-octane. 2.5mL of sample was transferred to a cuvette, and the absorbance was measured at 350 nm against pure iso-octane as a blank. Then, 0.5 mL of p-anisidine reagent was added, and the cuvette was shaken by hand. The cuvette was kept in the dark for 10 min before the second absorbance measurement was made.

The p-AV is given by the formula:

$$\rho - AV = D\ x\ [1.2\ x\ (AS2 - AB2) - (AS1 - AB1)/m] \quad (4)$$

Where, D is the volume of iso-octane used to dissolve oil sample (1 mL), AS1= Absorbance of the oil solution before reaction with the p-anisidine reagent, AS2 = Absorbance of the oil solution after reaction with the p-anisidine reagent, AB1= Absorbance of iso-octane before reaction with the p-anisidine reagent, AS2 = Absorbance of iso-octane after reaction with the p-anisidine reagent, and m = mass of the sample (20 mg).

Determination of conjugated dienes

Conjugated dienes were determined as described by Kūka *et al*. (2018). One hundred (100) mg of each sample was weighed into a test tube, and 5 mL of iso-octane was added to dissolve it. About 300 µL of each sample was transferred into a 96-well microplate. The absorbance reading of each sample solution was taken at 234 nm using a microplate reader (PowerWave HT microplate reader, BioTek). Absorbance was taken against 1% methyl stearate in iso-octane as a blank.

$$CD = A/\varepsilon l \quad (5)$$

Where

CD is the concentration of conjugated dienes in the sample

A is the sample absorbance in iso-octane, which varies across the samples

L is the path length, which equals 1 cm

ε is the molar absorptivity of 1% solution, which is 25250 M-1 ·cm -1 – molar absorptivity of linoleic acid hydroperoxide

The conjugated diene value (CD value) was calculated as follows:

$$CD\ value = [CD]x\ 5\ x\ 10\ 4/\mathrm{m} \quad (6)$$

where

5 x10^4 – a factor that encompasses the volume of iso-octane (50 mL) used to dissolve the oil sample for the determination of CD concentration in µmol,

m – sample weight

Determination of Thiobarbituric Acid Reactive Substance (TBARS)

TBARS was measured with a little modification in the method described by Zeb and Ullah (2016). Fifty (50) mg of the oil sample was homogenized in 1 mL of 50% glacial acetic acid solution at 50 °C for 2 min. The mixture was allowed to cool to room temperature (25 ℃). A 57.66 mg thiobarbituric acid (TBA) in 100 mL glacial acetic acid (4.0 mM) was prepared, and exactly 150 µL each of the sample solution and TBA were placed in microplate wells and heated in an oven (60 °C) for 60 min to develop a pink colour. The blank sample was prepared by adding 150 µL 50% acetic acid + 150 µL TBA in a microplate well. The calibration standard (1mM) was prepared by dissolving 31.35 mg of malondialdehyde tetrabutylammonium salt (MDA) in 100 mL of glacial acetic acid. This was diluted to give 0.2, 0.4, 0.6, and 0.8 mM. 150 µL of TBA was added to the same volume of MDA in the microplate

well. The samples were measured at 532 nm in a microplate reader (PowerWave HT microplate reader, BioTek). A calibration curve of absorbance was plotted against the concentration, and the concentration of the samples was determined and expressed as mmol MDA equivalents/g oil.

Thermal stability of shea butter, shea olein, and super shea olein fractions

The thermal stability of the shea fractions was assessed using the method described by Islam *et al.* (2023). An empty sealed pan was used as a reference, and lipid samples (6–8 mg) were firmly sealed in a 100 µL aluminium pan. At a rate of 20 °C per min, these samples were heated isothermally from 25 °C to 140 °C, and they were kept in the DSC furnace for 90 min. The profiles were analyzed using the DSC system software (ᵒstar, Mettler Tonado, Shelton, CT, USA). The temperature for the isothermal program was set at 140 °C.

Determination of Fatty Acid Composition

The procedures described by Wang *et al*. (2015) were used to prepare the fatty acid methyl esters (FAMEs): 10 mL screw-capped tubes containing 40 µL of treated shea olein were filled with 0.7 mL of potassium hydroxide (10 M) solution and 5.3 mL of methanol. For 1.5 h, the reaction was carried out at 55 °C, with 5 s of mixing every 20 min. 0.58 mL of sulfuric acid (10 M) solution was added after the mixture had cooled to room temperature. The reaction was then maintained at 55 °C for 1.5 h, with 5 s of mixing every 20 min. Three (3) mL of n-hexane was added and stirred for five minutes after the mixture had cooled to room temperature (25 ℃). The tubes were then centrifuged for five minutes, and the extracts were placed in the vial for analysis. A gas chromatography flame ionization detector (GC/FID) analysis using a Schidmazu instrument was conducted. The separation was performed on an RTX-5 capillary column, measuring 30× 0.25 mm in diameter with a film thickness of 0.25 µm. The operating conditions were carrier gas pressure (100 kPa), nitrogen with a split ratio of 1:100, injection temperature (250 °C), and the oven temperature was programmed to start at 50 °C for 2 min, then increased to 174 °C at a rate of 50 °C/min, and finally rise to 215 °C at 2 °C/min until the end of the analysis. The individual fatty acids were identified and characterized by comparing their retention times with the external FAME 37 standards (Korede *et al*., 2024).

RESULTS AND DISCUSSION

Extraction and fractionation of shea butter

The yield of shea butter and shea olein are as presented in Table 1. The conventional shea butter extraction process yielded 37.5% Crude Shea Butter (CSB), which is consistent with the result of Saba *et al*. (2022), who reported a yield of 38.7% for shea butter extracted with the traditional method. Shea butter yield is dependent on several processing steps involved in the method of extraction employed. Saba *et al*. (2022) recorded a yield of 31.7 to 36.4% for butter obtained from shea kernels roasted at 30 to 150 ℃ and 31.6 to 38.7% kneaded at speeds between 100 and 300 revolutions per minute (rpm). Meanwhile, a dissimilar result was reported by Abdul-Hammed *et al*. (2020) and Oussou *et al*. (2022), who obtained shea butter yields ranging between 44.65-48.73% and 32.36-33.34% for solvent and cold press extraction methods, respectively. A moderately high yield (66.90%) of shea butter was observed by Ajala *et al*. (2016) through optimized solvent extraction techniques. Variation in shea butter yield has been reported to be a combination of processing conditions, extraction methods, and shea kernel varieties (Lovett, 2015; Oussou *et al.,* 2022).

In Table 1, the shea olein yield ranged from 50.94 to 75.59%.

Table 2: Oxidative stability of shea fractions during fractionation

Sample	PV (meq O_2/kg)	AV	CD (mmol/g)	TBARS (mmol/g)
CSB	1.59 ± 0.00[a]	11.51±0.02[a]	5.00± 0.25[a]	0.14 ± 0.22[a]
DSOA	0.72 ± 0.05[b]	8.14± 1.02[b]	0.80± 0.11[b]	0.12 ± 0.01[a]
DSOB	0.32 ± 0.01[c]	7.28± 0.85b[c]	0.59± 0.00[c]	0.10±0.03[a]

The fractionation produced markedly different olein yields at the two temperatures at $p<0.05$: 75.59% olein at 5 °C but only 50.94% at −5 °C. The observed result indicates a large temperature dependence of the partition between olein (liquid fraction) and stearin (solid fraction) as reported by Perederic *et al*. (2020). Fractionation is a solid–liquid separation driven by the crystallization of high-melting triacylglycerols (TAGs). At warmer crystallization temperature (5 °C), fewer TAG species crystallized out, and more material remained in the liquid phase, producing a higher olein yield. At lower temperatures (−5 °C), more high-melting TAGs solidify and are removed as stearin, so the olein fraction becomes smaller.

Table 1: Yield of shea butter and its fractions

Process	**% yield (Olein)**	**% Yield (stearin)**
Shea Butter Extraction	37.5±0.82	
Fractionation at 5 ℃	75.59±0.64[a]	24.41±0.32[b]
Fractionation at -5 ℃	50.94±0.52[b]	49.06±0.41[a]

Results are mean values of two determinations ± standard deviation. Values in each column bearing different superscripts are significantly different at p<0.05

This behaviour aligns with the report of Kang *et al*. (2013), who observed a decrease in liquid fraction yield from 80.1 to 61.9% when the temperature was reduced to 21 ℃ from 37 ℃ during fractionation of palm stearin.

Peroxide value

The results of oxidative stability indices obtained during the fractionation of crude shea butter are presented in Table 2. Peroxide value (PV) varied significantly ($p<0.05$) ranged from 0.32 meq O_2/kg in second shea olein fraction (DSOB) to 0.72 meq O_2/kg in the first fraction(DSOA) and 1.59 meq O_2/kg in crude shea butter (CSB). A decrease in PV between 54.72 and 79.87% was observed when crude shea butter was fractionated at 5 °C and -5 °C. Fractionation at less than zero temperature (–5 °C, DSOB) resulted in the lowest PV, suggesting that more crystallization under lower temperature preferentially trapped hydroperoxide-laden triacylglycerols (TAGs) in the stearin fraction, leaving the olein fraction purer. This agrees with the findings of Gerlei *et al.* (2024) that cooling-induced crystallization helps to remove oxidized polar lipids and high-melting triacylglycerols (TAGs), thus decreasing the PV of the olein.

ρ-Anisidine value (AV)

The result of the ρ-anisidine value during fractionation is shown in Table 2; the result of the ρ-anisidine value during fractionation was significantly different ($p<0.05$). Anisidine value (AV), which constituted the secondary oxidation markers (aldehydes, ketones), it ranged from 7.49 to 11.51. The value was significantly higher in CSB (11.51) and lowest in DSOB (7.49). The larger extent of reduction at lower fractionation temperature demonstrated better segregation of secondary oxidation products into the crystalline (stearin) fraction. Aldehydes are more likely to be associated with polar compounds or polymerized species, and these are better eliminated under lower conditions due to a larger extent of crystallization and

larger partitioning into the stearin phase (Sharma *et al.,* 2022).

Conjugated Dienes

The conjugated diene (CD) values among the shea butter fractions are as shown in Table 2 and were significantly different (p<0.05) from each other. CD, which was the first lipid peroxidation, formed during the early stages of lipid oxidation when polyunsaturated fatty acids undergo double bond rearrangement, leading to a conjugated system (Ribourg-Birault *et al*., 2024). A downward trend was recorded among the fractions, from 5.00 mmol/g in CSB to 0.80 mmol /g (DSOA) and 0.59 mmol /g (DSOB). This suggests that conjugated hydroperoxides are extremely prone to fractionation, with the –5 °C process (DSOB) being more effective. This agrees with the finding of Bachari-Saleh *et al*. (2018) that lower temperature crystallization would entrap oxidized polyunsaturated components in the stearin, resulting in an olein with fewer dienic structures. This underscores the potential of fractionation as a tool to enhance the oxidative stability and quality of shea butter for various applications.

Thiobarbituric Acid Reactive Substances (TBARS)

TBARS values are as shown in Table 2, they were low and moderately stable in all samples, ranging from 0.10 mmol MDA/g (DSOB) to 0.14 mmol MDA/g (CSB). TBARS measures secondary oxidation products in oil, primarily malondialdehyde (MDA), formed from the breakdown of hydroperoxides (Nahm *et al.,* 2012). The lower TBARS at lower fractionation temperature suggest partial elimination of aldehydic secondary products besides primary peroxides. This suggests that fractionation not only physically removes high-melting TAGs but also improves the overall oxidative quality of the super shea olein fraction (Lv *et al.,* 2025).

Generally, fractionation alone clearly improved oxidative stability with reductions in PV, AV, CD, and TBARS. This result indicates that the fractionation process removed the oxidized TAGs and polar breakdown products preferentially into the stearin fraction, leaving the olein phase chemically cleaner.

Thermal stability of shea olein Fractions during Fractionation

The differential scanning calorimetry (DSC) curves for CSB, DSOA, and DSOB are as shown in Figure 2, it reveal a clear, progressive enhancement in thermal stability as the fat is fractionated. CSB exhibited the most intense thermal events, with pronounced exothermic and endothermic transitions and a significant endothermic dip of about (−17.35 mW), suggesting a broad range of phase and oxidative processes. These broad thermal events are characteristics of a complex mixture of triglycerides, free fatty acids, phospholipids, and other minor components that co-melt or decompose over a wide range of temperatures, as often observed in minimally processed fats and oils with heterogeneous compositions (Diaz-Diaz *et al.,* 2025). The broad baseline and overlapping transitions align with lower oxidative stability and compositional complexity, a behavior similarly reported in DSC studies of crude vegetable fats, where unresolved, multi-component transitions reflect diverse triacylglycerol populations and associated oxidation events (Islam *et al*., 2023). The prominent, wide endothermic peak in CSB can be attributed to the high energy absorbed during the melting of structurally diverse lipid fractions and impurity-associated components, which is typical of unrefined fat matrices compared to more uniform, refined fractions.

DSOA showed a clear reduction in exothermic intensity (approximately −12.93 mW) and a more stable baseline compared with CSB, indicating improved thermal behavior. Fractionation at 5 °C removed a portion of the high-melting triglycerides (notably stearic- and palmitic-rich species), enriching the shea olein phase with more unsaturated lipids and

producing smoother, less complex thermal transitions (Chikhoune *et al.,* 2020).

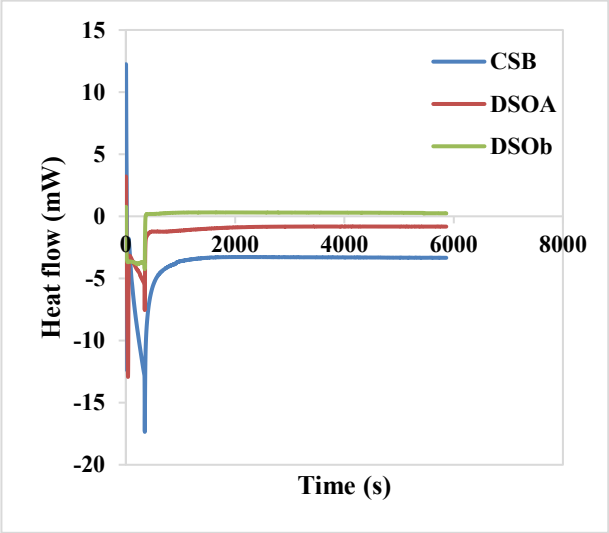

Figure 2: DSC isothermal measurement during fractionation of crude shea butter. CSB-crude shea butter; DSOA-shea olein; DSOB-super shea olein.

Fractionation processes concentrate unsaturated triglycerides in the olein fraction while segregating higher-melting saturated TAGs into the solid fraction, a pattern consistently observed in DSC studies of fractionated fats (Chikhoune *et al.,* 2020). The reduced peak intensity in DSOA also reflects the removal of oxidation-promoting impurities; degumming diminishes phospholipids and trace metals, which are known catalysts for oxidative reactions in fats and oils and contribute to exothermic transitions associated with oxidative decomposition (Wirkowska-Wojdyła *et al*., 2020). However, the remaining exothermic activity indicates that some saturated crystalline domains remain, which still influence melting enthalpy and oxidative susceptibility.

DSOB showed the smallest exothermic transition and the most stable DSC curve, with heat flow staying close to the baseline at -3.85 mW after the initial event. Fractionation at −5 °C allowed for more extensive separation of high-melting stearin fractions, producing a "super shea olein" enriched in low-melting, unsaturated triglycerides (mainly oleic and linoleic acids). This composition results in minimal crystallization enthalpy and better resistance to oxidation because of increased molecular fluidity and significantly fewer impurities (Marikkar *et al.,* 2020; Mulyono *et al*., 2023). The flatter baseline confirms DSOB as the most thermally stable fraction.

Overall, the DSC profiles show a clear thermal-stability trend: DSOB>DSOA>CSB in exothermic intensity, with stability increasing from crude butter to shea olein to super shea olein. This progression reflects the stepwise removal of high-melting triglycerides, impurities, and pro-oxidants during processing. In particular, lowering crystallization temperature during fractionation selectively increases the olein fraction in unsaturated fats, which has been linked to improved oxidative and thermal stability (Mulyono *et al.,* 2023).

Fatty Acid Composition of Shea Olein Fractions during Fractionation

Fatty acid composition changes of shea olein fractions during fractionation is presented in Table 3. There were significant differences (p<0.05) in the fatty acid composition of crude shea butter (CSB), shea olein (DSOA), and super shea olein (DSOB) fractions. Palmitic acid, elaidic acid, oleic acid, and arachidic acid were the major fatty acids contained in crude shea butter, shea olein, and super shea olein fraction. Palmitic acid ranged from 3.25% to 3.42%; elaidic acid, 6.55% to 9.02%; oleic acid, 47.83% to 56.23%; and arachidic acid, between 29.26% and 40.04%. Total saturated fatty acid (TSFA) ranged from 33.70% to 44.61%; total monounsaturated fatty acid (TMUFA), 54.71% to 65.25%; total polyunsaturated fatty acid (TPUFA), 0.42% to 1.05%; and total unsaturated fatty acid (TUFA), between 55.26% and 66.30%.

The fatty acid changes observed during fractionation indicated a clear, temperature-dependent partitioning system. The shea olein fraction recovered at the lower crystallization temperature (DSOB, −5 °C) was markedly enriched in oleic acid, TMUFA, and TUFA by about 17.57%, 21.09% and 19.98%, respectively. This is because as temperature decreases, additional

saturated or partially saturated fat crystallize out into the solid phase, concentrating oleic triacylglycerols in the liquide olein (TAGs) (Abdel-Razek *et al*., 2023; Yılmaz and Ağagündüz, 2022). This trend revealed that the extent of separation was temperature-dependent, as lower temperature (−5 °C) promoted more complete removal of high-melting TAGs, producing super shea olein with higher MUFA and lower SFA content. This aligns with the findings of Bansal and Kour (2022), Heddleson and Kodali, (2022) and Serunkuma, (2022), who reported higher concentrations of oleic acid in the fractionated high oleic sunflower oil, soybean oil, and canola oil at -60 °C compared to their respective parent oils. Higher oleic (MUFA) content generally improves oxidative stability compared to PUFA-rich oils and provides recognized dietary benefits (cardio-protective profile), while the lowered SFA and reduced high-melting TAG content give the olein a lower melting point, improved fluidity at ambient temperature, and stripped CSB-Crude shea butter; DSOA-shea olein @ 5 °C; and DSOB-super shea olein @ -5 °C. Results are mean values of two determinations ± standard deviation. Values in each column bearing the same superscripts are not significantly different (p<0.05).

natural antioxidants, which is advantageous for edible-oil applications, if well stabilized for long-term storage (Ullah *et al.,* 2016).

The long-chain saturated acids (arachidic acid, C20:0) and TSFA showed a sharp decrease of approximately 27.04% and 25.50%, respectively. This trend resulted from the preferential crystallization of high-melting TAGs (C20:0 and C22:0) into the stearin fraction, hence a sudden decline in C20:0 and TSFA in the super shea olein fraction at colder crystallisation temperatures. Lower crystallization temperatures promote the selective crystallization of high-melting triacylglycerols (TAGs), especially those containing long-chain saturated fatty acids (C20:0 and C22:0) into the stearin fraction, leaving the olein depleted in these fatty acids and lowering total saturated fatty acids (TSFA).

Table 3: % Fatty acid composition of shea butter fractions during fractionation

	CSB	DSOA	DSOB
C16:0	3.26± 0.01^{a}	3.25± 0.00^{a}	3.42± 0.00^{a}
C20:0	39.87± 0.00^{a}	40.04± 0.02^{a}	29.26± 0.01^{b}
C22:0	1.23± 0.01^{a}	1.32± 0.00^{a}	1.02± 0.01^{b}
C24:0	NIL	0.12± 0.01^{a}	NIL
C18:1 n9t	6.99± 0.01^{b}	6.55± 0.01^{b}	9.02± 0.03^{a}
C18:1 n9c	47.83 ±0.01^{b}	48.30± 0.00^{b}	56.23± 0.05^{a}
C18:2 n9c	1.23± 0.01^{a}	0.10± 0.01^{c}	0.64± 0.00^{b}
C20:3 n6	0.34± 0.02^{b}	0.32± 0.01^{b}	0.41± 0.01^{a}
TSFA	44.54± 0.02^{b}	44.61± 0.01^{a}	33.7± 0.01^{c}
TMUFA	54.71± 0.02^{c}	54.85± 0.01^{b}	65.25± 0.02^{a}
TPUFA	0.75± 0.04^{b}	0.42± 0.02^{c}	1.05± 0.01^{a}
TUFA	55.46± 0.00^{b}	55.26± 0.01^{c}	66.3± 0.01^{a}

This trend has been reported by Abdel-Razek *et al.* (2023) for shea butter fractionation and for other oil fractionation systems, where stearin fractions become enriched in high-melting saturated TAGs while olein shows increased unsaturation and iodine value. The removal of high-melting TAGs improves clarity at low temperatures, making the olein less prone to crystallization or cloudiness during cold storage, a quality essential for salad oil, cooking oil, frying applications, and soft margarine formulations.

The reduction in saturated fatty acids and enrichment in unsaturated ones improves the nutritional profile, making olein more heart-healthy (Mulyono *et al.,* 2023). Unlike very-long-chain SFAs, palmitic does not concentrate strongly in the removed solid fractions, so its relative abundance remains stable through fractionation. This behaviour is consistent with the findings of Helwani *et al*. (2021) during the TAG thermodynamic experiment on mid-chain SFA distribution during the fractionation process.

CONCLUSION

This study explores the critical relationship between the oxidative stability of shea olein and the fractionation process, directly addressing the existing knowledge gap regarding how stable shea olein remains throughout fractionation. The solvent fractionation method employed proved highly effective: it significantly increased shea olein yield while substantially minimizing the formation of both primary (hydroperoxides) and secondary (aldehydes, malondialdehyde) oxidation products. The process also markedly enhanced the thermal stability and optimized the fatty acid composition of the resulting olein fraction, particularly enriching it in oleic acid and other unsaturated fatty acids.

These improvements provide a safe, efficient, and low-chemical-intensity pathway to mitigate lipid oxidation, thereby preserving the inherent quality, nutritional value, and extended shelf life of shea olein. As a result, fractionated shea olein emerges as a highly stable, high-quality liquid oil ideally suited for diverse food applications. Importantly, these findings align closely with Sustainable Development Goal 12 (Responsible Consumption and Production) by promoting more efficient use of natural resources, reducing food loss and waste along the shea supply chain, and supporting cleaner, more sustainable production practices in the food industry. By unlocking the full potential of shea olein through a mild fractionation approach, this research contributes to both environmental sustainability and the delivery of healthier, more stable vegetable oils for global food systems.

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