



Effects of Refining Processes on the Physicochemical Properties of Some Selected Vegetable Oils

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Authors' contributions

This work was carried out in collaboration between both authors. Author CTO designed the study, wrote the protocol and wrote the first draft of the manuscript. Authors CTO and KKI managed the analyses of the study and literature searches. Both authors read and approved the final manuscript.

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ABSTRACT

The post refining processes effects on the physicochemical properties of some selected vegetable oils were studied using standard analytical procedures. The results obtained showed that specific gravity were unaffected after refining with values 0.900 (crude and refined palm oil), 0.916 (crude and refined palm kernel oil), and 0.917 (crude and refined soybean oil). Refractive index was 0 for all the vegetable oils as well as melting points of palm kernel oil and soybean oil which remained unaffected post refining. Drastic colour reduction after refining was also noted as well as the melting point of palm oil which fell from 38°C to 21 °C. Correspondingly, there was reduction in the chemical properties such as acid value (%FFA), peroxide value and saponification value. This study also revealed unsaponifiable matter showing no linear variation as it increased from 24.8% to 31.9% for crude and refined palm oil respectively and 25.05% to 33.15% for crude and refined soybean oil respectively with a decrease of 32.3% to 30.55% for crude and refined palm kernel oil respectively after refining. Hence, chemical properties are targeted and mostly affected in refining

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in a bid to getting an effective oil for human consumption while limiting the removal of nutritional content of the vegetable oil or fortification in cases of inadequacy.

Keywords: Vegetable oils; refining processes; physicochemical properties; oil extraction and fortification.

1. INTRODUCTION

Vegetable oils are regarded as an important component of the human diet. It is essential because it supplies nutrients, improves flavour, aids in the absorption of vitamins, and provides source of energy for our bodies [1] as well as fatty acids [2]. It belongs to the class of food; fats and oils, which is significantly seen in its various edible forms. Vegetable oil is a major source of vitamin E which can be seen as an antioxidant in the oil [1].

In a lay man's knowledge, vegetable oil is referred to as any oil from plant sources (either fruits or seeds), generally referred to liquid fat at ambient (room) temperature [1]. It is regarded to be a natural product of plant origin [3]. Many vegetable oils are consumed directly or used as ingredients in food e.g. palm oil. Reports have shown that approximately 75% of the world's production of oils and fats come from plant sources [4].

Oils can be categorised in different ways: the type of plant it was extracted from, the level of refinement, the method of extraction etc. [1]. Majorly, vegetable oils are usually named by their biological source such as palm oil, palm kernel oil, soybean oil etc. However, each oil has a range of physical, chemical and compositional parameter by which it can be categorised [5]. Although, specifications for refined oils may differ slightly from those of crude oils and bleached oils due to the prefix added before the biological source of the oil e.g. Crude Palm Oil (CPO), Refined Bleached Deodorised Palm Oil (RBDPO). These refining processes a times modify the chemical properties and constituents of these oils to the point of which could be detrimental to human health hence this work geared towards evaluating the effect of the refining processes on the physicochemical properties of commonly utilized vegetable oils viz a viz their health and shelf life implications.

2. OIL EXTRACTION TECHNIQUES

2.1 Palm Oil Extraction

In order to obtain quality palm oil, it is essential that the damage done to the fruit should be

minimal. Therefore, the handling of the bunches from the field to the sterilizers must be carried out with utmost care.

Prior to sterilisation done at high temperature to loosen the fruit is threshing which could be done manually with an axe or machete to cut the fruit-laden spikelet from the bunch stem or mechanically with a rotating drum or fixed drum equipped with rotary beater bars to detach the fruit from the bunch leaving the spikelet on the stem [6]. Sterilization with pressurised steam or steam pressure and cooking with hot water which follows immediately ensures the ease of mechanical stripping, preparation of kernel for further processing, prevention of free fatty acid increase in the oil, destroys oil-splitting enzyme etc is done in a sterilizer cage or large steam autoclaves [7]. Other pre-extraction processes like stripping and digestion prepares the fruit to facilitate oil extraction.

Isolation of the oil is achieved by two distinct methods from the digested material. While one system uses mechanical means (Screw press) involving pressure to ensure minimum oil residue in the pressed cake with an acceptable amount of broken nuts [6], the other uses hot water to leach out the oil leaving two products: a mixture of water, oil and solid impurities and a press cake which consist of fibres and nuts [7] which is separated on the advantage of difference in specific gravities of the crude oil components before storage in tanks [8].

2.2 Palm Kernel Extraction

Palm kernel is produced from the seeds (kernels) of oil palm usually by chemical and mechanical means [5]. It involves various processing units from pre-treatment down to extraction proper.

Kernel is pre-treated by cleaning (decorticating) which removes foreign materials that may damage the press and cracks the kernel to free the shells, nuts, fibre and dust [7]. Size reduction and flaking (sometimes cooked and conditioned) increases the surface area of kernels and rupture the cell, thus facilitating oil expression [5]. Aided with a screw press, the expander or expeller, the oil squeezes out the oil leaving the protein cake

with some percentage of oil to be solvent extracted [8].

Solvent extraction operation which supplements mechanical extraction sufficiently minimizes the residual oil in the cake. Hexane, with boiling point of 68.7°C, is widely used as a solvent in this case [6]. Solvent extraction operates in a counter current system in a Solvent Extraction Plant (S.E.P.). The cake is met by the oil-rich miscella (hexane and oil) and leaves the extractor as it is rinsed with pure hexane. Hexane in miscella and cake is recovered in succeeding operations through stripping and desolventization respectively with the escaping hexane vapours trapped by cold mineral oil spray to preclude hazard and maximize solvent recovery [9].

2.3 Soybean Oil Extraction

Soybean is economically important because of their high qualities and quantities of oil and protein. The initial preparatory steps for soybean for further processing (extraction) include cleaning, drying, cracking and conditioning. Drying considerably reduces the moisture content of the seed while dehulling results in removal of hulls from soybeans which is necessary for subsequent oil extraction [10]. In line with this, blanching (conditioning) which is essential to making soybean fit for human consumption is applied by cooking the soybean by boiling or application of steam to wet beans. This inactivates and eliminates the anti-nutritional factors [11]. Also, milling (size reduction) and flaking with an option of expanding is used to improve oil extraction, percolation and solvent drainage [12].

Conventionally, solvent extraction is used to recover oil from soybean. Mechanical de-oiling using hydraulic press and/or screw press has not been commercially practised due to low oil content of soybean, low extraction and damage on the proteins content of the meal [11]. Solvent (hexane) extraction of soybeans is a diffusion process [12] achieved by immersing solid in solvent, percolating solvent through seed of solids or by direct solvent extraction which recovers about 99% of the oil. The solvent, after extraction, is recovered from the mixture of solvent and extracted oil (miscella) by double effect evaporator; and steam stripping and from the meal by a desolventizing toaster and recycled [12].

2.4 Refining of Vegetable Oil: Palm Oil, Palm Kernel Oil and Soybean

According to Shahidi (2005_e), refining is the term liberally applied to series of processes designed to neutralise free fatty acids present in the oil by introduction of an alkali and centrifugal separation of the heavy insoluble materials [9]. It is also associated with the removal of phospholipids, colour bodies and other soluble and insoluble impurities. The purpose of refining is to remove undesirable components with the least possible damage to the triglycerides and maximum retention of the beneficial components [12,13]. After refining, a pure oil with desirable properties for the consumers such as taste, odour, light colour and stability is obtained. Generally, the refining routes of palm oil, palm kernel oil and soybean oil are quite identical considering the following basic processing steps: degumming, neutralisation, bleaching and deodorisation (steam refining) [14].

3. MATERIALS AND METHODS

3.1 Sample Collection

Crude vegetable oil samples of palm, palm kernel and soybean oils were obtained from Golden Oil Industries Limited, Onitsha; and the refined oil samples of the above company was obtained commercially from Eke Awka market all in Anambra State of Nigeria.

4. DETERMINATION OF THE PHYSICO-CHEMICAL PROPERTIES [15]

4.1 Specific Gravity

The weight of the empty pycnometer (specific gravity bottle) was taken and noted as (a) and the bottle subsequently filled with distilled water in such a manner as to prevent any entrapment of bubbles, stoppered and reweighed and noted as (b). The pycnometer was dried, filled with oil sample also preventing bubbles and the stopper properly inserted and weight noted as (c).

$$\text{Specific gravity} = \frac{c-a}{b-a}$$

4.2 Slip Melting Point

Into the oil sample that has been filtered and stirred, a capillary tube was inserted which forced about 10 mm of the oil sample into it. This was

chilled (scrubbed gently) against a piece of ice until the oil solidified. The capillary tube was placed in a refrigerator for about 15 minutes before it was attached to a thermometer such that the lower levels of the capillary tube and thermometer bulb were at the same level. With water (at 10°C) in a beaker on an electromagnetic heater, the thermometer was immersed with the capillary tube and heated gently. The heating continued until the oil becomes sufficiently fluid or begins to slip/run in the capillary tube; the temperature reading was taken immediately from the thermometer.

4.3 Colour

The glass cell of the Lovibond Tontimeter (Model E) was washed, cleaned and dried before it was filled with the oil sample that has been filtered; and placed in position. The colour was matched by sliding the red, yellow and blue colours of the Lovibond Tontimeter glasses until a perfect match was obtained while observing through the eye piece (pin hole). The colours were then reported in terms of Lovibond units.

4.4 Acid Value

The oil was stirred thoroughly and 5 grams and 10 grams of crude oil samples and refined oil samples respectively were accurately weighed into a conical flask. Added to it were 50 ml of absolute ethanol and 3 drops of phenolphthalein indicator solution. This was heated (warmed) and swirled while titrating with 0.1 N of NaOH until a faint pink colour which persisted for at least 30 seconds was observed.

4.5 Saponification Value

In a conical flask, 2 grams of the oil was weighed using an analytical balance and 25 ml of 12% alcoholic KOH was added to it. This was swirled and heated on a water bath until saponification was complete indicated by the appearance of an egg-like material and absence of an oily matter. 1 ml of phenolphthalein indicator was added to the saponified matter and titrated with 0.5 N of HCl while hot until the pink colouration disappeared with the appearance of a milky white solution. A blank sample titration was also carried out.

4.6 Unsaponifiable Matter

After the titration of the saponification value, one ml of 3 M KOH solution was added to the

solution and transferred into a separating funnel and was washed with 50 ml of distilled water. With 50 ml of diethyl ether, the solution was extracted and the extract (the colourless solution) was separated from the lower pink solution. 20 ml of water was used to wash the solution each time separating the extract from the residue until the wash water gave a neutral pH. Then, 20 ml of 0.5 M KOH and 20 ml of water was added, the solution swirled and the pink extract collected upon complete separation. The pink extract was heated in a crucible of known weight to dryness, cooled in a desiccator and re-weighed.

4.7 Peroxide Value

5 grams of the homogenous oil sample was weighed into a conical flask and 50 ml of acetic acid in isooctane solution was added. The solution was swirled followed by the addition of freshly prepared saturated solution of KI (0.5 ml) and swirled again for 2 minutes. It was covered with aluminium foil and kept in the dark for 5 minutes. Thereafter, 30 ml of distilled water and 1 ml of 1% starch solution were added and the solution titrated with 0.01 N solution of sodium thiosulphate until the dark/black colouration disappeared. The blank titration was also conducted simultaneously.

5. RESULTS AND DISCUSSION

5.1 Physical Properties

Table 1 highlights the physical properties of both the crude and refined oil samples under investigation. They exhibit similar trend with refining process having little or no significant change with regards to the refining of the oil with the exception of colour. Colour reduction is an important variation in the physical properties of the oil sample. The colour of the oil sample was reduced as the oil progressed from crude oil to refined oil. Bleaching and deodorisation (heating at a high temperature under vacuum) have been pin-pointed to be the major cause of this instability in colour [5]. This reduction or lightened colouration of the oil samples post refining could be attributed to the removal of pigments and other residues which could pose some health and hygienic risks. Melting point of palm oil which hugely decreased from 38°C for crude to 21°C for refined is also another deviation. This (melting point) can be accounted for by a post refining process, fractionation, which separates the refined oil sample into two fractions largely based on their melting point [9].

Other properties such as specific gravity and refractive index of the oil samples investigated were unaffected. Also in this trend were the melting point of Soybean Oil and the refractive indices of the oil samples. These variations in these physical properties could be attributed to impurities and traces of water in the crude oil samples which are usually taken care of during refining by adsorption, filtration and heating at high temperature (above 100°C).

5.2 Chemical Properties

As seen in Table 2, chemical properties are the ones that were largely affected in the course of the refining processes. With reference to acid value and percentage free fatty acid (%FFA) content, there was a decrease in its content from crude oil to refined oil. This was no surprise as the acid value (free fatty acid) was targeted specifically in refining via deacidification or neutralisation in order to reduce its toxicity to human [16]. Peroxide value follows the same trend. It is also seen that with the reduction in acid value (%FFA) between crude and refined oil, peroxide value decreased. Hence, acid value and peroxide value has a direct variation with each other. In other words, decrease in acid

value (free fatty acid) reduces its decomposition to volatile compounds (aldehydes and ketones) which causes rancidity in oil [17]; thus, stability and shelf life of the oil was increased because the peroxide value, which measures the level of deterioration in the oil, has decreased.

Saponification value decreased with the progression of the oils from crude to refined state. The decrease is understandable with the purification of the oil as the percentage free fatty acids and other fatty components in the oil have also been reduced [18].

In the same vein, this huge reduction in free fatty acid (FFA) in all the oil samples as shown in Table 2 shows reduced risk associated with FFA to cause insulin resistance and inflammation in the major insulin target tissues (skeletal muscle, liver and endothelial cells). Thus reducing the risk of resultant obesity, insulin resistance, inflammation and the development of type 2 diabetes (T2DM), hypertension, dyslipitemia, disorders of coagulation and antherosclerotic vascular disease (ASVD) [19].

However, unsaponifiable matter showed no linear series. In palm oil and soybean oil, it was

Table 1. Physical properties of various oil samples

Oil samples	Parameters	Specific gravity	Colour	Melting point (°C)	Refractive index
Crude palm Oil		0.900	20Y + 11R	38	0
Refined palm Oil		0.900	4Y + 0.8R	21	0
Crude palm kernel Oil		0.916	20Y + 1.5R	28	0
Refined palm kernel Oil		0.916	4Y + 0.7R	27	0
Crude soybean Oil		0.917	20Y + 2.4R	2	0
Refined soybean Oil		0.917	2Y + 0.1R	2	0

Table 2. Chemical properties of various oil samples

Oil samples	Parameters	Acid value (mgKOH/g)	%FFA (mgKOH/g)	Saponification value (mg/KOH)	Unsaponifiable matter (%)	Peroxide value (meqO ₂ /Kg)
Crude palm Oil		8.35	3.81	1572.483	24.8	3.49
Refined palm oil		0.13	0.061	1479.918	31.9	1.00
Crude palm kernel oil		11.17	4.18	1327.045	32.3	4.81
Refined palm kernel oil		0.18	0.064	1227.460	30.55	1.14
Crude soybean oil		1.94	0.98	1432.233	25.05	2.91
Refined soybean oil		0.15	0.076	1363.511	33.15	0.76

found to increase but decreased in palm kernel oil. Generally, the average unsaponifiable matter should decrease after refining with the level of reduction dependent on the refining route (physical or chemical) taken [20]. This rhymed with the result of palm kernel oil as shown in Table 2 because virtually all the refining processes leads to reduction in the unsaponifiable matter in one way or the other. Nevertheless, the rise in the unsaponifiable matter in palm oil and soybean oil other than the expected decrease is linked to some of the post refining processes especially vitamin fortification or other additives like vegetal squalene (a deodorisation distillate extracted by supercritical fluid method) re-introduced into the oil so as to increase the oxidative stability, effectively inhibit chemically induced colon, lung and skin tumourgenesis in rodents, several cosmetic applications amongst others [21].

6. CONCLUSION

Evidently, refining processes have more significant changes to chemical properties of the vegetable oils investigated than the physical parameter. Basically, the change is seen to be a general reduction in all the chemical properties. However, physical properties enjoy little or no effect while overlooking colour with significant reduction.

7. RECOMMENDATIONS

The significant reduction in acid value, peroxide value and percentage free fatty acid is encouraged as they lead to the improvement on the quality of the refined edible oil. So also is the decrease in saponification value, colour and melting point of refined palm oil. While commending this, the decrease in the unsaponifiable matter (in palm kernel oil) is highly unacceptable to some extent though it increases refining losses, its overall importance cannot be overemphasized. Hence, methods for isolation of these unsaponifiable matter (tocols, tocopherols, squalene, vitamins) should be devised and attached to the refining system to re-introduce them to the oil while limiting their refining effects due to its importance (stability, nutrition, medicine) which cannot be neglected.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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