A Critical Review on Vegetable Oils Refining: A Case for Local Reagents Application

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ABSTRACT

Vegetable oils contain impurities such as free fatty acids, phospholipids, and pigments that require removal through refining to improve its quality and usability. In Nigeria, traditional methods are mostly applied as a result of non-availability of required technology. Also, industrial refining methods often rely on imported chemical reagents, which increase production costs and limit local processing capacity. This review explores procedures, benefits and limitations of both traditional and industrial methods of vegetable oils refining. Also, the potential of locally sourced reagents, such as agricultural waste, as viable alternatives in the chemical and physical refining of vegetable oils are discussed. This will encourage circular economy and promote many of United Nations Sustainable Development Goals (UN SDGs), by using renewable materials in separation processes and adding values to the agricultural wastes. Emphasis is placed on the probable effectiveness, economic advantages, and environmental impact of using indigenous materials such as plant-based precipitants, agricultural waste-based alkali solutions and natural adsorbents for vegetable oils refining. Process optimization would help in providing the best condition at each stage of the refining operation and as well alternative routes based on different refining agents.

Keywords: vegetable oil; refining; local reagents; degumming; deacidification; decolorization; deodorization

INTRODUCTION

Fats and oils are essential components of the human diet and are classified as lipids. They are primarily composed of triglycerides, which are esters formed from glycerol and three fatty acid molecules. Although fats and oils share the same basic chemical structure, they differ in their physical state at room temperature: fats are solid, while oils are liquid due to differences in their fatty acid composition [1]. Fats and oils can be of animal or plant origin: Animal fats include butter, lard and tallow while vegetable oils include palm oil, soybean oil, sunflower oil and olive oil.

Global edible oil demand has witnessed a significant surge in recent decades, and was driven by high population growth rates worldwide and the globalization of food supply networks, as well as growing concerns about sustaining nutrition. Edible oils form a crucial component in human diets and contribute essential fatty acids, fat-soluble vitamins and energy, and flavor and texture and appearance to food items [2]; [3]. Crude vegetable oils, extracted from oil-bearing seeds and fruits such as palm kernel, soybean, sunflower, and groundnut, contain various impurities including free fatty acids (FFA), phospholipids (gums), pigments, waxes, and trace metals that can adversely affect the oil's stability, appearance, and edibility [4]. As developing economies adopt urban and semi-urban lifestyles, the demand for vegetable oils such as palm oil, soybean oil, sunflower oil, groundnut oil, coconut oil and palm kernel oil has increased, transforming refining into a crucial sector of food manufacturing and national healthcare systems [5]. To render the oil suitable for human consumption and industrial applications, refining processes are employed to remove these undesirable components.

Refining is imperative because such bioactive-rich crude oils also contain unwanted components such as free fatty acids (FFAs), phospholipids (gums), colored pigments (e.g., chlorophyll and carotenoids), moisture, metal ions, and volatility compounds which contribute off-odors [6]. Such impurities reduce the palatability and shelf life as well as pose potential risks to safety if not properly eliminated. Oil refining hence becomes a critical postharvest operation to obtain safety, palatability, and sellability. Traditional refining methods, dominant in subsistence or rural settings, are based on simple steps like sedimentation, boiling and manual filtering with natural materials. These are normally parts of cultural practice and require little infrastructure and are hence readily available even for smallholder processors [7]. While extremely simple in nature, traditional methods can provide a higher percentage of beneficial micronutrients but fall short in microbial safety, standardization, and shelf life [8].

Industrial refining procedures have become a norm worldwide and in major food companies. They involve high-tech and organized procedures such as degumming, neutralization, bleaching, and deodorization under systemically regulated chemical and thermal conditions. The outcome yields a final product with international standards of purity, taste, stability, and protection from oxidation [9]. Nevertheless, industrial refining's stringent process can destroy or even deactivate healthy nutrients such as tocopherols, phytosterols, and polyphenols, if not properly done [10].

Industrial refining of vegetable oils can be achieved through two major methods: physical refining and chemical refining. Physical refining relies mainly on steam distillation to remove free fatty acids and volatile compounds during the deodorization step, with prior degumming and bleaching stages [11]. It is considered more environmentally sustainable and economically attractive due to lower chemical usage and reduced effluent generation. Nonetheless, its effectiveness depends largely on the pretreatment efficiency, especially in removing phospholipids, as residual gums can lead to oil degradation during high-temperature deodorization. Chemical refining involves the degumming, followed by the neutralization of free fatty acids using an alkali solution, bleaching, and deodorization steps. This method is widely used due to its flexibility and efficiency in processing a wide range of oils with varying impurity profiles [1]. However, it generates considerable amounts of soapstock and wastewater, making it less environmentally friendly and costly in terms of waste handling.

The choice between physical and chemical refining methods depends on several factors which includes; the type of crude oil, impurity content, processing cost, environmental impact, and the desired quality of the final product. A comparative analysis of both methods provides critical insights into optimizing refining operations for improved oil quality, yield, and sustainability.

This review seeks to provide a critical analysis of the traditional and the industrial systems (chemical and physical refining) of refining oil based on strength and weakness in the areas of nutrition, economics, the environment as well as culture. Also, it will provide an insight into the application of local reagents in crude vegetable oils refining, especially in developing and underdeveloped countries.

EDIBLE OILS

Source and Composition

Edible oils come from various plant sources consisting primarily of seeds, nuts, and fruit. The major edible oils used globally include soybean oil, palm oil, peanut oil and groundnut oil, sunflower oil, rapeseed (canola) oil, coconut oil and palm kernel oil, among others. The sources of the oils vary geographically from one region to another according to agro-climatic adaptation, cultural preferences, and economic viability [2; 12]. These oils exist in crude form and usually come from solvent extraction or mechanical pressing and in a majority of cases provide a complex mixture of compounds. Triglycerides (triacylglycerols) form the greatest component of every dietary oil and contribute to over 95% of the oil by weight. Crude oils also contain a variety of non-triglyceride components like free fatty acids (FFA), phospholipids (gums), sterols, tocopherols, carotenoids, chlorophyll, waxes, and trace metals like iron and copper [3; 6].

These minor components may be beneficial or undesirable. While tocopherols (vitamin E) and phytosterols are associated with antioxidant and cholesterol-lowering properties, FFAs and metal impurities cause lipid oxidation, rancidity and off-flavors, and a reduced shelf life [9]. Chlorophyll pigments cause photochemical catalysis while phospholipids and waxes cause turbidity and emulsification issues in final products [13]. The diversity in the crude oil composition greatly affects the choice and intensity of refining procedures. An example is the high content of carotenoids and high-FFA in palm oil requiring a bleaching and a modified deodorization step to attain color maintenance and improvement in flavor stabilization [10]. Similarly, high phospholipid content in soybean oil requires effective degumming to prevent emulsification and darkening of the oil during storage [5]. The opposite applies with coconut oil's low level of unsaturation and high saturated fats content, which makes it relatively less prone to degradation and may even require less severe refining treatments if the end-use was virgin or cold-press consumption [14].

The presence of impurities and vulnerability to oxidative spoilage necessitates refining, not simply to enhance aesthetic and sensory qualities such as clarity, flavor, and fragrance but also in order to attain global food safety standards and trading specifications [15]. Refining techniques used therefore aim toward a fine balance as the unwanted components are eliminated, and bioactive compounds, giving nutrition and contributing to consumer health, retained. The Table 1 below shows different edible oils with their applications and limitations.

Table 1 Edible Oils, Applications and Limitations

Oil Type	Properties	Applications in Food System	Observations	Author/ Reference
Soybean Oil	High in polyunsaturated fatty acids (PUFAs); contains linoleic and linolenic acids; prone to oxidation	Used in frying, baking, margarine production, and salad dressings	Requires degumming due to high phospholipid content; often hydrogenated to improve stability	[2; 3]
Palm Oil	High in saturated and monounsaturated fats; rich in carotenoids and tocotrienols	Used in frying oils, margarine, shortening, processed snacks	Needs bleaching and modified deodorization due to carotenoid content and distinctive odor	[10]
Groundnut/ Peanut Oil	Rich in oleic and linoleic acids; good oxidative stability	Used in deep frying, cooking oil, confectionery	Popular for flavor and shelf stability; susceptible to aflatoxin contamination if poorly stored	[12]
Sunflower Oil	High in linoleic acid (standard type) or oleic acid (high-oleic type); contains vitamin E	Common in salad oil, mayonnaise, frying, and cooking	Refined to remove waxes and stabilize for longer shelf life	[5]
Coconut Oil	High in medium-chain saturated fatty acids (e.g., lauric acid); stable at high temperatures	Used in baking, confectionery, and traditional cooking	Virgin oil is minimally processed; refined oil is stable with low unsaturation	[14]
Rapeseed/ Canola Oil	Low in saturated fat; high in oleic acid and omega3 fatty acids	Used in salad dressings, baking, and cooking	Mild flavor and favorable fatty acid profile; requires mild deodorization	[2]
Olive Oil	Rich in monounsaturated oleic acid; contains polyphenols and antioxidants	Used in salads, sautéing, and Mediterranean dishes	Extra virgin oil is cold-pressed and unrefined; flavor and bioactives preserved	[9]
Rice Bran Oil	Contains γoryzanol, phytosterols, and tocopherols; moderate PUFA and MUFA composition	Used in frying, salad oils, and health-focused products	Good oxidative stability; requires dewaxing and high-temp deodorization	[6]
Avocado Oil	High in oleic acid and vitamin E; low in saturated fats	Used in cooking, salad dressing, and cosmetics	Increasing interest as a premium oil; cold-pressed varieties retain nutrients and flavor	[16]
Mango Kernel Oil	Moderate in saturated and unsaturated fats; potential in nonconventional oil sources	Used experimentally in margarine, soap, and biodiesel production	Underutilized by-product with economic potential; refining techniques under development	[17]

Classification of Fats and Oils

Fats and oils are classified based on their origin, physical state at room temperature, and degree of saturation. Generally, they are grouped into animal fats, vegetable oils, and marine oils depending on their source [18]. Animal fats such as lard, tallow, and butter are typically solid at room temperature due to their high content of saturated fatty acids. In contrast, vegetable oils like soybean, sunflower, and palm oil are mostly liquid at room temperature because they contain a higher proportion of unsaturated fatty acids [19]. Marine oils, derived from fish and other sea animals, are rich in omega-3 polyunsaturated fatty acids, known for their health benefits.

Fats and oils can be classified according to the predominant type of fatty acid present in their triglyceride molecules. The three main groups include saturated fatty acids (SFA), monounsaturated fatty acids (MUFA), and polyunsaturated fatty acids (PUFA). This classification is important as it influences the physical properties, stability, and nutritional value of the oil or fat.

Saturated fats are primarily composed of saturated fatty acids with no double bonds. They are usually solid at room temperature and more resistant to oxidation. Examples include coconut oil, palm kernel oil, and animal fats like lard and tallow [1]. Monounsaturated fats contain a high proportion of monounsaturated fatty acids, typically oleic acid. These fat are generally liquid at room temperature but may solidify at lower temperatures. They are considered heart-healthy fats. Examples include olive oil, canola oil, and high-oleic sunflower oil [20]. Polyunsaturated fats are rich in fatty acids with two or more double bonds, such as linoleic acid (omega-6) and alpha-linolenic acid (omega-3). The polyunsaturated oils are liquid at room temperature and are essential for human health but more prone to oxidation. Some examples of oils that exhibits these characteristics include sunflower oil, soybean oil, flaxseed oil, and fish oils [18]. This structural difference affects their stability, nutritional value, and susceptibility to oxidation [20].

Furthermore, fats and oils may be categorized as edible or non-edible, depending on their suitability for human consumption. Edible oils are refined to remove impurities and improve their sensory and nutritional properties while non-edible oils are commonly used in industrial applications such as soap production, biodiesel, and lubricants.

VEGETABLE OILS

Vegetable oils are triglycerides extracted from plant sources, widely used in food, cosmetics, pharmaceuticals, and industrial applications. They are primarily derived from oil-rich seeds or fruits such as soybean, sunflower, groundnut, palm, and palm kernel. The global demand for vegetable oils continues to rise due to their nutritional value, especially their content of essential fatty acids, fat-soluble vitamins (A, D, E, and K), and antioxidants [21]. In the food industry, vegetable oils serve as cooking mediums, flavor enhancers, and carriers for fat-soluble nutrients. They are composed mainly of unsaturated fatty acids, which have been associated with various health benefits such as reducing the risk of cardiovascular diseases [1]. However, the quality and stability of vegetable oils are affected by factors such as free fatty acid content, moisture, impurities, and oxidation. To enhance their quality and suitability for consumption and industrial use, crude vegetable oils often undergo refining processes such as degumming, neutralization (deacidification), bleaching, and deodorization [22].

Components of Vegetable Oils

Vegetable oils are triglyceride-rich substances extracted from plant sources such as seeds, nuts, and fruits. They serve as essential dietary fats and raw materials in food, pharmaceutical, and cosmetic industries. The quality and utility of vegetable oil are largely determined by its chemical composition, which includes triacylglycerols (TAGs), free fatty acids (FFAs), phospholipids, unsaponifiable matter, pigments, wax, and moisture [23].

TAGs are the predominant component of vegetable oil, typically constituting 95 – 98% of the total oil content [1]. They are esters formed from glycerol and three fatty acid molecules. The nature and arrangement of the fatty acids on the glycerol backbone significantly influence the oil's physical properties such as melting point, stability, and nutritional value [24]. The fatty acid profile of vegetable oil varies depending on the plant source. Fatty acids may be saturated (e.g., palmitic, stearic), monounsaturated (e.g., oleic), or polyunsaturated (e.g.,

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linoleic, linolenic). These fatty acids play a crucial role in determining the oil's health implications, oxidative stability, and industrial applications [25]. For instance, oils high in polyunsaturated fatty acids are more prone to rancidity but are considered heart-healthy. FFAs are formed by the hydrolysis of TAGs, particularly during poor storage or processing. High FFA content is undesirable as it contributes to off-flavors and reduced shelf life. FFAs are also a key parameter in assessing the degree of oil degradation and refining requirements [26].

Phospholipids are polar lipids, mainly found in crude oils, and are often referred to as gums. They are undesirable in refined oils because they reduce clarity and stability. Therefore, degumming is a crucial step during refining. Common phospholipids include lecithins and cephalins [4]. Unsaponifiable matter consists of components that do not form soap when reacted with alkali. It includes sterols, tocopherols (vitamin E), carotenoids, and hydrocarbons. These compounds contribute to the nutritional and antioxidant properties of the oil [27]. Tocopherols, in particular, help in preventing oxidative rancidity. Crude vegetable oils contain natural pigments such as chlorophyll and carotenoids. These pigments influence the color and oxidative stability of the oil. While carotenoids are considered beneficial due to their pro-vitamin A activity, excessive chlorophyll can promote photooxidation [28]. Waxes are esters of fatty acids with long-chain alcohols, commonly found in minor quantities in some vegetable oils. They can cause turbidity at low temperatures and are typically removed during dewaxing [29]. Moisture in oil accelerates hydrolysis and microbial spoilage. Volatile compounds may include aldehydes and ketones formed during oxidation. Both are undesirable in high-quality edible oils and are minimized during drying and deodorization processes [20].

Purification of Vegetable Oils

Treatment that eliminates undesirable and toxic components in crude oils is known as "refining" [30]. Refining of oil is a set of purification operations used to convert crude edible oils into stable, acceptable, and safe products suitable for consumption by human beings. The main objective is to remove impurities such as free fatty acids, phospholipids, pigments, and odorous compounds and retain or enhance the nutritional quality of the oil. Refining is practically mandatory for crude oils, that cannot be consumed as virgin oils, to provide a product with an attractive appearance, a neutral taste, and more resistance to oxidation. Likewise, it allows obtaining oils that are more suitable for various industrial uses and getting rid of undesirable substances such as pesticide residues, metal traces, polycyclic aromatic hydrocarbons, dioxin, and alteration products as well as minimizing oil loss during processing [31]. Refining methods are all integrated into conventional and commercial (or industrial) processes with different tools, effects, and levels of sustainability. The following sections discuss the traditional as well as commercial procedures in detail, beginning with historically significant traditional procedures.

Traditional Oil Refining

Traditional oil refining techniques are among the oldest and most traditional methods to purify food oils. Predominantly practiced in rural, artisanal, and smallholder communities, these methods rely on locally available low-technology, equipment, and procedures that have been passed down from generations. The fundamental steps often include boiling to force off water, sedimentation to allow the settling of heavier impurities, and filtering by hand, typically through cloth, clay, or woven sieves [7].

One of the strongest advantages of traditional refining processes is that they are inexpensive to operate. They require minimal infrastructure, burn biomass or firewood to do so, and use no expensive chemicals or high-tech equipment. This renders them energy-efficient and cheap to run, especially in underdeveloped or remote areas where industrial refining is a pipedream [32]. Also, such strategies are typically embedded in domestic value chains that support women and smallholder processors and promote rural livelihoods and food sovereignty [33].

Nutritionally, conventionally refining retains a higher percentage of good phytochemicals. Since these technologies do not involve extreme heat or chemical addition, bioactive compounds such as tocopherols (vitamin E), phytosterols, carotenoids, and certain polyphenols are better preserved [12]. These micronutrients have well-established antioxidant and cholesterol-lowering activities, which are partly accountable for the functional health benefits of conventionally processed oils [16].

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However, the traditional approach is not without significant drawbacks. Due to limited process control and hygiene standards, traditionally refined oils often exhibit high moisture content, elevated levels of free fatty acids (FFAs), and microbial contamination, which collectively contribute to rapid rancidity and shorter shelf life [32]. Also, the absence of standardization in parameters such as filtration efficiency, heating time, and temperature control leads to batch-to-batch variation in quality, color, flavor, and oxidative stability [7]). Also, safety concerns also take center stage. Non-treatment of contaminated water, outdoor use, and use of improvised containers (such as weakened fuel tanks or unclean containers) present heavy metal contamination or bacterial/yeast proliferation risks [32]. Such issues shortchange conventionally processed oils in meeting national and international safety specifications, making them less competitive in external, regional or informal trade circles [15].

Nonetheless, traditional oil refining methods are significant socio-economic and cultural aspects of numerous developing regions. Increased interest is developing to upgrade traditional technologies with intermediate technologies, i.e., improved boiling pots, sediment traps, and low cost filtration units, that could enhance quality without forsaking the nutritional and environmental gains of these age-old techniques [34].

Industrial Oil Refining

These operations are typically done in batch or continuous systems under very controlled thermal, chemical, and mechanical conditions in order to attain homogeneous quality of the product that meets international food safety and quality standards [9]. There are two main industrial technologies used for vegetable oils' refining, namely; chemical refining and physical refining. Physical refining eliminates undesirable compounds (deacidification) by distillation under a high vacuum with steam injection while chemical refining removes free fatty acids by soda neutralization [35].

Physical Refining Method

The process consists of same steps as in chemical refining, except for the alkali neutralization process [36]. The difference between chemical and physical refining is that chemical refining consists of removing free fatty acids by adding caustic soda and separating the soap by centrifugation [37], while in physical refining (also referred to as steam refining), free fatty acids and other compounds are removed by steam distillation, which is the last step of the entire process [38]. Indeed, physical refining is mostly considered for oils with high acidity [39]. In general, physical refining includes the following three main processing steps, which are degumming, bleaching and filtration (to eliminate color pigments) and deodorization (to eliminate free fatty acids and other volatile compounds).

The first step involves subjecting the oil to phosphoric acid reaction in the short-mix chemical refining process in order to remove phosphatides. It is the most important stage in refining stage and therefore, it must be done carefully [40]. Degumming efficiency for a given refined oil sample, is evaluated through an analytical test called "Degumming Efficiency". The efficiency, according to [41], is determined using Equation 1.

$$\text{Degumming Efficiency g/100 g)} = \frac{P_0 - P_d}{P_0} \times 100 \qquad 1$$

where P_0 is crude oil's phospholipids concentration (in ppm) and P_d is degummed oil's phospholipids concentration (in ppm).

The second step is bleaching (or decolorizing) with same objective as that in chemical refining (that is, reducing the levels of colored pigments such as carotenoids and chlorophylls), but it also further removes residues of phosphatides traces, phospholipids traces contaminants, lipid peroxidation products, and other impurities [42]. The oil is then mixed with acid activated bleaching earth or another adsorbent using the standard bleaching process temperature of 368 – 378 K (95 – 108 °C). The spent adsorbent along with some precipitated carotenoids and other impurities are then removed by filtration.

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The final step in the physical refining of oils is the simultaneous deacidification and deodorization. These combined processes are carried out under same conditions as for chemical refining with two main objectives which includes; removal of volatile components such as free fatty acids, different off-flavors and contaminants (pesticides, light polycyclic aromatic hydrocarbons, etc.), and thermal bleaching of colored pigments and peroxides. To obtain low phosphatides, better quality, and more flavor-stabilized oil during storage, the combined process is optimized using four parameters: the amount of stripping steam, time, pressure and temperature. Deodorization is usually carried out at temperatures greater than 473 K (>200 °C) with low vacuum pressure [41].

Chemical Refining Method

The initial step is the removal of the phospholipids (gums) from the crude oil through water, acid, or enzymes. Phospholipids are accountable for emulsification issues as well as darkening and destabilizing the oils during storage [6]. Chemical refining is the traditional method used since ancient times. It can be used for all fats and oils even when they have been slightly degraded. Each step of the refining process has specific functions for removing some undesirable compounds. Chemical refining follows six processes describe below. The first process in chemical refining is degumming with the goal of eliminating phospholipids and mucilaginous gums [43]. This is followed by neutralization, which allows the elimination of free fatty acids (FFA), phospholipids, metals, and chlorophylls [44]. Washing and drying are carried out immediately in order to eliminate residuals of soaps and water. The next stage is bleaching, carried out with the aims of eliminating pigments, peroxides, and residuals of both fatty acids and salts [43], and then dewaxing with main objective of removing waxes in the case of oils rich in waxes [37]. The final stage of chemical refining is deodorizing, which allows the elimination of volatiles, carotenoids, and free fatty acids in order for the oil to have pleasant aroma [36].

Degumming

Degumming is a crucial step in the refining process of vegetable oils. It allows the elimination of “gums” or “mucilage,” composed mainly of phospholipids from the crude oil as well as compounds such as carbohydrates, proteins, and trace of metals [30]. Phospholipids or phosphatides are naturally present in oils. These compounds are important biochemical intermediates in the growth and functioning of plant cells [45]. Phosphatidylcholine (PC), phosphatidylethanolamine (PE), phosphatidylserine (PS), and phosphatidylinositol (PI) are the major types of phospholipids that can be found in crude vegetable oils [46]. In general, vegetable oils contain hydratable and non-hydratable phospholipids [45]. These compounds can trap metallic ions (copper + iron) and prevent their catalytic activity related to free radical production in crude oils [47]. Moreover, the presence of these compounds in crude oils poses many problems for storage and processing. Phospholipids are often linked to heavy metals, which are catalysts in oxidation reactions and, sometimes, act as prooxidants in vegetable oils [48].

The incomplete removal phosphorus-rich components during alkaline neutralization creates a series of subsequent refining difficulties resulting in the formation of a dark color settling-in during storage [49]. Therefore, their elimination from crude oil is mandatory. Indeed, the degumming stage consists of elimination of all compounds (such as phospholipids, glycolipids, proteins, etc.) that can become insoluble through hydration [50]. There are four types of degumming processes; water degumming, acid degumming, dry degumming and enzymatic degumming.

Water degumming is usually done beforehand to remove hydratable phospholipids [47], where the gums recovered represent the raw lecithin [35]. Water degumming is more prevalent for oils like soybean, while acid or enzymatic degumming is used for oils containing more gums, i.e., sunflower and rapeseed oil [3; 6]. Acid degumming uses a concentrated acid combined with bleaching earth (1 to 3 g/100 g acid). The acid (0.05 to 1.2 g/100 g oil) is dispersed in oil at 353 – 373 K (80 – 100 °C). This acid dissociates the nonhydratable phosphatides into phosphatidic acid, and the phosphatidic acid is eliminated by centrifugation. The remaining amount is further adsorbed through bleaching earth. Generally, for acid degumming process, a strong acid is needed to precipitate the lipids that are majorly responsible for the gum formation. Phosphoric acid and citric acid have extensive reported as reliable reagent for this purpose [30; 49; 51; 52]. In order to meet SDGs goals on circular economy, strong acidic agricultural wastes, such as processed cassava effluent water, orange peel and pine apple peels can be employed for the acid degumming process. This will not only reduce processing cost of vegetable oils, but as well add values to this set of agricultural wastes and reduce environmental pollution caused by the wastes.

Dry degumming was developed for palm oil, palm kernel oil, and coconut-type oils containing small amounts of phospholipids. The dry degumming process combines the acid degumming step with the bleaching process, thus eliminating the water addition and centrifugation of the gums. This technique is carried out at 393 to 413 K (120 – 140 °C) under a reduced pressure [53]. Enzymatic degumming is a kind of biotechnological process in which a phospholipase, especially the phospholipase C, converts nonhydratable phospholipids into lysophospholipids [54]. These components are insoluble in oil and need to be removed by centrifugation [55].

Neutralization/ Deacidification

The second process of chemical refining of vegetable oils is neutralization, where the acidity of the oils is neutralized by an alkali solution. Acidity depends on the nature of the oil, which, in turn, depends upon its geographical origin, harvesting, seed crushing conditions, and storage duration [56]. Acidity is usually measured in terms of free fatty acids (FFAs) and it ranges from a value below 0.7 to 10 g/ 100 g, especially for some degraded oils. Free fatty acids content is expressed in g/ 100 g of oleic acid except for some oils such as palm oil where it is reckoned in g/ 100 g of palmitic acid, and coconut and palm kernel oils, where it is in g/ 100 g of lauric acid. Crude vegetable oils containing a high percentage of free fatty acids (by hydrolysis and/or oxidation) and must be refined to be edible [57]. The presence of free fatty acids in crude oils poses problem during storage and result in an undesirable color and odor in the final product). Free fatty acids influence the chemical quality and the organoleptic instability of oil [48]. In chemical refining, the oil is treated with an alkali solution, usually caustic soda, that reacts with the free fatty acids (FFAs) and converts them into soap stock according to the neutralization reaction in Equation 2 [58].

$$\mathrm{R-COOH\,(acid) + NaOH\,(base) \rightarrow R-COONa\,(soap) + H_2O\,(water)} \qquad 2$$

This step is crucial based on the fact that untreated FFAs catalyze oxidation, as well as off-flavor and rancidity development [2; 10]. Several agricultural wastes, such as cocoa pods, had been employed as alkali based medium in local soap production [59; 60; 61]. The application of these materials as neutralization reagents in vegetable oils refining will stimulate further research into the use of other agricultural wastes like kolanut pods, ackee seed pod, and others, as neutralization agents for vegetable oils, such as palm kernel oil, coconut oil, soybean oil refining.

Washing and drying

This operation is employed to eliminate alkaline substances (that is, caustic soda and excess soap), as well as last metallic and phospholipids traces and other impurities present in the oil from coming out of the reaction tank. In order to achieve this, the crude oil needs to be well prepared for this reaction otherwise because sizeable emulsions could take place and part of the soap may not be eliminated. Washing water should be carried out at very hot temperature of about 358 to 363 K (85 – 90 °C). The oil, free of gums, traces of soap stock, and other impurities, is pumped through a plate heat exchanger where it is heated by steam and then centrifuged after being mixed with water in a centrifugal mixer. After this treatment, water washed oil is dried with a vacuum dryer until the moisture level of the oil falls below 0.1% [62].

Bleaching/ Decolorization

Bleaching is another critical step in the refining process of oils [63]. It is a complex physical and chemical process employed in the refining of vegetable oils. The objective of bleaching (or decolorizing) is to reduce the levels of colored pigments (carotenoids and chlorophylls). It also further removes residue traces of phosphatide, soap, phospholipid contaminants, lipid peroxidation products, and other impurities and indirectly impacts the oil color [64]. To carry out bleaching, adsorption bleaching clays, activated carbon, special silica, or a combination of these are used [63; 65]. The bleaching earth is the most popular adsorbent for decolorization of oil and the most widely used adsorbent material by the oil industry [56]. Bleaching clay is favored over other adsorbents such as silica-based and activated carbon products due to its low cost and relatively high adsorption capacity. Indeed, bentonite is the most favored bleaching clay used in the oil industry [65].

In general, activated earth has no bleaching properties in their natural state. Their natural state chemical composition does not indicate that they can bleach. However, through activation which is the transformation of silicates into colloidal silica, they possess an important adsorbing power. Activation is a chemical reaction of strong inorganic acid (sulfuric or hydrochloric acids) at temperatures lying between 353 – 373 K (80 – 100 °C). The chemical treatment significantly changes their textural characteristics [66]. Strong acids act by substituting protons for cations while increasing notably the adsorbing surface. Bleaching earth's quality depends on the amount and the nature of acid used, the contact time, and the temperature [67]. The degree of bleaching is dependent upon the level of cation substitution by the hydrogen ions of the acid in the clay structure, according to Equation 3 [67; 68].

$$\text{Cation - clay} + 2H^+ \rightarrow \text{H - clay} + \text{Cation} \qquad 3$$

In order to obtain a high adsorption capacity in the bleaching of some oils, a mixture of activated carbon and bleaching earth is used in refining industries. In general, the amount of activated carbon must be in the range of 5 – 10 g/100 g bleaching earth. The usual method of bleaching occurs through the adsorption of pigments over an adsorbent material. In general, when an adsorbent comes into contact with oil, the adsorbent attracts to its surface, colored pigments and other compounds that need to be eliminated. This attraction condenses the molecules and they form a casing inside, thereby reducing the concentration of the adsorbed substance in oil. Langmuir's [69] and Freundlich's [70] equations theoretically give the adsorption capacity, according to Equations 4 and 5.

Langmuir: $$\frac{X_e}{(X/M)} = \frac{1}{A} + \frac{B}{A}(X_e) \qquad 4$$

Freundlich: $$\log\left(\frac{X}{M}\right) = N\log(X_e) + \log K \qquad 5$$

where M is the amount of adsorbent, X is the amount of the adsorbed substance, X_e is the residual amount of dissolved substance (at equilibrium), A and B are Langmuir constants, and K and N are Freundlich constants [65]. When equilibrium is reached, the adsorbent no longer acts upon the oil, but got discolored. The amount of adsorbent used ranges between 0.1 and 1g/ 100 g crude oil, depending on the crude oil quality. However, other higher-percentage bleaching materials can be used to meet final color requirements [67].

In order to bleach the oil, the pretreated oil is heated to 353 – 393 K (80 – 120 °C) under vacuum and afterward mixed vigorously in the bleacher with the adsorbent (bleaching earth or/and activated carbon). Usually, the treatment is done under a slight vacuum to prevent oxidation, which are usually enhanced by oil dispersion on earth particles [67]. After a retention time of 20 – 40 mins, the oil adsorbent mixture is filtered, as centrifugation is not desirable for this separation. Therefore, for efficient filtration, short filtration time and minimization of oil retention on the adsorbent matter are necessary [65].

Many agricultural wastes had been reported for preparation of carbonaceous materials used as adsorbent in oils bleaching. Omar et al. [71] reported the effective usage of 6 different seeds (cottonseed, peanut, sunflower, soybean, fababean and lupine) as carbonaceous materials for soybean oil bleaching. Amany et al. [72] reported the application of olive ash waste as adsorbent for regeneration of sunflower oil. Ismail et al. [73] reported the use dried press mud as adsorbent in crude palm oil refining. Salawudeen et al. [74] studied the performance of adsorbent prepared from oyster shell to bleach and reduce the acid value (AV) of palm kernel oil. Chairgulprasert and Madlah [75] utilized coffee husk ash for treating used palm oil and observed a removal of 73.7% in acid value. Butt et al. [76] reported effective palm oil bleaching using activated carbon prepared from neem leaves and waste tea. There are several agriculture waste with probable potentials as those reported by these researchers that can be applied as carbonaceous materials for vegetable oils bleaching. There is a need to steer research towards the application of agricultural wastes like snail shells, cowries, periwinkles, among others, as adsorbing medium for the bleaching operation. This will diversify the use of these materials, reduces wastages and increase local contents applications in vegetable oils refining.

Deodorization

The last stage in CPKO refining is deodorization which involves a high temperature and therefore, requires a great care. A deodorized oil is not only devoid of unpleasant aroma but as well devoid of any taste, even pleasant ones [5; 77; 78]. Deodorization is a simple distillation process that allows elimination of free fatty acids and removes odors, different off-flavor components, contaminants such as pesticides, light polycyclic aromatic hydrocarbons, and other volatile components [38; 79]. Deodorization also removes residues of mineral oil saturated hydrocarbons (MOSH) and mineral oil aromatic hydrocarbons (MOAH) [80]. A careful execution of this process improves the stability and color of the oil, while still preserving its nutritional value. Deodorization is a vacuum steam distillation process [79]. The process involves the passage of steam through layers of oil held in trays and heating to high temperatures 453 – 513 K (180 – 240 °C) using a high-pressure steam boiler. Utilizing a very high vacuum, between 2 and 8 mmHg, the process removes undesirable odors caused by aldehydes, ketones, alcohols, short-chain fatty acids, and thermolabile pigments [79]. It is a steam stripping of taste and odor conveying substances that are more volatile than oil. The thermodynamic equilibrium of the oil and dissolved matter (taste releasing substance) is given by Raoult's law according to Equation 6 [81].

$$\frac{PV_0}{PV} = \frac{V}{H} \qquad 6$$

where PV_0 is the partial pressure of the volatile components dissolved at a given temperature, PV is the partial pressure the oil would have at the same temperature, V is the number of moles of the volatile components, and H is the number of moles of oil. The obtained oil is subsequently conditioned under nitrogen to protect it from oxidation [82]. The careful execution of these processing steps ensures that fully refined oils possess good organoleptic and physicochemical qualities. All these good attributes could be achieved, for a particular oil, by optimizing the processing parameters at each stage of the refined operation, and based on the subsequent usage of the refined oil, either for consumption or industrial application [83].

Cumulatively, the processes of refining result in oils that are physically clear, chemically stable, microbiologically safe, and compatible for long storage and cooking. Commercial-scale refining also can be designed to fit the distinctive physico-chemical requirements of individual oils and their corresponding food applications, further contributing to market suitability and exportability [84]. However, the industrial process of refining give rise to nutritional and environmental concerns. The drastic temperatures and severe chemical processing used in bleaching and deodorization can lead to the breakdown of bioactive compounds like tocopherols, sterols, and polyphenols, which possess antioxidant and cholesterol-lowering activity [10]. Moreover, deodorization at extremely high temperatures, if not rigorously controlled, might result in the formation of undesirable compounds such as trans fatty acids and polymerized triglycerides, which have been implicated in adverse health effects [6; 13]. Also, industrial refining can lead to environmental problems, if not well carried out or managed. The use of enormous quantities of water, energy, and chemicals generates wastewater, spent bleaching earth, and emissions that need strict environmental management and waste valorization procedures to reduce pollution and operation costs [15; 17]. Therefore, all these concerns must be addressed in the optimum design of variables that affects products quality in order to provide different vegetable oils for different purposes and applications.

CONCLUSION

Refining is a crucial treatment for crude oils that cannot be consumed in their virgin state. This treatment improves the quality of the oil, extends its shelf life and makes it edible by the removal of undesirable components (phospholipids, free fatty acid, pigments, aromatic compounds) that are present in the crude oil. The contrast between traditional and industrial oil processing shows traditional oil processing methods are deeply rooted in livings and will probably retain larger amounts of bioactive nutrients while commercial processes provide products of uniform quality that meet industrial standards of safety, shelf life, marketability and economic scalability.

Oils with high level of free fatty acid require chemical method for effective refining, while those with low fatty acid requires physical method for refining. The two industrial refining methods have both their advantages and disadvantages in terms of gums and fatty acid removal, cost effectiveness, oil yields, environmental impact. Chemical method is costlier than physical method in long term, due to the use of raw materials like caustic soda, water supply and so on, but more feasible to operate in short term based on the huge steam requirements of physical method. Chemical method effluents (soap) when released into the environment causes pollution while physical methods is environmentally friendly. However, there are some factors that determine the choice of methods which are; fatty acid content, phospholipids content, desired oil quality, and so on.

Optimization of independent process variables with respect to these listed separation indices will help in determine the best condition at each stage of the refining process, which would eventually improve the economics of the refining process. The use of local reagents helps in reducing cost of production, preserve nutrients, reduce waste in the environment and reduce the level of pollution in the environment as this efficiently replace the use of chemicals in refining vegetables oil.

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