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REFINING RESIDUAL FRYING OIL AND INCORPORATING IT INTO THE PRODUCTION OF VEGAN GLYCERIN BASES

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Abstract: The main problem with vegetable waste generated by food processing and consumption is the disposal of residual frying oil in homes and retail establishments. Recycling is the best way to dispose of it, both from an environmental and public health perspective, as well as from a financial perspective, since the waste in question can be transformed into commercial products that can be sold and generate revenue. Therefore, the better use is made of residual frying oil, transforming it into other marketable products, the less impact it will have on the environment. Grease raw materials such as fats are found in large cities and can be used to produce toiletries, especially in the production of low-cost, high-quality glycerin bases used in the production of handmade soaps with recycled raw materials. In addition to the advantages of production, partnerships between the population and universities are promoted, complementing the benefits of the knowledge studied by academics. In view of the reuse of residual soybean oil from frying, which is often improperly discarded, from an environmental, economic and social perspective, a project was developed to train undergraduate chemistry students to develop glycerin bases from simple products such as residual frying oil, coconut oil, castor oil, glycerin, alcohol, commercial crystal sugar, hydrolate and water, and then be able to offer mini-courses to the internal and external community of the university. Several tests were carried out to improve the quality of the product, such as its affinity with the skin and its softness. Carrying out these tests is very important because, many times, this product is made at home in dangerous conditions, which, in addition to making the quality of the product questionable, can pose risks to the citizen who undergoes this procedure. In addition to the advantages of production, integration between the population and the university environment is promoted, sharing the benefits of the knowledge studied by the students.

Keywords: Used frying oil, Recycling, Vegan glycerin base, Handmade soaps.

INTRODUCTION

The main problem with vegetable waste generated by food processing and consumption is the disposal of residual frying oil in homes and retail establishments. Recycling is the best way to dispose of it, both from an environmental and public health perspective, as well as from a financial perspective, since the waste in question can be transformed into commercial products with sales value, generating revenue. Thus, the better use is made of frying waste, transforming it into other marketable products, the less impact it will have on the environment and the greater the value of animal sacrifice (BORÉM, 2010).

The main raw materials used to manufacture glycerin bases are fatty acids, fats and oils, which can be of animal or vegetable origin. Among the fats of animal origin, the most commonly used for soap production is beef fat, commonly known as tallow. Among the vegetable fats and oils most commonly used for this purpose, coconut oil, extracted from babassu (COSTA, 2011), palm oil and castor oil (extracted from castor beans) stand out.

Glycerin bases are special soaps used in the manufacture of soaps for human hygiene (MERCADANTE, 2010). They are of superior quality to soaps for cleaning the human body, due to the quality of the raw material used in their manufacture and the strict control in the manufacturing process (NATIONAL HEALTH SURVEILLANCE AGENCY, 2005).

A glycerin base considered ideal has a compact, transparent and odorless texture, retains its shape for a long time and is simple to manufacture. To achieve this objective, the animal fat (tallow) and vegetable oil must be as pure as possible (ARGENTIERE, 2001). The solvents used for this purpose are ethanol, glycerin and sucrose. Furthermore, when highly unsaturated oils such as soybean oil are heated, isomerization and migration of double bonds occur, leading to their conjugation. The conjugation of double bonds leads to the absorption of greater amounts of blue light, causing an increase in orange and brown colors in the oil. Therefore, the color of the oil will depend on the initial content of double bonds and the foods that are fried (LIMA, 1994).

According to Spitz (1991), oils and fats are the main ingredients used in the manufacture of laundry soaps and belong to the family of compounds called triglycerides, glycerol esters and fatty acids. The difference between an oil and a fat is in their physical state at room temperature: oils are in a liquid state while fats are in a solid state. (CDCC; SOAP PROPERTIES).

THEORETICAL FOUNDATION

DEFINITIONS AND CONCEPTS

Recycling and reusing materials are current issues that are increasingly gaining new supporters. This approach is extremely important for environmental protection (Green Chemistry) and the management of toxic materials with a long-life cycle. In addition to reducing waste, reusing materials also reduces the use of raw materials in the production of new products (JORGE, 2005). Green Chemistry encourages cleaner production with fewer industrial pollutants, ensuring that producers take greater responsibility for the products they produce.

Due to the increase in the generation of solid waste and changes in eating patterns, the consumption of ready-made and easy-to-prepare foods, including fried foods, has increased considerably. The increase in the consumption of fried foods in household and commercial environments results in greater generation of waste, among which vegetable oil attracts a lot of attention, as it is a material that is difficult to decompose and very harmful to the environment (OLIVEIRA, 2011). The increase in consumption was also encouraged by the greater variety of vegetable oils available on the market, such as: sunflower oil, canola oil, corn oil, almond oil, soybean oil, among others, with the most widely used still being soybean oil (CELLA, 2002).

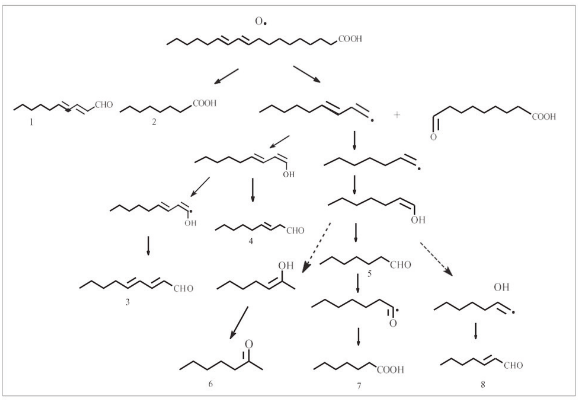
In view of the problems caused to the environment by the incorrect disposal of used cooking oil (frying oil), recycling and reusing it become viable and economical alternatives, as they enable the production of new products such as soap, biodiesel, paints, glycerin, among others (RODRIGUES et al, 2010; BARBIZAN et al, 2013; ZAGO NETO, 2022).

Residual frying oil, after being superficially cleaned and bleached, can be sent to companies as raw material for various products such as: varnish and paint, cleaning products (soap, disinfectant, detergent, etc.), glass paste, glycerol (pharmaceutical, food, perfumery, plastic, etc.), biofuel (COSTA, 2011).

FRYING OILS AND FATS

According to Filho (FILHO, 2013), oil used repeatedly in deep-frying undergoes deterioration, accelerated by the high temperature of the process, resulting in the modification of its physical and chemical characteristics (MORETTO, 1998). The oil becomes dark, viscous, its acidity increases and it develops an unpleasant odor, commonly called rancid, becoming exhausted, and then it is not recommended for further frying, as it gives an unpleasant flavor and odor to food, as well as acquiring chemical characteristics that are proven to be harmful to health (SOUZA, 2010; SANTOS et al, 2012).

However, as the oil degrades, its color tends to increase, due to the presence of residues that give color to the product and residues from the food itself that migrate to the oil. Furthermore, when highly unsaturated oils such as soybean oil are heated, isomerization and migration of double bonds occur, leading to their conjugation, Scheme 1. The conjugation of double bonds leads to the absorption of larger amounts of blue light, causing an increase in orange and brown colors in the oil. Therefore, the color of the oil will depend on the initial content of double bonds and the foods that are fried (LIMA, 1994).



Scheme 1: Products of thermooxidation of linoleic acid (18:2) (9,12)

1 = 2,4–decadienal; 2 = octanoic acid; 3 = 2,4-nonadienal; 4 = 3–nonenal; 5= heptanal; 6 = 2–heptanone; 7 = heptanoic acid; 8 = 2–heptenal.

Source: Kesler; Kriska; Németh, 2000 (21)

Oils and fats are the main ingredients used in the manufacture of laundry soaps and belong to the family of compounds called triglycerides, glycerol esters and fatty acids (SPITZ, 1991). The difference between an oil and a fat is in their physical state at room temperature: oils are in a liquid state while fats are in a solid state. (CDCC - SOAP PROPERTIES).

BLEACHING

Bleaching is the name given to any technological process whose objective is to remove or lighten the natural color of certain materials, generally organic materials such as textile fiber, cotton pulp, paper, cellulose, oils (Figure 1) and glycerin base (Figure 2). Bleaching is applied to obtain products of differentiated quality, when the shade of the natural color of the material is not appropriate for the desired purpose.

Figure 1: Unpurified oil and purified (bleached) oil.

Source: Own author, 2023.

Figure 2: Unbleached glycerin base and bleached glycerin base.

Source: Own author, 2023

Bleaching is a way of separating small undesirable components from a fat or oil, which can effectively mean the destruction of some of them (PATTERSON, 1992). However, it is important to emphasize that the technological process chosen as the bleaching route must not damage or alter the properties of the fat or oil and glycerin base.

CHROMOPHORES IN OILS AND FATS

The chromophores (Figure 3) most commonly found in oils and fats are: Chlorophyll, Carotenoids, Flavins, Tocophenols, Phosphatides and Sterols, which give the material shades of red and yellow in different intensities. The main chromophore found in vegetable oil is chlorophyll and in beef tallow it is carotenoid. "Carotenoids are easily the main source of the yellow/red colors in animal fat, with coloration being greatly affected by the diet of the cattle and consequently varying according to the season and location. More than 70 varieties of carotenoids are recognized. As a class, they are composed of isoprene units and contain both cyclic and acyclic formations." (PATTERSON, 1992).

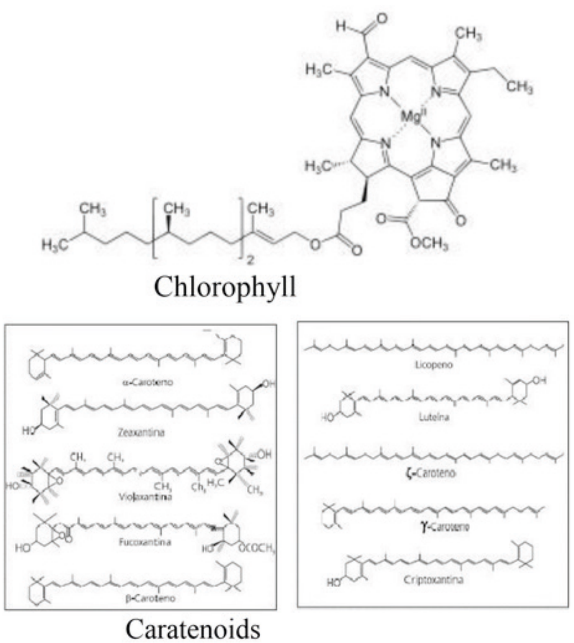


Figure 3: Typical structures of Chlorophyll and Carotenoids.

The chromophores present in oils, fats and saponification products can be removed through oxidation-reduction or bleaching reactions, also known as selective color removal.

CHEMICAL BLEACHING

Chemical bleaching (PATTERSON, 1992) can occur through an oxidation reaction with hypochlorite, chlorite, peroxides or perborates that break the double bonds of colored molecules, generating oxidized molecules.

Organic oxidation reactions are chemical phenomena in which an organic compound, subjected to an oxidizing agent (a substance that undergoes the phenomenon of reduction, i.e., gains electrons), thus undergoes oxidation (loss of electrons). There are several compounds that can be subjected to an organic oxidation reaction, but few can be oxidizing agents (MARIN, 2002). Some examples of oxidizing agents that can be used:

- Ozone (O_3)
- Oxygen peroxide (H_2O_2)
- Potassium dichromate ($K_2Cr_2O_7$)
- Potassium permanganate ($KMnO_4$)
- **Sodium hypochlorite (NaOCl)**

It is worth mentioning that all these oxidizing agents have nascent oxygens (free oxygen atoms that are commonly represented by [O]) when subjected to certain conditions, such as the presence of a strong acid or base. Nascent oxygens are responsible for the oxidation process (MARIN, 2002).

METHODOLOGY

TREATMENT OF VEGETABLE FRYING OIL

The residual vegetable oil was purchased from the local community (university restaurants and snack bars). The residual oil samples were transported to the Chemistry Laboratory of UTFPR - Pato Branco Campus, where they received specific treatment to make them suitable for the production of the glycerin base. The oil was filtered, separating the solid parts, then one part of hot water was added for every 3 parts of used oil, sodium hypochlorite was added (45 mL for 3 liters of oil), at a temperature between 70°C and 80°C. The mixture remained heated for 30 minutes and the temperature was strictly controlled to prevent the oil from decomposing. The mixture was then filtered to separate the oil and the impurities generated in this stage of the purification process. It was left to rest for 7 days. After this period, the oil is removed from the top using a siphon or a ladle or separatory funnel, and the water and a thin layer of oil that is in contact with it are discarded. Initially, to eliminate the water retained in the oil, the oil was heated on an electric plate for 30 minutes at 100°C under constant homogenization. To ensure the elimination of odorous substances, the oil remained for 24 hours in a drying oven at 60°C. Finally, the refined oil was stored for the production of the glycerin base and made available for physical-chemical characterization.

The physical-chemical characterization of the in natura and refined fatty materials was performed in terms of acidity index (AI), free fatty acid content (%AGL), moisture content (%H2O), saponification index (Is), and density (D), to verify whether the quality parameters found for the residual frying oil met the current technical specifications and to verify whether the treatment techniques for these raw materials were efficient.

PRODUCTION OF GLYCERIN BASE

Waste frying oil, babassu coconut fat and castor oil were used as saponifiable raw materials, improving the quality of the glycerin base obtained. A 1:1 ratio was used between the quantities of saponifiable raw materials; the amount of caustic soda was calculated based on the saponification indexes of the oils and fats used and the amount of sodium lye required at 29% was determined. Vegetable alcohol at 92.8°GL, glycerin and crystal sugar, the latter in a 50% solution (hydrolate), were used as transparency agents. The transparency agents were inserted into the formulation in the proportions of 1/3, 1/2 and 1/1 of the total mass of saponifiable raw materials. The sugar was introduced into the reaction mass in the form of syrup prepared by dissolving it with floral water (hydrolate), replacing pure water, at a temperature of approximately 50°C. The amount of hydrolate used to prepare the syrup was 1/3 of the sugar mass (NATIONAL INSTITUTE OF TECHNOLOGY, 1983). The bleaching agent (sodium hypochlorite) was added at 40°C under constant stirring. The formulation used was adapted from that found in specialized literature (NATIONAL INSTITUTE OF TECHNOLOGY, 1983).

To characterize the glycerin base produced, the following parameters were determined: free acidity or free alkalinity; insoluble in alcohol; pH; solidification time (hardness/softness), transparency, water solubility, moisture absorption, foam and odor (CARAZA et al, 1995; DIER et al, 2000; BRAZIL, 2015; MOUSSAVOU, 2012).

RESULTS

The use of vegetable oil at certain temperatures and for frying purposes contributes to its deterioration, to the growth of microorganisms, and to accelerate chemical decomposition reactions. The purpose of the clarification or bleaching process is to ensure an oil with uniform color, to add value to the purified oil when compared to residual oil, and to use it as a raw material in the production of glycerin bases, a process that requires high-quality starting fatty materials to meet consumer demands. Figure 4 shows some stages at different times: without treatment, after filtration, and mixed with the clarifying solution, maintained at a temperature of 70°C.

Figure 4: Steps in the frying oil bleaching process.

Source: Own author, 2022.

During the bleaching process, the mixture containing the frying oil and the clarifying solution changed color over time, in accordance with the change in its pH. Initially, after 5 minutes of heating, the liquid acquired a greenish-yellow coloration; after 15 minutes it became orange; after 30 minutes it became brown; and finally, after 45 minutes of heating, a light-yellow coloration appeared.

The clarified oil was transferred to a decantation funnel to remove undesirable substances by washing it repeatedly with boiling water until it maintained a clear appearance free of impurities, as illustrated in Figure 5.

Figure 5: Aqueous washing of residual oil.

Source: Own author, 2020.

Regarding clarification (bleaching), deodorization and clear appearance free of impurities, the refining process was efficient. Figure 6 shows the purified, deodorized, clarified oil available for the production of glycerin bases.

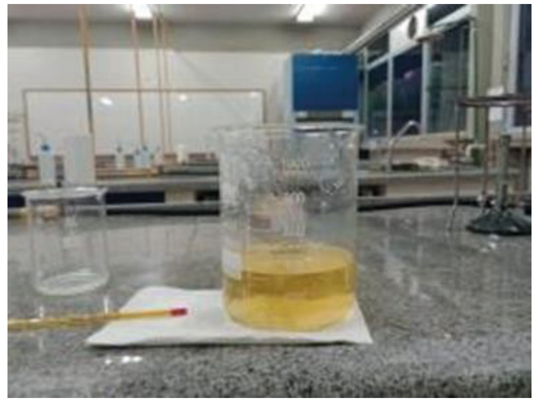


Figure 6: Refined frying oil

Source: Own author, 2022.

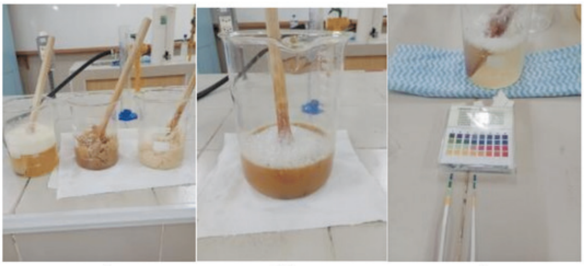
To produce glycerin bases, a series of solvents were used, such as: alcohol (ethanol), glycerin (glycerol or propanetriol) and sugar (sucrose). At this point, you must choose the proportion of soap and solvent to be used. Transparent bases must have between 40 and 60%, by weight of solvent, for 60 to 40% of "real soap", respectively. In this work, a proportion of 50% solvent and 50% "real soap" was used. The more solvent, the more transparent the soap, however, the less foamy it will be and the faster it will be used up in the bath, this is due to the smaller amount of soap contained in its weight.

Other problems may arise, such as the soap becoming softer than desired, forming water droplets on its surface in humid environments and wilting over time, Figure 7.

Figure 7: Glycerin bases in the hardening process.

Source: Own author, 2022.

The glycerinated base was produced with untreated residual oil and with treated oil, significant differences were observed in its final color, Figure 8.

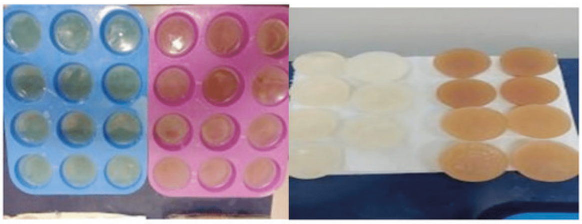


a) b) c)

Figure 8: **a)** Base mass with untreated and treated oil. b) Untreated glycerin base. c) Glycerin base with treated residual oil.

Source: Own author, 2022.

After the glycerin base solidified, the difference in color tones was observed, characteristic of the impurities contained in the residual oil, Figure 9.



a) b) a`) b`)

Figure 9: Glycerin base: a and a`) treated oil. b and b`) untreated oil.

Source: Own author, 2022.

In the hardness and softness test, basic reagents were initially used to monitor the solidification time, softness and drying. It started with sodium chloride, which helped with stability (solidification time), increasing from 72h to 2h, but interfered with transparency, leaving the glycerin base translucent, losing transparency and becoming very hygroscopic, with water droplets or sweat on the surface, Figure 10.

Figure 10: Glycerinated bases with sodium chloride.

Source: Own author, 2022.

After several tests with sodium chloride, another hardening and drying agent was chosen, sodium lactate. The results were observed instantly, after 30 minutes, it contributed to the formation of a more solid and dry product, and after 72 hours, the glycerin base was free of droplets on the surface and had excellent total transparency, Figure 11.

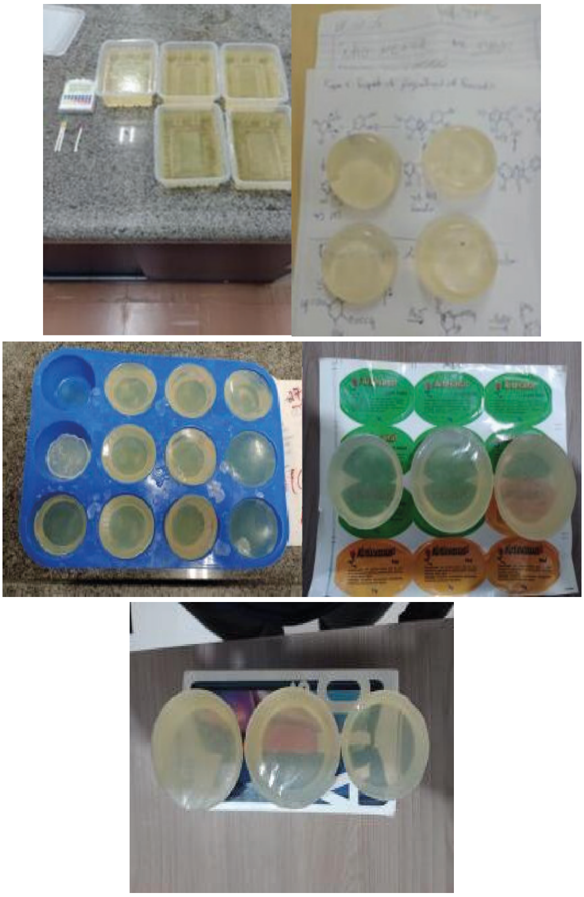


Figure 11: Glycerin bases with sodium lactate.

Source: Own author, 2023.

The results presented indicated that after the treatment of residual frying oil, it can be added to glycerin base formulations, without altering the characteristics of the final product, Figure 12.

Figure 12: Vegan glycerin bases.

Source: Own author, 2023.

CONCLUSIONS

The main challenge of this work was to develop vegan glycerin bases using the "Cold-Process" technique using residual frying oil, evaluating the physicochemical behavior of the samples, followed by the sensory evaluation of the products obtained.

The tests performed were important to establish the profile of the physicochemical characteristics of the formulations. The incorporation of this food waste (residual frying oil) may be economically viable for the continuous and increasing production of vegan glycerin bases, used in the production of handmade soaps as cleaning and body hygiene products. In addition, they can contribute to environmental sustainability and the generation of jobs and income.

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