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# **Treatment of Post-consumer Vegetable Oils for Biodiesel Production**

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Additional information is available at the end of the chapter

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## **1. Introduction**

The current energy model based on petroleum shows signs of exhaustion, which is aggravating, as besides energy source petroleum is used extensively for the production of plastics, clothing, fertilizers and medicine, moving a true "Petroleum Civilization" [1]. All the question of exhaustion of petroleum reserves and its derivatives and the search for renewable energy sources, is also highlighted the issue of waste, which daily becomes one of major problems for humanity. Worldwide, approximately 60 million tons of edible vegetable oils - which, in most cases, are used for frying various types of food - are produced, according to data from the United States Department of Agriculture Food, published in 2000. A significant number of these oils are eliminated directly into the environment, harming these aquatic and terrestrial environments [2].

Almost all energy consumed in the world comes from non-renewable sources of fossil fuels, which cause great environmental impact. Alternative fuels for diesel engines are becoming increasingly significant due to the decrease of petroleum reserves and thus, increasing its price, that reaches levels high enough to prevent its use. Also the environmental impact caused by emissions of gases generated from burning of fossil fuels have been reason for research on alternative energy sources [3,4].

Due to emission of toxic gases by discharges from diesel vehicles, hundreds of researches warn that different pollutants emanating from the exhausts lie in the main causes of degradation of air quality in large urban centers.

The recycling of post-processed oil is minimal and has restricted applications, one being the use in the detergent industry and most recently, as biodiesel. This can be defined as the mono-alkyl ester derived from long chain fatty acids, from renewable sources such as vegetable oils or animal fats obtained by transesterification process, use of which is associated with replacement of fossil fuels in engines compression ignition [5]. It can also be defined as a biodegradable fuel derived from renewable resources obtained from the reaction of vegetable oil and animal fats which, stimulated by a catalyst, react chemically with methanol or ethanol. This can be done with any fresh or post-consumer vegetable oil, waste or sludge. Several studies have shown that the obtaining of methyl and ethyl esters from soybean oil, canola, sunflower, palm, castor, and also post-consumer frying oil, is recommended, since it has lower incomplete combustion of hydrocarbons and lower emissions of carbon monoxide, particulate matter, nitrogen oxides and soot [3, 6].

The biodiesel obtained from post-consumer frying oil, according to studies, decreased smoke, demonstrating that has effective benefit in reusing this oil for biofuel production, featuring a more suitable destination to this agro-industrial waste that, in Brazil, is commonly discarded and/or partially reused, but often in inadequate ways [7].

Vegetable oils have many advantages as alternative fuels when compared to diesel: they are natural liquids, renewable, with high energy value, low sulfur content, low aromatic content and biodegradable. However, despite the use of these oils being favorable from the point of view of energy, its direct use in diesel engines is very problematic. Studies performed with various vegetable oils showed that its direct combustion leads to a series of problems: carbonisation in the injection chamber, contamination of the lubricating oil, among others [8].

The emission of toxic gases by motor vehicles is a major source of air pollution. In cities, these vehicles are responsible for the emission of harmful gases such as carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), nitrogen oxides (NO<sub>x</sub>), sulfur dioxide (SO<sub>2</sub>), hydrocarbons (HC), lead, smoke and particulates. Studies have been conducted in order to quantify and estimate the use of various energy sources on the increase of CO<sub>2</sub>. The main sources of energy considered more polluting in terms of CO<sub>2</sub> emissions are: Liquefied Petroleum Gas (LPG), natural gas, fuel oil and diesel oil [9].

In general, air pollution affects health, generating both acute effects such as eye irritation and coughing, which are temporary and reversible, and chronic effects, which are permanent and cumulative with demonstrations in the long run, of causing severe respiratory diseases. There may also be structural corrosion and degradation of buildings and work of art. In heavily polluted cities, these disturbances are exacerbated in winter with temperature inversion, when a layer of cold air forms a bell high in the atmosphere, trapping hot air and preventing dispersion of pollutants. Compared to different sources of emissions, the diesel has the highest emission of toxic gases, contributing to the rise of the various environmental scenarios, social and economic [10]. Due to this problem, various studies are being conducted with post-consumption vegetable oils for biodiesel production, therefore, is an alternative renewable fuel that releases less harmful gas emissions compared to conventional fossil fuel (diesel). The most common method of making biodiesel is by transesterification reaction of vegetable oils or animal fats, with a short chain alcohol [11].

Biodiesel in its pure form (B100) can allow the net emission of carbon dioxide (CO<sub>2</sub>) - the main from the Greenhouse Gas (GHG) emissions be reduced by 80%. This has a positive impact on the environment because it decreases air pollution in large urban centers (the B100 blend provides a 90% reduction of smoke and eliminate the sulfur oxide, responsible for acid rain), thus improving the quality of life and reduced spending in the health system population [12].

The recycling of post-consume discarded vegetable oils contributes to reduce the uncontrolled and harmful environmental disposal, and may have competitive price on fossil fuels. However, the use of this oil in biodiesel production requires treatment prior to transesterification reaction, which comprises the removal of contaminants solid particles and the appropriateness of color and odor. For this reason, the main objective in this research was to use clays of the northeastern semi-arid region of Paraíba/Brazil to evaluate its potential in the treatment of post-consumer vegetable oils for biodiesel production.

### 1.1. Post-consumer vegetable oils

Among renewable energy resources, the use of biomass, in its different forms (solid, liquid and gas), was intensively researched in recent years as an alternative to minimize adverse environmental impact and the uncertainty in future supply of fossil fuels. Despite the possible environmental benefits in the use of vegetable oils as a substitute for diesel, barriers economically and ethically motivated the search for alternative raw materials for biofuel production [13, 14].

Among the alternatives studied, the reuse of Waste Vegetable Oils (WVO) and fats of processes of frying various foods has been shown to be attractive because the advantage in that the vegetable oil as fuel after its use in the food chain, thus resulting in a second use, or even an alternative destination to a residue of food production destination [15]. Among the several aspects that motivated the study of vegetable oils as fuel potential are:

- It's (liquid) physical condition and its high specific energy content (MJ/kg fuel) when compared with other fuels derived from biomass;
- The fact that they are produced from different oilseeds (soybean, rapeseed, palm, etc.) under different climatic conditions;
- High energy productivity of some oilseeds (above 150 GJ/ha for palm oil);
- The possibility of using oil and its derivatives in high efficiency energy conversion engines, such as diesel engines.

The oils used in frying have important nutritional aspects, involving the transport of fat soluble vitamins, supply of essential fatty acids of the  $\omega$ 3 and  $\omega$ 6 series, precursors of eicosanoids, the energetic power and present a wide acceptance by the various social groups [16].

Studies conducted in the city of Valencia/Spain, concludes that it is attractive, the environmental point of view, obtaining biofuel from WVO. A selective collection system, established by the city council, supported the project to produce biofuel to supply 480 city buses, with a

demand of approximately 42,000 liters/day. The ultimate goal of the project was the elimination, large scale, the WVO plumbing the sanitary sewer system of the city, about 10,000 t/a [13].

In Brazil, it is common the use of soybean oil (nationally) and rice oil (in the south) to processes of frying food in shops. Soybean oil contains 15% of saturated fatty acids, 22% of oleic acid, 54% of linoleic acid and 7.5% linolenic acid. The rice oil contains about 20% of saturated fatty acids, 42% of oleic acid, 36% of linoleic acid and 1.8% of linolenic acid. Soybean oil, by presenting a lower composition of saturated fatty acids and higher in polyunsaturated fatty acids, is more susceptible to degradative processes [17].

The physical changes which occur in the oil or fat during the frying process include dimming, increase in viscosity, decrease in smoke point and foaming. Chemical changes can occur by three different types of reactions: the oils and fats can hydrolyze to form free fatty acids, monoacylglycerol and diacylglycerol; can oxidize to form peroxides, hydroperoxides, conjugated dienes, epoxides, ketones and hydroxides; and may decompose into small fragments or remains in the triacylglycerol and to associate, leading to dimeric and polymeric triglycerides [16,18].

During the process of frying oils and fats are exposed to the action of three agents that contribute to compromise their quality and modify its structure: the moisture from foods, which is the cause of hydrolytic alteration; oxygen, which in contact with the oil, for prolonged periods, causes oxidative modification and the high temperature in the operation, 180°C, causing thermal alteration [19].

The usage time of the oil varies from one establishment to another, mainly due to the lack of legislation to determine the exchange of post-consumer oil [7]. There is no single method by which it is possible to detect all situations involving the deterioration of oils in the frying process. The determination of the optimal point for disposal has significant economic impact resulting in a higher cost when oil is discarded before its effective degradation, and loss of quality of food, when discarded later. Some indicators used by restaurants and cafeterias, to determine the point of discharge of oil or fat are: color change, formation of smoke and foam during the frying process and changes in aroma and taste [20].

In frying temperature (170 to 180°C) occurs in reactions with air, water and food components. The oil and the vegetable fat used in frying process by immersion represent a major risk of environmental pollution since most commercial establishments (pubs, restaurants, coffee shops, etc.) and residential discard the residual oil into the sewer system difficult to treat these. However, this material can be used as raw material for biodiesel production [21, 10].

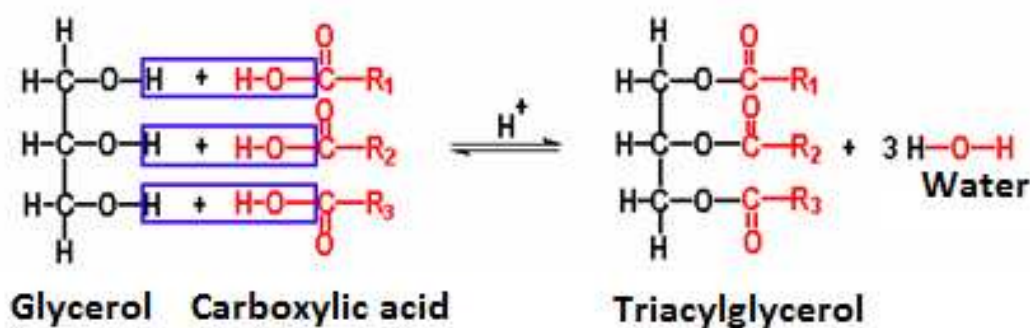
The transformation of the used cooking oil into biodiesel brings significant environmental improvements. Initially, the byproduct that would be discarded in the environment receives a new use, no longer willing improperly. Thus, reducing the consumption of fossil fuels (diesel oil) occurs, in addition to encouraging the use of renewable fuels.

For the manufacture of biodiesel, it is necessary to invest in the industry of purification and transformation. Biodiesel is biodegradable fuel derived from renewable sources (vegetable oil or animal fat) which can be obtained by different processes, such as cracking, esterification and transesterification [22].



The lipids are oils and fats insoluble in water, animal or vegetable source, and consist of triglycerides or triglyceride esters formed from glycerol and fatty acids. The present fatty acids are generally saturated carboxylic acids with 4 to 24 carbon units in the chain and unsaturated carboxylic acids with 10 to 30 carbons and 1 to 6 double bonds in the chain [23].

The vegetable oils are natural products consist of a mixture of esters of glycerol derivatives, which contain fatty acid chains from 8 to 24 carbon atoms having different degrees of unsaturation (Figure 1). Different species show variations in oil molar ratio between the different fatty acids present in the structure [7].



Source: [24].

**Figure 1.** Formating of Trigliceride: a molecule of glycerol and a molecule of fatty acid.

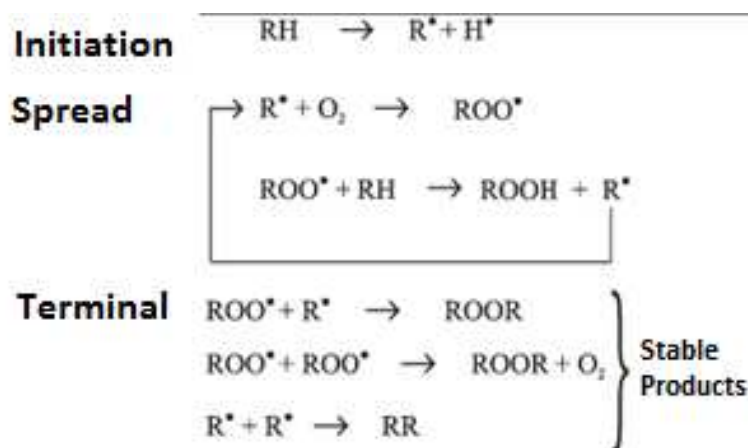
Firestone et al. [25] comment that in some countries such as Belgium, France, Germany, Switzerland, Netherlands, United States and Chile, there are rules on the conditions under which a vegetable oil used for frying should be discarded. But in Brazil, as in many other countries there are no laws and regulations establishing limits to the changes in these oils. An estimated damaged by oil frying process must be discarded when their content of polar compounds meet above 25%. Another aspect that must be considered is the percentage of free fatty acids, for which the laws set, limits around 1 and 2.5%.

One of the main causes of the degradation of oils and fats is rancidity, which is associated with the formation of organoleptically, creates unacceptable product due to occurrence of foreign odors and flavors, and the loss of product color, and inactivation of vitamins polymerization [26]. The rancidity can be classified as:

- Hydrolytic rancidity - occurs in the presence of moisture due to the action of lipases that catalyze the hydrolysis enzymes, releasing fatty acids, and
- Oxidative rancidity or oxidation occurs due to non-enzymatic action of lipoxygenase enzymes or by action, such as autoxidation and photooxidation.

According [17] consumption of fried foods and frozen pre-fried, induces higher intake of oil through the frying process. During these processes, there are several forms of lipid deterioration that compromises the quality of the oil, they are:

- Hydrolysis involves the cleavage of the glyceride ester with formation of free fatty acids, mono glycerides, diglycerides and glycerol. It is a reaction that occurs due to the presence of water at high temperatures, which can result in products with high volatility and high chemical reactivity;
- Consisting of degradative oxidation process in which atmospheric oxygen dissolved in the oil or reacts with unsaturated fatty acids, producing sensory unacceptable products with unpleasant smells and flavors for human consumption (Figure 2);
- Polymerization that occurs when two or more fatty acid molecules combine as a consequence of changes in the oxidation process and high temperatures.



Source: [27].

**Figure 2.** General scheme of the lipid oxidation mechanism.

Several studies with oil heated for long periods at high temperatures showed that the resulting product contains more than 50% of polar compounds which are degradation products of triglycerides (polymers, dimers, oxidized fatty acids, diglycerides and free fatty acids). These oils with high contents of polar compounds can cause severe irritation of the gastrointestinal tract, diarrhea, reduction in growth, and in some cases death of laboratory animals [28]

When oils are used at high temperatures or are reused, they release a toxic substance, acrolein, which interferes with the functioning of the digestive and respiratory system, mucous membranes and skin, and can even cause cancer [29].

The resulting polymers increase the viscosity of the oil. The frying process characteristics such as browning develops, an increase in viscosity, decrease in smoke point and foaming affecting the quality of the oil [16].

Brazil does not have any regulation that legally defines the monitoring of disposal for oil and frying fats. There are regulations governing the suitability of oil for consumption in Brazil, the NTA 50, citing some physicochemical items to control the suitability of this oil: iodine value, peroxide value and acid value, however not refer to oils and cooking fats [16].

## 1.2. Clays

According to Santos [30], clays are natural earth materials which exhibit fine-grained (typically with a diameter of less than 2  $\mu\text{m}$  particles) and are formed by chemically hydrated silicates of aluminum, iron and magnesium. These are composed of small crystalline particles of a limited number of minerals, clay minerals. In addition to these clay minerals, clays may also contain organic matter, soluble salts, particles of quartz, pyrite, calcite, and other residual amorphous mineral reserves. The main factors that control the properties of clays are the mineralogical and chemical composition of clay minerals of non-clay minerals and their particle size distributions; electrolyte content of exchangeable cations and soluble salts; nature and content of organic components and textural characteristics of the clay.

Brazil has industries that utilize different types of clays for several purposes: fabrications red ceramic, white ceramic, refractory materials; the manufacturers of rubber and plastics used as the active and inert fillers; metallurgical industry uses clays as binders for molding sands for the casting of metals and for pelletizing iron ores; industries of edible oils and petroleum use them as bleaching agents of vegetable and mineral oils; can also be used as thixotropic agents in mud for drilling for oil drilling and water; There are special clays are used as catalysts in cracking of oil to produce gasoline and are used for special purposes being used as filler for soap and tissues, as pigments for paints, in the manufacture of pharmaceutical products [30].

Determining the result of the technological properties of these properties whose function is to complement function test results traditional characterization as: X-ray diffraction, X-ray fluorescence, particle size analysis. With these results together with the results of the technical properties (physical and mechanical properties) can indicate the proper use of a clay and establish accurate or necessary for better performance properties to which the clay is subjected [31].

The importance and diversity of use of clays is a result of its particular characteristics. This difference makes the clays of the most used materials, either on his great geological variety or offers a set of essential and indispensable factors in numerous industrial processes [31].

The bentonite is a layered clay mineral composed montmorillonite that is an aluminosilicate trifórmico the type crystalline structure appearing as a layer of alumina octahedrons between two layers of silica tetrahedra with adjacent margins primarily. Their composition is variable due to ease of isomorphic substitutions (may contain FeO, CaO, Na<sub>2</sub>O and K<sub>2</sub>O), which causes a negative charge density on the surface of the smectite clay and require cations to compensate for these loads, the exchangeable cations [30].

In Brazil, the terms bentonite clay materials are used to montmorillonite without any information about the geological origin or mineralogical composition. The chemical composition and method of the unit cell of the "theoretical" montmorillonite or end of the series is  $(\text{Al}_{3,33}\text{Mg}_{0,67}) \text{Si}_8\text{O}_{20} (\text{OH}) 4.\text{M}^{+}_{10,67}$ , where  $\text{M}^{+1}$  is a monovalent cation. This formula shows that the unit cell has a negative electrical charge due to isomorphic substitution of  $\text{Al}^{3+}$  by  $\text{Mg}^{2+}$ . The cation  $\text{M}^{+}$  which balances the negative charge is called exchangeable cation since it can be changed in a reversible way, by other cations. The content of exchangeable cation, expressed in milliequivalents of cation per 100g of clay is called CEC - cation



exchange capacity. The cation  $M^+$  interplanar occupies the space of the two layers 1 and may be anhydrous or hydrated. As the size of the dry cation and the number of layers of water molecules coordinated to the cation, it may have different values of basal interplanar distance [32].

According Centre for Mineral Technology – CMT [33], is the term given to a smectite group of minerals consisting of: montmorillonite, beidellite, nontronite, hectorite and saponite, in which each of these minerals form a similar structure, but each is chemically different. The most common mineral in the economic deposits of smectite is montmorillonite group. The calcic and sodic varieties, based on exchangeable cation, are the most abundant.

Amorim et al. [34] commented that according to geologists, the bentonite is formed by devitrification and chemical alteration of volcanic ash. For many years, scholars have used the origin of these clays as part of its definition, but in some countries as their deposits were not originated by volcanic action, other definition came to be used: bentonite clay is composed of any clay mineral montmorillonite, smectite group the and whose properties are established by this clay mineral.

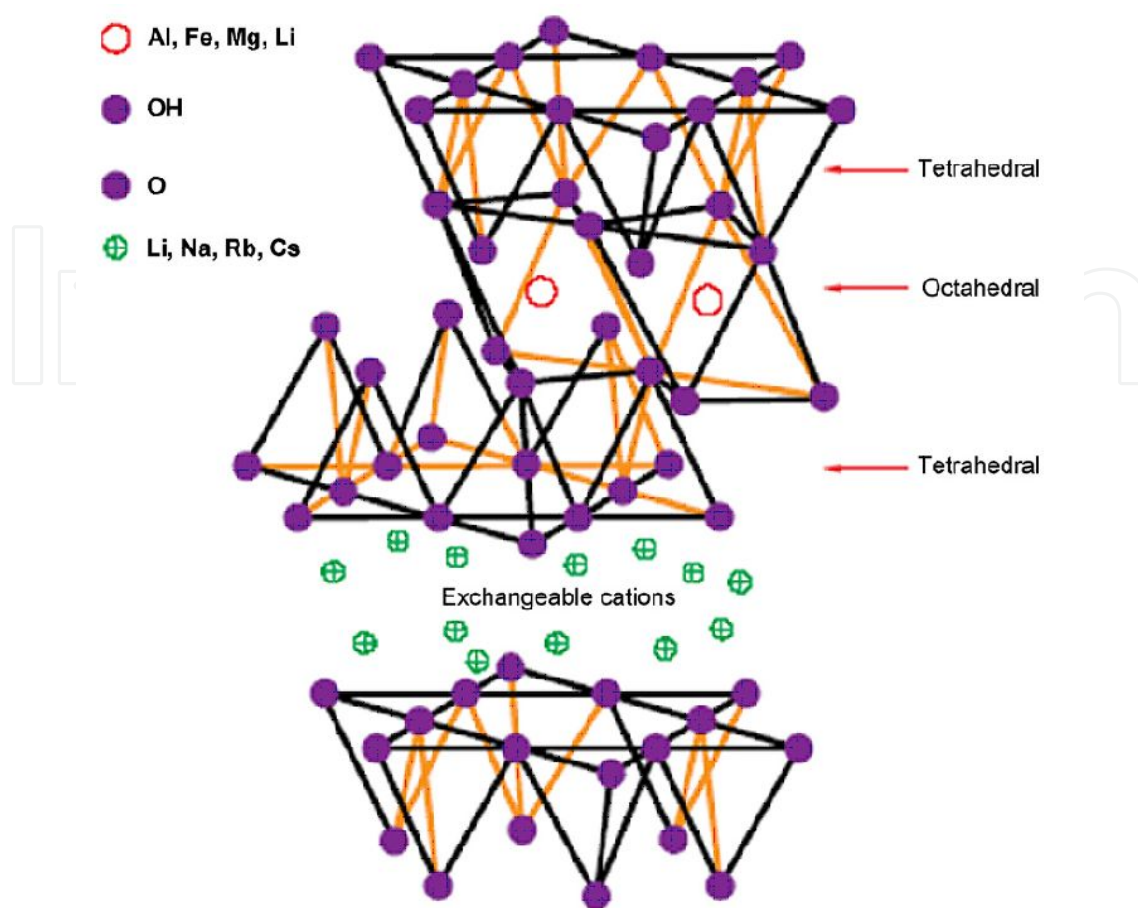
The bentonite clays have distinct and peculiar to increase to several times its original volume when wetted with water and form thixotropic gels in aqueous media at low concentrations, interplanar spaces reaching up to 100 Å, high surface area and cation exchange capacity. These are characteristics that make the bentonite a wide range of applications in various technological sectors from the preparation of nanocomposites by the use as decolorizing agent [35].

Deposits of bentonite clays of Paraíba form the largest, and the most important deposit is located in Brazil. Their occurrences are located in the city of Boa Vista, and its deposits are mines Lages, Bravo, Jua and Canudos. In 2004, Paraíba State was the main producer of crude bentonite with 88% of national production, followed by São Paulo (7.3%), Rio de Janeiro (4.4%) and Paraná (0.2%). The production of bentonite in Brazil, which focuses on two products, activated bentonite clay and dry ground, grew by 14% [34, 36].

According to data released by the National Department of Mineral Production – NDMP [37], the state of Paraíba is currently the most significant source of bentonite clay, bentonite deposits it's being located mainly in the city of Boa Vista. Its reserves amount to about 70% of bentonite clays throughout Brazil.

The national reserves of bentonite represent about 3% of world reserves. Brazilian production is around 300 000 t/a which represents 3% of world consumption. The average price of bentonite is about \$107/t, while the activated bentonite can reach \$1,800/t. Also according to [38], the market for bentonite is very concentrated in the United States, the world's largest producer and has high investments made in this industry, which has provided diversification in its use and application [38].

Clay minerals of the smectite (montmorillonite) group are composed of two layers of a tetrahedral silicate with an octahedral core sheet joined together by common oxygen atoms to the leaves and in the space between the sheets are adsorbed water molecules and exchangeable cations, which may be  $Ca^{2+}$ ,  $Mg^{2+}$  or  $Na^+$  or both (Figure 3) [30].



Source: [39, 40].

**Figure 3.** Crystal structure of the clay mineral montmorillonite.

The bentonite clay is classified according to their exchangeable cations present in [39]:

- Homocationica: when there is a predominance of a type of exchangeable cation such as sodium or calcium, so called sodic or calcic bentonite.
- Polycationic: when there is no predominance of one type of exchangeable cation. Cations such as sodium, calcium, potassium and others can be present in similar concentrations.

Treatment with acid serves to Dissolve some impurity of bentonite; replace calcium and other cations intercalated by ions  $H_3O^+$  hidroxônio and dissolve in the octahedral layers of two layers: one, some cations  $Mg^{2+}$ , Al,  $Fe^{3+}$  or  $Fe^{2+}$ . The acid treatment causes significant morphological changes in the crystal structure of montmorillonite during and after acid activation. The montmorillonites activated by acids, are commonly used for bleaching of edible oils and fats [40].

### 1.3. Clays for treatment of post-consumer vegetable oils

Clays have been used by mankind since antiquity for manufacturing ceramic objects, such as bricks and tiles, and more recently, in several technological applications. These are used as

adsorbents in bleaching processes in the textile and food industry, in processes of soil remediation and landfill. The interest in its use has been gaining momentum mainly due to the search for materials that do not harm the environment when discarded, the abundance of world reserves and its low price. In the oil industry, the clays that are used for bleaching these oils are called "bleaching earth", "soil bleach", "clarifying clay" or "adsorbent clay" to indicate that clays in the natural state or after chemical or thermal activation, have the property of coloring materials present in adsorbing mineral oils, animal and vegetable [32].

The bentonite clays according to Santos [32] can be classified according to their adsorptive properties: montmorillonitic bentonite-type clays, which are virtually inactive and inactivable; montmorillonitic inactive clays, but highly activatable by acid treatment; extremely active and activatable clays by acid treatment; active clays and whose activity is little affected by acid treatment; active clays whose activity is decreased by acid treatment.

According to the adsorptive and catalytic properties, the activated bentonite clays are used industrially as catalysts, adsorbents and catalyst supports. However, in terms of consumption, the most important use of this material and purification, bleaching and stabilization of vegetable oils. The adsorptive capacity of these materials increases with treatment with strong acid, typically sulfuric or hydrochloric acid are used. The presence of these acids modifies the structure of clays [41].

The adsorptive capacity of clay bleaching increases with the increase of the specific area. The bleaching earth adsorbs some better connection than others or even ceases to adsorb some. Polar or polarizable molecules are well adsorbed by bleaching earth. However, the adsorptive ability of the bleaching earth is reduced if the oil contains soaps or gums in excess to neutralize the acid sites of the same is true when there are many free fatty acids, which, as highly polar compounds occupy part of the surface of the clay mineral [26].

The power of bleaching clay may be due alone or in combination, the following factors: simple filtration, which corresponds to the retention of colored particles dispersed in oil in the capillaries clay; the selective adsorption of dissolved dyes and catalytic activity of the clay [32].

The time of bleaching oils suffer limitations due to the bleaching temperature. For this, we used 0.75% of smectite clays activated bleaching processes structured in three different temperature levels (82°C, 104°C and 138°C) and five levels of time (5 min., 10min., 15 min., 35min., and 55min.). It was observed that the red color of the oil fell to the lowest level when the highest temperature is used. At this temperature, however, the color began to darken oil from the time of bleaching, coming, at the end of the bleaching, become darker than the other two processes [26].

For an acid activated bentonite clay may be used as a decolorizing agent is necessary to have the following requirements: the pH is between 6.0 and 7.5; porosity between 60 and 70%; no catalytic activity in the case of edible oils and fats to prevent the generation of undesirable odors and tastes after bleaching; low oil retention in filtration and good filterability [40].

## 2. Materials and methods

The calcic clays used for the treatment of post-consumer vegetable oils were the bentonite clay (Figure 4) trade name Tonsil and Aporofo with a particle size of 200 mesh (0.074mm) mesh provided and identified by the company BENTONISA - The Bentonite Nordeste S/A, located in João Pessoa-Paraíba.



Source: Research data.

**Figure 4.** Calcium bentonite clay used for the treatment of post-consumer vegetable oils.

### 2.1. Post-consumption vegetable oil

Residual soybean oil, mixture of soybean oil and hydrogenated fat residual: samples of raw materials found in some homes in the city of Campina Grande-Paraíba were collected. These oils had a dark color and unpleasant odor. A sample of fresh vegetable oil from soybeans, Figure 5 was acquired in a business in order to make a comparison with the samples of vegetable oils untreated post-consumer and post-consumer-treated clays under study. Soybean oil was chosen because it is the most widely used in the domestic market and for having little commercial value in relation to other edible vegetable oils, such as olive oil, sunflower oil and corn oil.

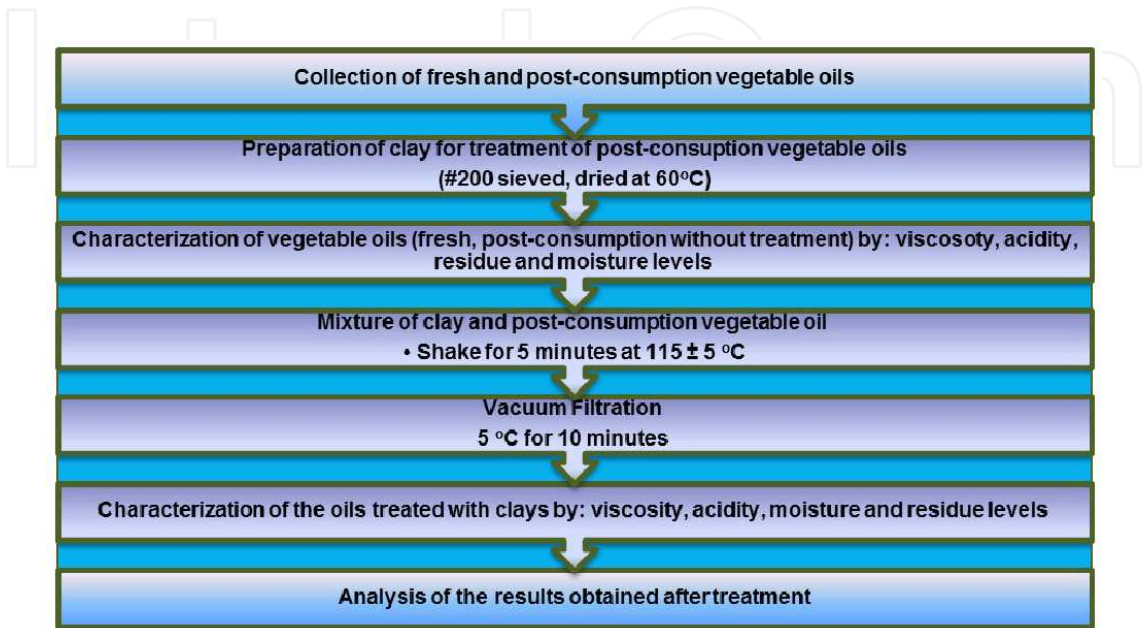


**Figure 5.** Samples of fresh vegetable oils (a) and post-consumer without treatment (b).



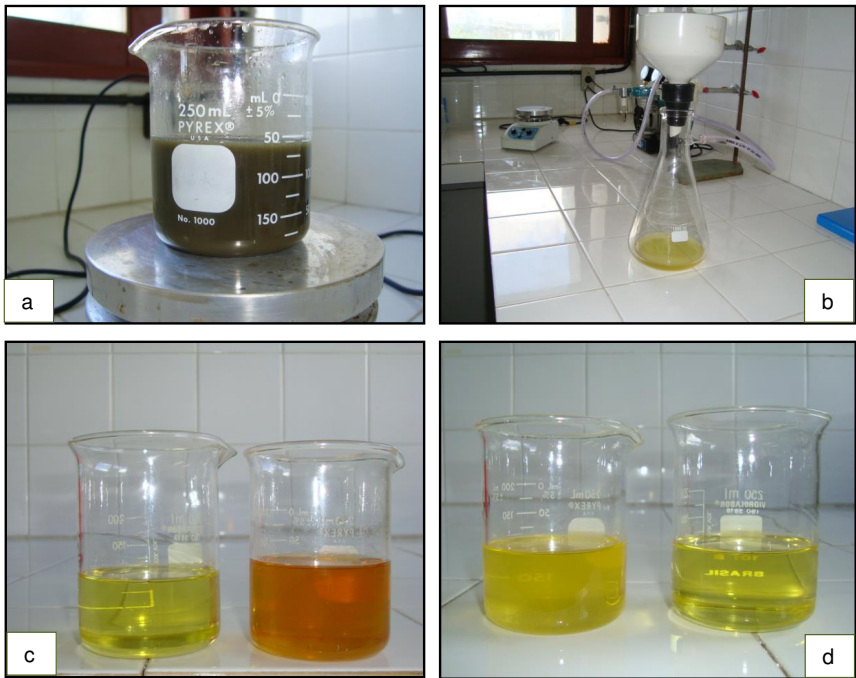
2.2. Methodology

Figure 6 shows the flowchart of the methodology used for the bleaching of treaties with calcic bentonite clay, Tonsil and Aporofo, Paraíba region of post-consumer vegetable oils. This method was adapted from de Santos [32] literature.



Source: Personal archive.

Figure 6. Steps in the treatment of post-consumer vegetable oils process.



Source: Research data.



**Figure 7.** Steps used to treat post-consumer vegetable oils: (a) mixing oil with clay, (b) filtration processes the oil with clay, (c) fresh oils and vegetable consumption without post-treatment and (d) post-consumer oil treated and fresh.

## 2.2.1. Characterization of post-consumer vegetable oils

### 2.2.1.1. Kinematic viscosity

The kinematic viscosities of fresh oils, post-consumer and post-consumer treated with Tonsil and Aporofo clays were measured by a CANNON-FENSKE viscometer thermostat of the brand Quimis according to ASTM 445, 220V, 40°C. For the determination of kinematic viscosity, was used an oil standard viscosity suitable for the viscometer/viscosity range. The standard viscometer is filled with oil by immersing the tube containing the oil bath, waiting 5 to 10 minutes for thermal equilibrium to occur. A reading is held on the 1st and second bulb, noting the result. This procedure is repeated eight times. Then makes an average of measurements and calculates the calibration factor of the tube:

$$F = \frac{V}{t} \quad (1)$$

F = Calibration Factor

V = Standard viscosity

t = Time spent in seconds

The stirred sample is transferred to a beaker and then the viscometer reservoir is filled with this sample, adapting a stopper at the end, in order to promote complete sealing, thus avoiding leakage of oil. The viscometer is then transferred to a thermostatic bath at a test temperature of 40°C. Then the stopper is removed allowing the flow of oil. It is noted that the time was spent for the oil to drain from the first to second and second to third meniscus viscometer. The kinematic viscosity is calculated by the formula described below, and the result is presented in mm<sup>2</sup>/s:

$$V_{(cin)} = T \times F \quad (2)$$

where:

V = Kinematic viscosity at the test temperature, in seconds.

T = Time in seconds obtained by the sample flow.

F = calibration factor.

### 2.2.1.2. Acidity

The acid content of the oils was determined by titration according to ASTM standard D664 24A. For this test, the following reagents are used: isopropyl alcohol (CH<sub>3</sub>CH(OH)CH<sub>3</sub>);

phenolphthalein indicator ( $C_2OH_{14}O_4$ ); barium hydroxide ( $Ba(OH)2.8H_2O$ ); potassium hydroxide (KOH); potassium hydrogen phthalate ( $C_8H_5KO_4$ ). To prepare the solution of 0.1 N KOH are weighed 5.6g of potassium hydroxide. The solution is transferred to a 1000mL volumetric flask, where it is allowed to stand for 24 hours.

After this time is added 2mL of barium hydroxide to this solution is allowed to stand for 24 hours. Is added 2mL of a solution of barium hydroxide precipitation and if the solution is left standing for 24 hours. If there is no precipitation, the solution is filtered with Millipore filter assembly. Then collects the filtered solution to calculate the factorization of 0.1 N KOH, weighting 0, 3500g of potassium. Hidrogenphthalate is added to the flask 50mL of distilled water and six drops of phenolphthalein indicator. Titrate with 0.1 N KOH It is a white 50mL of distilled water added six drops of phenolphthalein indicator. Titrate again with 0.1 N KOH, recording the volume required. The calculation of the factorization is performed by the following formula:

$$N = \frac{\frac{P \times 9,99}{100}}{0,2042 \times (A-B)} \times 56,1 = \quad (3)$$

Where:

P = weight of potassium hydrogen phthalate (grams)

A = Volume of spent KOH titration of potassium hydrogen

B = Volume of spent KOH titration white

V = Normal Concentration

M. Eq. 56.1 KOH =

Purity = 99.9 hidrogenphthalate

Constant = 0, 2042

Constant = 100

In the titration, solvent is titrated in the absence of oil. Initially weighed in an Erlenmeyer  $\pm$  2.5g of oil. Added 50mL Erlenmeyer flask with the solvent in the oil, the measuring cylinder and 4 to five drops of phenolphthalein. It is a plug inserted into the Erlenmeyer flask (magnet) for mechanical agitation. Drops of KOH solution are added to the Erlenmeyer flask until the appearance of a slight pink tint. It is noted the amount of KOH. The calculation is done by the NHS expressed below formula and the result is displayed in mg KOH/g.

$$\frac{\text{Factor (KOH Volume - Volume of White)}}{\text{Weight of the sample}} \quad (4)$$

### 2.2.1.3. Residue

The residue content of the oils was examined in a model centrifuge. 215, brand FANEM, voltage of 220 V. Two tubes are filled with 100 mL sample and then are placed in a centrifuge. The process is centrifuged for 30 minutes at 1,500 rpm.

The result of the residue content is presented in percentage (%).

### 2.2.1.4. Moisture content

The moisture content of fresh oils, untreated post-consumer and post-consumer treated were analyzed by means of a water condenser with the heating mantle, make Quimis, 220V, Q.321.24 model. Initially, it is checked whether the oil for contamination by water, through the test on a hot plate apparatus. Oil drops are dripped with a glass rod and verifies whether precipitation occurred this oil, i.e., if is detected the presence of water. After this procedure, other tests are initiated to know the amount of oil contamination by water. 0.01mL of sample and 100mL of Xilou into a 500mL flask are added. The water condenser is turned on and starts heating to a temperature of 150°C and adjusted so as to provide reflux for 2 to five drops/second. The process of distillation continued/continues until no more water appears nowhere in the unit, except in the collector. After distillation, the collector is cooled to room temperature. After this process, the reading of the volume of water in the sink is performed. The moisture content is calculated by the following formula:

$$\frac{\text{Moisture content (\%)} = \text{Volume of water in the collector (in mL)} \times 100}{\text{Sample Volume (mL)}} \quad (5)$$

The results of moisture content are presented in %.

Tests of kinematic viscosity, acidity levels, residue and moisture were conducted in the laboratory LUBECLEAN- Distributor Cleansing and Lubricants LTD, located in João Pessoa – Paraíba.

## 3. Results and discussion

### 3.1. Analysis of kinematic viscosity, acidity, residue and moisture content

The procedures adopted in this study allowed analyzing comparatively the results Tonsil and Aporofo bentonite clay in viscosity, the levels of acidity, residue and moisture from fresh vegetable oils, untreated post-consumer and post-consumer treaty. Table 1 illustrates these results.

As can be seen in Table 1, the oil treated with Tonsil clay had a lower viscosity compared to the crude oil and indicating the possibility of use as a biofuel is also a better efficiency than the Aporofo clay. The viscosity is a measure of the internal resistance to flow of a liquid, is an

important property of vegetable oils because its control feature is intended to maintain its lubricating the engines, as well as proper operation of systems and injection pumps fuel [7]. Values above or below the viscosity specified by the NAP (National Agency of Petroleum, Natural Gas and Biofuels) range can lead to excessive wear on parts self - lubricating the injection system, with an increased work and leak in the fuel pump, as well as providing inadequate fuel atomization, incomplete and with consequent increase in the emission of smoke and particulate matter combustion [42].

|                                | Fresh vegetable oil | Un-treated post consumption vegetable oil | Post consumption vegetable oil treated with Tonsil clay | Post consumption vegetable oil treated with Aporofo clay |
|--------------------------------|---------------------|-------------------------------------------|---------------------------------------------------------|----------------------------------------------------------|
| Viscosity (mm <sup>2</sup> /s) | 34,57               | 35,45                                     | 32,47                                                   | 35,33                                                    |
| Acidity (mg KOH/g)             | 0,64                | 2,90                                      | 2,44                                                    | 2,27                                                     |
| Residue (%)                    | 0,0                 | 0,1                                       | 0,0                                                     | 0,0                                                      |
| Moisture content (%)           | 0,0                 | 0,0                                       | 0,2                                                     | 0,3                                                      |

**Table 1.** Viscosity values, levels of acidity, and the residue moisture of fresh vegetable oils, untreated post-consumer and post-consumer and treated with Tonsil and Aporofo clay.

Viscosity is a measure of the resistance offered to the flow of diesel engines. The key is to provide a proper atomization of the oil and preserve its lubricating characteristics. Kinematic viscosity of the biodiesel increases with increasing carbon chain and is inversely proportional to the number of unsaturation present thereon. For the same unsaturated compound has a higher viscosity dependence on the configuration of the double bond (cis or trans) than the position of the same [43].

The viscosity directly influences the atomization; that is, the higher the viscosity, the greater the average size of the droplets of the fuel sprays in the combustion chamber. Accordingly, larger droplets resulting in poorer and slower burning mixtures damage the ignition and combustion efficiency. Therefore, an increase in viscosity increases the time delay in the ignition cycle diesel engines.

The viscosity of the biodiesel with increasing carbon chain length and degree of saturation and influences the combustion process in the combustion chamber of the engine. High viscosity causes heterogeneity in the combustion of biodiesel, due to decreased efficiency of atomization in the combustion chamber, causing the deposition of waste in the internal parts of the engine [45].

In Brazil, there was an attempt to make a single specification for biodiesel (B100) similar to those already existing in some countries. However, there are characteristics that differentiate Brazil, a tropical country, countries like those in Europe: the temperature, which is high during most of the year and another important factor, is that in Europe reproduces biodiesel from oils

of a single species vegetable, rapeseed. As in Brazil a wide diversity of species of potential use for the production of oils in many cases it is impossible to attain the viscosity values as specified. The specifications for conventional diesel and biodiesel in Brazil are: viscosity at 40°C - NAP 310/01 (diesel) and NAP 255/03 (biodiesel): 2.5-5.5 mm<sup>2</sup>/s. The viscosity of the biodiesel is considerably reduced compared to when the source oil is passed to a subsequent process which is the transesterification reaction (which is the step of conversion of the oil or fat to methyl or ethyl esters of fatty acids, which is the biodiesel) [46].

With respect to acid content found in the samples studied after consumption of processed vegetable oils, can be seen a decreased value compared to vegetable oil consumption without post-treatment. NAP Ordinance 42/2004 establishes a value of  $\leq 0.80$  mgKOH/g for biodiesel (B100) [42]. However, even if the treated vegetable oils do not present results of acidity within the values established by the NAP, these oils must undergo a subsequent treatment process that is the transesterification reaction. The acidity can partly reveal the condition of the oils and fats because the higher the number, the greater the hydrolysis of frying oil, with a consequent increase in fatty acid content. The ideal is that the oil is index less than 2mgKOH/g acidity, in order to have a good reaction yield in the production of biodiesel and also to avoid problems in diesel engines [5].

Argue that the acidity can be defined as the mass (in mg) of potassium hydroxide required to neutralize the free fatty acids not esterified. He also reveals the conservation status of biodiesel, because the hydrolysis of esters occurs with consequent lowering of pH due to the increased content of fatty acids over time [47].

The condition of the oil is closely related to the nature and quality of the raw material, with the quality and purity of the oil with the processing, and especially with the storage conditions. The breakdown of triglycerides is accelerated by heat and light as rancidity is almost always accompanied by the formation of free fatty acid.

The monitoring of acidity in the biodiesel is of great importance during storage, in which the change of values in this period can mean the presence of water. All the rules described above established maximum acidity of 0.5 mg KOH/g [45]. The acidity of biodiesel produced, measured in mg KOH per gram of sample, must be strictly within fixed parameters. The National Petroleum Agency recommends an acid, for any sample of biodiesel produced, less than 0.80 mgKOH/g.

A measure of acidity is a variable directly related to the quality of the oils, processing and storage conditions. According to Ordinance No.482 of National Health Surveillance Agency (NHTA 2), the acidity is one of the quality characteristics of various vegetable oils. The lipid materials undergo chemical changes during still in use as heat transfer medium. The acidity is determined by the amount of base required to neutralize the free fatty acids, the acidity increases with the deterioration of the oil during the exchange of heat, such as the frying process, for example [48].

High levels of acidity have a very adverse effect on the oil quality, as to make it unfit for human consumption or even for fuel purposes. Furthermore, the pronounced acidity oils can catalyze intermolecular reactions of triglycerides while affecting the thermal stability of the fuel in the



combustion chamber. Also, in the case of use of the fuel oil has a significant free acidity corrosive action on the metallic components of the engine. The acid is a crucial examination for oil and biodiesel since high acidity reaction makes it difficult to produce biodiesel, biodiesel while an acid may cause corrosion of the engine or deterioration of biofuel [8].

An analysis of the results, it is found that soybean oil, despite the relatively high level of acidity, which is a limiting factor of process yield, was higher in the transesterification reaction of the mixture of soybean oil/hydrogenated fat. The yields obtained with either soybean oil as with the mixture, indicate that these materials have significant potential for the production of methyl esters of fatty acids. The positive aspect of biodiesel can be explained by the fact of not having nitrogen or sulfur in structures. Thus, they do not contribute to the acidification of precipitation [13].

The contents of waste clay substantially removed the impurities that were present in the oils without treatment, since the oil recovery achieved by means of a first step which is the bleaching process, is one of the most important steps in refining vegetable oils and has a fundamental role to eliminate substances which color instability and oil (residue). In this step, the decolorization of the oil occurs through the adsorption of pigments, which can be done using clays as adsorbent material [24].

The method of treatment is aimed at reducing the amount of impurities and substances which color the oil. Many of these substances act as catalysts of undesirable reactions, such as oxidation, interfering negatively on the physicochemical characteristics of the oil [24].

With respect to moisture content, all results presented are within the specifications of the NAP. Claim that the oil quality influences the transesterification reaction. So is that the oil is ideal index less than 2.0mgKOH/g of oil and moisture content below 0.5% for the purpose of a good reaction yield in obtaining biodiesel acidity and avoids problems microemulsion, corrosion, among others [49].

With respect to the final destination of clays retained on the filter, these can be applied in layers of compression earthworks or can be converted to non-polluting clusters applicable in the formation of landfills [50].

#### 4. Conclusions

- Tonsil bentonite clay had a potential post-treatment in vegetable oil consumption more efficiently compared with the Aporofo bentonite clay, since clay removed many impurities from the oil.
- The post-consumer oil treated with Tonsil bentonite clay showed a viscosity less than the fresh oil and post-oil consumption without treatment, indicating an excellent adsorptive activity of the clay and the possibility of potential use oil as biofuel.
- Vegetable oils treated clay had a water content lower than after consumption untreated oil acidity.

- The oils treated and characterized for the levels of moisture and residue showed values within the standards established by the NAP.
- The post-consumer vegetable oils showed similar sensory and physicochemical characteristics, but differed substantially from fresh oil.
- After a period of storage, vegetable oils treated post-consumer showed stabilization of properties according to the requirements for processed oil.
- Tonsil bentonite clay may be considered more efficient for the post-consumer treatment vegetable oils since they showed better results than those treated with Aporofo clay.

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