





Article

Biodiesel and Bioplastic Production from Waste-Cooking-Oil Transesterification: An Environmentally Friendly Approach

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Abstract: Alternative sources of fuel have been a concern in the last few decades. The growth of urbanization and industrialization will lead to the exhaustion of fossil fuels, attracting studies on alternative routes. The main aim of this study was to produce biodiesel from waste cooking oil (WCO) by methyl transesterification using sodium hydroxide as a catalyst. For this, the physicochemical parameters of biodiesel were studied in triplicate (density, acidity, saponification, viscosity, corrosiveness to copper, visual appearance, and cloud point). An analysis by thin layer chromatography and infrared spectrometry was also performed. The increase in yield (83.3%) was directly proportional to the increase in the catalyst (0.22 g of NaOH). The infrared absorption spectra of WCO and biodiesel showed the presence of common and singular bands of each material. Furthermore, a simple and low-cost mechanism was proposed for purifying glycerol. The spectra of glycerol versus purified glycerin showed that the glycerin produced was pure, being used in the formulation of bioplastic. The product was checked for biodegradation and photodegradation, with incredible soil-degradation times of 180 days and photodegradation of only 60 days. In this way, biodiesel production from WCO showed environmentally friendly proposals and applicability. As the next steps, it is necessary to test the biodiesel produced in combustion engines and improve the bioplastic production, including a spectroscopic characterization and extensive biodegradation testing.

Keywords: bioplastic; waste cooking oil; optimization of oil; layer chromatography; infrared spectrometry

1. Introduction

Renewable energies obtained from plant sources are eminent solutions to produce fossil-fuel replacements. Biodiesel is a renewable, non-toxic fuel obtained from vegetable oils/animal fats. In comparison with petroleum fuels, biodiesel exhibits a low gas-emission profile [1,2]. Since 2008, there is a mandatory parameter to include biodiesel in commercial diesel [3]. In March 2021, the mandatory percentage became 13%. However, in September of this same year, the Brazilian Energy Policy Council approved the temporary reduction of 3%, due to the high appreciation of the cost of soy oil, which is considered the main raw material in the production of biodiesel [4].

The chemical process is involved in transesterification [5]. The mechanism consists of consecutive reversible reactions, in which 1 mol of triglyceride reacts with 3 mols of alcohol, resulting in 1 mol of glycerol and 3 mols of methyl or ethyl esters. Commonly, sodium or potassium hydroxide are used as catalytic agents [6,7]. The costs of raw materials and restriction of available vegetable oils are the critical points for biodiesel production [8,9]. The production of biodiesel from vegetable oils increased the cost up to 75%, resulting in 1.5 times higher than diesel obtained from petroleum [10]. Instead of this limitation, the use of waste cooking oil (WCO) reduces the cost by two to three times compared with virgin oils [11,12]. In Brazil, the estimate is around 1 billion liters of WCO that are dumped into sewerage systems each year causing environmental damage. The application of WCO can provide a sustainable energy matrix capable of avoiding an excessive increase in the final price of the product to the consumer [13].

Additionally, with the growth of the world population, there will be an increase in the demand for energy [14]. Thus, by 2030 there will be an estimated global oil consumption of about 17 million-billion-ton equivalent [15]. Part of the oil will be transformed in WCO by frying processes, in which the food is treated with hot oil at temperatures between 150 °C and 190 °C by immersion and contact with air [16]. This high temperature strongly affects the oil composition making its recycling for food uses difficult [17]. Alternatively, WCO can be collected and used as raw material for several industrial applications [16], including lubricants [18], cosmetics, solvents [19], and as an energy source, through direct burning [20] or as raw material for biodiesel production [21] as shown here.

There is an estimate that for every 1 m³ of biodiesel produced, approximately 0.1 m³ of glycerol is generated [22–24]. Simple alcohol glycerol (1,2,3-propanetriol, also named glycerin) is the backbone of the fatty acids, and it is the principal product obtained during transesterification of vegetable oils and animal fats [25–27]. The refining of glycerol involves the distillations [28], not involving a complex technology but increasing the cost [29]. The sub-product was commonly discarded forming a carcinogenic substance called acrolein [30]. Aiming at sustainable applicability with a high cost/benefit ratio, the resulting glycerol can be used as a plasticizer in the synthesis of bioplastics, biologically based polymer, derived from biomass, which is biodegradable [31]. Taking into consideration the prevailing challenge of plastic-waste management, the methodology shown here opens new perspectives in order to replace the common disposable plastics dependent on fossil-fuel extraction, with a bioplastic based in the transformation of WCO [32].

Finally, the production of biodiesel and bioplastic from WCO is particularly important because of the decreasing environmental problems caused due to fossil-fuel use. Additionally, this topic has been extensively studied in the last five years as shown in Table S1. Thus, this study proposed the transesterification of WCO to produce high-quality biodiesel and to provide a feasibility condition to use the residual glycerol.

2. Materials and Methods

2.1. Frying Oil Collection

The WCO was collected at the university restaurant of the Federal University of Tocantins, Campus of Gurupi using bottles. To optimize the transesterification reaction, a central composite design (CCD) was used.

2.2. Experimental Design

The study was designed based on four factorial points, four axial points, and two central points, totaling ten tests. The selected variables of methanol volume (mL) and sodium-hydroxide mass (g) are shown in Table 1. We also presented the limits of the variables (upper, central, and lower) to identify the maximum production yield. Using the experimental limits, we calculated the laboratory planning matrix in Statistica® 10.0 software, shown in Table 2.

Table 1. Independent variables and their respective experimental limits.

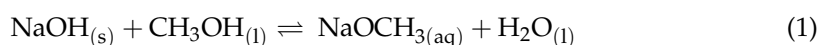
Independent Variables	Inferior Limit	Central Limit	Upper Limit
Sodium hydroxide (g)	0.10	0.15	0.20
Methanol (ml)	3.00	6.00	9.00

Table 2. Laboratory planning matrix.

Assay	Volume of Methanol (mL)	Mass of Sodium Hydroxide (g)
1st	3.00	0.10
2nd	3.00	0.20
3rd	9.00	0.10
4th	9.00	0.20
5th	1.75	0.15
6th	10.24	0.15
7th	6.00	0.08
8th	6.00	0.22
9th	6.00	0.15
10th	6.00	0.15

2.3. Chemical Procedures

The oil samples were filtered using a vacuum pump (brand Primatec and model 13) through the filter paper. Then, the catalytic mixture was prepared by dissolving the mass of sodium hydroxide in methanol as specified in Table 2. The catalyst and alcohol concentrations established in the planning matrix (Table 2) were used for each assay. First, the NaOH catalyst was dissolved in methanol, resulting in the formation of sodium methoxide (CH₃ONa) characterizing an exothermic reaction:



After the total dissolution of the catalyst, the mixture was added to 30 mL of oil heated to 60–65 °C and kept under mechanical stirring for 30 min using a hotplate with a temperature sensor (brand Edutec and model XMTD-701). At the end of the reaction period, the mixture passes through a funnel for complete phase separation. One phase is made up of biodiesel, which is less dense and lighter, and the other is made up of glycerol, which is darker and denser (Figure 1A). The glycerol contained in the lower part of the funnel was removed and packaged (Figure 1B) for further treatment and application in the synthesis of natural polymers. After removing the glycerol, the biodiesel supernatant phase was washed with 5 mL of distilled water at room temperature to remove both excess alcohol and catalyst and other water-soluble substances formed during the transesterification reaction (Figure 1C).

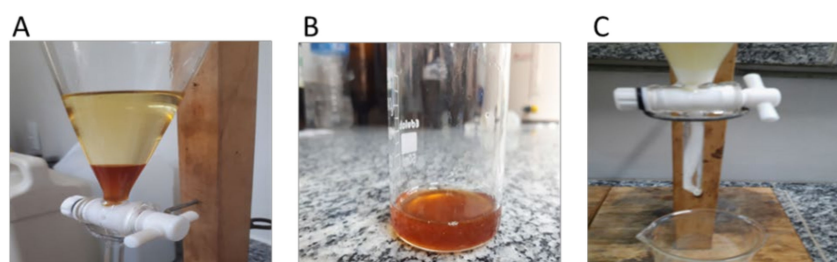


Figure 1. Chemical procedures for processing oil samples. (A) Decantation. (B) Glycerol. (C) Biodiesel wash.

Transesterification Process

The transesterification process is the main method for acquiring biodiesel, whether it is a basic, acidic, or enzymatic reaction. Its mechanism consists of several consecutive reactions of a reversible nature, in which 1 mol of triglyceride will react with 3 mols of alcohol in the presence of the catalyst [33,34]. Figure 2 shows the transesterification reaction of triacylglycerides with methanol in an alkaline medium to produce monoalkyl fatty-acid esters, where R''' represents the alkyl group of alcohol, while R' simulates the carbon chain of fatty acids. In this process, the alcohol ion initially attacks the carbonyl carbon of the triglyceride, resulting in the formation of a tetrahedral intermediate. Then, the intermediate compound reacts with the alcohol, regenerating the anion, allowing the rearrangement of the tetrahedral compound (intermediate), and leading to the formation of a fatty-acid ester and a diglyceride ($R''OH$ in Figure 2).

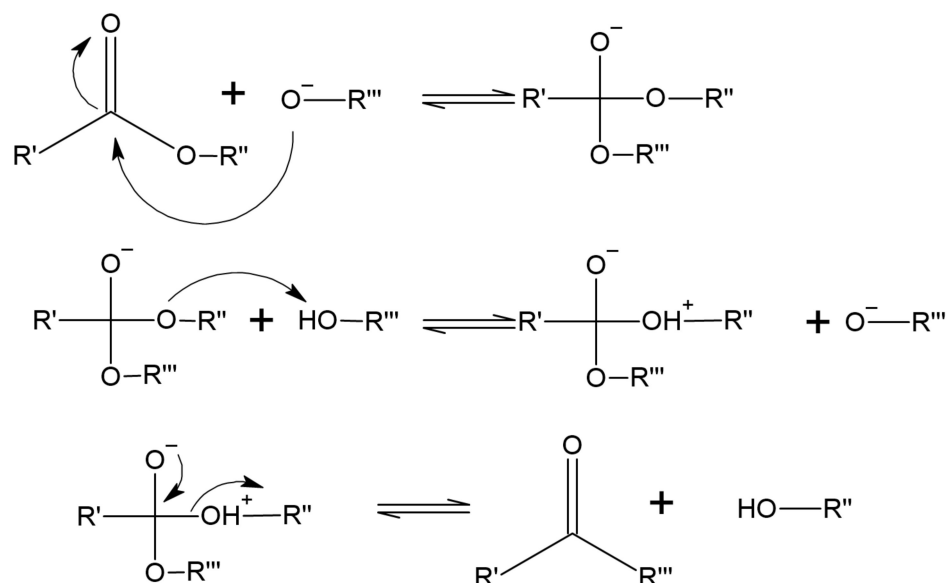


Figure 2. Transesterification reaction of triacylglycerides with methanol in an alkaline medium to produce monoalkyl fatty-acid esters (adapted from Solomons et al. (2014) [35]).

This process was repeated consecutively until the water reached a neutral pH. After removing the water, the biodiesel was filtered on filter paper and added with 5 g of anhydrous sodium sulfate, in which, when hydrated, it is able to remove any traces of water present in the medium. Subsequently, a new filtration on filter paper was carried out to remove the excess sodium sulfate formed. Thus, the biodiesel from purified frying oil was obtained (Figure 3).



Figure 3. Biodiesel obtained from WCO.

2.4. Determination of Biodiesel's Production Yield

At the end of the process, the production yield in each trial was determined as a function of the amount of biodiesel generated and the amount of oil used as raw material. Based on the yields obtained and applied to the CCD, the statistical optimization point for the production of biodiesel was determined (see Supplementary Material 1: Step by step of the production and physicochemical characterization of biodiesel and bioplastics were carried out).

2.5. Physicochemical Characterizations

The optimized biodiesel was checked for the density, the acidity index, the saponification index, the kinematic viscosity, the copper corrosivity, the cloud point, and the visual appearance [36] (see Supplementary Material 1 for details). The density was determined by the pycnometer technique. The acidity and saponification index were determined by the AOCS official method [37,38]. The kinematic viscosity was determined by the method of Stokes [39]. Copper corrosivity, on the other hand, followed the methodology adopted [40,41] in which a previously polished copper sheet was submerged in biodiesel and heated to 50 °C for 3 h. At the end of the process, the slide was washed with distilled water and compared with standard slides in different degrees of corrosion according to the Brazilian Agency for Petroleum, Natural Gas, and Biofuels (ANP) number^o 07/2008 and ANP number^o 14/2012 resolutions [42]. The cloud point was determined from the freezing of the biodiesel sample, recording the temperature at which crystal formation starts. Furthermore, the combustion potential of the generated biodiesel was evaluated in comparison with a sample of frying oil used as raw material, where both were submitted to burning [43].

2.6. Thin Layer Chromatography (TLC)

After the physicochemical characterization, the conversion of oil into biodiesel was qualitatively monitored through TLC [44]. To this end, a drop of biodiesel and a drop of frying oil were applied to a silica plate with a distance of 1 cm between each application and 1.5 cm from the bottom edge of the plate. Then, the plate was placed in a glass vat containing 20 mL of hexane (nuclear, MW 86.18 and 98.5% purity), 5 mL of ethyl ether (Nuclear, MW 74.12 and 99.8% purity), and 2.5 mL of glacial acetic acid (Synth, MW 60.05 and 99.7% purity) remaining at rest for 15 min. After percolating the solvent, the plate was removed and developed with iodine vapor, determining the retardation factor (R_f) of the sample due to the differential migration over the adsorbent layer.

2.7. Purification of Glycerol

For the purification, initially 25 mL of glycerol were acidified with 20 mL of 0.1% phosphoric acid and kept at rest for 30 min, consequently resulting in the phase separation of the mixture into free fatty acids on top, glycerin/methanol in the middle, and sodium phosphate in the lower phase. After phase separation, the glycerin/methanol fraction was neutralized at room temperature with the addition of 0.1 M NaOH solution until reaching a pH equal to 7, and the methanol was recovered by rota-evaporation at 70 °C (vacuum rotary evaporator, brand 7Lab, and model RE-DM). After extracting the alcohol, the glycerol proceeded to the bleaching stage. For this, 1.2 g of activated charcoal was added in 20 mL of glycerol, and the mixture was kept under mechanical agitation for 1 h in a hotplate (brand Edutec and model XMTD-701). Then, the activated carbon was removed by vacuum filtration (brand 7Lab and model RE-DM) with filter paper, thus obtaining purified glycerin.

2.8. Infrared Spectroscopy

Infrared spectroscopy of the biodiesel and glycerin samples was performed with the aid of a PerkinElmer brand spectrometer, model Spectrum Two, in the region of 400–450 cm^{-1} , with a resolution of 4 cm^{-1} , an average of 32 scans, and using a cesium-iodide sample port.

2.9. Synthesis of Bioplastic

Glycerol was used as a plasticizer in the synthesis of bioplastic. For this purpose, 5 mL of purified glycerin and 5 mL of acetic acid were added to 10 g of cornstarch dissolved in 60 mL of heated water (70 °C) kept under mechanical stirring for 15 min. After the reaction period, the still-hot solution was placed in a petri dish and dried in an oven at 40 °C for 24 h, resulting in the formation of bioplastic.

2.10. Moisture Content of the Bioplastic

The bioplastic was characterized to moisture content, water-solubility, thickness, biodegradation, and photodegradation potential. To determine the moisture content of the bioplastic, 4 cm^2 samples were previously weighed and dried in an oven at 105 °C for 4 h; after the drying period, the moisture was determined based on the ratio between the final mass and the initial mass of the samples. The mass lost by solubilization in water was determined by the equation:

$$pm = mi - mf/mi,$$

where: pm is the moisture percentage; mf is the final sample mass; and mi is the initial sample mass. For this purpose, bioplastic samples were submitted to drying in an oven (drying and sterilization oven, brand De Leo, and model DL SE 42L) at 100 °C for 24 h, obtaining the value of mi. Afterward, the dried samples were added with 80 mL of water and kept under mechanical agitation for 24 h (magnetic stirrer, brand Fisatom, and model 752A). At the end of the process, the samples were again submitted to drying in an oven, obtaining the value of mf.

2.11. Thickness and Degradation Analysis

The thickness of the bioplastic was determined through the arithmetic to mean of five random points in the sample, calculated with the aid of a disk micrometer (digital external micrometer, brand Mitutoyo and disc type 323-250-30) with a precision of 0.001 mm. To assess the effects of biodegradation, the 4 cm^2 bioplastic samples were kept covered with 5 cm of soil for 180 days, and the physical changes of the samples were visually evaluated. Degradation catalyzed by photodegradation was also evaluated with direct exposure of the sample to sunlight for 60 days.

3. Results

3.1. Biodiesel Production

The volumes of biodiesel produced and the conversion rates in percentage yield for the methyl transesterification reaction in ten (10) tests are shown in Table 3.

Table 3. Mass-yield values for biodiesel were obtained in different experimental routes.

Test	NaOH (g)	Methanol (mL)	Oil (mL)	Biodiesel (mL)	Biodiesel (%)
1st	0.10	3.00	30.00	17.00	56.60
2nd	0.20	3.00	30.00	28.00	93.30
3rd	0.10	9.00	30.00	14.00	46.60
4th	0.20	9.00	30.00	26.00	86.60
5th	0.15	1.76	30.00	21.00	70.00
6th	0.15	10.24	30.00	18.00	60.00
7th	0.08	6.00	30.00	10.00	33.30
8th	0.22	6.00	30.00	28.00	93.30
9th	0.15	6.00	30.00	18.00	60.00
10th	0.15	6.00	30.00	19.00	63.30

The biodiesel yield generated in each trial was defined as a process-dependent variable; so, using it in the CCD with the aid of the Statistica® 10 software, we can compare the response surface of the variables: the alcohol volume, the catalyst mass, and the mass yield of the transesterification (Figure 4).

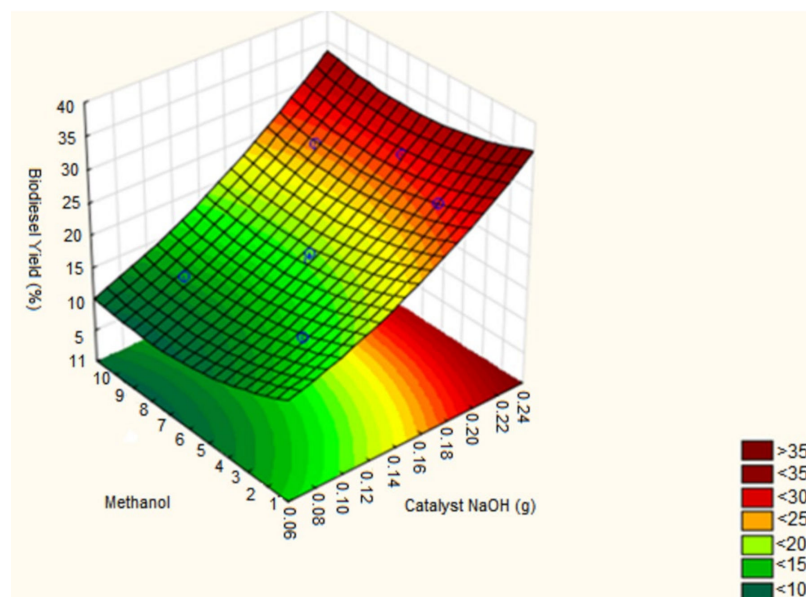


Figure 4. Response surface for frying-oil biodiesel mass-yield values.

The increase in yield was directly proportional to the increase in the catalyst. The methoxide anion facilitated the attack on the triglyceride ester group, resulting in faster conversion of biodiesel, since, in low amounts of catalyst, the in-situ formation was compromised. In the methanol axis (Figure 4), the lower values of alcohol reflect the lower effectiveness of methoxide-ion formation, while for higher values, the yield was influenced by the amount of catalyst in the medium. The effects of the studied variables can be observed in the Pareto chart (Figure 5). The highest values in the bars mean the most effective influence. The catalyst NaOH showed an affecting positive on yield, while the methanol presented the lowest influence.

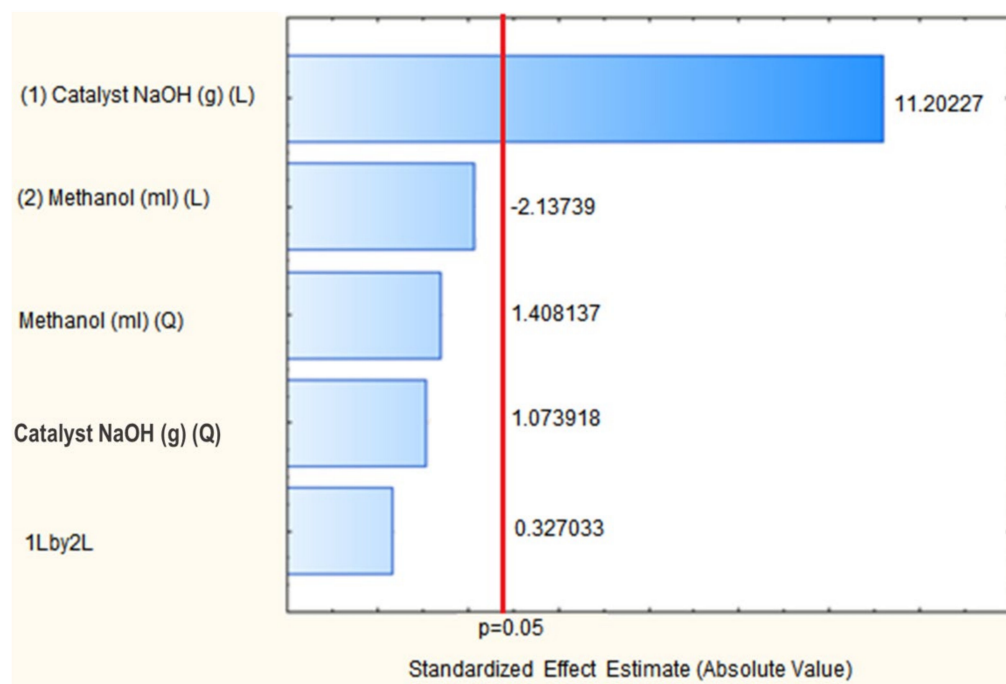


Figure 5. Pareto chart for the methyl transesterification reaction with a 95% confidence interval.

A linear regression model with predicted versus observed values experimentally is shown in Figure 6. The closer the data are to the straight identity, the better the quality of the proposed model. The data showed a regression of coefficient equal to 0.97. A similar relationship was found in a study on the optimization of biodiesel production carried out by Cavalcante et al. (2010) [45] and by Lima et al. (2013) [46] with a linear-regression coefficient of 0.92 and 0.96, respectively.

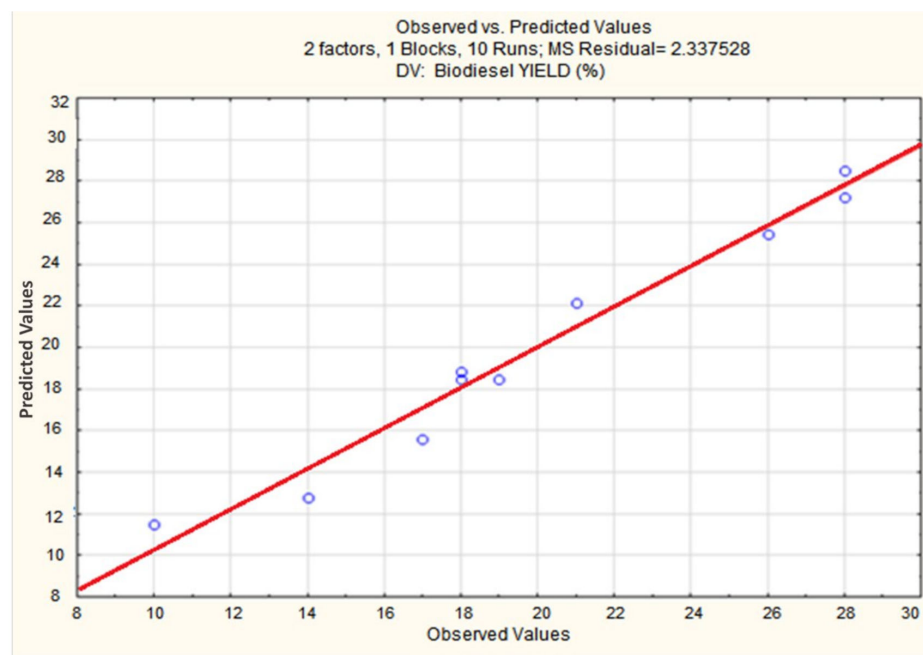


Figure 6. Predicted values vs. observed values.

The values that maximized the yield equal to 83.3% of biodiesel were: 0.22 g of sodium hydroxide, 10 mL of methanol, and a reaction time equal to 30 min under mechanical agitation at 60–65 °C. This yield was considered satisfactory, as it is estimated that fatty

residues can show a conversion yield of around 65% to 70% in esters [47]. The results of the physicochemical analysis of biodiesel, and for comparison with values established by ANP resolution number^o 45 [48] for biodiesel without blending with diesel (B100), are also shown in Table 4. The data presented confirm that the results obtained experimentally were consistent with the limits established by the ANP [48]. We observed a minimal increase in the acidity level because of our proposed derivative of the WCO raw source. This can be solved by applying a pre-treatment of WCO as degumming, acid catalysis, and adsorption, among others. In the combustion test, the biodiesel sample exhibited high efficiency with an unchanging orange flame for long periods as opposed to the low-burning frying-oil sample and resistance throughout burning (data not shown).

Table 4. Physicochemical analysis of the biodiesel produced.

Essay	Units	ANP 2014	WCO Biodiesel
Density at 25 °C	g/cm ³	0.85 to 0.90	0.88
Acidity level	mg KOH/g	0.50	0.51
Saponification index	mg KOH/g	–	105.00
Viscosity at 40 °C	cST	3.00 to 6.00	3.50
Corrosivity to copper	–	1.00	1.00
Fog point	°C	to 10.00	8.00
Aspect	–	–	Clear

In addition, the efficiency of the transesterification reaction was qualitatively monitored through TLC followed by the determination of the R_f of the biodiesel and WCO samples (Table 5 and Figure S2). The stationary phase used in chromatography had a polar characteristic, while the mobile phase composed of a mixture of hexane, ethyl ether, and acetic acid exhibited a nonpolar characteristic [49]. The highest R_f value means the greater distance traveled by the solute. Biodiesel has more non-polar compounds when compared to WCO, confirming the conversion of fatty acids present in the oil into an alkyl ester (biodiesel).

Table 5. R_f values were obtained experimentally.

	Biodiesel	WCO
R _f	0.63	0.40

The infrared absorption spectra of WCO and biodiesel showed the presence of common and singular bands of each material (Figure S1). Most parts of the spectra revealed a similar chemical structure. The bands at 1.377 and 1.100 cm⁻¹ attributed to stretch (O-CH₂) and (O-CH₂-C) of glycerides, respectively, were present in lower intensity in biodiesel, indicating the possible occurrence of the transesterification process. However, due to residual oil in biodiesel, these bands were not entirely absent from the biodiesel spectrum. The 1.197 and 1.436 cm⁻¹ bands assigned to the ν (O-CH₃) and δ (CH₃), respectively, were present only in biodiesel samples confirming the formation of biodiesel [50,51].

3.2. Glycerol Purifications and Application

Crude glycerol from biodiesel production was acidified with H₃PO₄ and left for 12 h before phase separation. To remove any salts/impurities that conferred color and odor to glycerin, we used adsorption with activated carbon.

The spectra of glycerol versus purified glycerin and the commercial version are available in Supplementary Material 1 and Figure S1. The results showed the absence of specific bands of the purified glycerin presenting in the glycerol spectrum. The bands appearing at the position of 3.005, 2.850, 1.736, and 1.557 cm⁻¹ are related to oil and biodiesel. Thus, their absence in the spectrum of purified glycerin indicates an adequate efficiency in the crude glycerin purification process. However, in the spectrum of purified glycerin, there

was a band at the height of 491 cm^{-1} , which was not present in the spectrum of crude glycerin. This band can be attributed to deformation since in the purification of glycerin, phosphoric acid was used, which was then neutralized with sodium hydroxide [52]. The green color resulted from the addition of an external color (artificial coloring). However, it is important to emphasize that in certain situations the color could indeed be related to some impurities and heterogeneity of the WCO samples that influence the color of the glycerin formed during the transesterification process [53]. However, this situation did not occur here, as the analysis via infrared spectroscopy makes it clear that the glycerin produced was pure (shown colorless).

Following recommendations [54], purified glycerin was used in the formulation of bioplastic, which had 20.64% moisture and 38.00% water solubility. The application was direct to biodegradable packages. The glycerin as a plasticizer in the formulation of bioplastic promoted homogeneity, clarity, a smooth appearance, and greater flexibility. The thickness was 2.78 to 3.00 mm considering the promisor due to the difficulties to manipulate viscous solutions. We observed the reduction in the polymeric matrix of the bioplastic with an opaque and brittle appearance (Figure 7). This phenome occurred because samples in contact with the soil suffered microbial action. The microorganisms digested the starch present in the sample, making the structure porous and permissive for enzymatic digestion [55]. In addition, when bioplastic samples were exposed to sunlight, the moisture content was significantly reduced, and the matrix weight became opaque and brittle (Figure 8).

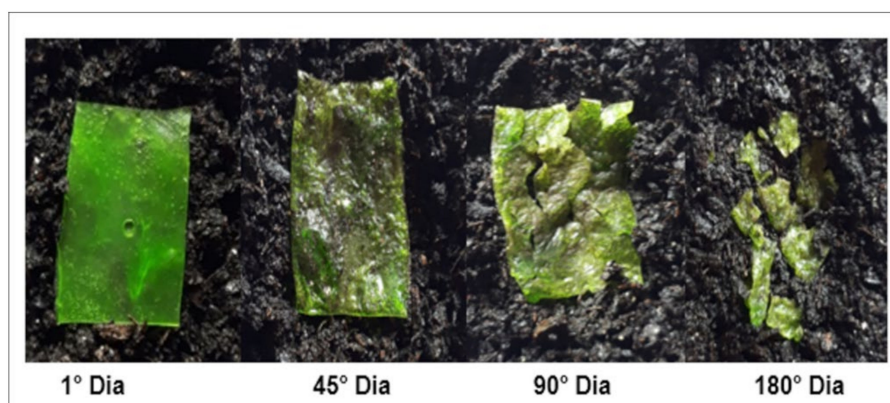


Figure 7. Biodegradation in soil.

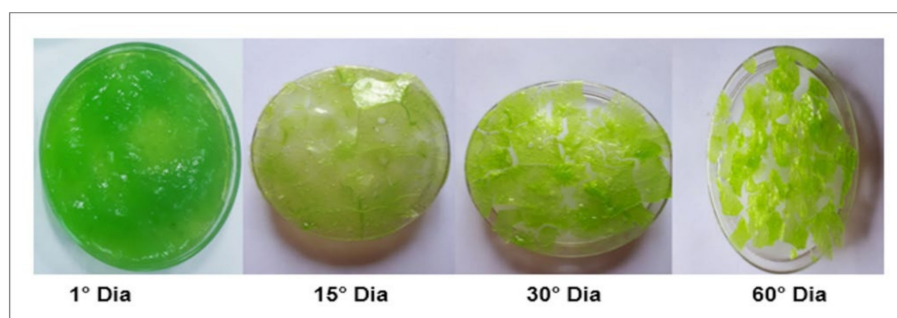


Figure 8. Photodegradation.

4. Discussion

The search for the reuse of natural resources to minimize the harmful action of man on the planet has to be strengthened. The current world population of 7.9 billion is expected to reach 8.6 billion in 2030, 9.8 billion in 2050, and 11.2 billion in 2100, according to the United Nations [56]. So, here, we applied a simple and inexpensive method of transforming WCO into biodiesel and bioplastic. The biodiesel produced here was within the strict standards

established by the ANP [48]. Therefore, its use is appropriate for combustion engines, since, here in Brazil, currently 10% of diesel is blended with biodiesel. This limit was reduced from 13 to 10% due to the price of agricultural commodities, mainly corn and soybeans [4].

Biodiesel is a well-known alternative fuel, and its production can be processed from several vegetable oils. Thus, the production of biodiesel is considered environmentally friendly due to the possibility to reuse oils from cooking, for example. The advantage of using WCO is that you do not compete with soy, corn, and other vegetable oils for food production. There are different feedstocks to be used as WCO sources for biodiesel production. Sharma et al. (2021) [57] evaluated six different raw materials for biodiesel production, including chicken oil; fat, oil, and grease; beef hotpot oil; mixed waste cooking oil; duck oil; and vegetable hotpot oil. As a result, the authors demonstrated the biochemical composition, fatty acids' profile, and properties of the produced biodiesel—these WCOs are promising candidates for biodiesel production. However, the commercialization of WCOs' biodiesel requires further investigation of produced biodiesel and the regulation of parameters involving engine performance, efficiency, and emissions, in addition to evaluating the quality and cost-effectiveness of the biodiesel produced.

We reinforce the importance of governmental (or private centers') collection streamlining to feed refineries and produce self-sustainable fuels and sub-products. Moreover, biodiesel does not contain aromatic hydrocarbons, and the content of sulfur is lower than diesel. Furthermore, the content of cetane is lower than diesel, improving engine combustion performance [58–60]. Here, we proposed the production of biodiesel from WCO and its applicability in diesel blend. Additionally, the unburned hydrocarbons in pure biodiesel fuel were reduced compared to the use of pure diesel [59].

Physicochemical analysis revealed that our biodiesel was experimentally consistent with the ANP [48] limits. A minimal-increase value in acidity was observed and can be solved by applying pre-treatment (degumming, acid catalysis, and adsorption, for example). For a yield equal to 83.3%, we maintained for 30 min the reaction containing 0.22 g of sodium hydroxide and 10 mL of methanol. The catalyst is responsible for the yield. We showed our variables studied in the Pareto chart. The NaOH showed a positive effect on the yield. A similar relationship was found in studies on the optimization of biodiesel production [45,46]. Reşitoğlu et al. (2012) [61] analyzed the main variables involved in the esterification process, including methanol/waste cooking-oils ratio, the amount of acid catalyst, the reaction time, and the reaction temperature. The authors showed that the optimum experimental conditions were obtained using methanol/WCO ratio 9/1, with 9 wt% sulfuric acid catalyst, reaction time 120 min, and reaction temperature 60°C to achieve the best biodiesel yield of 93.98%, which is a higher yield compared to our study (but with a longer time). Jalkh et al. (2018) [62] investigated the physicochemical properties of two food-industry waste products, including spent coffee grounds and WCO. The results showed that oxidation significantly affects the oils by increasing the release of fatty acids and the breaking of double bonds. The latter, in addition to polymerization and the release of high molecular weight compounds, increases the viscosities of the oils while retaining their Newtonian behavior. In our study, the viscosity at 40 °C was within the parameter established by the ANP [48].

The biodiesel production from WCO produces soap and glycerin subproducts. Glycerol was discovered in 1783 by the Swedish chemist Carl Wilhelm Scheele when treating natural oils with alkaline. However, at the time, the discovery of this substance did not generate a great impact in the scientific or industrial area. In 1811, the chemist Michel Eugene Chevreul named this substance glycerol, whose origin is from the Greek word "glykos," which means sweet. In 1866, the first industrial use of the substance was in the production of glycerol trinitrate, which is used in dynamite making. At the end of the 19th century, glycerol production increased continuously [63]. Glycerol is a tri-alcohol with three carbons; its official name (IUPAC) is 1,2,3-propanetriol. It is usually found as a triglyceride combined with, for example, fatty acids such as oleic, palmitic, and stearic acids. In the pure form, it is found in the normal conditions of temperature and pressure

(CNTP), and, in the liquid physical state, it is colorless, has sweet taste, and is odorless and very viscous. It is obtained from natural or petrochemical sources. In the raw form, it is in the form of a dark-brown viscous liquid, containing between 20 and 30% impurities, and being soap, alcohol (methanol or ethanol), monoacylglycerol, diacylglycerol, glycerol oligomers, polymers, and water [64].

The term glycerol applies only to the pure compound. Commercially, it is known as glycerin, which presents amounts greater than or equal to 95% of glycerol. The purification process of the sub-product of the transesterification of biodiesel starts with acidulation (with hydrochloric, sulfuric, or phosphoric acid) for the separation of glycerol and fatty acids from soap. During acidulation, a certain amount of salt is deposited in the lower phase of a three-phase liquid, the upper phase being by free fatty acids and the intermediate phase composed mainly of glycerol and alcohol. The recovered glycerol reaches concentrations above 80% (*w/w*), with variable amounts of water, dyes, and alcohol. Subsequently, the glycerol with excess acid is neutralized with NaOH solution and subjected to heat treatment (70 °C) to eliminate volatile components (alcohol recovery). To obtain a degree of purity greater than 95% (*w/w*) (grade food or pharmaceutical), the glycerol must be subjected to distillation under low pressure. Due to the physicochemical properties such as non-toxicity, the absence of color, and the odor of glycerol, this substance has a wide variety of applications. The main glycerol-consuming industries are cosmetics, soap, and pharmaceuticals, where glycerol is used in its raw form, mainly as a humectant [65]. The environmental impact is reduced using WCO in several categories including abiotic depletion, global warming, and photochemical oxidation. Here, we presented the synthesis of bioplastic, but, in fact, glycerin and its derivatives are widely used as a raw material in the food, pharmaceutical, and cosmetic industries [66]. Biodegradable plastics acquired visibility because they contribute to minimizing environmental complications due to the disposal of plastic waste [67].

The advantages to producing bioplastics are similar to biodiesel: it reduces the environmental impact and promotes an alternative to petroleum-plastic options. The biodegradation occurs when samples in contact with soil suffer microbial action by the digestion of starch. Bioplastic refers to innovative bio-based plastic polymers such as PLA (polylactic acid), PHA (polyhydroxyalkanoates), PHB (polyhydroxybutyrate), and starch blends, as well as microbial polymers such as polynucleotides, polypeptides, and polysaccharides. [68]. Meanwhile, biodegradability is caused by biological processes during composting and yields of carbon dioxide, water, inorganic compounds, and biomass at a rate similar to that of other known, compostable materials; it leaves no other recognizable or hazardous residue [69]. Consequently, bioplastic materials can have a wide range of biodegradability percentages and can be obtained from a wide range of renewable and non-renewable sources; hence, numerous classification systems based on different criteria have been developed to separate them [68]. Here, we proposed the application of cornstarch, which is already available in commercial packing materials with higher amylose content as compared to other starch sources. The bioplastic produced here has two main characteristics: it is biomass-derived and biodegradable [70], with incredible soil degradation times of 180 days and photodegradation of only 60 days. The photodegradation promotes the disintegration of the polymer chain by absorption of ultraviolet light. The proportion of starch to glycerin was 2:1 in this research. The glycerin is a plasticizer in the formulation of bioplastic-promoted homogeneity, clarity, smooth appearance, and greater flexibility. A previous study analyzed the following proportions: 1:0.5, 1:1, 2:1, and 2:2 and observed the better results using 1:0.5 and 2:1 (starch:glycerin). The photodegradation percentages were around 0.9 per day, requiring 105–200 days to degrade via sunlight fully [71].

Our study is a pilot model for a sustainable plant industry. We suggest a process with minimal residues disposed of for further treatment. Our optimization showed promising results in biodiesel conversion. Acidification of glycerin also demonstrated the useful application of this sub-product inside our process. We used a simple amid source and produced a bioplastic with a useful thickness in the order of 3.00 mm. Bioplastics are

widely applied in the food-package industry. We reinforce that biorefineries are sustainable options to engineer food waste, reducing the volume of waste and producing value-added products. In addition, the use of waste reduces the cost compared to conventional routes that use pure substrates. Finally, our study proposed a boosted research of WCO, valorizing the technologies and producing green chemical products.

5. Conclusions and Future Directions

We believe that the methodology was able to produce biodiesel in similar CCD parameters since biodiesel was efficiently produced (a yield of 83.3%) from the WCO by methyl transesterification using 0.22 g of NaOH as a catalyst. Many physicochemical parameters were evaluated in triplicate to verify the purity of the biodiesel produced. The infrared absorption spectra of WCO and biodiesel showed the presence of common and singular bands of each material. Moreover, the spectra of glycerol versus purified glycerin showed that the glycerin produced was pure, being used in the formulation of bioplastic. Finally, the bioplastic produced showed incredible soil-degradation times of 180 days and photodegradation of only 60 days. Thus, the use and reuse of WCO in biodiesel and bioplastic is an environmentally friendly approach to add value to a product available in large quantities around the world. Additionally, the methodology proposed here can help to solve two problems, which involve avoiding the improper disposal of WCO in the environment and the use of plastic products based on petrochemical compounds. From future perspectives, it is necessary to produce a larger volume of biodiesel and test it in combustion engines. In relation to bioplastic, it is necessary to characterize it and evaluate all its properties, including new tests of the biodegradation of the product. In the end, we dreamed of developing a machine that will be used at home or in the industry to convert WCO into biodiesel and bioplastic for use in cars and biodegradable packaging, respectively.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/en15031073/s1>, Table S1: List of 436 publications between 2022 to 2017 containing the terms “biodiesel,” “bioplastic,” and “waste cooking oil.” Supplementary Material 1: Step by step of the production and physicochemical characterization of biodiesel and bioplastics were carried out. Figure S1: Infrared spectrum: (a) frying oil; (b) crude biodiesel; (c) purified biodiesel. Figure S2: Thin layer chromatography: (A) biodiesel, (B) WCO.

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