

ETHYL BIODIESEL: MICROWAVE IRRADIATION AIDING ETHANOLYSIS OF WASTE COOKING OIL

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Abstract

We describe a methodology to produce biodiesel of excellent quality from waste cooking oil, NaOH catalyst and ethanol, by accelerating the transesterification reaction with microwave irradiation from an unmodified household microwave oven. The resulting Waste Cooking Oil Ethyl Esters were evaluated according to the physical and chemical properties demanded by regulatory standards for biodiesels, and a brief discussion of the meaning and scope of these quality control parameters directly related to biodiesel is also presented.

Keywords: Ethylic Biodiesel; Waste Cooking Oil; Microwave Irradiation; Biotechnology; Quality Control; Biofuel.

1. Introduction

In 1896, Rudolf Diesel introduced the first diesel engine, which had efficiency in the order of 26%. The fuel initially utilized was petroleum, followed in 1900 by vegetable oils, but because of economic reasons, mainly their high cost and low availability compared to petroleum, plant-derived oils were eventually abandoned as fuels [1-3].

The difference between fossil diesel and vegetable oils is mainly in the molecular weight of these two compounds, and also in the higher viscosity and density of vegetable oil compared to the mineral product. Fossil diesel consists of hydrocarbons with an average number of 14 carbons, whereas vegetable oils consist of glycerol triesters (the product of condensation between glycerol and long-chain fatty acids). The side chains of these fatty acids have 10-carbon atoms in the less-common, to 18 in the more-abundant types. The molecular weight of vegetable oils is approximately three times higher than that of fossil fuel [3,4].

The transesterification of vegetable oils such as soybean or sunflower, and of animal fats or other triglycerides using methanol or ethanol breaks down triglyceride molecules, producing a mixture of methyl or ethyl esters of the corresponding long-chain fatty acids, with glycerol as a co-product. The transesterification reaction occurs between the triglycerides and an alcohol in the presence of catalysts such as acids, alkalis, or enzymes (lipases) [5-8]. The molecular weight of these monoesters is similar to the molecular weight of fossil diesel. The similarities in both molecular weight and physical/chemical properties, such as lower viscosity and density, have stimulated the use of these esters in compression ignition engines as substitutes for fossil diesel, instead of vegetable oils in natura [4,9]. Biodiesel fuel has the following characteristics: it is virtually free of sulfur and aromatic compounds, has a cetane number equivalent to or higher than that of fossil diesel fuel, has an average oxygen content of approximately 11%, and has similar viscosity to, and a higher flash point than conventional fossil fuels. In economic terms, biodiesel fuel now occupies a specific market niche in the agricultural sector. Its production cost is relatively higher than that of commercial fossil diesel, but will decrease significantly with increased production and use on a larger scale, or when used cooking oil or animal fats are utilized as raw materials [9].

Biodiesel fuel is a domestic and “locally produced” renewable fuel, biodegradable, non-toxic, and has low emission profiles, thus being environmentally friendly. It is defined as the mono alkyl esters of long-chain fatty acids. To be used as a fuel, biodiesel must meet quality standards, i.e., ASTM D6751 in the USA, and EN 14214 in Europe [10,11]. These specifications prescribe the required properties of biodiesel fuel blend stock (B100) for middle distillate fuels at the time and place of delivery. The stated requirements may be applied at other points in the production and distribution system, as agreed between the purchaser and the supplier. The biodiesel specifications must include mono-alkyl esters of long-chain fatty acids derived from vegetable oils and animal fats, and must undergo chemical analysis for flash point, methanol, water and sediment, kinematic viscosity, sulfated ash, oxidation stability, sulfur, copper strip corrosion, cetane number, cloud point, acid number, carbon residue, total and free glycerin, phosphorus, reduced-pressure distillation temperature, atmospheric-equivalent temperature, combined calcium and magnesium, and combined sodium and magnesium [10,11].

In Brazil, biodiesel quality is controlled according to specifications established by ANP Regulation No 7 (ANP, Brazilian Government Petroleum, Natural Gas and Biofuels Agency) [12]. Its physical and chemical parameters, similar to chemical analysis of biodiesel in the USA and Europe, are analyzed following protocols covered by international guidelines, mainly from the American Society for Testing and Materials (ASTM), International Organization for Standardization (ISO), and/or European Committee for Standardization (CEN). Biodiesel fuels, when approved by ANP Regulation 7, can be blended in any concentration with petroleum-based diesel fuels to be used in existing diesel engines with little or no modification. Blends of biodiesel fuel with petroleum-based diesel fuel, established by Regulation 7, are designated BX, where X represents the percent by volume of biodiesel fuel in the blend [12].

In addition to the ecological and energy advantages of biodiesel fuel, we emphasize its technical and economic benefits based on the following considerations:

1. The use of ethyl biodiesel fuel increases engine durability, and because of its high lubricating power, the fuel consumption, ignition, and power of the engine remain unchanged.

2. Biodiesel fuel is particularly interesting for countries with large rural areas, allowing large-scale production of vegetable oils at low cost. With increased area planted for oil-producing crops, the output can be increased, and costs consequently reduced. Biodiesel production will also mean increasing industrial activity, with the creation of new jobs.
3. Biodiesel fuel production promotes studies of additional neglected, underutilized, and unexploited non-food oil plant species for biofuel production and;
4. Biodiesel promotes reduction in emissions of pollutant gases by the partial or total replacement of fossil diesel.

2. Material and Methods

The experimental procedure described here is generic and typical.

2.1. Materials:

The laboratory experiment required an unmodified household microwave oven (2450 GHz/560 W), a kitasato flask, a separation funnel, round-bottomed flasks, and a distillation system. In this experiment, waste cooking oil (WCO) was collected from restaurants, residences, hotels, etc, and was supplied by the Diamantina City Hall.

2.2. Methods:

For the production of Waste Cooking Oil Ethyl Esters (WCOEEs) biodiesel, transesterification reactions were performed employing WCO, under normal pressure and microwave irradiation [13].

The reaction progress and the complete transformation of mono-, di-, and triglycerides in vegetable oil into monoalkylesters was monitored using Thin Layer Chromatography (TLC) (Figure 1) and by Hydrogen Nuclear Magnetic Resonance Spectroscopy (^1H NMR) (Figure 2). TLC experiments were performed using silica-gel coated aluminum foils from Merck, prepared using two drops of acetic acid in 10 mL of a solution of a 95:5 mixture of hexane:ethyl acetate [14], and samples were taken every 20 s for 2 min, during the reaction progress. The relevant signals chosen for integration in ^1H NMR experiments are caused by the protons attached to the glycerol moiety of mono-, di-, or triacylglycerols in WCO (4.1 ppm and 4.3 ppm) and the signal of the α -methylene protons present in all esters derived from triglycerides (2.3 ppm, triplet), as well as the triplet at 2.67 ppm and quartet at 4.10 ppm indicate ethyl ester ($-\text{CO}_2\text{CH}_2\text{CH}_3$) formation.

2.2.1. Production of biodiesel mediated by microwave (MW) irradiation

The cooking oil / Anhydrous ethyl alcohol (99,3%)/ NaOH ratios used in the reactions were 100 mL / 80 mL / 1.10 g respectively.

In this experimental procedure, the WCO (Figure 3) was first filtered through silica-gel 60 mesh (10.00 g) to eliminate free fatty acids, polymeric substances, and water (Figure 4). The WCO had an acid value of 0.40 mg KOH and 0.02% water content prior to base-catalyzed transesterification. 80 mL of ethanol, previously treated with 1.10 g NaOH, was transferred to a beaker containing 100 mL of the filtered oil. This mixture was irradiated in the MW oven for 3 min at 560 W, and 10 mL of distilled water was added to help the subsequent separation process. The resulting mixture was transferred to a separation funnel and allowed to cool, where it separated into WCOEEs (upper phase) and glycerin (lower phase) (Figure 5). After the separation of the phases, the biodiesel was washed with successive additions of 15% by volume of distilled water under moderate agitation until neutral pH, and dried over anhydrous MgSO_4 (Figure 6). The glycerin phase was neutralized and slightly acidified with sulfuric acid under stirring, filtered, and transferred to a separation funnel, where it again formed two phases, the new upper layer containing free

fatty acids and some WCOEEs. The lower glycerin phase was neutralized with a concentrated solution of sodium hydroxide, and water and residual ethanol were removed by distillation. Upon cooling to room temperature, sodium sulfate precipitated and was filtered and recrystallized from boiling water, filtered again, washed with cold water, and dried in an oven at 80 °C for two hours. The “brown glycerin” obtained was purified by distillation under high vacuum (> 10 mmHg) in the presence of activated charcoal.

2.2.1. Characterization and Quality Control of Biodiesel Fuel

The sample of WCOEEs was sent to the Center for Monitoring and Research of the Quality of Fuels, Biofuels, Crude Oil and Derivatives – CEMPEQC, Araraquara, São Paulo, SP, Brazil, for fuel characterization. The sample was tested to determine the biodiesel fuel physical and chemical properties, according to ASTM, EN, and/or NBR Standard Methods, covered by ANP Regulation 7. Table 1 summarizes the Standard Methods used, as well as the specification limits recommended by the Regulation. The Standard Methods include several physical and chemical parameters such as relative density (ASTM D4052), oxidative stability (EN 14112), flash point (ASTM D93), kinematic viscosity (ASTM D445), carbon residue (ASTM D4530), copper corrosiveness (ASTM D130), cold filter plugging point (ASTM D6371), total acid number (ASTM D664), iodine value (EN 14111), and water content (ASTM D6304). Also, mass percentages of mono-, di-, and triglycerides (ASTM D6584), free and total glycerin (ASTM D6584), methyl or ethyl esters (EN 14103), and methanol or ethanol (EN 14110) were determined by Gas Chromatography with Flame Ionization Detector (GC-FID). The elemental content of biodiesel (Na, K, Ca, Mg, and P, NBR 15553) was also analyzed by Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES), while total sulfur (S, according to ASTM D4294) was analyzed by energy-dispersive X-ray fluorescence spectrometry (EDX).

The instruments employed in these analyses were an automatic densimeter (Anton Paar GmbH, model DMA4500), a Rancimat[®] (Metrohm Ion Analysis, model 873), a Pensky-Martens closed cup automatic flash point tester (Petrotest Instruments GmbH, model PMA 4), an automated kinematic viscosity measuring system (Tanaka Scientific Limited, model AKV-202), a micro carbon residue tester (Tanaka Scientific Limited, model ACR-M3), a copper strip corrosion tarnish tester (Petrotest Instruments GmbH), a cold filter plugging point tester (Tanaka Scientific Limited, model AFP-102), an automatic potentiometric titrator (KEM Electronics, model AT-500N2), a coulometric Karl Fischer titrator (Metrohm Ion Analysis, model 756), a gas chromatograph with flame ionization detector (Shimadzu Corporation, model GC-2010) coupled to a CTC Combi PAL headspace and liquid injector system (Shimadzu Corporation, model AOC-5000), an energy dispersive X-ray fluorescence spectrometer (Shimadzu Corporation, model EDX-800), and an inductively coupled plasma optical emission spectrometer (Thermo Scientific, model iCAP 6300 Duo).

2.2.1.1. Relative Density @ 20 °C (ASTM D4052): Relative density was also measured with an automatic oscillating U-tube densimeter and two integrated Pt 100 platinum thermometers (DKD traceable) with a stated accuracy of $5 \cdot 10^{-6} \text{ g} \cdot \text{cm}^{-3}$. The temperature of the densimeter was regulated to $\pm 0.001 \text{ K}$ with a solid-state thermostat. The densimeter was calibrated daily with both dry air and bi-distilled degassed water.

2.2.1.2. Water Content (ASTM D6304): This test method determines the sum of free water in biodiesel by Coulometric Karl Fischer Titration.

2.2.1.3. Flash Point (ASTM D93): This requirement ensures that the methanol or ethanol used in production is completely removed from the biodiesel fuel, because of both fire-safety concerns and the corrosive nature of alcohol.

2.2.1.4. Oxidative Stability @ 110 °C (EN 14112): The duration of the induction period is a measure of its resistance to oxidation. The EN 14112 method is based on the fact that in oxidated oils or fats, volatiles are formed at the end of the induction period. The oxidative stability of the biodiesel samples was evaluated at temperatures of 100 and 105 °C and air flow of 20 L.h⁻¹. In this method, the oxidation is induced by the passage of a constant air flow through the sample that is kept under constant temperature. The volatile products of the reaction, which were blown off with the air, were collected in distilled or deionized water and measured by the change in electrical conductivity of these liquids. During the course of the reaction, due to an increase in the conductivity, a curve is drawn from which the induction period is inferred. The most significant and undesirable instability change in liquid fuel with time is the formation of solids, also termed filterable sediments. During long-term storage, oxidation due to contact with air (autoxidation) is a legitimate concern with respect to maintaining fuel biodiesel quality.

2.2.1.5. Kinematic Viscosity @ 40 °C (ASTM D445): Adequate viscosity is required for lubrication and to prevent leakage in metal/metal seals, but viscosity must not be so high as to cause seizure of parts, particularly under low-temperature conditions. High-viscosity fuel can also cause higher injection pressures, leading to increased wear and shorter equipment life.

2.2.1.6. Carbon Residue (ASTM D4530): This test provides an estimate of the carbon-depositing tendencies of a fuel, and is designed to prevent the formation of deposits in the combustion chamber. In biodiesel samples, high levels of glycerides are expected to contribute to engine deposit formation and hence to a higher carbon residue.

2.2.1.7. Copper Corrosiveness, 3 h @ 50 °C (ASTM D130): Corrosion is of concern because of potential damage to copper components of fuel systems, but also because dissolved copper can catalyze oxidation reactions, leading to the formation of deposits and corrosive free acids. This requirement mirrors the ASTM D975 requirement for conventional petrol-diesel, and is designed to ensure that biodiesel is equally compatible with and resistant to oxidation by copper.

2.2.1.8. Cold Filter Plugging Point (ASTM D6371): The most important practical disadvantage of biodiesel is that it has a higher pour cold filter plugging point than mineral diesel oil. The cold filter plugging point measures the temperature at which paraffin or, in the case of biodiesel, ester structures, crystallize before injection, thereby blocking the filter. The ensuing lack of fuel can result in engine failure, mainly in cool to cold temperatures. The raw materials used in the manufacture of biodiesel influence the cold filter plugging point. In the case of rapeseed oil methyl ester this occurs at -12° C, and for palm oil at +15° C.

2.2.1.9. Total Acid Number (ASTM D664): This test measures the presence of corrosive free fatty acids and oxidation products by Potentiometric Titration. The total acid number or acid value is the total amount of potassium hydroxide necessary to neutralize the free acids in a biodiesel sample. This can be further improved by controlling the transesterification, cleaning, and drying processes. High acid values in the feedstock indicate an unrefined or poorly refined product oil source due to poor process control, such as ethanol carryover, and could also cause degradation of rubber parts in older engines, resulting in filter clogging.

2.2.1.10. Iodine Value (EN 14111): The iodine value is the amount of iodine, measured in grams, absorbed by 100 g of a given sample. The Iodine value (or Iodine number) is commonly used as a measure of the chemical stability of different biodiesel fuels against the oxidation described above. The Iodine value is

determined by measuring the number of double bonds in the mixture of fatty acid chains in the fuel by introducing iodine into 100 g of the sample being tested, and measuring how many grams of iodine are absorbed. Iodine absorption occurs at double-bond positions - thus a higher iodine value number indicates a higher quantity of double bonds in the sample, greater potential to polymerize, and hence lower stability.

2.2.1.11. Mono-, Di-, and Triglycerides and Free and Total Glycerin (ASTM D6584): A gas chromatography test method: Free Glycerin, which is a by-product of the transesterification process, causes injector deposits, which can clog the fuel system. Free Glycerin can cause fuel separation and materials compatibility problems. It can also build up in the bottom of storage and fuel tanks. Total Glycerin includes the sum of free glycerin and mono-, di-, and tri-glycerides, all reported as mass percent glycerin. This measures the level of free glycerin plus any unreacted oil or fats (mono-, di- or triglycerides) in the biodiesel. The unreacted glycerides have much higher boiling points than biodiesel or conventional diesel fuel, which can lead to injector engine deposits and may adversely affect cold-weather operation. ANP Regulation 7 does not set a standard limit for mono-, di-, and triglyceride content in the final product. However, the European biodiesel standard recommends that the mono-, di-, and triglyceride content should not exceed 0.2, 0.2, and 0.8, respectively.

Of all the individual standard methods that cover biodiesel analysis, probably the most important with regard to monitoring the actual refining process is ASTM D6584. Ideally, the level of free glycerin and any unreacted mono-, di-, or triglycerides in biodiesel will indicate how efficiently the transesterification reaction is proceeding. All the vegetable oil will react with the methanol or ethanol and will be converted to the methyl or ethyl ester. Analyzing the sample using this method will indicate if there are any unreacted triglycerides as well as any traces of free glycerin in the final product. ASTM D6584 describes a method for quantitatively determining free and total glycerin in methyl or ethyl esters (biodiesel) by GC using flame ionization detection (FID) technology. The detection range in this method is 0.005 to 0.05 mass % for free glycerin and 0.05 to 0.5 mass % for total glycerin. The sample is first derivatized with a silylating agent and then injected into an open tubular GC column packed with 5% phenylpolydimethylsiloxane. Calibration is achieved with two internal standards (butanetriol and tricaprin) and four reference materials. Mono-, di-, and triglycerides are determined by comparison with mono-olein, di-olein, and tri-olein, respectively. Conversion factors are then applied to the results for mono-, di-, and triglycerides to calculate the sample's bonded glycerin content. The total glycerin is the sum of the free and bonded glycerin.

2.2.1.12. Methanol or Ethanol (EN 14110): Monitoring residual methanol or ethanol in B100 is a matter of safety, since even small amounts of this material can lower the flash point. Moreover, residual alcohol can affect fuel pumps, seals, and elastomers, and result in poor combustion properties. ANP Regulation 7 sets a standard limit for methanol or ethanol content in the final product as 0.20 mass %, maximum. Of all the individual standard methods that cover biodiesel analysis, probably one of the most important concerns EN 14110. This standard method describes a method for quantitatively determining residual methanol or ethanol content in biodiesel by gas chromatography using flame ionization detection technology and coupled with a headspace system. Either polar or non-polar columns are allowed. EN 14110 can be applied to mixtures containing 0.01 to 0.5% methanol or ethanol. The biodiesel sample is heated in a sealed vial at 80 °C, and after attaining equilibrium, a defined amount of the gas phase is injected into the GC in an open tubular column packed with a polyethylene glycol stationary phase. Since the biodiesel matrix can influence the equilibrium between the methanol or ethanol concentrations in the liquid and gas phases, calibration standards must be prepared in methanol- or ethanol-free biodiesel. The EN 14110 biodiesel standard recommends preparation of a calibration curve containing 0.01, 0.1, and 0.5 mass % methanol or ethanol in biodiesel. An internal standard should always be used when applying manual headspace injection. When

using a headspace auto sampler, an internal standard is not necessary, but is recommended to increase the reliability of the results. 5 μL of 2-propanol is added to each standard and biodiesel sample.

2.2.1.13. Methyl or Ethyl Esters (EN 14103): This method provides verification that the ester content in biodiesel is greater than 96.5 mass %, while also allowing the characterization of the fatty acid methyl esters (FAME) composition. The ester content and linolenic acid methyl ester content are quantified by internal calibration with methyl heptadecanoate. An accurate characterization of fatty acid methyl esters (FAME) in biodiesel is essential for a more accurate calculation of the cetane index. The cetane number of biodiesel depends on the distribution of fatty acids in the original oil.

2.2.1.14. Sodium and Potassium (NBR 15553): Metals that are covered include Ba, Ca, Mg, Na, K, and Sn, although S, P, and Cl can be present in combined form. An application to biodiesel is obviously determining residual Na or K from the catalyst. The presence of metals in the biodiesel can cause operability problems due to formation of deposits and poisoning of emission-control devices, or can catalyze reactions that cause undesired products. The metals of interest include sodium (Na) and potassium (K), used as catalysts in biodiesel production. Fuel-injection equipment manufacturers have proposed to limit the content of Na and K (combined) to 5 ppm each. Metals were analyzed via NBR 15553 by inductively coupled plasma optical emission spectroscopy (ICP-OES) configured with dual view, for which the reported detection limits for Na and K in biodiesel after dilution with kerosene are 0.06 (Na 589.592 nm, radial view) and 0.14 (K 769.896 nm, axial view) $\mu\text{g kg}^{-1}$.

3.1.15. Calcium and Magnesium (NBR 15553): Calcium and magnesium are of concern because of soap formation. They may also be found in animal fats as a result of contact with non-lipid material. The metals of interest include magnesium (Mg) and calcium (Ca), used in adsorbents for purifying biodiesel. Fuel-injection equipment manufacturers have proposed to limit the content of Mg and Ca (combined) to 5 ppm each. NBR 15553 calls for analyzing Ca and Mg by ICP-OES. Ca is determined at 422.673 nm and Mg at 279.553 nm. Other wavelengths are acceptable if they are free from interference. Metals were analyzed via NBR 15553 by inductively coupled plasma optical emission spectroscopy (ICP-OES) configured with dual view, for which the reported detection limits for Ca and Mg in biodiesel after dilution with kerosene are 0.01 (Ca 315.887 nm, radial view) and 0.06 (Mg 279.553 nm, axial view) $\mu\text{g kg}^{-1}$.

2.2.1.16. Phosphorus (NBR 15553): This element can be carried over from vegetable oils, for example, from phospholipids present in all vegetable oils or glucosinolates in rapeseed-based biodiesel. It must be ensured that phosphorus is not found in "alternative" biodiesel sources, such as used frying oils or animal fats, which can come into contact with extraneous materials containing this element. The intent of this requirement is to protect exhaust catalysts, which are becoming more and more common on diesel equipment. Traces of phosphorus, resulting from phospholipids, can remain in vegetable oils after refining. Phosphorus can poison catalysts used for reduction of exhaust emissions. Phosphorus (P) was analyzed according to NBR 15553, by inductively coupled plasma optical emission spectroscopy (ICP-OES) configured with dual view, for which the reported detection limits for P in biodiesel after dilution with kerosene are 0.05 (P 178.766 nm, axial view) $\mu\text{g kg}^{-1}$.

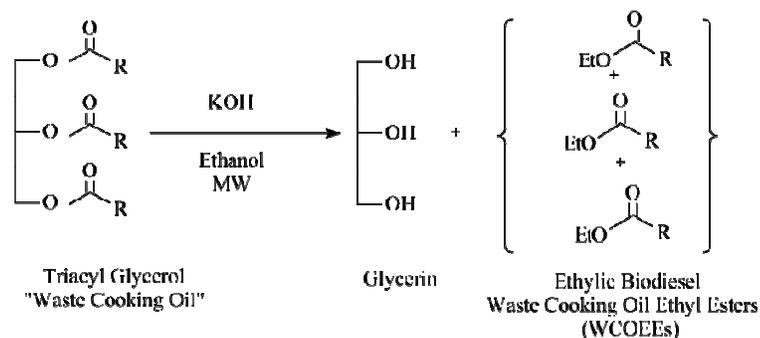
2.2.1.17. Sulfur (according to ASTM D4294): Sulfur, like phosphorus, is a potential catalyst poison and is carried over from vegetable oils, for example, from phospholipids present in all vegetable oils or glucosinolates in rapeseed-based biodiesel. Most biodiesel fuels inherently contain little or no sulfur, except possibly in rapeseed oil. The specification is important to show that biodiesel will not negatively affect

automotive catalyst systems. Sulfur is covered by ASTM D5453 and EN 20884, which determine sulfur content by UV fluorescence of the sample during its combustion and by wavelength-dispersive X-ray fluorescence spectrometry (WDX), respectively. As an alternative method, ASTM D4294 calls for sulfur analyses by energy-dispersive X-ray spectroscopy (EDX), as performed on petrol-diesel fuel.

3. Results and Discussion

In the present study, ethyl biodiesel fuels were successfully synthesized from waste cooking oil. All the waste cooking oil present was consumed during the reaction process, producing WCOEEs and glycerin (Equation 1).

Equation 1



The process developed here was conducted at normal pressure and microwave irradiation for 3 min. The transesterification reaction was also studied by reflux, but the reaction time was approximately 120 min. Therefore, more energy would be used in this process than the energy expended during the 3 min of microwave irradiation.

While apprising the effect of the NaOH catalyst amount on WCOEEs production, seven experiments were conducted with different concentrations (0%, 0.5%, 0.75%, 0.80%, 0.90%, 1.00%, 1.10%) of NaOH, and each experiment was repeated five times. In all experiments, an ethanol/ oil ratio of 80 mL: 100 mL was used. The reaction progress was monitored using Thin Layer Chromatography (TLC) and ¹H NMR Spectroscopy. As expected, no product appeared with 0% catalyst. Catalyst concentrations higher than 1.10% adversely affected WCOEEs production, resulting in soap formation and a lower ester yield.

The optimum yield (98%) of WCOEEs was gained at an ethanol/oil molar ratio of 7:1. Higher proportions (above 7:1) of ethanol had an adverse effect on WCOEEs production. At ethanol-to-oil molar ratios greater than 80 mL of ethanol: 100 mL of oil, separation of esters from glycerol was difficult. Unreacted ethanol, when present, can suppress the gravity decantation so that the apparent yield of WCOEEs decreases, because traces of glycerol may remain in the biodiesel phase [15,16].

3.1. Characterization and Quality Control of WCOEEs.

The sample of WCOEEs was tested to determine the biodiesel fuel quality according to ASTM, EN, and/or NBR Standard Methods established by ANP Regulation 7. Table 1 shows the specification limits of the standard methods and the sample results obtained for each requirement.

Table 1. Biodiesel Fuel Physicochemical Properties of Waste Cooking Oil Ethyl Esters (WCOEEs).

Physical and Chemical Properties	Units	Standard Method	Specification ANP Regulation 7	Limits	Results
Relative Density @ 20 °C	kg/m ³	ASTM D4052	850.0 – 900.0		879.4
Water Content, max.	mg/kg	ASTM D6304	500.0		397.6
Flash Point, min.	°C	ASTM D93	100.0		86.0
Oxidative Stability @ 110h °C, min		EN 14112	6.0		1.5
Kinematic Viscosity @ 40mm ² /s °C		ASTM D445	3.0 – 6.0		4.4
Carbon Residue, max	mass %	ASTM D4530	0.050		0.0
Copper Corrosiveness, 3 h- @ 50 °C, max		ASTM D130	1.0		1A
Cold Filter Plugging Point, °C max		ASTM D6371	19.0		- 1.0
Total Acid Number, max	mg KOH/g	ASTM D664	0.50		0.098
Iodine Value	g/100g	EN 14111	NA*		87.8
Monoglycerides			NA*		0.80
Diglycerides			NA*		0.50
Triglycerides	mass %	ASTM D6584	NA*		0.30
Free Glycerin, max			0.02		0.01
Total Glycerin, max			0.25		0.20
Methanol or Ethanol, max	mass %	EN 14110	0.20		0.019
Methyl or Ethyl Esters, min	mass %	EN 14103	96.5		97.4
Sodium + Potassium, max	mg/kg		5.0		1.7
Calcium + Magnesium, max	mg/kg	NBR 1553	5.0		0.1
Phosphorus, max	mg/kg		10.0		0.5
Total Sulfur, max	mg/kg	according to ASTM D4294	50.0		39.0

* NA – not applicable

3.1.1. Relative Density @ 20 °C (ASTM D4052): Relative densities out of the range can also indicate the presence of contaminants, and cause an incorrect injection amount of fuel in the chamber. The relative density of biodiesel is typically 880.0 kg/m³, significantly higher than typical petrodiesel, which ranges from 840.0 to 860.0 kg/m³.

3.1.2. Water Content (ASTM D6304): Free water is undesirable because it may promote microbial growth and corrode fuel-system components, causing excessive wear in fuel-injection equipment. The WCOEEs met the specification of 500.0 mg/kg maximum.

3.1.3. Flash Point (ASTM D93): The flash point for the biodiesel met the specification of 100.0 °C minimum. This requirement ensures that the alcohol used in preparation is completely removed from the final biodiesel.

3.1.4. Oxidative Stability @ 110 °C (EN 14112): The oxidative stability of the biodiesel did not meet the specification of 6 h, minimum. However, the biodiesel sample was tested without any added antioxidant.

3.1.5. Kinematic Viscosity @ 40 °C (ASTM D445): The kinematic viscosity for the biodiesel met the specification of 3.0 to 6.0 mm²/s.

3.1.6. Carbon Residue (ASTM D4530): The biodiesel samples tested met this requirement of 0.05 mass %, maximum.

3.1.7. Copper Corrosiveness, 3 h @ 50 °C (ASTM D130): The biodiesel samples exhibited a 1A slight tarnish, therefore easily meeting the standard requirement of 1.0, maximum.

3.1.8. Cold Filter Plugging Point (ASTM D6371): The cold filter plugging point of used cooking oil occurs at - 1.0 °C, which meets the specification limits of 19.0 °C, maximum.

3.1.9. Total Acid Number (ASTM D664): The biodiesel sample tested showed acid levels below the maximum limit of 0.5 mg KOH/g.

3.1.10. Iodine Value (EN 14111): ANP Regulation 7 does not set a standard limit for iodine value in the final product.

3.1.11. Mono-, Di-, and Triglycerides and Free and Total Glycerin (ASTM D6584): ANP Regulation 7 does not set a standard limit for mono-, di-, and triglyceride content in the final product. However, the European biodiesel standard recommends that the mono-, di-, and triglyceride content should not exceed 0.2, 0.2, and 0.8, respectively. The biodiesel sample met the free and total glycerin requirements of 0.02 and 0.25 mass % maximum, respectively.

3.1.12. Methanol or Ethanol (EN 14110): The biodiesel sample met the methanol or ethanol requirements of 0.20 mass % maximum.

3.1.13. Methyl or Ethyl Esters (EN 14103): The biodiesel sample met the specification for FAME content.

3.1.14. Sodium and Potassium (NBR 15553): The combined Na and K contents met this requirement.

3.1.15. Calcium and Magnesium (NBR 15553): The combined Ca and Mg contents did meet this requirement.

3.1.16. Phosphorus (NBR 15553): The P content did meet this requirement.

3.1.17. Sulfur (according to ASTM D4294): Following this methodology, we found that the S content did meet this requirement and note its applicability to biodiesel neat fuels.

4. Conclusion

We described a methodology for the production of ethyl biodiesel fuel (Waste Cooking Oil Ethyl Esters – WCOEEs) using microwave irradiation from an unmodified household microwave oven. The excellent quality of the biodiesel produced in this way from waste cooking oil was improved by the systematic determination of its several physical and chemical properties, following standard methods of analysis, in particular those established by ASTM, and the ANP Regulation 7 in Brazil.

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