



Biodiesel from Residual Oils: Less Environmental Impact with Sustainability and Simplicity

Rafael do Nascimento Pereira¹, Francisco Sávio Gomes Pereira^{2*},
Chesque Cavassano Galvão¹, Ana Maria Ribeiro Bastos da Silva¹,
Valdinete Lins da Silva¹, Maria Aparecida Guilherme da Rocha³
and Nelson Medeiros de Lima Filho¹

¹Department of Chemical Engineering, Federal University of Pernambuco – UFPE, Center of Technology and Geosciences, Recife, PE, Brazil.

²Federal Institute of Education, Science and Technology of Pernambuco – IFPE, Campi Recife and Ipojuca, Recife, PE, Brazil.

³Federal University of Pernambuco – UFPE, Coordination of Science Teaching of Northeast – CECINE, Recife, Brazil.

Authors' contributions

This work was carried out in collaboration between all authors. Authors CCG, MAGR and AMRBS participated in the execution of laboratory tests. Authors VLS and NMLF participated in literature review and planning of the article. Authors RNP and FSGP participated in execution of analysis, coordination, writing and text editing. All authors read, reviewed and approved the text of article.

Article Information

DOI: 10.9734/CSIJ/2016/29455

Editor(s):

(1) Nagatoshi Nishiwaki, Kochi University of Technology, Japan.

Reviewers:

(1) Reda Elkacmi, Hassan II University of Casablanca, Casablanca, Morocco.

(2) Salmah Ismail, Institute of Biological Sciences, University of Malaya, Malaysia.

Complete Peer review History: <http://www.sciencedomain.org/review-history/16850>

Original Research Article

Received 11th September 2016

Accepted 28th October 2016

Published 9th November 2016

ABSTRACT

This study shows viability energetic with residual frying oils. The oils collected and filtered were characterised in some analytical parameters and converted into biodiesel by homogeneous alkaline transesterification (molar ratio of 6:1, methanol: oil, 60 minutes, 60°C, and stirring of 300 rpm and 1% of NaOH). After reaction, decanted for 3 hours and purified with 0.5% phosphoric acid and distilled water. Heated at 110°C (water bath and vacuum distillation system) for the removal of residual methanol. The purified biodiesel was treated with anhydrous sodium sulphate, filtered and

*Corresponding author: E-mail: cientista.francisco@yahoo.com.br;

characterised in acid value, specific mass, kinematic viscosity, turbidity, water content and purity of ester. The results showed that the alkaline transesterification is a powerful tool for the conversion of saponifiable fatty acids into biodiesel, represented by the yield of 82% and 94.4% in purity of methyl esters, even with its demand for purification of the feedstock to reduce acidity and water content.

Keywords: Alkaline transesterification; frying; residual oils; sustainable energy; waste feedstocks.

1. INTRODUCTION

Frying is a fast preparation process at high temperatures, using vegetable oil or animal fat, and providing satiety, aroma, flavour and peculiar palatability characteristics to the fried food. Oil is exposed to high temperature in air and moisture during frying. A number of chemical reactions such as hydrolysis, and oxidative and thermal degradations take place under these conditions. Consequently, the quality of the frying oil and of the fried food is lost. It is one of the fastest ways for preparing certain types of food, widely used in households, commercial establishments and industries, generating great quantities of oils or fats used, normally without a specific destination or reuse purpose [1,2,3].

The environmental and social impacts caused by these oils used are considered devastating when such are disposed incorrectly, even if in a small scale. One litre of oil inadequately-disposed in a lake can lead to the contamination of 10,000 litres of clean water. Furthermore, it can cause the clogging of sewage systems, causing the accumulation of rubbish and rainwater retention, generating chaos in the urban areas. In the rivers, a barrier is formed in the water surface, making it difficult for light and oxygen to penetrate, with consequent death of fishes and other types of aquatic life. In the soil, it leads to impermeability, preventing the growth of vegetation in the area affected by the fatty material; it can also cause the release of gases such as hydrogen sulphide and unpleasant odour, maximizing the greenhouse effect [4,5,6].

In order to achieve the sustainability of production, the use of clean renewable energy (addresses environmental aspects by optimizing processes) and reverse logistic (recycling and reuse of materials) are of great importance. The use of waste cooking oils to produce biodiesel fits these concepts, given that this initiative avoids the inappropriate disposal of wastes and promotes the use of a sustainable fuel, reducing the costs of production and associated activities [2,7,8]. In this context of sustainability, a interesting example of synergy industrial, with oily waste recovery which could cause

environmental impacts, suggested in the study, was the recovered of the residual oil lost in extraction process of olive oil, in later applications as production of biodiesel, soap and glycerine or of oleic acid (useful in various industries) [9].

Biodiesel is widely used as an alternative fuel in various countries for displaying similar physicochemical properties to conventional diesel, with the main advantage of reducing harmful pollutants such as sulphur and others [10,11,12]. In Brazil and worldwide, the most predominant path for biodiesel production is the transesterification process, which consists in the reaction of triacylglycerol-rich (vegetable oils or animal fats) feedstocks with a short-chain alcohol (methanol or ethanol) in the presence of a catalyst (basic or acid), having fatty acid esters (Biodiesel) as products and glycerol (Glycerine) as a co-product [13,14].

The ultimate goal of researchers is to find biodiesel production paths to meet, at least, the requirements of simplicity, low cost, absence or minimal environmental risk and good energy effectiveness. Some research using residual oils as feedstocks for biodiesel production (methyl transesterification) can be seen in Table 1.

The main intention of work was show the simplicity of the alkaline transesterification in comparison with others (Table 1) routes, mechanisms and resources (acid, enzymatic, heterogeneous catalysis with solid catalyst, microwave, supercritical process, reactive distillation, among others [19]) in terms of operating conditions and technological resources, focusing on purification of feedstock, using common techniques and of domain technological widespread. In this particular case, the residual frying oil with a simple filtration using dual-layer (felt and qualitative filter paper). The characterization the oil (chromatographic profile) was not intention this study, hence the term simplicity. The focus was the biodiesel production anywhere in the world with residual oils. The work highlights also: (a) Environmental sustainability vision (generation of waste frying oil come increasing environmental problems in

Table 1. Biodiesel production by methyl transesterification with residual oils

Source, treatments and analysis of the oils	Reaction conditions	Treatments of purification of the biodiesel	Additional information	Ref.
Waste cooking oil of a restaurant; Used without any pretreatment; Density at 20°C = 0.9954 g.mL ⁻¹ ; Free fatty acid = 15.65%; Moisture = 0.1%.	Temperature = 65°C; Methanol oil ratio = 70:1 Time = 14-16 h. Stirring = 300 rpm Certain amount of 4 A° zeolites (absorb water) Catalyst/Quantity = H ₃ PW ₁₂ O ₄₀ .6H ₂ O (PW12) 0.1 mmol	Rotary evaporated at 50°C to excessive methanol, then formed two phases (methyl esters and glycerin, and the catalyst) PW12 decanted and treatment with methanol and drying under air. Methyl esters were treated by active carbon to dehydrate and discolor.	PW12 acid is an excellent water-tolerant and environmentally benign acid catalyst. Experiment in microscale (8 g of oil) Ester content = 87% (*)Gross yield (%) = uninformed. Calculates the conversion efficiency in terms of free fatty acids with results of 95.84%.	[15]
Fish oil Acid value = 10.04 mgKOH.g ⁻¹ ; Water content (wt,%) = 0.28; Iodine value (cg I ₂ g ⁻¹) = 164; Oxidation stability (110°C) (h) = 0.1 Waste oil, extracted from olive oil bagasse, Acid value = 21.85 mgKOHg ⁻¹ ; Iodine value = 71cgI ₂ g ⁻¹ . Dehydrated by heating at 100°C until constant weight.	Acid esterification Temperature = 65°C; Methanol oil ratio = 6:1 Time = 1h; Stirring = 900 rpm. Catalyst/Quantity = H ₂ SO ₄ / 2% (w/w) At ambient pressure Alkaline transesterification, divided in two steps. Temperature = 65°C; Methanol oil ratio = 6:1 Time = 1,5h (45 min/45min); Stirring = 900 rpm. Catalyst/Quantity = NaOH 1% (w/w)	Excess methanol was removed in a rotary evaporator, washed four times using distilled water (in equal volume), and dehydrated by heating at around 100°C, until constant weight was achieved. Final product was decanted overnight. Biodiesel purification - distillation under vacuum to remove excess methanol, washing once with a hydrochloric acid solution (0.2 wt.% (m/m)) and after three times with distilled water (in equal volume). Remaining water was finally removed by heating at around 100°C, until constant weight.	Use of Design of Experiments (DOE). JMP 5.0.1 software was used: Response Surface Design. Fish oil contains high content of PUFA and is very prone to oxidation. In the use for biodiesel production, is also detrimental, as it increases the acid value and reduces the quality of the oil, necessary caution during the storage to prevent oxidation. (*)Gross yield (%) = 73.0-75.5 Acid esterification (biodiesel of waste fish oil) Acid value (mg KOH.g ⁻¹) = 0.90 Density (kg.m ⁻³) = 891.8 Kinematic viscosity (mm ² s ⁻¹) = 4.41 Methyl ester content (wt.%) = 78.2 Alkaline transesterification	[16]

Source, treatments and analysis of the oils	Reaction conditions	Treatments of purification of the biodiesel	Additional information	Ref.
			Acid value (mg KOH.g ⁻¹) = 0.62 Kinematic viscosity (mm ² s ⁻¹) = 4.32 Methyl ester content (wt.%) = 75.5	
Waste canola oil collected from a University of Ottawa cafeteria Oleic acid, technical grade 90% (used to vary the FFA content) Range of FFA = 4.8-10%	Temperature = 65°C Transmembrane pressure 15 psi (103.4 kPa) Residence time = 84min Catalyst = sodium methoxide, 25 mass% in methanol solution Catalyst concentration = 1 wt.% above neutralization Methanol to oil molar ratio = 20:1	Permeate was poured into a separatory funnel and left to phase separate overnight. Permeate and retentate - neutralised using hydrochloric acid to quench the reaction. The FAME-rich phase of the permeate - treated using a rotary vacuum evaporator at 90°C and 0.9 bar (90 kPa) vacuum, for 40 min to remove any methanol and water present, centrifuged at 1500 rpm for 45 min, washed four times with distilled de-ionised water, at room temperature, using a biodiesel to water volume ratio of 2:1.	The tubular membrane module - ceramic membrane placed inside stainless steel housing, support material of the ceramic membranes was aluminum oxide (Al ₂ O ₃) and the selective layer was titanium dioxide (TiO ₂). Pore sizes ranging from 3 to 800nm were tested (ultrafiltration operating range and the microfiltration range). Content of ester, water and glycerides meet standard of ASTM D6751. Ester content = uninformed (*)Gross yield (%) = uninformed.	[17]
WFO from local restaurants FFA content (%) = 0.46; Water content (wt%) = 0.125; Viscosity at 40°C (cSt) = 37.56 Filtered, heated for 5 h at 150°C and filtered again (polar substance = 21%)	Temperature = 64°C; Methanol oil ratio = 6:1;9:1;12:1;15:1;18:1 Time = 3 min Stirring = 400 rpm (with a magnetic nucleus) Catalyst/Quantity = NaOH = 0.5%;1%;1.5% (w/w)	Methyl ester mixture obtained was immediately placed in an ice bath, centrifuging at 5000 rpm for 5 min. The product was washed with warm deionised water several times until the washed pH value was 7. After the washing procedure, anhydrous sodium sulphate was added to prevent water residue in methyl ester.	Alcoholysis reactions were performed in a microwave system. Batch microwave tests were conducted on single-mode operating systems, running at 2.45 GHz, with a power programmable from 1 to 1000 W. Content of ester = 82.8;94.6;96.87 (*)Gross yield (%) = 84.96;90.09;74.60	[18]

(*) Gross yield [(biodiesel/oil) x 100]

cities). In order to avoid this problem or add value to needy people - cooperatives, NGOs, and others, to be able to mount a biodiesel industry, even if not for use as fuel commercial, but homemade or in farm in everyday uses; (b) The use of measurement of turbidity as innovation in studies involving vegetable oils and biodiesel as an analytical parameter for assessing quality; (c) Attempt to break the paradigm that the transesterification route is very costly in treatment of feedstock and biodiesel purification and inhibition of reaction when acidity is above of 0,5% and the water content above 0.06% [15]. A good purification (classical techniques of filtration, neutralization, washing and drying) of the feedstock will greatly reduce this difficulty favouring production scales in zones rural, urban and industrial with high yields and purity. The issue this study is not unheard and not original, but the reaction conditions and the treatments of feedstock suggest ways simple and sustainable production of a renewable fuel much studied and well spread in the world.

Therefore, this work was aimed at showing the sustainable viability of the production of biodiesel using homogeneous alkaline transesterification from residual frying oils. The residual oils were collected, filtered, characterised and one of the samples converted into biodiesel; with the latter being characterised in terms of some analytical parameters crucial for its qualification as a biofuel.

2. MATERIALS AND METHODS

2.1 Materials and Reagents Used

Residual frying oils (samples collected for this study); Distilled water and Reagents Analytical Degree of Purity between 96% and 99.8%: methanol, ethyl ether, glacial acetic acid, hydrous ethanol, chloroform (all of Modern Chemistry); Sodium chloride, Anhydrous sodium sulphate; Phosphoric acid, Sodium thiosulfate, potassium iodate, sodium hydroxide (all of Merck); starch

and phenolphthalein (all of Dynamic); Analytical balance (Bioprecision, mod.FA-2104N); Hotplate with magnetic stirring (VelpScientifica, mod. ARE); water bath (Novatécnica, mod. NT 267); drying oven with temperature control and heated until 300°C (DeLeo, mod.6); moisture scale (Gehaka IV 2000); Fluctuation densimeter (Incoterm 5598; scale 0,700 – 1,000); Cannon Fenske Viscometers (WH2750 and 539A); Vacuum pump; Turbidimeter (Hach 2100N); Semi-analytical balance (Agabol 541); Submersible pump (Boyu SP 500) and Classical Laboratory Glassware.

2.2 Collect and Treating the Samples

The oils commonly used in the region and collected were sunflower, cotton and, mainly, soybean, in random mixtures in points of collect and in quantities. The sample collection was adapted from the recommendations of "Physicochemical methods for food analysis" of the Institute Adolfo Lutz [20]. The residual oils were collected in bars and restaurants in the surrounding areas of the University Campus of Federal University of Pernambuco (UFPE), using Polyethylene terephthalate (PET) bottles. The bottles were previously treated with sodium hypochlorite solution (2.5%), triple wash with distilled water and left upside down for 72 hours for drying. The clean and dry bottles were then distributed in selected collecting points, with the instructions to avoid the contamination of the samples; these oils were then collected from these points and subsequently investigated. The oils collected were stored in the dark in glass flasks of 2 L (Fig. 1a), at ambient temperatures (25-30°C) and at rest until being analysed. The oils stored collected were heated to 60°C in water-bath during 2 minutes, cooled and filtered through a filter bed (3 mm felt and qualitative filter paper with 24-48 µm) (Fig. 1b) using a vacuum pump. The filtered oils (Fig. 1c) were stored separately in the same preceding conditions until being further analysed.

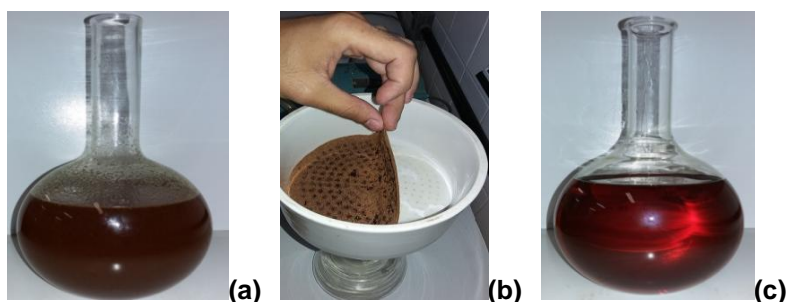


Fig. 1. Visual aspect of one of the samples of study
 (a) Frying oil before being filtered; (b) Detail of the filter bed (felt and filter paper underneath); (c) Filtered oil

2.3 Physicochemical Characterization of the Samples

The filtered oils were characterised in terms of the acid and peroxide values [20], specific mass (NBR 14065/ASTM4052), kinematic viscosity (NBR10441/ASTMD445) [21] and moisture content (GEHAKA IV 2000 balance, according to the operational procedure of the equipment) and turbidity (operational procedure from the turbidimeter HACH 2100N).

2.3.1 Acid value

About 2 g of each sample filtered of residual oil was weighed on an analytical balance and solubilized with 25 ml of solution ether-alcohol (2:1, neutral). It was then homogenized, and added two drops of phenolphthalein and titrated with NaOH 0.1 mol.L⁻¹ solution to become pink. The spent titrant volume was noted (in triplicate) and the average used in equation [20] below to calculate the acid value:

$$AV = (V \times f \times 5.61) / P$$

Where: V = volume of NaOH 0.1 mol.L⁻¹ spent on titration (mL). f = correction factor for the solution of NaOH 0.1 mol.L⁻¹. P = mass of sample (g). AV = acid value (mgKOH/g_{oil}).

The acid value can be expressed in terms of oleic acid (in percent) by [20] equation:

$$AV \text{ (in \% of oleic acid)} = AV \text{ (mg}_{KOH}/g_{oil})/1.99$$

2.3.2 Peroxide value

About 5 g of each sample of filtered residual oil was weighed on an analytical balance and solubilised with 30 mL of acetic acid/chloroform (3:2, v/v). Then it was homogenized and added 0.5 mL of saturated potassium iodide solution (fresh solution to avoid its degradation). The mixture was allowed to stand in the dark for 1 minute. Then they were added 30 mL of distilled water and 0.5 mL of 1% starch solution (blue color formation). The mixture was titrated with sodium thiosulphate 0.01 mol.L⁻¹ until the bluish tint disappeared and spent titrant volume was noted (in triplicate) and the average used in the equation [20] below to calculate the oil peroxide value:

$$PV = [(A-B) \times C \times f \times 1000] / P$$

Where: PV = peroxide value. A = volume required of the sample analyzed. B = volume

spent on white titration. N = normality of the sodium thiosulfate solution, 0.01 mol.L⁻¹. f = correction factor of sodium thiosulfate solution.

2.4 Biodiesel Production by Homogeneous Alkaline Transesterification

The reactor used was a 250 mL borosilicate glass bottle with two entrances flask and immersed in a thermostatically-controlled water bath with ethylene glycol at 60°C. The mixture was simultaneously stirred (water-bath and reaction medium) with two magnetic stirrers (Teflon coated) at 300 rpm (controlled by the stirring-hotplate, Velp Scientifica, mod. ARE) and monitored with a thermometer (mercury bulb, scale of 0-110°C, Incoterm, mod. 002/14) in the thermostatically-controlled water bath. The assembled system promoted homogenization, safety, reaction temperature-control and avoided moist entrance or material loss by volatilization (Fig. 2). The conditions chosen for the experiment were based on [14], with consequent adaptations for the feedstock type used (filtered residual frying oil).



Fig. 2. Assembling of the reaction system for the production of biodiesel

The alkaline transesterification was carried out at a molar ratio of 6:1 (methanol:oil), at 60°C, for 60 minutes, at a stirring speed of 300 rpm, 1.0% in mass of analytical sodium hydroxide as a catalyst (calculated in relation to the mass of oil used). The quantities used were of 150 g of oil, 40.1 mL of methanol (99.8%, approximately 31.65 g converted in volume with a density of 0.79 g.mL⁻¹) and 1.55g of sodium hydroxide (mass corrected from the theoretical mass calculated due to the purity of the reagent in 97%). In the end of the reaction, the material was

transferred to a separator funnel (dried and weighed) and naturally decanted for 3 hours. The system was subsequently weighed and the phases separated (Fig. 3b) and weighed for determining the reaction yield.

2.5 Purification of Biodiesel through Neutralization, Washing and Drying

Purification of biodiesel obtained was made with adapting the methodology of [22]. The impure biodiesel (light phase of transesterification) was treated using the proportion of 1:3 (biodiesel: purifying agent) to remove methanol residues and impurities (products formed in the reaction of neutralization of free fatty acids). The following purifying agents were used: 0.5% phosphoric acid solution and distilled water (Fig. 3c). The purification was monitored through the pH of the biodiesel until reaching neutrality (pH= 7) using strips Merck pH indicator (range from 0 to 14, with four colour scales). Four treatments were carried out: 2 with 0.5% phosphoric acid and 2 with distilled water. The treated biodiesel was transferred to a 250 mL round-bottom flask and attached to a simple distiller (with recirculation water in a closed circuit with a submerged pump) connected to a collecting flask in a vacuum system. The system was heated to 110°C for 30 minutes (in a thermostatically-controlled water-bath in ethylene glycol) and homogenised with a magnetic stirrer (300 rpm) for expelling any traces of occluded water and residual methanol. The product obtained in distillation received approximately 10% in mass of anhydrous sodium sulphate for the removal of remaining moisture. The mixture (biodiesel and anhydrous sodium sulphate) was homogenised for 10 minutes, filtered in qualitative filter paper with the vacuum pump and the biodiesel obtained (Fig. 3d) was transferred to an amber flask.

2.6 Characterization of the Biodiesel Produced

The biodiesel produced was characterised by some analytical parameters regulated by the ANP (Res. 45/2014) [23]: acid value (NBR 9866), specific mass (NBR 14065/ASTM 4052) and kinematic viscosity (NBR10441/ASTM D445), water content (NBR 11348/ASTM D6304, Karl Fischer) [21] and turbidity (operational procedure of the turbidimeter HACH 2100N) and ester content (EN 14103).

The determination of purity (ester content) of biodiesel Obtained was made utilized

experimental procedures and calculus based in [24] and [25]. For the analysis of the composition of the FAMES and to calculate the level of ester, a gas chromatograph Shimadzu 17A was used, with an FID detector and split/splitless injector; the capillary column used was the DB-WAX (30 m x 0.32 mm x 0.50 µm). The temperature of the injector was of 240°C and the temperature of the detector was of 260°C. The flow of the mobile phase (H₂) was of 1.7 mL.min⁻¹ and the division ratio (split) of 1:50. The methodology used is based on the standard: EN 14103: 2003, suitable for FAMES (methyl esters) between C14 and C24. Was weighed accurately about 250 mg of sample into a 10 ml flask, then added to 5 ml solution of Methyl heptadecanoate (C17, reference standard, Nu-Check Prep^l) using a volumetric pipette. After chromatographic analysis of the sample it is made the integration of the chromatogram from methyl myristate (C14) to the peak of the methyl ester C24:1. The ester content (EC), expressed as a mass fraction in percent is calculated using the following formula:

$$EC\% = \{[(\Sigma AT - AP) / AP] \times [(CP \times VP)/m]\} \times 100$$

Where:

ΣAT - Total peak area of the methyl esters between C14 and C24;

AP - area of the peak for Methyl heptadecanoate (C17);

CP - Methyl heptadecanoate concentration of the solution to be used (mg / ml);

VP - Methyl heptadecanoate volume of the solution to be used (ml);

m - mass of the sample (mg).

The result is generally expressed to one decimal place.

3. RESULTS AND DISCUSSION

3.1 Treatment and Characterization of the Samples

The residual oils heated to 60°C did not hamper the passage through the filter medium and displayed limpid characteristics, with little retention of residues. However, when reaching ambient temperature (25°C), colloidal materials in suspension appeared (Fig. 1a), with the oils becoming turbid. This turbidity was eliminated by a second cold filtration in similar conditions, with

a more difficult passage through filter medium and with a big retention of residues, making the oils limp (Fig. 1c) and acceptable for analysis and for the treatment of biodiesel conversion. Table 2 shows the parameters determined in the filtered residual oils [26].

The acid and peroxide values were used to evaluate the oil degradation before being used as a feedstock for biodiesel production. The high acid values of oils 1 and 3 can suggest a longer frying time-period, caused by the hydrolysis reactions with the development of free fatty acids, according with [1]. The peroxide value of

oil 1 was also high, with a certain link to the acid value. Oil 4 presented a very high peroxide value, but the smallest of acid values from all the samples investigated, contradicting the suggested acid-peroxide relation. One way or the other, it can be therefore concluded that these parameters are indicators of degradation of the classical fatty matrix (triacylglycerol), either in free fatty acids (acid value) or in oxidising compounds (peroxide value), corroborated for [18] in study with moringa oil of high acid and peroxide values and show that the frying oils are highly variable in terms of analytical characterisation [26], ratified for [2] which used

Table 2. Results of the analyses of filtered oils

Analytical parameters determined	Samples (oils)			
	1	2	3	4
Acid value (mgKOH.g ⁻¹ oil) (IAL-2008)	3.3	1.9	3.8	1.1
Acid value (% oleic acid) (IAL-2008)	1.65	0.95	1.91	0.55
Peroxide value (meqO ₂ .kg ⁻¹ oil) (IAL-2008)	8.8	1.7	4.9	23.3
Specific Mass (Kg.m ⁻³ at 20°C) (NBR 14065/ASTM D4052)	924	910	925	916
Kinematic Viscosity (mm ² .s ⁻¹ at 40°C) (NBR 10441/ASTM D445)	62.8	38.7	62.3	50.9
Water Content (mg.kg ⁻¹) (Balance GEHAKA IV 2000)	4,500	4,200	6,500	3,000
Water Content (%) (Calculated of the results of line previous)	0.45	0.42	0.65	0.30
Turbidity (NTU at 20°C) (Hach 2100N Turbidimeter)	63.4	33.2	35.7	34.8



Fig. 3. Steps in the production of biodiesel from filtered frying oil
 (a) Filtered frying oil (b) Separation of phases – impure glycerine in the bottom and impure biodiesel on the top
 (c) Purification step – washing with water (d) Purified biodiesel

frying oils (nine samples), in a study with pilot plant of 200 L for biodiesel production, with averages of acid value of $1.93 \text{ mgKOH.g}^{-1}$, peroxide value of $12.02 \text{ mEqO}_2.\text{kg}^{-1}$ peroxide and water content of $655.75 \text{ mg.kg}^{-1}$. Phan and Phan [27] also employed waste cooking oils (four samples) in biodiesel production, with acid value between $0.67 \text{ mgKOH.g}^{-1}$ and $3.64 \text{ mgKOH.g}^{-1}$ and peroxide value between $27.42 \text{ mEqO}_2.\text{kg}^{-1}$ and $33.47 \text{ mEqO}_2.\text{kg}^{-1}$. Felizardo et al. [28] also employed waste cooking oils (two samples) in biodiesel production, with acid values of $0.42 \text{ mgKOH.g}^{-1}$ and $2.07 \text{ mgKOH.g}^{-1}$. All authors ratify this wide variation of physicochemical features for samples of these fatty materials.

The specific mass and viscosity are common general physicochemical criteria for crude, refined or degraded (such as frying oils) vegetable oils [29]. After filtration, the frying oils displayed specific masses ranging from 910 to 925 kg.m^3 , within the range studied for vegetable oils by [30]; on the other hand, the kinematic viscosity was considered high when compared to refined soybean oil ($32.6 \text{ mm}^2.\text{s}^{-1}$), suggesting the presence of many colloidal compounds carried in the structure of fatty acids, and contributors to these values [26]. The soybean oil was used as a standard comparative material, with viscosity of $32.6 \text{ mm}^2.\text{s}^{-1}$ and specific mass of 913.8 kg.m^{-3} [30], due to its great use as a commercial and household frying oil. Phan and Phan [27], found values of average specific mass of 920 kg.m^{-3} and kinematic viscosity between $27.42 \text{ mm}^2.\text{s}^{-1}$ and $33.47 \text{ mm}^2.\text{s}^{-1}$ (average of $30.44 \text{ mm}^2.\text{s}^{-1}$), corroborated with the specific mass this study (average of 918.8 kg.m^{-3}), but the kinematic viscosity was very different, with averages of $30.44 \text{ mm}^2.\text{s}^{-1}$ and $53.7 \text{ mm}^2.\text{s}^{-1}$, respectively. This fact confirms the wide variation of physicochemical properties of frying oils.

The turbidity was measured in order to evaluate the intensity caused by the colloidal materials dispersed in such oils, with a possible negative influence in the production of biodiesel [29]. The sample 1 visibly displays darker colour than the others (2, 3 and 4), common characteristics for the oils with colloidal materials, ratified by its analytical result of 63.4 NTU for turbidity. Samples 1 and 3 exhibited higher water content and acid value, corroborating the acid-hydrolytic relation [26]. The water content or frying frozen foods can be associated with this increase of these substances (acids and water) in the oils [1].

3.2 Choice the Sample for the Alkaline Transesterification

In order to obtain high yields of esters in the alkaline transesterification, the oil used cannot exhibit acid values higher than 3% ($5.97 \text{ mg KOH/g oil}$). The free fatty acids present in the oil can react with the alkaline catalyst, forming soaps and reducing the efficiency, and even preventing the phase separation step [10,11]. Even though the oils used were previously filtered, they had already been refined, with their acid values (Table 2) as a prerequisite for biodiesel production by alkaline transesterification. Nonetheless, a previous neutralisation, washing and drying treatment is recommended in order to improve the production yield in esters [14].

One of the objectives of this study was based on the assumption of avoiding previous treatments intended to the samples, in order to reduce costs and to enable the comparison of the results obtained for biodiesel with the parameters indicated from the regulatory bodies. The samples were therefore only filtered, according to the description in 3.1. From the data analysis of Table 2, the oil 2 presented preferable characteristics for the alkaline transesterification process, in terms of acid and peroxide values, kinematic viscosity and turbidity.

3.3 Evaluation of the Reaction Performance and Yield

The amounts of volume and mass of pure biodiesel and impure glycerine are shown in Table 3, for calculating the reaction yield. The volume was measured with a cylinder graduate and the mass in an analytical balance.

The gross yield (%) of the process was calculated using the following equation:

$$Y\% = (m_{\text{biodiesel}} / m_{\text{oil}}) \times 100.$$

The yield of this alkaline transesterification reaction (60°C , 1% NaOH, molar ratio 6:1, methanol:oil) was of 82.0% with acid value of 1.9 mgKOH.g^{-1} (Table 2, sample 2). The sensory quality of the biodiesel produced and purified (Fig. 3d) was visibly remarkable. Felizardo et al. [28] also employed waste cooking oils (two samples) in biodiesel production, with acid value $0.42 \text{ mgKOH.g}^{-1}$ and $2.07 \text{ mgKOH.g}^{-1}$ obtained yields of 87.0% and 80.2% respectively, in the reaction conditions (60 minutes, 65°C , 1% NaOH

Table 3. Quantities of materials used in the alkaline transesterification

Oil used (sample 2)		Pure biodiesel		Impure glycerine	
Mass (g)	Volume (mL)	Mass (g)	Volume (mL)	Mass (g)	Volume (mL)
150 g	140 mL	123 g	40 mL	39 g	

Table 4. Parameters analysed from the biodiesel produced and respective normative references

Analytical parameters	EN (14214/2008)	ASTM (D6751-07b)	ANP (RES.45/2014)	Results of this study
Acid value (mgKOH.g ⁻¹ oil) (NBR 9866)	Max. 0.5	Max. 0.5	Max. 0.5	0.7
Ester content (% mass) (EN14103)	Min. 96.5	*	Min. 96.5	94.4
Specific mass (Kg.m ⁻³ at 20°C) (NBR 14065/ASTM D4052)	860-900	*	850-900	876
Kinematic viscosity (mm ² .s ⁻¹ at 40°C) (NBR 10441/ASTM D445)	3-5.5	1.9-6	3-6	4.3
Moisture content (mg.kg ⁻¹) (NBR 11348 / ASTM D 6304)	Max. 500	Max. 500	Max. 200	1,118
Turbidity (NTU at 20°C) (Turbidimeter Hach 2100N)	*	*	*	4.7

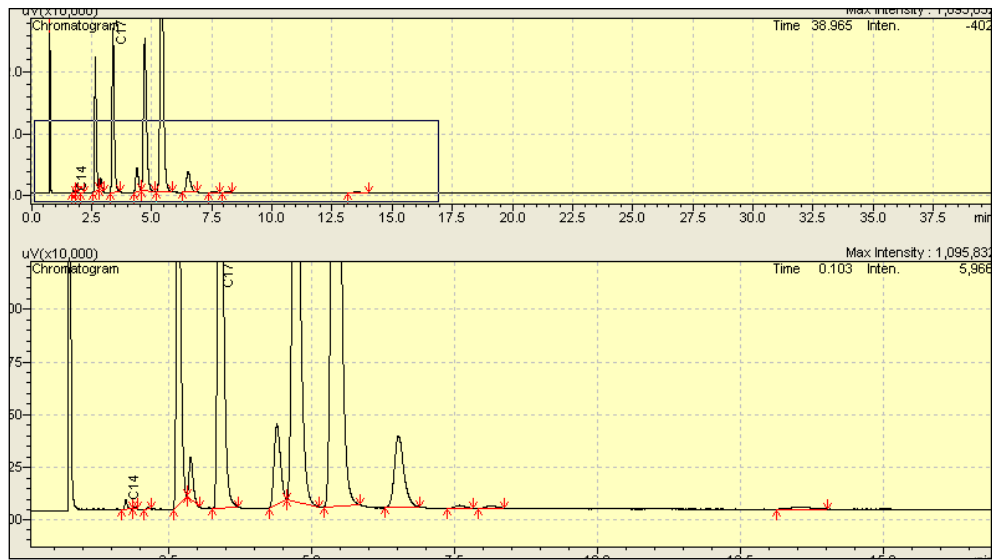
**Not specified in the standards*

as catalyst and the molar ratio 5.4:1, methanol:oil). Both studies had similarities and shows that the acid value is a very important parameter in this production, directly influencing in the reaction yields. On the other hand, the samples of [28] had water contents between 700 mg.kg⁻¹ and 1300 mg.kg⁻¹ and the this study, 4200 mg.kg⁻¹ (Table 2, sample 2), about 6 and 3,2 times more, respectively.

Table 4 shows the parameters analysed for the purified biodiesel in comparison with the values recommended by the European (EN 14214/2008), American (ASTM D6751-07b) and Brazilian standards (ANP RES. 45/2014) [23].

The acid values of the bibliographic references were: 0.43 mgKOH.g⁻¹ [27], 0.47 mgKOH.g⁻¹ [28] and 0.48 mgKOH.g⁻¹ [2], all according with the recommendations by the standards compared (Table 3). The acid value of this study (0.7 mgKOH.g⁻¹oil) remained above the maximum value recommended by the standards compared; this can be explained by the retained excess of phosphoric acid (neutralising solution) not removed during the washing step in the biodiesel purification process [26].

The contents of ester (purity of the biodiesel) of the bibliographic references were: 99.3% e 84.9%, respectively, for samples of oils with acid values of 0.42 mgKOH.g⁻¹ and 2.07 mgKOH.g⁻¹ [28], 88% to 90% for oils with acid values between 0.67 and 3.64 mgKOH.g⁻¹ [27] and 94.38%, for oil with acid value of 1.93 mgKOH.g⁻¹ [2]. The result this study was of 94.4% (Table 4). A reaction of alkaline methyl transesterification realized for [28] with oil (acid value of 0.42 mgKOH.g⁻¹ and 700 mg.kg⁻¹ of content water) and sodium hydroxide (1%) presented 99.3% of ester (purity of biodiesel), ratifying the viability of this method. This study and of the references had ester contents (purity of biodiesel) below of the minimum recommendations for standards Brazilian (ANP) and European (EN), showing that the acid value actually reduces reaction yield. A relevant comparison is the result of this study (Fig. 4, laboratory scale) and of the [2] (Pilot plant in artisanal scale) with similar analytical values, 94.4% and 94.38%, indicating that the alkaline route is interesting in terms of operational simplicity and quality of the final product.



Peak#	Compound Name	Ret.Tim	Area	Height	Conc.	Units	Mark	Compound ID#
1	C14	1.739	1285.5	457.9	0.00000	ppm		1
2		1.900	227.2	80.7	0.00000			
3		2.119	239.2	72.4	0.00000			
4		2.659	103244.2	21564.1	0.00000			
5		2.877	9523.1	2002.6	0.00000			
6	C17	3.392	166811.7	26509.2	0.00000	ppm		2
7		4.386	29478.0	3811.4	0.00000			
8		4.716	220772.4	24507.7	0.00000			
9		5.419	386753.2	40952.3	0.00000			
10		6.507	39056.3	3344.7	0.00000			
11		7.589	1907.6	153.9	0.00000			
12		8.122	1759.4	132.5	0.00000			
13		13.519	2549.7	107.4	0.00000			

(a)

B100_VIA ALCALINA								
Peak#	Compound	Ret,Time	Area	Height	Conc,	Units	Mark	Compound ID#
1	C14	1.739	1285,5	457,9	0	ppm		1
2		1.900	227,2	80,7	0			
3		2.119	239,2	72,4	0			
4		2.659	103244,2	21564,1	0			
5		2.877	9523,1	2002,6	0			
6	C17	3.392	166811,7	26509,2	0	ppm		2
7		4.386	29478	3811,4	0			
8		4.716	220772,4	24507,7	0			
9		5.419	386753,2	40952,3	0			
10		6.507	39056,3	3344,7	0			
11		7.589	1907,6	153,9	0			
12		8.122	1759,4	132,5	0			
13		13.519	2549,7	107,4	0			
	SOMA	963607,5						
	PI	166811,7						
	1	4,776618						
	2	0,197664						
	ÉSTER	94,4						

(b)

Fig. 4. Experimental information of the biodiesel obtained

(a) Chromatogram and record of the components; (b) Calculation of ester content (purity of biodiesel)

The specific mass of this study (876 kg.m^{-3} , Table 4) and of the references: 864 kg.m^{-3} to 900 kg.m^{-3} [28], 880 kg.m^{-3} [27] and 879.2 kg.m^{-3} [2], agree with normative recommendations (Table 4), close to the one reported by [30] for biodiesel from residual oil and demonstrating that this parameter is easily reached after the oil conversion and the purification of the product [14].

A higher viscosity of biodiesel affects the atomisation of fuel after the injection and, thus, ultimately increases the deposit forming on the engine [11]. The kinematic viscosity of this study ($4.7 \text{ mm}^2.\text{s}^{-1}$, Table 4) and of the references: 4.1 to $6.3 \text{ mm}^2.\text{s}^{-1}$ [28] and $4.89 \text{ mm}^2.\text{s}^{-1}$ [27], agree with normative recommendations (Table 4), exception for $6.3 \text{ mm}^2.\text{s}^{-1}$ (slightly above the acceptable limit by standards) in some samples of study of [28].

The water content of biodiesel was of approximately 26.6% of the content exhibited in the oil used in this investigation, but above the recommended by standards. Specific drying step for the removal of biodiesel was not carried out during the purification process as proposed in the methodology of [14], only distillation for the removal of excess methanol and treatment with anhydrous sodium sulphate and filtration with vacuum pump. Moecke et al. [2] found $495.74 \text{ mg.kg}^{-1}$ to water content for biodiesel produced. Nevertheless used oil with $655.75 \text{ mg.kg}^{-1}$, while this study with $4,200 \text{ mg.kg}^{-1}$ (about 6.4 times greater). Despite this very high value of water in the feedstock, the results in ester (purity of biodiesel are similar, about 94%). It is also noted maintenance of about 76.6% [2] and 73.3% (this study) in the amount of water present in the feedstock used and maintained in the purified biodiesel. The water content found in this study ($1,118 \text{ mg.kg}^{-1}$, Table 4) was above the limit accepted by the ANP (200 mg.kg^{-1}) and EN e ASTM (500 mg.kg^{-1}), requiring improvements in practises in the drying phase of the biodiesel produced.

The turbidity is a parameter not yet recommended as a quality criterion by the international standards for biodiesel. It can show a great relation between the sensorial aspect, purity of ester and the presence of few colloidal impurities [14]. The turbidity this study (4.7 NTU , Table 4) was around 7 times less in comparison to the oil used (33.2 NTU , Table 2), being possibly related to the purity of biodiesel in fewer colloidal species and easily monitored as quality parameter.

4. CONCLUSIONS

The methyl biodiesel obtained from the filtered frying oil exhibited a gross yield of 82.0%. The parameters specific mass and kinematic viscosity met the recommendations of the norms compared in this study. Its ester content of 94.4% (purity) was slightly lower than the minimum recommended (96.5%) by the Brazilian (ANP) and European (EN) standards. The water content and the acid value remained above the recommended and need to be improved in the purification step, in order to meet the regulatory requirements. Based on the results obtained in this study, it can be concluded that the frying oil is an excellent feedstock for biodiesel due to its simplicity in collection, transportation, stocking and of great production in all cities. Besides, the homogeneous alkaline path (the most conventional) is seen as very effective in the production of biodiesel, given the simplicity of its reaction, requiring less feedstock purification processes, making biodiesel more competitive when compared to petroleum diesel, especially more sustainable and with less environmental impact.

ACKNOWLEDGEMENTS

The authors thank the technical staff and managers of the Laboratories LEAQ, LAC, LPC and LCI of Department of Chemical Engineering of the UFPE and CECINE - UFPE by support during the experiments this work.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Sahin S, Sumnu SG. *Advances in Deep-Fat Frying of Foods*. Boca Raton: CRC Press Taylor & Francis Group; 2009.
2. Moecke EHS, Feller R, Santos HA, Machado MM, Cubas ALV, Dutra ARA, et al. Biodiesel production from waste cooking oil for use as fuel in artisanal fishing boats: Integrating environmental, economic and social aspects. *Journal of Cleaner Production*. 2016;135:679-688. Available:<http://dx.doi.org/10.1016/j.jclepro.2016.05.167>
3. ANVISA - Agência Nacional de Vigilância Sanitária. Informe Técnico nº 11, de 5 de

- outubro de 2004. Óleos e gorduras utilizados em frituras. Portuguese. Available:http://www.anvisa.gov.br/alimentos/informes/11_051004.htm. (Accessed 29 August 2016)
4. Math MC, Kumar SP, Chetty SV. Technologies for biodiesel production from used cooking oil - A review. *Energy for Sustainable Development*. 2010;14:339-345. Available:<http://dx.doi.org/10.1016/j.esd.2010.08.001>
 5. Giraçol J, Passarini KC, Silva Filho SC, Calarge FA, Tambourgi EB, Santana JCC. Reduction in ecological cost through biofuel production from cooking oils: An ecological solution for the city of Campinas, Brazil. *Journal of Cleaner Production*. 2011;19:1324-1329. Available:<http://dx.doi.org/10.1016/j.jclepro.2011.02.015>
 6. Rodrigues GT, Almeida GM, Alves RSV, Oliveira HSN. Estudo da viabilidade econômica de implantação de uma indústria de produção de biodiesel utilizando óleo de cozinha saturado no mun. de Campos dos Goytacazes. *Perspectivas online*. 2011;5(17):1-14. Portuguese. Available:http://www.seer.perspectivasonline.com.br/index.php/revista_antiga/article/view/475
 7. Samios D, Pedrotti F, Nicolau A, Reiznautt QB, Martini DD. Transesterification double step process modification for ethyl ester biodiesel production from vegetable and waste oils. *Fuel*. 2012;92(1):197-203. Available:<http://dx.doi.org/10.1016/j.fuel.2011.08.010>
 8. Skarlis S, Kondili E, Kaldellis JK. Small-scale biodiesel production economics: A case study focus on Crete Island. *Journal of Cleaner Production*. 2012;20(1):20-26. Available:<http://dx.doi.org/10.1016/j.jclepro.2011.08.011>
 9. Elkacmi R, Kamil N, Bennajah M, Kitane S. Extraction of oleic acid from Moroccan olive mill wastewater. *Biomed Research International*. 2016;(2016):9. Article ID 1397852. Available:<http://dx.doi.org/10.1155/2016/1397852>
 10. Knothe G, Gerpen JV, Krahl J. *The biodiesel handbook*. Champaign, Illinois: AOCS Press; 2005.
 11. Kegl B, Kegl M, Pehan S. *Green diesel engines - biodiesel usage in diesel engines*. London: Springer-Verlag; 2013.
 12. Islam A, Taufiq-Yap YH, Teo SH. *Advanced technologies in biodiesel: New advances in designed and optimized catalysts*. New York: Momentum Press – LLC; 2015.
 13. Guzzato R, Martini TL, Samios D. The use of a modified TDSP for biodiesel production from soybean, linseed and waste cooking oil. *Fuel Processing Technology*. 2011;92(10):2083-2088. Available:<http://dx.doi.org/10.1016/j.fuproc.2011.06.013>
 14. Pereira FSG, Brito Neto EX, Wei S, Galvão CC, Lima VF, Silva VL, Lima Filho NM. Produção de biodiesel metílico com óleo purificado de *Moringa oleifera* Lamarck. *Revista Virtual De Química*. 2016; 8(3):873-888. Portuguese. Available:<http://dx.doi.org/10.5935/1984-6835.20160063>
 15. Cao F, Chen Y, Zhai F, Li J, Wang J, Wang X, et al. Biodiesel production from high acid value waste frying oil catalyzed by superacid heteropolyacid. *Biotechnology and Bioengineering*. 2008; 101(1):93-100. Available:<http://doi.org/10.1002/bit.21879>
 16. Costa JF, Almeida MF, Alvim-Ferraz MCM, Dias JM. Biodiesel production using oil from fish canning industry wastes. *Energy Conversion and Management*. 2013;74: 17–23. Available:<http://dx.doi.org/10.1016/j.enconman.2013.04.032>
 17. Hasswa R, Dubé MA, Tremblay AY. Distribution of soap in a membrane reactor in the production of fame from waste cooking oil. *Canadian Journal of Chemical Engineering*. 2013;91(3):459-465. Available:<http://doi.org/10.1002/cjce.21686>
 18. Rahmanlar I, Yücel S, Özçinen D. The production of methyl esters from waste frying oil by microwave method. *Asia-Pacific Journal of Chemical Engineering*. 2012;7(5):698-704. Available:<http://doi.org/10.1002/apj.620>
 19. Kiss AA, Bildea CS. A review of biodiesel production by integrated reactive separation technologies. *Journal of Chemical Technology and Biotechnology*. 2012;87(7):861-879. Available:<http://doi.org/10.1002/jctb.3785>
 20. IAL - Instituto Adolfo Lutz. *Métodos físico-químicos para análise de alimentos*. 4ª ed.

- 1a ed. digital. SP, São Paulo; 2008. Portuguese.
Available:http://www.crq4.org.br/sms/files/file/analisedealimentosial_2008.pdf
(Accessed 10 January 2016)
21. ABNT - Associação Brasileira de Normas Técnicas. Normas diversas. Portuguese Available:<http://www.abnt.org.br/normalizacao/lista-de-publicacoes/abnt>
(Accessed 2 April 2016)
 22. Pereira FSG, Schuler ARP, Silva AMRB, Galvão CC, Pereira RN, Lima Filho NM, Silva VL. Turbidity and acidity as monitoring parameters in the purification of *Moringa oleifera* oil for biodiesel production. American Chemical Science Journal. 2016;16(3):1-9.
Available:<http://doi.org/10.9734/ACSJ/2016/28799>
 23. ANP - Agência Nacional do Petróleo, Gás Natural e Biocombustíveis. Resolução n.45/2014. Especificação do biodiesel e obrigações quanto ao controle da qualidade.
Available:<http://www.anp.gov.br/?pg=78463&m=&t1=&t2=&t3=&t4=&ar=&ps=&1470591068152.Portuguese>
(Accessed 10 January 2016)
 24. Pereira FSG, Galvão CC, Lima VF, Rocha MFA, Schuler ARP, Silva VL, Lima Filho MM. The versatility of the *Moringa oleifera* oil in sustainable applications. OCL. 2016; (In press).
Available:<http://doi.org/10.1051/ocl/2016027>
 25. Schuler ARP, Pereira FSG, Lima VF, Carvalho SLBV, Sobral AD. Chromatographic Characterization of potential feedstocks for biodiesel production. Chemical Science International Journal. 2016;17(2):1-10.
Available:<http://doi.org/10.9734/CSIJ/2016/29458>
 26. Pereira RN. Produção de biodiesel através da transesterificação de óleos residuais de frituras. TCC Grad. Eng. Quím. Universidade Federal de Pernambuco – UFPE; 2016. Portuguese.
 27. Phan AN, Phan TM. Biodiesel production from waste cooking oils. Fuel. 2008;87: 3490-3496.
Available:<http://dx.doi.org/10.1016/j.fuel.2008.07.008>
 28. Felizardo P, Correia MJN, Raposo I, Mendes JF, Berkemeier R, Bordado JM. Production of biodiesel from waste frying oils. Waste Management. 2006;26(5):487-494.
Available:<http://dx.doi.org/10.1016/j.wasman.2005.02.025>
 29. Pereira FSG, Silva AMRB, Galvão CC, Lima VF, Montenegro LGLA, Lima Filho NM, Silva VL. *Moringa oleifera* as Sustainable Source for Energetic Biomass. International Journal of Chemistry. 2015: 7(2): 177-185.
Available:<http://dx.doi.org/10.5539/ijc.v7n2.p177>
 30. Singh SP, Singh D. Biodiesel production through the use of different sources and characterization of oils and their esters as the substitute of diesel: A review. Renewable and Sustainable Energy Reviews. 2010;14:200-216.
Available:<http://dx.doi.org/10.1016/J.RSER.2009.07.017>

© 2016 Pereira et al.; This is an Open Access article distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/4.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Peer-review history:

The peer review history for this paper can be accessed here:

<http://sciencedomain.org/review-history/16850>