CSCanada
Advances in Petroleum Exploration and Development
Vol. 5, No. 2, 2013, pp. 83-88
DOI:10.3968/j.aped.1925543820130502.907

ISSN 1925-542X [Print]
ISSN 1925-5438 [Online]
www.cscanada.net
www.cscanada.org

A Simple Method for the Biodiesel Production by the Reuse of Different Types of Waste Frying Oils

Tiago Almeida Silva[a]; Antonio Carlos Ferreira Batista[a],*; Andressa Tironi Vieira[b]; Marcelo Firmino de Oliveira[b]

[a]Laboratory of Renewable Energy and Environment of Pontal, Faculty of Integrated Sciences of Pontal, Federal University of Uberlândia. Rua Vinte 1600, Tupã. 38304-402, Ituiutaba, MG, Brazil.
[b]Department of Chemistry, Faculty of Philosophy, Sciences and Letters of Ribeirão Preto, University of São Paulo. Av. Bandeirantes 3900, Monte Alegre. 14040-901, Ribeirão Preto, SP, Brazil.
*Corresponding author.

Support by CNPq and FAPEMIG, REBIO (Rede Mineira de Biocombustíveis), and FINEP CTINFRA I(2007).

Received 30 November 2012; accepted 18 June 2013

Abstract

A simple and complete method for the production and characterization of methylic and ethylic biodiesel from the main types of waste frying oils produced in Brazil was developed. The waste frying oils of soybean, canola, corn and sunflower were employed in the production of methylic and ethylic biodiesel by transesterification reaction via basic homogeneous catalysis. The transesterification reactions were performed at 40ºC during 40 min, using a catalyst percentage (KOH) equal to 2%. After separation of the phases biodiesel/glycerol, biodiesel was washed with 0.1M HCl aqueous solution, heated at 100 ºC to remove excess alcohol and finally filtered under vacuum with silica, a drying agent. The reaction yields were in the range 67.8-95.9%, quite satisfactory. The oxidative stability index was obtained for the oils as well as the biodiesel. Quality control of the original oil and of the methylic and ethylic biodiesels was accomplished by the TLC and GC-MS techniques. The results presented indicate the main waste frying oils produced in Brazil as potential sources of feedstocks for biodiesel production, which could aid in the development of the local cities that adopt programs to collect and reuse of waste oils. Furthermore, we emphasize that was obtained a route for biodiesel production greener, producing a biofuel substituent to mineral diesel by the reuse (or recycling) of waste.

Key words: Methylic biodiesel; Ethylic biodiesel; Waste frying oils

Silva, T. A., Batista, A. C. F., Vieira, A. T., & Oliveira, M. F. (2013). A Simple Method for the Biodiesel Production by the Reuse of Different Types of Waste Frying Oils. *Advances in Petroleum Exploration and Development*, *5*(2), 83-88. Available from: URL: http://www.cscanada.net/index.php/aped/article/view/j.aped.1925543820130502.907
DOI: http://dx.doi.org/10.3968/j.aped.1925543820130502.907

INTRODUCTION

Oil and its derivatives are the main non-renewable sources of energy[1]. Currently over 90% of all energy consumed in the world comes from non-renewable sources, and the oil is responsible for 33.1% this amount, as recently presented by the latest edition of the BP Statistical Review of World Energy[2]. However, it is predicted that over the next decades several of the current sources of oil can be extinguished[3, 4]. This fact along with economic concerns and environmental has encouraged the search for alternative energy sources such as wind, solar and biofuels[5-7]. Thus the replacement of fossil fuels has been driven by environmental, economic and social factors. In this context, a biofuel substitute of the mineral diesel which has been presented in numerous studies is the biodiesel[8-13].

In chemical terms, biodiesel is defined by the American Society for Testing and Materials (ASTM) as alkyl esters of long-chain carboxylic acids obtained from renewable sources like vegetable oils and animal fats[14, 15]. “Bio” represents the fact of the biodiesel to be obtained from renewable sources, in contrast with the mineral diesel fuel oil[15, 16].

The main advantages of biodiesel compared to mineral diesel are lower emission levels of CO_2 and particulate matter, use of renewable resources, which consequently alleviates the dependence of many countries

in relation to mineral diesel imported, is biodegradable, and when exposed the environment is degraded much faster than petroleum diesel[17, 19]. An important feature of biodiesel is its adaptability to the Diesel cycle engines without any mechanical modification, which has made it an alternative fuel for all the existing fleet[20, 21].

Biodiesel is frequently produced by the transesterification reaction, which consists in the reaction between vegetable oil (triacylglycerides) with a short chain alcohol (usually methanol or ethanol) in the presence of a catalyst (acid or basic), as schematically represented in Figure 1[22, 23].

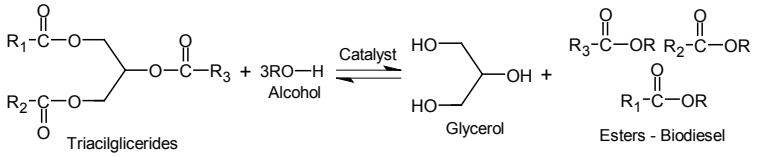

Figure 1
General Equation for a Transesterification Reaction

As seen biodiesel has many advantages over petroleum diesel in chemical and environmental terms, however, there are issues of technical level that must be studied so that biodiesel can be viable economically. One of this issues it the cost of feedstock, which approximately corresponds to 80% of the final cost of production. Thus, the search for alternative sources of feedstocks for biodiesel production and cheaper is an important need[10, 24].

In this context, the research on the biodiesel production from waste frying oils becomes very important, since with this practice is possible meet two eminent needs, first the removal of a pollutant from the environment and second the generating of an alternative fuel of the diesel. Moreover, it is a feedstock whose cost is minimal. Therefore the aim of this work was to develop a simple and efficient method for the production of methylic and ethylic biodiesels from the main types of vegetable oils used in frying in Brazil, soybean, canola, corn and sunflower oil via catalytic transesterification reaction.

1. MATERIALS AND METHODS

1. Biodiesel Production

The soybean, canola, sunflower and corn refined oils were purchased in local shops, and used without any pretreatment. Part of the oils were consumed in frying and collected after use to be employed in the synthesis of biodiesel. All waste frying oils were filtered before being subjected to the synthetic procedure in order to remove particulates that remained after frying.

The synthesis was performed by alkaline transesterification reaction via methylic and ethylic. Potassium hydroxide P.A. (KOH), methanol P.A. and ethanol P.A. were purchased from Sinth and used as received. The potassium methoxide form was obtained after adding 1.0 g of KOH at 14mL of methanol under stirring until the complete dissolution (exothermic reaction). The potassium ethoxide form was obtained after adding 1.0 g of KOH at 14 mL of a mixture methanol:ethanol 1:4 (vol:vol) under stirring until the complete dissolution. The alcoholic mixture methanol:ethanol was used for the ethylic route because the spontaneous phase separation was not obtained when used only ethanol. After the alkoxide preparation 50 g of oil was added, and the reaction system was kept under stirring at 40 ºC for 40 min.

The transesterification process was monitored by thin layer chromatography (TLC): the development of separation in hexane/ethyl acetate 95%/5% solution can exhibit a decrease of oil band and increase of biodiesel bands through the time.

After the decantation step, each biodiesel form was separated from glycerin and washed with HCl 0.1M solution. The biodiesel was heated at 100ºC to remove excess alcohol and finally filtered through a sintered plate glass filter containing silica, which acted as a drying agent.

1.2 Oxidative Stability Studies

The importance of this study consists of finding out up to which time point there is no formation of secondary compounds of oxidation, and to establish when the onset of increasing oxidation rate, peroxide index, oxygen absorption, and formation of volatile substances take place. The oxidative stability measurements were carried out using a 873 Rancimat equipment from Metrohm. The oil and the methylic and ethylic biodiesel samples were submitted to an air gas flow of 10 L/h, under a continuous heating at 110ºC±0.3ºC.

1.3 GC-MS Analysis

The chromatographic analysis of the biodiesel samples was carried out using an HP gas chromatograph, model CG 5890, series II, equipped with an HP1 column (100% dimethyl polysiloxane) with 30 m length and 0.2 mm internal diameter. The mobile phase consisted of H_2 and N_2 (30 L/min) and air (300 L/min). An injection volume of 0.5 μL was used in all the measurements. An injector temperature of 200 ºC was employed, and analysis was accomplished by using a temperature ramp from 80 to 200 ºC. The mass spectra of the main chromatographic peaks monitored in a mass spectrometer HP model 5988A, which was coupled to the chromatograph.

2. RESULTS AND DISCUSSIONS

The biodiesel production from waste frying oils is supported by two main factors, firstly because it is a waste whose cost is very low, which makes the biodiesel production cheaper and second for environmental reasons, since with this practice avoids the deposition of more one waste in the environment.

The amount of waste frying oil produced by snack bars, restaurants and residences in total is very large. In Brazil, it is found that the most widely used vegetable oil is soybean oil, and after the corn, sunflower and canola oil. Both were investigated in this work for the biodiesel production. The reaction yields obtained for all assays developed (16 in total) are shown in Table 1.

Table 1
Reaction Yields

Route	Yields (%)							
	Soybean		Corn		Canola		Sunflower	
	Ref*	Was**	Ref	Was	Ref	Was	Ref	Was
Methylic	95,3	95,9	92,7	86,8	94,3	91,0	93,3	93,8
Ethylic	83,3	77,9	81,3	67,8	81,5	78,9	85,7	72,1

*Ref – Refined Oil; ** Was – Waste Oil.

As can be seen from the data presented in Table 1 the yields obtained for reactions conducted via methylic were higher than those of ethylic via, in all cases. This result has also been observed by other authors, as Oliveira et al.[25]. In most assays the percentage of biodiesel produced from waste oils was less than that corresponding with the refined oil. This result can be correlated with the fact that waste oils present an advanced state of deterioration as a result of the degradation processes occurring during frying, as illustrated in Figure 2. However, yields are acceptable, so the methodology proposed in this work is a simple and feasible route for the biodiesel production from the main types of waste frying oils produced in Brazil.

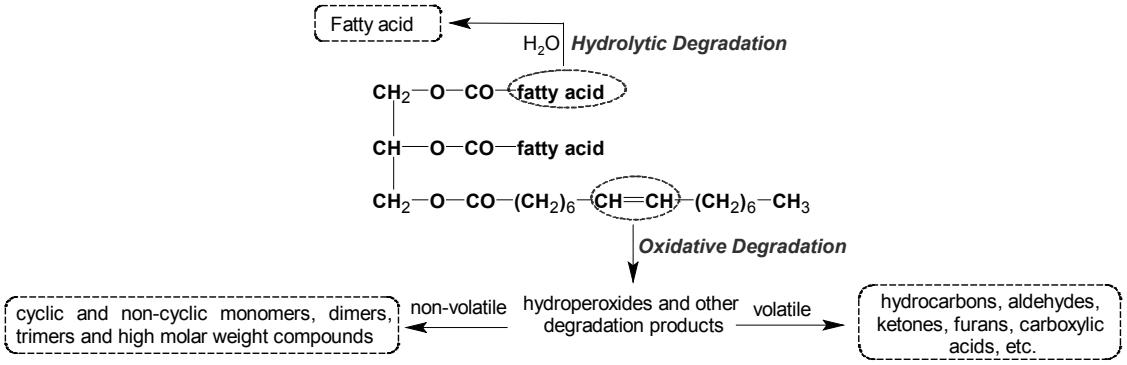

Figure 2
Degradation Process Suffered by Vegetable Oils During Frying[26]

After the steps of synthesis and refinement of biodiesel samples, the characterization of the biodiesel samples was performed. We evaluated the oxidative stability of biodiesel samples and the chemical composition by GC-MS. The results about oxidative stability index are reported in Table 2.

Table 2
Oxidative Stability Index Obtained for the Oils and the Methylic and Ethylic Biodiesels

Sample	Oxidative stability index (h)							
	Soybean		Corn		Canola		Sunflower	
	Ref	Was	Ref	Was	Ref	Was	Ref	Was
Oil	6,67	5,17	9,56	6,34	7,26	4,83	4,44	2,00
MB*	0,12	0,11	0,24	0,12	0,17	0,15	0,14	0,16
EB**	0,12	0,13	0,15	0,18	0,09	0,11	0,11	0,14

*MB – Methylic Biodiesel; **EB – Ethylic Biodiesel.

The oxidative stability index of refined oils and waste frying oils were analyzed for comparison. It was observed that the oxidative stability index decreased significantly for waste frying oils, confirming the fact that vegetable oils used in immersion frying suffer degradation. The oxidative stability index results for the biodiesel samples indicate a low stability, below that recommended by the Brazilian legislation (6 h at 110 ºC)[27]. In fact, in most studies in the literature, the oxidative stability index for biodiesel hardly reaches the standard value of 6 h, which

is also a feature and a problem to be solved biodiesel, its low oxidative stability[28].

All biodiesel samples were analyzed by GC-MS. Due to the large number of chromatograms obtained presents part of them, since the chromatographic profile of the samples allowed similar conclusions. In Figure 3 there are the chromatograms obtained for samples of biodiesel from corn and canola oil.

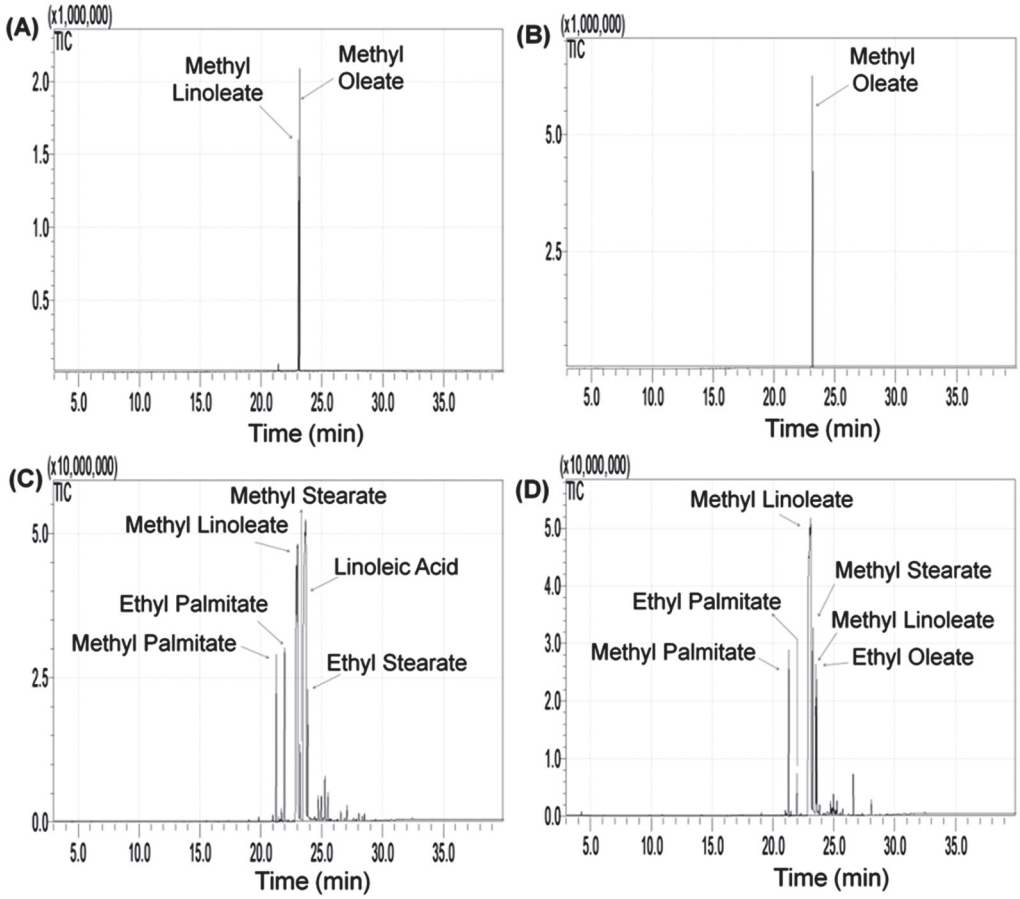

Figure 3
Chromatogram with Mass Spectrum Identification for Biodiesel Sample (A) Methylic Corn Waste Oil, (B) Methylic Canola Waste Oil, (C) Ethylic Corn Waste Oil, (D) Ethylic Canola Waste Oil

The main esters (methylic or ethylic) identified in all samples were palmitate, oleate, linoleate and stearate, in good agreement with previous works reported in the literature (Table 3), confirming the efficacy of the synthesis process. Due to use of the alcoholic mixture in the ethylic via, was found a mixture of methylic and ethylic in the ethylic biodiesel samples.

Table 3
Fatty Acid Composition of Soybean Oil, Canola, Corn and Sunflower

Fatty acid	Oil			
	Soybean	Canola	Corn	Sunflower
Palmitic C16:0	12,66 %	3,90 %	12,00 %	6,66 %
Stearic C18:0	3,96 %	1,10 %	2,90 %	4,32 %
Oleic C18:1 (9)	23,61 %	64,40 %	32,20 %	21,09 %
Linoleic C18:2 (9, 12)	55,26 %	20,40 %	52,20 %	67,78 %
Linolenic C18:3 (9, 12, 15)	4,52 %	9,60 %	0,70 %	0,15 %
Reference	[29]	[30]	[29]	[29]

CONCLUSIONS

The results of this work show the waste frying oils of soybean, corn, canola and sunflower as viable feedstocks for methylic and ethylic biodiesel production by the transesterification reaction. Thus the use of waste frying oils appears as an interesting alternative for the biodiesel production, which can be easily converted to biodiesel, and contribute to the local development of cities that to engage in projects to collect and reuse of this waste.

Previous studies of characterization of the methylic and ethylic biodiesel samples been performed with respect to oxidative stability index and chemical composition. It was observed a low value of stability for all samples analyzed. Therefore, further work should be done to improve this physic-chemical property. As to the chemical composition of biodiesel, all were in agreement with the composition cited by the literature, confirming the effectiveness of the catalytic process.

REFERENCES

[1] Christopher, K., & Dimitrios, R. (2012). A Review on Exergy Comparison of Hydrogen Production Methods from Renewable Energy Sources. *Energy & Environmental Science*, *5*, 6640-6651. Retrieved from http://dx.doi.org./10.1039/C2EE01098D

[2] BP Statistical Review of World Energy. (2012). Retrieved from http://www.bp.com/assets/bp_internet/globalbp/globalbp_uk_english/reports_and_publications/statistical_energy_review_2011/STAGING/local_assets/pdf/statistical_review_of_world_energy_full_report_2012.pdf

[3] Silva, T. A., Batista, A. C. F., & Vieira, A. T. (2012). A Brief Discussion of General Aspects of Biodiesel Production. *Brazilian Geographical Journal: Geosciences and Humanities research medium*, *3*(1), 80-89. Retrieved from http://www.seer.ufu.br/index.php/braziliangeojournal/article/view/13961/ 9674

[4] Vyas, A. P., Verma, J. L., & Subrahmanyam, N. (2010). A Review on FAME Production Processes. *Fuel*, *89*(1), 1-9. Retrieved from http://dx.doi.org/10.1016/j.fuel.2009.08.014

[5] Dresselhaus, M. S., & Thomas, I. L. (2001). Alternative Energy Technologies. *Nature*, *414*, 332-337. Retrieved from http://dx.doi.org./10.1038/35104599

[6] Mekhilef, S., Siga, S., & Saidur, R. (2011). A Review on Palm Oil Biodiesel as a Source of Renewable Fuel. *Renewable and Sustainable Energy Reviews*, *15*(4), 1937-1949. Retrieved from http://dx.doi.org/10.1016/j.rser.2010.12.012

[7] Koroneos, C., Spachos, T., & Moussiopoulos, N. (2003). Exergy Analysis of Renewable Energy Sources. *Renewable Energy*, *28*(2), 295-310. Retrieved from http://dx.doi.org/10.1016/S0960-1481(01)00125-2

[8] Körbitz, W. (1999). Biodiesel Production in Europe and North America, an Encouraging Prospect. *Renewable Energy*, *16*(10), 1078-1083. Retrieved from http://dx.doi.org/10.1016/S0960-1481(98)00406-6

[9] Oliveira, F. C. C., Suarez, P. A. Z., & Santos, W. L. P. (2007). Biodiesel: Possibilidades e Desafios. *Química Nova na Escola*, *28*, 3-8. Retrieved from http://qnesc.sbq.org.br/online/qnesc28/02-QS-1707.pdf

[10] Leung, D. Y. C., Wu, X., & Leung, M. K. H. (2010). A Review on Biodiesel Production Using Catalyzed Transesterification. *Applied Energy*, *87*(4), 1083-1095. Retrieved from http://dx.doi.org/10.1016/j.apenergy.2009.10.006

[11] Salvi, B. L., & Panwar, N. L. (2012). Biodiesel Resources and Production Technologies – A Review. *Renewable and Sustainable Energy Reviews*, *16*(6), 3680-3689. Retrieved from http://dx.doi.org/10.1016/j.rser.2012.03.050

[12] Albuquerque, M. C. G., Machado, Y. L., Torres, A. E. B., Azevedo, D. C. S., Cavalcante Jr., C. L., Firmiano, L. R., & Parente Jr., E. J. S. (2009). Properties of Biodiesel Oils Formulated Using Different Biomass Sources and Their Blends. *Renewable Ener*gy, *34*(3), 857-859. Retrieved from http://dx.doi.org/10.1016/j.renene.2008.07.006

[13] Rinaldi, R., Garcia, C., Marciniuk, L.L., Rossi, A.V., & Schuchardt, U. (2007). Synthesis of Biodiesel: a contextualized Experiment Proposal for the General Chemistry Laboratory. *Química Nova*, *30*(5), 1374-1380. Retrieved from http://dx.doi.org/10.1590/S0100-40422007000500054

[14] Silva, N. L., Maciel, M. R. W., Batistella, C. B., & Filho, R. M. (2006). Optimization of Biodiesel Production from Castor Oil. *Applied Biochemistry and Biotechnology*, *129*, 405-414. Retrieved from http://dx.doi.org/10.1007/9781597452687_33

[15] Zhang, Z., Dubé, M. A., McLean, D. D., & Kates, M. (2003). Biodiesel Production from Waste Cooking Oil: 1. Process Design and Technological Assessment. *Bioresource Technology*, *89*(1), 1-16. Retrieved from http://dx.doi.org/10.1016/S0960-8524(03)00040-3

[16] Knothe, G. (2010). Biodiesel and Renewable Diesel: A Comparison. *Progress in Energy and Combustion Science*, *36*(3), 364-373. Retrieved from http://dx.doi.org/10.1016/j.pecs.2009.11.004

[17] Chen, Y. H., Chen, J. H., Chang, C. Y., & Chang, C. C. (2010). Biodiesel Production from Tung (*Vernicia Montana*) Oil and Its Blending Properties in Different Fatty Acid Compositions. *Bioresource Technology*, *101*(24), 9521-9526. Retrieved from http://dx.doi.org/10.1016/j.biortech.2010.06.117

[18] Conceição, M. M., Candeia, R. A., Silva, F. C., Bezerra, A. F., Fernandes Jr., V. J., & Souza, A. G. (2007). Thermoanalytical Characterization of Castor Oil Biodiesel. *Renewable and Sustainable Energy Reviews*, *11*(5), 964-975. Retrieved from http://dx.doi.org/10.1016/j.rser.2005.10.001

[19] Sendzikiene, E., Makareviciene, V., & Janulis, P. (2006). Influence of Fuel Oxygen Content on Diesel Engine Exhaust Emissions. *Renewable Energy*, *31*(15), 2505-2512. Retrieved from http://dx.doi.org/10.1016/j.renene.2005.11.010

[20] Morshed, M., Ferdous, K., Khan, M. R., Mazumder, M. S. I., Islam, M. A., & Uddin, Md.T. (2011). Rubber Seed Oil as a Potential Source for Biodiesel Production in Bangladesh. *Fuel*, *90*(10), 2981-2986. Retrieved from http://dx.doi.org/10.1016/j.fuel.2011.05.020

[21] Lianhua, L., Pengmei, L., Wen, L., Zhongming, W., & Zhenhong, Y. (2010). Esterification of High FFA Tung Oil with Solid Acid Catalyst in Fixed Bed Reactor. *Biomass and Bioenergy*, *34*(4), 496-499. Retrieved from http://dx.doi.org/10.1016/j.biombioe.2009.12.014

[22] Manh, D. V., Chen, Y. H., Chang, C. C., Chang, M. C., & Chang, C. Y. (2011). Biodiesel Production from Tung Oil and Blended Oil via Ultrasonic Transesterification Process. *Journal of the Taiwan Institute of Chemical Engineers*, *42*(4), 640-644. Retrieved from http://dx.doi.org/10.1016/j.jtice.2010.11.010

[23] Silva T. A., & Batista, A. C. F. (2010). Production of Methylic and Ethylic Biodiesel from Peanut Oil Employing the Transesterification Reaction via Basic Homogeneous Catalysis. In: XVI Encontro Luso-Galego de Química, Aveiro, Portugal. *Livro de Resumos do XVI Encontro Luso-Galego de Química*, 234.

[24] Singh, S. P., & Singh, D. (2010). 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*, *14*(1), 200-216. Retrieved from: http://dx.doi.org/10.1016/j.rser.2009.07.017

[25] Oliveira, M. F. O., Vieira, A. T. , Batista, A. C. F., Rodrigues, H. S., & Stradiotto, N. R. (2011). A Simple and Fast Method for the Production and Characterization of Methylic and Ethylic Biodiesels from Tucum Oil via an Alkaline Route. *Journal of Biomedicine and Biotechnology*, *2011*, 1-4. Retrieved from http://dx.doi.org./10.1155/2011/238474

[26] Neto, P. R. C., Rossi, L. F. S., Zagonel, G. F., & Ramos, L. R. (2000). Production of Alternative Biofuel to Diesel Oil Through Transesterification of the Soybean Oil Used in Frying. *Química Nova*, *23*(4), 531-537. Retrieved from http://dx.doi.org/10.1590/S0100-40422000000400017

27] EN 14112: 2003. (2003). Fat and Oil Derivatives–Fatty Acid Methyl Esters (FAME). *Determination of Oxidation Stability* (Accelerated Oxidation Test).

[28] Ferrari, R. A., & Souza, W. L. (2009). Evaluation of Oxidation Stability of Sunflower Oil Biodiesel with Antioxidants. *Química Nova*, *32*(1), 106-111. Retrieved from http://dx.doi.org/10.1590/S0100-40422009000100020

[29] Jorge, N., Soares, B. B. P., Lunardi, V. M., & Malacrida, C. R. (2005). Physico-Chemical Alterations of Sunflower, Corn and Soybean Oils in Deep Fat Frying. *Química Nova*, *28*(6), 947-951. Retrieved from http://dx.doi.org/10.1590/S0100-40422005000600003

[30] Haagenson, D. M., Brudvik, R. L., Lin, H., & Wiesenborn, D. P. (2010). Implementing an in Situ Alkaline Transesterification Method for Canola Biodiesel Quality Screening. *Journal of the American Oil Chemists' Society*, *87*(11), 1351-1358. Retrieved from http://dx.doi.org/10.1007/s11746-010-1607-9

