

ENCIT-2018-0766 BIODIESEL PRODUCTION IN SMALL SCALE

Alisson Aparecido Vitoriano Julio

Universidade Federal de São João del Rei - UFSJ
alissonvjulio@gmail.com

Gustavo Rodrigues de Souza

Universidade Federal de São João del Rei - UFSJ
souzagr@ufsj.edu.br

Abstract. *This work analyzes a new and low cost way to produce biodiesel by transesterification of wasted frying oil and soya bean oil in natura. Therefore a small plant was manufactured in which a drill was used as stirrer.*

The built plant used wood, steel angle brackets and threaded bars. As a stirrer, a propeller was welded to the end of a rod and this was coupled to the drill chuck. A funnel was also constructed to separate glycerol and ester, with PET, PVC, hose parts and a gate valve. The rotation of the drill was controlled by a voltage variator, in which it was mounted next to the plant.

By means of transesterification, three main results were obtained: ester from recovered oil and ester from soya bean oil in natura with two different catalysts. Despite none of these had characteristics consistent with the ANP specification, the best case was a transesterification efficiency of 84%. The study was able to chart a way for further work, such as adding heat source to the plant to improve the efficiency of the reaction.

Keywords: *biodiesel, transesterification, wasted frying oil.*

1. INTRODUCTION

According to RIBEIRO and DIAS (2016), The National Program for the Production and Use of Biodiesel (PNPB) transformed family farming in the North and Northeast regions of Brazil. The cultivation of sunflower, castor plant and soybeans among small producers was introduced through long-term contracts between micro and small producers with Petrobrás, in order to provide raw material for biodiesel production. However, the program only bought raw material from this producer, which could produce its own fuel and make it a profitable business. It is in this context that production by means of simplified means applies: encouraging the raw material producer to be more ambitious and discover a new source of income or even using this source for own consumption in tractors, trucks and harvesting machines. Energy engineering is the area that seeks to improve the utilization of primary energy sources. Oil, coal, and all conventional means of energy have been explored. However, there are challenges related to the finite character of these inputs, as well as the environmental impacts arising from them.

The introduction of biomass in the world energy matrix is a function of the technological advance and the direct influence of energy engineering, which searches the best form of its use, managing the resources well from its taking, to the effective use of the energy. In spite of it's an old source of energy - perhaps the oldest one - being used to cook and heat environments with simple wood burning, for example, the modern use of biomass includes the generation of electricity, heat and the production of fuels. The use of sustainable resources has the great advantage of the low emission of polluting gases to the atmosphere and, so, it can be said that biomass is the resource that can play a leading role in the transition to sustainable energy generation. Biomass also deserves special attention because of its versatility, as it can be used as solid fuel in the form of briquettes and pellets for steam generation and also in the production of liquid fuels, such as biodiesel. The biodiesel has been used in addition or substitution to diesel to power compressed-engine vehicles and also to energy generation in order to minimize environmental impacts in agreement with KNOTHE et al. (2006).

The use of biodiesel is justifiable for several reasons: KNOTHE et al. (2006) claims that this is the only renewable fuel with direct application in any diesel engine, without the need to make adaptations; it is the most economically viable option among alternative fuels, in agreement with the text of RAMKUMAR and KIRUBAKARAN (2016); It is non-toxic, biodegradable and has an ignition point of 150 ° C which makes transport and handling safer (B.H.U.G., 2016).

According to data of average CO₂ emission in Brazil (ANP, 2009) by vehicles with diesel engine, the study of CORONADO (2010), shows that with biodiesel B100 the emission of this gas would be reduced by 78.45%. Falling from 32.2 tons to 6.94 tons emitted per vehicle, within a year. The current legislation requires that by March 2019 a minimum quantity of 10% of biodiesel in mineral diesel should be added to fuel fuels (Brazil Federal Law 13.263 of 2016). In terms of carbon dioxide, it can be stated, according to SHEEHAN et al. (1998), that the emissions caused by

the combustion of biodiesel are photosynthesized by the plants, while the carbon emitted in the atmosphere due to the burning of the fossil fuels, refers to the one stored in the terrestrial surface for centuries.

The study aims to check the viability of the production of biofuel, along with the fact that there are not many resources available, which would be the case of the small rural producers, based on family farming. It is also proposed the construction of a small plant to execute the reaction of transesterification of soybean oil and wasted frying oil in ester by ethylic route. In order to defer the fuels and obtain a variation of properties analyzed, three molar ratios will be used for the transesterification process and variants will be obtained in the results. Finally, it is proposed the subsequent separation of the reaction products and the characterization of the fuel obtained in order to know if it is possible to obtain a product according to ANP – National Agency of Petroleum, Natural Gas and Biofuels – standards of viscosity, specific mass and calorific value.

2. METHODOLOGY

2.1 Plant construction

The present work deals with an experimental research according to the procedures used. The research shows the possibility of becoming used oil in frying, and also, *in natura* oil - which is often wasted and ends up as pollutant in water reserves - in biofuel, by means of simplified methods.

In order to obtain the expected final product - soybean oil biodiesel - will be used of the chemical reaction of transesterification. The contact of the triglycerides present in the oil with the alcohol in the presence of agitation and with an alkaline catalyst characterizes the type of transesterification proposed. Though, to generate this reaction requires an agitator, which he proposed to build as part of the work.

With the proposition of constructing a plant to agitate the mixture in favor of the reaction previous cases in the literature such as LIN & CHEN (2017) that used a rotating cylindrical stirrer inside a beaker were investigated. In view of this proposal, it was decided to use the rotation capacity of a drill and to use as a stirrer a rod that could be coupled to the chuck of the machine.

In order to stabilize the mixture, it was decided that the drill should be positioned on a support and the first step was to design a prototype using software to define a starting point, and then in Fig. 1 is the first profile of the plant to be developed.

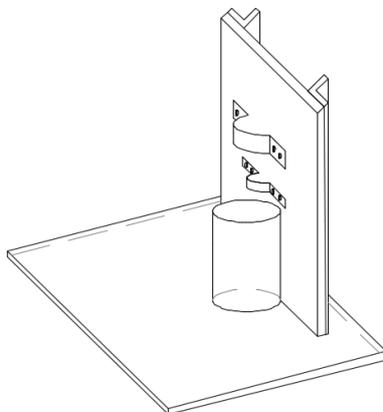


Figure 1. Outline of the biodiesel production plant

When putting into practice the construction of this prototype, wood was used for both plates, as it was a resource available at no cost. The wooden boards were coupled by screws and the support between them was guaranteed by means of steel angles. The impact drill, a FORT FT-2519 420W machine, was coupled to the structural plates by means of two threaded rods and a steel plate and for safety, threaded rods were also used to fix the machine around the chuck. As shown in Fig. 2. Such decisions were made for ease of construction, setting and availability of resources.



Figure 2. Prototype ready for operation

A separation funnel, Fig. 3, similar to a bromine funnel used for separating heterogeneous mixtures between liquids by decantation, was also constructed for the separation of ester and glycerol at the end of the transesterification reaction. This funnel was constructed with a PET bottle, a small PVC tube and a drawer valve of 12.7mm diameter each and a piece of hose. This equipment is very important to the work since, for the characterization tests of the ester produced, it must be separated from the secondary product, glycerine.



Figura 3. Separation funnel

Based on the study by LIN & CHEN (2017), who judged to be 200 rpm the best agitation speed to operate a transesterification, the challenge was to control the speed of the drill motor. It was decided to use a VARIAC TDGC2-3kVA voltage variator. Using a FLUKE 115 TRUE RMS multimeter and a MINIPA MDT-2245 C tachometer it was determined that for the mixer to operate at a constant speed of 200 rpm, the supply current should be approximately 1 A. In Fig. 4 the assembled circuit is presented and ready to perform the chemical reaction.



Figura 4. Circuit configured to process the chemical reaction

2.2 Work samples

To work with transesterification, according to MENEGHETI et al., 2013, 3 mole of carboxylic acid, in this case anhydrous ethanol, is required to react with the triglyceride, oil, and then to form ester and glycerol. However, in practice, it is necessary to use an excess of alcohol to increase the ester yield in the reaction and allow the separation of the glycerol. With this it was proposed to produce samples of molar ratio of 8: 1, 10: 1 and 12: 1 of ethanol to oil and as catalyst 1% by weight of sodium hydroxide was used.

The batch was small because of the capacity of the plant built as a reactor. The glass cylinder used behaves approximately two liters and as it is a test plant it was decided to use small quantities in order to have a greater control of the process. Since the reactants are in the liquid state, a device for applying the molar ratio is to use the specific mass and the molar mass to arrive at the coherent values for reaction. For soybean oil the value of 0.891 g / cm³ for specific mass and 282 g / mol of molar mass was used. For ethanol, the values were 0.789 and 46g / mol, for specific mass and molar mass, respectively. With the artifice of a spreadsheet for calculations, the measurements to be used in the experiment were shown in Tab. 1.

Table 1. Amounts for the production of biodiesel by alkaline catalysis

	8: 1 Batch			10: 1 Batch			12: 1 Batch		
	Volume amount (cm ³)	Molar amount (mol)	Weight amount (g)	Volume amount (cm ³)	Molar amount (mol)	Weight amount (g)	Volume amount (cm ³)	Molar amount (mol)	Weight amount (g)
Wasted fryied oil	200	0.632	178.2	250	0.789	222.75	150	0.474	133.65
Ethanol (C ₂ H ₅ OH)	300	5.056	232.55	460	7.89	363.35	332	5.688	261.61
NaOH	-	-	2.2	-	-	3.47	-	-	2.46

The reaction preparation procedure was done by measuring the quantities to be processed. From the time NaOH was mixed with ethanol the corresponding oil measure was added, heated to 100 ° C to remove moisture. The drill remains on for 40 minutes, timed, from the moment all the reagents were under its action, to process the ethyl ester transesterification. The process described, is also illustrated by Fig. 5.

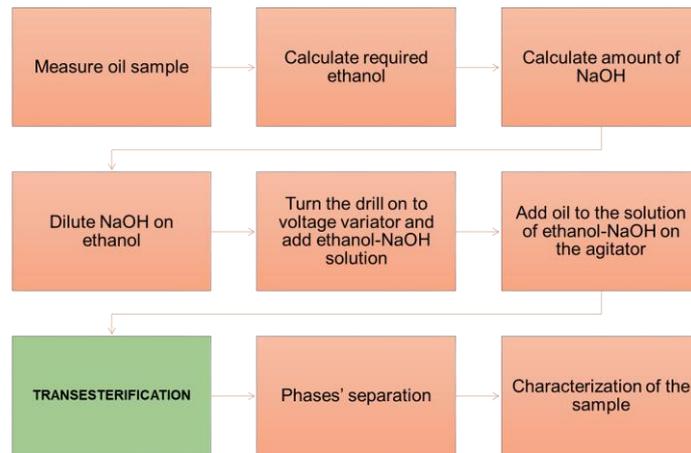


Figura 2. Process Flowchart

2.3 Experimental procedures

When it comes to the manufacture of a product it is important to characterize it so that it is compared to what is produced by others, or even if it is within certain established standardization. The biodiesel studied can be classified by its properties and for this it was taken measures of viscosity, specific mass and calorific value.

A MLW Rheo 340 viscometer, ball drop, was used to reach the dynamic viscosity values. The operation of the equipment is associated with the time the ball takes to reach the bottom of the flask, this time is marked by a stopwatch connected to the viscometer. In Eq. 1, the time taken to find the viscosity (μ) in millipascal second is used.

$$\mu = t.K.(M + A) \quad (1)$$

K is the constant of the flask used to store the fluid during the test, standardized at $0.005179 \text{ mPa.cm}^2 / \text{g}$; A is a constant associated with standardized instrument weight correction at $-0.0763 \text{ g} / \text{cm}^2$; M is the counterbalance mass and t is the elapsed time.

To obtain the Lower Heating Value (LHV), the Parr 1341 oxygen calorimeter pump was used. The calorimetric pump, adiabatic chamber and igniter set work to promote the combustion of the tested fuel and point out the temperatures at each point in order to generate a graph that serves as the basis for the calculations that lead to the value of the LHV. To compute the point temperatures, a digital thermometer, Minipa MT-450, was used, which by means of a thermocouple inserted inside the adiabatic chamber informed the temperature of each interval selected for analysis and sent data through a Wi-Fi connection to a computer with Minipa software.

Calculate the LHV depends on three equations. These depend on variables found in the temperature-by-time graph, the theoretical plot of the calorimetric pump is in Fig. 6.

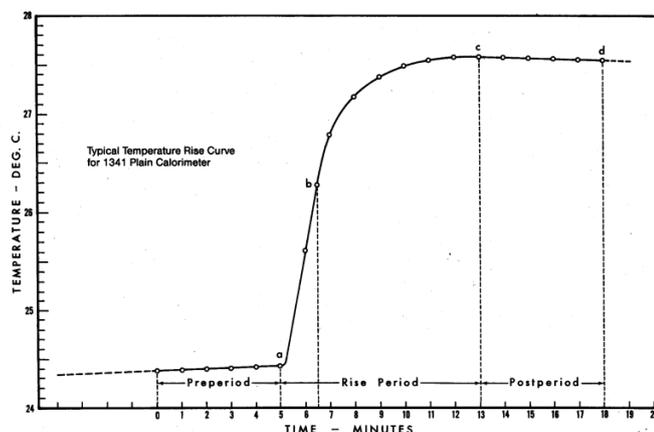


Figura 3. Calorimetric bomb's theoretical graph. Source: Manual of instructions Parr1341 Bomb Calorimeter (2008)

To reach the value of the LHV, the temperature correction is calculated first by Eq. 2, where a, b and c refer to the points that characterize the ignition, the combustion's rise, when 60% of the temperature increase is reached, combustion and post-ignition stability, respectively. Just as Ta, Tb and Tc indicate the temperature of these points. In addition to these values, the inclination of the stable first phase, R1, and the inclination of the increasing combustion curve, R2, are added together.

$$t = T_c - T_a - R1.(b - a) - R2.(c - b) \quad (2)$$

From the correction parameter it is possible to calculate the standardization energy (W). Eq. 3 expresses this magnitude, knowing that the value H represents the calorific value of the pump standardization sample. This sample is characterized by 1 g of benzoic acid in the solid state and the value of the calorific value is 26.434 MJ. The correction value is also necessary due to the ignition wire used in the work, which in this case is a 10 cm platinum wire. After burning, not all the thread is consumed, leaving a part of the pump. The remaining wire is measured and multiplied by a factor of 2.3 to complement the equation of the standardization energy, this is the factor e3.

$$W = \frac{(H.mH) + e3}{t} \quad (3)$$

With the standardization energy value in hand, the next step is to calculate the LHV of the sample. To do so, simply apply the known values of temperature correction (t), standardization energy (W) and calorie correction due to the ignition wire (e3) and divide them by the mass of the sample tested, according to Eq. 4.

$$LCV = \frac{(t.W) - e3}{m} \quad (4)$$

Finally, the simplest magnitude to obtain is the specific mass, it was used immersion densimeters to reach the values of specific mass. Since the instruments have a scale, calculations were not necessary to arrive at the result.

To calculate the reaction's yield, a sufficient amount of transesterification, use Eq. 5, V_{ester} is the volume of ester formed, and $V_{total\ product}$ the amount in milliliters of the entire product of the reaction. This ratio is represented by the letter η , the yield of the reaction.

$$\eta = \frac{V_{ester}}{V_{total\ product}} \quad (5)$$

3. RESULTS

The variables studied were measured properties and reaction yield in terms of ester formation. Another contributing factor for the results are the reagents, not all were in the best conditions for use, however they were used due to the availability of resources.

The transesterifications were conducted according to the ratio shown in Tab. 1 and the average yields for each ratio are given in Tab. 2, these data were calculated by the simple ratio of amount of ester separated per total amount of product.

Table 2. Average reaction's yield and average specific mass of waste frying oil biodiesel

Ratio	Reaction's Yield	Specific mass (g/cm ³)
8:1 Batch	52.20	0.8414
10:1 Batch	64.00	0.8305
12:1 Batch	73.65	0.816

More reactions were processed, but the raw material was the soybean oil *in natura*, sold in supermarkets. And then, it was determined to produce by the ratio 10: 1, the product characteristics of this reaction are in Tab. 3.

Table 3. Results for production with soybean oil *in natura*

	Reaction's Yield	Specific mass (g/cm ³)
1st Batch	74.76	0.845
2nd Batch	81.18	0.845

It was also produced biodiesel with a catalyst, still NaOH, but of different brand, that was made available at the end of the work and was in better conditions. A new 10: 1 sample was produced to be characterized and compared with the others already obtained. In Tab. 4 are the results for 10: 1 samples for the listed properties, where Biodiesel X refers to that produced from the waste frying oil, Biodiesel Y refers to the fuel produced from *in natura* soybean oil with the first catalyst and Biodiesel Z refers to the production with NaOH under better conditions, the second catalyst.

Tabela 3. Characterization of the produced fuels

Produced batches	Specific Mass (g/cm ³)	Kinematic Viscosity (mm ² /s)	LCV (MJ/kg)	Reaction's Yield (%)
Biodiesel X	0.835	2.430	22.78	61.00
Biodiesel Y	0.845	3.897	27.03	81.18
Biodiesel Z	0.815	3.314	26.49	84.00

According to OLIVEIRA, 2015, the LHV of biodiesel from soybean oil varies around 39.9 MJ / kg and as seen in Tab. 4 the value that shows the highest agreement is that of the fuel produced with soybean oil *in natura* (Y and Z). However, the value is still lower than that of biodiesel reported in the literature. This lower value implies that the fuel has less energy to be explored. The curves obtained for LHV calculation are shown in Fig. 7, 8 and 9.

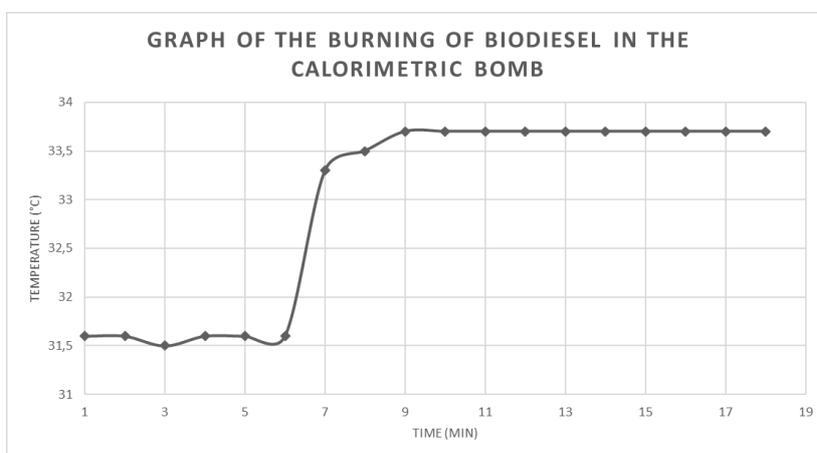


Figure 7. Graphic for calculating the LHV of the Biodiesel X

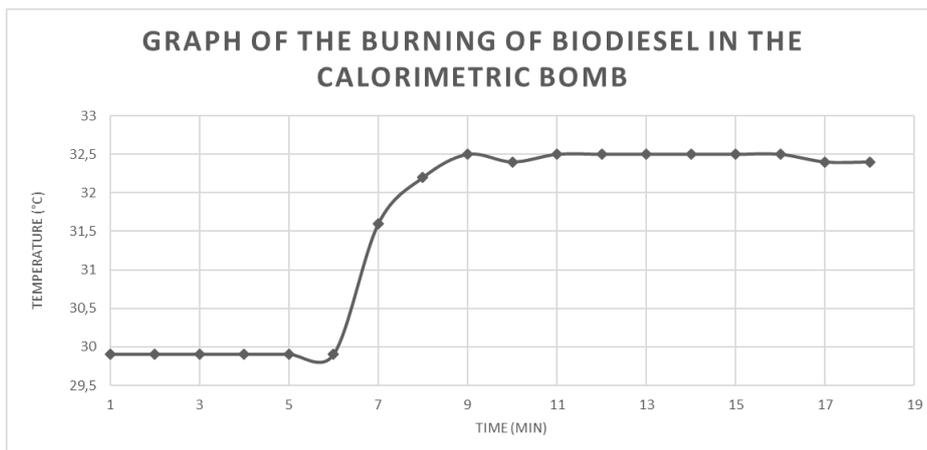


Figure 8. Graphic for calculating the LHV of the Biodiesel Y

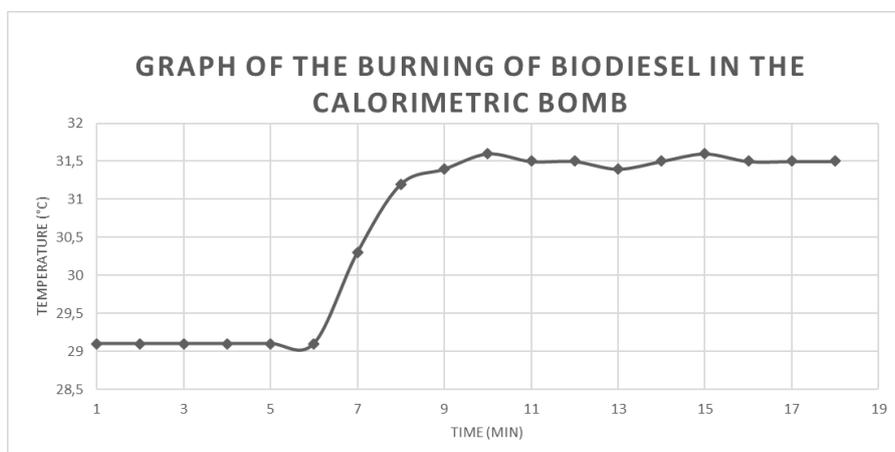


Figure 9. Graphic for calculating the LHV of the Biodiesel Z

The ANP dictates the rules of fuels in Brazil, therefore imposes, among other properties, viscosity and specific mass. According to the ANP standard, the specific mass of the ester must not have a density greater than 0.900 g / ml. According to the production of FERREIRA et al., 2013, the samples have an average of 0.861 g / cm³ which is more similar to the one found.

Regarding the viscosity values, the ANP imposes a maximum limit of 6 mm² / s at 40° C. Viscosity is the resistance of a fluid against shear deformation, and its value falls with temperature. Since the tests were conducted at 28° C and reached substantially lower values, the viscosity is another parameter short of the ANP standard.

Besides the presented values did not agree with the norms, as expected, there was also the obstacle of not being miscible to mineral diesel. One plausible justification is that the reaction was not complete, the time may have been short for the ester to be formed, and then it resulted in ester mixed with unreacted ethanol, which explains the smaller specific mass and small values of viscosity.

4. CONCLUSIONS

Using the experimental apparatus, results were obtained for specific mass, viscosity and lower calorific value. It is considered the best result of specific mass and viscosity those closest to the fuel commonly used in compression engines. Considering that S500 diesel fuel values range from 0.820g / ml to 0.865g / ml at 20° C for specific mass, the 10: 1 samples of recovered oil and the 10: 1 samples of *in natura* oil fall within this range. Viscosity at 40° C of the S500 has to vary between 2.0 mm² / s and 5.0 mm² / s. As the viscosity calculation experiment was conducted at a temperature of 28° C, it is imagined that the value will decrease with increasing temperature, and therefore the highest value obtained is considered the best. The best sample, with this, is the Biodiesel Y that presented 3.897 mm² / s.

For LHV, the best value obtained is the higher, that is, the one that has the most energy to provide. In this way, the best fuel in terms of calorific value is Biodiesel Y, with a value of 27.033 MJ / kg which is below the general average of biofuels produced with soybean oil – 39 MJ / kg – and, as expected, much lower than the value presented by mineral diesel of 43 MJ / kg.

Regarding to reaction's yield, the best scenario is the one acquired by the Biodiesel Z – 84% of ester after the transesterification. In spite of this number seems good, still is far from the results obtained by LIN & CHEN (2017), those are above 95%.

A simplified apparatus was created that met the reaction agitation and a funnel decanter, made of recyclable materials that allowed the easy separation of the two final products of the transesterification.

In general the results obtained were lower than expected, the values of viscosity, LHV and specific mass are outside the ANP, DIN and ASTM standards for what characterizes a quality biodiesel. Also, the resulting product was not mixed with S500, which should be characteristic of the ester.

5. REFERENCES

- ANP – National Agency of Petroleum, Natural Gas and Biofuels. Order nº 310 from december 27th, 2001. Establishes the specifications for the commercialization of automotive diesel oil throughout the national territory and defines obligations of the economic agents on the quality control of the product.
- ANP – National Agency of Petroleum, Natural Gas and Biofuels' statistics. CO₂ emissions in national territory in 2008. Brazil, 2009. <<http://www.anp.gov.br/estatisticas>>.
- B.H.U.G., “Biodiesel Handling and Use Guidelines”, Energy Efficiency and National Renewable Energy Laboratory, 5th edition, U.S. Department of Energy, November 2016.
- BIODIESEL STANDARDS GROUP LTD. Biodiesel Standards. <<https://www.biofuelsystems.com/specification.htm>>.
- BRAZIL. Federal Law number 13.263 from march 23rd, 2016. To regulate the percentage of adding biodiesel to diesel oil marketed in the brazilian territory. Brasilia, 2016.
- CORONADO, C. J. R. Thermoconomical Analyses of a Biodiesel Production: Thecnical, Economical and Ecological Aspects. 171f. PhD thesis in Mechanical Engineeirg. Faculdade de Engenharia do Campus de Guaratinguetá, Universidade Estadual Paulista, Guaratinguetá, 2010.
- FERREIRA, S. L.; SANTOS, A. M.; SOUZA, R. G.; POLITO, W. L. Influence of the Reaction Conditions of the Ester Content and Charecterization of Biodiesel via Etyhlic Route. Journal of ASTM International. 2013. v. 9, n. 5. <www.astm.org>.
- LIN, Jar-Jin.; CHEN, Yu-Wen. Production of biodiesel by transesterification of Jatropha oil with microwave heating. Journal of the Taiwan Institute of Chemical Engineers, v. 75, p. 43-50, 2017.
- KNOTHE, G.; GERPEN, J.V.; KRAHL, J.; RAMOS, L. P. The Biodiesel Handbook. São Paulo: Blücher, 2006.
- MENEGHETTI, Simoni P; MENEGHETTI, M. Roberto; YARIADNER, C. Brito. The Transesterification Reaction, Some Applications and Biodiesel Production. Química Nova Magazine, vol. 5, n. 1, 2013. <http://qnint.s bq.org.br/qni/popup_visualizarConceito.php?idConceito=66&semFrame=1>.
- OLIVEIRA, Melina Cais Jecic de. Diesel and Biodiesel of Murumuru and Soybean: Operational Performance of Agricultural Tractor in Tillage. Ph.D thesis, Universidade Estadual Paulista, College of Agrarian and Veterinary Sciences. Jaboticabal, 2015. <https://repositorio.unesp.br/bitstream/handle/11449/134252/oliveira_mcj_dr_jabo_int.pdf?sequence=4&isAllowed=y>.
- OPERATING INSTRUCTION MANUAL PARR 1341 OXYGEN BOMB CALORIMETER. PARR Instrument Company, 2008. <<https://www.parrinst.com>>.
- RAMKUMAR, S., KIRUBAKARAN, V. Biodiesel from vegetable oil as alternate fuel for C.I engine and feasibility study of thermal cracking: A critical review. Energy Conversion and Management. 118. 155-169. 2016.
- RIBEIRO, Dinalva Donizete and DIAS, Mariza Souza. Effects of the Programa Nacional de Produção e Uso de Biodiesel on the peasant territory in the rural settlement. Campo Grande, 2016. <<http://www.scielo.br/pdf/inter/v17n1/1518-7012-inter-17-01-0015.pdf>>.
- SHEEHAN, J., CAMOBRECO, V., DUFFIELD, J., GRABOSKI, M., SHAPOIRI, H., 1998 “ An Overview of Biodiesel and Petroleum Diesel Life Cycles”, National Renewable Energy Laboratory. U.S. Department of Energy, May 1998.

6. RESPONSIBILITY NOTICE

The author is the only responsible for the printed material included in this paper.