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Purification and characterization of glycerin obtained from soybean biodiesel production

The crude glycerin is a raw material which can be applied in a wide range of products, even with all its impurities, without the need for purification. However, the purification processes allow a wider application, making it more salable. With increasing demand for biodiesel, a glycerin excess is being released to the market. Therefore, the search for alternative treatments for the glycerin derived from the biodiesel production process is of utmost importance, ensuring biofuel production flow. This paper presents glycerin purification experiments done in a crude glycerin (64.44% of glycerol) obtained from the soybean biodiesel production, which was subjected to pre-purification process, purification with activated carbon and by ion exchange process. After the purification process the glycerin sample was characterized and compared with commercially used glycerin. The highest content of glycerol achieved was 94.22% corresponding to the steps of: pre-purification process (washing, acidification, separation, neutralization, salting-outing and evaporation); purification with activated carbon and by ion exchange process with mixed resin.

Keywords: Glycerol; Biodiesel; Purification; Ion Exchange; Sustainability.

Purificação e caracterização de glicerina obtida na produção de biodiesel de soja

A glicerina bruta é uma matéria-prima que pode ser aplicada em uma ampla gama de produtos, mesmo com todas as suas impurezas sem a necessidade de purificação. Porém, os processos de purificação possibilitam uma aplicação mais ampla, tornando-a mais vendável. Com o aumento da demanda por biodiesel, um excesso de glicerina está sendo liberado para o mercado. Portanto, a busca por tratamentos alternativos para a glicerina derivada do processo de produção de biodiesel é de suma importância, garantindo o fluxo de produção de biocombustível. Este trabalho apresenta experimentos de purificação de glicerina bruta (64,44% de glicerol) obtida da produção de biodiesel de soja, que foi submetida ao processo de pré-purificação, purificação com carvão ativado e por troca iônica. Após o processo de purificação, a amostra de glicerina foi caracterizada e comparada com glicerina comercialmente utilizada. O maior teor de glicerol obtido foi de 94,22%, correspondendo às etapas de: processo de pré-purificação (lavagem, acidificação, separação, neutralização, salting-outing e evaporação); purificação com carvão ativado e por processo de troca iônica com resina mista.

Palavras-chave: Glicerol; Biodiesel; Purificação; Troca Iônica; Sustentabilidade.

Topic: **Desenvolvimento, Sustentabilidade e Meio Ambiente**

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INTRODUCTION

It can be seen throughout history that various forms of energy have fueled human needs, but this power ever needs to be more efficient and sustainable. Today, the increase in power consumption occurs as humanity uses new technologies. Thus, biodiesel is an excellent biodegradable alternative to the replacement of diesel fuel, however, the growth of production has generated a large surplus of glycerin, which generally results in 10% by weight of the product of transesterification reaction. Called crude glycerin, has impurities such as water, methanol and organic material, which gives it a low commercial value.

Due to increased production of this by-product, arises the need for studies to purification methods so that they can rise to new applications for this glycerin, avoiding a possible discharge to the environment generating high environmental impact. It is necessary to perform a treatment in glycerin in order to achieve a better product value. For this, will be presented in this work some purification processes having the purpose of achieving a degree of purification which safely can be applied to new products. Treatment of glycerin or their direct recycling is necessary to increase the viability of the biodiesel production process, thereby allowing the fuel to become more competitive in the market.

Biodiesel and glycerin background

In its origin, diesel engines were able to function with crude oil and vegetable oils. Depending on the cost of oil at the time, the crude oil has become the fuel widely used in these engines and looking to improve the performance of engines, adjustments were made in the engines in order to use fossil fuel so that the use of vegetable oils now presents function problems due to the high viscosity, yielding deposits in various parts of the engine. Various techniques exist to reduce the viscosity of the vegetable oils, for example, the use of binary mixtures with petroleum diesel, pyrolysis, micro-emulsion and transesterification.

Biodiesel is a mixture of alkyl esters that can be produced from various raw materials (vegetable oils, animal fats, algae), being the transesterification, the most widespread process for the production of biodiesel. This transformation reduces the viscosity of the vegetable oils and animal fats, for example, making the biodiesel fully compliant with the diesel oil in almost all of its properties, allowing its use in diesel engines without the need for modifications. The main stages of the biodiesel production process are: preparation of raw materials; transesterification; separation and purification of the biodiesel. In the process glycerin is produced as a byproduct.

The transesterification is the most common chemical process for the production of biodiesel, in which a triglyceride reacted with an alcohol in the presence of a catalyst, thereby forming mono-alkyl esters (biodiesel) and glycerol. This reaction is reversible being necessary alcohol in excess to displace the equilibrium towards the desired product. The stoichiometry of the reaction is 3: 1 (3 mol of alcohol / 1 mol of triglyceride), being necessary the use of an acid catalyst, basic or enzymatic in order to accelerate the reaction.

Each triglyceride molecule reacts with three molecules of alcohol, occurring the production of a glycerol molecule and three fatty acid ester molecules. Methanol and ethanol are commonly used because of its low cost and appropriate physicochemical properties. A wide variety of triglycerides have been used, such as vegetable oils, animal fats, and others. The choice of the raw material varies depending on the regional supply and influences the production process, purification and quality of the final product.

Biodiesel is an alternative fuel that is becoming accepted in a steadily growing number of countries around the world (ALMEIDA et al., 2015; CAI et al., 2015; DERMIBAS, 2009; GIWA et al., 2014; GÜLÜM et al., 2015; KNOTHE, 2005; NAUTIYAL et al., 2014; ÖZTÜRK, 2015; PEREIRA et al., 2017; PEREIRA et al., 2014; PEREIRA et al., 2012; PEREIRA et al., 2011; PEREIRA et al., 2007). The increase in production of biodiesel also will result in increased byproduct glycerin, which increases proportionally with the production of biofuel because of its proportion being about 10% of total production. The compound obtained in the production of biodiesel is referred to as glycerin, due to mixing with impurities such as water, fatty acid, catalyst etc. However, for use in the pharmaceutical, chemical and in food industry, this glycerin needs to be subjected to a purification process.

Studies of glycerin purification indicate the need for development of new methods of purification according to the type of transesterification, the physical parameters and the glycerin quality. The choice of the appropriate method for the purification depends on many factors, such as: costs employed in the purification system and quality of the final product. Some of the most used glycerin purification techniques are: recovery, concentration, refining, distillation, bleaching and ion exchange.

Morales et al. (2013) purified the glycerin phase from palm-oil biodiesel by ion-exchange with cationic resins. A 96.6% purification level of glycerol was obtained. Hunsom et al. (2013) studied the adsorptive purification of crude glycerol (CG) using sewage sludge-derived activated carbons at a laboratory scale and ambient conditions. The adsorption time and the shaking rate influenced the adsorptive purification of CG. The highest content of glycerol achieved in the glycerin was 96.9% after three adsorption cycle.

Kongjao et al. (2010) studied the purification of crude glycerol derived from waste used-oil methyl ester plant. The experiment was carried out on a laboratory scale by using the combined chemical and physical treatments based upon repeated cycles of acidification to the desired pH. The results indicated that increasing the pH of the acidification step led to an increased yield of the glycerol-rich layer and decreased amount of inorganic salt and free fatty acids phase. At pH = 1, high purity glycerol (~93.34%) was obtained.

Glycerol with a purity of approximately 86% wt. was achieved in the work of Hajek et al. (2010). The glycerin formed by biodiesel production was submitted to neutralization and/or saponification process. In the research of Manosak et al. (2011), a sequential stage physicochemical refining of crude glycerol, derived from a waste used oil utilizing biodiesel (methyl ester) production plant, was performed by acidification, polar solvent extraction and activated carbon adsorption at a laboratory scale and ambient temperature. The highest glycerol purity obtained was 95.74%. A review about progress, prospect and challenges in glycerol purification process is presented by Ardi et al. (2015).

MATERIALS AND METHODS

The glycerin used in purification procedures was obtained from the Rheology Laboratory at Fluminense Federal University where they were available for use. The glycerin was obtained from soybean biodiesel production, using methanol and NaOH as catalyst. Details about the methodology used in the analysis can be found in Ferreira (2009) and ANVISA (2010).

Glycerin pre-purification

The pre-purification steps of the glycerin are detailed below.

Washing with solvent

A sample of 100 ml of glycerin was transferred to a separating funnel which was added about 30 ml of hexane, being the funnel capped and shaken. The mixture was left to stand for 24 hours for the separation of the phases. This step was aimed at extracting waste of esters and triglycerides. After separating, the hexane phase was recovered by using a rotary evaporator, weighing the residue.

Acidification

Because glycerin is rather viscous at room temperature, the sample was heated to 60 ° C. Then, slowly titrated with sulfuric acid (H_2SO_4 6N, 98%) until pH = 4, using measuring strips as an indicator of pH. Sulfuric acid reacts with the soap present in the mixture to form free fatty acids.

Separation

The acidified sample was placed in a separating funnel and allowed to stand for a period of 2 hours for phase separation. The light phase is composed of fatty acids and the heavy phase comprises glycerin, which was separated.

Neutralization

The sample was neutralized at room temperature with sodium hydroxide (NaOH 6N) until pH between 6.5 and 7.5 (pH measuring was made using indicator strips). Then the glycerin was filtered to retain soaps and other impurities.

Salting-Outing

Corresponds to the final step of pre-purification, this process is known as precipitation by antisolvent, having for its function to remove the salts formed during the acidification process and neutralization, a simple method in which ethanol PA was added to the samples in the ratio 2:1 relative to the volume of glycerin and waiting 24 hours for decant and thereafter, centrifuged for 5 min at 5000 rpm. For a better retention of impurities, glycerin was filtered using diatomite as filter medium.

Evaporation

The ethanol was evaporated using a rotary evaporator, in order to obtain only glycerin and water. The process was conducted until to obtain the initial quantity of alcohol used in salting-outing process so that it could be reused.

Adsorption with activated carbon

Activated carbon was used in the treatment for removal of color and odor of the glycerin sample as detailed next.

Activated carbon quantity

For color removal, tests were carried out using different activated carbon mass (1.0, 2.0, 3.0, 4.0 and 5.0 g) for each 50 ml of pre-purified glycerin solution (diluted 35% glycerin in water). Then, absorbance was measured in UV-Visible in wavelength corresponds to the color.

Contact time

The glycerin solution was left in contact with the activated carbon for a period of 15 consecutive hours, over that time, samples were taken after 1 and 5 hours, being measured: conductivity; pH and glycerol content. After that it was filtered using diatomite.

Purification of pre-purified glycerin by ion exchange

The resins used in this process were: C-160 (cationic) and A-133 (anionic) and a mixed resin (Purolite mark). To ensure good diffusion through the resin, in all cases the glycerin was diluted in distilled water at an average concentration of 35% pre-purified glycerin. Assays were performed passing the solution through the resins, first in series: through the cationic resin; then through the anionic resin and then through the mixed resin, and further, assays were performed individually with each type of resin, evaluating its effect by determining the electrical conductivity of glycerin, using a digital conductivity meter Tecnopon/MCA-150.

To evaluate the improved performance of resins and consequently obtain a better quality of glycerin, it was made four steps of ion exchange processes known as 1st, 2nd, 3rd and 4th: 1st. Resins in series - passing the solution through the cationic resin, then through the anionic resin and then through the mixed resin; 2nd. Resin individually - passing the solution through the cationic resin; 3rd. Resin individually - passing the solution through anionic resin; 4th. Resin individually - passing the solution through the mixed resin.

Glycerin characterization

Glycerol content

The glycerol content was measured using the method of sodium periodate that consist in the sample dilution using distilled water, followed by acidification with sulfuric acid 0.1 N to pH 4, using bromocresol green as indicator. After, the sample was neutralized with sodium hydroxide 0.05 N until reach blue color and adding 10 ml of sodium periodate, 60 g.l^{-1}. The sample was allowed to stand in the dark for 30 min, then was added 1 ml of 99.5% ethylene and again remained in the dark for further 20 min. Then, the sample was diluted to a volume of 30 ml with distilled water and titrated with sodium hydroxide 0.125 N.

Color analysis

The analysis was performed using a colorimeter, calibrated with standard color of 5, 100, 500 and 3,500 color unit.

Density

Previously, a pycnometer was washed, dried and weighed. Water was placed at the test temperature (28°C) and measured its mass. So, with the density of water at 28°C the volume of the pycnometer is determined. After that, the pycnometer is emptied, cleaned and dried. Then the sample was added in the same pycnometer at 28°C and the mass was measured. The difference between the obtained value and the mass of the pycnometer was the mass of the sample. The density of glycerin (ρ) is the ratio between the sample mass (m) and volume of the pycnometer (v).

Determination of the presence of chlorides

The titration was done in triplicate, approximately 0.5 g of each sample was diluted in 10 ml of distilled water with silver nitrate solution (1% w/v, PA) previously standardized with sodium chloride solution (0.01 N). As an indicator, it was used 1 ml of 5% (w/v) potassium chromate in the diluted sample, then, titrated to a reddish color.

Determination of alkalinity

The titration was done in triplicate, approximately 0.5 g of each sample was diluted in 10 ml of distilled water with sulfuric acid solution (0.01 N) previously standardized with standard sodium carbonate (0.01 N). As an indicator, it was used three drops of bromocresol green in the diluted sample, then titrated to a green color.

Determination of the presence of sulfates

It was used 300 ml of an aqueous solution of glycerin (10% w/v), it was added 3 drops of aqueous solution of chloric acid (10% w/v) and 5 drops of aqueous solution of barium chloride PA 1 % (w/v). After mixing, it should not be observed precipitation or turbidity.

Determination of the presence of sucrose

It was added 4 ml of glycerin in 6 ml of 0.5 M sulfuric acid, heating the mixture for 1 minute. After cooling, the mixture was neutralized with 0.5M sodium hydroxide solution. Then, it was added 5 ml of

Fehling's reagent and heated to boiling for 1 minute. Should not produce red brick precipitate.

Determination of the Presence of acrolein, glucose and of ammonium substances

It was mixed 5 ml of glycerin with 5 ml of aqueous solution of potassium hydroxide 10% (w/v). The mixture was heated to 60°C for 5 minutes. It should not be seen yellow color and it should not have release of ammonia.

Sodium content (Na^+)

It was used a flame spectrophotometer for the analysis of solutions prepared by 1000 ppm of sample of glycerin.

Determination of electrical conductivity

It was determined according to ASTM D1125-95 (2005) using a DIGMED/DM 31 equipment.

pH determination

The pH was determined according to ASTM D 1293-99 (2005) using a TECNAL/3MP equipment.

RESULTS

Characteristics of crude glycerin

Sample of crude glycerin from soybean biodiesel production was subjected to characterization of glycerol content and color, the results are shown in Table 1.

Table 1: Characterization of the crude glycerin of soybean biodiesel production

Parameter	**Crude glycerin**
Glycerol content (%)	64.44
Color (Pt-Co)	845

Glycerin pre-purification characterization

The pre-purification step of the crude glycerin was effective in removal most of the impurities. In Table 2 is shown the result of the characterization of the pre-purified glycerin sample from soybean biodiesel production. It can be observed that the glycerol content of the sample increased as compared to the sample of crude glycerin. A Glycerin to be considered blonde must have a minimum purity of 80%. Thus, the glycerin after the pre-purification process can already be considered blonde glycerin. With this purity, the glycerin may already be applied in the production of plastics, additives, biofilms, among others (MOTA et al., 2011).

Table 2: Characterization of the pre-purified glycerin

Parameter	**pre-purified glycerin**
Glycerol content (%)	85.45
Color (Pt-Co)	166
Sodium content Na^+ (ppm)	3.32

Adsorption with activated carbon

Activated carbon quantity

Visually, from 3 grams of activated carbon per 50 ml of glycerin it was sufficient to eliminate the color, according to absorbance measurements at the wavelength equivalent to color.

Contact time

Table 3 shows the results for the contact time of 50 ml of pre-purified glycerin with each 3 g of activated carbon. According to the results shown, it can be observed that the conductivity and pH remained nearly constant over time. The glycerol content decreased with time, indicating that the activated carbon was adsorbing the glycerol, which was not desired. In the case of the color, it can be seen that in only 1 hour of contact of the activated carbon with the glycerin was sufficient for complete removal of color.

Table 3: Carbon contact time analysis of the pre-purified glycerin

Contact time	Conductivity (µS/cm)	pH	Glycerol content (%)
1 hora	1162	10,71	82,15
5 horas	1209	10,21	53,34
15 horas	1212	10,72	51,29

Purification of pre-purified glycerin by ion exchange

Table 4 shows the results for the treatment of the glycerin using each resin individually and in series (5 hour of contact), after passing the pre-purified glycerin by the activated carbon (1hour of contact). The values of the glycerol content in all tests are displayed excluding the mass of water in the solution, since the use of water is needed to perform the entire experimental procedure.

According to the conductivity values shown in Table 4, it can be noted that: for the treatments performed with resins in series (Result A) and mixed resin (Result D) the conductivity of the solution decreased significantly; in the case of treatment with cation resin (Result B), the conductivity decreased, and in the treatments with anionic resin (Results C) the conductivity increased.

Regarding the pH, this remained acid in the case of glycerin solution treated with cationic resin (Result B). It remained basic to glycerin solution treated with the anionic resin (Result C) and near neutral when treated with the mixed resin and series resin (Results A and D). Concerning the values of the glycerol content, after passing through the activated carbon, it was observed that there was a small adsorption of glycerol in the process, however the glycerin passing through activated carbon is indispensable for the removal of color and odor. Making a comparison with treatment using different types of resin, it can be seen that the cation and anion resins, individually (Results B and C) had worse results keeping the glycerol content in a percentage lower than the samples of pre-purified glycerin and pre-purified glycerin treated with activated carbon. For the series resins (Result A), glycerol content remained close to the result of treatment with activated carbon. In the case of the mixed resin (Result D), it is observed that the glycerol content increased. This was probably due to the retention of compounds in the resin and little or no retention of glycerol, making the solutions more concentrated in glycerol content.

Table 4: Characterization of the crude glycerin, pre-purified glycerin, and pre-purified glycerin treated with activated carbon (1 hour of contact) and resins (5 hours of contact)

Sample	Conductivity (µS/cm)	pH	Gyicerol content (%)
Crude glycerin	7360	12.51	64.44
Pre-purified glycerin	1311	9.5	85.45
Pre-purified glycerin treated with activated carbon	1162	10.71	82.15
Pre-purified glycerin treated with activated carbon and resins in series (Result A)	29	6.4	85.01
Pre-purified glycerin treated with activated carbon and cationic resin (Result B)	1096	3.4	80.37
Pre-purification glycerin treated with activated carbon and anionic resin (Result C)	1645	11.78	76.12
Pre-purification glycerin treated with activated carbon and mixed resin (Result D)	13.77	7.8	94.22

Characterization of purified glycerin

The results of physicochemical analysis of purified glycerin (pre-purified glycerin treated with activated carbon and mixed resin), which showed the best results regarding the proportion of glycerol, are shown in Table 5. Table 6 shows the characterization of glycerin after the process of purification with activated carbon and ion exchange resin (mixed resin) compared to the properties of commercial pure glycerin. The pure glycerin used as a comparison was obtained in Synth Vegetable Glycerin USP ($C_3H_8O_3$) G287402 BJ lot.

Table 5: Characterization of pre-purified glycerin treated with activated carbon and by ion exchange with mixed resin.

Parameter	Purified Glycerin
Glycerol (%)	94.22
Alkalinity (%)	0.0010
Chlorides (%)	0.0034
Color (Pt-Co)	35.20
Na^+ (ppm)	5.333
pH	7.8
Conductivity (µS/cm)	13.77
Density at 28°C	1.00056 g/ml

Table 6: Comparison of pure commercial glycerin with glycerin purified with activated carbon and by ion exchange with mixed resin.

Parameter	Purified glycerin (with activated carbon and by ion exchange with mixed resin)	Pure commercial glycerin
Appearance control	Syrupy liquid, odorless, colorless	Syrupy liquid, odorless, colorless
Presence of chlorides	No presence of chlorides	No presence of chlorides
Determination of acrolein, glucose and ammoniacal substances	slightly yellowish, with no release of ammonia	Colorless, with no release of ammonia
Presence of sulfates	No presence of sulfates	No presence of sulfates
Determination of Sucrose	None sucrose	None sucrose
pH	7.8	6.65
Conductivity (µS/cm)	13.77	4.11
Glycerol content	94.22	≥ 95
Density	1.00056 g/ml (at 28°C)	1,25 g/ml (at 20°C)

CONCLUSIONS

The pre-purification of glycerin was effective for removal of impurities, salts and free fatty acids that make up the color and odor of glycerin. The activated carbon, whether or not retaining a small percentage of glycerol, was important for removing the color and odor of the pre-purified glycerin. Making a comparison with the types of resin used in the process of purification by ion exchange, it can be seen that the cation and anion resins, individually, were ineffective in the treatment, keeping the glycerol content lower than the sample of the pre-purified glycerin and treatment with activated carbon. For series resins, the results were unsatisfactory, with a percentage of purification only slightly higher compared to treatment with activated carbon, in order that it was the more costly treatment having used all types of resin. The most efficient result presented after the entire process is related with the processing of purification by ion exchange with the mixed resin, wherein the glycerol content increased considerable in the glycerin.

It is shown as well in this present study that the glycerin purified with activated carbon and by ion exchange using mixed resin has, in general, similar properties when compared with commercial pure glycerin. The purification of crude glycerin is important in order to achieve a better product value, rising new applications for this glycerin, avoiding a possible discharge to the environment generating high environmental impact. Treatment of crude glycerin or their direct use is important to increase the viability of the biodiesel production process, thereby allowing the fuel to become more competitive in the market and contributing to a more sustainable development.

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REFERENCES

ALMEIDA, V. F.; GARCÍA-MORENO, P. J.; GUADIX, A.; GUADIX, E. M.. Biodiesel production from mixtures of waste fish oil, palm oil and waste frying oil: Optimization of fuel properties, **Fuel Processing Technology,** v.133, p.152-160, 2015. **DOI:** https://doi.org/10.1016/j.fuproc.2015.01.041

ANVISA. Agência Nacional de Vigilância Sanitária. **Brazilian Pharmacopoeia.** 5 ed. Brasilia: ANVISA, 2010.

ARDI, M. S.; AROUA, M. K.; HASHIM, N. A.. Progress, prospect and challenges in glycerol purification process: A review, **Renewable and Sustainable Energy Reviews**, v.42, p.1164-1173, 2015. **DOI:** https://doi.org/10.1016/j.rser.2014.10.091

CAI, Z. Z.; WANG, Y.; TENG, Y. L.; CHONG, K. M.; WANG, J. W.; ZHANG, J. W.; YANG, D. P.. A two-step biodiesel production process from waste cooking oil via recycling crude glycerol esterification catalyzed by alkali catalyst, **Fuel Processing Technology**, v.137, p.186-193, 2015. **DOI:** https://doi.org/10.1016/j.fuproc.2015.04.017

DEMIRBAS, A.. Biofuels securing the planet's future energy needs, **Energy Conversion and Management**, v.50 n.9, p.2239-2249, 2009. **DOI:** https://doi.org/10.1016/j.enconman.2009.05.010

FERREIRA, M. O.. **Purification of crude glycerin obtained from the transesterification of cottonseed oil**. Dissertação (Mestrado em Engenharia Química) - Universidade Federal do Rio Grande do Norte, 2009.

GIWA, S. O.; CHUAH, L. A.; ADAM, N. M.. Fuel properties and rheological behavior of biodiesel from egusi (Colocynthis citrullus L.) seed kernel oil, **Fuel Processing Technology**, 122, 42-48, 2014. **DOI:** https://doi.org/10.1016/j.fuproc.2014.01.014

GÜLÜM, M.; BILGIN, A.. Density, flash point and heating value variations of corn oil biodiesel–diesel fuel blends, **Fuel Processing Technology**, v.134, p.456-464, 2015. **DOI:** https://doi.org/10.1016/j.fuproc.2015.02.026

HAJEK, M.; SKOPAL, F.. Treatment of glycerol phase formed by biodiesel production, **Bioresource Technology,** v. 101, p.3242-3245, 2010. **DOI:** https://doi.org/10.1016/j.biortech.2009.12.094

HUNSOM, M.; AUTTHANIT, C.. Adsorptive purification of crude glycerol by sewage sludge-derived activated carbon prepared by chemical activation with H_3PO_4, K_2CO_3 and KOH, **Chemical Engineering Journal**, v.229, p.334-343, 2013. **DOI:** https://doi.org/10.1016/j.cej.2013.05.120

KNOTHE, G.. Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters, **Fuel Processing Technology**, v.86, p.1059-1070, 2005. **DOI:** https://doi.org/10.1016/j.fuproc.2004.11.002

KONGJAO, S.; SOMSAK, D. S.; HUNSOM, M.. Purification of crude glycerol derived from waste used-oil methyl ester plant, **Korean J. Chem. Eng.**, v.27, n.3, p.944-949, 2010. **DOI:** https://doi.org/10.1007/s11814-010-0148-0

MORALES, L. J. G.; LÓPEZ, F. C.; RIOS, L. A.. Refining the glycerin phase from palm-oil biodiesel by ion-exchange with cationic resins, **J Chem Technol Biotechnol**, v.88, p.1978-1983, 2013. **DOI:** https://doi.org/10.1002/jctb.4054

MANOSAK, R.; LIMPATTAYANATEA, S.; HUNSOM, M. Sequential-refining of crude glycerol derived from waste used-oil methyl ester plant via a combined process of chemical and adsorption, **Fuel Processing Technology**, v.92, p.92-99, 2011. **DOI:** https://doi.org/10.1016/j.fuproc.2010.09.002

MOTA, C. J. A.; PESTANA, F. M.. By-products of Biodiesel Production. **Rev. Virtual Quim.,** v.3, n.5, p.416-425, 2011. **DOI:** http://dx.doi.org/10.5935/1984-6835.20110045

NAUTIYAL, P.; SUBRAMANIAN, K. A.; DASTIDAR, M. G.. Production and characterization of biodiesel from algae. **Fuel Processing Technology**, v.120, p.79–88, 2014. **DOI:** https://doi.org/10.1016/j.fuproc.2013.12.003

ÖZTÜRK, E.. Performance, emissions, combustion and injection characteristics of a diesel engine fuelled with canola oil–hazelnut soapstock biodiesel mixture, **Fuel Processing Technology**, n.129, p.183-191, 2015. **DOI:** https://doi.org/10.1016/j.fuproc.2014.09.016

PEREIRA, R. G.; TULCAN, O. E. P.; FELLOWS, C. E.; BRAZ, A. J. L.. Energy generation and exhaust emissions analysis in a stationary engine using palm biodiesel, palm oil and diesel. **Int J Oil Gas and Coal Technology**, v.16, n.4, p.402-421, 2017. **DOI**: https://doi.org/10.1504/IJOGCT.2017.10008349

PEREIRA, R. G.; TULCAN, O. E. P; FELLOWS, C. E.; SILVA, I. M.; SANTO FILHO, D. M. E.; LAMEIRA, V. J.; QUELHAS, O. L. G.. Energy generation using coconut biodiesel and coconut oil in a stationary engine**, Int J Oil Gas and Coal Technology**, v.7, n.4, p.450-473, 2014. **DOI:** https://doi.org/10.1504/ijogct.2014.062165

PEREIRA, R. G.; TULCAN, O. E. P.; FELLOWS, C. E.; LAMEIRA, V. J.; QUELHAS, O. L. G.; AGUIAR, M. E.; SANTO FILHO, D. M. E.. Sustainability and mitigation of greenhouse gases using ethyl beef tallow biodiesel in energy generation, **Journal of Cleaner Production**, v.29, n.30, p.269-276, 2012. **DOI:** https://doi.org/10.1016/j.jclepro.2012.01.007

PEREIRA, R. G.; TULCAN, O. E. P.; LAMEIRA, V. J.; SANTO FILHO, D. M. E.; ANDRADE, E. T.. Use of soybean oil in energy generation. in: KREZHOVA, D.. Recent trends for enhancing the diversity and quality of soybean products. **InTech Publishing,** Rijeka, p.301-320, 2011. **DOI:** https://doi.org/10.5772/17771

PEREIRA, R. G.; OLIVEIRA, C. D.; OLIVEIRA, J. L.; OLIVEIRA, P. C. P.; FELLOWS, C. E.; PIAMBA, O. E.. Exhaust emissions and electric energy generation in a stationary engine using blends of diesel and soybean biodiesel, **Renewable Energy**, v.32, n.14, p.2453-2460, 2007. **DOI:** https://doi.org/10.1016/j.renene.2006.05.007