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PLASMA-ASSISTED CATALYTIC ROUTE FOR THE PRODUCTION OF BIODIESEL

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Abstract. *The development of biofuels is increasing to reduce the dependence on fossil fuels and their impacts on climate change. Plasma-assisted catalytic reactors are promising strategies to produce biodiesel, since it runs at room temperature and atmospheric pressure. The objective of this work is to develop a plasma-assisted catalytic route for the production and purification of biodiesel. The basic homogeneous catalyst* $NaOCH_3$ *will be used together with the plasma reactor to favor the transesterification reaction. The reaction occurred at room temperature, atmospheric pressure, molar ratio of methanol and soybean oil of 6:1. After the reaction, the product were undergo purification steps that include decanting, acid washing and drying. Different production and purification conditions were tested and the highest ester content (63.7 ± 5) was obtained with* $NaOCH_3$ *0.1%, 15.6 kV and 30 min of reaction. With the purification method employed here, a clear and residue-free final product was obtained.*

Keywords: *Plasma catalysis, Homogeneous catalysis, Biodiesel, Soybean oil*

1. INTRODUCTION

Approximately 25% of CO_2 emissions come from the transport sector (IEA, 2019). Besides that, the emission of particulate matter by diesel vehicles represent a threat to human health and the environment (Yang *et al.*, 2019). The development of biofuels is increasing as they provide lower environmental impacts and to reduce dependence on fossil fuels. Biodiesel is a renewable, biodegradable, and non-toxic fuel that can replace fossil-based diesel, leading to the effective reduction of greenhouse gases emissions (Onukwuli *et al.*, 2017).

The conventional process for biodiesel production is based on the transesterification reaction, in which the triglycerides from oils reacted with alcohols to produce fatty acid alkyl ester (FAAE) and glycerol (Van Gerpen and Knothe, 2005). The transesterification reaction normally occurs in the presence of a catalyst as a promoter. The catalysts can be either acidic or basic in a heterogeneous or homogeneous phase, or enzymatic (Khodadadi *et al.*, 2020). Currrently, biodiesel is produced mainly using basic homogeneous catalysis and soybean oil is the main raw material used.

Advanced routes have been developed to reduce reaction time and temperature. In addition, the use of advanced technologies, such as plasma, can favor the use of cheaper raw materials, such as residual oils (Li *et al.*, 2019). Plasma-assisted catalytic reactors are considered promising strategies, as it is possible to produce biodiesel at room temperature and atmospheric pressure. In addition, the plasma associated with a catalyst provides a synergistic effect, making it possible to obtain high conversions in shorter reaction times (Palm *et al.*, 2022).

In addition to the production route, purification methods also directly influence the efficiency of biodiesel production. After the reaction to obtain biodiesel, the product formed undergoes some purification steps to obtain a biodiesel free of impurities. The purification steps are carried out with the purpose of separating by-products produced together with biodiesel, as well as separating remaining reagents such as excess methanol and the catalyst used. Several purification processes are found in the literature and industrially, and the efficiency of the purification steps will influence the maximum yield of the desired product and the productivity of the industrial plant. In addition, the efficiency of the purification steps is of great importance for the production of high quality biodiesel that meets the established national standards, influencing the performance of its use, as well as protecting the engines from possible damage (Bashir *et al.*, 2022).

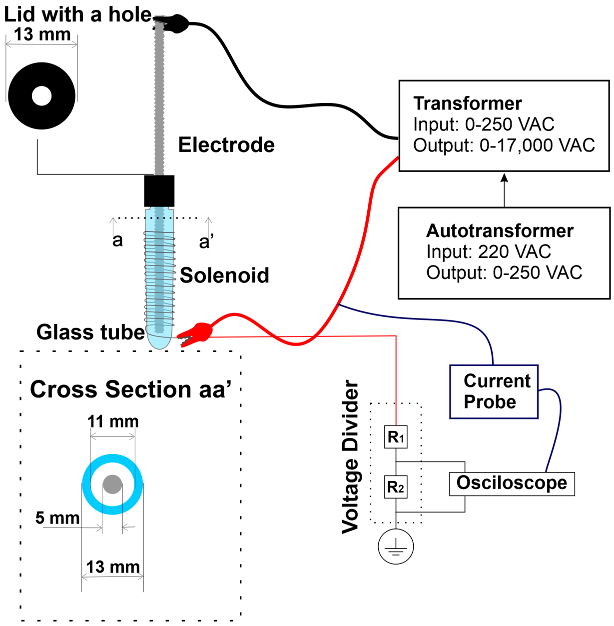
The objective of this work is to develop a plasma-assisted $NaOCH_3$ catalytic route for the production and purification of biodiesel from soybean oil at room temperature and atmospheric pressure.

2. MATERIALS AND METHODS

2.1 Plasma-catalytic rector

Transesterification reactions was performed in a dielectric barrier discharge (DBD) plasma reactor at atmospheric pressure. Figure 1 represents the scheme of the experimental setup. The plasma reactor was build with a 7 cm^3 boron silicate tube. The internal electrode consists of a 5mm diameter stainless steel rod placed in the center of the tube while the external electrode is a stainless steel wire placed as an spiral around the tube. The electrical discharges occurs inside the glass tube between the two electrodes. A plastic cap is used to remain the reactor closed while keeps the internal electrode concentric to the tube. The reactor runs under batch operation. Each run is performed with a 5 cm^3 of fresh reactants, keeping a void volume of 2 cm^3 filled with atmospheric air. The electrical discharges visually occurs in the liquid phase.

Figure 1. Scheme of the experimental setup used for transesterification reaction.



An autotransformer of alternating current was used connected to a transformer to provide a high operational voltage. The qualitative behavior of the transformer's input wave function is the same as the output signal. Autotransformer is single-phase and the transformer is two-phase. The DBD plasma was generated by regulating the voltage in the autotransformer.

2.2 Reactants

The transesterification reaction occurred between soybean oil and methanol (CH_3OH) in a molar ratio of 6:1. Degummed soybean oil donated by the company ADM do Brasil was used. Table 1 summarizes the reaction conditions such as catalyst content, time of reaction and plasma applied voltage.

2.3 Purification

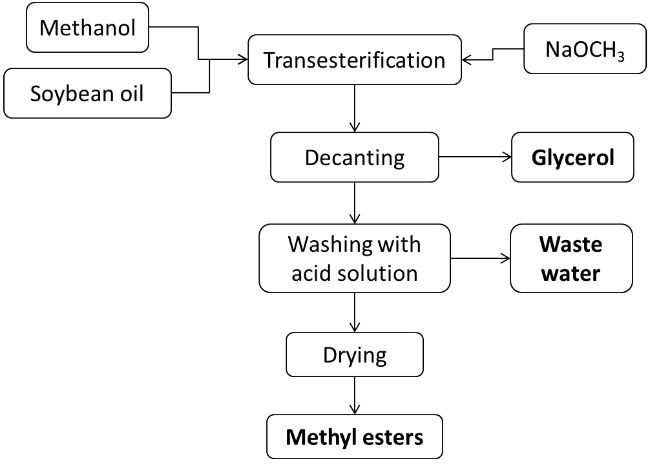
Purification is an important step to obtain high quality biodiesel, eliminating residues, catalysts and unreacted reagents. These residues can be glycerol, water or another component that may be present in the product after the transesterification reaction. Product purification is composed of three main steps: decanting, washing and drying. Figure 2 presents the

Table 1. Tested conditions with soybean oil in the plasma-assisted catalytic reactor.

Condition	Catalyst, mass content (%)	Plasma applied voltage (kV)	Reaction time (min)
I	$NaOCH_3$, 0,1%	15,6	30
II	$NaOCH_3$, 0,1%	15,6	19
III	$NaOCH_3$, 0,1%	3,1	30
IV	$NaOCH_3$, 0,2%	3,1	30
V	$NaOCH_3$, 0,5%	3,1	30

flowchart of the purification steps used in this work and the products generated in each phase. The methodologies used in each step will be detailed below.

Figure 2. Flowchart of the steps of production and purification of methyl ester from soybean oil.



2.3.1 Decanting

In this first step of purification, the product was placed in a separating funnel and product was separated into two phases. It was considered that the product of interest was the lightest phase and glycerol was the heaviest phase, since biodiesel has a density of 0.88 g/cm^3 and glycerol has a density of 1.26 g/cm^3. The separation process was analyzed after 30 min, 1 h, 2 h, 4 h, 6 h and 24 h of decantation. The glycerol was removed and weighed on an analytical balance (accurately of ± 0.001g) and the product that remained on top was collected and sent to the next purification step.

2.3.2 Washing

The second purification step consisted of washing the light phase generated in the decantation to remove the remaining catalyst, methanol and glycerol. The washing step was carried out with an acid solution in order to neutralize the pH of the product, which was found to be basic due to the catalyst used. The solution was prepared with a molar concentration sufficient to neutralize the basic catalyst, therefore, the molar concentration of acid depended on the mass content of the catalyst. The washing step was realized with acid solution with water heated at 85 °C, and at room temperature. In addition, it was tested the washing with fast agitation and with a slower agitation.

After washing with acid solution, the mixture was left decanting for 1 hour to separate phases. The residual water was removed of the funnel and your mass was measured on an analytical balance (accurately of ± 0.001g). After washing, the pH of the sample was checked with pH indicator paper. The mass of the sample was measured in an analytical balance (accurately of ± 0.001g), and sent to the next purification step.

2.3.3 Drying

Drying was the third and last step of biodiesel purification, with the objective of removing particles of water and methanol that remained after the washing step. Two different equipments were used in the drying process. Some samples were dried using an analog hot plate, heated to approximately 105 °C. Other samples were dried in a closed oven at 105 °C. To determine the drying time, the sample was left in the drying condition and checked at intervals of 4 hours, 6 hours, 12 hours and 24 hours.

2.4 Product characterizations

The product generated after the transesterification reaction and the purification steps was characterized by density and chromatographic procedure.

Density was determined as the ratio between the mass of the product and the volume, according to Eq. (1). The mass was determined using an analytical balance and the volume was determined with the aid of a graduated pipette. The uncertainty of equipment used at the analyses are presented at Table 2.

$$\rho_{sample} = \frac{m_{sample}}{V_{sample}} \tag{1}$$

Equipament	Capacity	Tolerance
Pipette	2 mL	±0,02
Balance	200 g	±0,0001

Table 2. Tolerance of equipments used on density analysis

The propagation of experimental uncertainty of density measurements was determined as defined in (INMETRO, 2008). The propagation of density uncertainty is the combined uncertainty of the mass and volume measurements, determined by the positive square root of the standard deviation, σ_ρ^2, as presented in Eq. (2), where σ is the tolerance of equipment.

$$\sigma^2_{\rho_{sample}} = (\frac{1}{V_{sample}})^2 \sigma^2_{balance} + ln(m_{sample})^2 \sigma^2_{pipette} \tag{2}$$

Samples that presented density close to the density of biodiesel of 0.88 g/mL were sent for analysis of ester content. The determination of the ester content was carried out according to the European standard test method EN 14103, using a gas chromatograph coupled to mass spectrometry (GC-MS). Ester content analyzes were performed at the Laboratory of Automotive Fuel Analysis (LACAUT), at the Federal University of Paraná (UFPR).

3. RESULTS

Below will be presented the results regarding to the different methodologies adopted in the steps of product purification, then the products of transesterification reaction is presented.

3.1 Purification methods

With Fig. 3 it is possible to observe that most of the residues formed in the process, after the transesterification reaction, were decanted in 1h. In the following hours, no major changes were observed in the decantation only in the opacity of the sample after 24 hours. From that, it was considered that the time of 1h was the most optimized, because the sample will still go through washing and drying steps that will improve the opacity of the sample.

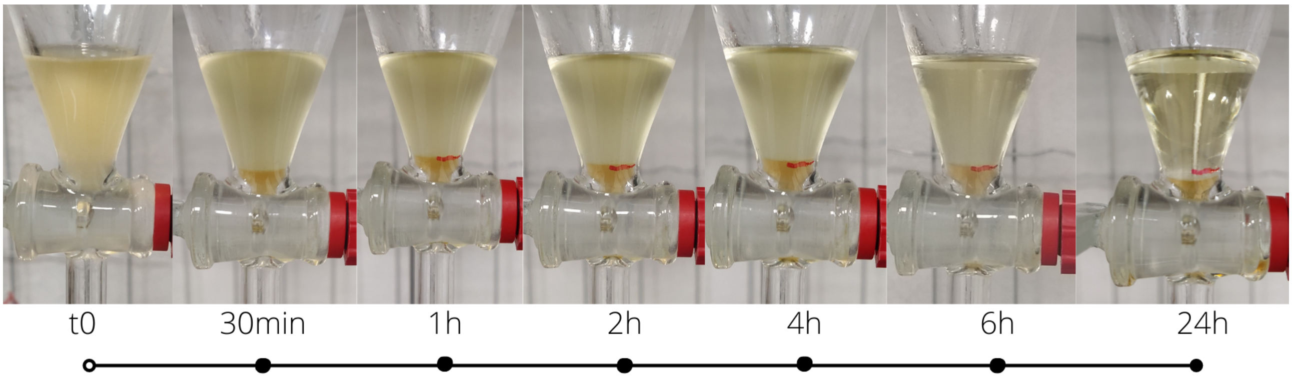


Figure 3. Photos obtained after different decantation times, after the transesterification reaction.

The washing process was tested under different conditions, such as with heated distilled water and at room temperature, and with slow and fast agitation. First, it was tested the washing with water at 85 °C. In this test, when adding the solution to the sample, the sample immediately became a whitish emulsion. Even after 1h of decantation, it was not possible to separate the sample from the formed emulsion. In the test using acid solution at room temperature, there was only emulsion formation depending on the agitation. According the stirring speed was increasing, more emulsion was formed. When the speed are small, few emulsion was observed. Thus, it was determined that the elevated temperature of the water and the stirring speed influence on formation of the emulsion and decreases the yield of the product of interest

Furthermore, initially, the exact volume of hydrochloric acid solution needed for each wash was prepared. As the amount of acid was small, the micropipette used had an error observed, the pH of the final products was not the same and in some cases more than one wash was necessary to neutralize the pH of the sample. To solve this problem, a larger volume of hydrochloric acid solution was prepared at the same desired molar concentration, and aliquots of this prepared solution were withdrawn to each washing.

Therefore, the methodology established for the washing step was just one wash with an acid solution at room temperature and at the ideal concentration to neutralize the pH of the sample, and with agitation in slow circular motions.

To remove the water and methanol it needs to dry the product. Initially was used an analogue hot plate, where heat is conducted through the plate to the base of the beaker. However, this equipment stays on the laboratory bench and open to the room temperature, so that wasn't efficient and was very difficult determine a single and repetitive process. From that, was used a stove, where the temperature can be selected with more precision and the heat inside of the chamber is uniform.

In tests with drying times of 4h, 6h and 12h, a few days after the purification process was observed a heterogeneous residual, that was attributed to the presence of water in the sample. The samples dried for 24h and 105 °Cin the oven did not show the formation of residues after a few days, so all the water and residues were evaporated and this was the method established for drying.

The standard methodology of purification was defined as 1h of decantation, washing with an acidic solution of HCl 37% at room temperature and slow stirring followed by a new decantation for 1h, and finally, drying for 24h in an oven at 105 °C. Figure 4 shows the appearance of the samples after the best purification conditions and that were forwarded to the characterization steps.

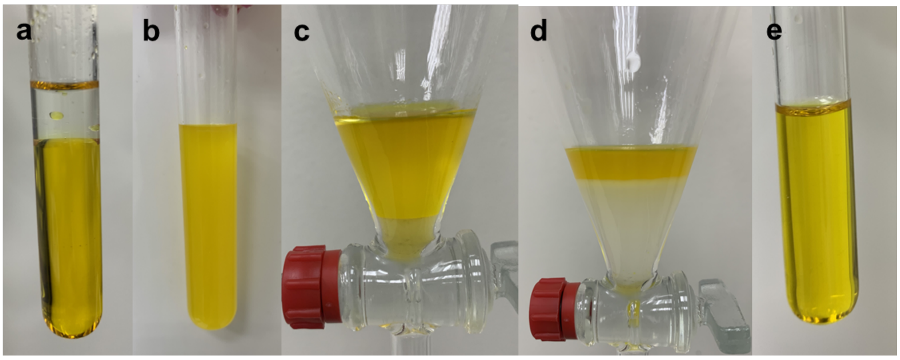


Figure 4. Photos of the different stages of production and purification of biodiesel: a) Reagents before the reaction; b) Products after the reaction; c) Separation of glycerol and biodiesel after 1h of decantation; d) Product after washing and another 1h of decanting; e) Final product after drying.

3.2 Product characterizations

After the purification step, the samples were characterized by density. Samples with a density of 0.88 g/mL were sent for ester content analysis. Table 3 presents the content of esters obtained in the transesterification reaction of soybean oil, for the conditions presented in Table 1.

Table 3. Conditions tested in the transesterification reaction of soybean oil and the ester contents obtained.

Condition	Catalyst	Plasma applied voltage, kV	Reaction time, min	Ester content, %
I	$NaOCH_3$ 0,1%	15,6	30	63,7 ± 5
II	$NaOCH_3$ 0,1%	15,6	19	58,4 ± 5
III	$NaOCH_3$ 0,1%	3,1	30	45 ± 5
IV	$NaOCH_3$ 0,2%	3,1	30	40,7 ± 5
V	$NaOCH_3$ 0,5%	3,1	30	54,9 ± 5

With the results presented in the Table 3 can be seen that the reaction with maximum voltage of 15.6 kV and 30 min of reaction was the condition that presented the highest ester content. The plasma applied voltage influences the conversion of triglycerides to esters because the high-energy electrons generated in the plasma collide with the reactant molecules and break the electron pairs of the unsaturated O–C bonds in the triglyceride, forming carbonated carbonyls. The carbonyl carbon of the excited triglyceride molecules becomes so weak that it can readily react with a methoxide anion (Purwanto *et al.*, 2020).

With the maximum voltage applied to the plasma, the highest ester conversions are obtained, however, it is also in this condition that the highest power applied to the plasma is obtained, and thus, the highest energy expenditure. Therefore, conditions were tested with a lower voltage applied to the plasma (3.1 kV) and with different levels of catalyst (conditions III, IV and V in the Table 3). It can be seen that the reaction was not sensitive with the change in mass contents from 0.1 to 0.2 % of $NaOCH_3$ (conditions III and IV), obtaining very similar values when considering the error tolerance range of ± 5%. On the other hand, increasing the catalyst content to 0.5% (condition V) it is obtained 54.9% of ester content. This result shows that the catalyst content is a sensitive factor in the conversion of biodiesel, as also observed by Wu *et al.* (2019).

4. CONCLUSIONS

The developed plasma reactor proved to be efficient in the transesterification reaction of soybean oil, even operating at room temperature and atmospheric pressure. In addition, the present work also presented a biodiesel purification methodology in which clear and residue-free biodiesel is obtained.

Of the conditions analyzed in the transesterification reaction with soybean oil, the routes with the highest voltages applied to the plasma (15.6 kV) had the highest ester contents (63.7% in 30 min of reaction and 58.4% in 19 min). Reducing the applied voltage from 15.6 kV to 3.1 kV, the ester contents obtained are also reduced. However, the reaction condition with 0.5% of $NaOCH_3$, 30 min of reaction and 3.1 kV of voltage applied to the plasma showed a conversion of 54.9%, close to the conversions obtained with 15.6 kV voltage applied to the plasma. Therefore, it is concluded that both the voltage applied to the plasma and the catalyst content are factors that influence the conversion of biodiesel and that they must be analyzed to obtain an optimized condition.

5. ACKNOWLEDGEMENTS

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