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Experimental parametric analysis of biodiesel synthesis in microreactors using waste cooking oil (WCO) in ethylic route

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Abstract

This study investigates biodiesel synthesis from waste cooking oil (WCO) using a microreactor completely 3D printed in metal. Production of biodiesel from WCO will inevitably lead to higher levels of free fatty acids (FFAs), since a hydrolysis reaction occurs with the water from food, turning triglycerides into FFAs when the refined vegetable oil is used for cooking. To overcome the negative effects of the FFA content on mass transfer and ultimately tend to decrease the ester conversion, its amount in oil feedstock must be reduced to lower values than 0.5% through a pretreatment step of esterification with an acid catalyst. Therefore, the two chemical processes were here parametrically investigated in an ethylic route: first, the reduction of the FFAs in the WCO using an esterification pretreatment, and then the conversion of the remaining triglycerides through an alkali-catalyzed transesterification. The partial factorial Taguchi analysis was used to explore parametric effects and greatly reduce the number of experiments needed. A biodiesel conversion of 98% was achieved at a temperature of 55 °C which is very close to the industrially acceptable level of conversion, but in only 2 min, which is much lower than the reaction times using traditional batch reactors.

Keywords Biodiesel · Microreactor · Waste cooking oil · Esterification · Transesterification

Abbreviations

A	Alcohol
ANOVA	Analysis of variance
CC	Catalyst concentration (%wt-oil)
C. F	Correction factor
DG	Diglycerides
E	Ethyl esters
ET	Electric tension (Volts)

f	Degrees of freedom
F	Variance ratio
FFA	Free fatty acids
G	Glycerin
k	Number of independent variables
L	Levels
m	Number of factors
MG	Monoglycerides
MR	Molar ratio (ethanol/oil)
MSA	Methane sulfonic acid
n	Number of experiments
P	Percent influence
r	Repetitions
RT	Residence time (min)
s	Number of levels
S	Sum of squares
S'	Pure sum of squares
S/N	Signal noise ratio
TG	Triglycerides
V	Variance
X	Independent variables
WCO	Waste cooking oil
Y	Result of a trial run

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\hat{Y}	Predicted response variable
\bar{Y}	Average of the response Y_i

Greek symbols

β	Regression coefficients
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Subscripts

e	Experimental error
i	Factor
T	Total
k, j	Counters

1 Introduction

World energy consumption has steadily increased since the dawn of the industrial revolution. Most of the energy currently produced is derived from fossil fuel energy sources (“BP Statistical Review of World Energy Statistical Review of World,” 2019). Concern about the depletion of these energy sources and their harmful impact on the environment, as well as their cost and limited supply, motivate the search for new alternative energy sources [1–6]. Recently, the use of renewable energy sources which are less harmful to the environment, such as solar, wind, hydro, biofuels, has increased significantly. One of the most important biofuels is biodiesel. Biodiesel, a fuel derived from renewable sources, is an attractive substitute for conventional diesel used in vehicles, as it has almost the same energy capacity as diesel. Furthermore, biodiesel is miscible with petrodiesel in any proportion and has several technical advantages over petroleum diesel, such as inherent lubrication, low toxicity, superior ash point, biodegradability, insignificant sulfur content and lower overall exhaust emissions [7–13]. Although biodiesel has several environmental advantages compared to fossil diesel, it is only cost competitive with government subsidies and mandates. Therefore, research and investment has been committed to reducing the cost of biodiesel production [21].

Biodiesel is made through the conversion of fatty acids to alkyl esters. Two commonly ways this is done through the transesterification of triglycerides and the esterification of free fatty acids (FFAs). Biodiesel synthesis through transesterification uses as raw material vegetable oils, animal fats or waste cooking oil (WCO) together with alcohol (methanol or ethanol are the most used) and/or without a catalyst [4–6, 11–20]. Esterification of FFAs to esters is performed using alcohol and an acid catalyst, and it is used for feedstocks that are high in FFAs [21]. Transesterification reaction is the most frequently used biodiesel production method due its moderate energy-consumptions and cost-effective process in comparison with the other methods.

The largest cost in biodiesel production is the cost of raw material (virgin vegetable oil), which accounts for nearly

75% of the cost of biodiesel production [6, 41–47]. Another disadvantage of biodiesel production using virgin vegetable oil is competition with human food production [6, 16, 41]. In this sense, the use of waste cooking oil for biodiesel production can be a suitable solution. In addition to lowering the cost of biodiesel production, it can reduce the environmental contamination, because the reusing of these waste greases can reduce the burden of the government in disposing of the waste, maintaining public sewers, and treating the oil wastewater [11, 41, 48].

Oil degrades with cooking through processes of oxidation at high temperature and hydrolysis from the water in the food leading to free fatty acids (FFAs) in the oil. Furthermore, WCO contains several contaminants such as water, food particles, and FFAs. These impurities have adverse effects on ester conversions when present in large quantities. FFAs present in feedstocks react with the alkali catalyst during transesterification creating soap. To use WCO in alkali-catalyzed transesterification biodiesel synthesis, several pretreatment steps are needed before transesterification [6, 20, 48, 49, 55, 56]. The food particles are removed with vacuum filtering, the water is removed through drying the oil, and the FFAs can be reduced through esterification. Thus, it is common to use a two-step chemical process: first, reducing the FFAs in WCO using an esterification pretreatment, and then converting the remaining triglycerides using alkali-catalyzed transesterification [20, 21, 55, 56].

The alcohols most commonly used for both esterification and transesterification are methanol and ethanol [52]. Methanol is more widely used in industry for biodiesel synthesis because of its low cost compared to ethanol [3]. Also, methanol is recoverable and makes purification easier [53]. Ethanol is cost competitive with methanol in areas where production is high, such as Brazil [41]. Ethanol also has the advantage of being derived from renewable sources, and it is safer to handle than methanol [54]. Few studies involving biodiesel synthesis in microreactors use ethanol as alcohol [26, 28, 31, 35]. The most of them perform the reaction using the methanol [14, 22–25, 27, 29, 30, 33–35]. The most common catalyst used in esterification is sulfuric acid; however, methane sulfonic acid (MSA) can also be used and it is safer to handle than sulfuric acid [57]. For alkali-catalyzed transesterification, KOH and NaOH are the most common catalysts used [58].

Biodiesel production processes are generically divided into the batch and continuous processes. The conventional reactors used in biodiesel production are stirred tank reactors or batch reactors. In batch processes, a set number of reactants are reacted, while in a continuous process the reactants are continuously fed into the system [21]. Many methods have been proposed for the process intensification of biodiesel synthesis, where microreactors have shown itself as the most promising one [6, 23]. This could allow biodiesel

synthesis to be carried out in microsystems faster and more energy-efficient in a continuous process. Advances in manufacturing allow for complex microsystems to be made very efficiently and cost-effectively. The high conversion rates achieved at very short residence times demonstrate the high efficiency of microreactors in biodiesel production [5, 14, 17, 19, 23–35]. This efficiency is achieved due to the short diffusion distance path between the reactants and the high surface area/volume ratio, which lead to intensified heat and mass transfer and consequently to improved reaction rates [10, 19, 23, 30, 33–40].

Although the amount of biodiesel produced by a single microreactor is not substantial, an advantage of the completely 3D printed microdevices is the easy possibility of scaling production, with the parallel use of a larger number of microreactors. The scaling of production using microreactors allows the construction of a portable biofuel production unit with several potentials such as the possible to generate energy biodiesel in remote areas.

In the literature, few studies report the synthesis of biodiesel in microreactors using waste cooking oil [43, 50, 51]. Mohadesi et al. [43] studied the production of biodiesel in a semi-industrial plant composed of microreactors using WCO, methanol and a homogeneous catalyst of potassium hydroxide (KOH). The biodiesel production rate was 5 L/h under ideal conditions. Experiments were carried out within different reaction times, and the highest percentage of biodiesel of 98.26% which was obtained in 120 s.

Aghel et al. [51] evaluated and optimized the production of biodiesel in a pilot scale microreactor using WCO. At a reaction temperature of 61.7 °C, catalyst concentration of 8.87% wt, methanol/oil molar volume ratio of 1.7: 3 and a residence time of 15 min, it reached the ideal conditions to obtain maximum purity of 93.41% biodiesel.

Given this, this study aims to experimentally analyze the parametric values for biodiesel synthesis with WCO using a 3D metal printed microdevice. In recent literature, most microreactors manufactured by 3D printing are made of polymeric materials [59–62], while few use metals [62–64]. This work has used the innovative microfluidic named as micromonolithic integrated reactor and heat exchanger (μ MIRHE) for biodiesel production proposed by [35], consisting of 10 microreactors stacked in parallel with 11 micro-heat exchangers and the reaction driven with rejected heat from a parallel thermal process.

Rather than using a resource-intensive full factorial experimental analysis, this work has implemented the partial factorial Taguchi analysis to explore parametric effects and greatly reduce the number of experiments needed. The two chemical processes were parametrically analyzed in an ethylic route: first, the reduction of the FFAs in the WCO through an esterification pretreatment, to reduce the recommended values of FFA content in oil to less than 0.5%,

avoiding then: the large amounts of soap in the mixture, the possible decrement in the mass transfer efficiency and some difficulties in the purification step, which all have adverse effects on overall biodiesel yields. And, secondly, the conversion of the remaining triglycerides through an alkali-catalyzed transesterification for the biodiesel production.

Several types of microreactors, resources based on resources such as microchannels, microcylinders, micro-grooves, appear as a promising technological alternative to improve efficiency in the production of biodiesel. Most of these studies use methanol, as the alcohol, and commercial vegetable oil. The present study provides two important environmental benefits: first, enabling the reuse of energy, thus increasing the overall energy efficiency of the process; second, allowing high yield reaction obtained starting from WCO and using ethyl instead of toxic methyl alcohol as a reagent. Methyl alcohol has an adverse environmental influence, therefore, for countries like Brazil, which produce large quantities of this product, the combined proposal, shown here, has a holistic advantage. The present work contributes to the understanding and analysis of the microreactor scheduling process applied to the synthesis of biodiesel using WCO and ethanol. It also advances in the presentation of an experimental plan for process optimization and identification of the element with the greatest contribution to the conversion of biodiesel.

2 Materials and methods

2.1 Microdevice

The so-named micromonolithic integrated reactor and heat exchanger (μ MIRHE) device used in this study has 10 microreactors stacked in parallel with 11 micro heat exchangers. This is the same device used in another study [35] to use a parallel thermal process to heat a working fluid that is then passed through the micro heat exchangers, heating the chemical process (esterification or transesterification) taking place in the microreactors layers. Figure 1a, b shows the internal structure of (a) microreactor and (b) micro heat exchanger. The dimensions and further details of the device can be seen in [35].

The microreactor design uses a Y-mixer, of channel length 13.34 mm, for the alcohol/KOH and oil reactants. The reaction takes place in a meandering square ($400 \mu\text{m} \times 400 \mu\text{m}$) microchannel reactor of 432.57 mm length. In the micro heat exchangers, heated water is distributed to 13 microchannels and heat is transferred to the microreactors placed in parallel to the heat exchangers. The final μ MIRHE was manufactured in chromium – cobalt alloy, and further details of the device can be found in [35].

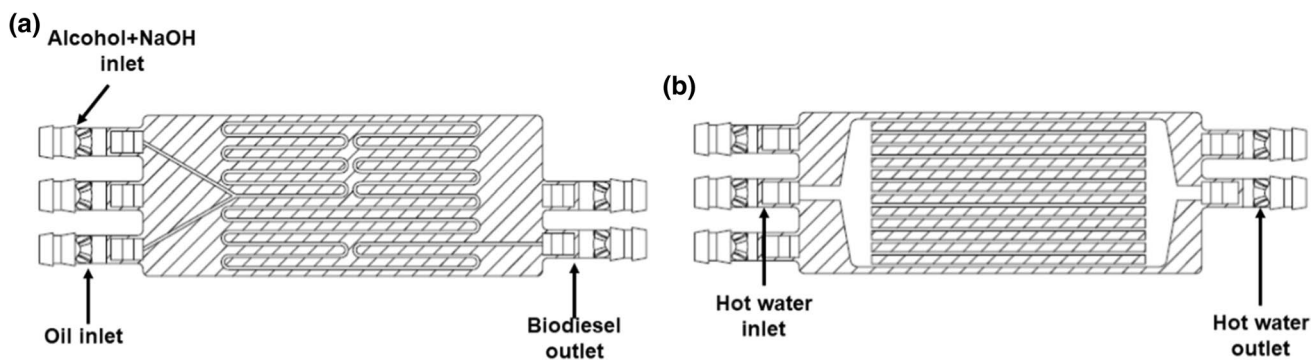


Fig. 1 Internal structure of **a** microreactor and **b** micro heat exchanger

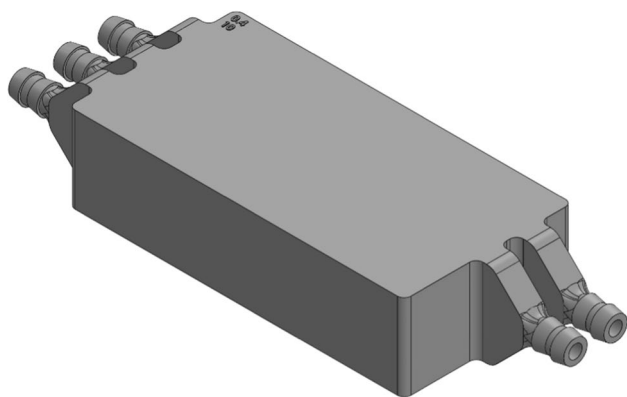


Fig. 2 3D view of the μ MIRHE device used in this study. Reprinted with permission from [35]. Copyright (2020) American Chemical Society

The reactants and heating fluid are attached to the entrance of the device by three barbed circular fittings with an interior diameter of 2 mm and a length of 6 mm. The three fluids are distributed to the various microreactors, and heat exchangers and the products are exited via two barbed circular fittings: one for the reacted final product and one for the water exiting the heat exchangers. A 3D view of the microreactor is shown in Fig. 2.

The 3D printing method of selective laser melting was employed for the device manufacturing, using the Mlab-R, from GE. This additive manufacturing equipment operates with an Ytterbium fiber laser of 100 W to selectively melt successive metallic powder layers. This specific design would be impossible to be achieved as a single monolithic unit without additive manufacturing.

2.2 Esterification of High FFA content oil

Esterification is a process option to produce biodiesel but is more frequently used as a pretreatment of poor-quality oils [65, 66]. It consists of a reversible reaction where FFA reacts with alcohol and the catalyst to produce FFA esters

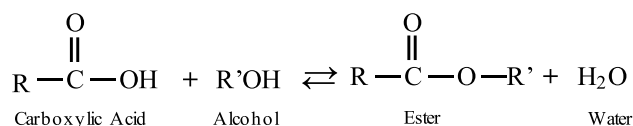


Fig. 3 Esterification of FFA and hydrolysis of a triglyceride

and water. FFAs are naturally found in oils or are generated during the cooking process, where the triglyceride from the oil reacts at high temperatures with water from food, increasing FFA content and also forming glycerol [67]. The reaction schemes of hydrolysis (backward direction) and esterification (forward direction) are, respectively, shown in Fig. 3.

2.2.1 Materials

To conduct the analyses of the esterification process, the main reactants needed are high FFA content oil, alcohol and acid catalyst. In order to create an oil with a high FFA content, chemical-grade oleic acid (75%), which is a very common FFA found in vegetable oils, was purchased and mixed with refined soybean oil. This mixture is chemically identical to poor-quality WCO for the purpose of this study and allows control and consistency over the mixture's initial FFA content. Ethanol (99%) was used as the alcohol and methane sulfonic acid (MSA) (>99%) was used as the catalyst in the esterification experiments. For titration analysis were used the following: phenolphthalein, ethanol (95%), NaOH pellets (98%), potassium biphthalate, ether, and distilled water.

2.2.2 Experimental Setup and Procedure

The conduction of the esterification experiments was carried out in the experimental setup, the schematic design of which is illustrated in Fig. 4.

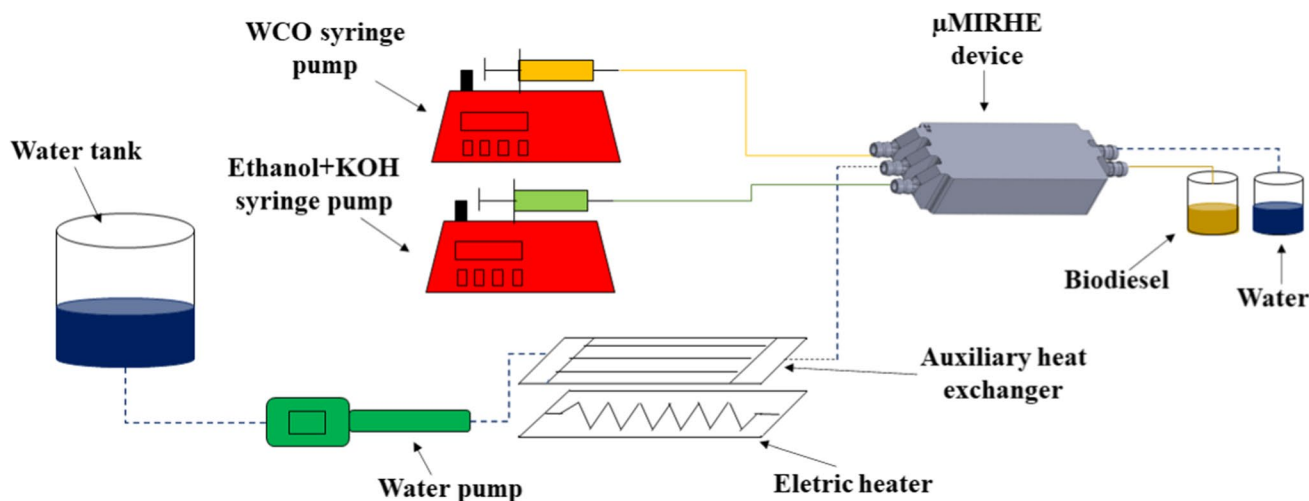


Fig. 4 Schematic of the experimental setup

The experimental configuration can be divided into two circuits: the biodiesel synthesis circuit (circuit 1) and the auxiliary heating circuit (circuit 2).

Circuit 1 is responsible for promoting the esterification/transesterification reaction and consists of two syringe pumps (New Era Pump Systems Inc., model NE 1000), the microdevice μ MIRHE and a vessel to collect the final product of transesterification reaction. The microdevice μ MIRHE is thermally insulated by polyurethane foam, which also serves as a support for the device.

Circuit 2 is responsible for heating the water that will heat the esterification/transesterification reaction in the μ MIRHE. This circuit is basically composed by the auxiliary heat exchanger coupled to an electric heater that is fed by a simple source of direct current (model PS-6100 from ICEL); a water tank and a helical rotor pump (NEMO Pumps—model NM003BY11S12B—NETZSCH) to supply water from the tank through the heating system to the microdevice and a vessel to collect the heating water.

To monitor temperatures, eight thermocouples were installed: In circuit 1, four of them monitor the external temperature of the microdevice and one the temperature of the final reaction product. In circuit 2, two thermocouples measure the temperature at the entrance and exit at the micro heat exchangers. A thermocouple is used to measure room temperature.

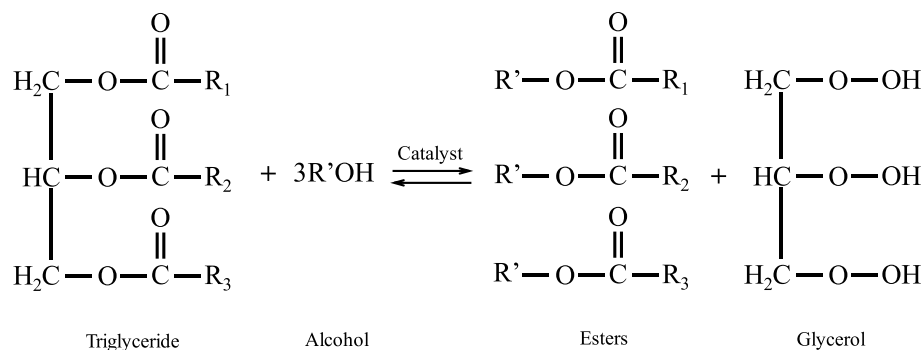
A data acquisition system (Agilent 34970-A) and a computer are used to capture the measurements of the thermocouples.

The experimental procedure for esterification begins with the preparation of a solution of ethanol and methanesulfonic acid catalyst ($\text{CH}_3\text{SO}_3\text{H}$) and, after that, the preparation of the oil, which is a mixture of refined soybean oil with oleic acid, is performed. Thereafter the solutions are

independently injected into μ MIRHE using syringe pumps. In the reaction heating, the distilled water from the tank passes through an auxiliary electrical resistance, where it is heated and directed to the heat exchangers into the μ MIRHE. The auxiliary electric heater simulates the recovery of waste heat from an external thermal source. This route is carried out using a water pump. Upon leaving μ MIRHE, the final product of the esterification is collected in a beaker immersed in an ice-water bath, which is intended to stop the esterification reaction. A separating funnel is used for phase separation, and then the oil is washed with distilled water at a temperature of 70 °C. Finally, the treated oil is dried with sodium sulfate. To determine the FFA content in the oil, a simple titration was used. The basic idea is to use an alkaline solution of known molarity to react with the FFAs present in the sample. The alkaline solution is added slowly to the sample and the phenolphthalein indicator is used to change the color of solution when it reaches the neutral pH. Then the FFA content is calculated using the volume of alkaline solution used and the weight of the sample.

2.3 Transesterification of WCO

Transesterification is most commonly method used in industry currently. It consists of a reaction involving a triglyceride (TG) source (mainly found in animal fats and vegetable oils) with an alcohol (methanol, ethanol, etc.) (A) to produce fatty acid esters (E) and by-product glycerol (G). This reaction occurs in three steps where each step corresponds to a change in the alkoxide groups, forming diglycerides (DG) and monoglycerides (MG), respectively. Transesterification reaction can be represented in general according to Fig. 5, where R_1 , R_2 , and R_3 correspond to long-chain hydrocarbons nominated fatty acid chains. These chains can vary a

Fig. 5 Transesterification of a triglyceride

lot depending on the feedstock used in the process and its length and amount of double bonds have a noticeable effect on the combustion and emission properties of the finished biodiesel [3].

2.3.1 Materials

The transesterification experiments were carried out using WCO from a local restaurant (Adega Perola) in Rio de Janeiro, absolute ethanol (99%) and potassium hydroxide (KOH) (98%) as the homogeneous basic catalyst.

2.3.2 Preparation of WCO

Impurities from WCO before transesterification are removed in two steps: first, a vacuum filter with paper is used to separate food particles remaining from the cooking process, and second the WCO is heated to roughly 120 °C for 1 h and simultaneously magnetically stirred to avoid hydrolysis, increasing the FFA content in the oil and also allowing the water to evaporate more quickly.

After drying process, the WCO was titrated to determine the FFA content. The FFA content found was very low compared to WCO used in the literature, but to bring down the FFA content further, the WCO was esterified using 5% wt. methane sulfonic acid, 20:1 alcohol to oil molar ratio, and residence time of 2 min using 17.5 Volts of electrical resistance tension to heat the water that is used in heating of reaction system. This was done several times over several days to accumulate enough to perform transesterification analysis. The oil is dried after each reaction. Once this was accumulated, a titration was performed to discover the new FFA content. The new FFA content met the standard of 0.5% FFA that is recommended in the literature [15].

Transesterification of triglycerides in the oil via acid catalyst also occurs during the esterification of FFAs. The transesterification with an acid catalyst is much slower than with an alkali catalyst but intermediary species (MGs and DGs) will be created. Table 1 summarizes the final FFA and intermediary species content measured just before the WCO was used for the alkali-catalyzed transesterification experiments.

Table 1 FFA content and intermediary species of WCO used in transesterification experiments

FFA Content in WCO		WCO Composition		
Before esterification	After esterification	MG	DG	TG
1.07%	0.5%	4%	3%	93%

2.3.3 Experimental setup and procedure

The equipment and experimental setup for the transesterification experiments are the same shown in Fig. 4.

The experimental procedure for the transesterification experiments starts with the preparation of the ethanol/KOH solution. Soon after, the WCO and the ethanol/KOH solution are pumped to the microreactors that make up the μ MIRHE. At this stage, syringe pumps with independent and controlled flows were used. Reaction heating is carried out using distilled water which is pumped through the auxiliary electrical resistance where it is heated. The final product of the transesterification reaction is collected in a beaker immersed in an ice-water bath. The separation of the biodiesel and glycerol phases is carried out using a separating funnel, and the biodiesel is washed with distilled water at a temperature of 75 °C. Finally, the biodiesel is dried in an oven with a temperature above 100 °C.

2.3.4 Biodiesel analysis

The analysis of the biodiesel was done using high-performance liquid chromatography (HPLC) from Thermo Scientific, model Ultimate™ 3000 and was performed on a column C18 column of 4.6 mm internal diameter and a 250 mm length with 5 μ m particulates of a 120 Å pore diameter, also from Thermo Scientific, model Acclaim™ 120.

2.4 Design of experiments

The purpose of this study is to optimize the parameters for the esterification of high FFA content oil and transesterification of WCO. To do this accurately and efficiently, a Taguchi

experimental methodology was implemented. Experimental procedures were put in place to obtain accurate and meaningful results. The following sections outline the procedures used as well as the decision making involved in choosing the methodological and procedural steps.

Design of experiments (DOE) consists of a series of experimental and statistical techniques that allow analyzing the influence of different disturbances in operational conditions at the outcome. First, it's necessary to choose what parameters (factors) will be evaluated and which range (levels) they will vary. The most common method is the full factorial design, where each factor is tested in each possible combination. However, it can be a very long process, especially if you have a lot of factors to analyze. Other methods are available to perform the same analysis reducing the number of experiments. The method used in this work was the Taguchi method. It makes use of the properties of orthogonal arrays which are denoted by $L_n(s^m)$, in an $n \times m$ matrix, where n is the total number of experiments, s is the number of levels, and m is the number of factors analyzed on the DOE.

In this type of arrays, columns are mutually orthogonal. By doing this, all the combinations of factor levels occur, and they occur an equal number of times. This allows for maximum experimental efficiency, using the least number of test runs [68]. The Taguchi method is applied according to the following steps:

1. Determine the parameters (factors) important to esterification/transesterification.
2. Design the experiments to test the parameters.
3. Conduct the experiments.
4. Analyze the results and determine the optimal conditions.
5. Run a confirmatory test with the optimal conditions.

The use of ANOVA enables one to statistically interpret the results regarding the influence of factors such as temperature, pressure or time, on one or more response variables. This methodology is based on the comparison of variances between and within each sample [69]. The main principle of ANOVA methodology is to divide the overall variability among its components, where the part of it corresponds to the quadratic sum difference between the total average response and the average response for the same level and the other part is related to random errors. The sum of squares is a measure of the deviation of the experimental data from the mean value of the data. Besides the sum of squares, other parameters are calculated according to equations bellow to analyze the optimum operational parameters [68]. The variance ratio (Eq. 1) is the ratio of variance because of a factor and variance due to the error term. This ratio is used to measure the significance of the

factor under investigation concerning the variance of all the factors included in the error term:

$$F = \frac{V_i}{V_e}, \quad (1)$$

where V_i (Eq. 2) is determined by the sum of squares of each trial sum result involving the factor divided by the degrees of freedom of the factor. Similarly, the variance is also calculated for the experimental error.

$$V_i = \frac{S_i}{f_i}, \quad (2)$$

$$V_e = \frac{S_e}{f_e}. \quad (3)$$

The pure sum of squares (Eq. 4) is the sum of square minus the degrees of freedom times the error variance:

$$S'_i = S_i - f_i V_e \quad (4)$$

The percent influence of each factor (Eq. 5) is the ratio of the factor sum to the total, expressed in a percent:

$$P_i = S'_i \frac{100}{S_T}. \quad (5)$$

A relationship between the predicted response variable and the independent variables is obtained using a complete quadratic model. The response variable for the esterification reaction is %FFA, while the response variable for the transesterification reaction is the %Ester. The mathematical form of the complete quadratic model is shown in Eq. (6).

$$\hat{Y} = \beta_0 + \sum_{k=1}^3 \beta_k X_k + \sum_{k=1}^3 \beta_{kk} X_k^2 + \sum_{k=1}^2 \sum_{j=k+1}^3 \beta_{kj} X_{kj}, \quad (6)$$

where \hat{Y} is the predicted response variable, X_k and X_{kj} are independent variables, β_0 is a constant, and β_k , β_{kk} , β_{kj} are the regression coefficients.

The main parameters that affect esterification and transesterification, and will be here analyzed via ANOVA, are catalyst concentration (CC), alcohol/oil molar ratio (MR), residence time (RT) and reaction temperature, through the electric tension (ET) imposed in the resistance. These parameters will appear in Eq. (6) as independent variables. In this ANOVA analysis, and they were varied in different levels, as presented in Tables 2 and 4, respectively, to esterification and transesterification.

The quality of the mathematical model is verified through the coefficient of determination (R^2) and the adjusted determination coefficient (R^2_{adj}) which are given by Eqs. 7 and 8

Table 2 Factors and level values for the esterification experiment matrix

Level	Catalyst concentration “CC” (%wt-oil)	Molar Ratio “MR”(ethanol/oil)	Resi- dence time “RT” (min- utes)
1	1	5:1	1
2	2.5	10:1	2.5
3	5	20:1	5

Table 3 Levels to be used for factors of each trial for esterification experiments

Trial #	CC	MR	RT
1	1	1	1
2	1	2	2
3	1	3	3
4	2	1	2
5	2	2	3
6	2	3	1
7	3	1	3
8	3	2	1
9	3	3	2

$$R^2 = \frac{\sum_{i=1}^n (\hat{Y}_i - \bar{Y})^2}{\sum_{i=1}^n (Y_i - \bar{Y})^2}, \quad (7)$$

$$R^2_{\text{adj}} = 1 - (1 - R^2) \left[\frac{n - 1}{n - (k + 1)} \right], \quad (8)$$

where \hat{Y} is the predicted response variable, Y_i is the result of trial run, \bar{Y} is the average of the response Y_i , k is the number of independent variables, and n is the number of experiments.

Since esterification experiments take longer than the transesterification, fewer experiments were performed. Alcohol-to-oil molar ratio, catalyst concentration and residence time were chosen to be the ones analyzed here, where the temperature was kept below ethanol's boiling point. An extensive search was done in the literature to find operational conditions as similar as possible, but unfortunately, the parameters used in the literature vary widely (even because the feedstocks are also different). A study with WCO with FFA content of 5%, Chai et al. [70] achieved optimum results (0.5% FFA) with a residence time of 2 h, a methanol to FFA molar ratio of 40:1, a temperature range of 55–65 °C, and a sulfuric acid concentration usage of 10% (wt.). In another study using surface response methodology, Goyal et al. [73] converted 14.6% FFA content *Jatropha curcas* oil to 0.34% FFA with a 6.5:1 methanol-to-oil molar ratio, a 1.5% wt. sulfuric acid concentration, 125 min of residence time, and at 50 °C. Using the same catalyst as this study, Hayyan et al. [72] reduced 9% FFA crude palm oil to 0.5% FFA using 8:1 methanol to oil ratio, 1% wt. methane sulfonic acid, for 30 min at 60 °C. Marchetti and Errazu [73] converted 95% of the FFAs in using a 6.126:1 ethanol to oil molar ratio, 2.261% wt. sulfuric acid, at 55 °C for 250 min. Khan et al. [74] optimized esterification parameters using a Taguchi method DOE and achieved a 95% reduction in FFA of a blend of crude rubber oil and crude palm oil with a 15:1

methanol to oil ratio, 0.5% wt sulfuric acid, at 65 °C for 3 h. Ouachab and Tsoutsos [75] used a high acid concentration of 20% sulfuric acid and was able to reduce FFA of olive pomace oil from 2.3 to 0.3% using a 35:1 methanol to oil ratio 40 °C for 60 min.

The catalyst concentration (CC) levels were chosen taking a relatively low value in the literature of 1% as the first level. A relatively high value in the literature of 5% was chosen as the upper bound for level 3. Level 2 value of 2.5% was used as a middle value between levels 1 and 3. The stoichiometric value of the reversible esterification reaction is a one to one alcohol to FFA molar ratio (MR); however, the alcohol-to-molar ratio is set above the stoichiometric value to drive the reaction to the product side. Also, we are dealing with two immiscible fluids in the oil and alcohol mixture and the reaction will only occur at the interface between the two liquids; therefore, the mass transfer of the mixture becomes very important when determining the alcohol to oil molar ratios to be used. The mass transfer of the system is largely determined by the reactor design. Using the same μ MIRHE microdevice described in Sect. 2.1, Costa Junior et al. [35] converted soybean oil to biodiesel using 20:1 ethanol to oil molar ratio with his best conversions, 99.6%, being achieved at less than 35 s. Although his study was with transesterification rather than esterification the oil dispersion in the alcohol mixture is the same. Therefore we have decided to use a lower bound (level 1) of 5:1 ethanol to oil molar ratio and an upper bound (level 3) of 20:1 with level 2 in between these two, at 10:1. The experimental studies described from the literature in the previous paragraph all used laboratory batch reactors; therefore, the residence times are much longer than the ones expected for the experiments in this study using microreactors. The range of residence times (RT) set was level 1:1 min, level 2: 2.5 min, and level 3: 5 min. Table 2 summarizes the factors and values of the levels used in this study for the esterification experiment. Table 3 displays the orthogonal array matrix of each trial for esterification experiments analyzed in this study. For the trials shown in Table 3, considering the density 0.91 g/cm³ and molar mass

182 g/mol, the oil flows rate vary from 0.7 to 0.1 ml/min, while the ethanol flows rate vary from 3.5 to 0.2 ml/min.

In the transesterification analyses, all parameters that influence this reaction were used as factors: temperature, catalyst concentration, alcohol/oil molar ratio and residence time.

In his study, Costa Junior et al. [35]. were able to convert 99.6% of soybean oil triglycerides to ethyl esters with a residence time of 35 s, using 1% NaOH catalyst, 20:1 ethanol to oil molar ratio and an electrical tension (temperature control) of 17.5 Volts. Residence times under 1 min are strenuous on the equipment used for the experiments, therefore the lowest residence time of 1 min is chosen for level 1 with increases of 1 min for each of the other levels up to 5 min (corresponding to level 5). To observe the effects of catalyst concentration, the best result from Costa Junior et al. [35], 1%, was taken as the middle value (level 3) and two lower values, 0.5% and 0.75%, are placed in levels 1 and 2, respectively, and two higher values, 1.25% and 1.5%, were placed at levels 4 and 5, respectively. For the ethanol to oil molar ratio, the molar ratio from the best result in Costa Junior et al. [35], 20:1, was placed in level 3. Two values below, 10:1 and 15:1, were placed in levels 1 and 2, respectively, and two values above, 25:1 and 30:1, were placed in levels 4 and 5, respectively. To observe the effect of temperature, we set the electrical tension (ET) of the resistance connected to the heat exchanger (described in Sect. 2). As pointed out by Costa Junior et al. [35]. when the resistance is set higher than 17.5 Volts, the reaction can reach undesired temperatures above the boiling point of ethanol. Therefore, the first level is set to 6 Volts and increased to 9 Volts for level 2, 12 Volts for level 3, 15 Volts for level 4 and the maximum of 17.5 Volts for level 5. The factors and level values for the transesterification experiments are summarized in Table 4. The orthogonal array matrix used for each trial of transesterification experiments is displayed in Table 5. For the trials shown in Table 5, considering the density 0.91 g/cm³ and molar mass 176 g/mol, the oil flows rate varies from 0.7 ml/min to 0.1 ml/h, while the ethanol flow rate varies from 5.5 to 0.2 ml/min.

3 Results and discussion

3.1 Esterification of high FFA content oil

In order to perform transesterification reactions, it is recommended that FFA content in oil feedstock must be less than 0.5%; otherwise, FFAs will react with the catalyst and produce soap and large amounts of soap in the mixture decreases mass transfer efficiency and makes purification more difficult which has adverse effects on overall biodiesel yields. WCO typically has FFA content

Table 4 Factors and level values for the transesterification experiment matrix

Level	Catalyst concentration "CC" (%wt-oil)	Molar ratio "MR" (ethanol/oil)	Residence time "RT" (minutes)	Electric tension "ET" (Volts)
1	0.5	10:1	1	6
2	0.75	15:1	2	9
3	1	20:1	3	12
4	1.25	25:1	4	15
5	1.5	30:1	5	17.5

Table 5 Levels to be used for factors of each trial for transesterification experiments

Trial #	CC	MR	RT	ET
1	1	1	1	1
2	1	2	2	2
3	1	3	3	3
4	1	4	4	4
5	1	5	5	5
6	2	1	2	3
7	2	2	3	4
8	2	3	4	5
9	2	4	5	1
10	2	5	1	2
11	3	1	3	5
12	3	2	4	1
13	3	3	5	2
14	3	4	1	3
15	3	5	2	4
16	4	1	4	2
17	4	2	5	3
18	4	3	1	4
19	4	4	2	5
20	4	5	3	1
21	5	1	5	4
22	5	2	1	5
23	5	3	2	1
24	5	4	3	2
25	5	5	4	3

larger than the recommended 0.5% but can be reduced using a pretreatment step of esterification with an acid catalyst. The feedstock used for esterification studies in the literature has a starting FFA content as low as 2% to as high as 100% FFA. So, an FFA content oil of 5.9% was created using a mixture of oleic acid (a common FFA) and soybean oil which is chemically identical to WCO for a well-controlled parametric study of the esterification procedure in the μ MIRHE microdevice. The esterification experiments were conducted using the high FFA content oil mixture, ethanol, and MSA (methane sulfonic acid) as

a catalyst in a microreactor device thermally driven by a parallel process.

The experimental results of the esterification runs obtained in this work are presented in Tables 6, and 7 shows the statistical results from the analysis of variance (ANOVA) for esterification. In addition, in Table 6 is presented the predicted FFA content given by Eq. (9). Equation (9) represents the mathematical expression obtained from the linear regression procedure applied by combining Eq. (6) and the observed results for FFA.

$$\begin{aligned} \%FFA = & 5.84 - 1.15(CC) + 0.034(CC)^2 \\ & + 0.096(MR) - 0.026CC(MR) \\ & - 0.005(MR)^2 - 1.13(RT) + 0.212(CC)(RT) \\ & + 0.049(MR)(RT) - 0.038(RT)^2. \end{aligned} \tag{9}$$

In Eq. (9), CC is the catalyst concentration, MR is the ethanol/oil molar ratio, and RT is the residence time.

Each trail run was conducted three times and the results averaged to provide more accurate final FFA value. The quality of the mathematical model was verified by the determination coefficient (R^2) and the adjusted determination coefficient (R^2_{Adj}) where both values were 100%.

The use of design of experiments (DOE) combined with ANOVA has already been applied with success in the biodiesel production for microreactors to understand the phenomena by Rahimi et al. [29]. and Dai et al. [30]. The

best results occurred with 5% wt-oil of catalyst, 20:1 ethanol to oil molar ratio, and residence time of 2.5 min. All the experiments were conducted at a maximum temperature in which the electrical tension was set to 17.5 Volts. The best result was in a trial run number 9, where the FFA content was decreased from 5.9% to $0.21\% \pm 0.05\%$ average over 3 runs which fall below the recommended 0.5%. In this trial run, the final products' average temperature leaving the reactor was measured to be 56 °C, 57 °C, and 56 °C for each run, respectively.

To get a sense of the potential impact of the results obtained here (a reduction of 5.9% FFA to $0.21\% \pm 0.05\%$ FFA in only 2.5 min), Table 8 presents some esterification experimental studies from the literature detailing some key parameter values for each of these studies. Most of the experimental results from the literature were obtained using spinning tanks reactors and were conducted using methanol; however, both Marchetti and Errazu [73] and Neumann et al. [76]. conducted their studies with ethanol. The work of Marchetti [66] fits as a good comparison with this study since ethanol is used as the alcohol as well as a similar catalyst concentration. Despite the similar operational conditions, Marchetti and Errazu [73] reduced FFA from 10.7 to 0.5% in 240 min, while this study showed FFA reduction from 5.9 to 0.2% in just 2.5 min, decreasing residence time and reinforcing so the great applicability of the μ MIRHE microdevice in the reduction of the residence time, keeping the high efficiency of the process.

Table 6 Esterification of high FFA content oil results

Trial #	CC	MR	RT	FFA					S/N
				Run1	Run2	Run3	Avg	Predicted	
(-)	(% wt MSA)	(EtOH/oil)	(min)						(-)
1	1.0	5:1	1.0	4.22	4.13	4.34	4.23 ± 0.11	4.23	- 12.53
2	1.0	10:1	2.5	3.83	3.29	3.67	3.60 ± 0.28	3.6	- 11.14
3	1.0	20:1	5.0	3.65	3.52	3.14	3.44 ± 0.27	3.44	- 10.74
4	2.5	5:1	2.5	1.47	1.5	1.44	1.47 ± 0.03	1.47	- 3.35
5	2.5	10:1	5.0	1.29	1.36	1.67	1.44 ± 0.20	1.44	- 3.22
6	2.5	20:1	1.0	2.32	2.01	1.99	2.11 ± 0.19	2.11	- 6.49
7	5.0	5:1	5.0	0.5	0.52	0.52	0.51 ± 0.01	0.51	5.79
8	5.0	10:1	1.0	0.43	0.39	0.48	0.43 ± 0.05	0.43	7.23
9	5.0	20:1	2.5	0.15	0.25	0.22	0.21 ± 0.05	0.21	13.52

Table 7 ANOVA table for esterification experiments

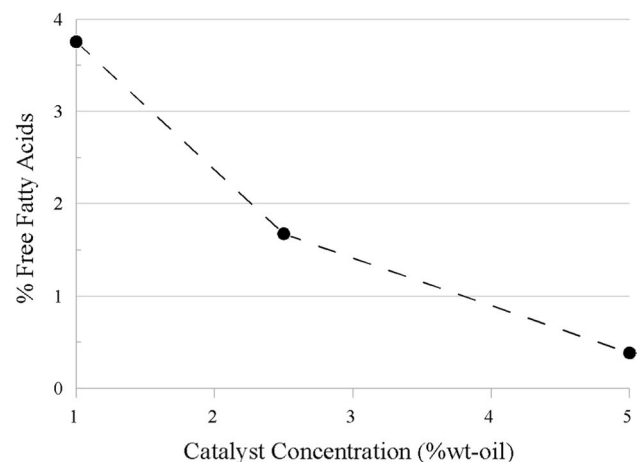
Source of variation (factor)	Degree of freedom <i>f</i>	Sum of squares <i>S</i>	Variance (mean square) <i>V</i>	Variance ratio <i>F</i>	Pure Sum of squares <i>S'</i>	Percent contribution <i>P</i>
CC	2	17.35	8.68	1332.23	17.34	96.20
MR	2	0.09	0.05	7.21	0.08	0.52
RT	2	0.46	0.23	35.47	0.45	2.56
Error	20	0.13	0.01	1	0.09	0.72

Table 8 Esterification optimization results in the literature using stirred tank reactors. Catalyst concentration in %wt-oil

Study	Key parameters	Conversion
Arora et al. [77]	20:1 (methanol/rice bran oil), 0.5% (H ₂ SO ₄), 90 (minutes), 60 °C	12% FFA to 1.8% FFA
Berrios et al. [78]	60:1 (methanol/FFA), 5% wt-FFA(H ₂ SO ₄), 120 min), 60 °C	3.5% FFA to 0.5% FFA
Brinks et al. [79]	20:1 (methanol/rapeseed oil), 0.1% (H ₂ SO ₄), 4 (hours), 70 °C	5% FFA to 0.2% FFA
Chai et al. [70]	40:1 (methanol/FFA), 10% wt-FFA (H ₂ SO ₄), 120 (minutes), 65 °C	5% FFA to 0.5% FFA
Ding et al. [80]	20% vol (methanol/WCO), 0.4%vol (H ₂ SO ₄), 5 (hours), 50 °C	34.4% FFA to 1.85% FFA
Goyal et al. [71]	6.5:1 (methanol/Jatropha oil), 1.5% (H ₂ SO ₄), 125 (minutes), 50 °C	14.6% FFA to 0.34% FFA
Hayyan et al. [72]	8:1 (methanol/crude palm oil), 1% (MSA), 30 (minutes), 60 °C	9% FFA to 0.5% FFA
Khan et al. [74]	15:1 (methanol/rubber seed/palm oil), 0.5% (H ₂ SO ₄), 180 (minutes), 65 °C	11.9% FFA to 0.6% FFA
Kostić et al. [81]	8.5:1 (methanol/plum stone oil), 2% (H ₂ SO ₄), 60 (minutes), 45 °C	15.8% FFA to 0.24% FFA
Marchetti et al. [73]	12.3:1 (ethanol/WCO), 5.1% (H ₂ SO ₄), 240 (minutes), 55 °C	10.7% FFA to 0.5% FFA
Neeharika et al. [82]	20:1 (methanol/FFA), 1% wt-FFA (MSA), 270 (minutes), 60 °C	22.5% FFA to 0.5% FFA
Neumann et al. [76]	6:1 (ethanol/oleic acid), 1.5% (H ₂ SO ₄), 120 (minutes), 74 °C	100% FFA to 15% FFA
Ouachab et al. [75]	35:1 (methanol/olive oil), 20% (H ₂ SO ₄), 60 (minutes), 40 °C	2.3% FFA to 0.3% FFA
Pisarello et al. [83]	15:1 (ethanol/sunflower oil), 1.14% (MSA), 30(minutes), 70 °C	18% FFA to 1.5% FFA
Maulidiyah et al.[91]	150 ml:60 ml (methanol/crude palm oil), 2 ml (H ₂ SO ₄), 120 (minutes), 60 °C	5.47% FFA to 0.57% FFA
Puangsang et al. [92]	10:1 (methanol/crude palm oil), 0.25% wt (HCL), 120 (minutes), 60 °C	13.81% FFA to 0.56% FFA
Present work	20:1 (ethanol/WCO), 5.0% (MSA), 2.5(minutes), 56 °C	5.9% FFA to 0.21% FFA

The analysis of catalyst concentration in the esterification reaction is an essential factor with an important role in the reaction and in the total cost of production [72]. The catalyst concentration (MSA) had by far the greatest percentage of contribution as presented by the ANOVA analyses (96.2%), followed by residence time and then molar ratio. Since the esterification reaction needs the catalyst presence to happen, its high influence is expected. To further investigate it, some of the average results presented in Table 6 were plotted in the means effect plot presented in Figs. 6, 7 and 8, having a graphic representation of this factor on the results. Figure 6 shows how steep FFA% can vary depending on the catalyst concentration. The catalyst concentration of 1% and 2.5% was insufficient to reduce the desired FFA for the transesterification reaction, and only with a catalyst concentration of 5% it was possible to reduce FFA content to the recommended value of 0.5% FFA. Higher catalyst concentrations did not contribute to the FFA reduction and may increase the cost of the pretreatment process due to extra and unnecessary catalyst use [72], so a catalyst concentration of 5% is sufficient for the operational conditions of the reaction of esterification.

The ethanol to oil molar ratio had the smallest effect on the variance with a percent contribution of just 0.52%, as shown in Table 7. From the main effect plot in Fig. 7, a

**Fig. 6** Catalyst concentration main effect plot for esterification

small reduction in the FFA content can be observed when the ethanol to oil molar ratio was raised from 5:1 to 10:1. The average FFA content was found to be slightly higher for the experiments conducted with ethanol to oil molar ratio of 20:1, but the difference is minimal and can be considered statistically similar to the result with ethanol to oil molar ratio of 10:1.

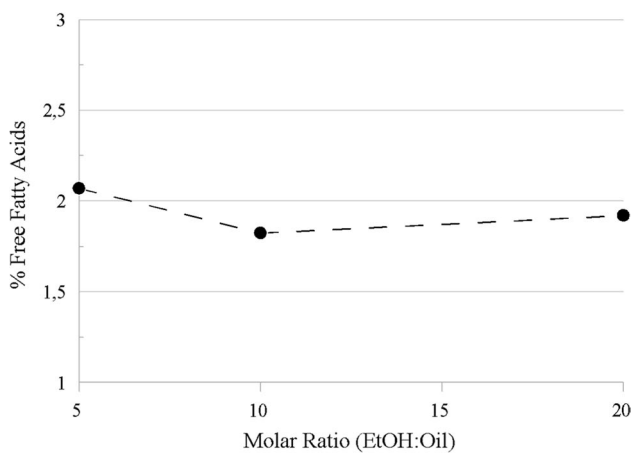


Fig. 7 Molar ratio main effect plot for esterification

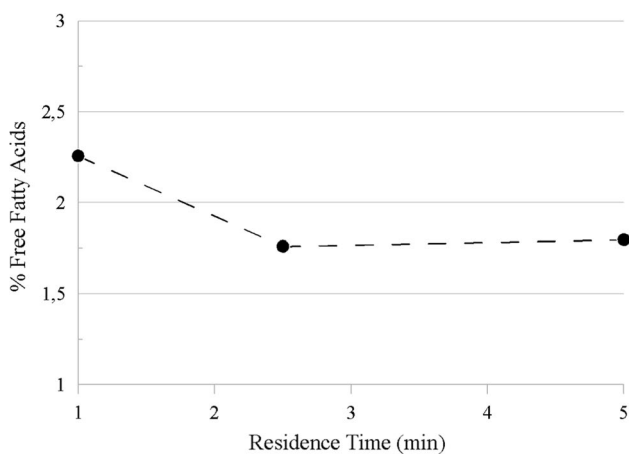


Fig. 8 Residence time main effect plot for esterification

None of the trials runs using ethanol to oil molar ratio of 5:1 (trial runs 1, 4, and 7 from Table 6) reduced the FFA content to values below 0.5% wt-oil. Raising the ethanol to oil molar ratio to 10:1 (trial runs 2, 5, and 8 from Table 6) improved the results, but the only trial run 8 with catalyst concentration of 5% wt-oil MSA was the FFA content reduced below the desired 0.5%. Ethanol to oil molar ratio of 20:1 was used for trial runs 3, 6, and 9 (Table 6). The best results in this study were achieved using ethanol to oil molar ratio of 20:1 in trail 9. However, in practice, the minimum amount of alcohol to achieve the desired result would be preferred, aiming to save money and to suppress or minimize the presence of the intermediary species in the transesterification purification. Most studies use batch processes where the reactants are constantly stirred for several hours and a lower amount of alcohol and catalyst can be used successfully. In continuous processes, the mass transfer of the reactants must be considered when analyzing. The reactor used in this study uses a simple Y-mixer to mix the reactants; the oil was better dispersed with an alcohol

molar ratio of 20:1. Also, many of the referenced studies used methanol which typically converts FFA at lower molar ratios than ethanol.

The residence time of the reaction also had a minimal effect on the variance of the results with a 2.56% contribution, as also presented in Table 7. In the main effect plot of Fig. 8, a reduction in the FFA content is observed when the residence time is increased from 1 to 2.5 min. No significant difference was observed when the residence time was increased from 2.5 to 5 min. This indicates that the reactants were already in equilibrium at 2.5 min.

A residence time of 1 min was used in trail runs 1, 6, and 8 (Table 6). Because the results largely correlate with the catalyst concentration, trial run 8 with a catalyst concentration of 5% wt-oil reduced the FFA content below the targeted 0.5%. Trial runs 2, 4, and 9 were conducted using a residence time of 2.5 min. The highest reduction of FFA occurred during trail 9 with a residence time of 2.5 min. Trials 3, 5, and 7 were done using a residence time of 5 min. None of these runs with the residence time of 5 min achieved the desired level of FFA reduction. The improvement in shortened residence times is where the major advantage of microreactors is observed. The residence times for batch reactors are typically 30 min to 2 h. The time saved using microreactors make this technology attractive to industrial producers looking to reduce costs and portability of biodiesel plant.

Despite the parameters discussed above, that can affect biodiesel production during reaction, purification step is also susceptible to affect the final amount of product available. The presence of water can cause the formation of emulsion [1], especially if the reaction product has a lot of mono or diglyceride (they are excellent emulsifiers). Besides, using ethanol as alcohol also makes the mixture more susceptible to emulsions. The formation of emulsions makes the purification step more time consuming and laborious.

3.2 Transesterification of WCO

After the preparation of WCO (where its FFA% was reduced from 1 to 0.5% and impurities were removed), transesterification was also performed in the μ MIRHE microdevice. Ethanol was chosen as the alcohol and KOH as the catalyst.

Table 9 presents the results obtained in each run with its respective operational conditions, and Table 10 shows the statistical results from ANOVA analysis for the transesterification. In addition, in Table 9 is presented the predicted yield of ester given by Eq. (10). Equation (10) represents the mathematical expression obtained from the linear regression procedure applied by combining Eq. (6) and the observed results for ester.

Table 9 Transesterification of WCO experimental results

Trial #	CC (% wt KOH)	MR (EtOH/oil)	RT (min)	Electric tension (ET) (Volts)	% Ester	
					Actual	Predicted
1	0.5	10:1	1	6±0.16	22	24.92
2	0.5	15:1	2	9±0.19	39	37.30
3	0.5	20:1	3	12±0.22	46	45.14
4	0.5	25:1	4	15±0.25	47	48.45
5	0.5	30:1	5	17.5±0.28	53	50.62
6	0.75	10:1	2	12±0.22	45	41.76
7	0.75	15:1	3	15±0.25	47	49.79
8	0.75	20:1	4	17.5±0.28	59	57.09
9	0.75	25:1	5	6±0.16	37	37.36
10	0.75	30:1	1	9±0.19	46	42.34
11	1.0	10:1	3	17.5±0.28	50	52.88
12	1.0	15:1	4	6±0.16	55	50.08
13	1.0	20:1	5	9±0.19	46	54.15
14	1.0	25:1	1	12±0.22	56	62.07
15	1.0	30:1	2	15±0.25	62	70.22
16	1.25	10:1	4	9±0.19	62	60.91
17	1.25	15:1	5	12±0.22	68	65.16
18	1.25	20:1	1	15±0.25	88	76.01
19	1.25	25:1	2	17.5±0.28	90	87.58
20	1.25	30:1	3	6±0.16	59	55.80
21	1.5	10:1	5	15±0.25	70	70.39
22	1.5	15:1	1	17.5±0.28	84	87.83
23	1.5	20:1	2	6±0.16	69	72.98
24	1.5	25:1	3	9±0.19	81	81.89
25	1.5	30:1	4	12±0.22	88	86.27

Table 10 ANOVA table for transesterification of WCO experiments

Source of variation (factor)	Degree of freedom <i>f</i>	Sum of squares <i>S</i>	Variance (mean square) <i>V</i>	Variance ratio <i>F</i>	Pure sum of squares <i>S'</i>	Percent contribution <i>P</i>
CC	4	5345.36	1336.34	34.14	5188.8	71.69
MR	4	541.36	135.34	3.46	384.8	7.26
RT	4	186.96	46.74	1.19	30.40	2.51
Tension	4	1069.76	267.44	6.83	913.2	14.35
Error	8	313.12	39.14	1	939.36	4.20

$$\begin{aligned}
\%Ester = & -31.19 + 120.404(CC) - 52.46(CC)^2 \\
& + 0.448(MR) + 0.615(CC)(MR) \\
& - 0.035(MR)^2 - 43.91(RT) - 39.29(CC)(RT) \\
& - 0.172(MR)(RT) - 5.091(RT)^2 \\
& - 8.52(ET) + 12.406(CC)(ET) + 0.114(MR)(ET) \\
& + 2.804(RT)(ET) - 0.617(ET)^2.
\end{aligned}
\tag{10}$$

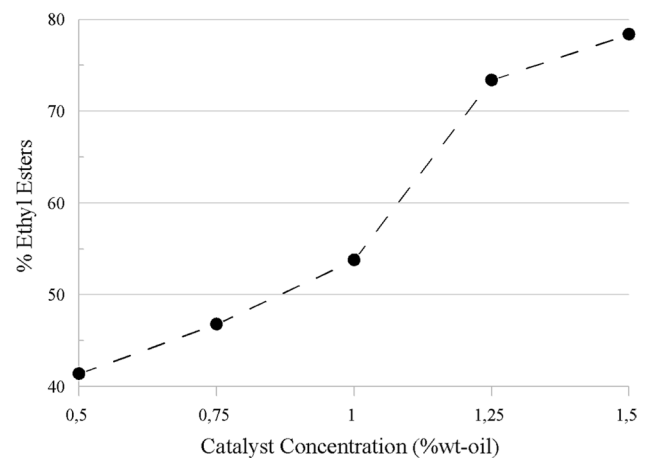
In Eq. (10), CC is the catalyst concentration, MR is the ethanol/oil molar ratio, RT is the residence time, and ET is the electrical tension.

The best condition found at this point was by trial 19, where 90% of ester yield was achieved with KOH concentration of 1.25%, ethanol to WCO molar ratio of 25:1, and residence time of 2 min. The system temperature was placed at its maximum in which the electrical tension of the auxiliary heat exchanger is set to 17.5 Volts which places the reactants just below the boiling point of ethanol. The appropriateness of the mathematical model was verified by the determination coefficient (R^2) and the adjusted determination coefficient (R_{Adj}^2) that in this case were 93.8% and 85.1%, respectively.

Table 11 Transesterification experimental results in the literature using spinning tank reactors. Catalyst concentration in %wt-oil

Study	Key parameters	Ester conversion
Abd Rabu et al. [87]	12:1 (methanol/WCO), 1% (NaOH), 120 (minutes), 70 °C	95%
Al-Hamamre et al. [84]	9.5:1 (methanol/WCO), 1% (KOH), 40 (minutes), 50 °C	98%
Anastopoulos et al. [86]	12:1 (ethanol/sunflower oil), 1% (NaOH), 2.5 (hours), 80 °C	81.4%
Atapour et al. [88]	9:1 (methanol/WCO), 0.72% (NaOH), 45 (minutes), 65 °C	92.05%
Encinar et al. [41]	12:1 (ethanol/WCO), 1% (KOH), 2 (hours), 78 °C	72.5%
Encinar et al. [54]	12:1 (ethanol/cynara oil), 1% (NaOH), 2 (hours), 75 °C	94.5%
Felizardo et al. [85]	4.8:1 (methanol/WCO), 0.6% (NaOH), 60 (minutes), 65 °C	99%
Keera et al. [52]	6:1 (methanol/soybean oil), 1% (NaOH), 60 (minutes), 60 °C	91%
Leung et al. [89]	6:1 (methanol/soybean oil), 1% (NaOH), 60 (minutes), 45 °C	93.5%
Leung et al. [89]	7:1 (methanol/WCO), 1.1% (NaOH), 60 (minutes), 60 °C	88.8%
Uzun et al. [90]	7.5:1 (methanol/WCO), 0.5% (NaOH), 30 (minutes), 50 °C	97%
Silva et al. [93]	3:1 (methanol/palm oil), 1.0% (NaOH), 60 (minutes), 52 °C	93%
Belkhanchi et al. [94]	6:1 (methanol/used frying oil), 1.0% (KOH), 60 (minutes), 18 °C	99.3%
Present Work	25:1 (ethanol/WCO), 1.25% (KOH), 2 (minutes), 56 °C	90%

It can be seen in Table 10 that the catalyst concentration showed a greater influence on ester yield, followed by electric tension, molar ratio and residence time. Similarly to the esterification process, the high catalyst influence was also expected. Table 11 summarizes some results from the literature that had used WCO in spinning tank reactors, along with the parameters used to obtain these results, where Al-Hamamre and Yamin [84] and Filizardo et al. [85] achieved conversions above the government-mandated 96% ester conversion for use in industry. Leung [11] shows a slight decrease in ester conversion, from 93.5 to 88.8%, by replacing soybean oil for WCO. Anastopoulos et al. [86], Encinar et al. [41] and Encinar et al. [54] used ethanol as the reacting alcohol used in transesterification; however, none of the studies achieved an ester conversion above 94.5%. Two different studies by the same author, Encinar et al. [41] and Encinar et al. [54], demonstrate how the use of WCO in place of refined oil can decrease overall conversions: In the [54] study, Cynara oil was reacted with ethanol for an ester conversion of 94.5%, while the [41] study ethanol reacted with WCO and had an ester conversion of just 72.5%. The results from this work compare very favorably with the studies in Table 11. The ester conversion of 90% from Table 9, trial 19, is larger than any of the studies using ethanol and WCO presented in Table 11. Also, when comparing the

**Fig. 9** Catalyst Concentration's main effect plot for transesterification

residence times the present study is far superior as the ester conversion of 90% was achieved in just 2 min residence time, while the studies in Table 11 achieved their results with residence times from 30 min to 2.5 h.

The KOH concentration contributed the most to the variance with a percent contribution of 71.69%. From the main effect plot in Fig. 9, the amount of ethyl esters created continued to increase with an increase in KOH concentration.

Table 12 Transesterification of WCO experimental results with MR=25:1, RT=1 min and electric tension ET=17.5Volts

Catalyst load (%wt KOH)	% Ester (-)
1.6	92
1.7	93
1.8	97
1.9	98
2.0	90

From 0.5 to 1.0% (%wt-oil) catalyst concentration, a steady increase was observed. A large jump in the conversion % is seen with a catalyst concentration jump from 1.0 to 1.25%, and then another steady increase is seen from 1.25 to 1.50% catalyst concentration.

In order to confirm it, the best values found for MR, RT, and voltage controlling temperatures were chosen to run more experiments varying the concentration above 1.5% until 2.0%. The results are summarized in Table 12. The ester conversion on WCO was increased up to 98% with 1.9% KOH, and the conversion then decreased to 90% when KOH concentration was increased to 2.0%, suggesting the best catalyst concentration for our system is in fact 1.9%. The analysis of the ideal catalyst concentration in microreactors is very important in the transesterification process, since the use in excess of catalyst will increase production

cost and will increase the complexity of the separation of the ester and glycerol phases.

For comparison purposes, Table 13 shows some results from the literature for the transesterification reaction performed in microreactors using refined vegetable oil in different operational conditions. Al-Dhubabian [23], Sun et al. [14], Wen et al. [25], Dai et al. [30], and Sun et al. [2] used methanol in their studies, where Wen et al. [25], Dai et al. [30], and Sun et al. [2] achieved nearly total conversion in residence times of 28, 14.9, and 17 s, respectively. Arias et al. [26], Santana et al. [31], Chen et al. [28], and Costa Junior et al. [35] used ethanol in their studies, and therefore Santana et al. [31] and Costa Junior et al. [35] achieved near-total conversion with residence times of 12 and 35 s, respectively.

It's worth to be commented that even though working with WCO brings into the picture a great challenge on the mass transfer process for biodiesel production, this Table 13 confirms that the results obtained with μ MIRHE microdevice in this work match pretty well the high ester conversion presented by the literature for both WCO and refined vegetable oil.

According to Table 10, ethanol to molar ratio had a contribution to the variance of 7.26%. The transesterification reaction is a reversible reaction and must occur with excess alcohol to favor the direct reaction and increase the formation of ethyl esters in the reaction. From Fig. 10, it can be

Table 13 Transesterification experimental results in the literature using microreactors. Catalyst concentration in %wt-oil

Study	Key parameters	Ester conversion
Al-Dhubabian [23]	7.2:1 (methanol/soybean oil), 1% (NaOH), 10 (minutes), 25 °C	91%
Dermibas [15]	6:1 (methanol/rapeseed oil), 1% (NaOH), 6 (minutes), 60 °C	98.8%
Wen et al. [25]	9:1 (methanol/soybean oil), 1.2% (NaOH), 28 (seconds), 56 °C	99.5%
Dai et al. [30]	8.5:1 (methanol/soybean oil), 1.2% (KOH), 14.9 (seconds), 59 °C	99.5%
Sun et al. [2]	8:1 (methanol/cottonseed oil), 1% (KOH), 17 (seconds), 70 °C	99.5%
Arias et al. [26]	25:1 (ethanol/castor oil), 1% (NaOH), 10 (minutes), 50 °C	96.7%
Santana et al. [31]	9:1 (ethanol/sunflower), 1% (NaOH), 12 (seconds), 50 °C	99.53%
Chen et al. [28]	12.7:1 (ethanol/soybean oil), 1% (NaOH), 5.6 (minutes), 60 °C	81%
Costa Junior et al. [35]	20:1 (ethanol/soybean oil), 1% (NaOH), 34 (seconds), 52 °C	99.6%
Pavlović et al. [95]	3:1 (methanol/sunflower oil), 0.1 g/g (NaOH), 10 (minutes), 60 °C	51.2%
Mohadesi et al. [96]	2.25vol:vol (WCO/methanol), 8.5% (calcined cow bone), 60 (seconds), 63.1 °C	99.24%
Present Work	25:1 (ethanol/WCO), 1.9% (KOH), 2 (minutes), 56 °C	98%

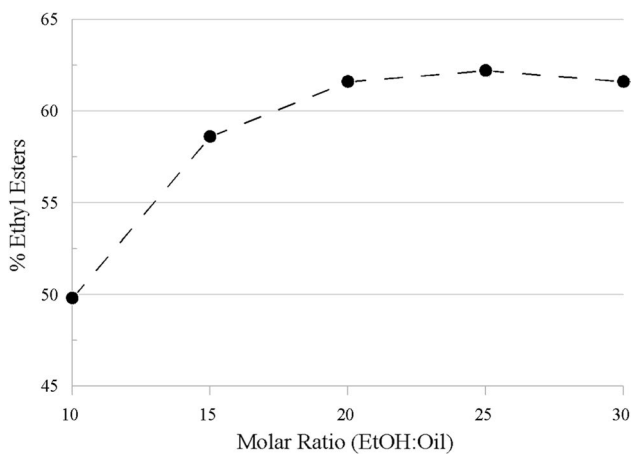


Fig. 10 Molar ratio main effect plot for transesterification

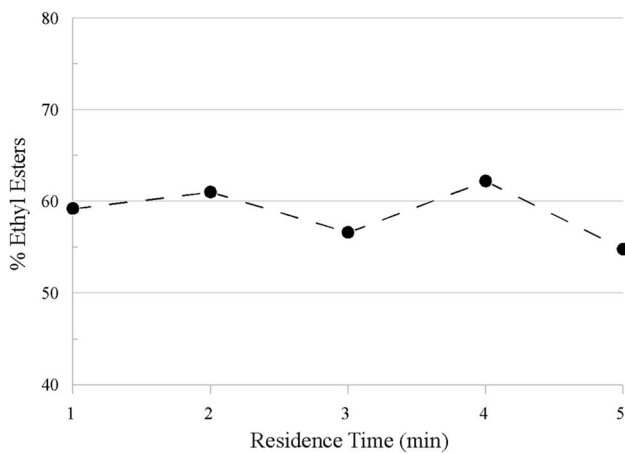


Fig. 11 Residence time main effect plot for transesterification

seen a large jump in ethyl esters conversion when the molar ratio increased from 10:1 to 25:1. In this figure, a slight decrease in ethyl esters is observed with an increase in the molar ratio from 25:1 to 30:1. This can be attributed to the difficulty in separation process of glycerin from biodiesel [41].

Residence time had a lower effect in variance for transesterification reaction with 2.51%, shown in Table 10. An average result from each level of the factor is plotted in the main effects plot (Fig. 11). From the main effect plot, a small rise in ethyl ester conversion can be seen raising the residence time from 1 to 2 min. A slight decrease in ethyl esters occurred increasing the residence times from 2 to 3 min. Then the ethyl ester conversion increased slightly when the residence time was 4 min and then slightly decreased when the residence time was 5 min. Usually, when transesterification is performed using pure refined oil, side reactions such as saponification or hydrolysis that occur simultaneously are ignored. When using WCO

Table 14 Electrical tension levels and their corresponding measured temperatures of the products leaving the reactor

Level	Electric tension (Volts)	Product temperature (°C)
1	6 ± 0.16	35 ± 4
2	9 ± 0.19	40 ± 4
3	12 ± 0.22	45 ± 4
4	15 ± 0.25	50 ± 4
5	17.5 ± 0.28	55 ± 4

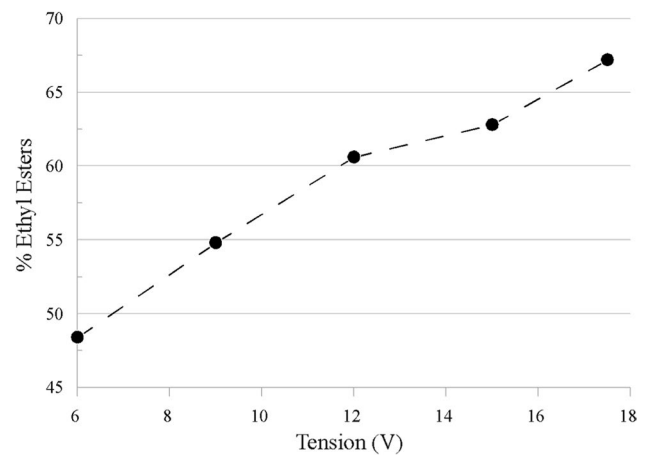


Fig. 12 Temperature main effect plot for transesterification

can have a noticeable effect on the conversion and can explain some of the differences within an average of the different residence times. The fact that a partial factorial experimental design was used also explains some of the differences from the expected results. Overall, the effect of residence time did not have much of a contribution at all on the variance of the response, so it can be concluded that the reaction is in equilibrium after 1–2 min of residence time. The high yields of ethyl esters in relatively short residence times in microreactors are due to the short distance of diffusion and consequent intensification of heat and mass transfer, which shows the advantage of producing biodiesel in microreactors.

The temperatures measured at the outlet of the reactor during experiments are displayed in Table 14; along with corresponding electrical tension, the auxiliary heat exchange system was set for the experiment. The temperature of the reaction had the second-largest percent contribution to the variance of 14.35%. An average result from each level of the factor is plotted in the main effect plot (Fig. 12). From the main effect plot, it is observed that the conversion of triglycerides to ethyl esters increased steadily as the electrical tension was increased, thus increasing the temperature. These results match well with the

literature of biodiesel synthesis with ethanol. The ester conversion is greatest when the temperature is just below the boiling point of ethanol, which is the maximum temperature while keeping the mixture in the liquid–liquid phase. It is worth noting that the heating of the transesterification reaction in the μ MIRHE is carried out using micro heat exchangers, which allows the use of rejected heat from a secondary process where heat rejection is high, such as from the cooling of high-quality photovoltaic cells concentration.

4 Conclusions

Several types of microreactors, based on microchannels, micropins, microgrooves, etc., appear as a promising technological alternative to improve efficiency in the continuous synthesis of biodiesel. Most of these studies use methanol, as the alcohol, and commercial vegetable oil. The present study provides three important benefits toward sustainability: first, enabling the recovery of waste heat, thus increasing the overall energy efficiency of the process; second, promoting the reuse of waste cooking oil, thus reducing disposed residues; third, allowing for high yield reaction using WCO and ethyl, instead of toxic methyl alcohol, as a reagent. Methyl alcohol has an adverse environmental effect, therefore, for countries like Brazil, which produce large quantities of ethanol, the ethylic route has a holistic advantage. The present work also contributes to the proposition of an experimental plan for process optimization and identification of the parameters with the greatest contribution to the biodiesel conversion.

In this work, biodiesel production was performed in a 3D metal printed microdevice using alternative feedstocks to evaluate the feasibility of the process in different strategies. Taguchi method was applied in both situations so that it could be possible to analyze which parameters have a relevant influence on ester yield. First, an esterification reaction was performed using a simulated high content FFA oil and ethanol as the working alcohol and MSA as an acid catalyst. The best results were obtained using 5% of catalyst, 20:1 of MR and RT of 2.5 min, where FFA content was reduced from 5.9 to 0.21%. The experimental results of the esterification reaction proposed in this work were compared with experimental results presented in the literature. The results available in the literature show that to obtain ideal FFA content for the transesterification reaction (<0.5%), stirred tank reactors take from 30 to 120 min. In this work, a reduction of FFA content to 0.2% was achieved in just 2.5 min, which makes the use of the μ MIRHE device feasible and efficient to conduct the esterification reaction.

After that, transesterification was performed using a WCO collected from a local restaurant with an initial FFA content of 1.0%, with ethanol as the alcohol and KOH as the catalyst. Initially, WCO was pretreated and then the Taguchi experimental plan was carried out in the same microdevice and heating conditions. The best result of 90% ester conversion was obtained at 1.25% of KOH, MR of 25:1, RT of 2 min and electrical tension of 17.5 Volts. Extra experiments were done aiming to investigate how far the catalyst concentration could be increased and still have positive effects on ester conversion, increasing catalyst amount to 1.9% leading to a higher ester conversion of 98%, for the same MR of 25:1, RT of 2 min and electrical tension of 17.5 Volts. The experimental results of the transesterification reaction proposed in this work were also compared with the experimental results from the literature. The literature results show that high yields of ethyl esters were obtained in residence times between 12 s and 10 min. In this work, a high yield of ethyl ester (98%) was achieved in 2 min, demonstrating the feasibility of using the μ MIRHE device for the efficient production of biodiesel using WCO, ethanol and KOH. The high yield of ethyl esters in low residence times is due to the use of the microreactor technology applied to biodiesel production through transesterification. These microreactors offer fast reaction rates as they have a high surface area/volume ratio and a short molecular diffusion distance that enhance heat and mass transfer. Another important factor for the high yields of ethyl esters at low residence times is the increase in the reaction temperature in these microreactors, as high reaction temperatures can decrease the oil viscosity, which increases the reaction rate at low reaction times.

From the factors analyzed with the Taguchi method, all of them seem to have individually positive effects on ester conversion between the levels analyzed. While catalyst concentration proved to be the biggest contributor to the variances in the final results in both reactions, molar ratio and residence time were responsible for only a small part of it. Temperature caused a relevant impact on the variance when added in the experimental plan for the transesterification reaction. The use of WCO showed itself as a great alternative in biodiesel production, as well as the use of microreactor in the process, which presented superior results when compared to traditional reactors.

The amount of biodiesel produced by a single microreactor is not substantial; however, its production increases when a large amount of them are staggered and operated in parallel mode. In this work, the manufactured device contains 10 microreactors in parallel (μ MIRHE) achieving high yields of ethyl ester, proving the efficiency of the microsystems for this application. The perspective of using a larger number of μ MIRHE devices in parallel arrangement could substantially increase the amount of produced biodiesel and thus fulfill

the commercial demand for a small portable system. The next step in the present research thus involves the design and assembly of a portable demonstration unit with 24 similar microdevices in parallel, thus comprising 240 microreactors.

This work has as motivation and potential application the conception of small-scale portable units for decentralized sustainable production of biofuels, enabled by the development of such innovative modular microdevices (μ MIRHE), which allow for the easy scaling up of the production to meet the raw materials availability and specific needs in each application and situation. Furthermore, sustainability is reinforced by the preferential use of the ethylic route, the recovery of waste heat from other processes, and the reuse of cooking oils.

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