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FABRICATION AND EXPERIMENTAL ANALYSIS OF A MICRO-REACTOR FOR BIODIESEL PRODUCTION

José Martim Costa Junior[1]
Carolina Palma Naveira Cotta[1]
Jeziel da Silva Nunes[2]
[1]Lab. of Nano and Microfluidics and Microsystems, LabMEMS, Mechanical Engineering Prog. –COPPE/UFRJ – Rio de Janeiro
[2]Mechanical Engineering Dept., Federal Center for Technological Education – CEFET/RJ- UnED Itaguaí
josemartim2005@gmail.com
carolina@mecanica.coppe.ufrj.br
jezielnunes@oi.com.br

Abstract. *In this study, a novel approach is presented for the micro fabrication and sealing of a microfluidic device to perform the role of a micro-reactor for biodiesel synthesis, made on a brass metal. The microfluidic device contains a Y-junction architecture, with a 400 µm squared cross section micro channel engraved using a micro-milling technique and sealed by welding, with tin as an adhesion material. This method provides a simple way to fabricate microfluidic devices for use in industrial applications, such as in the production of biodiesel, which require high temperatures, high pressures, and relatively high chemical resistance. To illustrate the applicability of the device, a biodiesel synthesis through a transeterification reaction of soybean oil, ethanol and NaOH was evaluated for different resident time and the conversion of triglycerides in ethyl esters of fatty acids was analyzed at room temperature. The analysis of biodiesel produced in these micro-reactors was performed by liquid chromatography high performance (HPLC).*

Keywords: *biodiesel, micro-reactor, transesterification, FAEE (fatty acid ethyl esters)*

1. INTRODUCTION

Due to the increased cost of petroleum, the reduction of petroleum reserves and increasing environmental concerns, there is great interest in developing alternative fuel sources, such as biodiesel (Dennis *et al.*, 2008; Sun *et al.*, 2010; Leung *et al.*, 2010). Biodiesel, which is produced from vegetable oils and animal fat, is biodegradable, nontoxic and have low emission profiles, making it more environmentally friendly than the diesel produced from petroleum (Meher *et al.*, 2006; Dennis *et al.*, 2008).

Biodiesel is commonly produced by transesterification reaction of vegetable oils, frying oils or animal fats with short-chain alcohols, such as methanol or ethanol, in the presence of a catalyst (Sun *et al.*, 2008). Normally, biodiesel is produced in conventional batch reactors and the transesterification process in this reactors uses high residence time (one hour to several hours) and high temperatures (Demirbas, 2008; Wen *et al*, 2009; Charoenwat and Dennis, 2009). Due to the high residence time, many researchers have been studying ways to reduce this reaction time to promote biodiesel production more efficiently (Pengmei *et al.,*2010; Falahati *et al.,* 2012; Rahimi *et al.,* 2014).

Various types of reactors are being developed in order to improve the production of biodiesel. Among these reactors, we can highlight the reactors based on microchannel , also called micro-reactors. These micro-reactors can achieve rapid reaction rates because they present a high ratio surface area per volume, which improves the heat and mass transfer, and short diffusion distance (Kobayashi *et al.,* 2006; Hessel *et al.,* 2005; Lee *et al.,* 2011; Xie *et al.,* 2012). These micro devices have presented a high yield of biodiesel at low residence times in biodiesel production (Salic and Zelic, 2011; Xie *et al.,* 2012).

Sun *et al*. (2008) accomplished the synthesis of biodiesel using unrefined rapeseed oil and cottonseed oil, methanol and KOH in micro-reactors capillaries with internal diameters of 0.25 mm, and found that the residence time is greatly reduced using micro-reactors in comparison with a conventional batch reactor, but the residence time in micro-reactors should be controlled to avoid biodiesel saponification with KOH. At a residence time of 5.89 min, the authors obtained a yield of 99.4% of methyl esters in a concentration of 1% wt of KOH using a mole ratio of methanol/oil 6:1 and a temperature of 60°C.

Wen *et al*. (2009) developed zigzag microchannel reactors to improve the efficiency of the alkali-catalyzed synthesis of biodiesel homogeneously and observed that the residence time for the high conversion of methyl ester was significantly reduced using an optimized microchannel reactor compared to a conventional agitated reactor. These micro-reactors also exhibited lower consumption of energy per gram for the same amount of biodiesel for biodiesel synthesis. At a residence time of 28s and temperature of 56°C, the yield of methyl ester reached 99.5% in a microchannel in zigzag optimized using a molar ratio methanol/oil 9:1 and a concentration of 1.2%wt of NaOH.

Charoenwat and Dennis (2009) experimentally studied the conversion of vegetable oil methyl esters of fatty acids as a function of residence time and of temperature in a capillary reactor with internal diameter of 500 μm connected to a micromixer Y and noted that the time residence in the capillary reactor significantly decreases compared with the same level of conversion in a batch reactor. Arias *et al*. (2012) developed micro-reactors in a T, Omega and Tesla geometries, manufactured in PDMS, and produced biodiesel from castor oil and ethanol. Using a concentration of 1 wt% of NaOH and a temperature of 50 °C, conversions were achieved 96.7, 95.3, and 93.5% using micro-reactors in the Tesla, Omega and T forms, respectively.

The objectives of this work is to describe the fabrication process of a metal micro-reactor based on micro channels and then analyze a biodiesel synthesis using soybean oil, ethanol and the NaOH catalyst, as a function of reaction time at room temperature. The micro-reactor, which is composed of micro channels with a square section 400μm x400μm, was made in brass and the micro channels were engraved by the machining process and hermetically sealed using tin as the adhesion material. The results of the synthesis in the micro-reactor were measured by means of HPLC (high-performance liquid chromatography).

2. FABRICATION OF MICROREACTOR

A base, wherein the structure of the micro channels was milled, and a cover, used to hermetically seal the device, compose the proposed micro-reactor. The base and the cover were made on brass and have a rectangular shape with 25mm wide, 40mm long and 3mm thick.

The micro-reactor consists basically of two access channels in the Y shape which converges to a simple reaction channel with a length 395.35 mm. All micro channels have a square section of 400μm x400μm. The two incoming connections and one outgoing connection to the outside were made on the external surface of the base plate. Figure 1.a shows a schematic draw of the device and Figure 1.b shows the positions of the connections to the external surface of the base plate.

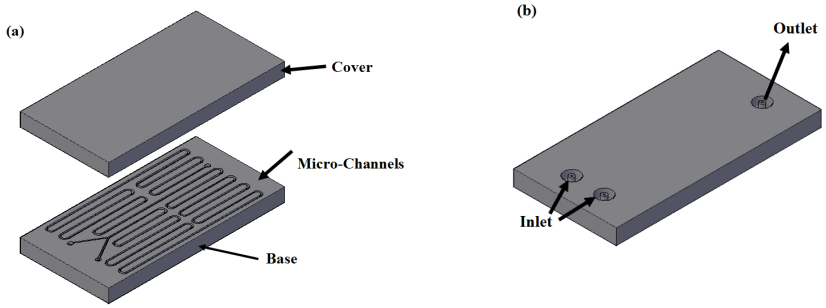
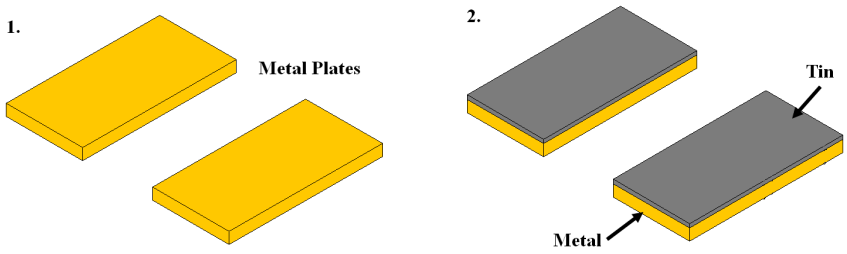


Figure 1. (a) Schematic draw of the micro device; (b) Inlet and outlet connections.

The micro channels were made through micro-machining process, which used a micro-milling device with computerized numerical control (CNC Minitech Machinery), that have a maximum rotation speed of 60,000 rpm and a displacement accuracy of 1μm. The manufacturing procedure used to manufacture the micro reactors, is schematically shown in Figure 2 and consists basically of four steps:

- Preparation of the base and cover surfaces (Fig. 2.1);
- Deposition of a tin layer (Fig. 2.2);
- Engraving of micro channels on the base plate using the micro-milling device (Fig. 2.3);
- Sealing of the base and cover plates (Fig. 2.4).



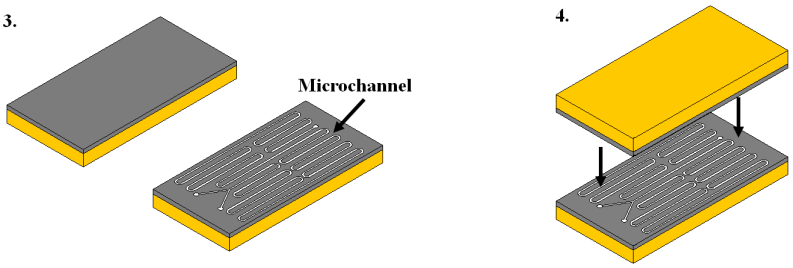


Figure 2. Schematic representation of the microfabrication process of a micro-reactor (1- surface preparation; 2 – tin deposition on the surface; 3 – engraving of the microchannel pattern; 4 – sealing of the microsystem).

The first step of the process, preparation of surfaces, has the purpose of removing the imperfections from the surfaces of the base plate, and cover, and in this sense, is made a facing step using a 3mm diameter tool bit (Figua 3.a). In the second step, the plates are heated up 200°C and a liquid tin layer is deposited over the surface. In the third step, shown in Figure 3.b, the inlet and outlet holes are drilled and the micro channel pattern is engraved on the surface with tin through of the milling process using a 0.4mm tool bit. In the last step, the device is hermetically sealed by assembling the base and cover plates aligned and compressing against each other in a thermal and pneumatic press (PLS By Metalnox 150) at 85 psi in a 230°C, for approximately 75min (Figure 3.c). Then, the plates were allowed to cool down to room temperature while maintaining the pressure of 85 psi.

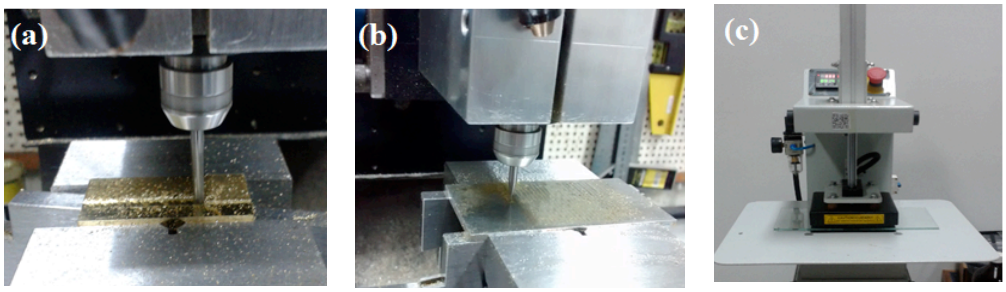


Figure 3. Machining operations used in the manufacture of the microfluidics device (a) Facing; (b) milling operation; (c) sealing.

Figure 4 shows the base plate at various stages of the manufacturing process, described in Figure 2. Figure 4.a shows the metal plate after the facing step, Figure 4.b shows the metal plate after the tin deposition, Figure 4.c shows the engraved micro channels and Figure 4.d shows the external face of the base plate with the three communication holes.

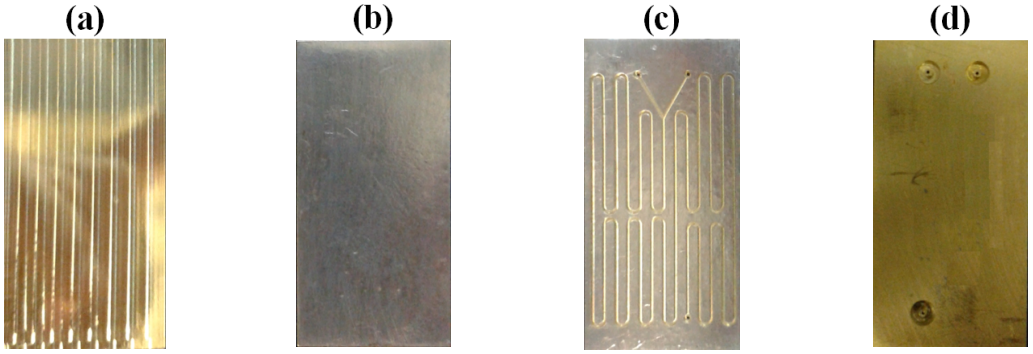


Figure 4. Fabrication steps for the micro device: (a) metal plate after the facing procedure, (b) metal plate with the tin layer, (c) the base plate with the engraved micro channels, and (d) the external face with three communication holes.

3. EXPERIMENTAL SETUP

The presented biodiesel synthesis was based on the transesterification of triglycerides (vegetable oil from soybean of food-grade, purchased at a local market) with absolute ethanol (99 Gl) purchased from B'Herzog, in the presence of an alkaline catalyst (sodium hydroxide - NaOH - from Petroquimios) yields esters of fatty acids and glycerol. The second order and reversible kinetics is presented in the following Figure 5 (Noureddini and Zhu, 1997).

$$Triglyceride + Ethanol \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Diglyceride + Ethyl\ Ester$$

$$Diglyceride + Ethanol \underset{k_4}{\overset{k_3}{\rightleftharpoons}} Monoglyceride + Ethyl\ Ester$$

$$Monoglyceride + Ethanol \underset{k_6}{\overset{k_5}{\rightleftharpoons}} Glycerol + Ethyl\ Ester$$

Figure 5. Second order and reversible kinetics reaction in the biodiesel production.

Where k_1 to k_6 are the kinetic rate constants of the reaction. Diglyceride and monoglyceride are intermediate products and the final products are the glycerol and ethyl ester, which is biodiesel.

3.1 Experimental Procedure

An experimental setup, shown in Figure 6, was assembled to perform the micro reactor here fabricated in a biodiesel synthesis application. The experimental setup is composed of: a micro-reactor; an electrical resistance in constantan, that can work as heater (for future analyses of the temperature influence in the reaction), of 10 ohms coupled to a flux meter and a thermocouple; two syringe pumps (NE 1000); a vessel for collecting of the end product in the transesterification reaction, immersed in a bath of water with ice which allows to stop the reaction, and thus evaluate the efficiency/performance of the micro reactor; a source of direct current with controlled voltage; a data acquisition system (Agilent 34970-A), for reading data provided by thermocouples and flux meter; a computer for data acquisition; and four thermocouples, being two located in each entrance of the micro device, the other located at the exit of the micro device and the last one, measuring the ambient temperature.

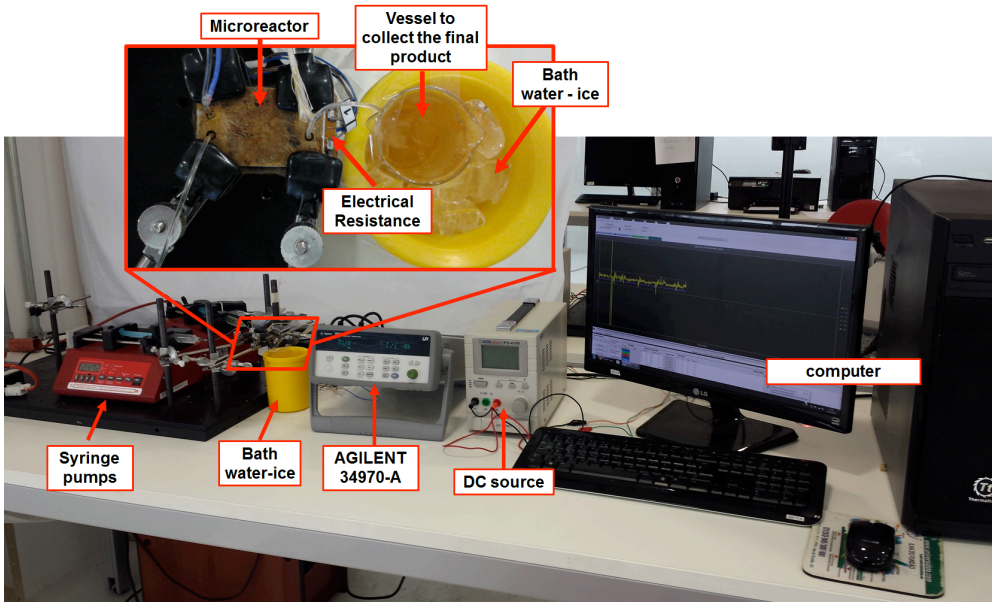


Figure 6. Experimental setup for biodiesel production.

The solution ethanol/NaOH and soybean oil are pumped into the micro-reactor through two independent syringe pump in a controlled flow rates. The final product is collected in a vessel immersed in a bath with ice-water, which is used to stop the transesterification reaction. The collected product is placed in a funnel that allows the separation of the two phases, the fatty acid ethyl esters (FAEE), that is the biodiesel, at the top and the glycerol at the bottom. Finally the ethyl esters are washed with distilled water at a temperature of 50°C for 15 minutes to remove catalyst residues and glycerol.

The analysis of the ethyl esters were made through a high-performance liquid chromatography (HPLC) from Thermo Scientific, model Ultimate™ 3000, and were performed on a column also from of Thermo Scientific, model Acclaim™ 120. All analyses were carried out in triplicate and the chromatograms were analyzed by the software Chromeleon 6.80.

4. RESULTS AND DISCUSSION

4.1 Micro-reactor Characterization

After that the micro channel was machined on the tinned surface, microscopic images of various parts of the surface were obtained to analyze, quality and quantitative, the manufacturing process. Figure 7.a shows the engraved microchannel on the surface of the base plate of the micro device. Figure 7.b shows an enlarged image of the region shown inside the rectangle in Figure 7.a. The widths of the channel in this region were analyzed and measured, and an example of the generated 3D image, including a measurement profile along the channel width, is shown in Figure 7.c. After 40 measurements in different points along the whole micro channel, the average width of the micro channel was 401 ± 4µm, and the average depth of the micro channel was 396.4 ± 1.42µm.

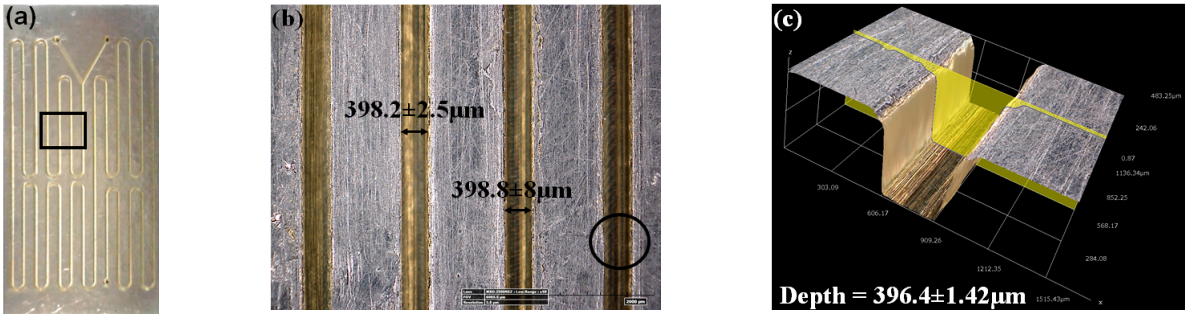


Figure 7.; (a) Fabricated micro reactor and the selected region presented in next figure (b); (b) Microscopic image of the selected region indicated by (a) by a rectangle; (c) 3D image of a selected region presented in (b) by a circle.

The quality of sealing process and the final product was verified through a destructive test by cutting the device along the dashed line shown in Fig. 8.a and them examining the cross section of the micro channel. A microscopic image of the obtained cross section from the selected region indicated by a rectangle in Fig. 8.a is presented in Figure 8.b. After 15 measurements, the average width of the micro channel was 377.8 ± 10,2µm and the average height of the micro channel was 390.7 ± 44,3µm. It was observed that there was no obstruction blocking the channel and the device was completely and controlled sealed, as it is also presented in more detail in Figure 9. The tin layer is presented in a closer view in Figure 10, and the average height of this layer was measured to be 44.75 ± 10µm.

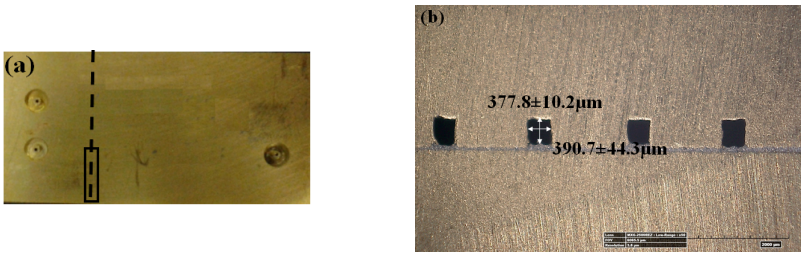


Figure 8. (a) External image of the sealed device, indicating the region where the device was sectioned and the microscopic images were obtained; (b) Microscopic image of the cross section.

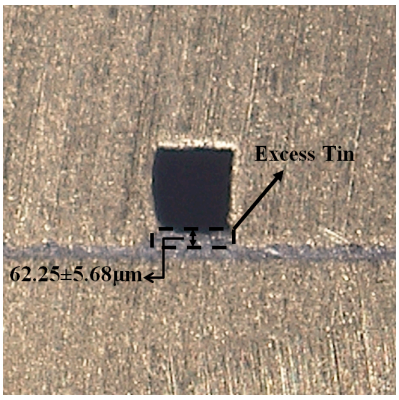


Figure 9. Enlarged image of the second microchannel of Figure 8.b.

Figure 10. Detailed image of the tin layer

4.2 Biodiesel Synthesis

To analyze the applicability of the fabricated micro-reactor, a biodiesel synthesis was conducted from ethanol and soybean oil using NaOH as a catalyst. The experiments were conducted at room temperature (approximately 23°C) for a molar ratio ethanol/oil 12:1, a quantity of catalyst of 1.0 wt% (based on oil weight), and seven different residence times (1 min, 3mim, 5min, 8min, 10min, 13min and 15min) was analyzed by adjusting the flow rate of the oil and ethanol + NaOH currents. Three experimental replicates were done for four of these seven analyzed residence times, (1min, 5min, 10min, and 13 min), in order to analyze the repeatability of the experimental procedure.

Figure 11 shows the profile of yield of FAEE, fatty acid ethyl esters that is the biodiesel, along the residence time using the seven reaction times, previously described, with the respective uncertainty bars provided from the HPLC analysis. It is worth mentioning that the values of the measurements of yield of FAEE made in HPLC, were ranging between 0.086% and 2.26% of the yield of FAEE. In this Figure 11 we can observe an increasing rate of FAEE yield of 30.57 ± 0.2 % to 47.2 % ± 0.7 % with an increasing residence time from 1 min to 15 min, where it reaches maximum conversion (57.5 ± 0.86 %) with 10 min. However a reduction in the biodiesel conversion can be observed from 10min to 15min (57.5 ± 0.86 % to 47.2 % ± 0.7 %), due to the possibility of having occurred biodiesel saponification with NaOH (Sun *et al*., 2008).

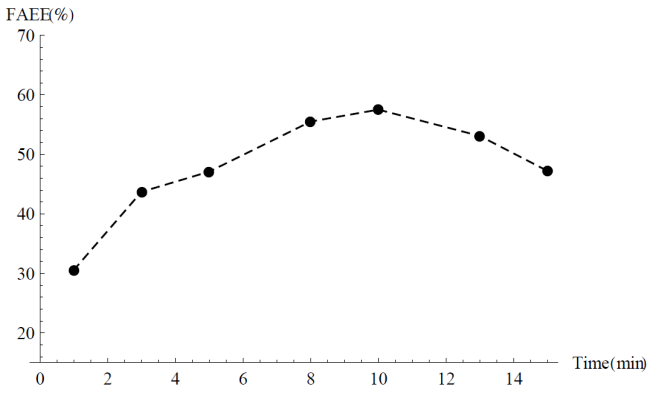


Figure 11. Evolution of profile of yield of FAEE over time.

Figure 12 below shows the repeatability of the experiments analysis. In this figure, it is observed that for the residence time of 1 min there is a large agreement of results and for other times it is observed a better agreement of the results, Showing that the experiment procedure, specially the finally step when the ethyl esters are washed, needs to be reviewed to improve it's repeatability, for example changing and/or controlling the amount water used in this process.

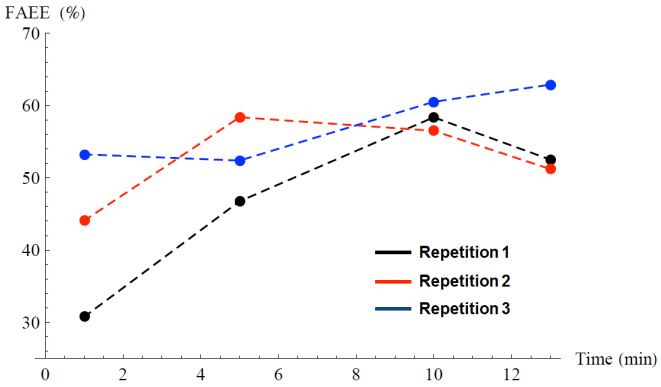


Figure 12. Repeatability of experiments.

Figure 13 shows the average profile of FAEE (fatty acid ethyl esters) yield and its average standard deviation over the residence time that comes from the previous analysis of repeatability presented in Figure 12. In this figure we observe an increase of the average yield of FAEE of 42.7 ± 6:53 to 58.47% ± 1.16% with increasing residence time of 1 min to 10 min, where it reaches maximum conversion (58.47 ± 1.16%). The maximum average standard deviation was 6.53% for residence time of 1 min and minimum was 1.16% for residence time of 10 min.

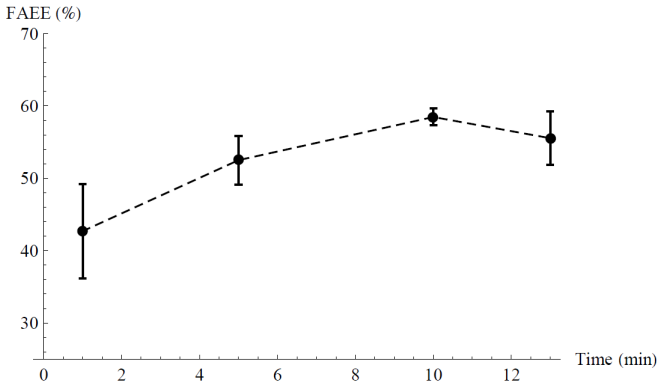


Figure 13 - The profile of average yield of FAEE over time and their average standard deviations.

5. CONCLUSIONS

In this work, it was shown the manufacturing process of a micro-reactor made completely in metal. Microscopic images was used to observe the quality of the machined microchannel and noticed that the micro machining process used is suitable for the manufacture of the micro reactor. The sealing of device was made using tin as the adhesion material, and by microscopic images of the cross section of the device was observed that this technique was also well suited. To show the applicability of the reactor, a biodiesel synthesis from soybean oil and ethanol using NaOH as catalyst, was presented. The synthesis of biodiesel was carried out at room temperature, with a molar ratio ethanol/oil 12:1, concentration of NaOH of 1 wt% and in various reaction times. The yield of fatty acid ethyl esters (FAEE) was analyzed over time and the maximum average yield of FAEE obtained was 58.47 ± 1.16% with a residence time of 10 min.

6. ACKNOWLEDGEMENTS

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