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MICROREACTOR FABRICATION BY PHOTOLITHOGRAPHY AND ANALYSIS FOR SYNTHESIS OF BIODIESEL

Kelvin Chen, kelvinchen89@gmail.com
Carolina Palma Naveira-Cotta, carolina@mecanica.ufrj.br
José Martim Costa Junior, josemartim2005@gmail.com
Arthur Berbert de Azevedo, arthur.b.azevedo@gmail.com

Laboratory of Nano and Microfluidics and Micro-Sistems - LabMEMS, Mechanical Eng.Dept. - POLI & COPPE/UFRJ, Rio de Janeiro, Brazil

Abstract. *This work presents an analysis about microreactors of different geometries for the biodiesel synthesis. The microreactors were made by a polymeric substrate with the photolithography technique. Simulations were made using the computational fluid dynamics software ANSYS-CFX. They show the flow behavior through the microchannels. Experiments were performed to produce biodiesel, with syringe pumps injecting alcohol and oil with specified flow, to control the alcohol/oil molar ratio. Ethanol and soybean oil were used to produce biodiesel with sodium hydroxide as catalyst. For these experiments, Omega and Tesla shaped microreactors were produced. Samples were prepared to chemical analysis to discover the percentage of oil converted in biodiesel. It has been shown that is possible to produce biodiesel in microreactors resulting in 81% of conversion in this work.*

Keywords: *microreactor, biodiesel, photolithography*

1. INTRODUCTION

Most part of energy nowadays is provided by nonrenewable sources. Therefore, new technologies has been studied to develop another energy sources. An alternative commonly used for the replacement of some fuels is the biodiesel, which has similar properties to mineral diesel. Even though the usual biodiesel synthesis process is well established, it needs some improves in many ways. Hence, the process intensification via microreactors seems to be a promising way to improve the biodiesel synthesis.

The microreactors, by presenting small dimensions, becomes appropriate to control the mixture of the reagents with very low Reynolds number and laminar flows, besides using small amount of reagents and to being able easily and quickly test a great number of reaction configurations (Tabeling, 2003). Therefore, using this microdevices has some advantages like to control small volumes of reagents, safety, low cost, low consumption, low energy demand and the most important in this work, the possibility to increase the efficiency in the biodiesel synthesis.

Microreactors are already used to produce biodiesel. Optimized microchannels with zigzag geometry were developed to the continuum synthesis of biodiesel (Wen *et al.*, 2009). With this devices they achieved a 99.5% conversion in biodiesel with residence time of 28 seconds. Microstructured reactors was developed to the transesterification of cottonseed oil and methanol with KOH as catalyst (Sun *et al.*, 2010). The reaction system included a micromixer that was connected to either a stainless steel capillary or a polytetrafluoroethylene tube. With this device they reached a 99.5% of conversion and a residence time of 17 seconds.

The present work deals with fabrication of microreactors on a low cost polymeric substrate using the photolithography technique. This approach using the conventional photolitography process combined with a low cost polymer was developed by Fernandes and Ferreira (2006) and use a photoresist based in urethane and acrylate oligomers (UA). This technique has the advantage of being very simple and produces microreactors relatively inexpensive. For the biodiesel synthesis, in this work were used ethyl alcohol and soybean oil and sodium hydroxide (NaOH) as catalyst.

2. FABRICATION BY PHOTOLITOGRAPHY

The photolithography fabrication process consists to transfer a geometric pattern through a photomask to a chemical photoresist via selective illumination of the photoresist using the ultra-violet (U.V.) radiation as the energy source.

In general, this micro-fabrication process can be described in five main steps:

1- Preparation and deposition of the photoresist;
2 - Exposure of the photoresist by the U.V. radiation;
3 - Removal of the unexposed polymer using a special solution called "developer";
4 - Sealing the microchannels;
5 - Communication of the micro-channels with the outside world.

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The figure 1 shows schematically these five steps of the micro-manufacturing process via photolithography.

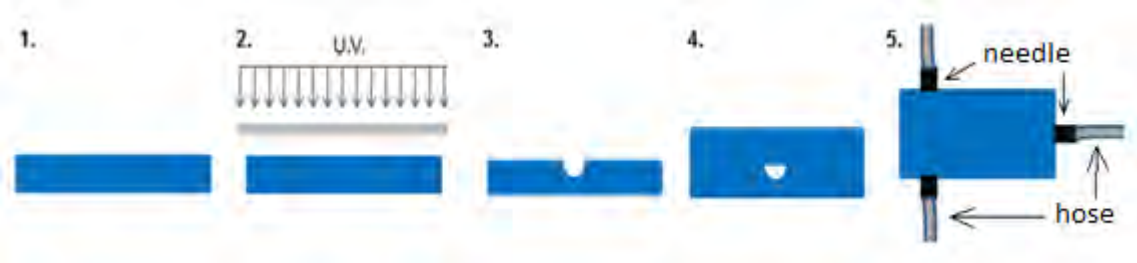

Figure 1 - Scheme of the photolithography micro-fabrication process

Figure 2 shows the geometry of the patterns with respective dimensions. Figure 3 shows the step of preparation and deposition of the photoresin (a viscous, liquid polymer) in a region bounded with a frame above the photomask. The photopolymer used is from AZ Srl®. The photomask consists in a transparency paper with the geometric pattern printed to be transferred to the resist. The photomask acts like a barrier, preventing the U.V. exposure of some parts of the resist, resulting in a selective exposure of the polymer. Therefore, the resist protected by the photomask, remains as a viscous liquid while the resist exposed become polymerized. Figure 4 shows the polymer getting in to exposition machine to be exposure by the U.V. radiation.

The exposure time determines the depth of channel that will be manufactured, since the greater the exposure time further polymerization will suffer the photoresist so that the channels are less deep. However, the exposure time may vary according to the polymer used and the photo exposition machine employed so that one must make a calibration of the process until reaching the desired dimensions. In this work the exposure time for the base manufactory was 24 seconds.

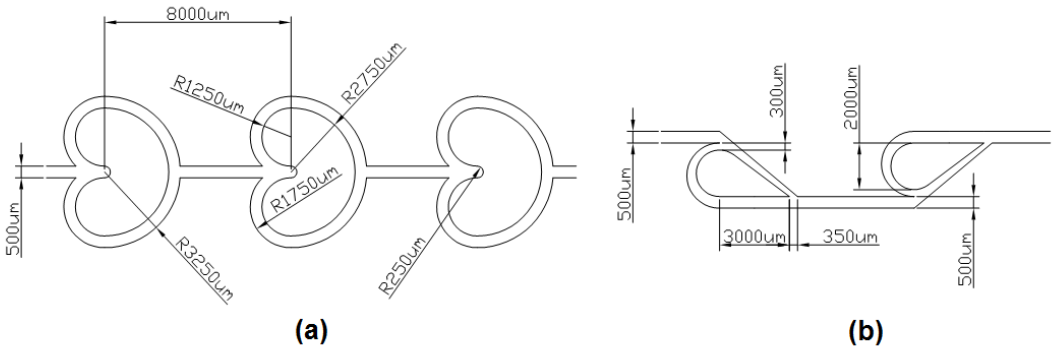

Figure 2 – Geometry of the pattern to be printed on the photomask with respective dimensions. (a) Omega geometry. (b) Tesla geometry.

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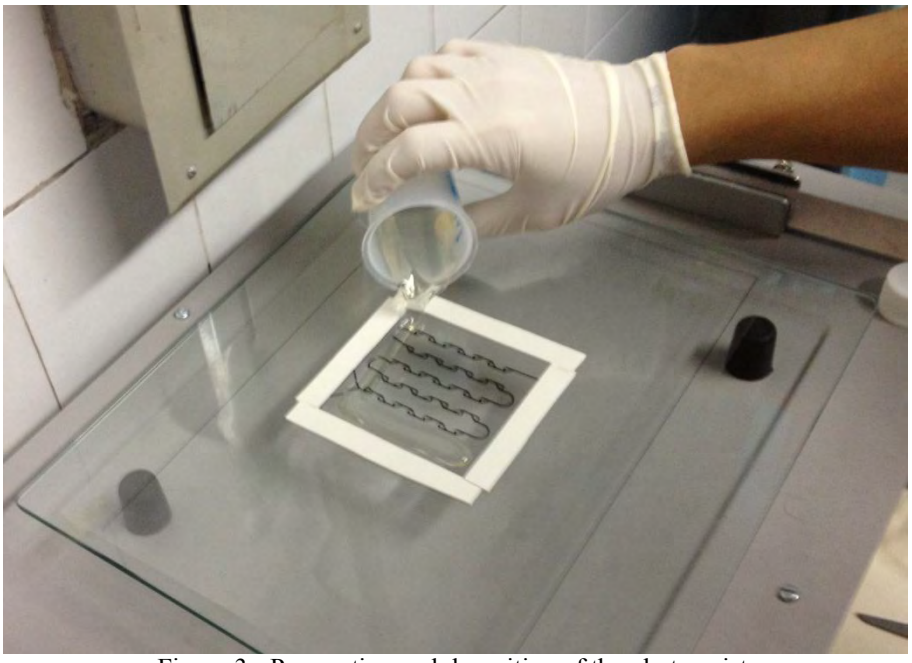

Figure 3 - Preparation and deposition of the photoresist.

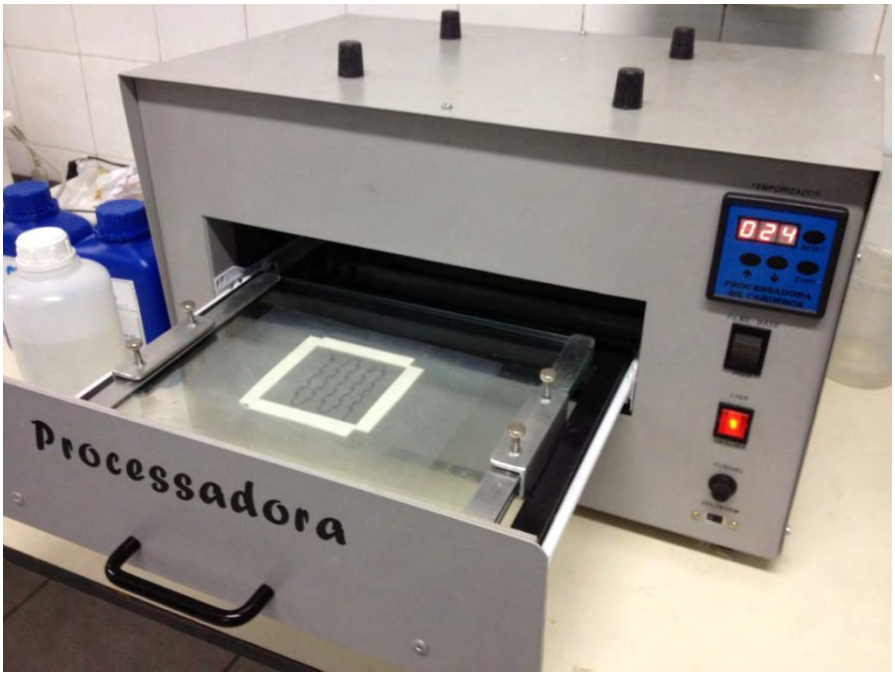

Figure 4 - Exposure of the photoresist by U.V. radiation

The next step in the microfabrication process is the removal of the remaining liquid resist. It consists to put the microsystem in an ultrasonic cleaner with a develop solution. In this work, the develop solution is a mixture of water and detergent. After the bath, with a thin brush, we remove the remaining resist. At the end of this step, it is possible to see the microchannels formed on the polymer. Figure 5 shows the microsystem being detached from the mask after polymerization has occurred. The next step in the manufacturing process is the development step, and it is performed in an ultrasonic bath containing water and detergent, as shown in figure 6.

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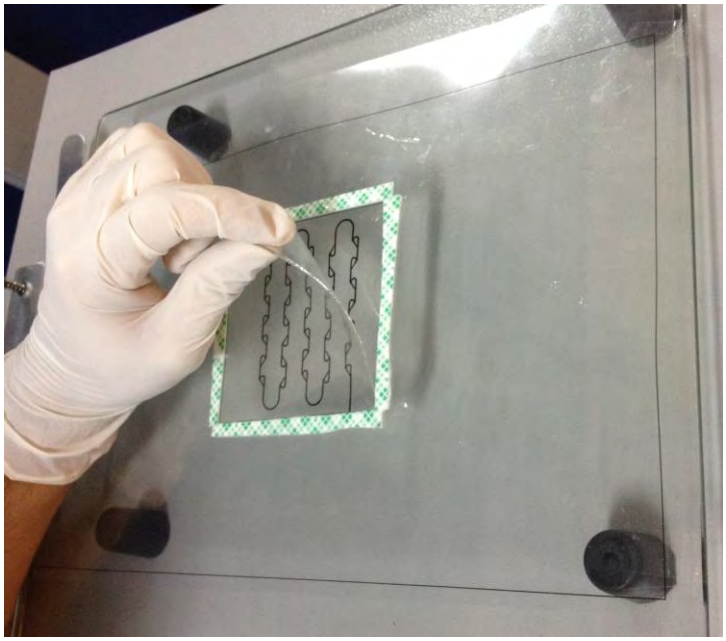

Figure 5 - Removal of the base with the microchannels.

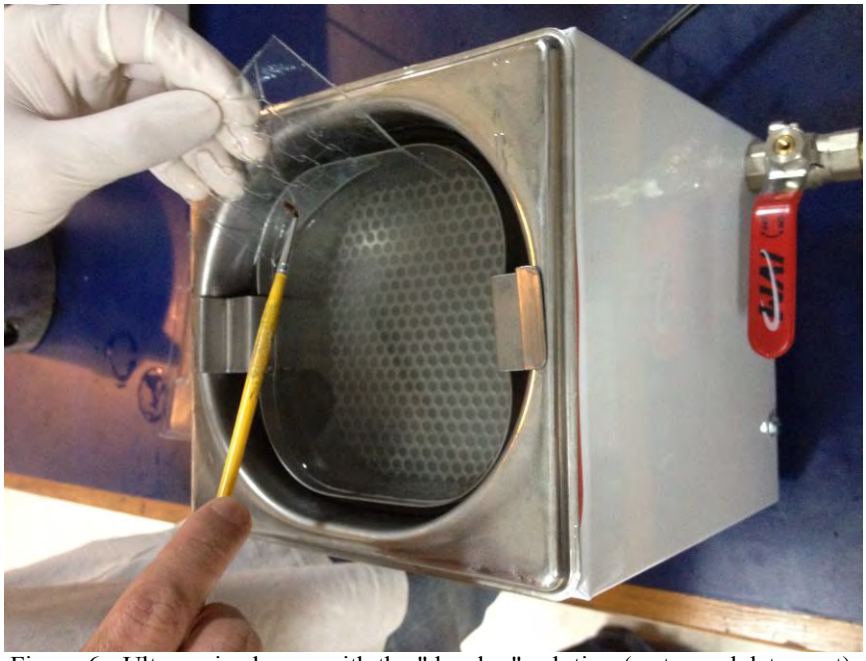

Figure 6 - Ultrasonic cleaner with the "develop" solution (water and detergent).

For the sealing process, is necessary to create a lid to cover the microchannels on the base of the microsystem because they are exposed and we cannot manipulate any fluid in their interior. The cover was made in the same way of the base, but without the photomask because we do not want to transfer any pattern to it. The time exposure of the cover is smaller than the base because we want to create a thin layer of non polymerized resist. As it was mention before, the exposure time depends on the polymer, and in this work the time exposure for the lid was 18 seconds. This thin film is necessary because it will promote the adhesion of the base and the cover providing a direct chemical bond (i.e., an intermolecular and without intermediate layers) between the cover and the base. The set of the base and cover is exposed again to the U.V. radiation with an imposing flow of argon gas in order to provide an oxygen-free atmosphere around the substrate. This atmosphere free of oxygen helps to improve the adhesion between the cover and the base. Figure 7 shows how the union of the cover and base is done and figure 8 illustrate the step of sealing.

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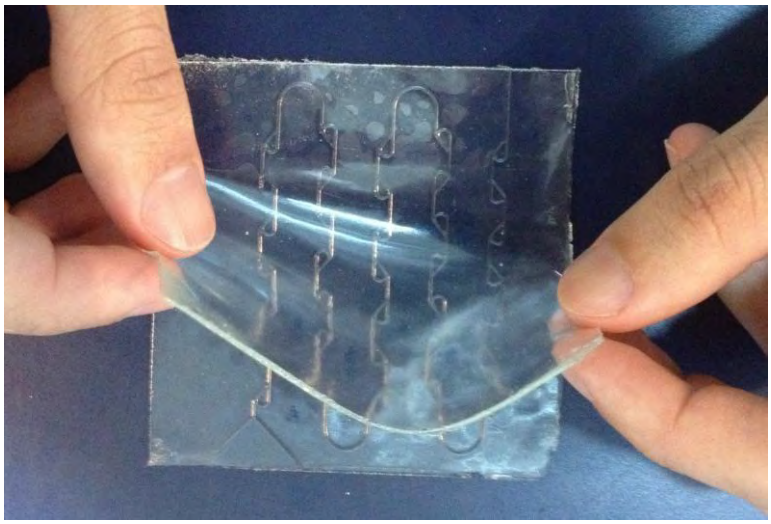

Figure 7 - Union of base and lid

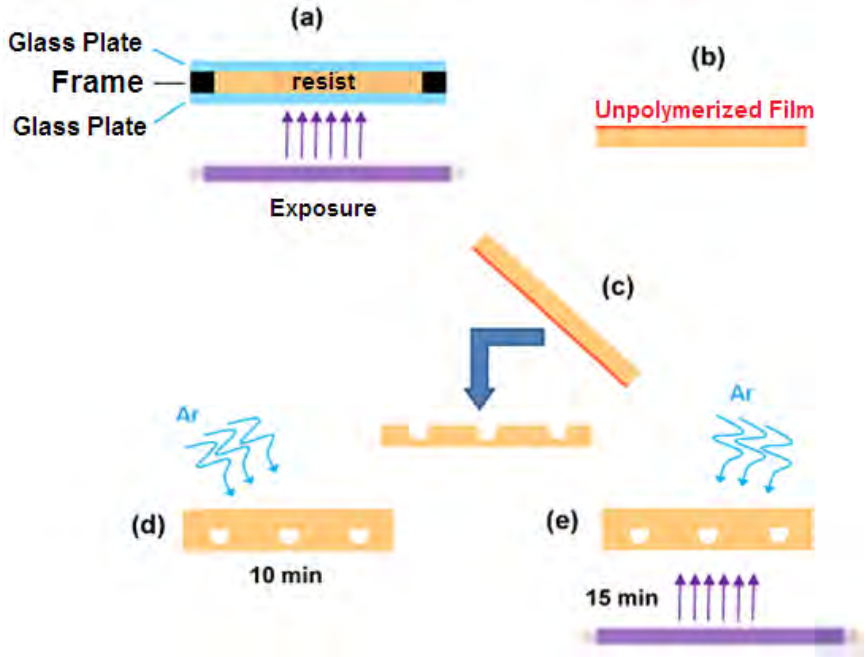

Figure 8 - Scheme of the fourth step: the sealing process. (Fonseca, 2008)

The last step is the communication of the microchannels with the outside world. In the present work, this connection was made through commercial hypodermic needles and hoses. Figure 9 shows the two microreactors made for this work, with a Tesla geometry (Fig. 9a) and with an Omega geometry (Fig. 9b). Figure 10 and 11 shows details of the geometry and the dimensions measured by electron microscopy. As we can see, the real dimensions of the microchannels are slightly smaller than the dimensions of photomask. It happens because the dimensions are dependent of the time exposure. With longer periods of exposure the dimensions are smaller and with lower periods the dimensions are larger.

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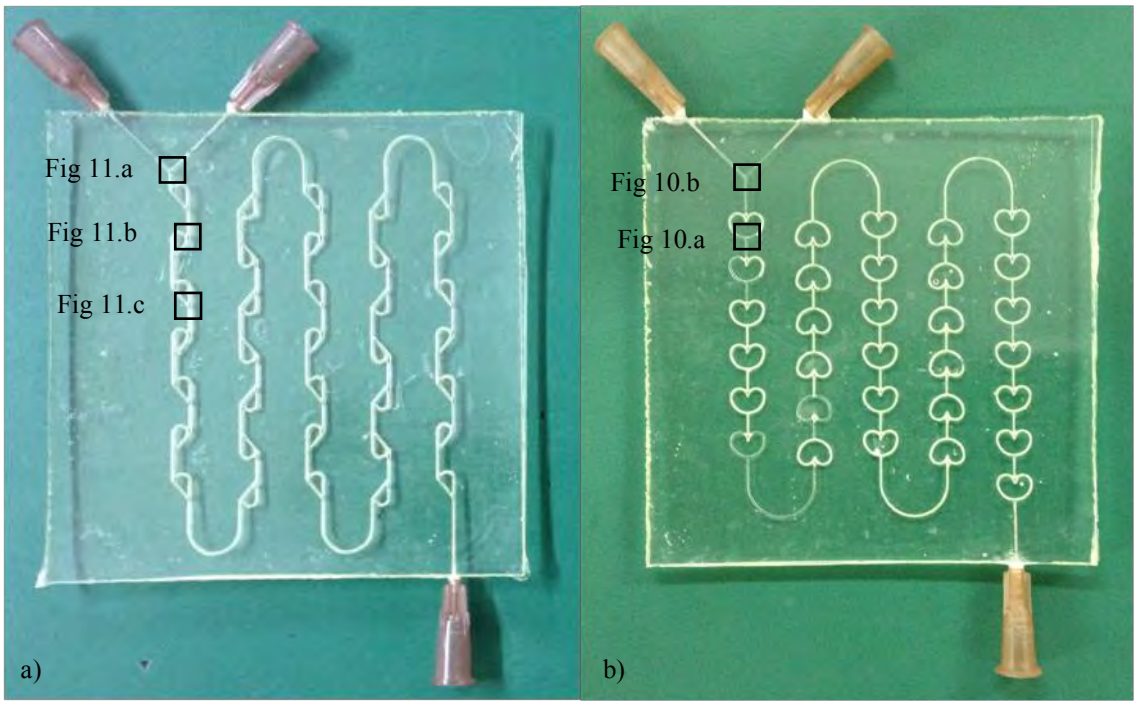

Figure 9 - Microreactors manufactured with the micro-channels communicated with the outside world through hypodermic needles. (a) Tesla geometry. (b) Omega geometry.

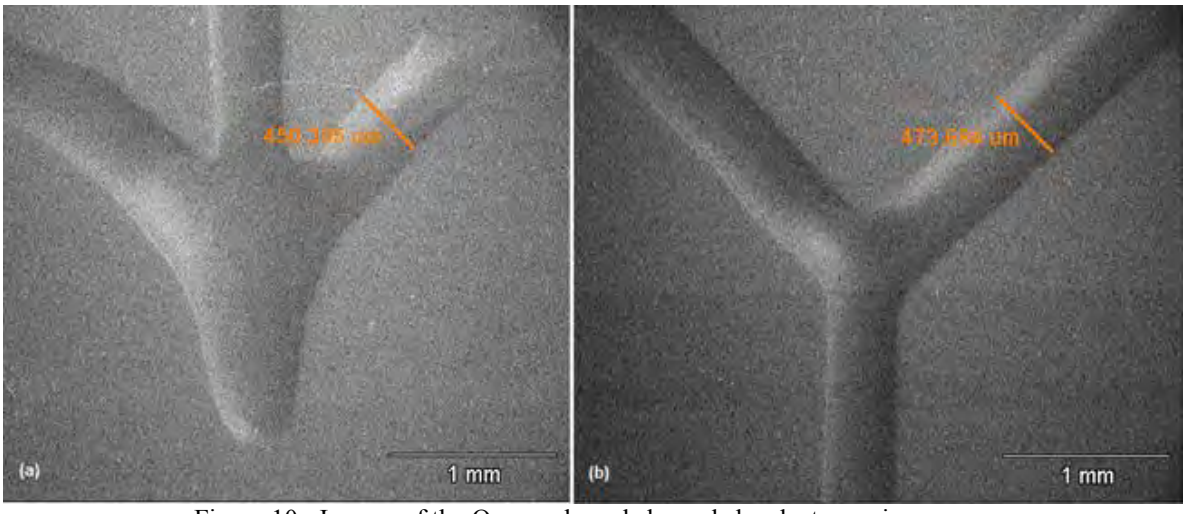

Figure 10 - Images of the Omega shaped channels by electron microscopy.

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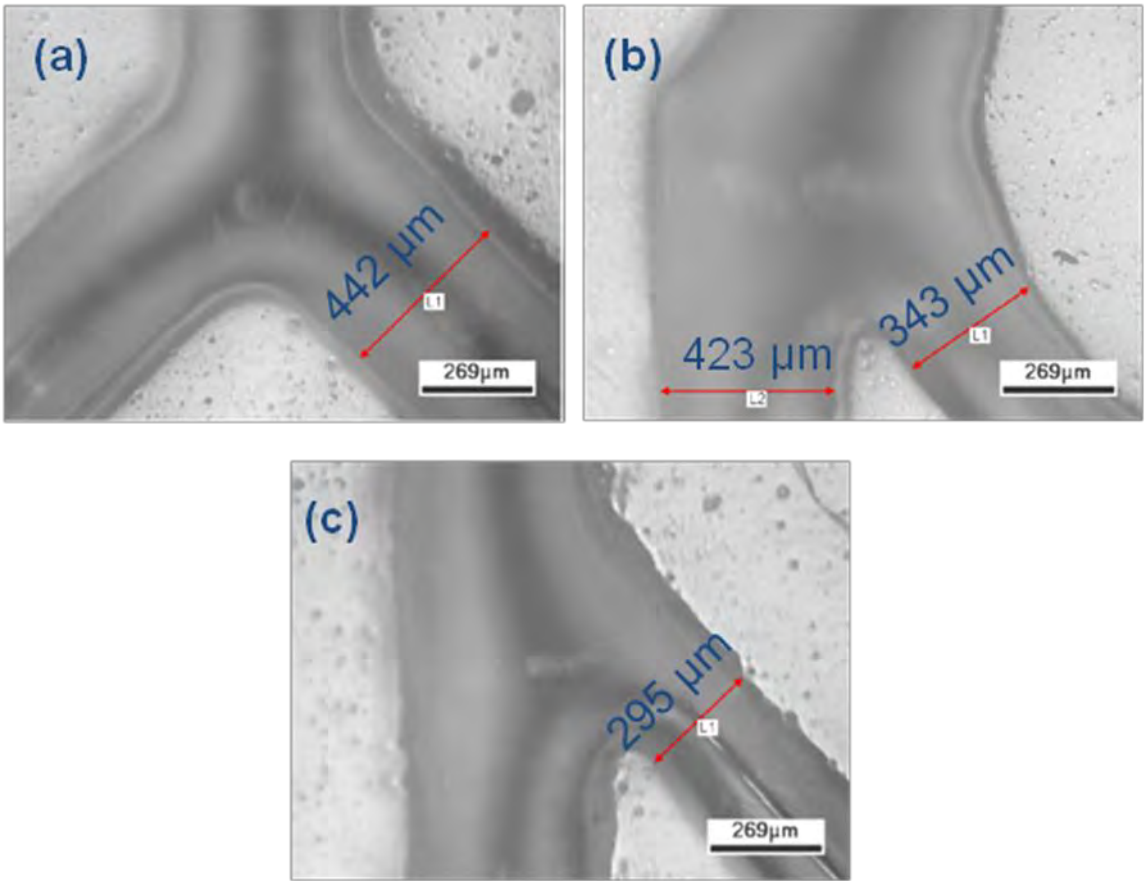

Figure 11 - Image of the Tesla shaped channels by electron microscopy.

3. NUMERICAL SIMULATION

Simulations of the flow and mixing has been performed using ANSYS CFX 12.0. Three geometries of micro-channels were studied and compared (Straight, Tesla and Omega). Fluids with the same properties of soybean oil and ethyl alcohol were used in the simulation. The chemical reactions were not taken into account.

Both of access channels (one for the alcohol and the other for the oil) were tested with a flow rate of 1.5 ml/min resulting in a low Reynolds number, then the flow was treated as laminar. Tab.1 shows the properties of the fluids used in simulation. Figure 12 shows the geometry of the microchannels simulated.

Table 1- Properties of the fluids used in simulation.

Properties	Fluid 1	Fluid 2
Fluid	Ethyl Alcohol	Soybean Oil
Density (kg/m³)	789	922
Molar Mass (g/mol)	46.07	874.8
Viscosity (Pa.s)	0.001197	0.059

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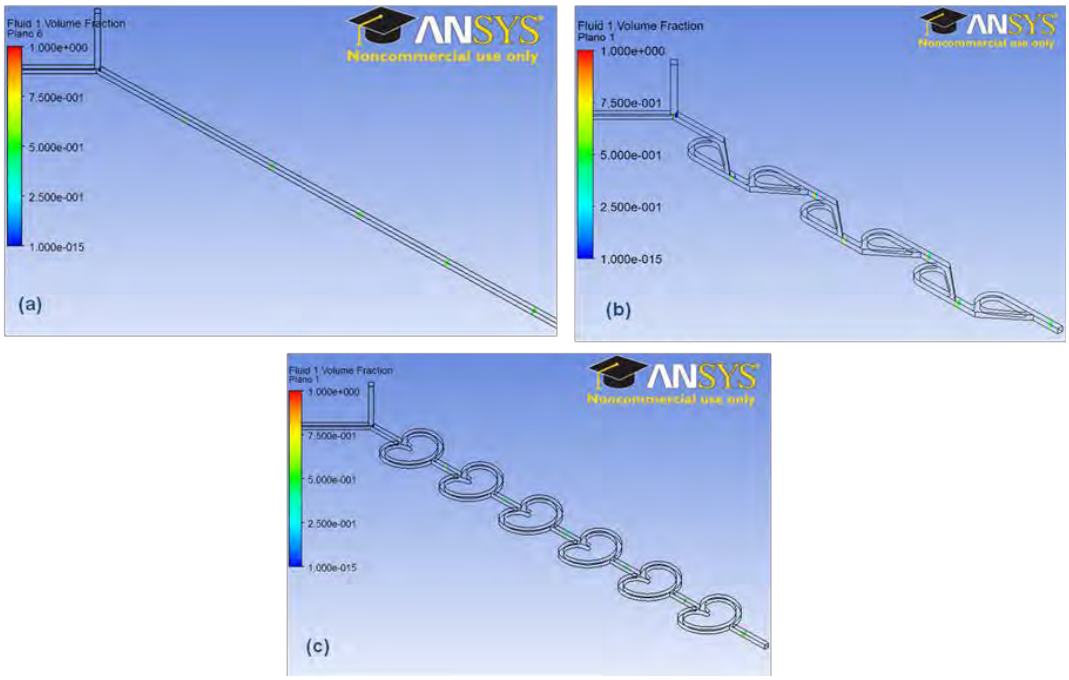

Figure 12 - Geometry of microchannels. (a) Straight. (b) Tesla-shaped. (c) Omega-shaped.

The mixing length of the microchannels simulated were 50mm for Omega and Straight and 45 mm for Tesla. The microchannels simulated has the same dimensions of the figure 2. Table 2 shows the quantity elements used in simulation.

Table 2 - Quantity of elements of each geometry.

Geometry	Straight	Tesla	Omega
Total number of nodes	144370	215054	377583
Total number of tetrahedron	184387	284093	514073
Total number of pyramids	6293	9693	21820
Total number of prismas	198247	291845	501074
Total number of elementos	388927	585631	1036967

Figure 13 shows the behavior of the mixture in the microchannels with different geometries, generated through the numerical simulations in ANSYS CFX, with the positions of each section. The blue color means the oil concentration and the red means alcohol. As we can see, both Tesla and Omega microchannels geometries have better mixture quality than the straight. The numbers in the figure indicate the position of the section (in mm). The position of the sections is measured from the junction of the access channels. Figure 14 shows the comparison of the section positioned in 42mm far from the junction.

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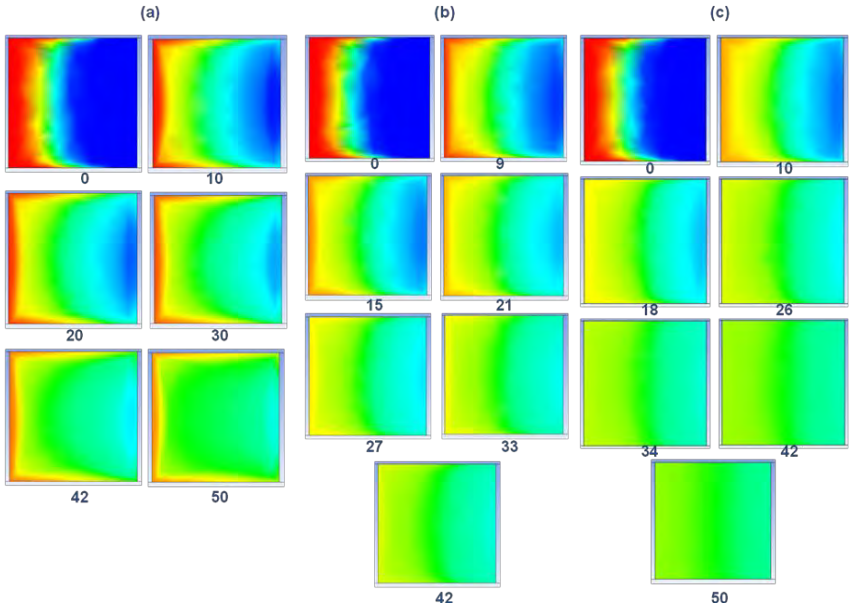

Figure 13 - Detail of the sections of the micromixers with the respective positions of the section (mm). (a) Straight; (b) Tesla; (c) Omega.

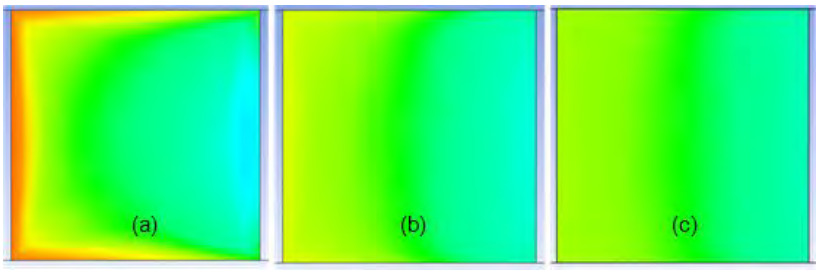

Figure 14 - Visual comparison of the mixture in each micromixer.

We chose five points to compare the concentration of alcohol in each micromixer. The figure 15 shows the location of each point. Tab. 3 shows the values of concentration of alcohol in each point.

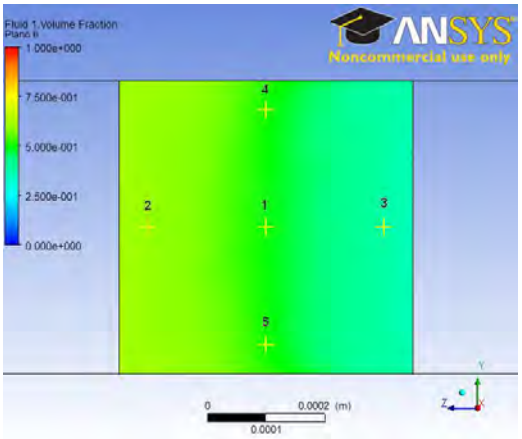

Figure 15 - Location of the points, for the comparison between the 3 micromixer.

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Tabela 3 - Values of alcohol concentration in each point.

	Values of alcohol concentration		
Geometry	Straight	Tesla	Omega
Point 1	0.44	0.50	0.50
Point 2	0.69	0.63	0.61
Point 3	0.27	0.37	0.39
Point 4	0.54	0.50	0.51
Point 5	0.54	0.52	0.51

4. BIODIESEL SYNTHESIS USING MICROREACTORS

Experiments were performed with microreactors with Tesla and Omega geometry. The reagents for the biodiesel synthesis were ethyl alcohol, soybean oil and NaOH as catalyst.

The first step was prepare a solution of ethyl alcohol and NaOH. The amount of catalyst was equivalent to 1wt.% (based on oil weight). Two syringe pumps, one filled with soybean oil and the other filled with the solution of ethyl alcohol and NaOH and, were connected to the access needles of the microreactor by little hoses. With the syringe pumps, we could control both of the reagents flow. The microreactor was positioned above a thin aluminum plate in contact with a resistance connected to a power supply. The purpose of the resistance was to supply a heat source to the microreactor, improving the reaction in the microchannels and the purpose of the thin aluminum plate was to homogenize the temperature prescribed by the resistance. The set of aluminum plate, resistance and microreactor was fixed in an acrylic support. The resistance is turned on until the plate temperature reaches approximately 80°C. The oil is heated and maintained to a temperature of 40°C. With the desired temperatures reached, the experiment is started. The microreactor is empty in the beginning of the experiment. The syringe pump containing alcohol is turned on a little time before the oil to avoid oil flowing alone in the channel. With the syringe pumps working, oil and alcohol flowed in the microchannels inducing the transesterification reaction of the soybean oil. The outlet was connected to a collection flask. Four thermocouples was strategically positioned to collect temperature data of the oil inlet, microreactor outlet, aluminum plate and room temperature. Figure 16 shows the experimental setup. It consists in: a) syringe pump filled with solution of ethyl alcohol and NaOH. b) syringe pump filled with soybean oil. c) acrylic support with the microreactor fixed. d) collection flask. e) power supply. Figure 17 shows the details of the experimental setup.

Figure 16 - Experimental setup. (a) syringe pump filled with solution of ethyl alcohol and NaOH. (b) syringe pump filled with soybean oil. (c) acrylic support with the microreactor fixed. (d) collection flask. (e) power supply.

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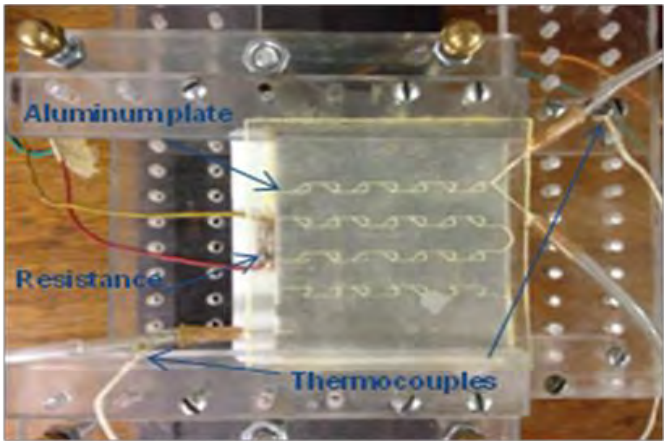

Figure 17 - Details of the support with the micromixer, the resistance and the aluminum plate.

5. RESULTS AND DISCUSSION

After the experiments performed, samples were analyzed in order to evaluate the percentage of soybean oil converted in biodiesel. The samples were analyzed through the Nuclear Magnetic Resonance Spectroscopy of hydrogen.

With the thermocouples strategically positioned in the experimental setup, we could analyze the temperatures developed in the experiment. Four thermocouples were used (named as T1, T2, T3 and T4). They measured temperature of the aluminum plate connected to the resistance (T3), the soybean oil inlet (T4), the microreactor outlet (T2) and the room temperature (T1). Figure 18 shows the temperature profile of the experiment. Only the temperature of oil inlet was measured. The alcohol temperature was not measured because of some complications with the alcohol inlet, like obstruction of the channel access and we did not want to cause more complications placing a thermocouple in the alcohol inlet.

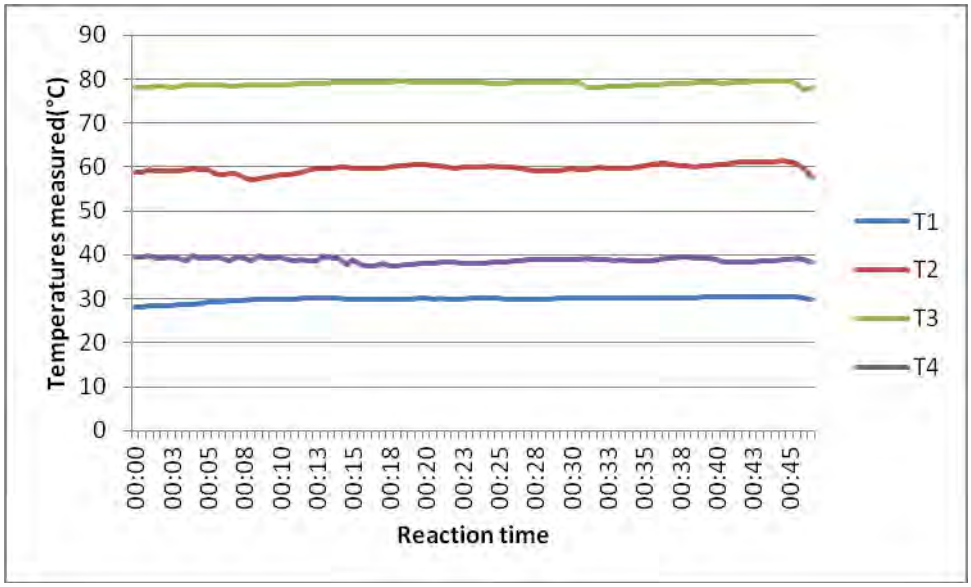

Figure 18- Temperatures measured in the respective thermocouples. T1: Room temperature. T2: Microreactor outlet temperature. T3: Aluminum plate temperature. T4: Soybean oil inlet.

The parameters used in this experiment are described in Tab.4. With this parameters, we achieved 81% of soybean oil converted in biodiesel and a residence time of 5.6 minutes. Figure 19 shows the spectrographic analysis of this sample. The spectrographic shows basically the response of the atoms of hydrogen in differents chemical bonds. The hydrogen reacts in different ways depending of the chemichal bonds in different mollecules and the peaks show these reactions. Integrating the curve, we can quantify the products.

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Table 4 - Parameter used in the sample analyzed.

Microreactor	Tesla Geometry
Catalyst	1wt.%
Soybean oil flow	0.009 ml/min
Ethyl alcohol flow	0.007 ml/min
Molar ratio of alcohol/oil	12.7
Outlet temperature	60°C
Residence time	5.6 minutes
Conversion	81%

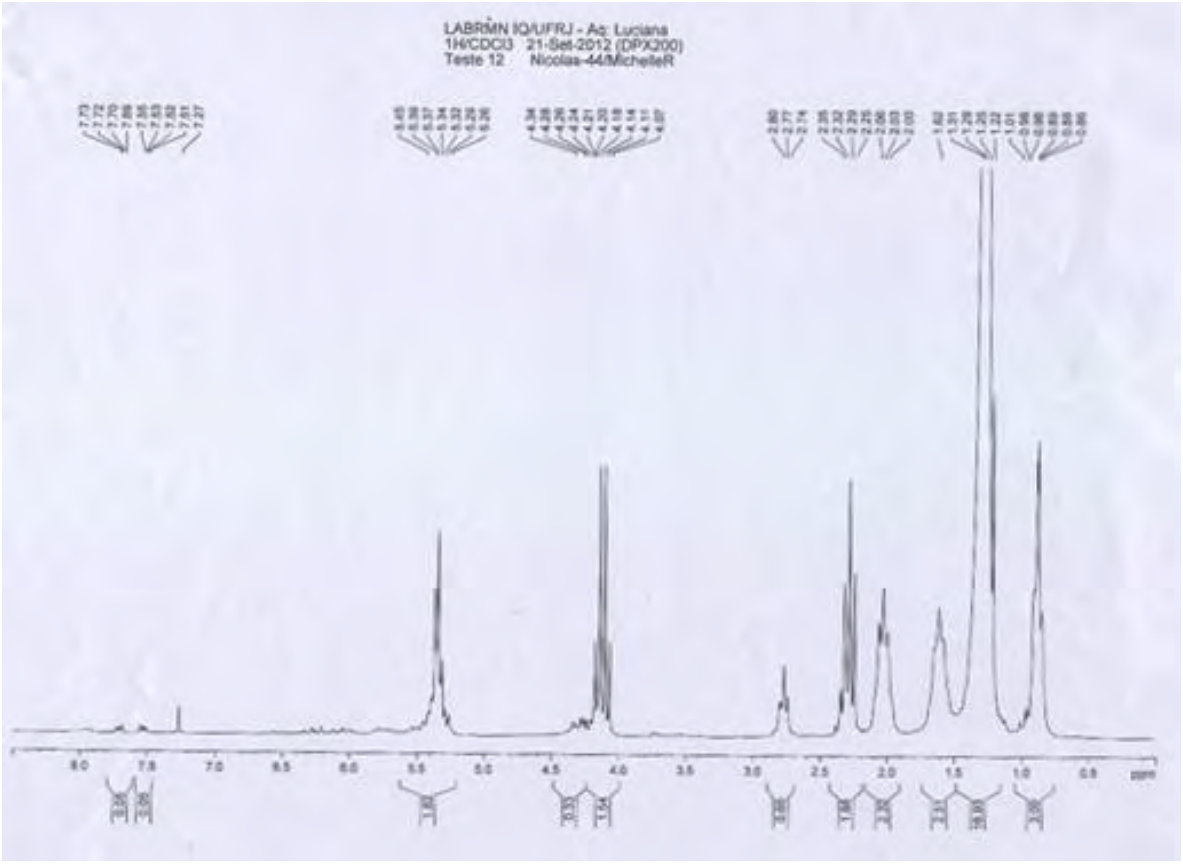

Figure 19 - Spectrographic analysis of the sample.

6. CONCLUSIONS

This work described the photolithography technique on a polymeric substrate to manufacture relative inexpensive and satisfactory microreactors for biodiesel synthesis.

Experiments were performed with soybean oil and ethyl alcohol with NaOH as catalyst. Using syringe pumps the reagents flow were controlled. Prescribed temperature was imposed in the base of the microreactor by a thin aluminum plate in contact with a resistance connected to a power supply. With the parameters specified in Tab.1, we achieved a 81% of conversion in biodiesel.

With microreactors, the reaction time of the alcohol and soybean oil, with the parameters described previously, was reduced from several minutes or hours in the conventional biodiesel synthesis process to some minutes. It showed that miniaturization has advantages for chemical reactions due to increase of the superficial area-volume ratio.

7. ACKNOWLEDGEMENTS

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9. RESPONSIBILITY NOTICE

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