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Numerical Study of Mixing and Reaction for Biodiesel Production in Spiral Microchannel

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Many microdevices have been tested in order to enhance the interaction between vegetable oil and alcohol to raising the conversion into biodiesel. However, many microdevices have some complexities in manufacturing and/or operation process. Consequently, this work studied numerically the use of a Spiral-micromixer for mixing and reaction of *Jatropha curcas* oil and ethanol for the production of biodiesel. The simulated microdevices had 200 μm in height and width. The mixing of the fluid was analyzed with Reynolds numbers from 0.67 to 100 and reaction studies were carried out for the same Reynolds numbers and a residence times ranging from 0.2 to 1,000 s. The Spiral-micromixer showed the highest mixing between the oil and ethanol. The highest conversion of vegetable oil in biodiesel was obtained with the T-micromixer (average of 51.8 %) and for the Spiral-micromixer (average of 50 %) for Reynolds number studied. An increment in residence time increased conversion, and the maximum conversion achieved was 98,48 % and 99,99 % for T-micromixer and Spiral-micromixer, respectively. The efficiency of mixing and reaction process can be increased and high conversion ratios obtained using this type of micromixer.

1. Introduction

Recently, great advances have been made in the area of miniaturization of the system. The application of these systems in fluid flows led to the creation of a new area of knowledge, the microfluidics. The tools developed in this area allowed to obtain great benefits in microscale processes. Some advantages include smaller amounts of reagents and samples, shorter reaction time and lower cost of manufacturing of this microdevices. This can lead to faster development of new products and processes for the industry. These new features can help solve current problems of society, such as the search for new fuels that can reduce use of petroleum. In this quest, biodiesel presents itself as an important alternative because it uses in its production vegetable oils or animal fats, is a renewable fuel and contribute less to the greenhouse effect. The biodiesel can be produced by chemical reaction (transesterification) of a vegetable oil (triglycerides) with a short-chain alcohol such as ethanol, in the presence of a basic, acid or enzyme catalyst (Gerpen, 2005). Thus, the high mixing of reactants results in higher conversions in biodiesel.
Despite the advantages of using microdevices in the synthesis of biodiesel, the difficulty of the mixture of species due to the tendency of laminar flow in this scale emerges as one of the greatest challenges in this area. To solve this issue several geometries have been proposed to promote mixing between vegetable oil and alcohol and increase the efficiency of biodiesel production. Some examples of geometries are: reactor with wire coil (Aghel et al., 2014); T-mixer, J-mixer, rectangular interdigital micromixer, slit interdigital micromixer (Sun et al., 2010); Tesla-, Omega-, and T-shaped (Martínez Arias et al., 2012). But an interesting geometry that has not been used in the synthesis of biodiesel was Spiral-Micromixer. This geometry is characterized by channels with curved trajectory which generate centrifugal effects on the fluids that flow in these channels, increasing the mixing of the chemical species (Sudarsan and Ugaz, 2006). Therefore, in this work we studied numerically the mixture and reaction of *Jatropha curcas* oil and ethanol for biodiesel production in T-Micromixer and Spiral-Micromixer. According to the studies found in the literature, this is the

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first work that studies the biodiesel production in Spiral-micromixer. This investigation is only qualitative and more studies are needed to quantify the results.

2. Computational Model

The T-micromixer and Spiral-micromixer are shown in Figure 1. All mixers have the rectangular cross-section. The length of inlet channel (L_e), distance between the inlet mixer and the point of mixing of the fluid was 400 μm and the height (B) was 200 μm. The width was 100 μm for entry length (W_e) and 200 μm for mixing channel (W_m). The total mixing length (L_m) channel was 35,100 μm. ANSYS ICEM 14.0 was used to create numerical meshes (subdivision geometry/domain in a finite number of control volumes) of micromixers. The geometries were discretized with tetrahedral elements. The number of control volumes were varied between 1,140,000 (T-micromixer) and 2,431,549 (Spiral-micromixer).

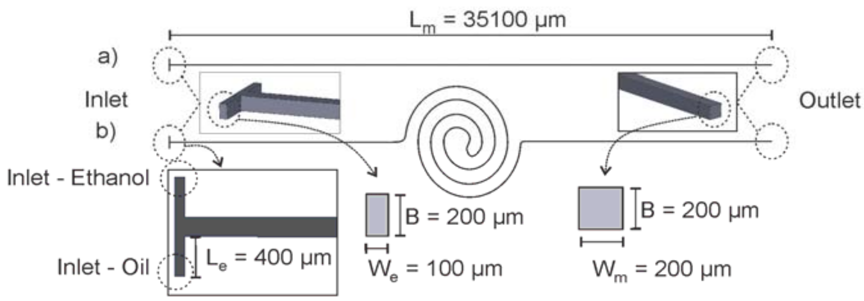

Figure 1: Micromixers used in this study; (a) T-micromixer and (b) Spiral-micromixer.

The physical properties of oil and ethanol are taken for a temperature of 40 °C; the density of *Jatropha curcas* oil and ethanol are 911.2 and 789 kg m^{-3}, respectively; the dynamic viscosities are 3.482×10^{-5} m^2 s^{-1} for *Jatropha curcas* oil and 1.50×10^{-6} m^2 s^{-1} for ethanol. The fatty acid composition of *Jatropha curcas,* information used to calculate the molecular weight of *Jatropha curcas* oil, was obtained from Tapanes et al. (2008). The molecular weight of the *Jatropha curcas* oil is 879.23 kg $kmol^{-1}$.

The software used for the fluid dynamic and reactive study was ANSYS CFX-14.0. This program of fluid dynamics general purpose solves the equations of mass and momentum using the finite volume method. Multicomponent, laminar, incompressible and isothermal steady-state flows were considered in all simulations. It was adopted for all simulated cases, high-resolution scheme for the advective terms. All numerical analyzes were performed at 40 °C. Different Reynolds numbers ranging from 0.67 to 100 were used. To calculate the inlet velocity used as boundary conditions for both fluids corresponding to Reynolds numbers specified, the dimensions of the mixing channel and the properties of vegetable oil (viscosity) were used. The diffusion coefficient of the alcohol in oil was calculated using the Wilke-Chang equation (Bird et al., 2002) and is equal to 1.2×10^{-9} m^2 s^{-1}.The static pressure was set to zero at the outlet and no-slip condition was applied on the walls. A convergence criterion of RMS (root mean square) of 1×10^{-5} was established (Cortes-Quiroz et al., 2014), and the number of iteration was set between 500 and 5000. For mixing study, oil was used as constraint and for reaction study inert oil was included as a constraint in simulation to ensure the mass fraction restriction $\left(\sum Y_i = 1\right)$. The simulations were solved in parallel processing. The computer nodes are composed of 8 Intel Xeon 3 GHz processors with 16 GB of RAM, which use Linux Suse 64-bit operating system.

The mixing index was calculated based on the standard deviation of the mass fraction of the oil in a normal cross-section of flow direction according to Eq. (1):

$$\sigma = \sqrt{\frac{\sum \left(Y_i - \bar{Y} \right)}{N}} \tag{1}$$

where σ is the variance of the mass fraction, Y_i is the mass fraction of the sampling point *i*, $\bar{Y}$ is the average and N is the number of sampling points inside the cross section. In each plane, N exceeded the number of 400 sampling points and these plans were equidistant from each other. The efficiency of the mixture of vegetable oil and ethanol was calculated using the parameter shown in Eq. (2):

$$M = 1 - \sqrt{\frac{\sigma^2}{\sigma_{max}{}^2}} \tag{2}$$

where M is the mixing index and $\sigma_{máx}$ is the maximum variation over the range of data. The variation is maximum for fluids unmixed and minimal for completely mixed fluids.

The transesterification reaction contains a series of consecutive and reversible reactions. In the presence of basic catalyst there is the reaction of triglycerides (TG) with alcohol (A) to form diglyceride (DG) and ethyl ester (E). In the second part of the reaction there is the conversion of the diglyceride into monoglyceride (MG) and ethyl ester, and finally there is the conversion into glycerol (GL) and ethyl ester (Freedman et al., 1984). The overall reaction of triglycerides with alcohol is given by Eq. (3):

$$TG + 3A \longleftrightarrow GL + 3E \tag{3}$$

Considering the reaction order of (A), (E) and (GL) equal to zero (Tapanes et al., 2008), the reaction rate is shown in Eq. (4):

$$\left(-r_{TG}\right) = k_1 C_{TG}{}^{\alpha} \tag{4}$$

From Tapanes et al (2008), α is equal to 1.266 and k_1 to 0.1830 using KOH (0.8 %) as catalyst, and was applied in the numerical simulations.

3. Results and Discussion

3.1 Mixing in micromixer

The mixing index at the outlet of micromixers as a function of the Reynolds number is shown in Figure 2. The Spiral-micromixer showed the highest mixing index, with average values of 0.99. The highest value for the T-Micromixer was 0.90. The Figure 3 shows the mass fraction of micromixers for Reynolds number of 10. At low Reynolds number (Re = 0.67, 2 and 5) the fluids within the mixing channel have low speeds, which causes a high residence time. In these circumstances the mixture of oil and alcohol is dominated by diffusion of species. As the residence time decreases when the Reynolds goes from 0.67 to 5 the mixing index also decreased until reach a minimum and then begins to rise. This behavior was also observed by Alam et al. (2014), Orsi et al. (2013), Alam and Kim (2012) and Ansari and Kim (2009). However, with increasing flow rate, other mixing mechanisms start to occur: advection. Advection causes a disturbance in the flow, increasing the mixture of species (Alam and Kim, 2012). This could explain why the mixing index increased with the increase of Reynolds number after 10 in the T-micromixer. If only diffusion between fluids were responsible for the quality of mixture, the increasing of velocity would decrease the mixing index, since higher velocity promotes smaller residence time in the micromixer, which would imply in a shorter time to triglyceride molecules travels over to the opposite side. The advection phenomenon also improved the mixing of fluids in microchannels in Alam and Kim (2009) and Ansari and Kim (2012).

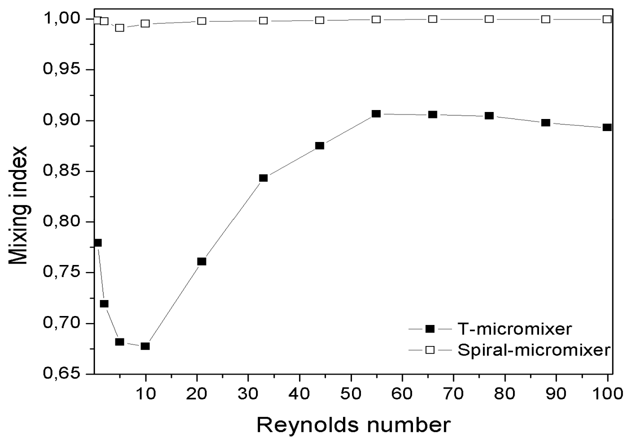

Figure 2: Mixing index as a function of Reynolds number for T- and Spiral-micromixer.

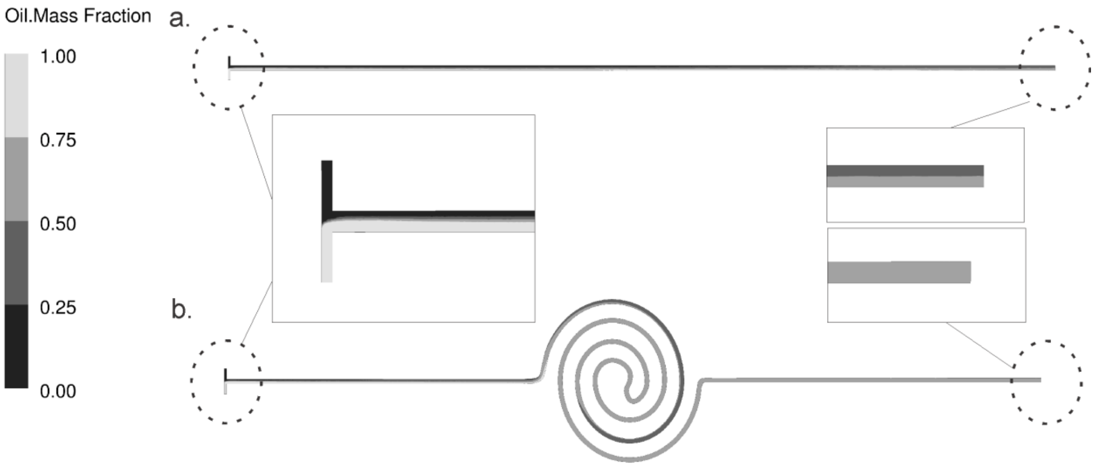

Figure 3: Mass Fraction distribution of oil in the (a) T-micromixer and (b) Spiral-micromixer at Re = 10.

In curved channels centrifugal effects pulls the fluid that is near the inner wall toward the outer wall while the fluid that is near the outer wall is drawn into the channel. Because the channel is in a spiral shape, this behavior is maintained throughout the spiral until the center of the spiral, when the fluid returns and change their positions (Sudarsan and Ugaz, 2006). This type of movement can explain the high mixing index values for the Spiral-micromixer. Diffusive effects found on T-Micromixer channels are also present in the Spiral-micromixer as shown by Sudarsan and Victor (2006). However, in the case of Spiral-Micromixer, diffusion and centrifugal effects seem to favor the mixing of the species in the same way. In low Reynolds (Re = 0.67, 2 and 5) the maximum value for the index mixing was 0.9982. In high Reynolds numbers (10-100) the maximum value found was 0.9991, which leads us to conclude that both low and high Reynolds number, the Spiral-Micromixer is efficient in the mixture of vegetable oil Jatropha curcas and ethanol.

3.2 Reaction in micromixers

Initially the reaction between oil of *Jatropha curcas* oil and ethanol was performed for the same Reynolds numbers used to study the mixing index. The conversion of the vegetable oil as a function of the Reynolds number is shown in Figure 4. The highest conversions of vegetable oil in biodiesel were obtained with T-micromixer, with an average of 51.8 %, and for the Spiral-micromixer (50 %). The conversion obtained in all micromixers decreases as the Reynolds number increases from 2 to 10 and after it, is practically constant and is not affected by the variation of Reynolds number between 10-100.

The residence time of the fluid inside the micromixers is inversely proportional to the mean velocity in the mixing channel. As the dimensions of the channel are kept constant, increasing the Reynolds number increases the velocity and decreases the residence time. Thus, the reactants don´t have enough time to react and the reaction is not complete at the exit of the channel, which could explain the low yields obtained. With a mixing channel length of about 0.0351 m and a reaction time ($\tau = 1/k_1$) of 5.46 s for T-micromixer, the mean velocity could not exceed the value of 0.0064 m s^{-1} which means a Reynolds number smaller than 1, which explains why in Reynolds equal to 2, the yield of 56 % was the highest obtained. In the Spiral-Micromixer was also observed that at low Reynolds the yield is higher (In Reynolds equal to 2, the yield is 60 %) and then decreases. This leads us to conclude that both diffusion and centrifugal effects favor the mixture, but for the reaction between species, the diffusion seems to favor more the yield.

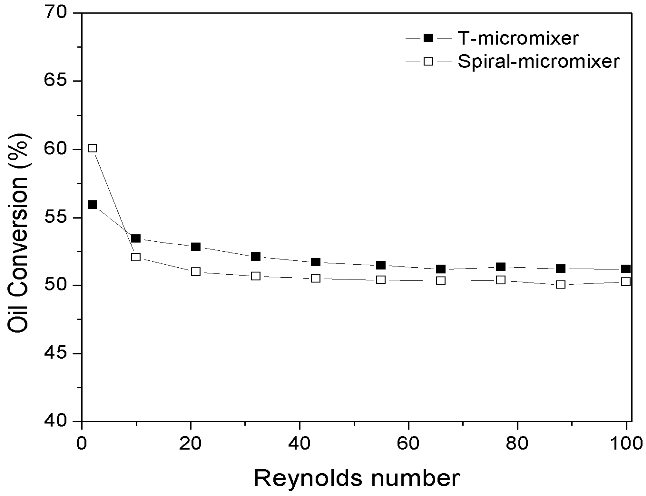

Figure 4: Conversion of vegetable oil in Biodiesel as a function of Reynolds number.

As the residence time appears to play a key role in the conversion of *Jatropha curcas* oil in both micromixer, Figure 5 shows the variation of conversion as a function of residence time. As can be seen, an increment in the residence time increased conversion and the maximum conversion achieved was 98,48 % in T-micromixer and 99,99 % in Spiral-micromixer. After a residence time of 40 s, there are not significant variations in the conversion of *Jatropha curcas* oil.

When the residence time is 0.2 s, still a low value for the conversion of oil (56.4 % to T-micromixer, 63.92 % to Spiral-micromixer), while in 10 s the conversion is 96 and 99.71 % to T-micromixer and Spiral-micromixer, respectively. As mentioned above the characteristic reaction time is 5.46 s, considering the first-order reaction. In 0.2 s, the reagents still do not have enough time to react in the mixing channel and reaction is incomplete. But when the residence time is increased, the molecules have enough time to diffuse in micromixers, which can show that diffusion effects play an important role in the reaction for both micromixers according to our simulations.

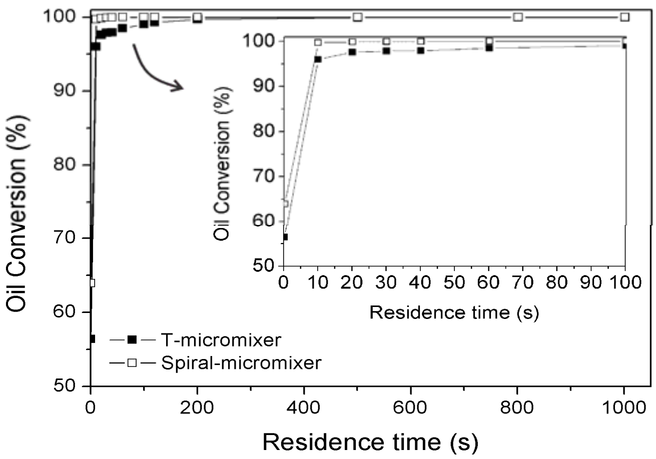

Figure 5: Conversion of vegetable oil in Biodiesel as a function of Residence time.

4. Conclusions

The mixture and the reaction between oil of *Jatropha curcas* and ethanol were studied in T-micromixer and Spiral-micromixer. The Spiral-micromixer showed the highest mixing index, with an average values of 0.99. The highest conversion of vegetable oil in biodiesel was obtained with the T-micromixer, with an average of 51.8 % when the conversion is a function of Reynolds number. An increment in residence time increased the conversion and the maximum conversion achieved was 98,48 % and 99.99 % for the T- and Spiral-micromixer, respectively. After a residence time of 40 s, there are not significant variations in the conversion of the *Jatropha curcas* oil. This work numerically showed the potential of the Spiral-micromixer to produce biodiesel in microdevices, however this investigation is only qualitative and more studies are needed to quantify the results.

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