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THEORETICAL ANALYSES OF THE FLOW PATTERNS IN THE BIODIESEL PRODUCTION

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Abstract. *This work presents a theoretical study of different types of flow inside microreactors for biodiesel synthesis, using two immiscible fluids: methanol and soybean oil in the presence of a catalyst (NaOH). Two flow patterns were studied: stratified flow, that is a laminar flow with a fixed interface between the immiscible fluids, and segmented flow, that is spherical droplets of one fluid, in motion, surrounded by the other fluid. This problem is here modeled through the Navier-Stokes equation and mass transfer equation coupled with a second order kinetic equations, assuming homogeneous, reversible and elementary chemical reactions. The mathematical model was solved using the finite element method using the multiphysics platform COMSOL. The main objective is to compare the influence, in the biodiesel synthesis, of different flow patterns in order to achieve higher conversions of triglycerides to biodiesel with lower residence times.*

Keywords: *microreactor, biodiesel, flow patterns, stratified flow, segmented flow*

1. INTRODUCTION

Most of the energy in use worldwide comes from non-renewable resources. Therefore, new renewable energy sources have been researched, like biodiesel, as an alternative to petroleum. Biodiesel, as a renewable and environmentally friendly fuel, has been widely produced and its demand continues to grow. The usual process of biodiesel production is the transesterification of vegetable oils. Even though the process of biodiesel production is well established in stirred tank reactors, new technologies have been developed to overcome problems like long reaction times, low production efficiency and high operation cost and energy consumption. Hence, the microreactors emerge as a potential technology due to their characteristics of low volume of materials manipulation, resulting in a safer process, lower energy and reactants inputs and process intensification, due to their reduced dimensions that result in decrease of diffusion path length and a substantially enhance of surface area-to-volume ratio (Martinez, *et al*., 2012).

The main distinction in segmented flow, unlike the stratified flow, is to create discrete volumes of one fluid, such as bubbles or droplets, called dispersed phase, which is immiscible in another fluid that surrounds the droplet, called continuous phase. Droplet flow in microchannels offers potentially further improvement in heat and mass transfer due to the enhancement of surface area-to-volume ratio, resulting in considerable reduction of transfer times and higher efficiency (Xu *et al*., 2005, Fischer *et al*., 2010, Han *et al*., 2011). Results showed that in some cases like the liquid-liquid extraction processes of acids and alcohol in a membrane dispersion mini-extractor, the mass transfer efficiency could be as much as 100%, with a mass transfer time less than 0.5 s (Xu *et al*., 2005). Enhancement of heat transfer in microchannels was achieved introducing droplets or slugs of an immiscible liquid into the main flow. It can be seen that the heat transfer in segmented flow is considerably higher compared with the case of single liquid flow, increasing the Nusselt Number in 400% (Fischer *et al*., 2010). Higher values of conversion of oil to biodiesel can be obtained with segmented flow too. With segmented flow of methanol in sunflower oil inside microtubes reactors with 800 μm and 300 mm of length, the oil conversion reached 100% within a residence time of 100 s (Guan *et al*., 2009). Furthermore, the segmented flow has the advantage of controlled manipulation of the fluids in its droplets sizes as well as in its frequency and spacing that result in significant reduction of consumption of samples and reactants (Surya *et al*., 2015).

In this context, the present work deals with theoretical analyses of the transesterification of soybean oil with methanol, in the presence of a catalyst, inside a microreactor. Two different flow patterns were considered and critically compared: stratified flow and segmented flow. The first model addresses a stratified flow with a plan and fixed interface between the two immiscible phases (soybean oil and methanol+catalyst). The second model addresses a segmented flow, composed by droplets of methanol (as the dispersed phase) surrounded by a continuous fluid (soybean oil). In both cases, the mathematical models that describe the flows and the non-linear problem of mass transfer coupled with chemical reaction are solved using the finite element method through the computation platform COMSOL Multiphysics 4.4. A parametric analysis was done to evaluate the effects of the residence time, dimensions of microreactor (height, diameter, and length), temperature, drop quantity and drop size, in the improvement of mass transfer and biodiesel conversion.

2. PHYSICAL PHENOMENON AND MATHEMATICAL MODEL

The transesterification reaction is the main process to produce biodiesel. It consists in a reaction of a vegetable oil (triglycerides) with an alcohol in presence of a catalyst yielding esters of fatty acids and glycerol. In this work it was considered a second order and reversible reaction according to the following Eq. (1) (Noureddini and Zhu, 1997). The triglyceride considered in this study was the soybean oil and the alcohol was methanol.

$$\begin{aligned} &Triglyceride(TG) + Methanol(M) \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Diglyceride(DG) + Methyl\ Ester(ME) \\ &Diglyceride(DG) + Methanol(M) \underset{k_4}{\overset{k_3}{\rightleftharpoons}} Monoglyceride(MG) + Methyl\ Ester(ME) \\ &Monoglyceride(MG) + Methanol(M) \underset{k_6}{\overset{k_5}{\rightleftharpoons}} Glycerol(GL) + Methyl\ Ester(ME) \end{aligned} \tag{1}$$

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 methyl ester, which is biodiesel.

In this work, it was considered two types of flow: stratified flow and segmented flow. The modeling of a stratified and segmented flow is described below. Both types of flow are modeled with the same transesterification reaction accorded to Eq. (1), showed previously.

2.1 Stratified flow

In this first case it was considered a stratified flow inside a microreactor composed by two rectangular parallel plates ($w>>H$) of width w, height H and length L. It was considered that soybean oil and methanol formed a two-phase flow configuration with a thin fixed interface between fluids and the velocity profile was fully developed inside the microreactor. The thicknesses of the soybean oil (H_{TG}) and methanol (H_M) layer are dependent of the dynamic viscosities and volumetric flow rates of these two species. Figure 1 shows a schematic representation of the microreactor of parallel plates. Figure 2 shows a schematic representation of velocity profile for the stratified flow between methanol and soybean oil phases in a parallel plates geometry microreactor.

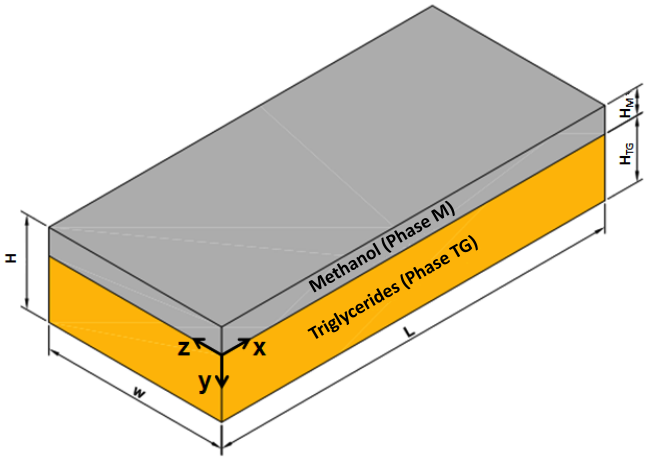

Figure 1 – Scheme of the microreactor of parallel plates with stratified flow.

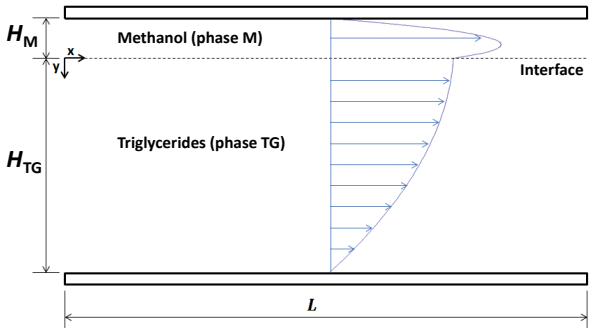

Figure 2 – Scheme of velocity of phases in the stratified flow in parallel plates.

The velocity profile for triglyceride and methanol phases, between parallel plates, were obtained from the Navier-Stokes and continuity equations with the following assumptions: steady state system, velocity and gravity in the directions x and z are equals to zero, pressure drop along x direction is constant, constant physical properties. For the boundary conditions it was assumed no slip conditions at the walls and continuity of velocity and shear stress at the interface. Since $w>>L$, it was adopted a 2-D model (x,y) for this stratified case. Thus, the equation that describes the velocity profile of the triglyceride specie $u_{TG}(y)$, and the methanol, $u_M(y)$, can be written as presented by Eqs. (2.a,b) and m, a and b are presented in Eqs. (3.b-d), where a is the ratio of the heights of triglycerides and methanol and b is the ratio of dynamic viscosities of triglycerides and methanol.

$$u_{TG}(y) = m\left[1+\frac{\left(b^2-a\right)y}{aH_{TG}(1+b)}-\frac{\left(b(a+b)\right)y^2}{aH_{TG}H_M(1+b)}\right]; \qquad u_M(y) = m\left[1+\frac{\left(b^2-a\right)y}{H_{TG}(1+b)}-\frac{(a+b)y^2}{H_{TG}H_M(1+b)}\right] \tag{2.a,b}$$

The pressure drop, ΔP, is related to the volumetric flow rate of the triglyceride specie Q_{TG}, by the following equation (Al-Dhubabian, 2005), where μ_{TG} and μ_M are the dynamic viscosities of the specie *TG* and *M*, respectively, *w* is the width and *L* the length of the microreactor.

$$\Delta P = \frac{2\mu_M L Q_{TG}(a+b)}{wH_M^2 H_{TG}(1+b)\left[1+\left(\frac{b^2-a}{2a(1+b)}\right)-\left(\frac{a+b}{3a(1+b)}\right)b\right]};\quad m=\frac{\Delta P H_{TG} H_M}{2\mu_M L}\left(\frac{1+b}{a+b}\right);\quad a=\frac{\mu_{TG}}{\mu_M};\quad b=\frac{H_{TG}}{H_M} \tag{3.a-d}$$

The mathematical model for the mass transfer problem is described below in Eqs. (4.a-d) with the assumptions of: a steady and isothermal system, constant physical properties, the velocity profile of products and intermediates is the same of the triglycerides, there is no diffusion of triglycerides, products and intermediates to the methanol phase and only the methanol diffuses to the triglycerides phase through the interface and the domain of study is limited to the triglycerides phase. The model consists of the follow advection-convection equation, where C_i is the concentration of specie *i* (*TG, DG, MG, M, ME, GL*), R_i is the reaction term of the specie *i* and D_i is the diffusion coefficient of specie *i*. At the entrance of microreactor (x=0) in the triglycerides phase, there is only presence of triglyceride and a constant concentration C_{TG0} is adopted. At the interface between triglycerides and methanol phases (y=0), from the hypothesis that there is no diffusion of triglycerides, intermediates and products species through the interface, a constant concentration of methanol C_M^* is imposed and the boundary conditions of no flux through the interface were established for all the other species. At the end of the microreactor (x=L) and at the wall (y=H_{TG}), the boundary conditions considered is no flux for all species.

$$u_{TG}(y)\frac{\partial C_i}{\partial x} = D_i\left(\frac{\partial^2 C_i}{\partial x^2}+\frac{\partial^2 C_i}{\partial y^2}\right)+R_i;\qquad i = TG, DG, MG, GL, M \text{ and } ME$$

$$\textbf{At entrance:}\quad C_{TG}(0,y)=C_{TG0};\qquad C_i(0,y)=0;\qquad i = DG, MG, M, GL \text{ and } ME$$

$$\textbf{At interface:}\quad C_M(x,0)=C_M^*;\qquad \left.\frac{\partial C_i}{\partial y}\right|_{y=0}=0;\qquad i = TG, DG, MG, GL \text{ and } ME \tag{4.a-d}$$

$$\textbf{At end and wall:}\quad \left.\frac{\partial C_i}{\partial x}\right|_{x=L}=0;\qquad \left.\frac{\partial C_i}{\partial y}\right|_{y=H_{TG}}=0;\qquad i = TG, DG, MG, GL, M \text{ and } ME$$

The term R_i represents the contribution of the transesterification kinetics for the mass transfer process. The kinetic expression for each specie is shown in Tab. 1:

Table 1 – Kinetic equation (R_i) for the specie *i*.

Specie *i*	$\boldsymbol{R_i}$
TG	$-k_1 C_{TG} C_M + k_2 C_{DG} C_{ME}$
M	$-k_1 C_{TG} C_M + k_2 C_{DG} C_{ME} - k_3 C_{DG} C_M + k_4 C_{MG} C_{ME} - k_5 C_{MG} C_M + k_6 C_{GL} C_{ME}$
DG	$k_1 C_{TG} C_M - k_2 C_{DG} C_{ME} - k_3 C_{DG} C_M + k_4 C_{MG} C_{ME}$
MG	$k_3 C_{DG} C_M - k_4 C_{MG} C_{ME} - k_5 C_{MG} C_M + k_6 C_{GL} C_{ME}$
GL	$k_5 C_{MG} C_M - k_6 C_{GL} C_{ME}$
ME	$k_1 C_{TG} C_M - k_2 C_{DG} C_{ME} + k_3 C_{DG} C_M - k_4 C_{MG} C_{ME} + k_5 C_{MG} C_M - k_6 C_{GL} C_{ME}$

2.2 Segmented Flow

This second case addresses a segmented flow in a tubular microchannel of circular section of diameter *d* and length *L*. The two-phase flow here considered, is composed by spherical droplets of a disperse phase (methanol) surrounded by a continuous phase (soybean oil). Figure 3 and 4 shows a scheme of the microreactor in a segmented flow, showing the dimensions and the two phases. It is considered that the droplet remains spherical along the microchannel. The velocity profile was obtained from Navier-Stokes and continuity equations with the following assumptions: steady state system, velocity in the direction x is equal to zero, pressure drop along x direction is constant, constant physical properties. It is considered that the spherical droplets behave as a spherical rigid particle, resulting in a velocity equal to zero at its surface (Clift *et al.*, 1978 and Wylock *et al.*, 2010). The model simulated in this work is in cylindrical coordinates and two dimensional (x,r) due the fact that the cross section is circular and the droplets are spherical, so we can consider an axisymmetric flow inside the microchannel. The Eqs. (5.a-g) show the equations of the velocity profile of segmented

flow with their respective boundary conditions. U_∞ is the velocity at the inlet of the microreactor and ρ_{TG} and μ_{TG} are the density and dynamic viscosity of the continuous phase (triglycerides), $\mathbf{u}=(u_r,u_x)$ is the velocity vector with the r and x components and p is the pressure.

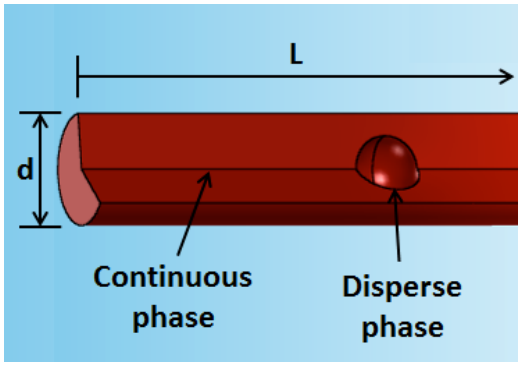

Figure 3 – Scheme or the microreactor in a segmented flow.

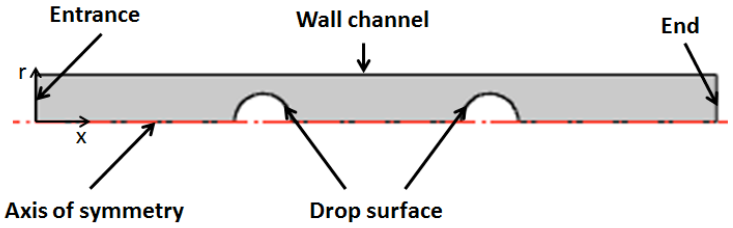

Figure 4 – Details of microreactor in a segmented flow.

$$\frac{1}{r}\frac{\partial(ru_r)}{\partial r}+\frac{\partial u_x}{\partial x}=0$$

$$\rho_{TG}\left(u_r\frac{\partial u_r}{\partial r}+u_x\frac{\partial u_r}{\partial x}\right)=-\frac{\partial p}{\partial r}+\mu_{TG}\left(\frac{\partial^2 u_r}{\partial r^2}+\frac{\partial^2 u_r}{\partial x^2}-\frac{u_r}{r^2}+\frac{\partial^2 u_r}{\partial x^2}\right)$$

$$\rho_{TG}\left(u_r\frac{\partial u_x}{\partial r}+u_x\frac{\partial u_x}{\partial x}\right)=-\frac{\partial p}{\partial x}+\mu_{TG}\left(\frac{\partial^2 u_x}{\partial r^2}+\frac{1}{r}\frac{\partial u_x}{\partial x}+\frac{\partial^2 u_x}{\partial x^2}\right) \qquad (5.a\text{-}g)$$

Entrance : $u_r=0;\quad u_x=U_\infty;$ **End :** $\left(-p\mathbf{I}+\mu\left(\nabla\mathbf{u}+(\nabla\mathbf{u})^T\right)\right)\cdot\mathbf{n}=\mathbf{0}$

Drop Surface : $\mathbf{u}=\mathbf{0}$ **Wall Channel :** $\mathbf{u}=\mathbf{0}$

The mathematical model of the mass transfer problem is described below with the following assumptions: steady and isothermal system, constant physical properties, the velocity profile of products and intermediates is the same of the triglycerides, there is no diffusion of triglycerides, products and intermediates to the methanol phase and only the methanol diffuses to the triglycerides phase through the surface of the droplet and the domain of study is limited to the triglycerides phase. The model consists of the follow advection-convection showed in Eqs. (6.a-d) where C is the concentration and i is the respective specie (TG, M, DG, MG, GL, ME). The boundary conditions are similar to the stratified flow case, so at the entrance of microreactor (x=0) a constant concentration C_{TG0} was adopted, at the surface of the droplet an equilibrium constant concentration of methanol C_M^* is imposed and the boundary conditions of no flux through the interface were established for all the other species and at the end of the microreactor ($x=L$) and at the wall ($r=d/2$), the considered boundary conditions are no flux for all species. The R_i term represents the contribution of the transesterification and is the same of the stratified flow, shown in Tab. 1.

$$u_r\frac{\partial C_i}{\partial r}+u_x\frac{\partial C_i}{\partial x}=D_i\left(\frac{\partial^2 C_i}{\partial r^2}+\frac{1}{r}\frac{\partial^2 C_i}{\partial x^2}+\frac{\partial^2 C_i}{\partial x^2}\right)+R_i \qquad i=TG,DG,MG,GL,M \text{ and } ME$$

Entrance : $C_{TG}(0,y)=C_{TG0};\quad C_i(0,y)=0;\quad i=DG,MG,M,GL \text{ and } ME$ (6.a-d)

Drop surface: $C_M=C_M^*;\quad \mathbf{n}\cdot\nabla C_i=0;\quad i=TG,DG,MG,GL \text{ and } ME$

End and wall channel : $\mathbf{n}\cdot\nabla C_i=0;\quad i=TG,DG,MG,GL,M \text{ and } ME$

3. RESULTS

The input data used in the present study for both, stratified and segmented flow, came from the literature (Al-Dhubabian, 2005), and it is shown in Tab. 2. To facilitate the results analyses, from now on, we will use a dimensionless form of the concentration (F) and coordinates (X, Y, R), described by Eqs. (7.a-d). The conversion of triglycerides (CTG) is defined in Eq. (7.e). $F_{TG,outlet}$ is the dimensionless concentration of triglycerides at the end of microreactor. The residence time (RT) is calculated according to Eq. (7.f) where *Total Volume* is the total volume of microreactor, *Area* is the cross section area and u_{AV} is the average velocity, defined in Eq. (8.b).

Table 2 – Input data for simulation (Al-Dhubabian, 2005)

Expression	Value	Expression	Value
μ_{TG} [Pa.s]	5.825×10^{-2}	k_1 [mol/(m³.s)]	4.368×10^{-6}
μ_M [Pa.s]	5.47×10^{-4}	k_2 [mol/(m³.s)]	9.623×10^{-6}
ρ_{TG} [kg/m³]	885	k_3 [mol/(m³.s)]	1.88×10^{-5}
C_{TG0} [mol/m³]	1014	k_4 [mol/(m³.s)]	1.074×10^{-4}
C_M^* [mol/m³]	4461.6	k_5 [mol/(m³.s)]	2.117×10^{-5}
D_{TG} [m²/s]	1.58×10^{-9}	k_6 [mol/(m³.s)]	9.0×10^{-7}
D_M [m²/s]	1.182×10^{-10}		
D_{DG}, D_{MG} D_{GL}, D_{ME} [m²/s]	1.38×10^{-9}		

$$F_{TG}=\frac{C_{TG}}{C_{TG0}};F_M=\frac{C_M}{C_{TG0}};$$
$$X=\frac{x}{L};Y=\frac{y}{H_{TG}};R=\frac{r}{(d/2)} \quad (7.a\text{-}g)$$
$$CTG(\%)=100\times\left(1-F_{TG,outlet}\right);$$
$$RT=\frac{Total\,Volume}{u_{AV}\times Area}$$

The COMSOL implementation was made following the steps: a) definition of constants and parameters, presented in Tab. 2; b) geometry of the microchannel with its dimensions; c) modeling, choosing the physics of the problem. For this work, it was chosen reaction engineering, transport of species and laminar flow; d) mesh; e) results.

Firstly, a mesh convergence analysis was made before the simulations in order to evaluate the stabilization of the results. The meshes considered for this analysis were triangular with maximum dimensions listed in Tab. 3 and 4. It was considered a large numbers of points along the microchannel length and was evaluated the values of F_{TG}. Tables 3 and 4 show the mesh convergence analysis for both types of flow at some points considered. As we can see, the results for different meshes are very similar, resulting in relative errors less than 1% for both cases.

Table 3 – Mesh convergence: segmented (RT=11.5min)

	Maximum element size (mm)			
Position	**0.0107**	**0.00831**	**0.00665**	**0.00309**
X=0.2	0.275651	0.279123	0.281287	0.281372
X=0.4	0.136627	0.138078	0.138967	0.139
X=0.6	0.101059	0.101596	0.101922	0.101934
X=0.8	0.091721	0.091913	0.092027	0.092031

Table 4 – Mesh convergence: stratified (RT=0.41min)

	Maximum element size (mm)			
Position	**0.03**	**0.01**	**0.007**	**0.005**
X=0.2	0.97758	0.98199	0.98241	0.982664
X=0.4	0.94424	0.95191	0.95255	0.95295
X=0.6	0.90161	0.91184	0.91268	0.913191
X=0.8	0.8541	0.8658	0.86677	0.86735

3.1 Stratified flow

For the simulations of the microreactor with stratified flow, we define the Reynolds Number Re and the entrance length x_L in Eqs. (8.a-d). Table 3 shows some geometric entities used for the case of stratified flow. The microreactor volume (Total Volume) used in residence time calculation takes also into account the total internal volume of the device (Al-Dhubabian, 2005), also considering the amount related to the input and output shafts of the microreactor, while the volume considered in the stratified flow simulations takes into account only the volume between plates, which is a little different of the total volume. $Diam_h$ is the hydraulic diameter, $u_{AV,TG}$ is the average velocity of the phase triglycerides.

Table 5 – Geometric entities of microreactor with stratified flow.

Expression	Values	
b	5.4286	
L [mm]	23.3	
w [mm]	10.5	
h [μm]	100	200
H_{TG} [μm]	84.44	168.89
H_M [μm]	15.56	31.11
Total Volume [cm³]	0.023	0.046

$$Diam_h=\frac{4wH_{TG}}{2(w+H_{TG})}$$
$$u_{AV,TG}=\frac{1}{H_{TG}}\int_0^{H_{TG}}u_{TG}(y)dy \quad (8.a\text{-}d)$$
$$Re_{TG}=\frac{\rho_{TG}u_{AV,TG}Diam_h}{\mu_{TG}}$$
$$\frac{x_L}{Diam_h}\approx\frac{0.6}{1+0.035Re}+0.056\,\mathrm{Re}$$

The higher values of Re and x_L achieved in this work are for the case of H=200 μm, RT=0.43 min, which results in a Re=0.00507915, ensuring laminar flow, and x_L=199.518 μm, justifying the assumption of fully developed flow.

For the verification of the problem, the simulation results of this work were compared with the literature data from Al-Dhubabian (2005), using the finite element method, and Pontes *et al.* (2015), using the Generalized Integral Transform Technique. The comparison of the profile of dimensionless triglycerides and methyl esters are shown in Fig. 5.a,b. As can be seen, a good agreement between the results provides from this work and the two different works from the literature was achieved.

Figure 5 shows the dimensionless concentration profile of triglyceride and methyl esters along X with H_{TG}=100 μm for different fixed residence times RT. In this analysis can be concluded that the concentration of triglyceride decreases

(Fig. 5.a), consequently, the concentration of methyl esters increases (Fig. 5.b) along the channel due the chemical reaction effects. The influence of the time that the reactants are exposure to reaction condition shows that for higher residence times, higher conversion of triglycerides was achieved, i.e., more triglycerides were reacted along the microchannel resulting in a lower concentration of triglycerides at the channel end (X=1), as shown in Fig. 5.a.

Figure 6 presents a comparison between the conversion of triglyceride for two different microchannel heights, 100 and 200 μm. It is observed that for a same residence time, the 100 μm microchannel height presents higher conversion than that of 200 μm. This effect occurs because lower channel heights present higher surface area-volume ratio and lower diffusion paths, ensuring higher mass transfer rate and better conversions for a fixed residence time, RT.

Figure 7 presents the influence of the temperature in the conversion. Four constant temperatures were adopted to the isothermal flow from 25 up to 60ºC, temperature next, but below to the methanol boiling point. The temperature influences the initial step of the transesterification, which is ruled by the chemical reaction, achieving higher conversions in shorter residence times. For a same microchannel height, the results showed that a higher and faster conversion can be achieved for higher temperature.

The relations of the kinetic rate constants at different temperatures are given by the Arrhenius equation below in Eq. (9), where $k_{j,n}$ is the kinetic rate constant j (j=1,2,…,6) from Eq. (1) at the temperature T_n, A_j is the pre-exponential constant and $R_{Constant}$ is the universal gas constant. Due the absence of the data for microfluidics devices, in this analysis it was used activation energy data from batch system (Noureddini and Zhu, 1997) to investigate the temperature effects in the reaction.

Table 6 – Parameters used in Arrhenius equation.

Reaction	Pre-Exponential Factor A [mol/(m³.s)]	Energy Activation E [cal/mol]
$TG \rightarrow DG$	19098.9	13145
$DG \rightarrow TG$	185.051	9932
$DG \rightarrow MG$	6.90966×10^{9}	19860
$MG \rightarrow DG$	5.70388×10^{6}	14639
$MG \rightarrow GL$	1.08361	6421
$GL \rightarrow MG$	9.68433	9588

$$k_{j,n} = A_j Exp\left[-\frac{E_j}{R_{\text{Constant}} T_n}\right]; \quad j = 1,\ 2,\ ...,\ 6 \tag{9}$$

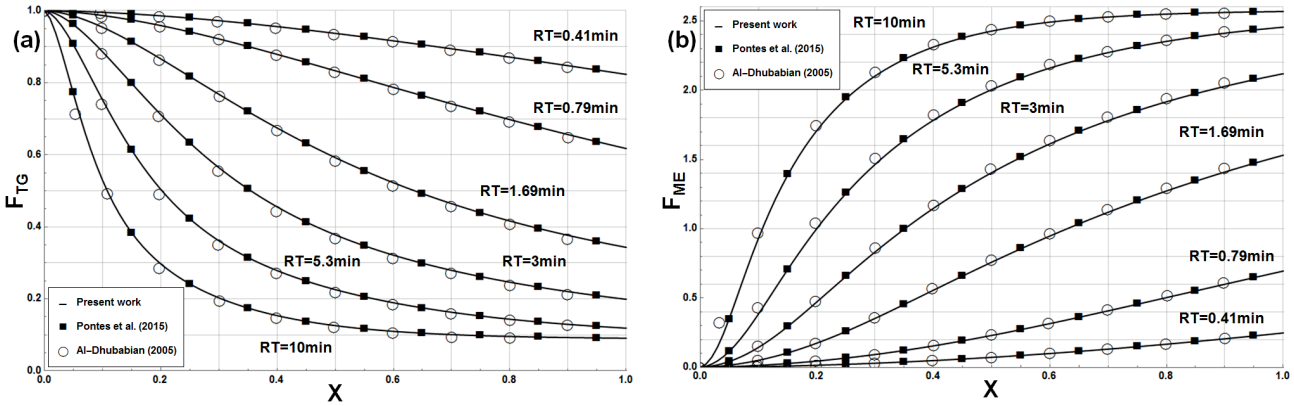

Figure 5 – Dimensionless concentration profile along the channel at Y=0.5: a) Triglycerides; b) Methyl Esters.

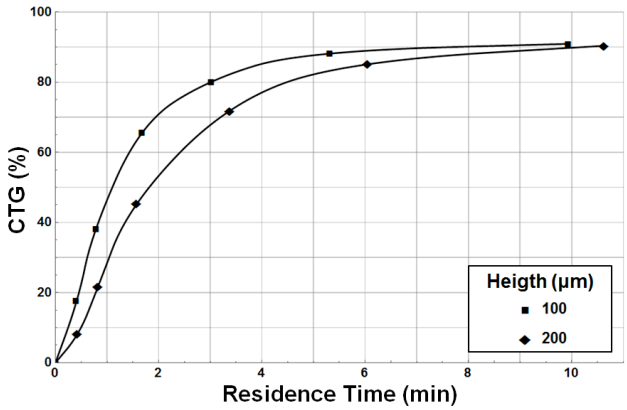

Figure 6 – Conversion of triglyceride for two different microchannel heights: 100 and 200 μm.

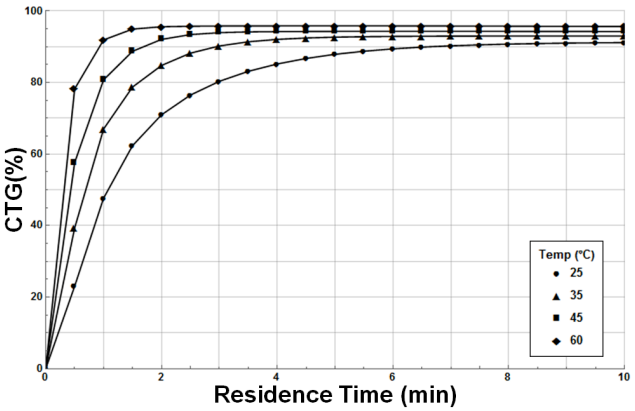

Figure 7 – Conversion of triglycerides for different temperatures for microchannel of 100 μm height.

3.2 Segmented flow

First of all, the segmented flow was compared with Wylock *et al.* (2010) that solved a problem of flow around rigid particles of CO_2 surrounded by water. The verification was done comparing the drag coefficient $(\overline{C}_D)$, described in Eqs. (10.a-c), where $\overline{C}_{DP}$ and $\overline{C}_{DF}$ are the form drag and friction drag coefficients, respectively, and ϕ is the angle of a point at the surface of the drop and the symmetry axis, starting at the front of the droplet. The next step was to verify the mass transfer problem, comparing with Dani *et al.* (2006) that solved a problem of mass transfer around rigid particles with two generic fluids. The verification was done comparing the average Sherwood Number (Sh_m), described in Eq. (10.f), where p_s is the pressure at droplet surface, Sh_L is the local Sherwood Number and ζ_s is the vorticity at the droplet surface defined in Eqs. (10.d) and (10.e), respectively. Figure 8 shows the comparison of the drag coefficient of the simulation results in this work with Wylock *et al.* (2010) and Fig. 9 shows the comparison of the Sh_m with Dani *et al.* (2006). As can be seen in Fig. 8 and 9, both, flow and mass transfer problem, achieved a good agreement with the literature.

After the verification, a parametric analysis was done to study the influence of different parameters in the conversion like droplet size and quantity of droplets, with the input data showed in Tab. 5. The molar ratio of methanol-oil is equal to 7.2, and it was changed the number of droplets and its size so that the molar ratio remains constant. Figure 10 shows the conversion of triglycerides of a microchannel with 200 μm of internal diameter for different values of *size* and *qt*, where *size* is the ratio of the droplet diameter and microchannel diameter and *qt* is the quantity of droplets equaled spaced along the microchannel length. Table 6 shows some values of *CTG* for different *size* and *qt*.

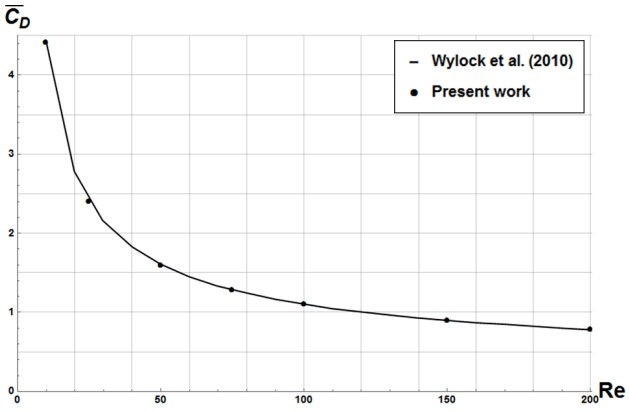

Figure 8 – Comparison of $\overline{C}_D$ with Wylock *et al.* (2010).

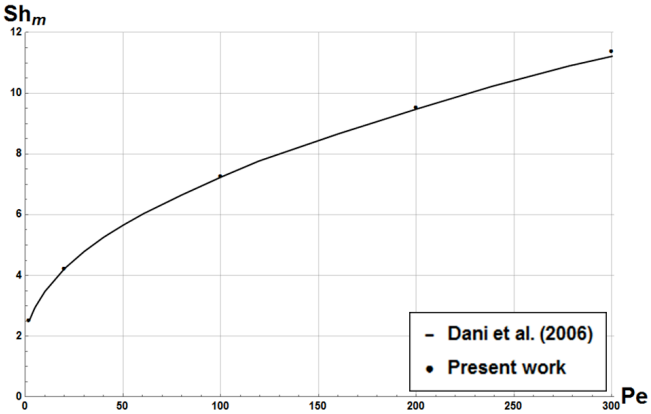

Figure 9 – Comparison of Sh_m with Dani *et al.* (2006).

Table 7 – Entities of segmented flow.

Expression	Values		
d [μm]	200		
L [mm]	60		
T [°C]	25		
Methanol-Oil Molar Ratio	7.2		
size	0.8809	0.6991	0.6108
qt	150	300	450

$$\overline{C}_{DP} = \int_0^{\pi} \frac{p_s}{\rho U_\infty / 2} \sin 2\phi d\phi;$$

$$\overline{C}_{DF} = \frac{4}{\mathrm{Re}} \int_0^{\pi} \frac{(d_G/2)}{U_\infty} \left(\frac{\partial}{\partial \phi} + \cot\phi \right) \zeta_s \sin 2\phi d\phi; \qquad (10.a\text{-}f)$$

$$\overline{C}_D = \overline{C}_{DP} + \overline{C}_{DF}; \qquad \zeta_s = \nabla \times \mathbf{u}$$

$$Sh_L = -2 \left. \frac{\partial C}{\partial r} \right|_{at\ surface\ drop} \qquad Sh_m = \frac{1}{2} \int_0^{\pi} Sh_L(\phi) \sin\phi d\phi$$

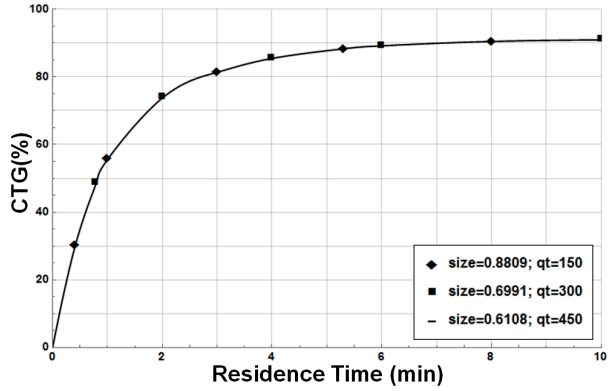

Figure 10 – *CTG* for different *size* and *qt* with *d*=200 μm.

Table 8 – CTG (%) for different RTs.

***RT* (min)**	**Case**		
	size=0.8809 *qt*=150	*size*=0.6991 *qt*=300	*size*=0.6108 *qt*=450
0.41	26.4913	24.019	23.0341
0.79	44.9841	42.7042	41.7882
1.69	67.4961	66.4941	66.1299
3	80.0751	79.5645	79.3627
5.3	87.7266	87.5632	87.4972
10	90.829	90.8127	90.8057

3.3 Comparison of microreactors with stratified and segmented flow

After the analysis of two different flow patterns, a comparison of conversion was made between both flows with a same $Diam_h$=200 μm, showed in Fig. 11 and the results of conversion is showed in Tab. 6 for different residence times.

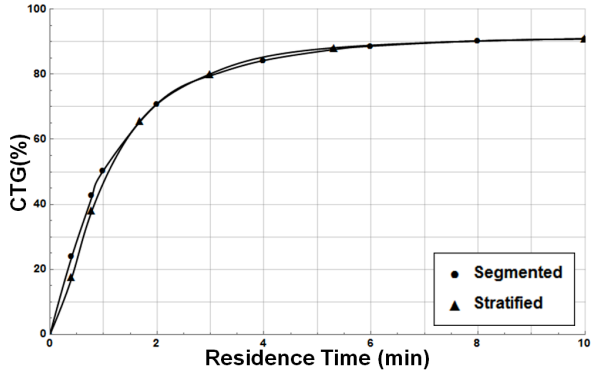

Figure 11 – Comparison of *CTG* for two types of flow.

Table 9 – *CTG* (%) for microreactors with stratified and segmented flow for the same $Diam_h$=200 μm.

RT (min)	Stratified	Segmented
0.41	17.6665	26.4913
0.79	38.2532	44.9841
1.69	65.6933	67.4961
3	80.1142	80.0751
5.3	88.1337	87.7266
10	90.9217	90.829

As we can see in Fig. 11, the microreactor with segmented flow has a higher conversion for lower residence times. For higher residence times, both of types of flow achieved a very similar conversion, with a bit higher conversions for the case of stratified flow. It is expected better conversion for the case of segmented flow, since with droplets it is achieved higher surface areas. It might not have happened here, due to the simplicity of the model adopted that consider the drop as a rigid particle, neglecting the intern flow inside the droplet. Also, the model adopted imposes a constant equilibrium concentration at the drop surface, not taking into account the diffusion of the other species through the drop surface, since for smaller droplets the resistance of diffusion tends to decrease, causing more interaction of the reactants, which leads to better conversions. Therefore, the results for the segmented flow may have achieved a sub estimated conversion.

4. CONCLUSIONS

In this work was shown a study modeling the transesterification reaction of biodiesel in microreactors for two types of flow: stratified and segmented flow. Also, a nonlinear problem of mass transfer with kinetic rate terms was modeled and solved. The solution method adopted was the Finite Element Method through the software COMSOL Multiphysics. Solutions were verified with other works and presented good agreement with data from the literature.

For the microreactor with stratified flow, it was observed that for higher residence times higher conversions of triglycerides were obtained, because the reactants have more time for chemical reaction. Also, a higher conversion was obtained for the smaller microchannel height case, due to greater surface area/volume ratio and smaller diffusion paths. Furthermore, it was observed that higher constant temperatures favor the increment of the kinetic rate constants and consequently improve the chemical reaction. It is also noted that the temperature effects occurs in the early reaction.

For the case of microreactor with segmented flow, it was observed that for different values of *size* and *qt* the conversion of triglycerides was very similar, with a little advantage for the droplet of higher size, which was not expected, since droplets with smaller dimensions result in higher ratios of surface area-volume. It might happens due to the simplicity of the model used at this stage of work, where a constant concentration at interface is adopted and does not take into account the consumption of the methanol inside the droplet.

A comparison with both types of flow showed that the segmented flow obtained higher conversion than the stratified flow for lower residence times. For higher residence times, both of types of flow achieved a very similar conversion, with a bit higher conversions for the case of stratified flow. It was expected higher conversions with segmented flow, due to the higher surface area-volume ratio, which was partially achieved, due to the simplicity of the model adopted.

Suggestions for future work include the addition of a complete model, including the recirculation of fluid inside the drop and take into account the diffusion through the interface of the methanol inside the drop instead of adopt a constant concentration at the interface between fluids.

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