EVALUATION OF THE INFLUENCE OF MIXER ROTATION THROUGH COMPUTATIONAL FLUID DYNAMICS SIMULATION OF A CONTINUOUS STIRRED-TANK REACTOR FOR BIODIESEL PRODUCTION FROM EXPERIMENTAL KINETIC DATA

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ABSTRACT

In the present work, a computer simulation was performed through computational fluid dynamics (CFD) for a Continuous Stirred-Tank Reactor, starting from experimental data on the kinetics of the transesterification reaction between soybean oil methyl acetate, using an enzyme as a catalyst, the *Candida Antartica*. A volume was proposed for the reactor so that the average residence time of the reaction mixture was sufficient for the expected yield, based on the data obtained by the Matlab®, was obtained at the exit of the reactor. The simulation of the reactor operation was of a continuous process with constant reagents flow rates made using commercial software ANSYS®. The impeller chosen was of the type inclined straight blades, the simulations were made by varying the rotation speed of the mixer where an increase in reaction yield was observed until the rotation of 120 RPM, above this speed, no real gain was observed in the amount of biodiesel obtained.

Keywords: biodiesel, CFX, CSTR, simulation

NOMENCLATURE

F_x	molar flow rate, mol/s
G_A	term of generation, mol/s
k	kinetic constant
m	mass, kg
Q	flow, m^3/s
t	time, s
u	velocity, m/s
V	volume, m^3
TG	Triglyceridies
DG	Diglyceridies
MG	Monoglyceridies
MMA	Molar mass of the specie A

Greek symbols

ρ	specific mass, kg/m^3
μ	dynamic viscosity, Pa.s

1. INTRODUCTION

The search for renewable energy sources has been the subject of research around the world, in order to seek new sources to replace fossil fuel. In this scenario, the Brazil shows a great potential for biodiesel production, because it is obtained from vegetable oils (Santos, 2016). The development of systems and components for sustainable energy, biofuels, more precisely biodiesel, are show an alternative for a sustainable development (Pontes et. al., 2017).

The Brazilian law forces the addition of 5% of biodiesel to fossil diesel, in order to reduce the environmental impact and encourage the production of renewable fuel (Lobo et. at., 2009). The biodiesel is a biodegradable and renewable biofuel, derived from mono-alkyl esters of long-chain fatty acids. Coming from biological resources such as vegetable oils, animal fat, or even frying oils Haas, 2006).

The reaction of fatty acids (triglycerides) with a lower alcohol (methanol or ethanol) or an acetate (methyl or ethyl) is describe in Equation 1.1.

$$\text{Triglycerides} + 3\,\text{Alcohol} \rightarrow 3\,\text{Ester} + \text{Glycerol} \quad (1.1)$$

However, this global reaction is composed of three consecutive and reversible steps, where the triglyceride forms diglycerides and monoglycerides in sequence, as shown in Equations 1.2, 1.3 and 1.4.

$$TG + R-OH \rightarrow DG + \text{Éster} \quad (1.2)$$

$$DG + R-OH \rightarrow MG + \text{Éster} \quad (1.3)$$

$$MG + R-OH \rightarrow \text{Glycerol} + \text{Éster} \quad (1.4)$$

To be considered biodiesel, the minimum methyl ester content is 96.5%, determined by chromatographic method, as provided for in standard EN 14214 and RANP 07/08 [3].

Several routes to obtain biodiesel can be used, with various combinations of reagents and catalysts, the most used route is the one that uses vegetable oil and anhydrous ethanol as reagent catalyzed by sodium hydroxide (NaOH), but acids are also widely used in catalysis. Homogeneous, oxides and enzymes when it comes to heterogeneous catalysis (Santos, 2016).

The biological route uses an enzyme (lipase) as a catalyst that can be immobilized in the reaction medium or can be dissolved in it. In recent years, research on this route has increased a lot, especially in Asian countries. The enzymatic route has been shown to be quite viable with yields that exceed 90%, but the reaction temperature has to be extremely controlled, because if it exceeds 43°C, the enzyme will denature, completely losing its function in an irreversible way. The main advantage of the enzymatic route is the characteristic of heterogeneous catalysis, the catalyst can be separated at the end of the reaction in a simple way, centrifuged or filtered (Xu, et al., 2005).

The determination of the kinetic constants for the synthesis of biodiesel from oil and methyl acetate as reagents catalyzed by the enzyme *Candida Antarctica* was determined by Xu, et al. (2005)., obtaining the six constants of the partial reactions, methyl acetate has an advantage in compared to ethanol because it disfavors competing saponification reactions. From this fact, several reagents and catalysts can be used favoring the production of biofuel, since, depending on the region and local characteristics, the synthesis is not limited. Of course, the profitability of the process is the main parameter to be analyzed Peng et. al., (2013).

1.1 Stirred reactors

Continuous stirred-tank reactors (CSTR), also known as a perfect mix reactor, has as its basic characteristic that the concentration is uniform inside the reactor, considering the concentration at its outlet (Folgler, 2012 and Levenspiel, 1972). The industrial processes continuous and batch way can be use stirred reactors, the advantage of the continuous process is the constant yield after the start-up time, the disadvantage is that for biochemical processes there is a greater chance of contamination of the medium, especially in case of feedback (Folgler, 2012).

Mixed reactors demand strong temperature control due to the condition that the reaction rate is constant throughout the reactor. For stirred reactor, it is important to carefully pre-analyze its behavior under abnormal operation due to its sensitivity to cooling and stirring parameters (Jiang et.al., 2018).

The equation for the minimum volume equation to obtain the consumption of X from component A.

$$V = \frac{F_{A0}(1-X)}{-r_{outlet}} \quad (1.5)$$

Poley and Magalhães (2014), studied transesterification in a mechanically stirred reactor. Obtaining a good fit of the component concentrations to the experimental kinetic data, however the impeller rotation speed did not change the yield.

The determination of the kinetic constants for the reaction of biodiesel production is the subject of several works, the value of the constants is extremely important to determine the limiting reaction, as well as to measure the chemical equilibrium, since the yield of the reaction is linked to this parameter, the reaction rate equation is changed only by the reactant concentrations and by changes in the kinetic constants, these in turn are only sensitive to temperature, so the fact of mixing of the reaction system can be linked to the value of the concentrations (Atkins and De Paula, 2008 and Chang et. al. 2008).

The objective of this work was to validate, through computer simulation, experimental data of the synthesis of biodiesel for a mixed reactor in steady state, analyzing the response to different rotations of the stirrer to evaluate the interference in the reaction yield.

2 PHYSICAL PROBLEM AND MATHEMATICAL MODELING

The problem to be modeled consists of a mixed stirred reactor fixed in the center of the equipment, in steady state with two inlets with the same feed mass flow and only one outlet at the end of the equipment. The intention is to evaluate if there is a gain in reaction yield only by increasing the impeller rotation (mass transfer). Mathematical modeling, through equations, seeks to physically represent a phenomenon. Thus, the model chosen in relation to the problem is of fundamental importance (Vergel, 2013). The CFX proposes the resolution in each control volume (mesh) of the equations of conservation of mass, energy and momentum, so that at each interaction between all points the error in the balances tends to have the lowest possible residual.

2.1 Methodology of solution in the computational fluid dynamics

In this work, the finite volume method (FVM) was used. The numerical results of the MVF were obtained using the commercial software ANSYS CFX 15 to solve the systems of partial differential equations (Maliska, 2004).

The method consists of dividing the study geometry into small control volumes, which is known as a numerical mesh. The equations are obtained through a balance of mass, momentum and energy. Values are calculated on discrete regions of the geometry. The MVF allows the use in unstructured meshes, making it very flexible for use in complex geometries, as in the case of a stirred reactor with the presence of an impeller.

Hexahedra always produce better results, even for highly complex turbulent flows, however CFX is a software that works primarily with unstructured meshes composed of tetrahedral (Poley, 2014). The computational modeling of the problem in CFD usually involves problem identification, pre-processing, numerical solution and post-processing. The ANSYS CFX software has packages that allow geometry modeling and mesh generation, however, the geometry can be imported from other software such as AUTOCAD or *Solidworks*, always observing if the language is compatible so that there is no unnecessary work.

2.2 Geometry

The volume of reactor are determined for the same system, through Matlab, evaluating only the volume necessary for the minimum yield of 96.5% of ester production as required by the current standard (SANTOS, 2016). For this work, it was decided to use a CSTR reactor stirred by a mixer of the type inclined straight blades, the reactor volume is approximately 2.5 m³, with an internal diameter of 1.16 m and a height of 2.33 m so that the relationship is H=2.D; the mixer has a diameter of 60% of the reactor internal diameter, being 0.7 m Folgler, 2012).

The software used to design the equipment was *DesignModele*, which is available in the Workbench® software package. The geometry construction technique was divided into two stages: first the impeller design and then the construction of the tank geometry surrounding the impeller. The impeller was placed at a height of 50 cm from the bottom of the reactor, randomly, as the position will not be a parameter for evaluating the yield of the reaction in this work. However, noting that the position and number of blades is a parameter that interferes with the conditions and model of the process. Both the reactor and the impeller are show in the figures below.

Two opposite inlets were placed on the sides of the tank, in order to try to increase the homogenization in the first volumes of the reactor. The fluid outlet was positioned at the bottom of the reactor to rely on the gravity factor, thus dispensing with equipment to displace fluid. However, the position of the output, as well as the inputs, can also be a factor in the study regarding the yield of the reaction. The outlet diameter is twice the diameter of the inlets in the amount of 20 cm.

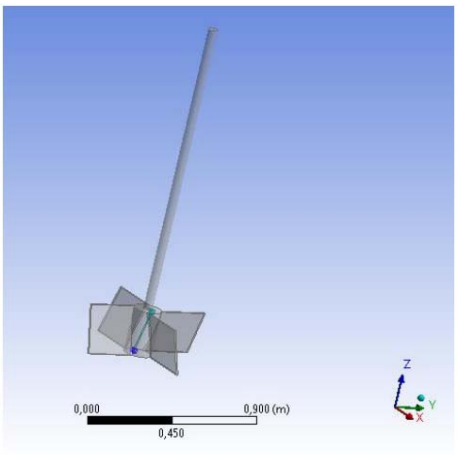

Figure 1 – Impeller of reactor in CFX

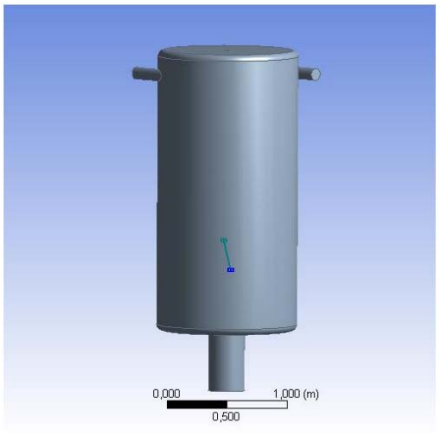

Figure 2 – Reactor in CFX

2.8 Mesh and setup

The mesh was developed in the ANSYS® Meshing software, present in the Workbench package, being generated in a standard way, with tetrahedral-type volumes. In order to obtain a better response to the results, it was decided to refine the upper and lower parts of the tank walls, as well as the impeller blades. The parameters of the components were taken from the literature and from the ASPEN PLUS® software database, which has an example model of a biodiesel production plant, shown in the tables below.

The simulation was performed in a steady state with separate feeding of triglycerides and methyl acetate, but both with a mass flow rate of 0.5 kg/s. To model the problem, the equipment was divided into two domains, the impeller domain and the tank domain. The impeller domain was configured as an immersed solid that has the possibility of rotating around a defined axis. This condition can only be used because it is not of interest to this work to study the heat and mass transfer that can

occur between the fluid and the impeller blades. The tank domain (reactor) was defined as a fluid and static domain, as the material of variable composition. The density of the domain can be accepted as the density of the mixture brought in the experiment studied with the value of 900 Kg/m³. The gravitational acceleration parameter was inserted at the value of 9.8 m/s² of the –z axis, with the element methyl acetate as a "constraint" and the others with transport.

Table 1 – physical-chemical proprieties of reaction components

Component	Molar mass (Kg/Kmol)	Density x10^{-1}(g/cm³)	heat capacity Cp (J/Kg.K)
Triglyceride	882	8.908	1960
Diglyceride	668	8.450	1956
Monoglyceride	454	9.850	1968
Methyl acetate	74	9.320	508
Biodiesel	288	8.630	2400
Triacethylglycerol	228	12.620	2187

The kinetic velocity constants were used obtained from the work of [5] and are shown in the table below:

Table 2 – kinetic constants of reactions (adapted)

Constates(L.mol-1 .min-1)	L/mol.min (x10^{-2})	m³/mol.s (x10^{-3})
K_1	3.11	1.866
K_2	1.76	1.056
K_3	11.24	6.74
K_4	12.71	7.62
K_5	11.29	6.71
K_6	9.15	5.49

The CFX only considers mass flows, all rate equations had to be multiplied by the molar pass of each species in order to go from mole to mass, the equation 2.1 shown the generation term and table 3 shown the reactions for the all composts.

$$r_A = G_A \times MMA \quad (2.1)$$

Table 3 – equations of components of the reaction

Compost	G_A
Triglycerides	$\frac{d[TG]}{dt} = k_1.[TG].[A] + k_2.[DG].[Bio]$
Diglycerides	$\frac{d[DG]}{dt} = k_1.[TG].[A] - k_2.[DG].[Bio] - k_3.[DG].[A] + k_4.[MG].[Bio]$
Monoglycerides	$\frac{d[MG]}{dt} = k_3.[DG].[A] - k_4.[MG].[Bio] - k_5.[MG].[A] + k_6.[Gly].[Bio]$
Biodiesel	$\frac{d[Bio]}{dt} = k_1.[TG].[A] - k_2.[DG].[Bio] + k_3.[DG].[A] - k_4.[MG].[Bio] + k_5.[MG].[A] - k_4.[Gly].[Bio]$
Triacethylglicerol	$\frac{d[Gly]}{dt} = k_5.[MG].[A] - k_4.[Gly].[Bio]$
Methyl acetate	$\frac{d[A]}{dt} = -\frac{d[Bio]}{dt}$

3 RESULTS

The convergence calculations were performed using an ASUS computer with an Intel Core i7® processor, taking an average time of 6 days for the total convergence of the residues (mass, energy and momentum). The time is show to be high due to the high complexity of the problem where there is no chemical reaction and internal rotation of the system. It is also possible to see that the residue mass of monoglycerides does not reach the minimum residue value, but remains constant after reaching a value close to 10^{-4}. It is not ideal, but because of the constancy and because all other variables have reached the minimum value, the result is analyzed in order to recognize whether the model represents the experimental model well. The residual limit was set at 10^{-4} for all parameters. Conversion results are shown in the Figures 3.1, 3.2 and 3.3.

3.1 Conversion of biodiesel

The formation and consumption of the system's constituents is obtained exactly as expected, showing that the kinetic model can indeed be applied to the case. Simulation results show a start at the top of the tank with an increase during flow to the bottom. When plotting a plane on the XY axis, we can see the mass fraction of biodiesel during the process.

When analyzing the streamlines inside the reactor, we are observe that the displacement of the lines inside the reactor follows a curvilinear trend, as already mentioned, the highest concentration of biodiesel is

located at the bottom of the reactor, following exactly what is proposed for the calculation of this type of reactor.

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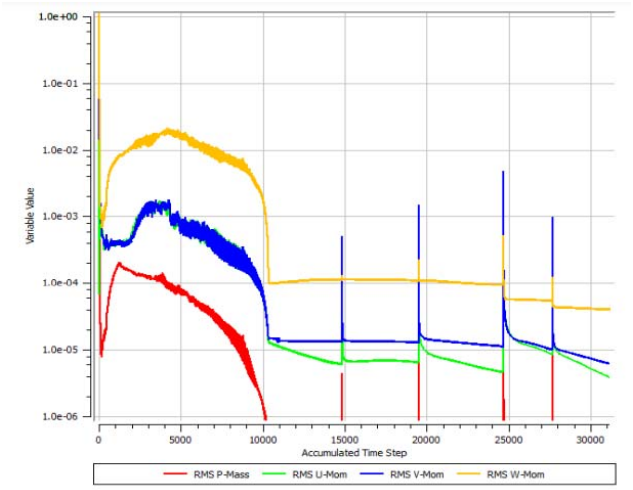

Figure 3.1 – graphic of convergence of the mass and U, V, W momentum.

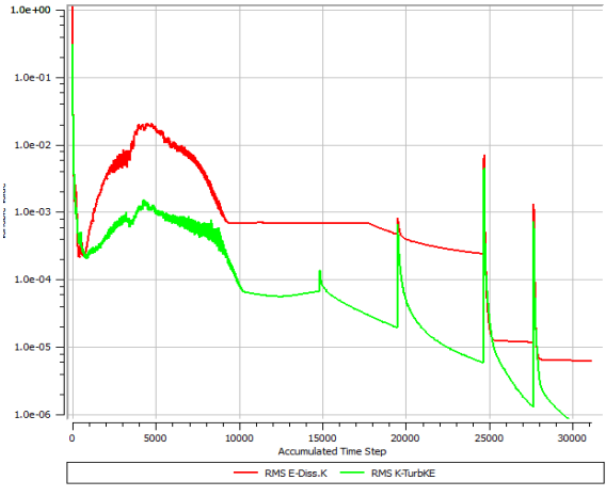

Figure 3.2 – Graphic of the k-ε convergence.

From 120 RPM there is no significant variation in the increase in the mass fraction of biodiesel. When compared with the experimental data obtained by (Xu et. a., 2005) we noticed that the conversion obtained in the CFD, about 95% at 120 RPM, is about 0.11% lower than the experimental result, which shows the ability of the simulation to report the experimental process. It is worth noting that the mixing is not considered as a parameter in the chemical kinetics equation (Atkins and De Paula, 2008 and Chang et. al. 2008).

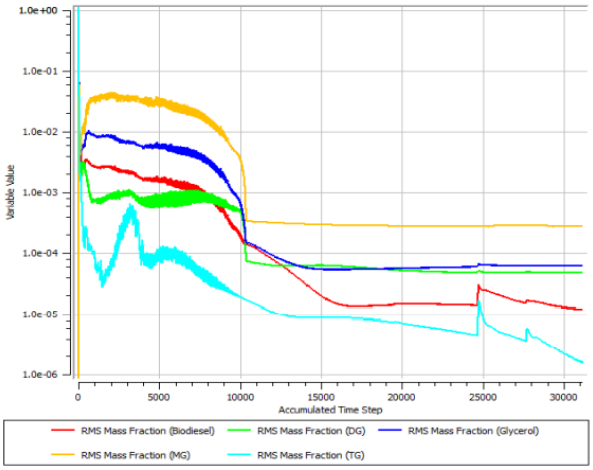

Figure 3.3 – Graphic of the convergence for all components of reaction

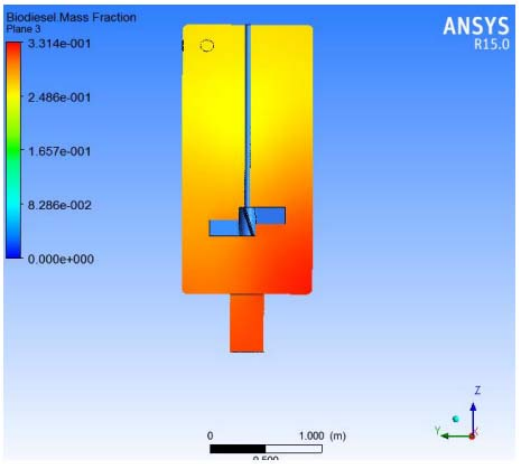

Figure 3.4 – conversion of Biodiesel in plane YZ

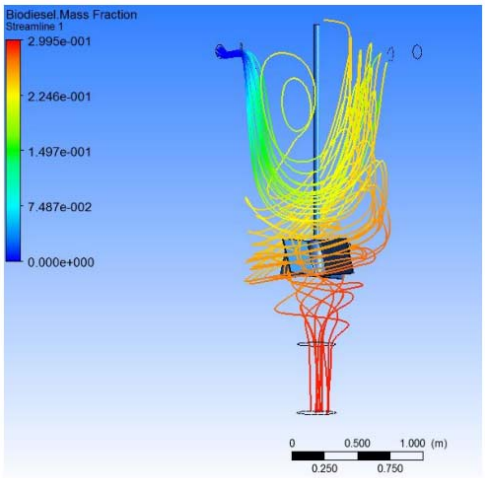

Figure 3.5– Streamlines in the reactor

Table 4 shows the values for the reaction yield for different impeller rotation.

Table 4 – yield biodiesel from different rotation of impeller

Rotation speed (rotations per minute)	Yield value (%)
0	82
20	90
40	90
60	91
80	92
120	95
140	95
160	95

4 – CONCLUSION

Note that the model used in CFX actually depicts a CSTR type reactor, showing a rapid conversion of triglycerides into biodiesel. However, the amount of biodiesel obtained in the simulation is lower than that obtained experimentally for the kinetic model using the enzyme *Candida Antartica* obtained through batch reaction. This can be explained by the fact that the dynamics of the fluids inside the reactor stirred by an impeller changes the concentration of the reactants inside the reactor at all times.

It is also seen that an increase in impeller rotation speed increases the conversion of triglycerides into biodiesel, up to a limit of 120 RPM from this rotation. The gain in the production of biodiesel is negligible, thus bringing a real stirred reactor closer to the ideal concept of the CSTR, or mixed reactor, where all concentrations inside the reactor are equal to the output.

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