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MODELLING AND SIMULATION OF TUBULAR REACTORS PACKED WITH A BED OF INERT PARTICLES AT SUPERCRITICAL CONDITIONS

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Abstract. The usage of tubular reactors for triglycerides transesterification process at supercritical condition has gained contrast as a promising technology to large-scale continuous production of biodiesel. Among the features which make this technique feasible, it is possible to highlight the use of low quality oils, absence of catalyst and smaller reaction time when compared to conventional processes.The intensification of continuous processes is possible applying mixing promoters, which purpose is reducing the mass transfer resistances as a consequence of increasing the contact between the components. A bed of inert particles inserted in a pipeline might work as a mixing promoter. Thus, this study aims to examine the triglycerides alcoholysis process at supercritical conditions in a tubular reactor fulfilled with inert particles. Two types of fillings were considered in this study: glass and stainless steel 316.The Method of Lines was selected to solve the proposed mathematical model. The use of stainless steel spheres had better simulation results and this behavior occur mainly due to the thermal properties of this material.

Keywords: Transesterification, Supercritical Conditions, Tubular Reactor, Inert Particles, Modelling.

1 Introduction

The pioneer works applying supercritical conditions in batch reactors date from 2001 and had the aim to establish the operation ranges which resulted in the highest ester yields, as well as to enable the determination of the kinetic data, according to Santiago [1].

Rebouças [2] affirms that supercritical transesterification in a tubular reactor has the main advantage of continuously producing biodiesel along time coupled to easy control and operation of the process, even under elevated pressure conditions.

The use of beds in reactors has the intention to intensify the reactional and mass transfer effects. According to Atmakidis & Kenig [3], this is due to the presence of regions which present high resistance to flux, provided by the low porosity and a flow profile which tends to stagnate, in a manner in which the molecules that lie in these spaces remain longer in the bed. Due to this, the reaction rates are higher in these locations.

Qiao *et al* [4], in their work applying soybean oil in the alcoholysis reaction with methanol in supercritical conditions, analyzed the influence of varying temperature, pressure and the types of inert packing beds in the biodiesel production in tubular reactors. They realized that with the decrease in particle size, there was an increase in biodiesel production, which could be justified by the increase of the homogeneity between the phases due to the insertion of the bed and the improvement of the contact promoted by the smaller particles in the packing.

In this manner, the present study aims to evaluate the influence of two different bed configurations (one constituted of glass and another of 316 stainless steel) on the conversion of triglycerides employing a tubular reactor under supercritical conditions packed with a bed of particles.

2 Methodology

The mathematical modelling was made considering the variations in concentration and temperature along time and in the axial direction (denoted by letter z) of the reactor. The mass and energy microscopic balances were developed based on the models of Santiago [1] and Aris & Amundson & Sundaresan [5], respectively, with the following simplifying hypothesis: (i) Constant operation pressure of 15 MPa; (ii) oil:alcohol molar ratio of 1:40; (iii) flux is predominantly in the axial direction (Aris-Taylor simplification); (iv) reversible pseudo-1st order reaction; (v) reaction kinetics given by Arrhenius' law; (vi) specific heat approximated by the average value. Items (iv) and (v) can be describe by Eqs. (1) and (2) respectively:

$$r_A = k_1 C_A C_B - k_2 C_C C_{\mathrm{Gl}}. \tag{1}$$

$$k_j = k_{0,j} * e^{\left(\frac{-\mathrm{Ej}}{R * T_F}\right)}. \tag{2}$$

where $\mathbf{C_A}$ is the molar concentration of triglycerides; $\mathbf{C_B}$ is the molar concentration of alcohol; $\mathbf{C_C}$, the ester molar concentration and $\mathbf{C_{Gl}}$ is the molar concentration of glycerin, $\mathbf{T_F}$ is the fluid temperature, $\mathbf{k_j}$ is the rate constant of the *j* reaction, the index *j* refers to the direct (j = 1) or reverse reaction (j = 2) and the parameters $\mathbf{k_{0,j}}$ and $\mathbf{E_j}$, are respectively, the pre-exponential factor and the activation energy.

To develop the mass and energy balances, a classic formulation represented by Eq. (3) was used and analysis were made considering a differential element of volume of the tubular reactor packed with a bed of inerts, as shown in Fig. 1:

$$\text{Accumulation} = \text{Inlet} - \text{Outlet} + \text{Generation} - \text{Consumption}. \tag{3}$$

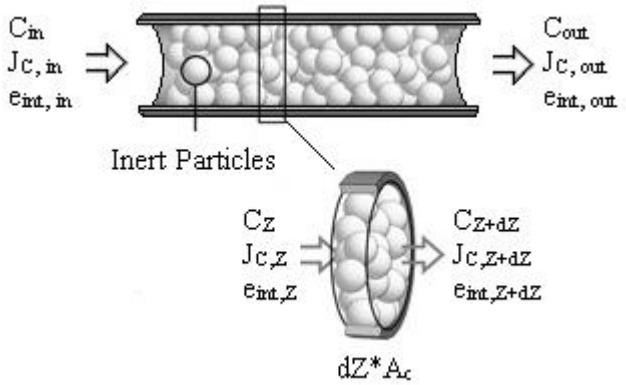

Figure 1. Schematic representation of the particle bed and the differential element of volume inside the reactor. **Adapted from Ding *et al.* [6]**

For the mass balance, the diffusive flux ($J_{C,Z}$) was considered and estimated by Fick's equation, according to Eq. (4):

$$J_{C,Z} = -D_Z A_C \frac{\partial^2 (C_{i,Z})}{\partial z^2}. \tag{4}$$

Considering the Eq. (3) and making the due mathematical manipulations, a generic equation for mass balance is found (Eq.5), as shown below:

$$\frac{\partial C_{i,Z}}{\partial t} + v_z \frac{\partial C_{i,Z}}{\partial z} = D_Z \frac{\partial^2 C_{i,Z}}{\partial z^2} \pm r_A. \tag{5}$$

where $C_{i,Z}$ is the concentration of the component *i* (A, B, C e Gl), v_Z is the average flow velocity in the axial direction, D_Z is the axial dispersion coefficient and ε is the bed porosity.

The energy balance was based on the heat transfer phenomena through conduction in the axial direction (for the solid) and the heat exchanged between the fluid and the particle bed. Those effects can be seen in the following equations:

$$(1-\varepsilon) * C_{P,S} * \rho_S \frac{\partial T_S}{\partial t} = k_S \frac{\partial^2 T_S}{\partial z^2} + \mathrm{UA}(T_F - T_S). \tag{7}$$

$$\varepsilon * C_{P,F} * \rho_F \frac{\partial T_F}{\partial t} + v_z \frac{\partial T_F}{\partial z} = -\mathrm{UA}(T_F - T_S). \tag{8}$$

where the Eqs.(7) and (8) are the energy equations to, respectively, the solid and the fluid. $\mathbf{C_P}$ refers to the average specific heat, **ρ** is density, **T** is temperature, $\mathbf{k_s}$ is the thermal conductivity of the material which constitutes the bed and **UA** is the global heat transfer coefficient between the fluid and the solid. The indexes ***S*** and ***F*** represent the solid and fluid properties, respectively.

The mass and energy balances form a system of partial differential equations, which are related to each other, making necessary to solve them simultaneously. The Method of Lines was used, discretizing the spacial domain by the finite differences technique in N fixed intervals, so that the convective terms (first order derivatives) were approximated by backward differences, while the diffusive terms (second order derivatives) were approximated by central differences.

The simulations were employed considering two types of materials to constitute the bed: steel and glass.

For the numerical solution of the model, the modeling and simulation interface EMSO (Enviroment for Modeling, Simulation and Optimization) was used. According to Soares [7], this software is an environment process simulator development with equations oriented paradigm, which allows the user

to build processes flowsheets and diagrams or models by a user-friendly graphical interface. It is disposable at the developer's site for free download.

The differential-algebraic system was numerically integrated by a BDF method, implemented in the software. The reaction kinetic parameters, the dispersion coefficient, the oil:alcohol molar ratio, the specific heat and the densities were obtained from literature. To initialize the system, it was considered that only the reagents presented non-null concentration and that the fluid and solid were at the temperature of 298K. The simulations were done to reach the temperatures of 573K and 673K in the reactor.

3 Results

The results of the simulations are presented in Figs. 2 and 3. Figure 2 shows the conversions of triglycerides in biodiesel, while Fig. 3 presents the temperature distribution along the length of the reactor.

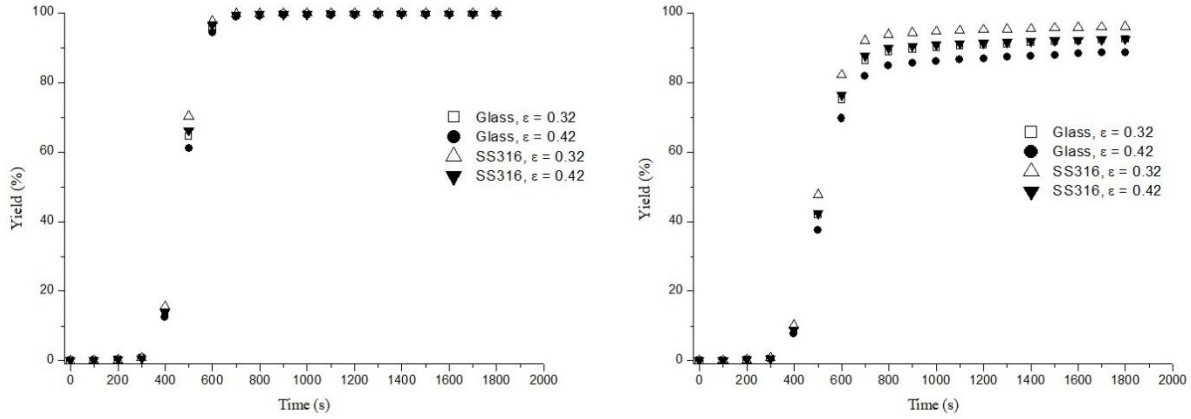

Figure 2. Conversion of the reaction for steel and glass, considering two bed porosities for each, for a initial temperature condition of (a) 673K (left) e (b) 573K (right). **Own authorship**

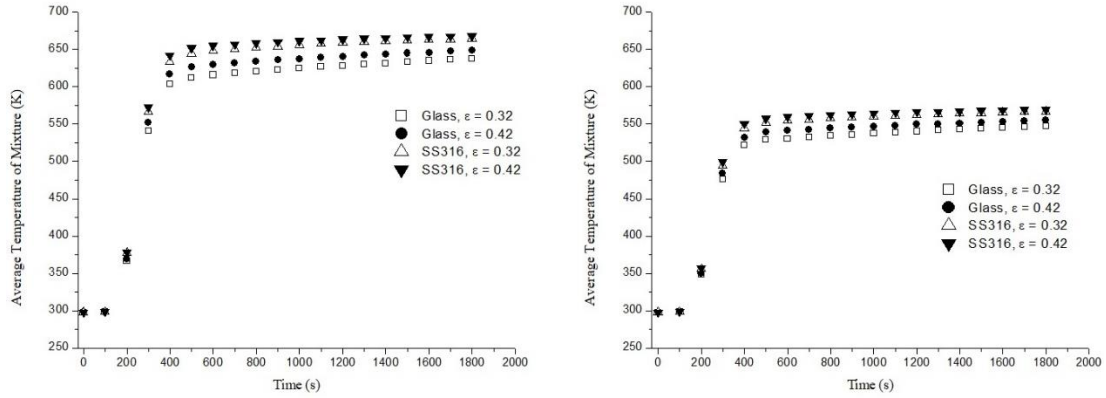

Figure 3. Average temperature distribution of the fluid over time, considering the interactions with beds of inerts of different porosities and materials, at set-point condition of (a) 673K (left) e (b) 573K (right). **Own authorship.**

As can be observed in Fig. 2 (b), the conversions obtained using a bed of inerts composed of smaller porosity ($\varepsilon = 0.32$) and steel spheres provide the best conversions. Such behavior can be explained based on two perspectives: the intensification of the mass transfer and reaction phenomena by inserting the packing in the reactors, as well as the heat transfer mechanisms between the fluid and the particles,

which greatly depend on the material that constitutes the bed.

Steel provides smaller resistance to heat transfer when compared to glass, which is the behavior observed in Fig. 3. Due to its high thermal conductivity, the fluid reaches higher temperatures in a bed composed of steel particles. This effect influences directly the kinetic parameters of the reaction, since the reaction kinetics applied follows Arrhenius' law.

Besides this, the effect of mass dispersion employed in the model is also influenced by temperature, since the increase in temperature results in the decrease of dispersion coefficient, according to Santiago [1]. Such explanation contributes so that the reaction kinetics presents bigger protagonism, providing higher conversions as the fluids temperature is increased.

The reduction of the porosity increases the contact between the substances, guaranteeing a better homogeneity of the mixture, according to Fig. 3 (a). In this case, the available superficial area, as well as the reaction area for the reagents will also be higher due to the bed porosity, confirming the explanation proposed by Qiao *et al* [4].

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