MODELING AND SIMULATION OF PROCESS CONTINUOUS PRODUCTION OF BIODIESEL FROM SOYBEAN OIL USING IMMOBILIZED CANDIDA ANTARCTICA IN FLUIDIZED BED BIOREACTOR

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Abstract. *The objective this work was investigated a new route for biodiesel production using Immobilized Candida Antarctica in continuous Fluidized Bed Bioreactor. Conventionally, Biodiesel (fatty acid methyl esters) is produced by transesterification in which, oil or fat is reacted with a monohydric alcohol in presence of a catalyst. In recent years, the use of lipases as biocatalysts for biodiesel production has become of great interest due to its environment friendly. But some alcohols such as methanol inactivated the lipases to some extent and the enzymatic stability was poor. In order to enhance the stability of the lipase, three-step methanolysis was adopted, however, glycerol, as one of the products was easy to adsorb on the surface of lipase resulting in serious negative effect on the enzymatic activity. For to solve problems was used the interesterification kinetics of triglycerides and methyl acetate for biodiesel production was modeled. A heterogeneous model describing the interesterification process in an immobilized enzyme fluidized-bed bioreactor was developed. A simplified model based on Ping Pong Bi Bi with substrate competitive inhibition mechanism was proposed to describe the reaction kinetics of the interesterification.The model without any adjustable parameters was used to predict the interesterification process. The key parameters which measured the extent of external and internal mass-transport resistances, as well as the degree of back-mixing were quantified and discussed. The fluidized-bed bioreactor considered in this investigation is composed of two phases: a fluid phase comprised mainly of the triglycerides and methyl acetate and the product (Biodiesel); and a solid phase which is the immobilized enzyme. The effects of some operating and design parameters on the performance of the fluidized-bed bioreactor were also analyzed. The model was also tested for its sensitivity to changes in hydrodynamic parameters. (Times New Roman, Italic, 10 pt)*

Keywords*: Biodiese, Lipase, Interesterification, Fluidized Bed*

1. INTRODUCTION

Biodiesel is mono-alkyl esters of long chain fatty acids derived from renewable vegetable oils and animal fats. Biodiesel (fatty acid methyl esters) is produced by transesterification in which, oil or fat is reacted with a monohydric alcohol in presence of a catalyst. In the transesterification of vegetable oils, a triglyceride reacts with an alcohol in the presence of a strong acid or base, producing a mixture of fatty acids alkyl esters and glycerol. The overall process is a sequence of three consecutive and reversible reactions, in which monoglycerides are formed as intermediates. The stoichiometric reaction requires 1 mol of a triglyceride and 3 mol of the alcohol. However, an excess of the alcohol is used to increase the yields of the alkyl esters and to allow its phase separation from the glycerol formed. The alcohols employed in the transesterification are generally short chain alcohols such as methanol, ethanol, propanol butanol, and methyl acetate.

Biodiesel has become more attractive recently because of its environmental benefits and the fact that it is made from renewable resources (Schuchardt et al., 1998). The transesterification of vegetable oils with methanol or ethanol as well as the main uses of the fatty acid methyl esters are studied in this paper. The general aspects of this process and the applicability of different types of catalysts (acids, alkaline metal hydroxides, alkoxides and carbonates, enzymes and non-ionic bases, such as amines, amidines, guanidines and triamino(imino)phosphoranes) (Jordan and Gutsche, 2001); (Fangrui and Hanna, 1998); (Filippis et al., 1995); (Antolín et al., 2002) are described, and ambient or elevated pressures and temperatures.

Conventionally, biodiesel was produced by transesterification of triglycerides and alcohols in the presence of an acid or an alkaline catalyst. In recent years, the use of lipases as biocatalysts for biodiesel production has become of great interest due to its environment friendly. However, some alcohols such as methanol inactivated the lipases to some extent and the enzymatic stability was poor. In order to enhance the stability of the lipase, three-step methanolysis was adopted, however, glycerol, as one of the productswas easy to adsorb on the surface of lipase resulting in serious negative effect on the enzymatic activity (Xu et al 2003), (Dossat et la 1999) and (Du et al 2004).

In order to solve the above-mentioned problems, we previously reported that using methyl acetate as acyl acceptor instead of methanol for biodiesel production could enhance the stability of the lipase significantly and in the process, triacetylglycerol instead of glycerol would be produced and it has been demonstrated that triacetylglycerol had no

negative effect on the activity of the lipase. Moreover, triacetylglycerol was an important by-product with a higher value than glycerol and this novel route was thought to be very promising for large scale production of biodiesel.

2. MODEL DEVELOPMENT

2.1 Kinetic Model

The enzymatic model used to describe the interesterification kinetics was based on the model Ping Pong Bi Bi with competitive inhibition for the substratum. The equation of that mechanism is shown:

$$V_i = \frac{V_{\max}[TG][AM]}{K_{M_{TG}}[AM]\left(1+\frac{[MA]}{K_I}\right)+K_{M_{AM}}[TG]+[TG][AM]} \quad (1)$$

where V_i was the initial reaction rate; [TG] and [A] the initial molar concentrations of triglycerides and methyl acetate, respectively; K_{mTG} and K_{mA} the apparent Michaelis constants for triglycerides and methyl acetate, respectively; K_i the apparent inhibition constant of methyl acetate and Vmax the initial maximum velocity of the reaction. The kinetic constants are shown in Table 2.1(Xu et al 2005).

Table 1 Parameters kinetics.

Parameters	Value
V_{max} (mol/lmin)	1.9
K_{mTG} (mol/l)	1.0
K_{mA} (mol/l)	16
K_i (mol/l)	0.0455

2.2 Solid Phase Mass Balance

The fluidized-bed bioreactor considered in this investigation is composed of two phases: a fluid phase comprised mainly of the substrate (oil and methyl acetate) and the product (Biodiesel); and a solid phase which is the immobilized enzyme. The following assumptions are employed in the model: (1) the system is isothermal; (2) the movement of reactant within the biocatalyst can be described mathematically by Fick's law of diffusion where the effective diffusion coefficient is constant and independent of concentration; (3) the enzyme activity is uniform throughout the particle; (4) the fluid phase back-mixing can be quantified by an axial dispersion coefficient.

The general mass balance equation governing the concentration distribution in the fluid phase of the biocatalyst is given by:

$$D_L\frac{d^2C_f}{dZ^2}-U_0\frac{dC_f}{dZ}-(1-\varepsilon)r_V \quad (2)$$

and the Danckwert's boundary conditions are:

$$when\ Z=0,\ -D_L\frac{dC_f}{dZ}+UC_f=UC_f \quad (3)$$

$$when\ Z=L,\ \frac{dC_{x,P,S}}{dZ}=0 \quad (4)$$

This set of boundary conditions, that is equations 7 and 8, is widely used in modeling immobilized enzyme fluidized-bed bioreactors

2.3 Solid Phase Mass Balance

The general mass balance equation governing the concentration distribution in the fluid phase of the biocatalyst is given by equation (5).

$$\frac{dC_s}{dZ}=k_m(C_f-C_s) \quad (5)$$

with the boundary conditions given by:

$$when\ Z=0,\ C_s=0 \quad (6)$$

2.4 Evaluation of the relevant parameters

The relevant parameters relating to the dispersion coefficient, external mass-transfer resistance and bed voidage are evaluated using correlations obtained from the literature and are given below.

2.4.1 Dispersion coefficient

The dispersion coefficient, D_L, in the fluidized-bed containing light, non-porous, solid particles was evaluated using the correlation of (Tang and Fan 1990) given by Equation (7) below.

$$D_L = \frac{U_0 H}{Pe} \tag{7}$$

$$\frac{1}{Pe} = 4.35\left(\frac{\rho_s}{\rho_f}\right)^{2.64} \varepsilon^{1.467} \tag{8}$$

The external particle-liquid mass-transfer coefficient was obtained using the correlation of Nore et al. (1992) given by:

$$k_m = 1.1\left(\frac{U_0}{\varepsilon}\right)^{0.43} D_p^{0.24} \tag{9}$$

The bed porosity in the bed is determined by the mechanics of fluidization. Hence, a realistic mathematical expression for the bed fluidization is necessary. For bed of uniform spherical particles, the following relation was proposed. The (Richardson and Zaki 1954) relates bed voidage to the upflow superficial liquid velocity given as:

$$\varepsilon = \left(\frac{U_0}{U_t}\right)^{1/n} \tag{10}$$

The terminal velocity given by Equation (2.11) was obtained using the correlation of Khan and Richardson (1990).

$$U_t = \frac{\mu}{\rho_f D_p}\left(2.33 Ga^{0.018} - 1.53 Ga^{-0.016}\right)^{13.3} \tag{11}$$

where

$$Ga = \frac{\left(\rho_s - \rho_f\right)\rho_f D_p^3 g}{\mu^2} \tag{12}$$

The fractional conversion, Y, shown in Fig. 1 against the flow rate is defined by Equation (13).

$$Y = \frac{C_0 - C_L}{V_{\max}\, L/u} = \frac{X}{\theta} \tag{13}$$

where θ dimensionless residence time.

3 RESULTS AND DISCUSSION

The modeling equations presented here constitute a system of non-linear boundary value problems which were solved by finite difference techniques. The details of solution methodology are omitted here for the sake of brevity.

Figure 1 shows the concentration of each composition triglycerides, methyl acetate and biodiesel against the height of the fluidized bed. From the Figure 2, it can be observed that, the model indicate the high concentration of biodiesel were reached in the end of the reactor. Indicating that the dispersion has influences in the interesterification of triglycerides for biodiesel production with methyl acetate.

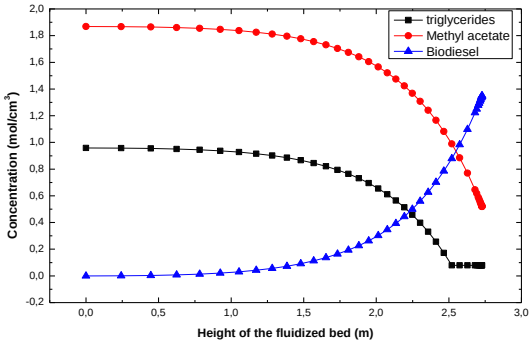

Figure 1. The concentration of triglycerides, methyl acetate and biodiesel.

The Figure 2 show the conversions obtained for the model for fluidized bed in function of the dimensionless residence time. It can be observed that the measure that the dimensionless residence time increases the values of the conversions increased. Therefore, they are high necessary times of residence for the reactor to reach high conversions.

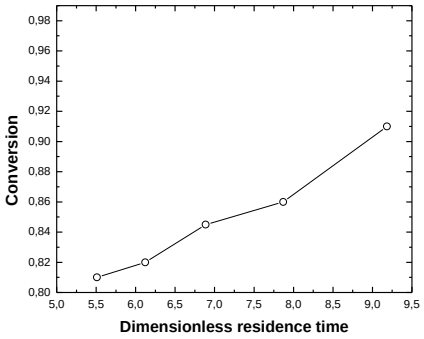

Figure 2 Conversion in fluidized bed bioreactor

Another parameter of common interest in the design of fluidized bed reactors is the Peclet number which is the measure of the degree of back-mixing in the flow vessel. As the Peclet number approaches infinity plug-flow behavior is approached, while complete mixing is approached for a Peclet number approaching zero. It is obvious from the plot of Peclet number against the dimensionless residence time. The according Equations 2.7 and 2.8 when the value the Peclet increases the dispersion coefficient value decrease. This is also indicative of dominance of mixing over segregation. Thus, the conversion increases when the value de Peclet increases.

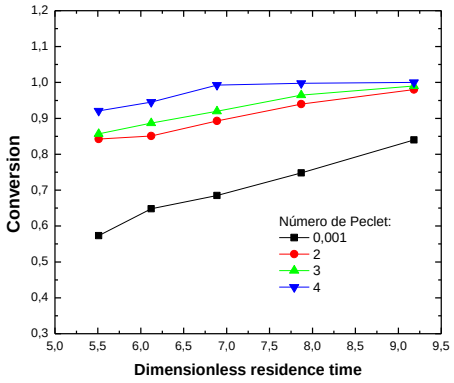

Figure 3 Effect of number of Peclet on the conversion de the fluidized bed.

4 CONCLUSIONS

In this work a continuous fluidized bed bioreactor model with Immobilized Candida Antarctica in continuous Fluidized Bed Bioreactor was developed for simulating the steady-state performance of a bioreactor for production biodiesel.

It was examined effect Peclet number and dimensionless residence time at conversion in fluidized bed. It the Peclet number decreases with the increase conversion production of biodiesel. It can be observed that conversion increased when the dimensionless residence time increased.

The model can be used to simulate the biodiesel production by interesterification in fluidized bed bioreactor and the results of the simulation were satisfactory.

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