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The synthesis of biodiesel via enzymatic ethanolysis of the sunflower and palm oils: kinetic modeling

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Biodiesel is an alternative fuel produced from renewable resources. It can be synthesized through the catalytic transesterification reaction of edible/non-edible oils or animal fats. Methanol and ethanol are the most used alcohols. The difficulties related with the synthesis using alkaline and acid catalysts are not found when an immobilized lipase is used and it encourages the researches in this field. The Ping Pong Bi Bi mechanism taking into account the competitive inhibition of the alcohol on the activity of lipase Lipozyme IM has been proposed to represent the kinetics of the enzymatic transesterification in many references in the literature, but the kinetic modeling of the enzymatic ethanolysis for the production of biodiesel has not been widely studied. In this work the synthesis of biodiesel via enzymatic ethanolysis of sunflower and palm oils were investigated with kinetic parameters fitted to experimental data retrieved from the literature. The model was successful in reproducing the experimental data of batch reactors at the beginning of the reaction, but after approximately 2-3 hours the Michaelis-Menten model showed to be more adequate to fit the experimental results.

KEYWORDS: Ping Pong Bi-Bi, Michaelis-Menten, enzymatic ethanolysis, sunflower oil, palm oil.

1. Introduction

Biodiesel is an alternative for the diesel derived from oil. It is environmentally friendly since is derived from renewable and biodegradable sources lowering emissions of particles, sulfur, carbon monoxide and hydrocarbons (Demirbas, 2007; Meher et al. 2006). The declining of fossil fuels resources and the possibility of decreasing the dependency on foreign energy supply has contributed for the increasing in the search for alternative fuels like biodiesel. It can be synthesized from animal fats or several vegetable oils such as soybean, palm, sunflower, and cotton. The transesterification (or alcoholysis) is a reaction where the triglycerides are transformed into fatty acid alkyl esters using an alcohol in the presence of a catalyst which can be an acid, base, or an enzyme (free or immobilized). Methanol and ethanol are the alcohols most used and since the reaction is reversible an excess of alcohol is usually required. In Brazil bioethanol is advantageous due to its enormous availability. Although the alkaline alcoholysis is fast, it requires a pretreatment of the raw materials with high water or free fatty acid contents. This pretreatment is applied to reduce the soap formation and to

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facilitate the separation of biodiesel and glycerol (Meher et al., 2006). The synthesis that uses acid and alkaline catalysts are mostly employed, but difficulties in the glycerol recovery, catalyst removal and purification steps have motivated several researches with enzymatic reaction since such problems are inexistent when biodiesel is made via this rout. The main drawbacks of this technology are the high costs of enzymes and their inhibition due to the presence of the alcohol. Works that deal with modeling of enzymatic ethanolysis for the production of biodiesel are not often found in the literature. This work presents a study of the kinetics of the enzymatic ethanolysis of palm and sunflower oils for the production of biodiesel with immobilized lipase Lipozyme IM. Ping Pong Bi Bi and Michaelis-Menten were the kinetic the models employed with experimental data taken from Selmi and Thomas (1998) and Oliveira and Alves (2000).

2. Kinetic Modeling

Lipase alcoholysis of triglycerides involves a two-step mechanism where the products of each step are released between additions of the substrates which are in accordance with the Ping Pong Bi Bi model (Fjerbaek et al., 2009). The rate expression for the overall transesterification reaction of the triglycerides based on this model is given by Equation (1).

$$r = \frac{V_{max} \cdot [oil] \cdot [alc]}{Km_{oil} \cdot [alc] \cdot \left(1 + \frac{[alc]}{Ki}\right) + Km_{alc} \cdot [oil] + [oil] \cdot [alc]} \quad (1)$$

where r is the initial rate of reaction; *[oil]* and *[alc]* are the molar concentrations of oil and alcohol, respectively; Km_{oil} and Km_{alc} represent the biding constants for the oil and alcohol; K_i is the inhibition constant of the alcohol, and V_m denotes the maximum initial rate for the reaction. The rate of an enzymatic reaction depends on factors such as enzyme load, pH, temperature, and substrates concentration. Although several studies in the literature report that Ping Pong Bi Bi model is suitable to represent the kinetics of the enzymatic transesterification reaction of triglycerides, simplifications such as Michaelis-Menten kinetic model can be used to fit experimental data when one of the substrates is in large excess in the reaction medium (Paiva et al., 2000). The Equation (2) shows the Michaelis-Menten rate expression.

$$r = \frac{V_{max,app} \cdot [oil]}{K_{m,app} + [oil]} \quad (2)$$

where $V_{max,app}$ is defined as $V_{max} \cdot$ *[alc]* which denotes the apparent maximum rate, and $K_{m,app}$, which is defined as $Km_{oil} \cdot [alc] \cdot (1 + [alc]/Ki)$, is the apparent Michaelis-Menten constant. Shimada et al. (2002) reported that the inhibition of the enzyme is a consequence of its contact with an immiscible polar phase which contains alcohol and glycerol in the presence of the apolar oil phase. As used by Steinigeweg et al. (2004), a pseudo homogeneous kinetic model with the rate per unit of enzyme load, was applied in this work. It was combined with the Ping Pong Bi Bi model to describe the reaction rate as given by Equation (3).

$$(-r_i) = -\frac{1}{m_{cat}} \cdot \frac{1}{V} \cdot \frac{dNi}{dt} = \frac{V_{max} \cdot [oil] \cdot [alc]}{Km_{oil} \cdot [alc] \cdot \left(1 + \frac{[alc]}{Ki}\right) + Km_{alc} \cdot [oil] + [oil] \cdot [alc]} \quad (3)$$

where $(-r_i)$ is the initial reaction rate; m_{cat} is the mass of enzyme; V denotes the reaction mixture volume; and dNi/dt is the number of moles of species i reacted per unit of time.

2.1 Kinetic parameters

The experimental data of the ethanolysis of sunflower oil was taken from Selmi and Thomas (1998), whereas Oliveira and Alves (2000) was the source of data for palm oil. In both cases the authors studied the ethanolysis of the oils catalyzed by immobilized lipase Lipozyme IM. The reaction with palm oil was conducted at ambient pressure, 40°C, initial molar ratio ethanol (pure) to oil of 3:1, enzyme load of 0.075g per 1.425 mmol of oil (7.5% w/w based on weight of oil), initial oil concentration of 0.036 mol/L, reaction volume of 40 cm^3, and using n-hexane as solvent. The authors mentioned an accuracy of ±10% in their values of conversion. In the case of sunflower oil, the reaction was carried out in solvent-free medium at ambient pressure, 50°C, initial molar ratio ethanol to oil of 3:1, initial oil concentration of 0.3617 mol/L, enzyme load of 0.4g per 5.7 mmol of oil and reaction volume of 15.8 cm^3. No information was reported regarding the accuracy of conversion data.

Based on the kinetics discussed above, a model of a batch reactor was applied. It comprises a system of four ordinary differential equations representing the mole balances on each species. The oil and biodiesel were treated as pseudo components. The rate expression is given by Equation (3). The conversion of oil (X_{oil}) is given by Equation (4), where $nO(t)$ and nO_0 represent the number of moles of oil at a given time t and at the beginning of the reaction, respectively.

$$X_{oil} = 1 - \frac{nO(t)}{nO_0} \quad (4)$$

Combining the Equations (4) with (3) and rearranging for the concentration of the oil yields the Equation (5).

$$\frac{dnO}{dt} = \frac{-m_{cat} \cdot V_{max} \cdot nO(t) \cdot nO_0 \cdot \left[\theta_A - 3 \cdot \left(1 - \frac{nO(t)}{nO_0}\right)\right]}{Km_{oil} \cdot nO_0 \cdot \left[\theta_A - 3 \cdot \left(1 - \frac{nO(t)}{nO_0}\right)\right] \cdot \left\{1 + \frac{CO_0 \cdot \left[\theta_A - 3 \cdot \left(1 - \frac{nO(t)}{nO_0}\right)\right]}{Ki}\right\} + Km_{alc} \cdot nO(t) + nO(t) \cdot CO_0 \cdot \left[\theta_A - 3 \cdot \left(1 - \frac{nO(t)}{nO_0}\right)\right]} \quad (5)$$

where dnO/dt is the number of moles of oil reacted per unit time; θ_A represents the initial ethanol to oil molar ratio; and CO_0 is the initial oil molar concentration. The number of moles rate of the other species (dNi/dt) can be expressed by the stoichiometric relationship (Equation (6)) where A, E, and G represent ethanol, ethyl esters (biodiesel), and glycerol, respectively.

$$\frac{dnO}{dt} = \frac{1}{3} \cdot \frac{dnA}{dt} = -\frac{1}{3} \cdot \frac{dnE}{dt} = -\frac{dnG}{dt} \quad (6)$$

The applicative Mathcad v.14 was used to fit the kinetic parameters by means of the *Odesolve* routine employing the adaptive step-size algorithm that combines the fourth with the fifth-order Runge-Kutta methods. The parameters are listed in Table 1.

3. Discussion and Results

The comparison between the experimental and predicted conversions for the sunflower and palm oils is illustrated in Figures 1 and 2, respectively. In both cases, the Ping Pong Bi Bi model, reproduced the experimental data successfully only at the beginning of the reaction (below 2h).

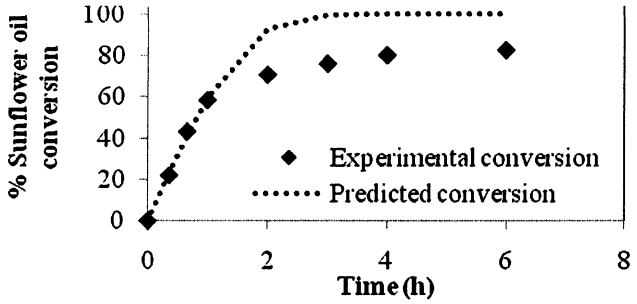

Figure 1- Sunflower oil conversion at 50ºC, 0.0702 g enzyme per mmol oil, 3:1 ethanol to oil molar ratio.

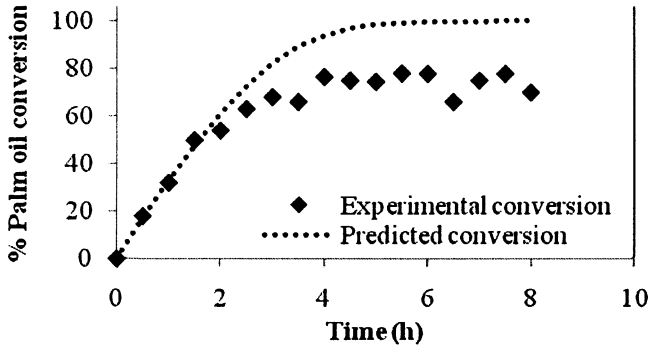

Figure 2- Palm oil conversion at 40ºC, 0.0526 g enzyme per mmol oil, 3:1 ethanol to oil molar ratio.

According to these plots it is clear that the reaction with sunflower is faster compared to palm oil which can be explained by the higher initial concentration of the reactants in the case of sunflower, since this reaction was performed without solvent. Additionally, the temperature for the ethanolysis of sunflower was 10°C higher. The Ping Pong Bi Bi parameters shown in Table 1 are in compliance with this observation. Regarding the oil binding constants, they have the same order of magnitude in both reactions, but Km_{oil}

sunflower < Km_{oil} palm oil, which favors the rate of the sunflower reaction. Also Km_{alc} sunflower << Km_{alc} palm oil, which yields higher rate for the sunflower oil reaction. As far as inhibition constants are concerned, K_i palm << K_i sunflower oil. Therefore, starting the ethanolysis of both oils with the same initial alcohol to oil molar ratio, 3:1, and practically the same enzyme load, even in the presence of the solvent, the enzyme is more likely to exhibit inhibition in the ethanolysis of palm oil. Although V_m palm > V_m sunflower, the other parameters favors the rate for the later, which leads to a higher rate for sunflower oil.

In order to predict the experimental data after 2 hours of reaction the Michaelis-Menten mechanism was investigated. The rate equation for the reactor is given by Equation (7). The combination of Equations (2), (4), written in terms of molar concentration of oil, and (7), followed by integration within the boundary conditions, $CO=CO_0$ at t=0h and CO=CO at time *t*, yields the rate equation for the Michaelis-Menten model (Equation (8)). The modified integrated rate expression is represented by Equation (9):

$$(-r_{oil}) = -\frac{1}{m_{cat}} \cdot \frac{dCO}{dt} \tag{7}$$

$$t = \frac{K_{m,app}}{V_{max,app}} \cdot \ln\frac{1}{1-X_{oil}} + \frac{CO_0 \cdot X_{oil}}{V_{max,app}} \tag{8}$$

$$\frac{1}{t} \cdot \ln\frac{1}{1-X_{oil}} = \frac{V_{max,app}}{K_{m,app}} - \frac{CO_0 \cdot X_{oil}}{K_{m,app} \cdot t} \tag{9}$$

The kinetics parameters ($K_{m,app}$ and $V_{max,app}$) for both oils were determined from the slopes of $1/t \cdot \ln(1/1-X_{oil})$ versus X_{oil}/t plots. The results with their respective linear regression correlation parameters, R^2, are shown in Table 1. The absolute deviations between experimental and calculated conversions (below 0.1000 for both oils) indicate that the Michaelis-Menten model describes adequately the enzymatic conversion for times above 2h.

Table 1- Kinetic parameters: Model 1 (Ping Pong Bi Bi), Model 2 (Michaelis-Menten)

Parameter	Sunflower oil		Palm oil	
	Model 1	Model 2 (R^2=0.9469)	Model 1	Model 2 (R^2=0.9954)
V_{max} (mol/L·h·g_{cat})	1.119	-	5.899	-
$V_{max,app}$ (mol/L·h·g_{cat})	-	0.0237	-	4.164×10^{-4}
Km_{oil} (mol/L)	0.16	-	0.219	-
Km_{alc} (mol/L)	0.95×10^{-4}	-	0.257	-
K_i (mol/L)	1.2	-	0.025	-
$K_{m,app}$ (mol/L·h·g_{cat})	-	0.245	-	0.021

4. Conclusion

Two models were employed to describe the kinetics of the enzymatic ethanolysis of sunflower and palm oils with lipase Lipozyme IM. The model based on the Ping Pong Bi Bi mechanism with competitive alcohol inhibition, was able to reproduce satisfactorily the experimental conversions only at the beginning of the reaction. For times above two hours the Michaelis–Menten model showed better agreement than the former. The kinetic parameters were determined by fitting the experimental data and they were found to be qualitatively consistent with the proposed mechanisms under the conditions of the reactions.

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