

PAPER • OPEN ACCESS

Inverse problem analysis for identification of reaction kinetics constants in microreactors for biodiesel synthesis

To cite this article: P C Pontes and C P Naveira-Cotta 2016 *J. Phys.: Conf. Ser.* **745** 032101

View the [article online](#) for updates and enhancements.

Related content

- [Improvement of estimation method for physical properties of liquid using shear horizontal surface acoustic wave sensor response](#)
Kazuya Takayanagi and Jun Kondoh
- [Estimation of liquid properties by inverse problem analysis based on shear horizontal surface acoustic wave sensor responses](#)
Kento Ueda and Jun Kondoh
- [Reconstruction of river bed topography from free surface data](#)
A F Gessese, M Sellier, E Van Houten et al.

Recent citations

- [Estimation of kinetic coefficients in micro-reactors for biodiesel synthesis: Bayesian inference with reduced mass transfer model](#)
José et al



IOP | ebooks™

Bringing you innovative digital publishing with leading voices to create your essential collection of books in STEM research.

Start exploring the collection - download the first chapter of every title for free.

Inverse problem analysis for identification of reaction kinetics constants in microreactors for biodiesel synthesis

P C Pontes^{1,2} and C P Naveira-Cotta¹

¹Dept. of Mechanical Engineering and Dept. of Nanoengineering
COPPE/UFRJ – Universidade Federal do Rio de Janeiro
Cx. Postal 68503, Cidade Universitária, Rio de Janeiro, RJ, Brazil, 21945-970

²UNIFESSPA – Universidade Federal do Sul e Sudeste do Pará
Santana do Araguaia, PA, Brazil, 68560-000

E-mail: carolina@mecanica.coppe.ufrj.br

Abstract. The theoretical analysis for the design of microreactors in biodiesel production is a complicated task due to the complex liquid-liquid flow and mass transfer processes, and the transesterification reaction that takes place within these microsystems. Thus, computational simulation is an important tool that aids in understanding the physical-chemical phenomenon and, consequently, in determining the suitable conditions that maximize the conversion of triglycerides during the biodiesel synthesis. A diffusive-convective-reactive coupled nonlinear mathematical model, that governs the mass transfer process during the transesterification reaction in parallel plates microreactors, under isothermal conditions, is here described. A hybrid numerical-analytical solution via the Generalized Integral Transform Technique (GITT) for this partial differential system is developed and the eigenfunction expansions convergence rates are extensively analyzed and illustrated. The heuristic method of Particle Swarm Optimization (PSO) is applied in the inverse analysis of the proposed direct problem, to estimate the reaction kinetics constants, which is a critical step in the design of such microsystems. The results present a good agreement with the limited experimental data in the literature, but indicate that the GITT methodology combined with the PSO approach provide a reliable computational algorithm for direct-inverse analysis in such reactive mass transfer problems.

1. Introduction

Biodiesel is a biodegradable and non-toxic product with physico-chemical properties very similar to conventional diesel fuel and which can be obtained from renewable energy sources [1]. It is usually obtained from the transesterification reaction between alcohol and triglyceride in the presence of a catalyst. Although extensively studied, the conventional biodiesel production in batch reactors demands a significant energy consumption and high residence time [2].

The microreactors are a promising alternative for the transesterification reaction, since they offer a higher surface area volume ratio for the reaction system and therefore enable the achievement of higher heat and mass transfer rates in short diffusion distances, providing high triglycerides conversion rates at low residence times, as discussed in the literature [3-4].



The enhanced conditions within the microreactor significantly alters the values of the kinetic constants, since they show fairly different values for the batch case [2] compared to those in microreactors [3,4]. Furthermore, depending on the experimental conditions, one can observe different values for the kinetic constants [4]. That is, the kinetic constants are sensitive to the various possible configurations to carry out the transesterification reaction.

Determining the kinetic constants is not an easy task, since besides an adequate experimental apparatus, it is necessary to formulate a mathematical model to represent the complex liquid-liquid flow that is established within the microreactors with the associated mass transfer and chemical reaction effects. This model, under the hypothesis of second order chemical reactions [2,3], presents nonlinearities that couple the species balance equations involved in the transesterification reaction, requiring the use of numeric or hybrid (numeric-analytical) solution methods. The parameter estimation procedure can be understood as an optimization process of an objective function, which represents a metric of the distance between the real data and the data predicted by the model, and should be based on statistical concepts, to enable an adequate results interpretation. In this context, a widely used procedure is the maximum likelihood method, which maximizes the likelihood of observing the real data from the model predictions. The literature presents different optimization methods that can be used in the inverse analysis [5-7].

This work presents an approach to estimate the kinetic constants in highly nonlinear models using a hybrid method to solve the mass transfer direct problem, associated with a heuristic method for optimization of the objective function, resulting in an interesting and effective approach to carry out the inverse analysis in such class of problems. The analytic-numerical method known as the Generalized Integral Transform Technique (GITT) [8,9], which originates from the Classical Integral Transform Technique (CITT) [10], is then used to solve the nonlinear coupled system of partial differential equations that govern the concentration potentials of the species involved in the transesterification reaction under isothermal conditions. To minimize the objective function, the heuristic method of Particle Swarm Optimization (PSO) is employed, as proposed by Kennedy and Eberhart [11]. This method is based on the social behavior of various species and it has successfully solved a number of complex optimization and parameter estimation problems [5,6,11].

2. Direct Problem

The solution of the Navier-Stokes equations for the case of fully developed two-phase stratified laminar flow of two immiscible Newtonian fluids, with constant physical properties in a parallel plate microreactor and disregarding field forces, is given by [12]:

$$u_{TG}(y) = \frac{y[(H - H_{TG})(H + H_{TG} - y)\mu_{TG} + H_{TG}(H_{TG} - y)\mu_A]\Delta P}{2L\mu_{TG}[(H - H_{TG})\mu_{TG} + H_{TG}\mu_A]} \quad (1a)$$

$$u_A(y) = \frac{(H - y)[-(H - H_{TG})(H_{TG} - y)\mu_{TG} + H_{TG}(H - H_{TG} + y)\mu_A]\Delta P}{2L\mu_A[(H - H_{TG})\mu_{TG} + H_{TG}\mu_A]} \quad (1b)$$

where the fluids are usually triglycerides (soybean oil) and alcohol with catalyst (methanol and sodium hydroxide), μ_{TG} and μ_A are the dynamic viscosities of the oil and alcohol, respectively. H and H_{TG} are the heights of the microchannel and of the interface, L is the microreactor length, and ΔP is the constant pressure drop along the microreactor.

The triglyceride layer height, H_{TG} , and the pressure drop, ΔP , can be determined through the solution of equations (1c) and (1d), respectively:

$$\frac{Q_{TG}}{Q_A} = \frac{H_{TG}^2\mu_A[(3H^2 - 2HH_{TG} - H_{TG}^2)\mu_{TG} + H_{TG}^2\mu_A]}{(H - H_{TG})^2\mu_{TG}[(H - H_{TG})^2\mu_{TG} + (4H - H_{TG})H_{TG}\mu_A]} \quad (1c)$$

$$\Delta P = -\frac{12LQ_{TG}\mu_{TG}[(H-H_{TG})\mu_{TG}+H_{TG}\mu_A]}{H_{TG}^2W[(H_{TG}^2+2HH_{TG}-3H^2)\mu_{TG}-H_{TG}^2\mu_A]} \quad (1d)$$

where W is the microreactor width and Q is the volumetric flow rate.

The dimensionless diffusive-convective-reactive mass transfer equations for the species concentrations within the microreactors, disregarding the axial diffusion term and assuming that the reactive effects occurs predominantly in the phase initially composed by triglycerides [3], are:

$$U_{TG}(Y)\frac{\partial F_s(X,Y)}{\partial X} = \xi_s \frac{\partial^2 F_s(X,Y)}{\partial Y^2} + \zeta G_s, \text{ where } s = TG, DG, MG, B, A, GL \quad (2a)$$

$$F_{TG}(0,Y) = 1, F_s(0,Y) = 0, \text{ where } s = DG, MG, B, A, GL \quad (2b,c)$$

$$\left. \frac{\partial F_s}{\partial Y} \right|_{Y=0} = 0, \text{ where } s = TG, DG, MG, B, A, GL \quad (2d)$$

$$F_A(X,1) = F_{Ao}, \left. \frac{\partial F_s}{\partial Y} \right|_{Y=1} = 0, \text{ where } s = TG, DG, MG, B, GL \quad (2e,f)$$

where the source terms G_s represent the reversible second order chemical reactions for each species involved in the transesterification, according to Table 1 below:

Table 1: Dimensionless reaction terms for the species involved in the transesterification [3].

Species s	G_s
TG	$-k_1 F_{TG} F_A + k_2 F_{DG} F_B$
A	$(-k_1 F_{TG} - k_3 F_{DG} - k_5 F_{MG}) F_A + (k_2 F_{DG} + k_4 F_{MG} + k_6 F_{GL}) F_B$
DG	$(k_1 F_{TG} - k_3 F_{DG}) F_A + (-k_2 F_{DG} + k_4 F_{MG}) F_B$
MG	$(k_3 F_{DG} - k_5 F_{MG}) F_A + (-k_4 F_{MG} + k_6 F_{GL}) F_B$
GL	$k_5 F_{MG} F_A - k_6 F_{GL} F_B$
B	$(k_1 F_{TG} + k_3 F_{DG} + k_5 F_{MG}) F_A + (-k_2 F_{DG} - k_4 F_{MG} - k_6 F_{GL}) F_B$

where k_1 to k_6 are the kinetic constants. The dimensionless groups were defined as:

$$F_i = \frac{C_i}{C_{TGo}}, F_{Ao} = \frac{C_A^*}{C_{TGo}}, X = \frac{x}{L}, Y = \frac{y}{H_{TG}}, U_{TG} = \frac{u_{TG}}{u_{TG,Av}}, \zeta = \frac{LC_{TGo}}{u_{TG,Av}}, \xi_s = \frac{LD_s}{u_{TG,Av} H_{TG}^2} \quad (3a-g)$$

where C is the dimensional concentration in the triglyceride phase, C_A^* is the equilibrium concentration of the alcohol at the interface, C_{TGo} is the concentration of triglycerides at the entrance of the microreactor, D is a diffusion coefficient, U is the dimensionless velocity profile and $u_{TG,Av}$ is the average velocity of the triglyceride phase. MG , DG , B and GL are related to intermediary reactants monoglycerides and diglycerides and to the products biodiesel and glycerol, respectively.

A hybrid solution via GITT of this nonlinear PDE system is then proposed. Initially, so as to homogenize the boundary condition defined in equation (4b), the following filter is proposed:

$$F_A(X,Y) = F_{Ah}(X,Y) + F_{Ao} \quad (4)$$

Two eigenvalue problems with known analytical solution [13] are proposed, according to Table 2, in order to satisfy the different boundary conditions and provide the basis to build the concentration potential of the species as orthogonal eigenfunction expansions.

From the orthogonality property of the eigenfunctions, the following transform-inverse formulae for the species concentration fields are constructed:

$$\bar{F}_{Ah,i}(X) = \int_0^1 \tilde{\Gamma}_i(Y) F_{Ah}(X,Y) dY, \quad \bar{F}_{s,i}(X) = \int_0^1 \tilde{\Psi}_i(Y) F_s(X,Y) dY, \quad \text{where } s = TG, DG, MG, GL, B \quad (7a,b)$$

$$F_{Ah}(X,Y) = \sum_{i=1}^{\infty} \tilde{\Gamma}_i(Y) \bar{F}_{Ah,i}(X), \quad F_s(X,Y) = \sum_{i=1}^{\infty} \tilde{\Psi}_i(Y) \bar{F}_{s,i}(X), \quad \text{where } s = TG, DG, MG, GL, B \quad (8a,b)$$

Table 2: Eigenvalue problems and corresponding analytical solutions

	Alcohol species	Other species
Eigenvalue problems	$\frac{d^2\Gamma_i}{dY^2} + \beta_i^2\Gamma_i = 0$ $\left. \frac{d\Gamma_i}{dY} \right _{Y=0} = 0, \Gamma_i(1) = 0$	$\frac{d^2\Psi_i}{dY^2} + \mu_i^2\Psi_i = 0$ $\left. \frac{d\Psi_i}{dY} \right _{Y=0} = 0, \left. \frac{d\Psi_i}{dY} \right _{Y=1} = 0$
Normalized eigenfunctions and eigenvalues	$\tilde{\Gamma}_i(Y) = \sqrt{2} \cos(\beta_i Y)$ $\beta_i = (2i-1)\pi/2$ $i = 1, 2, 3, \dots$	$\tilde{\Psi}_i(Y) = \begin{cases} 1 & \text{if } \mu_i = 0 \\ \sqrt{2} \cos(\mu_i Y) & \text{if } \mu_i \neq 0 \end{cases}$ $\mu_i = (i-1)\pi, \quad i = 1, 2, 3, \dots$

The integral transformation of the filtered partial differential equations, together with their boundary conditions in the X direction, can be performed by the integral transform operator with the respective eigenfunction for each species along the Y domain. The transformed system obtained is given by:

$$\sum_{j=1}^{\infty} O_{1,ij} \frac{d\bar{F}_{s_j}}{dX} + \xi_s \mu_i^2 \bar{F}_{s_i} = \zeta \bar{G}_{s,ijk}, \quad \text{where } s = TG, DG, MG, B, GL \quad (9a)$$

$$\sum_{j=1}^{\infty} O_{2,ij} \frac{d\bar{F}_{Ah_j}}{dX} + \xi_{Ah} \beta_i^2 \bar{F}_{Ah_i} = \zeta \bar{G}_{Ah,ijk} \quad (9b)$$

$$\bar{F}_{TG_i}(0) = \bar{f}_{1,i}, \quad \bar{F}_{Ah_i}(0) = \bar{f}_{2,i}, \quad \bar{F}_{s_i}(0) = 0, \quad \text{where } s = DG, MG, B, GL \quad (9c-e)$$

where the various coefficients can be analytically determined via symbolic computation [14] and are defined as:

$$\begin{aligned} O_{1,ij} &= \int_0^1 U_{TG}(Y) \tilde{\Psi}_i(Y) \tilde{\Psi}_j(Y) dY, \quad O_{4,ijk} = \int_0^1 \tilde{\Psi}_i(Y) \tilde{\Psi}_j(Y) \tilde{\Psi}_k(Y) dY, \quad O_{7,ij} = \int_0^1 \tilde{\Gamma}_i(Y) \tilde{\Psi}_j(Y) dY, \\ O_{2,ij} &= \int_0^1 U_{TG}(Y) \tilde{\Gamma}_i(Y) \tilde{\Gamma}_j(Y) dY, \quad O_{5,ijk} = \int_0^1 \tilde{\Gamma}_i(Y) \tilde{\Psi}_j(Y) \tilde{\Gamma}_k(Y) dY, \quad \bar{f}_{1,i} = \int_0^1 \tilde{\Psi}_i(Y) dY, \\ O_{3,ijk} &= \int_0^1 \tilde{\Psi}_i(Y) \tilde{\Psi}_j(Y) \tilde{\Gamma}_k(Y) dY, \quad O_{6,ijk} = \int_0^1 \tilde{\Gamma}_i(Y) \tilde{\Psi}_j(Y) \tilde{\Psi}_k(Y) dY, \quad \bar{f}_{2,i} = -F_{Ao} \int_0^1 \tilde{\Gamma}_i(Y) dY \end{aligned} \quad (10a-i)$$

The term $\bar{G}_{s,ijk}$ represents the transformed reaction kinetic terms, according to Table 3.

Equations (9) form an infinite system of nonlinear coupled ordinary differential equations for the transformed concentrations of the species in the transesterification process, which is required to be numerically solved. The built in function NDSolve of the *Mathematica* system can be employed for this purpose [12], providing automatic error controlled continuous solutions in the form of interpolation function objects along the X coordinate. After the numerical solution of the transformed system, the original potentials can be recovered through the inverse formulae defined in equations (8a-b).

The concentrations of the species in the transesterification can also be presented in terms of flow averaged potentials, defined as follows:

$$F_{A,Av} = \frac{\sum_{i=1}^{\infty} \int_0^1 U_{TG}(Y) \tilde{\Gamma}_i(Y) dY \bar{F}_{Ah_i}(X)}{\int_0^1 U_{TG}(Y) dY} + F_{Ao}, \quad F_{s,Av} = \frac{\sum_{i=1}^{\infty} \int_0^1 U_{TG}(Y) \tilde{\Psi}_i(Y) dY \bar{F}_{s_i}(X)}{\int_0^1 U_{TG}(Y) dY} \quad (11a-b)$$

where $s = TG, DG, MG, GL, B$.

Table 3: Transformed reaction terms

Species s	$\bar{G}_{s,ijk}$
TG	$\sum_{k=1}^{\infty} \sum_{j=1}^{\infty} \left(-k_1 O_{3,ijk} \bar{F}_{TG_j} \bar{F}_{Ah_k} + k_2 O_{4,ijk} \bar{F}_{DG_j} \bar{F}_{B_k} \right) - k_1 F_{Ao} \bar{F}_{TG_i}$
A	$\sum_{k=1}^{\infty} \sum_{j=1}^{\infty} \left[O_{5,ijk} \left(-k_1 \bar{F}_{TG_j} - k_3 \bar{F}_{DG_j} - k_5 \bar{F}_{MG_j} \right) \bar{F}_{Ah_k} + \right.$ $\left. + O_{6,ijk} \left(k_2 \bar{F}_{DG_j} + k_4 \bar{F}_{MG_j} + k_6 \bar{F}_{GL_j} \right) \bar{F}_{B_k} \right] + F_{Ao} \sum_{j=1}^{\infty} O_{7,ij} \left(-k_1 \bar{F}_{TG_j} - k_3 \bar{F}_{DG_j} - k_5 \bar{F}_{MG_j} \right)$
DG	$\sum_{k=1}^{\infty} \sum_{j=1}^{\infty} \left[O_{3,ijk} \left(k_1 \bar{F}_{TG_j} - k_3 \bar{F}_{DG_j} \right) \bar{F}_{Ah_k} + O_{4,ijk} \left(-k_2 \bar{F}_{DG_j} + k_4 \bar{F}_{MG_j} \right) \bar{F}_{B_k} \right] +$ $+ F_{Ao} \left(k_1 \bar{F}_{TG_i} - k_3 \bar{F}_{DG_i} \right)$
MG	$\sum_{k=1}^{\infty} \sum_{j=1}^{\infty} \left[O_{3,ijk} \left(k_3 \bar{F}_{DG_j} - k_5 \bar{F}_{MG_j} \right) \bar{F}_{Ah_k} + O_{4,ijk} \left(-k_4 \bar{F}_{MG_j} + k_6 \bar{F}_{GL_j} \right) \bar{F}_{B_k} \right] +$ $+ F_{Ao} \left(k_3 \bar{F}_{DG_i} - k_5 \bar{F}_{MG_i} \right) +$
GL	$\sum_{k=1}^{\infty} \sum_{j=1}^{\infty} \left(k_5 O_{3,ijk} \bar{F}_{MG_j} \bar{F}_{Ah_k} - k_6 O_{4,ijk} \bar{F}_{GL_j} \bar{F}_{B_k} \right) + k_5 F_{Ao} \bar{F}_{MG_i}$
B	$\sum_{k=1}^{\infty} \sum_{j=1}^{\infty} \left[O_{3,ijk} \left(k_1 \bar{F}_{TG_j} + k_3 \bar{F}_{DG_j} + k_5 \bar{F}_{MG_j} \right) \bar{F}_{Ah_k} + \right.$ $\left. + O_{4,ijk} \left(-k_2 \bar{F}_{DG_j} - k_4 \bar{F}_{MG_j} - k_6 \bar{F}_{GL_j} \right) \bar{F}_{B_k} \right] + F_{Ao} \left(k_1 \bar{F}_{TG_i} + k_3 \bar{F}_{DG_i} + k_5 \bar{F}_{MG_i} \right)$

An important parameter in the chemical reaction system is the residence time which provides an average time that a species is subjected to diffusive, advective and reactive effects inside the microreactor. Since it was assumed that the reaction occurs only in the triglyceride phase, then it may be calculated by equation (12a) below. The triglyceride consumption can then be evaluated in terms of the fractional conversion, according to equation (12b).

$$\tau = \frac{\text{Triglyceride layer volume}}{\text{Triglyceride volumetric flow}}, \quad \text{ConversionTG}(\%) = \left(\frac{F_{TG,AV}(0) - F_{TG,AV}(1)}{F_{TG,AV}(0)} \right) \times 100 \quad (12a-b)$$

3. Inverse problem

Assuming a normal distribution error and independent measurements with constant error, the objective function may be represented by the least squares function:

$$F_{obj} = \sum \left[\text{ConversionTG}(\%)^{Exp} - \text{ConversionTG}(\%)^{Cal} \right]^2 \quad (14)$$

To minimize the objective function F_{obj} , the heuristic method PSO will be used. In this method various particles are distributed in the search region, where each one adjusts its position in the parameters space according to its own experience (his best position found) and the experience of its neighboring points (best position found by the swarm), through to the following relationships:

$$\mathbf{x}_i^{j+1} = \mathbf{x}_i^j + \mathbf{v}_i^j, \quad \mathbf{v}_i^j = \alpha^j \mathbf{v}_i^{j-1} + \beta \mathbf{r}_{1i} (\mathbf{S}_i - \mathbf{x}_i^j) + \beta \mathbf{r}_{2i} (\mathbf{S}_g - \mathbf{x}_i^j) \quad (15a,b)$$

where: $\mathbf{x} \rightarrow$ Parameters vector. $\mathbf{x} = \{\bar{k}_1, \bar{k}_2, \bar{k}_3, \bar{k}_4, \bar{k}_5, \bar{k}_6\}$, where original constant is given by $k_i = 10^{-\bar{k}_i}$; $\mathbf{S}_i \rightarrow$ Best position found by i -th particle; $\mathbf{S}_g \rightarrow$ Best position found by the swarm; $\mathbf{v} \rightarrow$ Inertia term; $\beta \rightarrow$ acceleration constant, typically equal to 2 or 1.5; $\alpha^j \rightarrow$ Controls the inertia of the particle and generally should decrease over the iterations. It is zero at the first iteration and equal to one in the second. Here taken as $\alpha^j = j^{-1}$; $j > 0$; $\mathbf{r} \rightarrow$ Random number vector obtained from an uniform distribution between 0 and 1; $\beta \mathbf{r}_{1i} (\mathbf{S}_i - \mathbf{x}_i^j) \rightarrow$ Natural tendency of the particle to return to the best place found; $\beta \mathbf{r}_{2i} (\mathbf{S}_g - \mathbf{x}_i^j) \rightarrow$ Tendency of the particle to migrate to the best place found by the swarm;

For the first iteration the particles are generated as randomly computed points in the parameters space where the objective function should be evaluated. Figure 1 presents the PSO algorithm scheme:

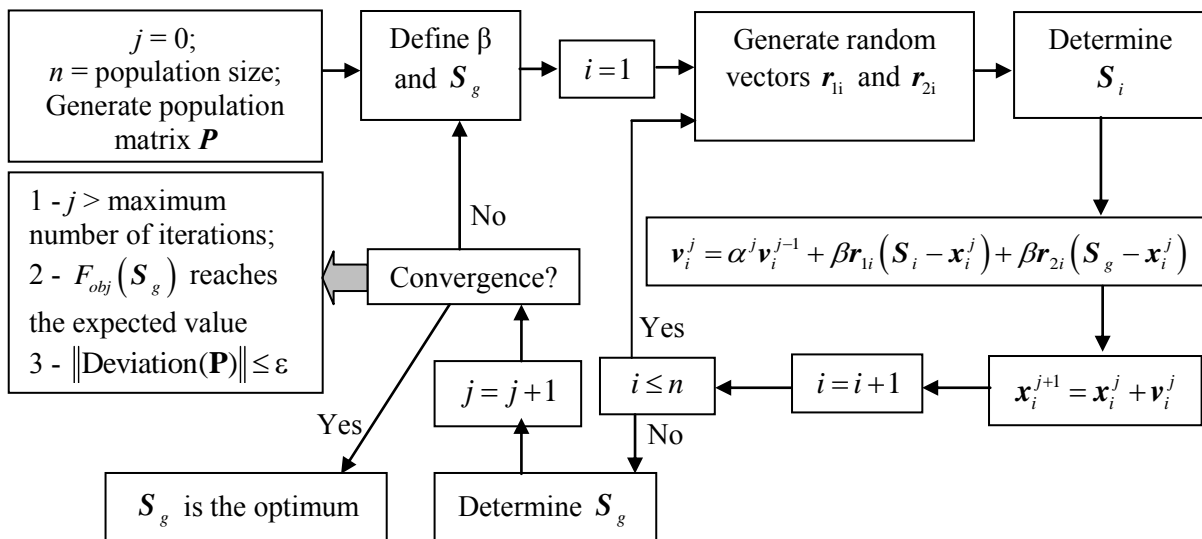


Figure 1: Iterative algorithm scheme for the PSO. Adapted from Colaço et al. [8].

4. Results

Table 4 presents the parameters used in the direct simulation of the species concentrations, while the kinetic constants are given further ahead, in Table 6. Table 5 presents a convergence analysis of the average concentration potential for the triglyceride species along the microreactor. It can be observed an excellent convergence of up to six significant digits for different residence times. The PSO was applied considering a swarm with 200 particles distributed in a region established by the parameter coefficient \bar{k}_i range, from 1 to 9. The advantage of working with the exponent argument \bar{k}_i is the reduction of the search region and the high possibility to identify parameter combinations that lead to better results, even for fairly different values of the original parameters. β was adopted equal to 1.5.

Table 6 presents a comparison among the values of the objective function and of the triglycerides conversion, as evaluated with the kinetics constants obtained from the literature and those estimated with the PSO method. One may observe an improved agreement from the constants estimated by PSO.

Table 4. Parameters used in the simulation.

Parameter	Value	Parameter	Value	Parameter	Value
μ_{TG}	5.825×10^{-2} [Pa.s]	Q_{TG}/Q_A	3.402	$D_{MG}, D_{DG}, D_{GL}, D_B$	1.38×10^{-9} [m ² /s]
μ_A	5.47×10^{-4} [Pa.s]	C_{TGO}	1014 [mol/m ³]	ρ_{TG}	885 [kg/m ³]
D_{TG}	1.58×10^{-9} [m ² /s]	F_{Ao}	4.4	W	0.0105 [m]
D_A	1.182×10^{-10} [m ² /s]	L	0.0233 [m]	H	100×10^{-6} [m]

Table 5. Convergence of the average concentration potentials of the triglyceride species along the microreactor for different residence times.

NT	$F_{TG,Av}(X)$					
	$\tau = 0.5\text{min}$			$\tau = 10\text{min}$		
	$X = 0.1$	$X = 0.5$	$X = 0.99$	$X = 0.1$	$X = 0.5$	$X = 0.99$
10	0.993096	0.914803	0.774554	0.526718	0.124018	0.090661
20	0.993099	0.914791	0.774538	0.526707	0.124018	0.090661
30	0.993099	0.914790	0.774537	0.526706	0.124018	0.090661
40	0.993099	0.914790	0.774536	0.526706	0.124018	0.090661

Table 6. Reaction kinetics constants [mol/(m³s)] estimated and conversion of triglyceride evaluated with the kinetic constants from the literature [3] and [15] and those estimated in this work (PSO)

Constant	Al-Dhubabian [3]	Dennis [15]	PSO	τ	Exp. [3]	Num. [3]	Num. (PSO)
k_1	4.368×10^{-6}	4.27×10^{-6}	3.170×10^{-6}	0.41	12.33	20.36	15.90
k_2	9.623×10^{-6}	9.69×10^{-6}	2.461×10^{-6}	0.79	36.98	40.68	35.70
k_3	1.880×10^{-5}	2×10^{-5}	5.378×10^{-5}	1.69	66.56	66.78	66.31
k_4	1.074×10^{-4}	1×10^{-5}	2.874×10^{-4}	3	84.48	80.57	83.98
k_5	2.117×10^{-5}	2.99×10^{-5}	1×10^{-1}	5.3	89.5	88.29	90.13
k_6	9.000×10^{-7}	9.04×10^{-7}	3.221×10^{-2}	10	91.1	90.95	90.88
F_{obj}	0.00949	0.01962	0.00152	-	-	-	-

Figure 2a shows the reasonable agreement of the experimental results with both theoretical results, from the present approach and from ref.[3], employing the same set of kinetic constants from [3]. However, Figure 2b illustrates the improvement of the present theoretical results against the experiment, once the newly estimated parameters are employed in the simulation.

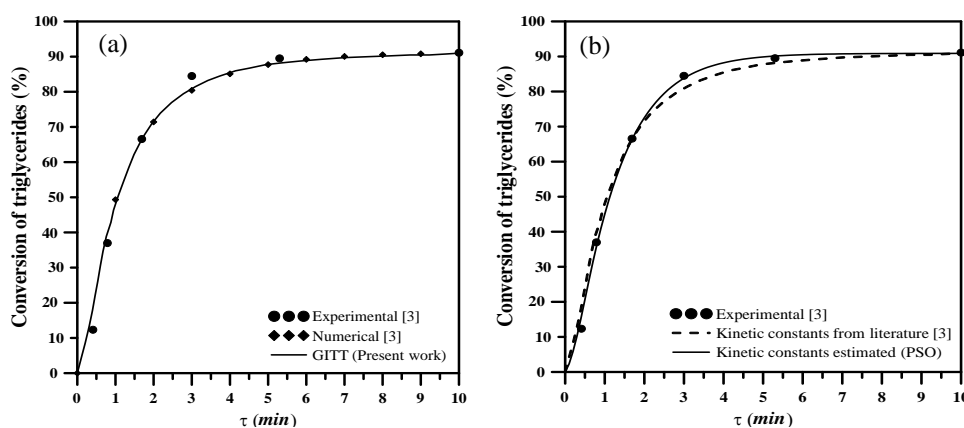


Figure 2. Conversion of triglycerides.

5. Conclusion

This paper presents a viable and interesting approach to estimate the kinetic constants in a nonlinear coupled mass transfer model for biodiesel synthesis in microreactors, by minimizing the objective function that approximates the prediction of the theoretical model to available experimental data. The combination of the hybrid GITT method, for the direct problem solution, and PSO optimization, for the inverse problem analysis, provides an efficient computational algorithm that successfully identified the parameters that resulted in improved agreement of the prediction of the theoretical model, as compared to the available experimental data.

References

- [1] Xie T, Zhang L and Xu N 2012 Biodiesel synthesis in microreactors *Green Process Synth* vol 1 pp 61-70.
- [2] Nouredini H and Zhu D 1997 Kinetics of transesterification of soybean oil *Journal of the American Oil Chemist's Society* vol 74 n 11 pp 1457-1463.
- [3] Al-Dhubabian A A 2005 Production of biodiesel from soybean oil in a micro scale reactor *Thesis (M.Sc)* Oregon State University (Corvallis, USA).
- [4] Richard R, Thiebaud-Roux S and Prat L 2013 Modelling the kinetics of transesterification reaction of sunflower oil with ethanol in microreactors *Chem. Eng. Science* vol 87 pp 258-269.
- [5] Schwaab M and Pinto J C 2007 *Análise de dados experimentais I. Fundamentos de estatística e estimação de parâmetros* (Rio de Janeiro: E-Papers).
- [6] Colaço M J, Orlande H R B and Dulikravich G S 2006 Inverse and optimization problems in heat transfer *J. of the Braz. Soc. Of Mech. Sci. & Eng.* Vol 28 n 1 pp 1-24.
- [7] Özisik M N and Orlande H R B 2000, *Inverse Heat Transfer: Fundamentals and Applications* (New York: Taylor & Francis)
- [8] Cotta R M 1993 *Integral Transforms in Computational Heat and Fluid Flow* CRC Press, USA.
- [9] Cotta R M and Mikhailov M D 1997 *Heat conduction: Lumped Analysis. Integral Transforms. Symbolic Computation*, Wiley-Interscience, Chichester, UK.
- [10] Mikhailov M D and Özisik M N 1984 *Unified Analysis and Solution of Heat and Mass Diffusion* John Wiley.
- [11] Kennedy J and Eberhart R 1995 Particle swarm optimization *Proc. of IEE International Conference on Neural Networks* (Piscataway: NJ) pp. 1942-1948.
- [12] Pontes P C, Naveira-Cotta C P, Macedo E N and Quaresma J N N 2015 Integral transform analysis of three-dimensional mass transfer in the transesterification process in microreactors *Proc. of the 7th international symposium on advances in computational heat transfer CHT-15 ICHMT* (Piscataway: NJ).
- [13] Özisik M N 1993 *Heat Conduction* (New York: John Wiley & Sons).
- [14] Wolfram S 2008 *The Mathematica Book* Cambridge-Wolfram Media, IL.
- [15] Dennis B H, Jin W, Cho J and Timmons R B 2014, Inverse determination of kinetic rate constants for transesterification of vegetable oils *Inverse Problems in Science and Engineering*, 16:6, 693-704.