

Approximation error model (AEM) approach with hybrid methods in the forward-inverse analysis of the transesterification reaction in 3D-microreactors

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This work advances the approximation error model approach for the inverse analysis of the biodiesel synthesis using soybean oil and methanol in 3D-microreactors. Two hybrid numerical-analytical approaches of reduced computational cost are considered to offer an approximate forward problem solution for a three-dimensional nonlinear coupled diffusive-convective-reactive model. First, the Generalized Integral Transform Technique (GITT) is applied using approximate non-converged solutions of the 3D model, by adopting low truncation orders in the eigenfunction expansions. Second, the Coupled Integral Equations Approach (CIEA) provides a reduced mathematical model for the average concentrations, which leads to inherently approximate solutions. The AEM approach through the Bayesian framework is illustrated in the simultaneous estimation of kinetic and diffusion coefficients of the transesterification reaction. For this purpose, the fully converged GITT results with higher truncation orders for the 3D partial differential model are employed as reference results to define the approximations errors. The results highlight that either the non-converged solutions via GITT or the reduced model solution obtained via CIEA, when taking into account the model error, are robust and cost-effective alternatives for the inverse analysis of nonlinear convection-diffusion-reaction problems.

Keywords: Approximation error model; integral transforms; improved lumped approach; GITT; CIEA; MCMC; hybrid methods; microreactors; biodiesel synthesis.

Nomenclature

C^*	dimensional concentration, mol m ⁻³
C	dimensionless concentration
D^*	diffusion coefficient, m ² s ⁻¹
D	diffusion parameter in the exponential format
e	vectors containing the measure error derived randomly from a known distribution function
\bar{e}	vectors containing the mean values of the measurement error distribution
G	kinetic terms
H	total height of the microreactor, m
H_{TG}	interface position inside the microreactor, m
J	sensitivity matrix
j	reduced sensitivity coefficient
k	kinetic constants, m ³ mol ⁻¹ s ⁻¹
L	total length of the microreactor, m
N	number of measurements
n	number of parameters to be estimated
NT	truncation order of the transformed system
nt	number of accepted states in the MCMC method
\mathbf{p}	vector of parameters
$\bar{\mathbf{p}}$	vectors containing the mean values of \mathbf{p}
\mathbf{p}^*	candidate vector of parameter in the MCMC method
q	probability distribution function
Q	volumetric flow rate, m ³ s ⁻¹
U	dimensionless velocity profile or uniform distribution
u	dimensional velocity profile, m s ⁻¹
Vol	volume, m ³
W	total width of the microreactor, m
W	covariance matrix for experimental measurements error
W_{Ap}	covariance matrix for approximation error

\mathbf{W}_p	covariance matrix for parameters
$\tilde{\mathbf{W}}$	covariance matrix combining the experimental and approximation errors
x, y, z	dimensional spatial coordinate, m
X, Y, Z	dimensionless spatial coordinate
\mathbf{y}	vector of measurements

Greek symbols

α	search step in the MCMC method
μ	dynamic viscosity, Pa. s
ξ, ζ, ω	dimensionless group
ρ	density, kg/m ³
$\boldsymbol{\varepsilon}$	vector containing the model approximation error
ε	increment for calculus of derivative
κ	kinetic parameter in the exponential format
$\boldsymbol{\eta}$	distribution of measurements and approximate errors
$\bar{\boldsymbol{\eta}}$	vector with the mean values of $\boldsymbol{\eta}$
$\boldsymbol{\Gamma}$	covariance matrix of \mathbf{p}
$\boldsymbol{\Gamma}_{\boldsymbol{\eta}\mathbf{p}}$	covariance matrix of $\boldsymbol{\eta}$ and \mathbf{p}
σ	standard deviation
$\hat{\sigma}$	reference standard deviation
τ	residence time, min
π	probability distribution function

Subscripts and superscripts

A	referring to the alcohol
Ac	referring to the accurate solution
Av	referring to the average potential
Ap	referring to the approximate solution
B	referring to the biodiesel
DG	referring to the diglyceride

Exp	referring to the experimental measurements
GL	referring to the glycerol
i	counter
MG	referring to the monoglyceride
p	referring to intermediates and products of reaction
s	referring to the species
Sim	referring to the simulated measurements
TG	referring to the triglyceride

1 - Introduction

Inverse analysis has great relevance in engineering and physical sciences, with its mathematical and statistical background being readily available in various sources (Beck and Arnold, 1977; Alifanov, 1994; Migon and Gamerman, 1999; Özisik and Orlande, 2000; Kaipio and Somersalo, 2004; Gamerman and Lopes, 2006; Schwaab and Pinto, 2007). The MCMC method is a widely used Bayesian method that allows the statistical inference about unknown parameters from its *posterior* probability density, considering the measurements and the related uncertainties through the *likelihood* function and any *prior* information from the unknown parameters (Migon and Gamerman, 1999; Gamerman and Lopes, 2006; Özisik and Orlande, 2000; Orlande, 2015). This method is especially suitable when it is unfeasible to find an analytical solvable posterior distribution and/or a large parameter space is involved, allowing for the Bayesian inference application even in rich and complex models. To speed up the MCMC calculations, approximate solutions can replace a more accurate forward problem treatment meeting constraints in the computing time, but at the same time ensuring accuracy in the inverse analysis, by using the so-called Approximation Error Model (AEM) approach. The error when approximate forward solutions are used can be accounted through statistical quantities obtained from a sampling procedure of the difference between approximate and accurate solutions. Such information can then be inserted in the *likelihood* function as an approximation error (Kaipio and Somersalo, 2004; Nissinen *et al.*, 2008, 2009, 2011a, 2011b; Lamien and Orlande, 2013; Orlande *et al.*, 2014, Pacheco *et al.* 2015, Lamien *et al.* 2017, 2019).

In this work, a robust and efficient statistical inversion approach is implemented to estimate the kinetic and diffusion coefficients of the biodiesel synthesis in 3D-microreactors within the Bayesian framework through the Metropolis-Hastings algorithm in the Markov Chain Monte Carlo (MCMC) method. Forward analysis for diffusive-convective-reactive processes governed by nonlinear coupled multidimensional mathematical models is not a straightforward computational task and hybrid techniques are particularly attractive since they combine numerical and analytical approaches to construct more accurate and cost-effective solutions, as compared to purely numerical approaches. The so-called Generalized Integral Transform Technique (GITT) is an example of a hybrid method that has been successfully applied in the solution of various flow, heat and mass transfer problems (Aparecido *et al.*, 1989; Cotta, 1990, 1993, 1994, 1998; Cotta and Mikhailov, 1997, 2006; Cotta *et al.*, 2013; 2015; 2016a; 2016b; 2018a; 2018b, Pontes *et al.*, 2018, Serfaty and Cotta, 1990). Derived

from the Classical Integral Transform Technique (CITT) (Mikhailov and Özisik, 1984; Özisik, 1993), the GITT is based on analytical eigenfunction expansions and numerical transformed potentials, obtained, respectively, from the solution of a suitable eigenvalue problem and of an infinite nonlinear coupled ordinary differential system. This transformed system usually depends on a single independent variable, and, therefore, its numerical solution demands much less computational effort than the original multi-dimensional model, making the GITT a successful technique for performing the time-consuming computational task inherent to inverse analysis (Naveira-Cotta *et al.*, 2010a, 2010b, 2011a, 2011b; Knupp *et al.*, 2012a, 2012b, 2013; Cotta *et al.*, 2016a; Abreu *et al.*, 2014, 2018).

Another interesting alternative of reducing the computational effort in forward-inverse analysis is the so-called Coupled Integral Equations Approach - CIEA (Aparecido and Cotta, 1989; Cotta and Mikhailov, 1997; Regis *et al.*, 2000; Naveira *et al.*, 2009; Sphaier *et al.*, 2017; Kakaç *et al.*, 2018; Costa Junior and Naveira-Cotta, 2019). The CIEA is a problem reformulation tool that has been employed in the simplification of diffusion and convection-diffusion problems via averaging processes in one or more of the involved space coordinates. The resulting lumped-differential formulations offer substantial improvement over classical lumping schemes in terms of accuracy, without introducing additional mathematical complexity in the corresponding final simplified differential equations to be handled. The CIEA has also been successfully applied to a few forward-inverse analyses in different contexts (Lamien and Orlande, 2013; Orlande *et al.*, 2014; Costa Junior. *et al.*, 2018; Costa Junior and Naveira-Cotta, 2019), where it should be pointed out the contribution in combining the improved lumped-differential formulation with the Approximation Error Model (Orlande *et al.*, 2014, Pacheco *et al.*, 2015).

The idea of combining the AEM with hybrid methods is here further explored. The physical problem used to demonstrate the proposed combined approach is the biodiesel synthesis in microreactors via the transesterification reaction, which is a process that has been widely explored in the literature due to the high conversion rate of triglyceride obtained with low residence time and temperature levels compared to traditional processes performed in conventional batch reactors (Al-Dhubabian, 2005; Guan *et al.*, 2009, 2010; Xie *et al.*, 2012; Billo *et al.*, 2015; Pontes *et al.* 2017, Costa Junior and Naveira-Cotta, 2019, Costa Junior *et al.* 2019). Biodiesel is generally defined as the mono alkyl esters of long chain fatty acids derived mainly from the transesterification reaction between triglycerides, obtained from renewable raw materials such as vegetable oils or animal fats, and alcohol, usually methanol or ethanol, in the presence of a catalyst (Noureddini and Zhu, 1997; Xie *et al.*,

2012). It is considered a non-toxic and biodegradable product with physical-chemical properties very similar to those of conventional diesel and that presents low emissions of carbon, sulfur, particulate matter and unburned hydrocarbons (Meher *et al.*, 2006; Dennis *et al.*, 2008; Xie *et al.*, 2012). Microreactors favor the reaction of the immiscible reagents in the transesterification, since the molecular diffusive effects occur more rapidly due to the significant reduction in the diffusion path length (Malengier *et al.*, 2012), resulting in more effective mass and heat transfer processes. However, due to the complexity of this application, many effects influence the biodiesel yields, such as the complex liquid-liquid interaction established in the reactive system, the reaction kinetic mechanism, the solubility of the components (De Boer and Bahri, 2009), the types of reagents and their molar feed ratio, the temperature of the system and the types and concentration of the catalysts, posing some difficulties to develop an optimized design of the microreactors for the biodiesel production. Thus, computational simulation plays a crucial role in determining the chemical kinetic and diffusion coefficients and, for that purpose, mathematical models and methodologies for forward-inverse analysis have been addressed in the literature (Al-Dhubabian, 2005; Dennis *et al.*, 2008; Richard *et al.*, 2013; Pontes *et al.*, 2016, 2017; Costa Junior and Naveira-Cotta, 2019, Costa Junior. *et al.*, 2020a, Costa Junior. *et al.*, 2020b).

The goal of this work is to simultaneously estimate the kinetic and diffusion coefficients of the transesterification with soybean oil and methanol in microreactors, by using simulated experimental data and approximate solutions obtained from a diffusive-convective-reactive nonlinear multicomponent 3D model (Pontes *et al.*, 2017; Costa Junior and Naveira-Cotta, 2019). The fully converged solutions derived through the GITT approach from the 3D mathematical model are considered as the accurate reference results (Pontes *et al.*, 2017). Two alternative low-cost approximate solutions are then explored, one from a reduced model derived by the CIEA and the other directly obtained from the GITT approach, but considering non-converged solution with low truncation orders in the eigenfunction expansions. The error analysis is performed only once, within a *prior* range considered for the parameters, and then approximate solutions combined with the approximation error approach are used in the inverse analysis leading to a significant reduction in the overall computational time. A sensitivity analysis together with the sequential experimental design are also presented to identify possible linear dependence among the parameters and to identify which residence times should be chosen to take the experimental measurements. In light of experimental limitations, only data on the average concentrations of four species at the microreactor outlet are considered to be available, for a few values of residence time, from the simulated data.

2 - Forward-Problem: formulation and solution methodology

The forward-problem here addressed has been posed in (Pontes *et. al.*, 2017) and it consists in determining the concentration profile of the species involved in the transesterification in microreactors from the knowledge of inlet and boundary conditions, reaction mechanism, geometry and parameters of the physico-chemical process.

The mathematical model for the biodiesel production in microreactors considers the hypothesis of continuous fully developed stratified laminar and incompressible flow of oil and alcohol, both as Newtonian fluids, where the significant reactive effects occur only in the oil phase (Al-Dhubabian, 2005; Pontes *et. al.*, 2017). Figure 1 illustrates a scheme of the velocity profile for the stratified flow of oil and alcohol in a microsystem obtained from the analytical solution based on the Classical Integral Transform Technique (CITT) (Pontes *et. al.*, 2017).

[Figure 1 near here]

Since this mathematical model assumes that the reaction is carried out mainly in the oil phase, the residence time τ can be written as a ratio between the volume and the volumetric flow rate of the oil species, in the form:

$$\tau = \frac{\text{Vol}_{\text{TG}}}{Q_{\text{TG}}} = \frac{LWH_{\text{TG}}}{Q_{\text{TG}}} \quad (1)$$

where Vol_{TG} is the volume of oil layer, Q_{TG} is the oil volumetric flow rate, L and W are the length and width of the microreactor, and H_{TG} is the position of the interface between the oil and the alcohol. Different volumetric flow rates lead to different residence times. By assuming the transesterification as a second order and reversible reaction (Noureddini and Zhu, 1997; Al-Dhubabian, 2005; Pontes *et. al.*, 2017), the dimensionless mathematical model for the concentration of the species in the transesterification mass transfer problem is then given by (Pontes *et. al.*, 2017):

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

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

$$\left. \frac{\partial C_s}{\partial Y} \right|_{Y=0} = \left. \frac{\partial C_s}{\partial Z} \right|_{Z=0} = \left. \frac{\partial C_s}{\partial Z} \right|_{Z=1} = 0, \text{ where } s = \text{TG,DG,MG,B,A,GL} \quad (2d-f)$$

$$C_A(X,1,Z) = C_{A0}, \left. \frac{\partial C_s}{\partial Y} \right|_{Y=1} = 0, \text{ where } s = \text{TG,DG,MG,B,GL} \quad (2g,h)$$

with dimensionless groups defined as:

$$C_s = \frac{C_s^*}{C_{\text{TGo}}^*}, C_{A0} = \frac{C_{A0}^*}{C_{\text{TGo}}^*}, X = \frac{x}{L}, Y = \frac{y}{H_{\text{TG}}}, Z = \frac{z}{W}, \quad (2i-q)$$

$$U_{\text{TG}} = \frac{u_{\text{TG}}}{u_{\text{TG,Av}}}, \zeta = \frac{LC_{\text{TGo}}^*}{u_{\text{TG,Av}}}, \xi_s = \frac{LD_s^*}{u_{\text{TG,Av}}H_{\text{TG}}^2}, \omega = \frac{H_{\text{TG}}^2}{W^2}$$

where C_{TGo}^* and C_{A0}^* are the dimensional inlet concentration of triglycerides and the equilibrium concentration of alcohol at the interface, respectively, $u_{\text{TG,Av}}$ is the average velocity for the oil stream (TG), U is the dimensionless velocity profile and D^* is the diffusion coefficient of each species. G_s are the chemical kinetic terms for each species, where k_1 to k_6 are the kinetic constants, according to the following equations:

$$G_{\text{TG}} = -k_1 C_{\text{TG}} C_A + k_2 C_{\text{DG}} C_B \quad (2r)$$

$$G_A = -k_1 C_{\text{TG}} C_A + k_2 C_{\text{DG}} C_B - k_3 C_{\text{DG}} C_A + k_4 C_{\text{MG}} C_B - k_5 C_{\text{MG}} C_A + k_6 C_{\text{GL}} C_B \quad (2s)$$

$$G_{\text{DG}} = k_1 C_{\text{TG}} C_A - k_2 C_{\text{DG}} C_B - k_3 C_{\text{DG}} C_A + k_4 C_{\text{MG}} C_B \quad (2t)$$

$$G_{\text{MG}} = k_3 C_{\text{DG}} C_A - k_4 C_{\text{MG}} C_B - k_5 C_{\text{MG}} C_A + k_6 C_{\text{GL}} C_B \quad (2u)$$

$$G_{\text{GL}} = k_5 C_{\text{MG}} C_A - k_6 C_{\text{GL}} C_B \quad (2v)$$

$$G_B = k_1 C_{\text{TG}} C_A - k_2 C_{\text{DG}} C_B + k_3 C_{\text{DG}} C_A - k_4 C_{\text{MG}} C_B + k_5 C_{\text{MG}} C_A - k_6 C_{\text{GL}} C_B \quad (2w)$$

The mathematical model defined by equations (2) is here solved through the GITT approach, as detailed in (Pontes *et. al.*, 2017). Also, the alternative reduced model is obtained by the CIEA approach, as presented in further detail in (Costa Junior and Naveira-Cotta, 2019). Both methodologies are described for the present application in the Electronic Supplementary Material which is associated with this article. The GITT methodology is employed in providing both the accurate reference results, through the fully converged solution for sufficiently large

truncation orders, and the alternative low-cost approximate solution, considering fairly low truncation orders in the eigenfunction expansions. In the CIEA approach, the system of lumped-differential equations for the average concentrations results in being not dependent on the diffusion coefficients D_{TG}^* and D_P^* , due to the zero flux boundary conditions at the reactor walls for these species, but retains the influence on the diffusion coefficient for the alcohol, as discussed in (Costa Junior and Naveira-Cotta, 2019). On the other hand, the non-converged solutions developed by GITT conserve the information about all diffusion coefficients, even for very low truncation orders in the eigenfunction expansion.

After the solution of the forward problem the average concentrations, $C_{s,Av}(X)$, can be evaluated from:

$$C_{s,Av}(X) = \frac{\int_0^1 \int_0^1 U_{TG}(Y,Z) C_s(X,Y,Z) dY dZ}{\int_0^1 \int_0^1 U(Y,Z) dY dZ} \quad (3)$$

3 – Inverse problem: Bayesian inference with MCMC and approximation error

The inverse problem here addressed to determine the kinetic and diffusion coefficients of the transesterification reaction shall consider the two approximate solutions previously mentioned: lumped reformulation based on the CIEA approach (one-dimensional reduced model) and GITT solution with a low truncation order (three-dimensional model with non-converged solution). The relative merits of the alternative cost-effective solutions shall then be critically examined.

In the estimation procedure, only the concentrations of the triglyceride, diglyceride, monoglyceride and biodiesel species are considered as available data, since, usually, after the reaction, the alcohol and glycerol species are separated from the product (Costa Junior and Naveira-Cotta, 2019). In addition, this information is considered to be available only at the microreactor outlet ($X=1$), in light of the experimental difficulties in measuring concentrations along the reactor length.

3.1 - Sensitivity analysis and sequential experimental design

Before addressing the estimation of the unknown parameters, a sensitivity analysis and a sequential experimental design are proposed, in order to give some insights regarding the influence of each additional experimental data in the inverse problem solution.

Specially in the application here considered, the characterization of the biodiesel sample is commonly performed by gas chromatography analysis, which is a sophisticated, time consuming, and expensive technique, which makes the analysis of a larger number of samples undesirable. Therefore, the sequential experimental design improves the estimation and helps to reduce time and costs in the experimental campaign, since its output information gives the best sequence of experiments to be performed.

Here, each experiment leads to four responses which are the concentrations of the TG, DG, MG and B species. Each species is considered as a sensor for the concentration measurements, which allows to define (Özisik and Orlande, 2000):

$$\frac{\partial \vec{C}^T(\mathbf{p})}{\partial \mathbf{p}} = \begin{bmatrix} \frac{\partial}{\partial p_1} \\ \frac{\partial}{\partial p_2} \\ \vdots \\ \frac{\partial}{\partial p_n} \end{bmatrix} [\vec{C}_1 \quad \vec{C}_2 \quad \dots \quad \vec{C}_N] \quad (4a)$$

where $\vec{C}_i = \{C_{i,TG}, C_{i,DG}, C_{i,MG}, C_{i,B}\}$, $i = 1, 2, \dots, N$. Here, n represents the dimension of the parameters vector and N is the number of measurements per species for different residence times. Then, the sensitivity matrix $\mathbf{J}(\mathbf{p})$ can be written as:

$$\mathbf{J}(\mathbf{p}) = \begin{bmatrix} \frac{\partial \vec{C}_1^T}{\partial p_1} & \frac{\partial \vec{C}_1^T}{\partial p_2} & \frac{\partial \vec{C}_1^T}{\partial p_3} & \dots & \frac{\partial \vec{C}_1^T}{\partial p_n} \\ \frac{\partial \vec{C}_2^T}{\partial p_1} & \frac{\partial \vec{C}_2^T}{\partial p_2} & \frac{\partial \vec{C}_2^T}{\partial p_3} & \dots & \frac{\partial \vec{C}_2^T}{\partial p_n} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \frac{\partial \vec{C}_N^T}{\partial p_1} & \frac{\partial \vec{C}_N^T}{\partial p_2} & \frac{\partial \vec{C}_N^T}{\partial p_3} & \dots & \frac{\partial \vec{C}_N^T}{\partial p_n} \end{bmatrix} \quad (4b)$$

where the derivative $\frac{\partial \vec{C}_1^T}{\partial p_1}$ is calculated as:

$$\frac{\partial \vec{C}_1^T}{\partial p_1} = \left[\begin{array}{c} \frac{\partial C_{TG}}{\partial p_1} \\ \frac{\partial C_{DG}}{\partial p_1} \\ \frac{\partial C_{MG}}{\partial p_1} \\ \frac{\partial C_B}{\partial p_1} \end{array} \right]_{\tau=\tau_1} \quad (4c)$$

The other derivatives in the complete sensitivity matrix are calculated following the proposed idea presented in equation (4.c), where $\mathbf{p} = \{k_1, k_2, k_3, k_4, k_5, k_6, D_{TG}^*, D_A^*, D_P^*\}$ is the vector of parameters to be estimated and D_p^* is considered to be the same for all intermediates and products of reaction (DG, MG, GL, B), following Al-Dhubabian (2005). The analysis of the sensitivity coefficients helps to identify those parameters with lower magnitudes or linear dependence with respect to the others, in order to reduce the ill-condition nature of the inverse problem and lead to more accurate and precise estimates (Özisik and Orlande, 2000).

To perform the linear dependence analysis, the reduced sensitivity coefficients are commonly applied:

$$j_{s,i} = p_i \frac{\partial C_s}{\partial p_i}, \text{ where } s = TG, DG, MG, B \quad (4d)$$

The reduced sensitivity coefficients attenuate problems related to different orders of magnitude observed in the sensitivity coefficients and, consequently, helping to perform a more appropriate linear dependence analysis among them. The derivative of $\frac{\partial C_s}{\partial p_i}$ is here computed by using the finite difference method in forward formulation with an increment ϵp_i that is proportional to the parameter value (Özisik and Orlande, 2000):

$$\frac{\partial C_s}{\partial p_i} = \frac{C_s(p_1, p_2, \dots, p_i + \varepsilon p_i, \dots, p_n) - C_s(p_1, p_2, \dots, p_i, \dots, p_n)}{\varepsilon p_i} \quad (5)$$

Besides the analysis of the reduced sensitivity coefficients, the matrix $\mathbf{J}(\mathbf{p})$ is employed to develop a sequential experimental design to identify those experiments that maximize the determinant of the matrix $\mathbf{J}^T \mathbf{J}$ reducing the uncertainty in the parameter estimation (Pinto *et. al.* 1990, 1991; Schwaab and Pinto, 2007).

In this work, possible experiments were proposed for different reaction residence times, while keeping unchanged the reaction temperature, triglyceride to alcohol molar ratio, catalyst concentration, type of reagents, and the microreactor geometry. The determinant of the matrix $\mathbf{J}^T \mathbf{J}$ is maximized sequentially during the addition of information on each residence time in the matrix \mathbf{J} , aiming to reach the best combination among them.

The GITT solution for the complete 3D model with a sufficiently high truncation order, in light of the error control capabilities through a proper convergence analysis, is taken as the reference benchmark result and the synthetic experimental data arises from applying noise to this “true value”. Synthetic measurements for the average concentrations of triglyceride, diglyceride, monoglyceride and biodiesel species are considered to be taken at the reactor outlet, for a few selected values of the residence time.

3.2 - Bayesian inference with approximation error

In a Bayesian inference approach, a limited set of available information is used to reduce the uncertainties present in an inferential or decision-making problem (Orlande, 2007; Orlande, 2015). New information can be considered and added to the previous set according to Bayes' theorem, building the necessary basis to apply the statistical inversion approach by adopting the following hypotheses:

- 1 - All variables included in the model are modeled as random variables;
- 2 - The randomness describes the degree of information concerning their realization;
- 3 - The degree of information concerning these values is coded in probability distributions;
- 4 - The solution of the inverse problem is the *posterior* probability distribution;

The Bayes' theorem can be written as:

$$\pi_{posterior}(\mathbf{p}) = \pi(\mathbf{p}|\mathbf{y}^{Exp}) = \frac{\pi(\mathbf{y}^{Exp}|\mathbf{p})\pi_{prior}(\mathbf{p})}{\pi(\mathbf{y}^{Exp})} \quad (6a)$$

where $\pi(\mathbf{y}^{Exp}|\mathbf{p})$ is the *likelihood* function which provides the uncertainties and conditional probability of a given vector of parameters \mathbf{p} lead to the vector of observed measurement \mathbf{y}^{Exp} , $\pi_{prior}(\mathbf{p})$ is the *prior* distribution containing the information and uncertainties about the parameters before observing the measurements \mathbf{y}^{Exp} , which in this work will be considered as truncated Gaussian distribution for diffusion coefficients and Uniform for kinetic coefficients, $\pi(\mathbf{y}^{Exp})$ is the marginal probability density of the measurements that plays the role of a normalizing constant, and $\pi(\mathbf{p}|\mathbf{y}^{Exp})$ is the *posterior* distribution density which provides the uncertainties and conditional probability to obtain \mathbf{p} given the observations \mathbf{y}^{Exp} .

Assuming that the measurements errors are additive, independent of \mathbf{p} and follow a Gaussian distribution with zero mean and with a known covariance matrix \mathbf{W} , the *likelihood* function can be defined as:

$$\pi(\mathbf{y}^{Exp}|\mathbf{p}) = (2\pi)^{-N/2} |\mathbf{W}|^{-1/2} \exp\left[-\frac{1}{2}(\mathbf{y}^{Exp} - \mathbf{y}^{Sim}(\mathbf{p}))^T \mathbf{W}^{-1} (\mathbf{y}^{Exp} - \mathbf{y}^{Sim}(\mathbf{p}))\right] \quad (6b)$$

where, \mathbf{y}^{Exp} is the vector containing the synthetic experimental data generated from the mathematical model, and \mathbf{y}^{Sim} is the calculated potential based on the adopted mathematical model. Matrix \mathbf{W} is written as:

$$\mathbf{W} = \begin{bmatrix} \sigma_1^2 & 0 & \cdots & 0 \\ 0 & \sigma_2^2 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & \sigma_N^2 \end{bmatrix} \quad (6c)$$

where σ represents the standard deviation of the observed measurements.

Eventually, information on the parameters are accessible and might be represented as a Gaussian *prior* distribution, and can be incorporated in the inverse analysis in the form:

$$\pi_{prior}(\mathbf{p}) = (2\pi)^{-n/2} |\mathbf{W}_p|^{-1/2} \exp\left[-\frac{1}{2}(\mathbf{p} - \bar{\mathbf{p}})^T \mathbf{W}_p^{-1} (\mathbf{p} - \bar{\mathbf{p}})\right] \quad (6d)$$

where $\bar{\mathbf{p}}$ and \mathbf{W}_p are the known mean and covariance matrix for \mathbf{p} , respectively.

Assuming the solution via GITT for the complete 3D model with a higher truncation order is the existing “truth”, $\mathbf{y}_{Ac}^{Sim}(\mathbf{p})$, so the vector of synthetic experimental data \mathbf{y}^{Exp} arises from applying a noise based on a known probability distribution function for the measurement errors into the vector containing the accurate values, $\mathbf{y}_{Ac}^{Sim}(\mathbf{p})$, according to equation (6e):

$$\mathbf{y}^{Exp} = [\mathbf{y}_{Ac}^{Sim}(\mathbf{p})] + \mathbf{e} \quad (6e)$$

where \mathbf{e} is a vector containing the experimental noise.

Once the proposed approximate solution, $\mathbf{y}_{Ap}^{Sim}(\mathbf{p})$, does not coincide with that “true” one, $\mathbf{y}_{Ac}^{Sim}(\mathbf{p})$, then \mathbf{y}^{Exp} will, at the end, float around the vector of approximate solutions, $\mathbf{y}_{Ap}^{Sim}(\mathbf{p})$, according to (Kaipio and Somersalo, 2004; Nissinen *et. al.*, 2008, 2009, 2011a, 2011b; Lamien and Orlande, 2013; Orlande *et. al.*, 2014, Pacheco *et. al.* 2015, Lamien *et. al.* 2017, 2019):

$$\mathbf{y}^{Exp} = [\mathbf{y}_{Ap}^{Sim}(\mathbf{p}) + \boldsymbol{\varepsilon}(\mathbf{p})] + \mathbf{e} \quad (6f)$$

where $\boldsymbol{\varepsilon}(\mathbf{p})$ is a vector containing the information about the discrepancy between approximate and accurate models. Equation (6f) can be written in a simpler form as:

$$\mathbf{y}^{Exp} = \mathbf{y}_{Ap}^{Sim}(\mathbf{p}) + \boldsymbol{\eta}(\mathbf{p}) \quad (6g)$$

$$\boldsymbol{\eta}(\mathbf{p}) = \mathbf{e} + \boldsymbol{\varepsilon}(\mathbf{p}) \quad (6h)$$

The calculation of $\boldsymbol{\eta}(\mathbf{p})$ including the error in the measurements, \mathbf{e} , and the approximation error, $\boldsymbol{\varepsilon}(\mathbf{p})$, can be done in a reasonable simple way by assuming $\boldsymbol{\eta}(\mathbf{p})$ like a

Gaussian distribution. This assumption ensures effective results making possible to rewrite equation (6b) taking into account the error of the approximate model in the *likelihood* function, as shown below (Kaipio and Somersalo, 2004; Nissinen *et. al.*, 2008, 2009, 2011a, 2011b; Lamien and Orlande, 2013; Orlande *et. al.*, 2014, Pacheco *et. al.* 2015, Lamien *et. al.* 2017, 2019):

$$\pi_{Ap}(\mathbf{y}^{Exp} | \mathbf{p}) = (2\pi)^{-N/2} |\tilde{\mathbf{W}}|^{-1/2} \exp \left[-\frac{1}{2} (\mathbf{y}^{Exp} - \mathbf{y}_{Ap}^{Sim}(\mathbf{p}) - \bar{\boldsymbol{\eta}})^T \tilde{\mathbf{W}}^{-1} (\mathbf{y}^{Exp} - \mathbf{y}_{Ap}^{Sim}(\mathbf{p}) - \bar{\boldsymbol{\eta}}) \right] \quad (6i)$$

where $\bar{\boldsymbol{\eta}}$ and $\tilde{\mathbf{W}}$ are defined as (Kaipio and Somersalo, 2004; Orlande *et. al.*, 2014):

$$\bar{\boldsymbol{\eta}} = \bar{\mathbf{e}} + \bar{\boldsymbol{\varepsilon}} + \Gamma_{\boldsymbol{\eta}\mathbf{p}} \Gamma^{-1} (\mathbf{p} - \boldsymbol{\mu}) \quad (6j)$$

$$\tilde{\mathbf{W}} = \mathbf{W} + \mathbf{W}_{Ap} - \Gamma_{\boldsymbol{\eta}\mathbf{p}} \Gamma^{-1} \Gamma_{\mathbf{p}\boldsymbol{\eta}} \quad (6k)$$

where $\bar{\mathbf{e}}$ is the mean of \mathbf{e} , $\bar{\boldsymbol{\varepsilon}}$ is the mean of $\boldsymbol{\varepsilon}(\mathbf{p})$, $\boldsymbol{\mu}$ is the mean of \mathbf{p} , Γ is the covariance matrix of \mathbf{p} , \mathbf{W}_{Ap} is the covariance matrix of $\boldsymbol{\varepsilon}(\mathbf{p})$ and $\Gamma_{\boldsymbol{\eta}\mathbf{p}}$ is the covariance matrix of $\boldsymbol{\eta}$ and \mathbf{p} .

Equations (6j,k) are simplified regarding the hypothesis of Gaussian measurement errors with zero mean used for *likelihood*, which leads to $\bar{\mathbf{e}} = \mathbf{0}$, and neglecting the dependence between $\boldsymbol{\eta}$ and \mathbf{p} , which implies in $\Gamma_{\boldsymbol{\eta}\mathbf{p}} = \mathbf{0}$, resulting in the following expressions:

$$\bar{\boldsymbol{\eta}} \approx \bar{\boldsymbol{\varepsilon}} \quad (6l)$$

$$\tilde{\mathbf{W}} = \mathbf{W} + \mathbf{W}_{Ap} \quad (6m)$$

Statistical properties of $\boldsymbol{\varepsilon}(\mathbf{p})$ are calculated only once, before the estimation procedure, through a Monte Carlo simulation of the difference between the accurate and approximate solutions, $\mathbf{y}_{Ac}^{Sim}(\mathbf{p}) - \mathbf{y}_{Ap}^{Sim}(\mathbf{p})$, within the *prior* intervals assumed for the parameters. The sampling obtained is used to calculate mean and standard deviation which will be used in the approximation error model approach. This task in general requires a much lower computational

effort if compared to the complete parameter estimation procedure via MCMC using the more accurate solution in the estimation step.

3.3 - MCMC through Metropolis-Hastings algorithm

Markov Chain Monte Carlo (MCMC) method is based on a collection of a large sample of a given probability function via a stochastic process such that the value \mathbf{p}^i , given all previous values $\mathbf{p}^{(0)}, \mathbf{p}^{(1)}, \mathbf{p}^{(2)}, \dots, \mathbf{p}^{(i-1)}$, depends only on $\mathbf{p}^{(i-1)}$, not mattering the past to predict a future state, where from that it is possible to extract some desired information (Gamerman and Lopes, 2006).

Here the adopted MCMC method was based on a "random walk" in the space of $\pi(\mathbf{p}|\mathbf{y}^{\text{Exp}})$ that converges to a stationary distribution, and which allows to summarize its information in central and dispersion values that give an idea of its variability (Migon and Gamerman, 1999). For this, the initial states also called burning sampling, which comprise the evolution of the chain up to its steady behavior, must be eliminated.

To promote the random walk in the MCMC method, the Metropolis-Hastings algorithm is used to establish a mechanism for accepting a candidate state \mathbf{p}^* obtained from an auxiliary probability distribution $q(\mathbf{p}^*, \mathbf{p}^i)$ given the current state \mathbf{p}^i . The MCMC method with Metropolis-Hastings algorithm for the parameter estimation can be schematized as illustrated in figure 2:

[Figure 2 near here]

The randomness for the search step to get the candidate points in the MCMC method can be inserted by using a uniform distribution according to:

$$p_j^* = p_j^i \{1 + \alpha(2w - 1)\}, 1 < j < n, n = \text{number of parameters} \quad (7)$$

where α is the search step and w is a random number uniformly sampled in the range $[0,1]$.

The acceptance rate of the MCMC must be observed in order to avoid that the chain stays around the same state for an excessive number of iterations or that many new states are

not accepted. The movements of the chain must be dosed to make it move throughout the domain of $\pi_{Ap}(\mathbf{p}|\mathbf{y}^{\text{Exp}})$ with large displacements that have real chances of acceptance.

4 - Results and discussion

The computed code was implemented in the *Mathematica* 10.0 platform (Wolfram, 2016), using the *NDSolve* routine to numerically solve the system of ODEs for the transformed potentials that results from the GITT approach, and in the solution of the reduced model for the average potentials, through the CIEA approach. Table 1 presents the parameters adopted for the simulation, obtained in the literature (Al-Dhubabian, 2005; Costa Junior and Naveira-Cotta, 2019).

[Table 1 near here]

The concentrations of the species were evaluated for different residence times, which for a fixed geometry are obtained by varying of volumetric flow rates of the reagents, according to equation (1).

Since, experimentally, the measurements of the species concentrations are performed only on reaction products collected at the outlet of the microreactor, even though the GITT solution provides the analytical local information within the reactor, the results further presented are mainly based on the comparison of the average concentration of the species, that were constructed through Eq. 3.

Figure 3 illustrates the accurate and approximate dimensionless average concentrations of the species along the residence time, obtained through CIEA and GITT with different truncation orders: $NT = 2, 5$ and 40 . The concentration of triglyceride decreases throughout the residence time, Fig. 3a, while the biodiesel and glycerol species increase, Figs. 3e,f, respectively. The intermediate species diglyceride and monoglyceride are initially formed, reach a maximum and decrease as the reaction progresses to equilibrium (Figs. 3c,d, respectively). The $GITT_{NT=40}$ solution is here assumed to be the most accurate one while the other are considered approximate solutions. It is possible to notice that, the $GITT_{NT=5}$ and $GITT_{NT=40}$ solutions present, at the graphic scale, a fairly good adherence between themselves, for all the species. However, the solutions $GITT_{NT=2}$ and 1D-CIEA slightly differ from that one derived via $GITT_{NT=40}$.

[Figure 3 near here]

Table 2 presents the CPU time required for the solutions through $GITT_{NT=40}$, $GITT_{NT=5}$, $GITT_{NT=2}$ and 1D-CIEA, during a single solution of the forward problem. This comparative evaluation of computational time was performed on a desktop microcomputer with Intel Core i7-7500U CPU @ 2.70GHz-2.90GHz. The accurate solution $GITT_{NT=40}$ required a computational time of only 102s, which though not optimized, can be considered fast enough for a multidimensional nonlinear forward problem of six coupled species, but would not be fast enough to be applied in the present stochastic approach for inverse problem analysis. The two proposed approximate solutions, 1D-CIEA and $GITT_{NT=2}$ required a computational time nearly 6500 and 15000 times smaller than the accurate solution, $GITT_{NT=40}$, respectively, and therefore, they are preferable to perform the parameter estimation in the present work.

[Table 2 near here]

To evaluate the reduced sensitivity coefficients of the kinetic and diffusion coefficients, the exponential format $k = 10^{\kappa}$ and $D^* = 10^D$ is used, where κ and D are the new parameters to be estimated, instead to the original value “k” and “D*” (Costa Junior. and Naveira-Cotta, 2019). The exponential format for the parameters has been proposed since it allows to reduce the search interval for the parameters in the MCMC method and promotes a desirable increment in the sensitivity of the concentrations, facilitating an extensive investigation within the search interval with small values for the search step (Costa Junior. and Naveira-Cotta, 2019).

The sensitivity analysis and the sequential experimental design, which demand more accurate information about the physical phenomenon, were performed with the accurate solution $GITT_{NT=40}$. Figure 4 illustrates the reduced sensitivity coefficients evaluated for the different species TG, DG, MG and B, and indicates a linear dependence among some of them, notably between κ_4 and κ_5 and between κ_2 and κ_6 . Comparing Figures 3 and 4, it is observed that the reduced sensitivity coefficients related to the parameters κ_1 , κ_2 , κ_3 , κ_4 , κ_5 , κ_6 and D_A present large amplitudes, of the same magnitude as the species concentrations, which somehow favors the inverse analysis. However, the reduced sensitivity coefficients related to the parameters D_{TG} and D_p have lower amplitudes in comparison to the concentrations of the

species and the other parameters, and thus an increased difficulty in their estimation is expected.

It is also observed that, for low residence times, some sensitivity coefficients have a value very close to zero, which suggest inadequate times for the collection of experimental data, despite being a desirable result in the biodiesel production process.

[Figure 4 near here]

For the sequential experimental design, 40 different residence times in the range from 0.5 to 20 minutes, equally spaced by 0.5 minutes, are considered as candidates to be experimented, and the determinant of the matrix $\mathbf{J}^T\mathbf{J}$ is maximized through the sequential experimental design method.

Also, in the sequential experimental design, the quality of information carried by each species into the inverse problem procedure was evaluated to justify which species must be used in the likelihood. Each species, triglyceride, diglyceride, monoglyceride and biodiesel, was evaluated singly and combined among them. The analysis of the matrix $\mathbf{J}^T\mathbf{J}$, Fig. 5a, indicates an order of importance for the species to be considered in the measurement process (i.e.: B, DG, MG and TG), aiming at a better combination of results to be used in the estimation process. As can be seen, the information added through the triglyceride species does not imply in a significant change in the determinant of $\mathbf{J}^T\mathbf{J}$, so the concentration of this species could be in principle disregarded in the inverse procedure without losing information in the estimations. However, since information on this species is generally available experimentally, the triglyceride concentration was also considered in subsequent inverse analyzes.

Figure 5b illustrates the gain in the determinant of $\mathbf{J}^T\mathbf{J}$ considering, or not, the sequential experimental design for the case where four species would be experimentally available. The red triangle curve represents the determinant of $\mathbf{J}^T\mathbf{J}$ taking into account the list of 40 candidates, of residence times, in an ascending order from 0.5 to 20 minutes, equally spaced of 0.5 minutes. And the black circle curve shows the increment observed in the determinant of $\mathbf{J}^T\mathbf{J}$ when the same number of cases (40 at total) was considered in a sorted sequence, derived from the sequential design procedure. It can be noticed that the sequential design improves values for the determinant of $\mathbf{J}^T\mathbf{J}$ up to the twentieth candidate, from that

point and beyond there is no significant difference in the order of sub sequential candidates. For this reason, the inverse analysis from this point on was performed considering measures for the first 20 candidates indicated by the sequential experimental design: 5.5min, 2.5min, 18.5min, 0.5min, 1.5min, 11min, 4.5min, 2min, 20min, 1min, 6.5min, 11.5min, 4min, 19.5min, 3min, 5min, 10.5min, 19min, 3.5min, and 6min.

[Figure 5 near here]

The synthetic experimental data were simulated from the accurate solution (GITT with NT= 40) evaluated in the 20 residence times mentioned before. At each residence time, the dimensionless average concentrations for the 4 species (TG, DG, MG and B) at the reactor outlet are obtained, totaling 80 synthetic experimental data. The exact solution was disturbed by a Gaussian noise with zero mean and a standard deviation $\sigma = \hat{\sigma} C^{\text{Sim}}$ in accordance with the following expression:

$$C^{\text{Exp}} = C^{\text{Sim}} + \sigma N(0,1) \quad (8)$$

Although lower values for $\hat{\sigma}$ were investigated, such as $\hat{\sigma} = 0.01$ and $\hat{\sigma} = 0.03$, only the results for $\hat{\sigma} = 0.05$ will be here presented since such estimations have more discrepant values with respect to the original exact parameters.

Information about the approximation error in modeling is evaluated through a Monte Carlo simulation involving the difference between the accurate and approximate solutions, $C_{Ac}(\mathbf{p}) - C_{Ap}(\mathbf{p})$, for different vectors \mathbf{p} randomly generated from uniform distributions. Table 3 presents the reference values and limits of the parameters considered in the sampling procedure used in the construction of information about the model error. Mean and standard deviation, for this approximation error, were calculated from this sampling and used in the approximate *posterior* formulation, Eq. (6i), for those residence times chosen for the inverse analysis.

[Table 3 near here]

It is also worth commenting that, in the sampling process, the variation of 5% in the parameters (in exponential format as here proposed) leads to a wide variation in the actual

kinetic coefficient value higher than 37%. On the other hand, this variation on the kinetic coefficients may lead to more the 370% of variation on the dimensionless concentration for the species TG, DG, MG and B, as can be observed in Figure 6.a. These curves illustrate that 5% variation in the parameters is sufficient to create sampling curves (light grey curves) that cover a very wide region around the exact solution (solid black line). Figure 6b exemplifies the model error curves for the species TG evaluated by the difference between the $GITT_{NT=40}$ and $GITT_{NT=2}$, respectively, for an illustrative number of 200 samples of different vectors \mathbf{p} , and therefore 200 calculations of the difference between the accurate and approximate solutions. The number of samples, NS, must be evaluated to ensure a sampling which provides a fully converged value for the mean and standard deviation of the error. In this sense, Figure 6c shows the convergence analysis referring to the mean value of the error calculation between models for species TG, where it is noticed that a sampling with NS = 1000 is satisfactory to ensure, at this graphical scale, a converged behavior to appropriately describe the mean of the error.

The same convergence analysis was performed for all other species for both approximate solutions, $GITT_{NT=2}$ and 1D-CIEA, even not being presented here. For all cases, the sampling number of NS = 1000 was suitable to perform the statistical analysis on the approximation error.

Figure 6d illustrate the converged mean of the error for the species TG and B generated for the $GITT_{NT=2}$ and 1D-CIEA, where it is possible to notice that the error profiles have behavior completely distinct from those observed in the average concentration, but both $GITT_{NT=2}$ and 1D-CIEA error curves present similar tendency.

[Figure 6 near here]

For all kinetic coefficients, a non-informative Uniform *prior* was assumed, while for the diffusion coefficients, a truncated Gaussian *prior* was considered with mean based on a correlation available in the literature (Al-Dhubabian, 2005) and standard deviation of 5%. For the *priors'* range, for all parameters, a wide search interval for the MCMC was set as 50%, up and down, of the exact value of each parameter. Tables 4 and 5 present the result for the estimation of the parameters “ κ ” and “ D ” carried out with the approximate solutions, $GITT_{NT=2}$ and 1D-CIEA, respectively, considering 80 synthetic measurements with a deviation $\hat{\sigma} = 0.05$ for the concentration of species TG, DG, MG and B evaluated in the 20 residence times

indicated by the sequential experimental design. The MCMC was performed with an acceptance rate smaller than 50% for a total of 200000 accepted states. The parameter estimation was obtained through the calculation of the mean values and the quantiles of 99% for the credibility interval, both calculated from the accepted states after neglecting the burning period of 100000 states.

Tables 4a,b present the results obtained with the approximate solution $GITT_{NT=2}$, with and without taking into account the approximation error information in the estimation procedure, respectively. Similarly, Tables 5a,b present the results for the estimations obtained via 1D-CIEA, with and without, the approximation error information in the estimation procedure, respectively.

The estimated parameters for the situation where the approximation error information was taken into account presented a relative error lower than 7.70% with respect to the original exact values for kinetic and diffusion coefficients, and the credibility intervals are enveloping all exact reference values of them. Results for the estimation without taking into account the approximation error information for both approximate solutions ($GITT_{NT=2}$ and 1D-CIEA) present more expressive relative error such as 8% which suggests a poorer estimation, certainly due to the absence of the approximation error information. The credibility intervals from the estimation without the approximation error information does not include, for some parameters, their exact values and this seems like a deformation of the approximate *posterior* domain which led to less accurate estimations. These cases are illustrated in the table 4b,5b in shaded form.

[Table 4a near here]

[Table 4b near here]

[Table 5a near here]

[Table 5b near here]

Figure 7 shows the evolution of the Markov chains of the parameters for the $GITT_{NT=2}$ approximate solution, evaluated with the approximation error information considering three different initial guesses: black curve for $\mathbf{p}^0 = 0.5\mathbf{p}_{\text{exact}}$; red curve for $\mathbf{p}^0 = 0.8\mathbf{p}_{\text{exact}}$; and blue curve for $\mathbf{p}^0 = 1.5\mathbf{p}_{\text{exact}}$. These results illustrate the convergence and agreement of the MCMC with approximation error model for different initial guesses, including those away from the exact value. Even for a wide range of initial guesses, the estimation converges to a region around

the exact value of the parameters. It is also worth mentioning that a variation of 50% made in the initial guesses of the parameter, in the exponential format, represents a variation higher than 100% in the actual kinetic coefficients.

[Figure 7 near here]

Figure 8 presents the final comparison for the original accurate result for the concentrations of all four measurable species. The obtained concentrations with the exact parameters via $GITT_{NT=40}$ are presented as the black solid lines, the synthetic measurements with a standard deviation of $\hat{\sigma} = 0.05$ are presented by the red symbols. The estimated concentrations, using the $GITT_{NT=2}$ solution in the inverse analysis, are presented by the blue stars with dashed line, and their respective credibility intervals of 99% are represented by the black dashed line.

Once the equilibrium region in the iterative process of the MCMC is reached, after the burning period, the *posterior* prediction for each species was computed and stored for each state of MCMC, and from this *posterior* sample it was possible to calculate the mean and the quantiles of 99% to the estimated value of the concentration and its credibility interval. All estimated results show a good adherence to the experimental synthetic data recovering most of them, and in particular the agreement between the estimated curve and the exact one can be observed.

[Figure 8 near here]

5 – Conclusions

This work presents a methodology that allows to markedly reduce the computational effort in the estimation of the kinetic and diffusion coefficients for the transesterification reaction in microreactors, using approximate solutions and an information about the approximation error. The hybrid method GITT was used to construct an accurate solution for the forward problem governed by a multicomponent diffusive-convective-reactive nonlinear coupled 3D mathematical model, with sufficiently high truncation orders, such as $NT = 40$, while two approximate solutions were considered, one obtained by a 1D model reformulated via an improved lumped analysis (CIEA) and another one obtained from the 3D model itself solved by

GITT but with low truncation order, as low as only two terms ($NT = 2$) in the eigenfunction expansion.

The “exact” GITT solution (with a high truncation order, $NT = 40$) was used to perform the sensitivity analysis and the sequential experimental design for the problem, where it was possible to verify that the representation in exponential format for the kinetic and diffusion coefficients, $k = 10^k$ and $D^* = 10^D$, instead of its original properties k and D^* , increases the sensitivity of the new parameters to be estimated as exponents (k and D). From evaluating the $\det(\mathbf{J}^T \mathbf{J})$ it was indicated that replicating the experiments in the increasing order of the residence time proposed in a list of 40 different residence times as candidates, from 0.5 until 20min with increment of 0.5min, is not the best alternative to maximize $\det(\mathbf{J}^T \mathbf{J})$ and a sequence of 20 experiments collected and sorted from the original list of 40 candidates was presented and considered as the synthetic experimental measurements.

The approximation error information was obtained from a Monte Carlo simulation of the difference between the accurate and approximate solutions performed in a sampling generated from uniform distributions with means in the exact values of the parameters and 5%, for more and less, as interval limits. From a convergence analysis of the mean of the error, it was found a number of samples $NS = 1000$ as a satisfactory amount to represent the profile of the error representation along residence time.

The *likelihood* function was constructed using synthetic measurements with standard deviation of $\hat{\sigma} = 0.05$ for the triglyceride, diglyceride, monoglyceride and biodiesel species, and the MCMC was employed using approximate solutions with and without their approximation error information. The estimation of the parameters in the exponential format 10^k and 10^D were demonstrated for the case $\hat{\sigma} = 0.05$ with relative errors lower than 8.0% compared to the exact values when the approximation error was considered. If this approximation is not considered, the error on estimative increases and a deformation in the credibility intervals occur and consequently the exact values are not recovered for all parameters. The computational time was fairly low, reaching as much as 1.71h and 4.72h for CIEA and $GITT_{NT=2}$, respectively, in the microcomputer configuration adopted. The estimated potentials were recovered with strong adherence to the simulated data, which indicates that the combination of approximate solutions together with the information on approximation errors generates accurate results and fast algorithms for the inverse problem analysis.

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Table 1. Parameters used in the simulation of the concentration of species involved in the transesterification reaction with methanol and soybean oil at 25°C (Al-Dhubabian, 2005, Costa Junior and Naveira-Cotta, 2019).

Table 2. Computational time for accurate and approximate solutions of the forward problem.

Table 3. Reference values and limits of the parameters κ and D considered in the sampling procedure in the error model approach.

Table 4a. Results for $\hat{\sigma} = 0.05$ and credibility interval of 99% using the approximate solution from 3D GITT_{NT=2} and the approximation error information.

Table 4b. Results for $\hat{\sigma} = 0.05$ and credibility interval of 99% using the approximate solution from 3D GITT_{NT=2} without the approximation error information.

Table 5a. Results for $\hat{\sigma} = 0.05$ and credibility interval of 99% using the approximate solution from CIEA and the approximation error information.

Table 5b. Results for $\hat{\sigma} = 0.05$ and credibility interval of 99% using the approximate solution from CIEA without the approximation error information.

Figure 1. Scheme of (a) the stratified flow between oil (soybean) and alcohol (methanol) within a microreactor; (b) the velocity profile for the fully developed stratified flow in microreactors.

Figure 2. Scheme of the MCMC with Metropolis-Hastings algorithm for parameter estimation procedure.

Figure 3. Accurate and approximate average concentration profile for the species in the transesterification reaction: (4a) triglyceride, (4b) alcohol, (4c) diglyceride, (4d) monoglyceride, (4e) biodiesel and (4f) glycerol.

Figure 4. Reduced sensitivity coefficients evaluated for the exponential representation “ 10^K ” and “ 10^D ” for the kinetic and diffusion coefficients. (6a) j_{TG} ; (6b) j_B ; (6c) j_{DG} and (6d) j_{MG} .

Figure 5: Analysis of the determinant of $\mathbf{J}^T \mathbf{J}$ investigating (5a) the best arrangement order for the four potentials in the matrix \mathbf{J} considering the sequential experimental design and (5b) the improvement providing by using of this optimum design.

Figure 6. Error analysis. (6a) Sampling of error curves for TG with number of samples equal to 200, NS = 200; (6b) Convergence analysis for the mean of the error for TG with approximate solution by GITT_{NT=2}; (6c) Mean of the error for TG and B and (6d) for DG and MG with approximate solution by GITT_{NT=2} and by CIEA.

Figure 7. Markov chains for parameters obtained from approximate error approach through GITT_{NT=2} assuming different initial guesses. Black curve: $\mathbf{p}^0 = 0.5\mathbf{p}_{\text{exact}}$; red curve: $\mathbf{p}^0 = 0.8\mathbf{p}_{\text{exact}}$; and Blue curve: $\mathbf{p}^0 = 1.5\mathbf{p}_{\text{exact}}$;

Figure 8: Results for the synthetic data with $\hat{\sigma} = 0.05$, estimated curves and their credibility intervals of 99% for (8a) triglyceride, (8b) biodiesel, (8c) diglyceride and (8d) monoglyceride.

Table 1

Parameter	Value	Parameter	Value
μ_{TG} [Pa.s]	$5.825 \cdot 10^{-2}$	μ_A [Pa.s]	$5.47 \cdot 10^{-4}$
ρ_{TG} [kg m ⁻³]	885	H[m]	$400 \cdot 10^{-6}$
D_{TG}^* [m ² s ⁻¹]	$1.58 \cdot 10^{-9}$	H_{TG} [m]	$356.592 \cdot 10^{-6}$
D_A^* [m ² s ⁻¹]	$1.182 \cdot 10^{-10}$	k_1 [m ³ mol ⁻¹ s ⁻¹]	$4.368 \cdot 10^{-6}$
D_P^* [m ² s ⁻¹]	$1.38 \cdot 10^{-9}$	k_2 [m ³ mol ⁻¹ s ⁻¹]	$9.623 \cdot 10^{-6}$
C_{TGo}^* [mol m ⁻³]	1014	k_3 [m ³ mol ⁻¹ s ⁻¹]	$1.88 \cdot 10^{-5}$
C_{A0}	4.4	k_4 [m ³ mol ⁻¹ s ⁻¹]	$1.074 \cdot 10^{-4}$
Q_{TG}/Q_A	3.4	k_5 [m ³ mol ⁻¹ s ⁻¹]	$2.117 \cdot 10^{-5}$
L[m]	$2.33 \cdot 10^{-2}$	k_6 [m ³ mol ⁻¹ s ⁻¹]	$9.0 \cdot 10^{-7}$
W[m]	$400 \cdot 10^{-6}$		

Table 2.

Solution	CPU time ⁽¹⁾	CPU time reduction with respect to the GITT _{NT=40} solution
3D – GITT _{NT=40}	101.2328s	-
3D – GITT _{NT=5}	0.1239s	817
3D – GITT _{NT=2}	0.0156s	6489
1D – CIEA	0.0070s	14461

⁽¹⁾ in a DESKTOP-T0TAGFG Intel(R) Core(TM) i7-7500U CPU @ 2.70GHz 2.90GHz with RAM of 8GB

Table 3.

Parameter	Exact value	Inferior Limit	Superior Limit
κ_1	-5,35972	-5.62770	-5.09173
κ_2	-5,01669	-5.26752	-4.76586
κ_3	-4,72584	-4.96213	-4.48955
κ_4	-3,96900	-4.16745	-3.77055
κ_5	-4,67428	-4.90799	-4.44057
κ_6	-6,04576	-6.34805	-5.74347
D_{TG}	-8.80134	-9.24141	-8.36128
D_A	-9.92738	-10.4238	-9.43101
D_P	-8.86012	-9.30313	-8.41711

Table 4a

Total computational time ⁽¹⁾ : 4.32h						
Search step: $2.0 \cdot 10^{-3}$; Acceptance: 44.00%						
Parameter	Initial Guess	Exact value	Estimated	Minimum	Maximum	Error (%)
κ_1	-2.67986	-5.35972	-5.23226	-5.40104	-4.94061	2.37800
κ_2	-2.50834	-5.01669	-4.95242	-5.07705	-4.69741	1.28105
κ_3	-2.36292	-4.72584	-4.37707	-4.80132	-4.02673	7.38011
κ_4	-1.98450	-3.96900	-3.66313	-4.07241	-3.31520	7.70646
κ_5	-2.33714	-4.67428	-4.61141	-4.69829	-4.51891	1.34496
κ_6	-3.02288	-6.04576	-6.03114	-6.10960	-5.95595	0.24185
D_{TG}	-4.40067	-8.80134	-8.89102	-9.76302	-8.07658	1.01893
D_A	-4.96369	-9.92738	-10.27336	-11.21084	-9.85875	3.48511
D_P	-4.43006	-8.86012	-8.27231	-9.06810	-7.62360	6.63435

⁽¹⁾ in a DESKTOP-T0TAGFG Intel(R) Core(TM) i7-7500U CPU @ 2.70GHz 2.90GHz with RAM of 8GB

Table 4b.

Total computational time ⁽¹⁾ : 3.57h						
Search step: $2.0 \cdot 10^{-3}$; Acceptance: 47%						
Parameter	Initial Guess	Exact value	Estimated	Minimum	Maximum	Error (%)
κ_1	-2.67986	-5.35972	-5.39955	-5.46939	-5.32628	0.74318
κ_2	-2.50834	-5.01669	-5.06979	-5.13565	-5.00246	1.05847
κ_3	-2.36292	-4.72584	-4.77795	-4.87654	-4.66998	1.10254
κ_4	-1.98450	-3.96900	-4.03333	-4.12840	-3.91947	1.62101
κ_5	-2.33714	-4.67428	-4.66791	-4.72480	-4.61061	0.13635
κ_6	-3.02288	-6.04576	-6.02765	-6.08604	-5.97200	0.29951
D_{TG}	-4.40067	-8.80134	-8.80501	-9.23042	-8.03627	0.04171
D_A	-4.96369	-9.92738	-9.93274	-10.04956	-9.83064	0.05396
D_P	-4.43006	-8.86012	-8.17955	-8.45854	-7.79879	7.68125

⁽¹⁾ in a DESKTOP-T0TAGFG Intel(R) Core(TM) i7-7500U CPU @ 2.70GHz 2.90GHz with RAM of 8GB

Table 5a

Total computational time ⁽¹⁾ : 1.71h						
Search step: $2.3 \cdot 10^{-3}$; Acceptance: 41%						
Paramete	Initial	Exact	Estimated	Minimum	Maximum	Error (%)
r	Guess	value				
κ_1	-2.67986	-5.35972	-5.29992	-5.40199	-5.20718	1.11559
κ_2	-2.50834	-5.01669	-4.9868	-5.08809	-4.88792	0.59587
κ_3	-2.36292	-4.72584	-4.51221	-4.76127	-4.3117	4.52044
κ_4	-1.98450	-3.96900	-3.76492	-4.0118	-3.55905	5.14180
κ_5	-2.33714	-4.67428	-4.6038	-4.6931	-4.50385	1.50771
κ_6	-3.02288	-6.04576	-5.97438	-6.06365	-5.87371	1.18064
D_A	-4.96369	-9.92738	-10.0121	-10.0817	-9.93321	0.85320

⁽¹⁾ in a DESKTOP-T0TAGFG Intel(R) Core(TM) i7-7500U CPU @ 2.70GHz 2.90GHz with RAM of 8GB

Table 5b

Total computational time ⁽¹⁾ : 1.70h						
Search step: $1.5 \cdot 10^{-3}$; Acceptance: 35.4%						
Paramete r	Initial Guess	Exact value	Estimated	Minimum	Maximum	Error (%)
κ_1	-2.67986	-5.35972	-5.22998	-5.27678	-5.18624	2.42063
κ_2	-2.50834	-5.01669	-4.97135	-5.02172	-4.92484	0.903698
κ_3	-2.36292	-4.72584	-4.31178	-4.38817	-4.23931	8.76163
κ_4	-1.9845	-3.96900	-3.62813	-3.71185	-3.54966	8.58831
κ_5	-2.33714	-4.67428	-4.55212	-4.59894	-4.50604	2.61351
κ_6	-3.02288	-6.04576	-5.96144	-6.01498	-5.90869	1.39464
D_A	-4.96369	-9.92738	-10.1184	-10.1516	-10.0843	1.92433

⁽¹⁾ in a DESKTOP-T0TAGFG Intel(R) Core(TM) i7-7500U CPU @ 2.70GHz 2.90GHz with RAM of 8GB

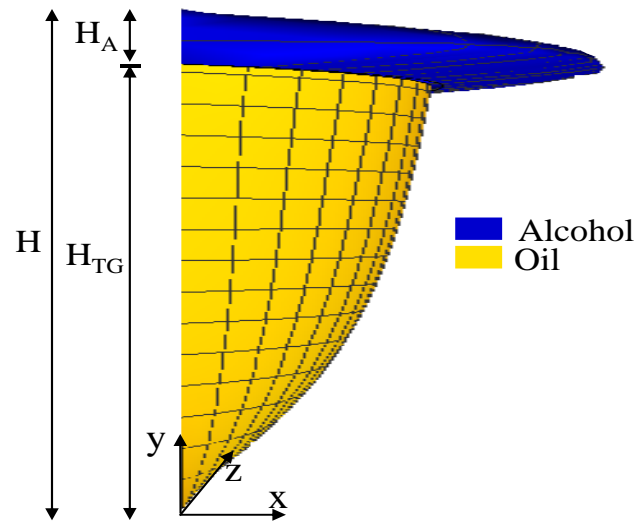


Figure 1

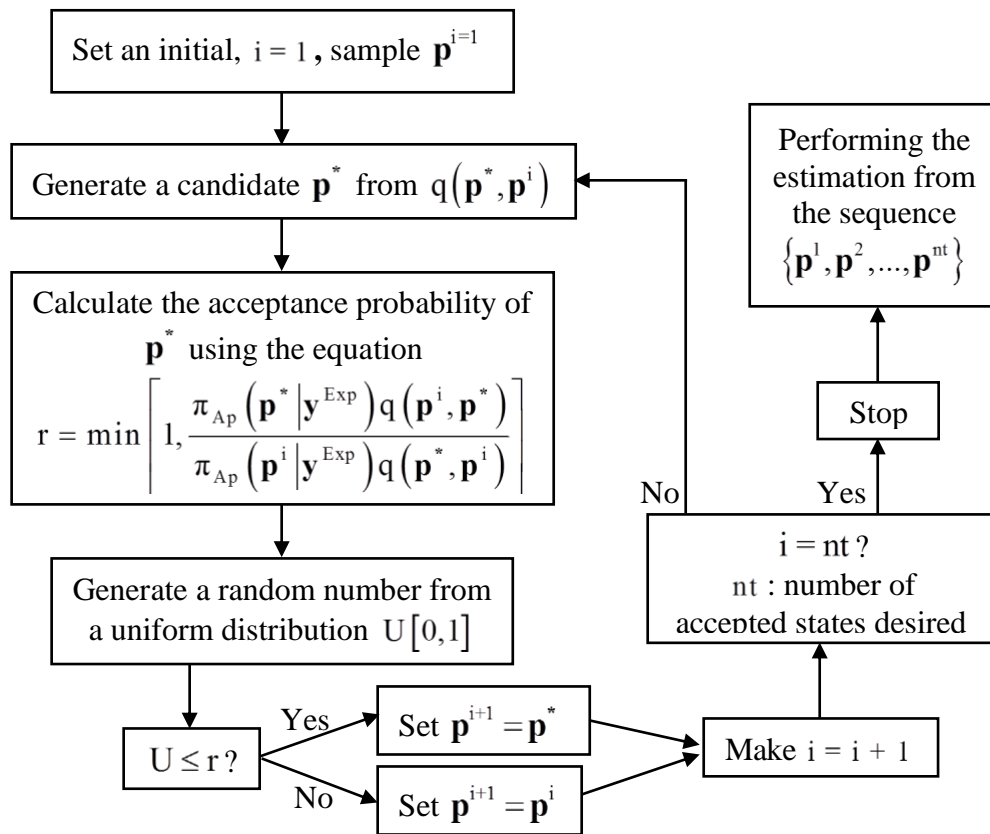


Figure 2

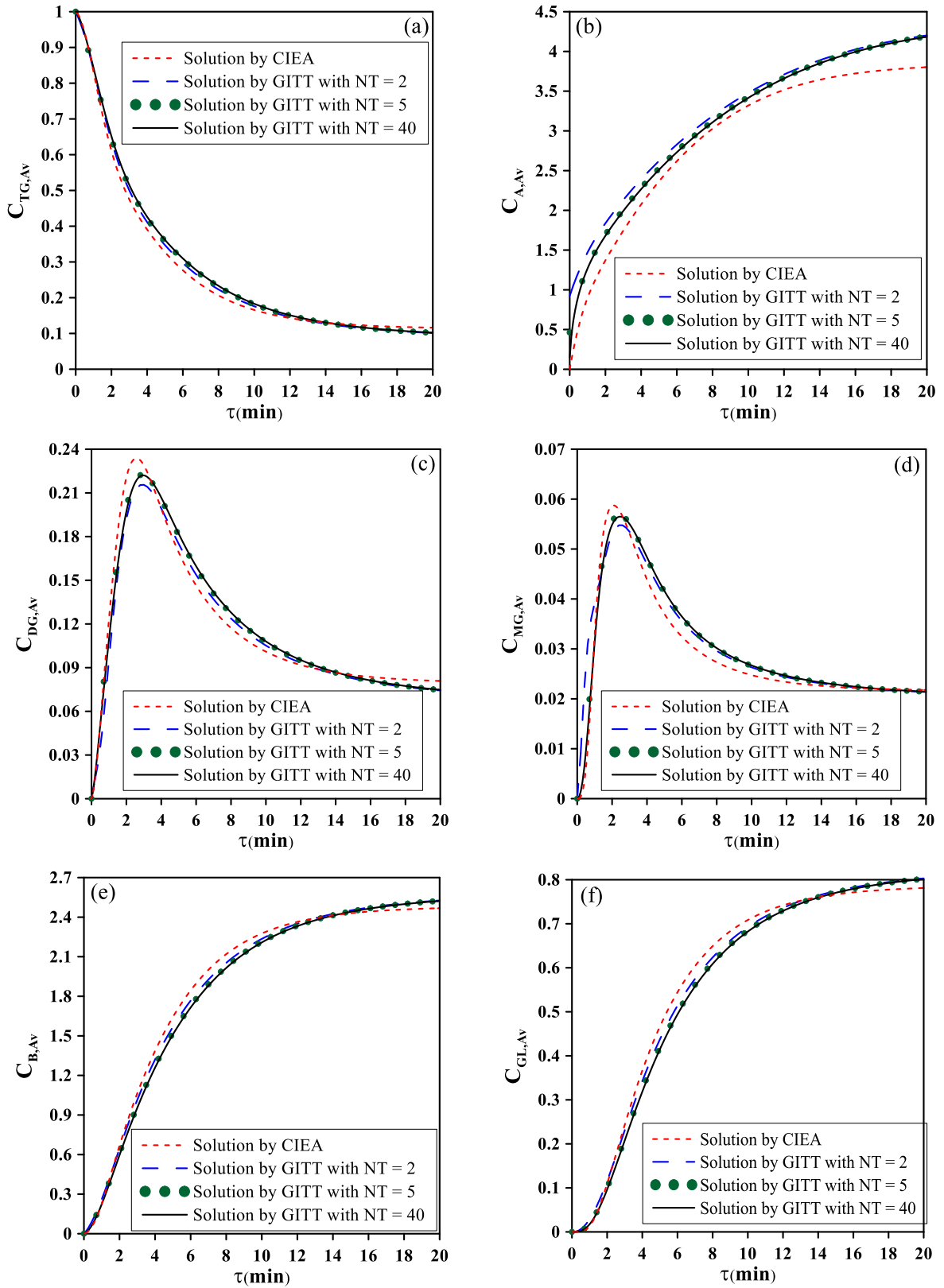


Figure 3

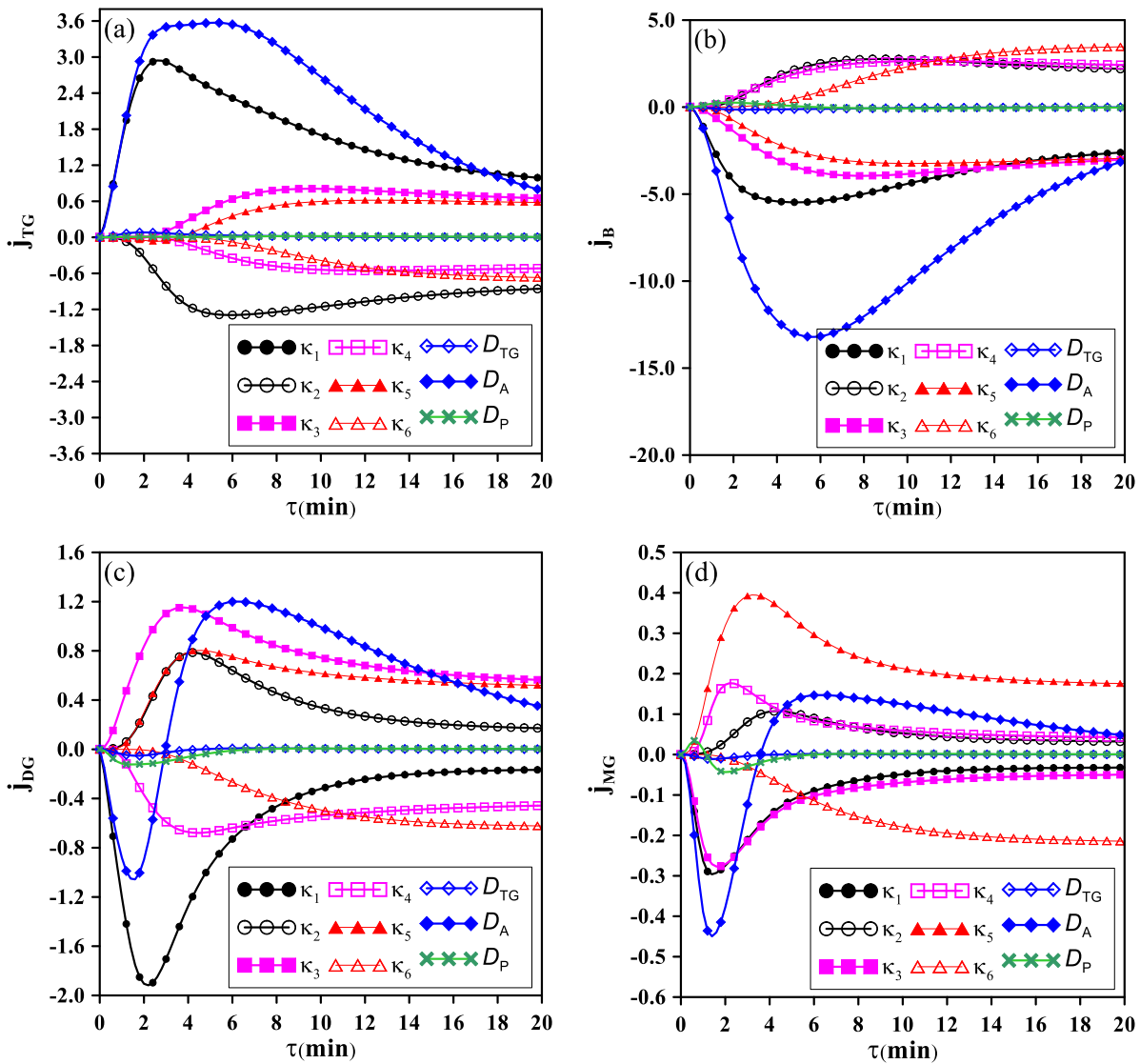


Figure 4

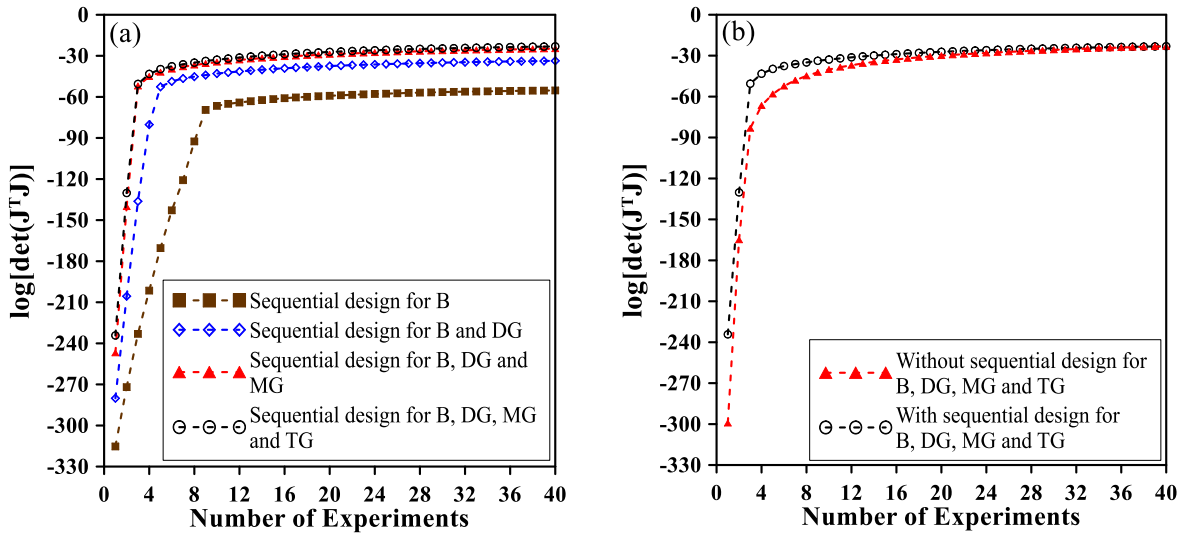


Figure 5

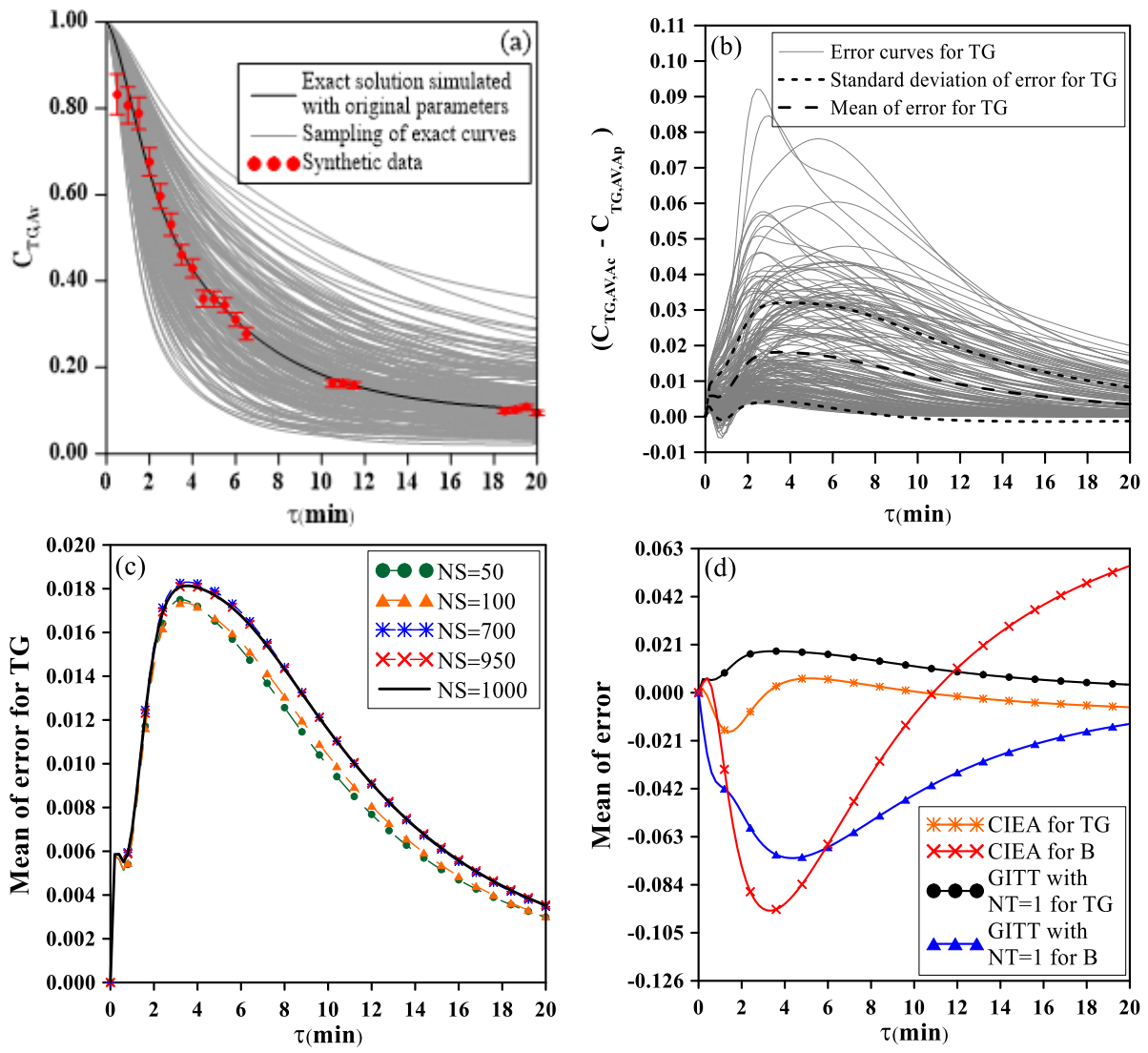


Figure 6

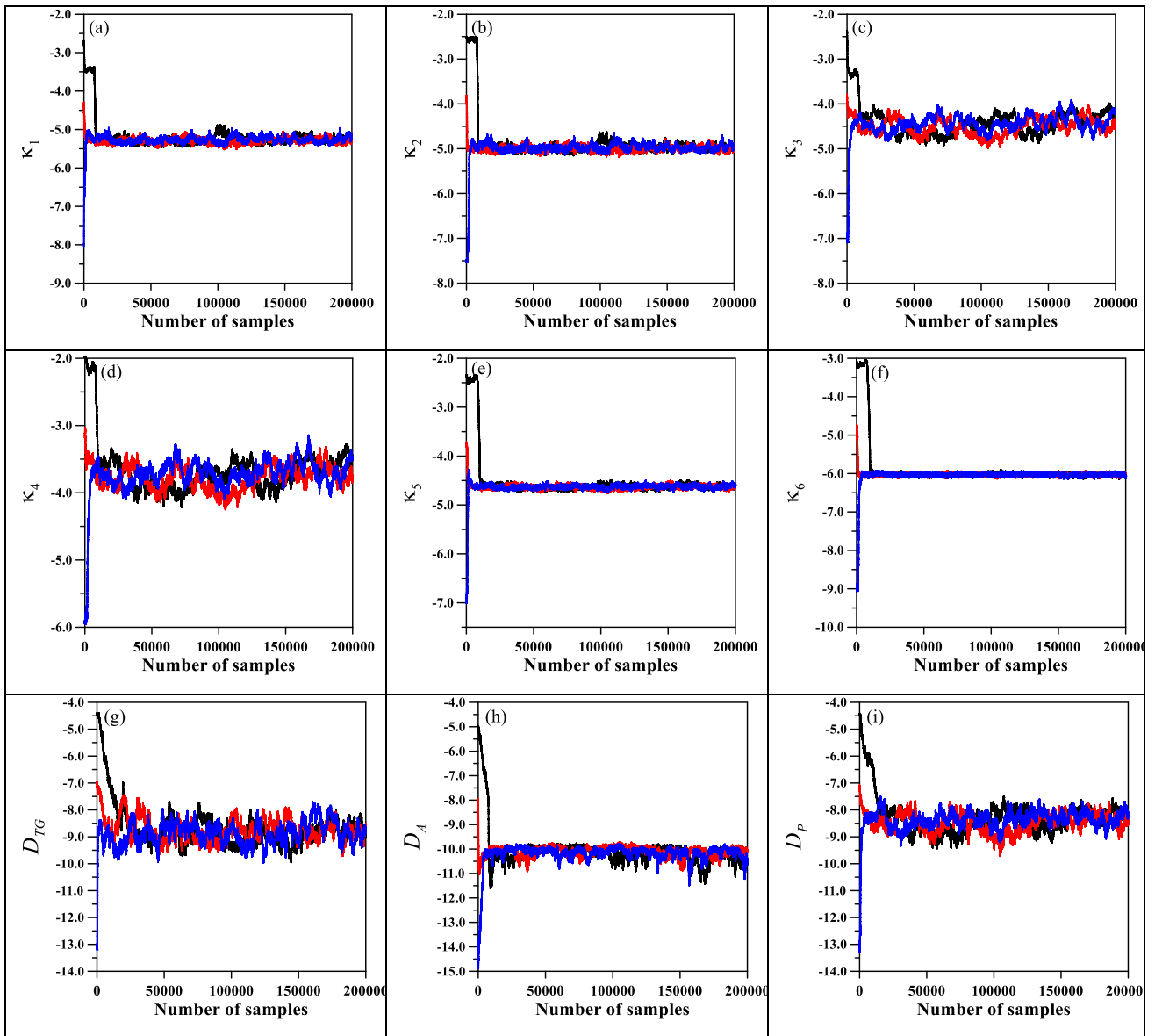


Figure 7.

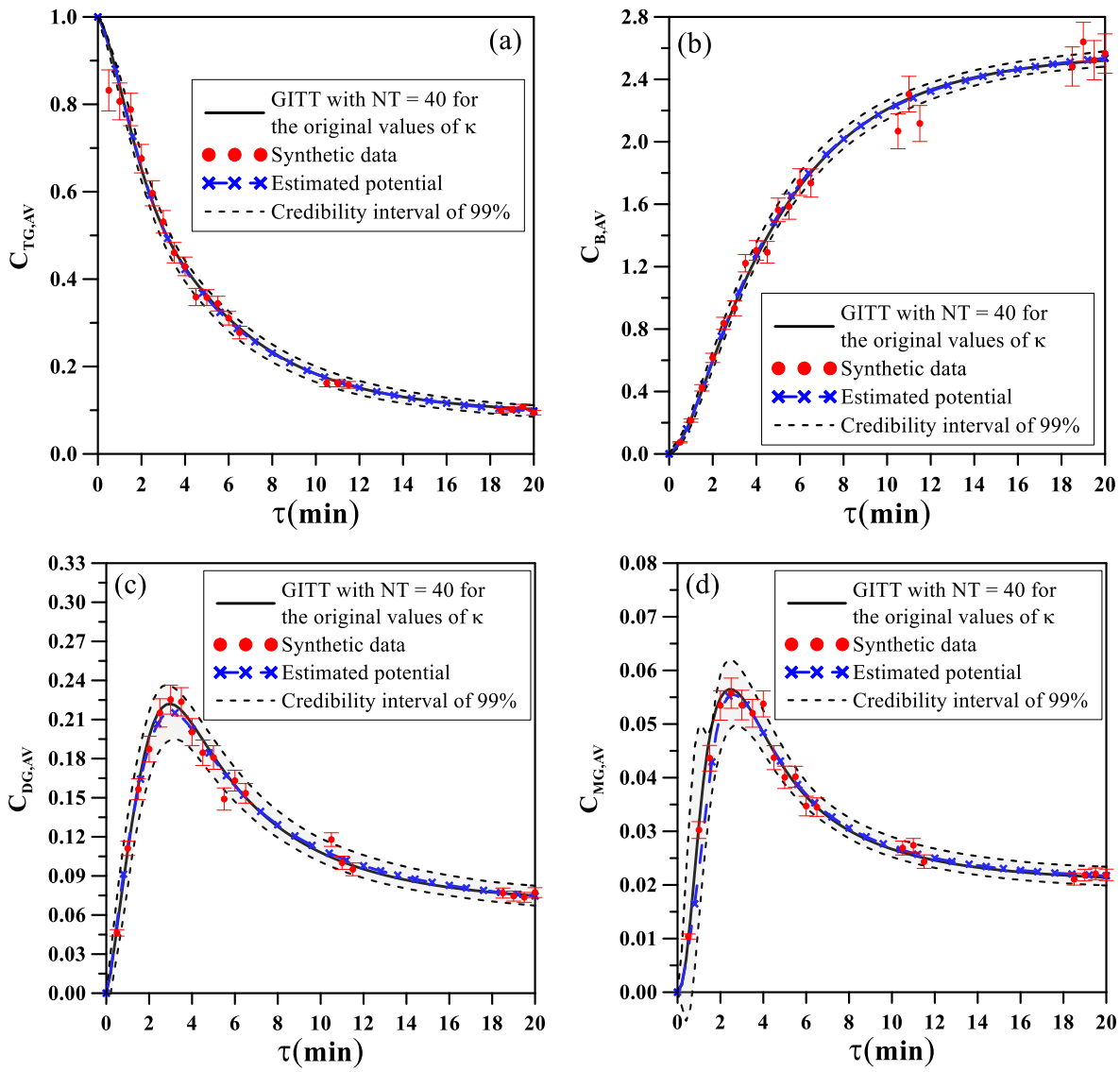


Figure 8