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ESTIMATION OF PARAMETERS IN THE HYDRODYNAMIC CHARACTERIZATION OF REACTOR CSTR

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Abstract: *The distribution of residence time (RTD) is a technique applied to different types of reactors and it is possible diagnosing issues during the operation. This analysis makes the process more efficient and predicts the main output properties of the current reactor. Aiming at this, this study seeks to rate the performance of five hydrodynamic models for determination of the RTD. These models contain parameters related to death volume and bypassing. The estimation of those parameters was performed by using the Markov Chain Monte Carlo Technique (MCMC). The reactor used was the CSTR, the results obtained from the estimation of parameters indicate that the death volume phenomenon influences 62% of the flow approximately, while the bypassing has almost a null influence. This propriety makes the uniparametric model of death volume be the most appropriate one to describe the experimental data.*

Keywords: *RTD,CSTR, parameter estimation, MCMC*

1. INTRODUCTION

The flow characteristics of the reactors are linked to their efficiency and performance. Several factors cause non-idealities and that analysis should be done on a case-by-case basis. The flow profile in real reactors can change away from the profile of ideal reactors dramatically, providing that each element of fluid have different tracks and, therefore, distinct output times. The cause of this discrepancy can be reflux zones, death zones, bypassing, high and low circulation with interconnection, preferred paths which are more likely to appear in larger units or in the process of viscous mixtures, causing a significant reduction in the overall yield of the process (Fogler, 2009; Simões, 2006; Lemos *et. al.*, 2002). Figure 1 shows a basic scheme of a dead-volume tank reactor bypassing.

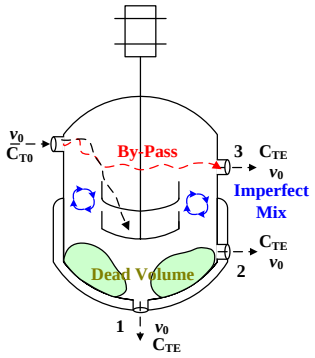


Figure 1. Reasons to non-idealities (Moreira *et al*, 2017).

The study of hydrodynamic is essential to evaluate the performance by detecting operational and design problems. This investigation is performed through the analysis of residence time distribution (RTD), this is based on the profile of residence time distribution E(t), the cumulative distribution function of residence times, F(t) and the medium time (Levenspiel, 2000).

The RTD can be described from the profile of concentration of the tracer in the reactor. Five (5) mathematical models were used to estimate the concentrations measured experimentally. This was performed because the models have parameters to represent the anomalies (dead volume and bypass).

At this scenario the purpose in this work is to apply the Bayesian technique Markov Chain Monte Carlo (MCMC) in order to estimate the parameters of the models used. This methodology joins the knowledge from the experimental data and mathematical model.

The parameters were estimated considering the uniform distribution as the prior distribution of probability within the interval [0 1]. This distribution was chosen because the only information known is that the parameters are a fraction of the volume, therefore it is necessary to use the distribution with equal probability to any parameter in the interval [0 1].

The experimental set up was a reactor CSTR using injection blue methylene tracer in the form positive step, obtained samples in the specific frequency and the concentration was evaluated using a spectrophotometer.

2. EXPERIMENTAL SET UP

The CSTR reactor (Figure 2) was assembled with material of low cost and easy arranging. The following materials were used: Trash PVC 5,5, water box adapter, Ball PVC log, garden nozzle, submersible aquarium pump of 180 liters/hour, mechanical stirrer and spectrophotometer Shimadzu UV-1800.

Figure 2. CSTR reactor used in the tests.

As shown in Figure 2, the reactor has different effluent collection points and different stem positions, which can operate in different flow regimes. The samples were collected at the middle outlet of the reactor with the rod positioned in the center. 20 liters of the solution containing the blue methylene tracer with a concentration of 0.258 mol/liter were prepared. Prior to initiating the experiment it is necessary to reach a steady state, then the experiment is initiated by activating the stopwatch and switching the water supply to the solution containing the tracer. The tests were performed with continuous stirring at 100 rpm. The effluent samples were collected in 15 mL falcon tubes on progressive time intervals, 20 seconds to 1 minute, and were performed until the inlet and outlet concentrations were the same. The collected samples were evaluated on a spectrophotometer model UV-1800 da Shimadzu.

3. DIRECT PROBLEMS – HYDRDYNAMIC MODELING

The used models are obtained by applying mass balance in transient regime in relation to the concentration of tracer in the outflow of the reactor, regarding a positive step experiment with constant stimulus without any tracer addition before the initial time. The tracer concentration in the reactor is calculated by the convolution integral, the concentration of the inlet (Levenspiel, 2000).

Model 1 - Reactor with Dead Volume (V_m)

In an ideal scenario of the continuous stirred tank reactor (CSTR), the composition, temperature and reaction rate are uniform. The reactor can be represented by a mathematical model of reduced dimensions, the residence time being the same for all molecules (Fogler, 2009; Levenspiel, 2000). The transient mass balance considering a step-type injection is, Equation (1):

$$v_0 C_{T0} - v_0 C_{TE} = V \frac{dC_{TE}}{dt} \tag{1.a}$$

Subject to the following initial conditions:

$$\begin{aligned} t &= 0 \qquad C_{TE} = 0 \\ t &> 0 \qquad C_{TE} = C_{T0} \end{aligned} \tag{1.b,c}$$

The system (1) is applied as the basis for models 1,2 and 3. For this, the following considerations are regarded:

$$Vs = \alpha V;\ v_b = \beta v_o; \tau = \frac{V}{v_o} \tag{2}$$

This model considers that the reactor contains a region in which reaction does not occur, named death volume, evaluated as a separate tank:

$$C_{TE}(t) = C_{T_0}\left[1 - e^{-\left(\frac{t}{\alpha\tau}\right)}\right];\quad F(t) = 1 - e^{-\left(\frac{t}{\alpha\tau}\right)};\quad E(t) = \frac{1}{\alpha\tau} e^{-\left(\frac{t}{\alpha\tau}\right)} \tag{3.a-c}$$

where C_{T0} is the concentration of the tracer, t is the time, τ it is spatial time and α is the kinetic parameter related to the dead volume.

Model 2 - Reactor with Bypassing (V_b)

This model considers that the reactor contains a flow deviation in the volumetric inflow, characterized by a flow that does not pass through the reactor:

$$C_{TE}(t) = C_{T_0}\left[1 - (1-\beta) e\left(\frac{(1-\beta)t}{\tau}\right)\right]; F(t) = 1 - (1-\beta) e^{-\left(\frac{(1-\beta)t}{\tau}\right)}; E(t) = \frac{(1-\beta)^2}{\tau} e^{\frac{(1-\beta)t}{\tau}} \tag{4.a-c}$$

where β is the kinetic parameter related to the flow deviation.

Model 3 - Reactor with flow deviation and dead volume (V_m and V_b)

In this model, the death volume is evaluated as a separate tank. In addition, there is a bypassing in the incoming volumetric flow rate. The variation of residence time is the parameter adjustment that characterizes each phenomenon.

$$C_{TE}(t) = C_{t_0}\left[1 - (1-\beta) e\left(\frac{(1-\beta)t}{\alpha\tau}\right)\right]; F(t) = 1 - (1-\beta) e^{-\left(\frac{(1-\beta)t}{\alpha\tau}\right)}; E(t) = \frac{(1-\beta)^2}{\alpha\tau} e^{\frac{(1-\beta)t}{\alpha\tau}} \tag{5.a-c}$$

Model 4 - Two CSTRs interconnected with different exchange flow rates

In this model, it is considered that the reactor has two different mixing zones: the first located near the stem, featuring an ideal CSTR of perfect mixing; and the second located far from the stem and near the bottom of the reactor, which may be characterized by its low agitation. The mass balance for this system generates the following differential system of linear equations, Equations (6):

$$\alpha\tau \frac{dC_{T1}(t)}{dt} = C_{T_0} + (1-\beta) C_{T2} - (1+\beta) C_{T1};\quad (1-\alpha)\tau \frac{dC_{T2}(t)}{dt} = \beta C_{T1} - (1-\beta) C_{T2} \tag{6.a-b}$$

Subject to the following initial conditions:

$$\text{In } t = 0 \; C_{T0} = C_{T1} = C_{T2} \; ;$$
$$\text{In } t^{1} 0 \; C_{T0} = C_{T0} \; ; C_{T1} = C_{T1}; C_{T2} = C_{T2}; \tag{6.c-d}$$

Model 5 - Two CSTRs interconnected with equal exchange rates

This model considers that the reactor presents distinct mixing zones within it, specifically a zone of high quality agitation, located near the stirring rod that characterizes CSTR ideal of perfect mixing and another of low agitation and both of equal volumes, as described by Equations (7):

$$\alpha\tau \frac{dC_{T1}(t)}{dt} = C_{T_0} + \beta C_{T2} - (1+\beta)C_{T1}; \quad (1-\alpha)\tau \frac{dC_{T2}(t)}{dt} = \beta C_{T1} - \beta C_{T2} \tag{7.a-b}$$

Subject to the following initial conditions:

$$\text{In } t = 0 \; C_{T0} = C_{T1} = C_{T2} \; ;$$
$$\text{In } t^{1} 0 \; C_{T0} = C_{T0} \; ; C_{T1} = C_{T1}; C_{T2} = C_{T2}; \tag{7.c-d}$$

After all models are shown to simulate the concentration of the tracer, by the equations presented below, the residence time distribution function, E(t) is evaluated (Eq. 8). Then, the cumulative distribution function of residence times, F(t) is defined (Eq. 9), the medium time (tm) is defined (Eq.10), the variance σ^2 (Eq.11) and the asymmetry s^3 (Eq.12).

$$E(t) = \frac{C_T(t)}{\int_0^{\infty} C_T(t)dt} \tag{8}$$

$$F(t) = \int_0^t E(t)\, dt \tag{9}$$

$$t_m = \frac{\int_0^{\infty} tE(t)dt}{\int_0^{\infty} E(t)dt} = \int_0^{\infty} tE(t)dt \tag{10}$$

$$\sigma^2 = \int_0^{\infty} (t - t_m)^2 E(t)dt \tag{11}$$

$$s^3 = \frac{1}{\sigma^{1,5}} \int_0^{\infty} (t - t_m)^3 E(t)dt \tag{12}$$

4. INVERSE PROBLEMS – MARKOV CHAIN MONTE CARLO

The Bayesian Inference methodology used was the Monte Carlo via Markov Chain to estimate the parameters of the models. The Bayesian Statistics consists essentially in using all available information in order to reduce uncertainty in inference. As new information becomes available, it is combined with prior information to form the basis of statistical processes. The formal mechanism for combining the new information and the previously available is Bayes' Theorem (Beck, 1977; Özisik and Orlande, 2000; Kaipio, 2004; Gamerman, 2006; Ehlers, 2007):

$$\pi_{\text{posterior}}(\mathbf{P}) = \pi(\mathbf{P}|\mathbf{Y}) = \frac{\pi(\mathbf{P})\pi(\mathbf{Y}|\mathbf{P})}{\pi(\mathbf{Y})} \tag{13}$$

where $\pi_{\text{posterior}}(\mathbf{P})$ is the posterior probability density ; $\pi(\mathbf{P})$ is the a prior probability density; $\pi(\mathbf{Y}|\mathbf{P})$ is the probability function and $\pi(\mathbf{Y})$ is the probability density of the measurements, representing the normalization constant.

The purpose of the MCMC method is to obtain a sample of the posterior distribution and to calculate sample estimates of the characteristics of this distribution. The rationale is that as the number of iterations increases the more the chain gradually converges to an equilibrium distribution (Orlande, 2011).

The algorithm is summarized in the following steps ((Metropolis et al, 1953 Hastings, 1970;)Kaipio,2004; Lee,2004).

a. Initialize the chair iteration counter t = 0 and declares an initial value P $^{(0)}$.

b. Sample a candidate point $\mathbf{P}^*$ from the proposed distribution;

$$\mathbf{P}^* = \mathbf{P}^{(t-1)}\left(1 + w\varepsilon\right) \tag{14}$$

where ε it is variable N (0, 1) and w is the search step.

c. Calculate the probability of acceptance of the candidate value through the Metropolis-Hastings:

$$\alpha\left(\mathbf{P}^{(t-1)}\middle|\mathbf{P}^*\right) = \min\left\{1, \frac{\pi\left(\mathbf{P}^* \mid \mathbf{Y}\right) p\left(\mathbf{P}^*, \mathbf{P}^{(t-1)}\right)}{\pi\left(\mathbf{P}^{(t-1)} \mid \mathbf{Y}\right) p\left(\mathbf{P}^{(t-1)}, \mathbf{P}^*\right)}\right\} \tag{15}$$

d. Generate by random a number u with uniform distribution, this is $u \sim U(0,1)$.

e. If $u \le \alpha\left(\mathbf{P}^{(t-1)}\middle|\mathbf{P}^*\right)$, accept the new value and do $\mathbf{P}^{(t)} = \mathbf{P}^*$, otherwise, it is done $\mathbf{P}^{(t)} = \mathbf{P}^{(t-1)}$;

f. Return to step 2 while some converge criteria is not satisfied.

5. RESULTS AND DISCUSSIONS

In order to apply the technique MCMC, a prior distribution was considered of probability for the parameters of the uniform distribution limited between 0 and 1. This probability distribution was chosen because of lack of previous information about the parameters. Therefore, the probability distribution must be the same probability to any physically possible parameter (uniform probability distribution). This also limits the fact that the parameters represent a fraction of the reactor volume, thus these have to be greater than or equal to zero (negative volume is not possible) and under or equal to 1 (because the maximum value for the dead volume and due to the flow deviation is the volume of the reactor). The parameters used in the simulations are presented in the Tab.1.

Table 1. Values of the parameters

N	Number of states	1.10^6
W_{uni}	Search step for models 1 and 2	5.10^{-3}
W_{bi}	Search step for models 3,4 and 5	1.10^{-4}
σ	Standard deviation measurement	$5\%C^{Meas}$

The Figure 3 shows, respectively, the evolution of the Markov chains to the parameters α and β for all models used.

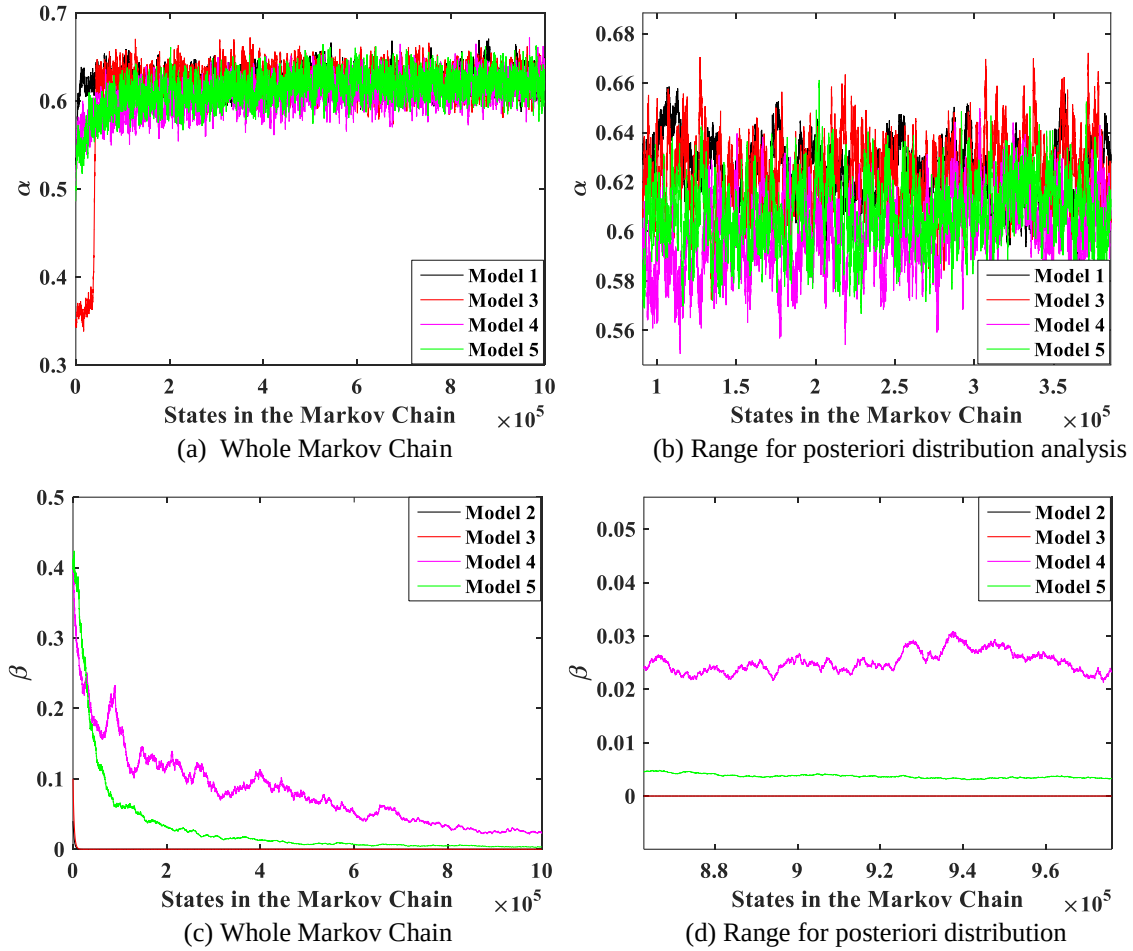
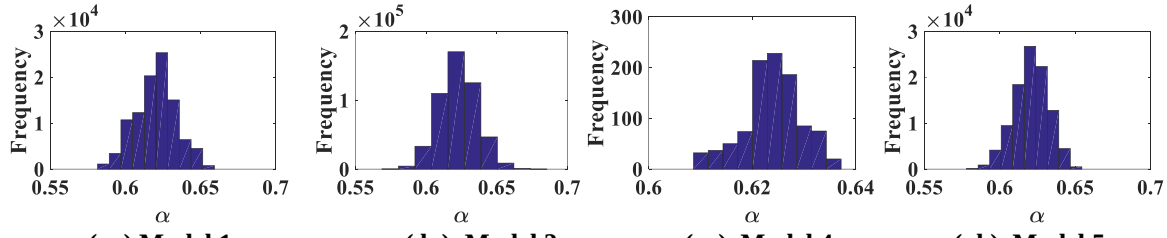


Figure 3. Evaluation of Markov Chain

Figure 3a shows that in order for the chain to achieve equilibrium around 10^5 states were necessary. These 10^5 states are called burn-in states and samples of the posterior distribution of parameter are the states after the burn in states. Figure 3b shows that for all models that contain the parameter α are converged to a value around 0.62. These shows the consistency of the technique in estimate values close to the parameters in different models. The parameter α represent the dead volume in all models. The estimated value of α means that the tracer did not pass through 62% of the reactor. On the contrary, Figure 3b shows that the parameter β tends to zero for the models 2, 3 and 5. Unfortunately, the Markov chain reference of model 4 does not achieve the equilibrium and probably the value estimated would be close the value of others models if the Markov chain had achieved the equilibrium. Therefore, it is considered that the value to β is zero and that the tracer is not influenced by the rotation of mechanical stirrer. The histogram of posterior probability distribution of the kinetic parameters α and β are shown in Figure 4 and it is clear to all cases that the uncertainties are low confirming that the solutions are accurate.



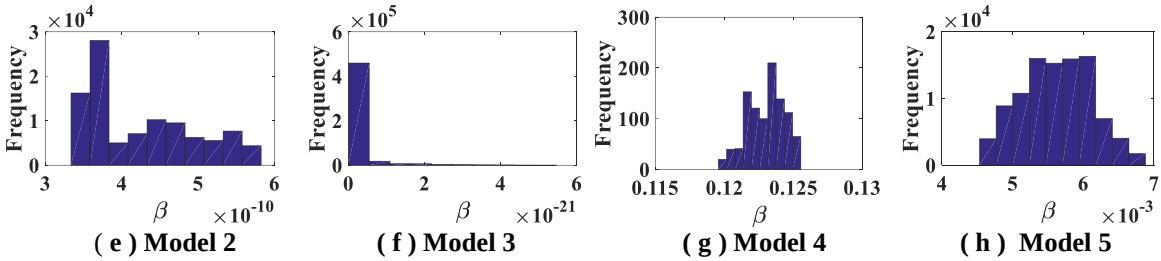


Figure 4. Histogram of the posterior probability distribution of the parameter α and β for all models.

After estimate of direct problem parameters (all 5 models) are solved with samples of the posterior distribution, multiple profiles of concentration are obtained because for each sample one profile of concentration is generated. Then to represent the profile concentration was considered the mean of the samples generated and these are shown in Figure 5.

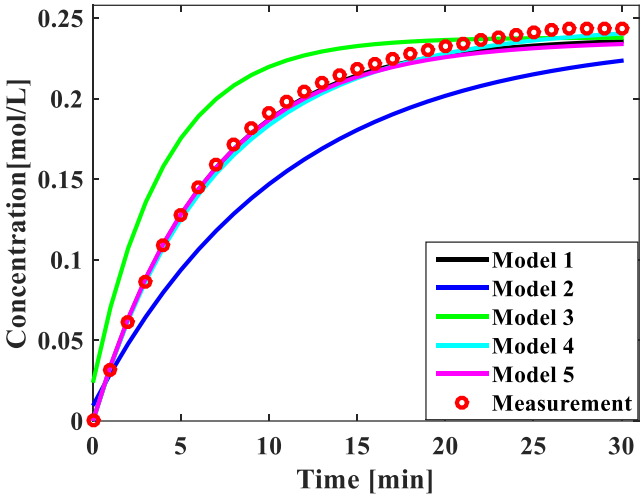


Figure 5. Comparison among the measurement concentration and those obtained through proposed models.

Figure 5 shows the concentration profile of the tracer simulated with the parameter estimation for all models studied and the experimental concentration. It is possible see that just Models 2 and 3 do have a good agreement between concentration simulated and experimental. These comparisons reveals that the effect of the death zone is so much higher than the by-passing. As Model 2 have just parameter β (by-passing) this results in model 2 not able to simulate the profile of concentration with a good agreement with the experimental concentration. Besides the concentration, the others reference profiles to verify if the model can represent the phenomenon is the E(t) and F(t) profiles, and the comparison of those profiles are shown in the Figures 6 and 7.

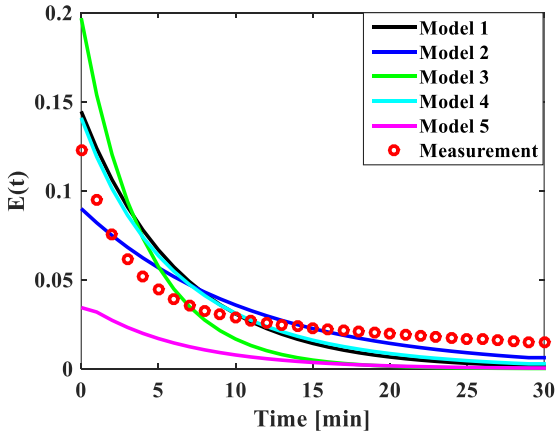


Figure 6. Comparison among the simulated and experimental E(t).

Figure 6 reveals that just Models 1 and 4 have a good agreement between the experimental and simulated E(t). The fit of simulated and experimental E(t) are not as good as the concentration (Refer to Figure 6) because the experimental data used to estimate the parameters was only the concentration of the tracer. Therefore it is expected that the agreement among simulated and experimental data be better to concentration then to E(t) and F(t). The comparison among simulated and experimental data to F(t) is shown in the Figure 7.

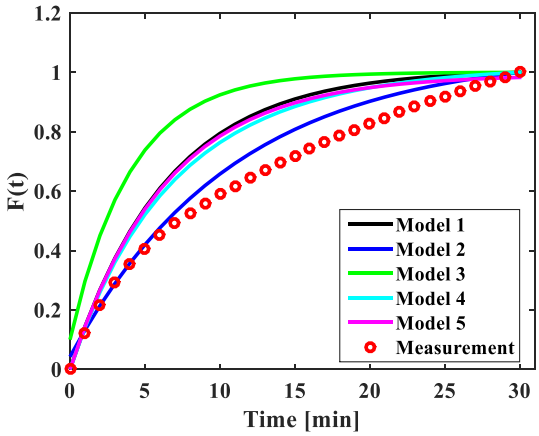


Figure 7. Comparison among the simulated and experimental F(t).

Figure 7 reveals that the models studied do not recover well the F(t). As mentioned previously, the lack parameter information makes the estimations more difficult. In the future work, the functions E(t) and F(t) will be regarded in the likelihood function to improve the estimations. In the end, the moments of RTD is shown in Table 2.

Table 2. Moments of RTD

Model	t_m (min)	σ^2 (mim^2)	s^3 (mim^3)
Experimental	5,76	31,04	19,70
1	5,66	30,58	22,22
2	8,08	49,49	23,52
3	3,20	17,36	17,84
4	6,17	36,61	23,94
5	5,96	44,12	31,14

Table 2 shows that Model 1 has the moments (tm, σ^2 and s^3) closer to the experimental value. So, after all comparison among simulated and experimental values to concentration of tracer, F(t), E(t), tm, σ^2 and s^3 **it** is possible say that Model 1 is the best model among the 5 models studied to characterize the reactor CSTR in the conditions used in the experimental set up.

6. CONCLUSION

In this work Markov Chain Monte Carlo was applied to estimate parameters of 5 different models, the estimations were performed using 10^6 states. The value found to parameter α was 0.62, this means that the tracer flows just in 62% of the volume of reactor and this value was estimated to all models. In other hands, the parameter β was estimated and the value is too small and is possible be considered zero. Therefore the flow is not affected for the by-pass zone.

The comparison among the simulated and experimental data of concentration, E(t), F(t)), tm, σ^2 and s^3 revealed that Model 1 was the best model to characterize the reactor CSTR used, despite being the simplest model that has the parameter α.

7. ACKNOWLEDGEMENTS

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9. RESPONSABILITY NOTICE

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