A new Monte Carlo-based approach for addressing stiff chemical kinetics.

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Highlights
- New pointwise Monte Carlo method for chemical kinetics modeling.
- Effectiveness of handling the quasi-steady state situation by Monte Carlo.
- Addressing the partial equilibrium situation via the use of importance sampling.

1. Introduction

Modeling reactive systems such as biomass pyrolysis or combustion is a complex challenge due to the heterogeneous nature of biomass [1]. It is a process involving multi-scale phenomena spatially and temporally [2], requiring appropriate coupling strategies between the different scales. When addressing the chemical kinetics of those reactive systems, a large variation of reaction characteristic times can be observed, which usually increases with the complexity of the specialized molecules, leading to stiff numerical issues [3]. In this study, we will introduce a Monte Carlo (MC) method that has proven effective in dealing with systems involving physical phenomena over wide ranges of spatial and temporal scales [4, 5]. Our methodology entails addressing a "toy model" of a reacting system that consists of three first-order reactions as in Figure 1, resulting in a system of coupled ordinary differential equations (ODEs), in an isothermal regime. For insightful purposes, we will investigate non-stiff and stiff cases.

$$A \; \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \; B \; \overset{k_2}{\longrightarrow} \; C$$

Figure 1. Chemical reaction network for the toy model.

2. Methods

The key point of the present work is to reformulate the system of ODEs as a system of coupled expectations that can be solved by a MC algorithm. This approach is applied within an isothermal regime. In the non-stiff case, no particular treatment was required. However, in the stiff case, two scenarios are investigated: one where the intermediate species forms slowly but is rapidly consumed (k_2, $k_{-1} >> k_1$), which analytically corresponds to the quasi-steady state (QSS) approximation [6]; and another where the intermediate species forms rapidly but is consumed slowly (k_2, $k_{-1} << k_1$), which analytically corresponds to the partial equilibrium (PE) approximation [6]. To handle the PE scenario, the exploration of importance sampling technique [7] is conducted.

3. Results and discussion

The evolution of the three species under isothermal conditions is computed using two methods for comparison purposes: backward differentiation formulas (BDF) [8] and MC, which is a pointwise approach. Therefore, each result (provided with an error bar) relies on a MC run and is estimated independently from the others (**Figure 1**, **Figure 2a**, and **Figure 2b**). For the non-stiff case, the results

are shown in **Figure 1**, and for the stiff case for QSS and PE situations, the results are respectively displayed in **Figure 2a** and **Figure 2b**.
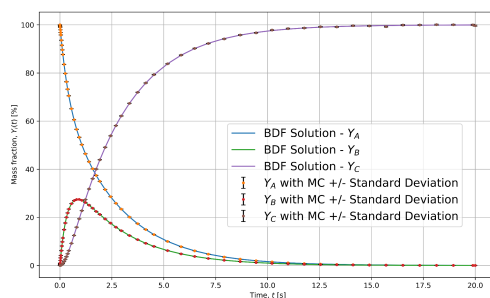

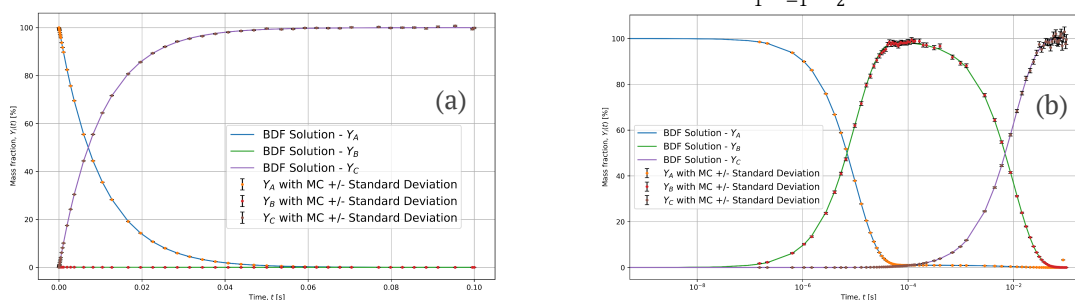**Figure 1.** Non-stiff case: The kinetic rate constant ratios are equal to 1 ($k_1, k_{-1}, k_2 = 1\ s^{-1}$).

Figure 2. a) QSS stiff case: $k_1 = 10^2\ s^{-1}$, $k_{-1} = 10^3\ s^{-1}$ and $k_2 = 10^5\ s^{-1}$. b) PE stiff case: $k_1 = 10^5\ s^{-1}$, $k_{-1} = 10^3\ s^{-1}$ and $k_2 = 10^2\ s^{-1}$.

4. Conclusions

The MC method provides results comparable to BDF solutions for the three involved species in the non-stiff case within the isothermal regime. However, in the stiff case, particularly with the PE situation, rare events with significant weights occur while treating the species B. Nonetheless, by employing importance sampling to mitigate these rare events, MC has demonstrated effectiveness in overcoming this numerical challenge. Additionally, the MC method adequately handles the QSS situation. Future work in progress aims to extend this methodology to the non-isothermal regime by coupling kinetics with a heat transfer model.

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