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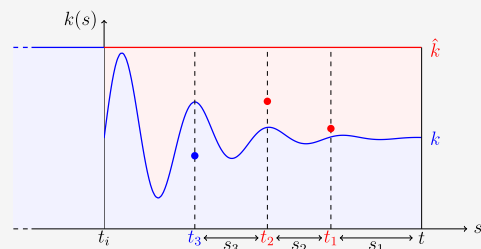
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A Monte Carlo-Based Strategy to Assess Complex Kinetics: Application of the Null-Reaction Method to DAEM

Yaniss Nyffenegger-Péré,* Marion Carrier, Simon Eibner, Mouna El Hafi, Manel Nasfi, and Abderrahim Sahim

ABSTRACT: The distributed activation energy model (DAEM) is widely used in chemical kinetics to statistically describe the occurrence of numerous independent parallel reactions. In this article, we suggest a rethink in the context of a Monte Carlo integral formulation to compute the conversion rate at any time without approximation. After the basics of the DAEM are introduced, the considered equations (under isothermal and dynamic conditions) are respectively expressed into expected values, which in turn are transcribed into Monte Carlo algorithms. To describe the temperature dependence of reactions under dynamic conditions, a new concept of null reaction, inspired from null-event Monte Carlo algorithms, has been introduced. However, only the first-order case is addressed for the dynamic mode

due to strong nonlinearities. This strategy is then applied to both analytical and experimental density distribution functions of the activation energy. We show that the Monte Carlo integral formulation is efficient in solving the DAEM without approximation and that it is well-adapted due to the possibility of using any experimental distribution function and any temperature profile. Furthermore, this work is motivated by the need for coupling chemical kinetics and heat transfer in a single Monte Carlo algorithm.



■ INTRODUCTION

DAEM Background. The efficient utilization of biomass has never been as critical as it is today, with the need to develop more efficient renewable biomass conversion technologies. For decades, the scientific community has developed numerous chemical models through different approaches to cover a wide range of complex systems. The development of these chemical kinetic models has made it possible to control the selectivity and kinetics of the reactions.

Pyrolysis of natural polymers is often described by various degradation schemes (reaction patterns) resulting in numerous chemical species. These degradation pathways are in general associated with rates and therefore with reaction models. However, the most challenging part remains to capture all the details of a complex and multiphasic process and to develop a detailed kinetic model based on fundamental chemistry. For this reason, lumped species are used when global kinetic models for the pyrolysis of complex fuels are applied. Among the variety of global kinetic models, including single-step, finite, and infinite multistep reactions reviewed by Burnham et al.,¹ distributed reactivity models are used. More specifically, the distributed activation energy model (DAEM) has proven to be convenient,² as it mathematically transcribes a set of independent and parallel reactions of first-order or particular-order reactions as a distribution of reactivity expressed by the activation energy distribution, $p_E(E)$.

When it comes to assessing solid-state reactions, it implies tracking the transformation of reactants. In thermal analysis and, more specifically, thermogravimetric analysis, the weight loss is measured, and the extent of conversion expressed as follows:

$$\alpha(t) = \frac{m_0 - m(t)}{m_0 - m_f} \quad (1)$$

where m_0 is the initial mass of the reactant, $m(t)$ is the reactant mass at a specific time t , and m_f is the final mass of the reactant. The temperature dependence of the kinetic rate constant, $k_E(t)$, in chemical kinetics is conveniently described by the Arrhenius law as follows:

$$k_E(t) = A_E(T(t)) \exp\left[-\frac{E}{RT(t)}\right] \quad (2)$$

where $A_E(T(t))$ is the pre-exponential factor depending on the temperature time evolution $T(t)$, E is the activation energy, and R is the universal gas constant. The reaction rate constant,

$k_E(t)$, can then be parametrized as a function of the kinetic parameters and its dependence on the extent of conversion, $\alpha_E(t)$, by the mathematical reaction model, $f(\alpha_E(t))$. A wide range of mathematical models for $f(\alpha_E(t))$ exist, and its choice depends on the homogeneous and heterogeneous nature of the reaction, on the physical state of reactants and products, and on the reaction network. There are three major types of reaction model, which can be classified according to their accelerating, decelerating, and sigmoidal reaction profiles. Here, the most common example of a decelerating model is a reaction-order model:³ $f(\alpha_E(t)) = \gamma_E(t)^n$, in which $\gamma_E(t) = 1 - \alpha_E(t)$ is the fraction unreacted and n is the reaction order. The evolution of $\gamma_E(t)$ is controlled by the following differential equation:

$$\begin{cases} \frac{d\gamma_E(t)}{dt} = -k_E(t)\gamma_E(t)^n \\ \gamma_E(t_i) = \gamma_{i,E} \end{cases} \quad (3)$$

in which the conversion rate at the initial time, $t_i = 0$, is equal to 1 and the value of $\gamma_{i,E}$ is equal to 1 when the reaction starts because none of the mass has been converted.

When a kinetics evaluation is conducted, knowledge of the sample temperature is paramount. However, this can be difficult to measure because of thermal lag (the temperature difference existing between the sample environment and its bulk). Indeed, thermal transfer resistance can have an important effect on the evaluation of intrinsic kinetic parameters, and then appropriate corrections must be made,⁴ such as the temperature profile.⁵ As kinetically controlled isothermal pyrolysis is rarely achieved, linear heating ramps, $\beta = dT(t)/dt$, corresponding to the heatup phase of the particles, are often considered.⁶ The difficulty of integrating the reaction rate will depend on the thermal history and the chosen reaction model. Under non-isothermal conditions (often called dynamic mode), the integration becomes difficult and does not have an analytical solution.² When the hypothesis that the temperature increases linearly with time is made, this is a strong assumption and also an important starting point to develop the present statistical approach to solve an integral with a minimum of error, whatever the temperature profile.

The idea of coupling a robust chemical kinetic model with a comprehensive heat and mass transfer computational code to model the whole process at a particle level has never been more important, as it could improve any modeling predictions and therefore improve technology efficiency. Perré et al.⁷ recently developed a DAEM introducing the heat capacity of the sample, thus allowing the DAEM to be successfully validated using very different temperature–time profiles. In this study, an approach is suggested to deal with any temperature profile and to open up new perspectives on a possible coupling between the chemical kinetics and heat equations.

The DAEM describes an infinite number of independent reactions, where a unique activation energy is given for each reaction. Statistically, we introduce a mean conversion rate, $\bar{\gamma}(t) = 1 - \bar{\alpha}(t)$. This mean conversion rate is a statistical mean over all possible activation energies from the considered system. As there are an infinite number of reactions, the activation energies are distributed over a density probability, denoted as $p_E(E)$. Hence, at a time t_0 the mean conversion rate

is the sum of all reaction contributions over the possible range of activation energies:

$$\bar{\gamma}(t_0) = \begin{cases} \int_0^{+\infty} \exp\left(-\int_0^{t_0} k_E(t) dt\right) p_E(E) dE & n = 1 \\ \int_0^{+\infty} \left[1 - (1 - n) \int_0^{t_0} k_E(t) dt\right]^{\frac{1}{1-n}} p_E(E) dE & n \neq 1 \end{cases} \quad (4)$$

where the expression is dependent on the reaction order, n . One can distinguish two regimes: the isothermal mode, where the temperature T is kept constant, and the non-isothermal configuration, where the temperature is time-dependent and so is the reaction rate.

Solving these equations is challenging and requires iterative loops of double integral functions that lead to significant numerical complications.⁸ Several numerical techniques have been proposed to tackle this problem of double integration, such as Simpson's 1/3 rule⁹ and the trapezoidal rule,¹⁰ which change the limits of the activation energy integral, or Gauss–Hermite integration.^{11,12} The double exponential term in the DAEM, which disappears in the isothermal process, is one of the primary sources of the numerical challenges. Please et al.¹³ reviewed the existing approaches to simplify the double exponential term in the non-isothermal pyrolysis of coal. By considering the original statistical nature of DAEM, one can think of using a stochastic method of resolution. Here we propose this approach by estimating the activation energy distribution of the DAEM using a Monte Carlo integral formulation that has already been widely used in the radiative heat transfer community.¹⁴

When referring to Monte Carlo in chemical kinetics, the most recurrent terminology is kinetic Monte Carlo (KMC). KMC is used to simulate elementary processes for each molecule or each site; then the dynamic changes are modeled by the master equation, where the parameters are, for each site, the probability of state change.¹⁵ This method requires describing the whole system, and the solving computation time increases according to a probabilistic combination of states at any given time and by a transition rate matrix to determine the switching between states. This probabilistic approach has been used to determine bond formation probabilities and therefore follow species with a large reaction network during thermal degradation.¹⁶ Other Monte Carlo algorithms have been used in conjunction with the Boltzmann distribution and percolation equations to describe bond formation, improving the prediction of bond populations during coal pyrolysis.¹⁷ More recently, this random number generation tool has been used to randomly generate coordinates of a derivative thermogravimetric curve and directly determine kinetic parameters.¹⁸ By using an asymptotic technique to approximate the solution, the authors unfortunately introduced a bias.

Here we propose another Monte Carlo approach, which needs no approximation, to solve the DAEM based on an integral formulation, as initially proposed by Metropolis and Ulam,¹⁹ who introduced the Monte Carlo method. This approach, consisting of determining the quantity expressed as a sum or integral, will be quoted as the Integral Formulation Monte Carlo approach in the next sections.

The Use of Fictitious Events. The origin of our work was the similarity between eq 4 for the first-order reaction and a quantity from the radiative transfer corpus called the mean transmissivity. The mean transmissivity, like the mean conversion rate, is an averaged quantity, but over the frequency domain. The transmissivity itself describes the attenuation of light along a spatial direction through a material medium. Thus, a strict parallel has been made between these quantities: one averaged over the activation energy range and the other over the frequency range. Also, for each the quantity of interest is a propagation, over the time domain for the conversion rate and over the spatial domain for the transmissivity. In both corpuses, a kinetic transport equation describes our problems. That is why it is more intuitive to write the mean conversion rate over the time domain than over temperature: the representation of propagation through the time domain is quite clear and continuous, whereas over the temperature domain it is not. In radiative transfer, a same resolution difficulty appears when the medium is heterogeneous. The mean transmissivity is difficult to solve even statistically. However, Galtier et al.²⁰ introduced, in an integral Monte Carlo scheme, the null-collision technique, which permits the use of Monte Carlo to solve such equations.

Historically, the method of fictitious events took off in three different physics communities in the late 1960s: plasma physics, neutronics, and semiconductor physics. This method was then adopted by other disciplinary fields and is often given different names. In plasma physics, Skullerud²¹ used this technique to statistically sample a collision time of charged particles in plasma. This method has strongly influenced the plasma culture.^{22–27} The technique is not exclusively called “null collisions”, and there are several other names: null event, pseudocollisions, fictitious collisions, hole tracking, Woodcock scattering, delta scattering, pseudoscattering, or maximum cross section by Marchuk.²⁸ On the other hand, in neutronics, some authors^{29,30} introduced the method in this community, followed by the works of others^{31–34} who implemented the same method in various simulation codes of neutron transport. Finally, during the same period, other scientists^{35,36} used fictitious events in semiconductor physics. From 1985, application to the dynamics of rarefied gases appeared.^{37–39} The method was adapted to other areas: image synthesis from 2010, or medical radiotherapy^{40,41} and tomography^{42,43} from the beginning of the 2000s. However, none of these statistical approaches have ever used an integral formulation like that proposed by Galtier in the field of radiative transfer. This work has had multiple consequences and inspired a lot of research. First, it helped the radiative community to treat heterogeneous media.^{44,45} It is now a reference in this community and even used in the film industry.⁴⁶ Second, the null-collision method has found a wide range of applications in physics: cloud rendering,⁴⁷ combustion chambers,⁴⁸ and also gas kinetics.⁴⁹ A null-collision review was written by El Hafi et al.,⁵⁰ providing more details. The fictitious events concept is also used in KMC chemistry for “computational speed-up upon coarse-graining illustrated in adsorption–desorption” in the context of heterogeneous catalysis.^{51,52}

Our objective is to solve the DAEM by taking an integral Monte Carlo approach using the fictitious events method to solve the non-isothermal configuration. This method introduces the new concept of the null-reaction phenomenon into the chemical kinetics corpus.

■ COMPUTATIONAL METHODS

As the rate conversion equations (eq 4) emerge from an energy probability distribution, they will be treated as such by the Monte Carlo integral approach. First, the isothermal case is considered for any reaction order, and second, the dynamic (non-isothermal) mode is considered, where the concept of null reaction is useful. For any condition, the conversion rate at an observation time, t_0 , and for any order can be written more concisely than eq 4 as follows:

$$\bar{\gamma}(t_0) = \int_0^{+\infty} p_E(E) \gamma_E(t_0) dE \quad (5)$$

where the mean conversion, $\bar{\gamma}(t_0)$, is the average of the conversion rate, $\gamma_E(t_0)$, over the activation energy distribution, $p_E(E)$. It can be noted that in the integral Monte Carlo one estimates the observable $\bar{\gamma}(t_0)$ at a given time, unlike in the usual approaches using discretization, where we evaluate the total field. This expression is mathematically defined as an expected value $\bar{\gamma}(t_0) = \mathbb{E}(W)$. However, the Monte Carlo integral method is based on the expected value: if one can express a quantity as an expected value, this quantity can be approximated by the arithmetic mean of a large number of realizations w of the random variable W . Here the Monte Carlo weight $w = \gamma_E(t_0)$ is obtained by sampling an activation energy according to the distribution function $p_E(E)$. The greater the number of realizations, the more the arithmetic mean converges to the expected value.

Also, all statistical realizations are independent and tend toward a normal distribution according to the central limit theorem. The Gaussian standard deviation is interpreted as the statistical error in our estimation. That is a real advantage of the integral Monte Carlo approach: one can estimate a quantity with a corresponding error bar which is inversely proportional to the square root of the realization number. If the number of realizations were infinite, the error term would be zero. Thus, the above equation can be estimated by a Monte Carlo integral approach.

Several choices are possible for the energy distribution. The only condition is that it must be normalized over the definition space: $\int_0^{+\infty} p_E(E) dE = 1$. These choices rely on the complexity of the kinetics in the presence of homogeneous and/or heterogeneous reactions and on experimental observations. A common distribution choice is a Gaussian distribution (or several):

$$p_E(E) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(E - E_0)^2}{2\sigma^2}\right] \quad (6)$$

where σ is the standard deviation and E_0 is the Gaussian mean, which are fixed in accordance with the nature of the reactant. It is important to mention that for some complex processes such as pyrolysis, the reactivity distribution tends to be asymmetric, and therefore, the use of a Gaussian distribution may be not realistic.⁸ To better describe the thermal behavior of natural polymers, a combination of Gaussian distributions can be used to appropriately represent the reactivity distribution. As a result, the distribution $p_E(E)$ can be expressed as a linear combination of different distributions weighted by factors.²⁸ A DAEM combining three Gaussian functions has been suggested by Wang et al.⁵³ to describe the concomitant

degradation of cellulose, hemicelluloses, and lignin. It is important to mention that the Gaussian distribution is not normalized on the $[0, +\infty]$ interval. In the following parts, different expressions for $\gamma_E(t_0)$ for both the isothermal and dynamic regimes will be used.

Isothermal Configuration. In the isothermal case, the temperature is time-independent and constant. Thus, the reaction rate constant, k_E , is dependent only on the activation energy and, for a given energy, $\gamma_E(t_0)$, which is constant and expressed by

$$\gamma_E(t_0) = \begin{cases} \exp(-k_E t_0) & n = 1 \\ [1 - (1 - n)k_E t_0]^{1/(1-n)} & n \neq 1 \end{cases} \quad (7)$$

For any reaction order, the above expressions are analytical. Hence, the estimation of the mean conversion rate in the isothermal regime for any reaction order is quite straightforward: to obtain a realization, one needs to sample an energy according to $p_E(E)$ and inject this value into the above expression according to the reaction order of interest. Directly from the mathematical expression of the mean conversion rate, there is an algorithmic procedure to estimate this value (Algorithm 1). The isothermal case is fully handled by the Monte Carlo method, whatever the value of the reaction order.

Algorithm 1 Monte Carlo algorithm for isothermal mode of the DAEM

- 1: Sample an energy from $p_E(E)$
- 2: if $n = 1$ then
- 3: $w = \exp(-k_E t)$
- 4: else
- 5: $w = [1 - (1 - n)k_E t]^{1/(1-n)}$
- 6: end if

Dynamic Configuration. In the non-isothermal case, eq 4 cannot be treated directly by Monte Carlo because of the integral inside the exponential for the first-order case or the integral raised to the power of $1/(1 - n)$ for any other order. Indeed, the purpose is to also express $\gamma_E(t_0)$ as an expected value. The property $\mathbb{E}(\mathbb{E}(f(X))) = \mathbb{E}(f(X))$ is respected if $f(X)$ is a linear function. If the function is nonlinear, as here with the exponential or the power of $1/(1 - n)$, it will be not possible to write the mean conversion rate as a unique expected value and estimate it by Monte Carlo. In the following, we propose a solution only for the first-order case.

In this case, the exponential attenuation of the reaction rate is problematic due to the dependence on the integral over time inside eq 4. The objective is to rewrite this expression in such a way that the attenuation of the rate occurs in a homogeneous medium.

First, we introduce an upper bound of the reaction rate constant, denoted as \hat{k}_E , to make the temporal attenuation homogeneous. This term can be expressed as the reaction rate constant with an additional term: $k_E = k_{E,n}(t) + k_E(t)$, where the quantity $k_{E,n}(t)$ is a contribution depending on time, which can be interpreted as a possibility of occurrence of null reactions. For a given activation energy, this corresponds to an upper-bound constant through time (Figure 1).

Second, we introduce \hat{k}_E directly into the differential kinetic equation (eq 3) as an additional attenuation. The conversion rate for only one reaction is expressed for the first-order case by

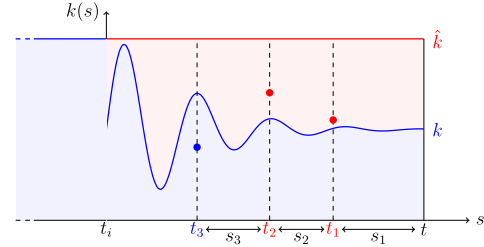


Figure 1. Time evolution of the rate constant from the time of observation, t , to the initial time, t_i . The rate constant upper bound, \hat{k} , is represented in red and is constant in time for a given activation energy.

$$\frac{d\gamma_E(t)}{dt} = -\hat{k}_E \gamma_E(t) + \hat{k}_E \gamma_E(t) - k_E(t) \gamma_E(t) + k_E(t) \times 0 \quad (8)$$

To express eq 3 in a statistical form, we have added a $k_E(t) \times 0$ contribution to use it in the next step of our statistical formulation. One has to consider that the above formulation does not change the underlying chemistry. Then we reformulate eq 8 in order to introduce a statistical view:

$$\frac{d\gamma_E(t)}{dt} = -\hat{k}_E \gamma_E(t) + \hat{k}_E [P_r(t) \times 0 + P_n(t) \gamma_E(t)] \quad (9)$$

where $P_r(t) = k_E(t)/\hat{k}_E$ is the probability of occurrence of a real reaction at a time t . The complementary probability, $P_n(t) = 1 - P_r(t) = \hat{k}_E(t)/\hat{k}_E$ is interpreted as a null-reaction event, which corresponds to an event where the reaction is not happening. Thus, by introducing a supplementary contribution of the reaction, $k_{E,n}(t)$, fictitious reactions are happening. To continue to satisfy the initial rate expression, this action must bring no change in the kinetic process, invoking the principle of null reaction.

From the differential formulation (eq 9), one can write the conversion rate in an integral form as a Fredholm equation (see the Appendix for the mathematical background):

$$\gamma_E(t_0) = \int_0^{+\infty} d\tau p_{\mathcal{T}}(\tau) \{ \mathcal{H}(\tau > t_0 - t_i) \times 1 + \mathcal{H}(\tau < t_0 - t_i) [P_r(t_0 - \tau) \times 0 + P_n(t_0 - \tau) \gamma_E(t_0 - \tau)] \} \quad (10)$$

where $p_{\mathcal{T}}(\tau) = \hat{k}_E \exp(-\hat{k}_E \tau)$ is the probability density allowing us to sample a time interval τ . In fact, the integral Monte Carlo formulation is interpreted as a transport equation through time by starting from the time of observation and going backward in time. At a time $t_0 - \tau$, the corresponding reaction for the activation energy chosen may happen or not, depending on the value of $k_E(t_0 - \tau)$.

Finally, by introducing the previous expression in the mean conversion rate (eq 5), it is now possible to estimate this quantity by Monte Carlo for the non-isothermal regime at first order. Practically, as for the isothermal mode, an activation energy is sampled according to $p_E(E)$. Considering a simple activation energy E , the upper bound of the kinetic rate \hat{k}_E is constant on the time domain, it is feasible to sample a time τ from $p_{\mathcal{T}}(\tau)$. If $\tau > t_0 - t_i$, then the reaction at this activation energy is not occurring, and the Monte Carlo weight retained is 1 (the Heaviside function $\mathcal{H}(\tau > t_0 - t_i)$ assesses this condition when $\tau > t_0 - t_i$). This statement makes sense: if no

reaction happens at all, the value will be always 1, as will the mean conversion rate, since no mass has been converted. If $\tau < t_0 - t_i$, a reaction may happen. Now, due to null-reaction addition at this time $t_0 - \tau$, a reaction could be real with the discrete probability $P_r(t_0 - \tau)$ or fictive according to $P_n(t_0 - \tau)$. If the reaction is real, the weight is zero: the conversion is complete. On the other hand, if the reaction is fictive, we need to estimate $\gamma(t_0 - \tau)$, the conversion rate at time $t_0 - \tau$. Consequently one needs to re-estimate eq 10. In fact, the use of the null-reaction method allows us to sample a time interval thanks to the $p_{\mathcal{T}}(\tau)$ distribution by homogenizing the time attenuation. The consequence is the recursivity of the method. As for the isothermal configuration, there is a corresponding algorithmic procedure to estimate this value (Algorithm 2).

Algorithm 2 Monte Carlo algorithm for DAEM dynamic mode at order $n = 1$

```

1: Sample an energy from  $p_{\mathcal{E}}(E)$ 
2: Sample a time interval  $\tau$  from  $p_{\mathcal{T}}(\tau)$ 
3: if  $(\tau > t_0 - t_i)$  then
4:    $w = 1$ 
5: else
6:   pick a random number  $r$ 
7:   if  $(r < P_r(t_0 - \tau))$  then
8:      $w = 0$ 
9:   else
10:    goto 2.
11:  end if
12: end if

```

The choice of the upper rate constant value, \hat{k}_E , is of paramount importance for this approach: it will contribute to CPU time optimization. Indeed, at a time t_i , the closer the upper value of the reaction rate constant is to the real reaction rate constant, the more fictive reactions will happen. For each fictive reaction, one needs to compute γ_E , which can be time-consuming if too many reactions of this type occur. Hence an appropriate value must be selected for this upper bound: it could be an upper rate constant value over the total time range, or one could discretize the time domain into several intervals where in each part an upper rate constant value is defined.

RESULTS AND DISCUSSION

As a proof of concept, we applied our method in both isothermal and dynamic regimes for some practical illustrations.¹ In the following, all of the Monte Carlo simulations (labeled as M-C) are compared to discrete numerical approaches for validation. In the following figures, the Monte Carlo error bars are 68% confidence intervals.

Isothermal Mode. The mean conversion rate under isothermal conditions is estimated by Monte Carlo according to a first-order reaction scheme for a given temperature and pre-exponential factor. The activation energy was assumed to be obtained from a Gaussian distribution described by a mean energy, E_0 , with the standard deviation as a free parameter. Indeed, the standard deviation has an important impact on the statistical results, as shown in Figure 2, where this parameter was varied. The mean conversion rate, $\bar{\gamma}$, is equal to 1 at the initial time, as there has been no mass loss. Through time $\bar{\gamma}$ decreases until reaching zero if enough time is given. The different evolution curves in Figure 2 correspond to different Gaussian standard deviation values determined by Cai et al.⁵⁴ to describe the pyrolysis of lignocellulosic biomass. For a wide activation energy distribution with a large standard deviation such as $\sigma = 30,000$ J/mol, the reactivity profile (the Gaussian distribution) is broader and corresponds to the degradation of

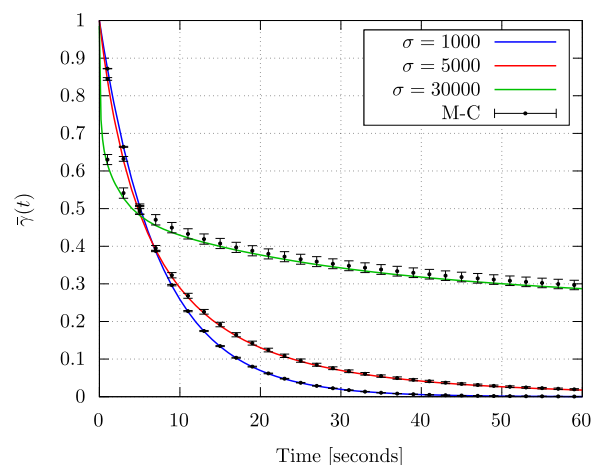


Figure 2. Effect of the Gaussian standard deviation on the statistical results against the time. The temperature is fixed at 773 K, and the Gaussian energy distribution is centered at $E_0 = 220$ kJ/mol. The pre-exponential factor has a value of $A = 10^{14}$ s⁻¹. The solid lines are computed with a trapezoidal rule to be compared to the Monte Carlo estimations (M-C).

the complex and heterogeneous lignin structure over a large activation energy range. Narrower activation energy distributions with smaller standard deviation values of 1000 and 5000 J/mol give narrower reactivity profiles and are used to describe cellulose and hemicellulose pyrolysis, respectively.⁵⁴ Statistically, the wider the distribution is, the greater is the sampling probability of activation energies far away from the mean activation energy of the Gaussian, E_0 . This implies a broader diversity for the Monte Carlo weight calculation, which results in slower convergence for the same number of Monte Carlo realizations. Indeed, as represented in Figure 2, for a given amount of Monte Carlo realizations, the statistical variance is smaller when the Gaussian standard deviation decreases. Inversely, if it tends to zero, one will sample a unique activation energy, so the weight will always be the same: the Monte Carlo algorithm is then called “null variance”.

For this same configuration, there are no severe difficulties in estimating $\bar{\gamma}$ for several orders of reaction in the isothermal mode, as shown in Figure 3. A chemical reaction is usually described by an interaction between reacting species at the molecular level, and the notion of molecularity is used to account for the number of molecules participating in this reaction, which can be monomolecular, bimolecular, or trimolecular. The chemical reaction rate depends on the reactant concentrations and their related power exponents, which are the reaction orders. In the presence of complex reactions, therefore with several reactants, the overall reaction order is the sum of the power exponents of the reactants.⁵⁵ Thus, the Monte Carlo method captures the dynamics of different reaction orders quite well: no variance is introduced when the order is changed.

Dynamic Configuration. In this section, we show the feasibility of the proposed method under non-isothermal conditions for the first-order case in typical configurations: one is described by a Gaussian energy distribution, and another is a configuration where the energy distribution results from experimental measurements and the pre-exponential factor depends on the activation energy.

As said above, reaction orders different from 1 are not treated due to the nonlinearity of the problem. Also, there is no

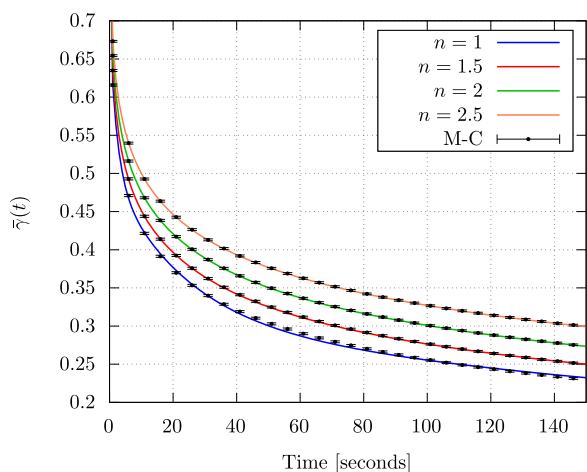


Figure 3. Effect of the reaction order, n , on the mean conversion rate evolution under isothermal conditions. The temperature is fixed at 773 K, and the Gaussian energy distribution is centered at $E_0 = 220$ kJ/mol with the Gaussian standard deviation fixed at $\sigma = 30,000$ J/mol. The pre-exponential factor has a value of $A = 10^{14}$ s $^{-1}$. The solid lines are computed with a trapezoidal rule to be compared to the Monte Carlo estimations (M-C).

need to study the influence of the reaction order under dynamic mode, as both the reaction rate constant, $k_E(t)$, and the reaction model, $f(\alpha_E(t))$, vary simultaneously, giving rise to sigmoidal curves that prevent the determination of the reaction model type.

Analytical Distribution of Activation Energies. We considered a furnace at the initial temperature of 443 K and heated up at a constant ramp (β) of 10 K/min, which is typical of slow pyrolysis conditions. Here the value of the pre-exponential factor was fixed, and the distribution of activation energies was Gaussian. For several values of the standard deviation of the Gaussian distribution, the mean conversion reaction rate was computed by Monte Carlo through time (Figure 4). Contrary to the isothermal mode, the Gaussian

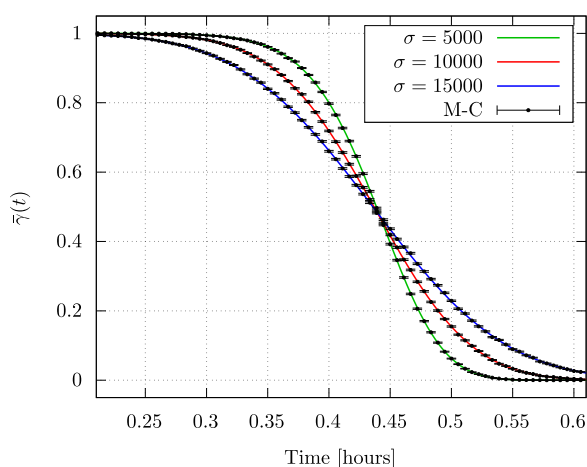


Figure 4. Evolution in time of the mean conversion rate for a heating ramp of 10 K/min for different Gaussian standard deviations. At $t_i = 0$ s, the initial temperature is 443 K. The activation energy distribution is Gaussian and centered on $E_0 = 220$ kJ/mol. The pre-exponential factor is $A = 10^{14}$ s $^{-1}$. The continuous curve was computed with a Gauss-Hermite quadrature to be compared to the Monte Carlo estimations (M-C).

standard deviation has no impact on the convergence of the statistical estimator. Indeed, the selected weights are not dependent on this parameter; this was the case for the isothermal configuration. However, for each σ value, the variance significantly increases when the reaction is fast; in other words, when the mean conversion rate starts to notably decrease. The cause is due to the reaction rate statistics where the weight can take the value of 0 or 1 when the extent of conversion reaches its maximum value.

Experimental Distribution of Activation Energies. Using the integral Monte Carlo approach, the activation energy sampling does not necessarily require an analytical distribution. It is possible to sample a distribution of activation energies from experimental data. This is an interesting approach because we are not assuming a predefined function (e.g., Gaussian(s), Weibull, etc.) for the activation energy distribution, in the same way as the model-free or isoconversional kinetic approaches, where no reactional models are assumed in the first place. They allow the determination of apparent kinetic parameters, and the accuracy and precision of resulting values depend on the differential or integral character of the collected data.³ However, one needs to use an experimental strategy allowing the control of a pure kinetic regime to obtain it, such as the method proposed by Miura and Maki⁵⁶ to retrieve the energy distribution from experimental data and also to determine a pre-exponential factor depending on the activation energy. Despite concerns related to the use of the Miura-Maki integral method demonstrated by Cai et al.,⁵⁷ the primary objective of Miura and Maki was to determine a true energy distribution from isoconversional analysis, which we believe to be an adequate approach, as an infinitely sequential reaction model could provide further insights in terms of pyrolysis stages (e.g., degradation scheme) and associated levels of reactivity if heat and mass transfer limitations are adequately removed from data sets. To justify the utility of our method in an experimental context, in the following section we propose to find the same mean conversion rate estimated by Miura and Maki from the same experimental energy distribution (see Figure 6 in the Appendix). Furthermore, Miura and Maki provided a pre-exponential factor depending on the activation energy from the following expression: $A_E = 10^{15} \exp[0.08(E - 250)]$ with E in kJ/mol. The calculation details to sample an energy from a discrete distribution can be found in the Appendix. The mean conversion rate was estimated by Monte Carlo with the null-reaction method for the same heating ramp and configuration as that used by Miura and Maki⁵⁶ (Figure 5). To establish a strict comparison, the value was plotted against the temperature.

Hence, there are no difficulties in treating an experimental activation energy distribution and its dependence on the pre-exponential factor.

Temperature Evolution Consideration. An interesting fact is that one needs to evaluate the reaction rate constant, $k_E(t)$, only for testing whether a reaction occurs or not at time t . There is no need to know the value of $k_E(t)$ for every time location, but only for t . A direct consequence is that the value needed to determine the reaction rate can be extremely complex and estimated by other models or experimentally measured. For this reason, we can use any form of the pre-exponential factor and apply the same reasoning on the temperature profile. It is straightforward to use a linear heating ramp as an analytical formulation of temperature. One can also use an exponential profile of temperature, which would model

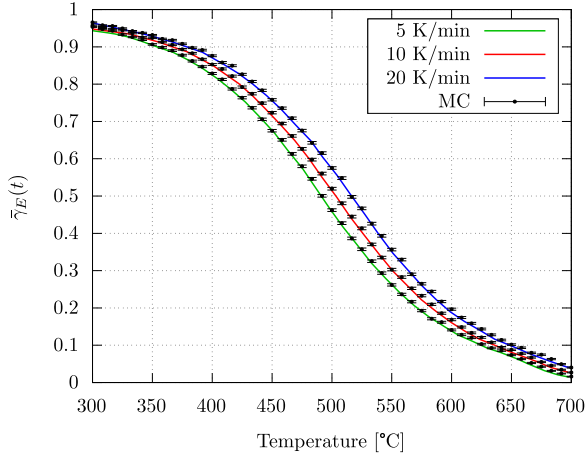


Figure 5. Mean conversion rate time evolution for different heating ramps. The Monte Carlo values (M-C) are compared to the data of Miura and Maki (continuous curves) for an initial temperature of 303.15 K.

in a better way a biomass sample inserted in a furnace preheated at fixed temperature:⁵

$$T(t) = T_f[1 - \exp(-t/t_c)] + T_0 \quad (11)$$

where T_f is the furnace final temperature, T_0 is the initial furnace temperature, and t_c is a characteristic time of temperature evolution.

In radiative transfer, a similar property occurring by the use of fictitious events, the absorption coefficient (the equivalent of the kinetic rate in our case), only needs to be known at a given spatial point. If the absorption coefficient is expressed as an expected value, Galtier et al.⁵⁸ showed that it is possible to couple the radiative transfer to a spectral model without calculating that coefficient. The same question can be addressed here: is it feasible to couple simultaneously chemical kinetics with a heat transfer model providing the temperature? In order to achieve this, one needs to express the kinetic rate constant, k_E , as an expected value. The question is open, but recent studies^{59–62} showed that the temperature could be expressed as an expected value in k_E .

CONCLUSIONS

A new method to solve the distributed activation energy model (DAEM) based on the Monte Carlo integral formulation was developed. This method resolution is inspired by the statistical nature of the model and the proposition made by the radiative transfer community. For the first time, an exact DAEM resolution method with no statistical bias is introduced, and each value of the conversion rate has an associated and estimated confidence interval. With this method, any activation energy distribution (analytical or experimental), any function for the pre-exponential factor, and any temperature profile (heating ramp or experimental data) can be used and the reaction kinetics assessed.

For future investigations, the coupling of chemical kinetics with a thermal model (such as a heat equation) will be considered. This is a concept that has already been demonstrated in radiation physics by coupling the radiative transfer to the absorption coefficient model,⁵⁸ while other research coupling heat transfer phenomena is ongoing.^{59–62}

There are some remaining considerations, such as varying the reaction order from 1 under dynamic conditions. Recent

techniques in nonlinear Monte Carlo could open up some interesting perspectives.⁶³

Another outlook could be the sensitivity estimation, meaning that the derivative of the mean conversion rate with respect to a parameter (such as the Gaussian standard deviation or the heating ramp parameter) could be studied. This could be useful for inversion strategies but also to understand the underlying chemistry dependences. Such an implementation is straightforward because the Monte Carlo estimation for a value and these sensitivities have no computational additional cost as they are evaluated in a single algorithm.⁶⁴

APPENDIX

Differential Equation to Integral Formulation

Introducing a function $f(t)$ depending on the parameter t that is attenuated through time according to $k(t)$ can be done by adding an additional term from a fictitious event:

$$\begin{cases} \frac{df(t)}{dt} = -k(t)f(t) = -\hat{k}f(t) + \hat{k}S(t) \\ f(t_i) = f_i \end{cases} \quad (12)$$

in which

$$S(t) = \frac{1}{\hat{k}}[-k(t)f(t) + \hat{k}f(t)] = \left[1 - \frac{k(t)}{\hat{k}}\right]f(t) \quad (13)$$

A solution of eq 12 is

$$f(t) = f_i \exp[-\hat{k}(t - t_i)] + \int_0^{t-t_i} \hat{k} \exp(-\hat{k}\tau) S(t - \tau) d\tau \quad (14)$$

Because

$$\begin{cases} \int_0^{t-t_i} \hat{k} \exp(-\hat{k}\tau) S(t - \tau) d\tau \\ = \int_0^{+\infty} \hat{k} \exp(-\hat{k}\tau) S(t - \tau) \mathcal{H}(\tau < t - t_i) d\tau \\ \exp[-\hat{k}(t - t_i)] = \int_0^{+\infty} \hat{k} \exp(-\hat{k}\tau) \mathcal{H}(\tau > t - t_i) d\tau \end{cases} \quad (15)$$

$f(t)$ can be written in integral form as follows:

$$\begin{aligned} f(t) = \int_0^{+\infty} d\tau \hat{k} \exp(-\hat{k}\tau) [\mathcal{H}(\tau > t - t_i) \times f_i \\ + \mathcal{H}(\tau < t - t_i) S(t - \tau)] \end{aligned} \quad (16)$$

Substituting the expression for the source term S from eq 13 gives

$$\begin{aligned} f(t) = \int_0^{+\infty} d\tau \hat{k} \exp(-\hat{k}\tau) \left\{ \mathcal{H}(\tau > t - t_i) \times f_i \right. \\ \left. + \mathcal{H}(\tau < t - t_i) \left[1 - \frac{k(t - \tau)}{\hat{k}} \right] f(t - \tau) \right\} \end{aligned} \quad (17)$$

Finally, one can introduce the complementary probability of $[1 - k(t - \tau)/\hat{k}]$ to express $f(t)$ as an expected value:

$$f(t) = \int_0^{+\infty} d\tau \hat{k} \exp(-\hat{k}\tau) \left\{ \mathcal{H}(\tau > t - t_i) \times f_i + \mathcal{H}(\tau < t - t_i) \left[\frac{k(t - \tau)}{\hat{k}} \times 0 + \left(1 - \frac{k(t - \tau)}{\hat{k}} \right) f(t - \tau) \right] \right\} \quad (18)$$

Energy Sampling from a Distribution

In our configuration, a simple numerical method exists to sample an activation energy from a Gaussian distribution. Otherwise, the inverse cumulative density function (CDF) method can be used.⁶⁵ When dealing with the Miura–Maki energy distribution,⁵⁶ an activation energy is sampled from the CDF. In Figure 6, the blue curve represents the Miura–Maki energy distribution and the red curve the corresponding CDF (which varies between 0 and 1).

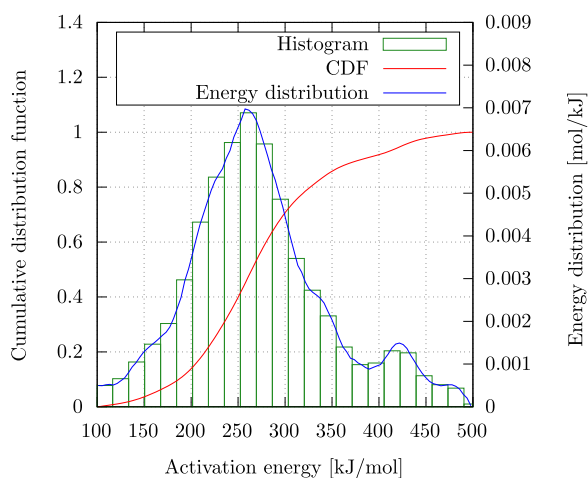


Figure 6. Representation of the activation energy distribution from Miura and Maki⁵⁶ and its corresponding CDF.

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Notes

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ADDITIONAL NOTE

¹The source code is available online at https://gitlab.com/yanissnp/DAEM_MC. It relies on Star-Engine libraries (<https://gitlab.com/meso-star/star-engine>).

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