Additional Information

A full probabilistic analysis of a randomized kinetic model for reaction-deactivation of hydrogen peroxide decomposition with applications to real data

J.-C. Cortés · A. Navarro-Quiles · J.-V. Romero · M.-D. Roselló

Abstract The classical kinetic equation has been broadly used to describe reaction and deactivation processes in chemistry. The mathematical formulation of this deterministic nonlinear differential equation depends on reaction and deactivation rate constants. In practice, these rates must be calculated via laboratory experiments, hence involving measurement errors. Therefore, it is more realistic to treat these rates as random variables rather than deterministic constants. This leads to the randomization of the kinetic equation, and hence its solution becomes a stochastic process. In this paper we address the probabilistic analysis of a randomized kinetic model to describe reaction and deactivation by catalase of hydrogen peroxide decomposition at a given initial concentration. In the first part of the paper, we determine closed-form expressions for the probability density functions of important quantities of the aforementioned chemical process (the fractional conversion of hydrogen peroxide, the time until a fixed quantity of this fractional conversion is reached and the activity of the catalase). These expressions are obtained by taking extensive advantage of the so called Random Variable Transformation technique. In the second part, we apply the theoretical results obtained in the first part together with the principle of maximum entropy to model the hydrogen peroxide decomposition and *aspergillus niger* catalase deactivation using real data excerpted from the recent literature. Our results show full agreement with previous reported analysis but having as additional benefit that they provide

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a more complete description of both model inputs and outputs since we take into account the intrinsic uncertainties involved in modelling process.

Keywords Random kinetic differential equation · Probability density function · Random Variable Transformation technique · Principle of Maximum Entropy · Chemical real data

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1 Preliminaries

Catalysis is a branch of chemical kinetics and it has an extensive number of applications, such as the production of alcoholic beverages by fermentation and the manufacture of vinegar by ethanol oxidation [8]. In [1], catalysis was firstly recognized as a wide-ranging natural phenomenon and Berzelius defined catalysis as the decomposition of bodies by the catalytic force. Then, catalysis is the process by which the rate of a chemical reaction is increased using a catalyst. A catalyst is a material that accelerates a chemical reaction without affecting the position of the equilibrium and thermodynamics of the reaction [9]. A particular catalyst is the *catalase*, an enzyme that decomposes hydrogen peroxide to water and oxygen [4].

Our investigation is inspired by a recent publication [11], where authors estimate the kinetic parameters for H_2O_2 enzymatic decomposition and for catalase deactivation. Taking into account the enzymatic reaction kinetics and the phenomenon of deactivation, the kinetic model can be described via the following coupled system of nonlinear differential equations

$$\frac{\mathrm{d}C_S(t)}{\mathrm{d}t} = -k_R\, C_E(t)\, C_S(t), \quad \frac{\mathrm{d}C_E(t)}{\mathrm{d}t} = -k_D\, C_E(t)\, C_S(t), \quad t > 0, \quad (1)$$

with initial conditions $C_S(0) = C_{S_0} > 0$ and $C_E(0) = C_{E_0} > 0$. For more details about the construction of the kinetic model, see [11] and references therein. In model (1), $C_S(t) > 0$ and $C_E(t) > 0$ are the concentration of hydrogen peroxide and the concentration of enzyme at the time instant t, respectively. Parameters $k_R > 0$ and $k_D > 0$ are the reaction and deactivation constants. Let $a(t) = C_E(t)/C_{E_0} > 0$ be the dimensionless activity of the catalase, then model (1) is equivalent to

$$\frac{\mathrm{d}C_S(t)}{\mathrm{d}t} = -k_R^*\, a(t)\, C_S(t), \quad \frac{\mathrm{d}a(t)}{\mathrm{d}t} = -k_D\, a(t)\, C_S(t), \quad t > 0, \quad (2)$$

with initial conditions $C_S(0) = C_{S_0}$ and $a(0) = 1$, and being $k_R^* = C_{E_0}\, k_R > 0$. From (2), it is clear that $C_S(t)$ and $a(t)$ are decreasing functions since their derivatives are negatives. So, $C_S(t) < C_{S_0}$ and $a(t) < 1$ for all $t > 0$. To solve the non-linear system (2), we introduce the fractional conversion of hydrogen peroxide $X(t) = (C_{S_0} - C_S(t))/C_{S_0} \in (0, 1)$, which allow us to

rewrite the foregoing system of differential equations as a single nonlinear differential equation. To this end, let first us observe that model (2) can be written as

$$\frac{\mathrm{d}X(t)}{\mathrm{d}t} = k_R^* \, a(t) \, (1 - X(t)), \quad \frac{\mathrm{d}a(t)}{\mathrm{d}t} = -k_D \, a(t) \, C_{S_0}(1 - X(t)), \quad t > 0, \quad (3)$$

with initial conditions $X(0) = 0$ and $a(0) = 1$. Dividing $\mathrm{d}a/\mathrm{d}t$ by $\mathrm{d}X/\mathrm{d}t$ and using the initial conditions, we can obtain the activity of the catalase in terms of the fractional conversion X,

$$a(X) = 1 - \frac{k_D}{k_R^*} C_{S_0} X. \quad (4)$$

Then, substituting Equation (4) in the first differential equation of (3), we obtain the following nonlinear differential equation for $X(t)$,

$$\frac{\mathrm{d}X(t)}{\mathrm{d}t} = (k_R^* - k_D \, C_{S_0} X(t))(1 - X(t)), \quad t > 0, \quad (5)$$

with initial condition $X(0) = 0$. The solution of this initial value problem is

$$\begin{cases} X(t) = \dfrac{1 - \mathrm{e}^{\left(k_R^* - k_D C_{S_0}\right) t}}{C_{S_0} \frac{k_D}{k_R^*} - \mathrm{e}^{\left(k_R^* - k_D C_{S_0}\right) t}} & \text{for } k_D \, C_{S_0} \neq k_R^*, \\[4mm] X(t) = 1 - \dfrac{1}{k_R^* \, t + 1} & \text{for } k_D \, C_{S_0} = k_R^*. \end{cases} \quad (6)$$

In practice, the reaction ($k_R > 0$) and deactivation ($k_D > 0$) parameters are usually estimated via laboratory experiments. Particularly, in [11], an interval estimation of the reaction rate constant k_R^*, at a fixed initial concentration of hydrogen peroxide C_{S_0}, is established after repeatedly performing a certain chemical experiment. Values of k_D were found from the values of k_R^*, using non-linear regression. Since model parameters are computed through experiments, they involve measurement errors and uncertainties, thus it is more natural to treat them as random variables rather than deterministic constants. In this paper, we assume that both rates are absolutely continuous random variables, $k_R^*(\omega)$ and $k_D(\omega)$, defined on a common complete probability space $(\Omega, \mathcal{F}, \mathbb{P})$, where $\omega \in \Omega$ denotes a simple outcome or elementary event of the sample space Ω. As a consequence, the kinetic model (5) is formulated by a random differential equation, and then, its solution is a stochastic process that can be derived from the deterministic solution established in (6),

$$X(t, \omega) = \frac{1 - \mathrm{e}^{\left(k_R^*(\omega) - k_D(\omega) \, C_{S_0}\right) t}}{C_{S_0} \frac{k_D(\omega)}{k_R^*(\omega)} - \mathrm{e}^{\left(k_R^*(\omega) - k_D(\omega) \, C_{S_0}\right) t}} \in (0, 1), \quad \forall \omega \in \Omega. \quad (7)$$

Note that, to determine the expression of the solution stochastic process (7), we have utilized that $k_R^*(\omega)$ and $k_D(\omega)$ are continuous random variables, then $\mathbb{P}[\omega \in \Omega : k_D(\omega) \, C_{S_0} = k_R^*(\omega)] = 0$, in other words, the second case defining the deterministic solution (6) can be neglected.

For the sake of generality, hereinafter we will assume that the positive rates $k_D(\omega)$ and $k_R^*(\omega)$ are absolutely continuous random variables with a joint probability density function (PDF), $f_{k_D,k_R^*}(k_D,k_R^*)$, defined on a certain domain $\mathcal{D}_{k_D,k_R^*} \subset \mathbb{R}^+ \times \mathbb{R}^+$. In case $k_R^*(\omega)$ and $k_D(\omega)$ are independent random variables, the joint PDF can be factorized by means of the product of their respective marginals PDFs, $f_{k_D}(k_D)$ and $f_{k_R^*}(k_R^*)$, $f_{k_D,k_R^*}(k_D,k_R^*) = f_{k_D}(k_D)f_{k_R^*}(k_R^*)$.

In the deterministic framework, the main mathematical goal in dealing with the kinetic model (5) is to compute its solution in order to describe the dynamics of the fractional conversion of hydrogen peroxide $X(t)$, see reference [11]. In contrast, when the kinetic model is randomized, the goal is also to compute the main statistical functions of the solution stochastic process, such as the mean and the variance. And, if possible, a major goal is to determine the first probability density function (1-PDF), $f_{X(t)}(x)$, that provides a full probabilistic description of the solution stochastic process, $X(t,\omega)$, at every time instant t. Indeed, via $f_{X(t)}(x)$ we can calculate every one-dimensional moment, $\mathbb{E}\left[(X(t,\omega))^k\right] = \int_0^1 x^k f_{X(t)}(x)\,\mathrm{d}x, \quad k = 1,2,\ldots$, where $\mathbb{E}[\cdot]$ denotes the expectation operator. In particular, from this latter expression we can easily obtain the mean and the variance functions, which are defined by

$$\mu_X(t) = \mathbb{E}\left[X(t,\omega)\right], \quad \sigma_X^2(t) = \mathbb{E}\left[(X(t,\omega))^2\right] - (\mathbb{E}\left[X(t,\omega)\right])^2, \qquad (8)$$

respectively. In addition, the 1-PDF allows us to determine, for example, the probability that the fractional conversion of hydrogen peroxide lies in a set of interest, say $[x_1,x_2]$, and the probability that this rate exceeds a given level $\hat{x}$

$$\mathbb{P}\left[x_1 \le X(t,\omega) \le x_2\right] = \int_{x_1}^{x_2} f_{X(t)}(x)\,\mathrm{d}x, \quad \mathbb{P}\left[X(t,\omega) > \hat{x}\right] = \int_{\hat{x}}^1 f_{X(t)}(x)\,\mathrm{d}x.$$

Furthermore, the 1-PDF is useful to construct confidence intervals. Let $\alpha \in (0,1)$, for each time instant $\hat{t} \ge 0$ fixed, we can built the $(1-\alpha)\%$-confidence interval $[x_1(\hat{t}), x_2(\hat{t})]$ as follows

$$\int_0^{x_1(\hat{t})} f_{X(\hat{t})}(x)\,\mathrm{d}x = \frac{\alpha}{2} = \int_{x_2(\hat{t})}^1 f_{X(\hat{t})}(x)\,\mathrm{d}x. \qquad (9)$$

The paper is organized into three sections. In Sect. 2, we provide a complete probabilistic description of the randomized kinetic model previously introduced. For the sake of clarity, we divide Sect. 2 in several subsections where different chemical quantities of interest are considered. In Subsect. 2.1, a closed-form expression of the 1-PDF of the fractional conversion of hydrogen peroxide, $X(t,\omega)$, is determined. Subsect. 2.2 is addressed to compute the distribution of the time until a given quantity of above mentioned conversion rate is reached. In Subsect. 2.3, we determine the 1-PDF of the activity of the catalase, a fundamental quantity in the catalysis process. We complete Sec. 2 by computing the probability distributions of the fractional conversion rate, $X(t,\omega)$, and of the activity of the catalase, $a(t,\omega)$ in the long-term, i.e. as

$t \to \infty$. This study is developed in Subsect. 2.4. In Sect. 3, all the theoretical results established in Sect. 2 are applied to model the hydrogen peroxide decomposition and *aspergillus niger* catalase deactivation using real data excerpted from the recent literature. Our main conclusions are drawn in Sect.4.

2 Probabilistic description of the kinetic model

In this section we provide a full probabilistic description of the kinetic model introduced in Sect. 1. This description is based on the computation of the PDF of different quantities of interest, including its solution, via the Random Variable Transformation (RVT) technique. The RVT method, stated in Theorem 1, allows us to determine the distribution of a random vector coming from mapping another random vector whose PDF is known.

Theorem 1 (Random Variable Transformation technique [12]) *Let* $\mathbf{u}(\omega) = (u_1(\omega), \dots, u_n(\omega))^\top$ *and* $\mathbf{v}(\omega) = (v_1(\omega), \dots, v_n(\omega))^\top$ *be* n-*dimensional absolutely continuous random vectors. Let* $\mathbf{r} : \mathbb{R}^n \to \mathbb{R}^n$ *be a one-to-one transformation of* $\mathbf{u}$ *into* $\mathbf{v}$, *i.e.,* $\mathbf{v} = \mathbf{r}(\mathbf{u})$. *Assume that* $\mathbf{r}$ *is continuous in* $\mathbf{u}$ *and has continuous partial derivatives with respect to* $\mathbf{u}$. *Then, if* $f_{\mathbf{U}}(\mathbf{u})$ *denotes the joint PDF of vector* $\mathbf{u}(\omega)$, *and* $\mathbf{s} = \mathbf{r}^{-1} = (s_1(v_1, \dots, v_n), \dots, s_n(v_1, \dots, v_n))^\top$ *represents the inverse mapping of* $\mathbf{r} = (r_1(u_1, \dots, u_n), \dots, r_n(u_1, \dots, u_n))^\top$, *the joint PDF of vector* $\mathbf{v}(\omega)$ *is given by*

$$f_{\mathbf{V}}(\mathbf{v}) = f_{\mathbf{U}}(\mathbf{s}(\mathbf{v})) |J_n|,$$

where $|J_n|$ *is the absolute value of the Jacobian, which is defined by*

$$J_n = \det\left(\frac{\partial \mathbf{s}^\top}{\partial \mathbf{v}}\right) = \det\begin{pmatrix} \dfrac{\partial s_1(v_1, \dots, v_n)}{\partial v_1} & \cdots & \dfrac{\partial s_n(v_1, \dots, v_n)}{\partial v_1} \\ \vdots & \ddots & \vdots \\ \dfrac{\partial s_1(v_1, \dots, v_n)}{\partial v_n} & \cdots & \dfrac{\partial s_n(v_1, \dots, v_n)}{\partial v_n} \end{pmatrix}.$$

The key point when applying this result in the setting of random differential equations, and in particular in dealing with the randomized kinetic model, is to calculate the 1-PDF of the corresponding solution stochastic process, $X(t)$, by choosing an adequate one-to-one transformation $\mathbf{r}$, being $X(t)$ one of its components, so that the Jacobian of $\mathbf{r}$ is computable. As it shall be seen throughout this paper, the RVT method will be extensively applied in our subsequent developments defining adequate mappings, $\mathbf{r}$, in each case and assuming the distribution of the random vector $(k_D(\omega), k_R^*(\omega))^\top$ is known. Finally, we point out that the RVT method has been successfully applied to study random differential equations modelling problems in many applied areas, see for example [6,3,7,5].

2.1 Distribution of the fractional conversion of hydrogen peroxide $X(t, \omega)$

From the expression of the solution stochastic process, given in (7), and considering $t > 0$ fixed, we apply the RVT method with the following choice in Theorem 1: $\mathbf{u}(\omega) = (k_D(\omega), k_R^*(\omega))^\top$ and $\mathbf{v}(\omega) = (v_1(\omega), v_2(\omega))^\top$, where, for each $\omega \in \Omega$, the components of vector $\mathbf{v}$ are defined by the following transformation $\mathbf{r} : \mathbb{R}^2 \to \mathbb{R}^2$,

$$v_1 = r_1(k_D, k_R^*) = \frac{1 - \mathrm{e}^{\left(k_R^* - k_D C_{S_0}\right)t}}{C_{S_0} \frac{k_D}{k_R^*} - \mathrm{e}^{\left(k_R^* - k_D C_{S_0}\right)t}}, \qquad v_2 = r_2(k_D, k_R^*) = C_{S_0} k_D / k_R^*.$$

Observe that for every $\omega \in \Omega$, the solution $X(t, \omega)$ is v_1, so we know that by construction $v_1 \in (0, 1)$. The inverse mapping, $\mathbf{s} : \mathbb{R}^2 \to \mathbb{R}^2$, of $\mathbf{r}$ is given by

$$k_D = s_1(v_1, v_2) = -\frac{v_2 \log\left(\frac{1-v_1}{1-v_1 v_2}\right)}{C_{S_0} t (1 - v_2)}, \qquad k_R^* = s_2(v_1, v_2) = -\frac{\log\left(\frac{1-v_1}{1-v_1 v_2}\right)}{t(1 - v_2)}. \tag{10}$$

Let us check that the inverse mapping $\mathbf{s}$ is well-defined. First, observe that

$$1 - v_1 v_2 = \frac{k_R^* - C_{S_0} k_D}{k_R^* - C_{S_0} k_D \, \mathrm{e}^{(C_{S_0} k_D - k_R^*)t}} > 0. \tag{11}$$

To show the positiveness of this expression we distinguish two cases:

- Case 1: Let us assume that $v_2 > 1$ (or equivalently that $C_{S_0} k_D - k_R^* > 0$). Then, the numerator and the denominator in (11) are both negative, as a consequence $1 - v_1 v_2 > 0$. Moreover, since $v_2 > 1$ one gets $0 < 1 - v_1 v_2 < 1 - v_1$, thus $\log((1 - v_1)/(1 - v_1 v_2)) > 0$, and from (10), one deduces that k_D and k_R^* are both positive, as required for consistency with model formulation.
- Case 2: Let us assume that $v_2 < 1$ (or equivalently that $C_{S_0} k_D - k_R^* < 0$). This entails the numerator and the denominator in (11) are both positive, thus $1 - v_1 v_2 > 0$ too. As a consequence, the logarithmic term $\log((1 - v_1)/(1 - v_1 v_2))$ in (10) is well-defined. Even more, from $v_2 < 1$ one gets $1 - v_1 v_2 > 1 - v_1 > 0$, then $\log((1 - v_1)/(1 - v_1 v_2)) < 0$, and again, k_D and k_R^* are both positive, as required.

On the other hand, the absolute value of the Jacobian of $\mathbf{s}$ is

$$|J_2| = \frac{\log\left(\frac{1-v_1}{1-v_1 v_2}\right)}{C_{S_0} t^2 (1 - v_1)(1 - v_2)(-1 + v_1 v_2)} \neq 0.$$

Then, applying RVT method, we obtain the PDF of random vector $\mathbf{v}(\omega) = (X(t, \omega), C_{S_0} k_D(\omega)/k_R^*(\omega))$ in terms of $f_{k_D, k_R^*}(k_D, k_R^*)$, which is assumed known,

$$f_{v_1, v_2}(v_1, v_2) = f_{k_D, k_R^*}\left(-\frac{v_2 \log\left(\frac{1-v_1}{1-v_1 v_2}\right)}{C_{S_0} t (1 - v_2)}, -\frac{\log\left(\frac{1-v_1}{1-v_1 v_2}\right)}{t(1 - v_2)}\right)$$

$$\times \frac{\log\left(\frac{1-v_1}{1-v_1 v_2}\right)}{C_{S_0} t^2 (1 - v_1)(1 - v_2)(-1 + v_1 v_2)}.$$

Marginalizing with respect to the random variable, $v_2(\omega)$, and taking $t > 0$ arbitrary, the 1-PDF of the solution stochastic process, $X(t, \omega)$, is given by

$$
f_{X(t)}(x) = \int_{\mathcal{D}(v_2)} f_{k_D, k_R^*} \left(-\frac{v_2 \log\left(\frac{1-x}{1-x\,v_2}\right)}{C_{S_0} t(1-v_2)}, -\frac{\log\left(\frac{1-x}{1-x\,v_2}\right)}{t(1-v_2)} \right)
$$
$$
\times \frac{\log\left(\frac{1-x}{1-x\,v_2}\right)}{C_{S_0} t^2(1-x)(1-v_2)(-1 + x\,v_2)} \, \mathrm{d}v_2,
\tag{12}
$$

where $\mathcal{D}(v_2)$ denotes the domain of random variable, $C_{S_0} k_D(\omega)/k_R^*(\omega)$, that must be contained in $(0,1) \cup (1, \infty)$.

2.2 Distribution of the time $T(\omega)$

In this subsection, we compute the distribution of the time, $T(\omega)$, until a fixed quantity of fractional conversion of hydrogen peroxide $\rho \in (0,1)$ is reached. So, first we need to solve

$$
\rho = \frac{1 - \mathrm{e}^{\left(k_R^* - k_D C_{S_0}\right)t}}{C_{S_0} \frac{k_D}{k_R^*} - \mathrm{e}^{\left(k_R^* - k_D C_{S_0}\right)t}},
$$

for t. This yields

$$
t = \frac{\log\left(\frac{1 - C_{S_0} k_D/k_R^* \rho}{1 - \rho}\right)}{k_R^* - C_{S_0} k_D}.
\tag{13}
$$

Now, we show that this time is well-defined, i.e. $t > 0$. Let $\rho \in (0,1)$ fixed, so $1 - \rho > 0$. We distinguish two cases:

- Case 1: Let us assume that $1 - C_{S_0} k_D/k_R^* \rho > 1 - \rho$. Then, $k_R^* - C_{S_0} k_D > 0$ and $(1 - C_{S_0} k_D/k_R^* \rho)/(1 - \rho) > 1$, so $\log((1 - C_{S_0} k_D/k_R^* \rho)/(1 - \rho)) > 0$. Thus according to (13), one deduces that $t > 0$.
- Case 2: Let us assume that $0 < 1 - C_{S_0} k_D/k_R^* \rho < 1 - \rho$. The second inequality entails $k_R^* - C_{S_0} k_D < 0$ and $(1 - C_{S_0} k_D/k_R^* \rho)/(1 - \rho) < 1$, thus $\log((1 - C_{S_0} k_D/k_R^* \rho)/(1 - \rho)) < 0$. In this manner, the expression (13) yields $t > 0$ too.

Summarizing, the time defined by (13) is always positive, and as a consequence, the following random variable

$$
T(\omega) = \frac{\log\left(\frac{1 - C_{S_0} k_D(\omega)/k_R^*(\omega)\,\rho}{1 - \rho}\right)}{k_R^*(\omega) - C_{S_0} k_D(\omega)}, \quad \omega \in \Omega,
$$

is well-defined on the conditional probability space $(\Omega, \mathcal{F}, \mathbb{P}\left[\cdot|C\right])$, where $C = \{\omega \in \Omega : 1 - C_{S_0} k_D(\omega)/k_R^*(\omega)\,\rho > 0\} \in \mathcal{F}$. Now, we apply the RVT method

to compute the distribution of $T(\omega)$ in the foregoing conditional probability space. Let us denote $\mathbf{u}(\omega) = (k_D(\omega), k_R^*(\omega))^\top$, and for every $\omega \in \Omega$ define $\mathbf{v}(\omega) = (v_1(\omega), v_2(\omega))^\top$ via the following deterministic transformation $\mathbf{r} : \mathbb{R}^2 \to \mathbb{R}^2$

$$v_1 = r_1(k_D, k_R^*) = \frac{\log\left(\frac{1 - C_{S_0} k_D / k_R^* \rho}{1-\rho}\right)}{k_R^* - C_{S_0} k_D}, \ \ v_2 = r_2(k_D, k_R^*) = 1 - C_{S_0} k_D / k_R^* \rho.$$

Now, we compute the inverse mapping $\mathbf{s} = \mathbf{r}^{-1} : \mathbb{R}^2 \to \mathbb{R}^2$, isolating parameters k_D and k_R^*,

$$k_D = s_1(v_1, v_2) = \frac{(1 - v_2)\log\left(\frac{v_2}{1-\rho}\right)}{C_{S_0} v_1(-1 + v_2 + \rho)}, \quad k_R^* = s_2(v_1, v_2) = \frac{\rho \log\left(\frac{v_2}{1-\rho}\right)}{v_1(-1 + v_2 + \rho)}. \tag{14}$$

Since we are working on the conditional space $(\Omega, \mathcal{F}, \mathbb{P}[\cdot|C])$, it is guaranteed that $v_2 > 0$, so $v_2/(1-\rho) > 0$ and the term $\log((v_2)/(1-\rho))$ is well-defined. Moreover, using the same reasoning exhibited in the study of previous Cases 1 and 2, it can easily checked that rates k_D and k_R^* are both positive, as required in the model setting. The Jacobian of the inverse mapping $\mathbf{s}$ is

$$J_2 = -\frac{\rho \log\left(\frac{v_2}{1-\rho}\right)^2}{C_{S_0} t^3 (1 - v_2 - \rho)^2}.$$

Then, given a fixed $\rho \in (0, 1)$, according to Theorem 1, the PDF of the random vector $(v_1(\omega), v_2(\omega))$ is given by

$$f_{v_1, v_2}(v_1, v_2) = f_{k_D, k_R^*}\left(\frac{(1 - v_2)\log\left(\frac{v_2}{1-\rho}\right)}{C_{S_0} v_1(-1 + v_2 + \rho)}, \frac{\rho \log\left(\frac{v_2}{1-\rho}\right)}{v_1(-1 + v_2 + \rho)}\right) \frac{\rho \left|\log\left(\frac{v_2}{1-\rho}\right)^2\right|}{C_{S_0} v_1^3 (1 - v_2 - \rho)^2}.$$

Marginalizing with respect to $v_2(\omega) = 1 - C_{S_0} k_D(\omega)/k_R^*(\omega) \rho$, we obtain the PDF of the time $T(\omega)$ in the conditional probability space $(\Omega, \mathcal{F}, \mathbb{P}[\cdot|C])$

$$f_T(t; \rho) = \int_0^\infty f_{k_D, k_R^*}\left(\frac{(1 - v_2)\log\left(\frac{v_2}{1-\rho}\right)}{C_{S_0} t(-1 + v_2 + \rho)}, \frac{\rho \log\left(\frac{v_2}{1-\rho}\right)}{t(-1 + v_2 + \rho)}\right) \frac{\rho \left|\log\left(\frac{v_2}{1-\rho}\right)^2\right|}{C_{S_0} t^3 (1 - v_2 - \rho)^2} dv_2. \tag{15}$$

Remark 1 Note that in our previous theoretical development the PDF, $f_T(t; \rho)$, has been calculated on a conditional probability space under the restriction defined by the event $C = \{\omega \in \Omega : 1 - C_{S_0} k_D(\omega)/k_R^*(\omega) \rho > 0\}$, however in practice once the distributions of input random variables $k_D(\omega)$ and $k_R^*(\omega)$ are fixed via appropriate probabilistic methods, the aforementioned condition must be checked prior to application of expression (15). This issue will be commented in the example exhibited in Sect. 3.

2.3 Distribution of the activity of the catalase $a(t, \omega)$

In formula (4) the deterministic activity of the catalase in terms of the solution $X = X(t)$ is introduced. Substituting the fractional conversion given in (6) and randomizing the input parameters, $k_D(\omega)$ and $k_R^*(\omega)$, we obtain the following expression for the randomized activity, $a(t, \omega)$, which is a stochastic process

$$a(t, \omega) = \frac{k_R^*(\omega) - C_{S_0} k_D(\omega)}{k_R^*(\omega) - C_{S_0} k_D(\omega) \, \mathrm{e}^{-(k_R^*(\omega) - C_{S_0} k_D(\omega))t}}. \qquad (16)$$

To compute the 1-PDF of $a(t, \omega)$, we first fix $t > 0$ and then we apply Theorem 1 with the following choice $\mathbf{u}(\omega) = (k_D(\omega), k_R^*(\omega))^\top$ and $\mathbf{v}(\omega) = (v_1(\omega), v_2(\omega))^\top$ and the mapping $\mathbf{r} : \mathbb{R}^2 \to \mathbb{R}^2$, $\mathbf{r} = (r_1, r_2)$, such that

$$v_1 = r_1(k_D, k_R^*) = \frac{k_R^* - C_{S_0} k_D}{k_R^* - C_{S_0} k_D \, \mathrm{e}^{-(k_R^* - C_{S_0} k_D)t}}, \;\; v_2 = r_2(k_D, k_R^*) = k_R^* - C_{S_0} k_D.$$

The inverse mapping $\mathbf{s} : \mathbb{R}^2 \to \mathbb{R}^2$ of $\mathbf{r}$, $\mathbf{s} = \mathbf{s}^{-1}$ is given by

$$k_D = s_1(v_1, v_2) = \frac{(1 - v_1)v_2}{(1 - \mathrm{e}^{-v_2 t})C_{S_0} v_1}, \qquad k_R^* = s_2(v_1, v_2) = v_2 + \frac{(1 - v_1)v_2}{(1 - \mathrm{e}^{-v_2 t})v_1}.$$

being its Jacobian $J_2 = \frac{-v_2}{v_1^2 C_{S_0}(1 - \mathrm{e}^{-tv_2})}$. Then, the PDF of random vector $\mathbf{v}(\omega)$, defined via the foregoing transformation, is

$$f_{v_1, v_2}(v_1, v_2) = f_{k_D, k_R^*}\left(\frac{(1 - v_1)v_2}{(1 - \mathrm{e}^{-v_2 t})C_{S_0} v_1}, v_2 + \frac{(1 - v_1)v_2}{(1 - \mathrm{e}^{-v_2 t})v_1}\right) \frac{|v_2|}{v_1^2 C_{S_0}|1 - \mathrm{e}^{-tv_2}|}.$$

Finally, marginalizing with respect to the second component of the random vector $\mathbf{v}(\omega)$, and taking $t > 0$ arbitrary, we obtain the 1-PDF of the activity of the catalase $a(t, \omega)$,

$$f_{a(t)}(a) = \int_{\mathcal{D}(v_2)} f_{k_D, k_R^*}\left(\frac{(1 - a)v_2}{(1 - \mathrm{e}^{-v_2 t})C_{S_0} a}, v_2 + \frac{(1 - a)v_2}{(1 - \mathrm{e}^{-v_2 t})a}\right) \frac{|v_2|}{a^2 C_{S_0}|1 - \mathrm{e}^{-tv_2}|} \mathrm{d}v_2, \qquad (17)$$

where $\mathcal{D}(v_2)$ denotes the domain of the random variable, $k_R^*(\omega) - C_{S_0} k_D(\omega)$, that must be contained in $\mathbb{R} \setminus \{0\}$.

2.4 Long-term behaviour of $X(t, \omega)$ and $a(t, \omega)$

An important issue in dealing with the dynamics of chemical reactions is to know the long-term behaviour of specific chemical quantities of interest. In our setting, we will study the asymptotic behaviour of the fractional conversion of hydrogen peroxide, $X(t, \omega)$, and the activity of the calatase, $a(t, \omega)$. Since both are stochastic quantities, the aforementioned asymptotic analysis will be performed from a probabilistic standpoint. To this end is convenient to introduce

the following probability $p_1 := \mathbb{P}[\{\omega \in \Omega : Y(\omega) := k_R^*(\omega) - k_D(\omega)C_{S_0} > 0\}]$ as well as the following RVs,

$$Z(\omega) := Y(\omega)/k_R^* = 1 - C_{S_0}k_D(\omega)/k_R^*(\omega), \ L(\omega) := k_R^*(\omega)/(C_{S_0}k_D(\omega)). \ (18)$$

Then taking into account expressions (7) and (16), one deduces that, in the long-term, the two following cases take place,

$$\text{Case 1:} \quad \begin{cases} X(t,\omega) \xrightarrow[t\to\infty]{} 1, \\ a(t,\omega) \xrightarrow[t\to\infty]{} Z(\omega), \end{cases} \quad \text{w.p. } p_1,$$

$$\text{Case 2:} \quad \begin{cases} X(t,\omega) \xrightarrow[t\to\infty]{} L(\omega), \\ a(t,\omega) \xrightarrow[t\to\infty]{} 0, \end{cases} \quad \text{w.p. } 1 - p_1,$$

where w.p. stands for "with probability". Notice that $\mathbb{P}[\{\omega \in \Omega : Y(\omega) = 0\}] = 0$ since $Y(\omega)$ is a continuous RV.

The value of probability p_1, corresponding to Case 1, i.e. when the fractional conversion tends to its maximum value and the activity of the catalase continues because of there is still hydrogen peroxide to be decomposed, can be computed by applying Theorem 1. Specifically, taking the mapping $\mathbf{r} : \mathbb{R}^2 \to \mathbb{R}^2$, $r_1(k_D, k_R^*) = k_R^* - k_D C_{S_0}$ and $r_2(k_D, k_R^*) = k_D$, one obtains

$$p_1 = \int_0^\infty f_Y(y)\mathrm{d}y, \text{ where } f_Y(y) = \int_0^\infty f_{k_D, k_R^*}(k_D, y + k_D C_{S_0})\,\mathrm{d}k_D. \quad (19)$$

Additionally, we can obtain the long-term (conditional) distribution of catalase, i.e. of RV, $Z(\omega)$, subject to condition $Y(\omega) > 0$ (restriction in Case 1). Indeed, first let us observe that the conditional PDF of $Z(\omega)|Y(\omega) > 0$ is given by

$$f_{Z|Y>0}(z) = \frac{\int_0^\infty f_{Z,Y}(z,y)\mathrm{d}y}{\int_0^\infty f_Y(y)\mathrm{d}y} = \frac{1}{p_1}\int_0^\infty f_{Z,Y}(z,y)\mathrm{d}y. \quad (20)$$

Now, we compute the joint PDF, $f_{Z,Y}$, taking advantage of Theorem 1 again. We now define the mapping $\mathbf{r} : \mathbb{R}^2 \to \mathbb{R}^2$ with $r_1(k_D, k_R^*) = (k_R^* - k_D C_{S_0})/k_R^* := Z$ and $r_2(k_D, k_R^*) = k_R^* - k_D C_{S_0} := Y$, whose Jacobian of the inverse transformation is given by $J_2 = -Y/(C_{S_0}Z^2)$. Therefore, the joint PDF is given by

$$f_{Z,Y}(z,y) = f_{k_D, k_R^*}\left(\frac{y(1-z)}{zC_{S_0}}, \frac{y}{z}\right)\left|\frac{-y}{C_{S_0}z^2}\right|.$$

Substituting this expression in (20), one gets

$$f_{Z|Y>0}(z) = \frac{1}{p_1}\int_0^\infty f_{k_D, k_R^*}\left(\frac{y(1-z)}{zC_{S_0}}, \frac{y}{z}\right)\frac{y}{C_{S_0}z^2}\mathrm{d}y.$$

Using an analogous reasoning, it is not difficult to obtain that the PDF of RV, $L(t,\omega)$ given that $Y(\omega) < 0$ (restriction in Case 2), is given by

$$f_{L|Y<0}(l) = \frac{1}{1-p_1}\int_{-\infty}^0 f_{k_D, k_R^*}\left(\frac{y}{C_{S_0}(-1+l)}, \frac{ly}{-1+l}\right)\frac{-y}{C_{S_0}(1-l)^2}\mathrm{d}y,$$

which provides the asymptotic distribution of fractional conversion in the case that the hydrogen peroxide is decomposed and the activity of the catalase finishes.

3 Application to real data

In this section, all the theoretical results established in Sect. 2 will be applied to model the reaction and deactivation by catalase of hydrogen peroxide decomposition at a given initial concentration using real data. In Table 1 we show data of fractional conversion of hydrogen peroxide, X_i, for different time instants t_i, $i \in \{1, 2, \ldots, 6\}$, in hours. In reference [11, Fig.2], the author obtained this data from an experimental analysis. This process is achieved under a given isothermal conditions and it takes place in a spectrophotemeter tank or isothermal bath reactor. The experiment has been carried out at $40°\text{C}$ taking as initial concentration of hydrogen peroxide $C_{S_0} = 0.015$ mol/L by *aspergillus niger* catalase $C_{E_0} = 2.5\text{U/mL}$.

t_i	0.24	0.49	0.74	0.99	1.24	1.48
X_i	0.30	0.48	0.61	0.68	0.73	0.74

Table 1 Fractional conversion X_i, for 0.015 mol/L hydrogen peroxide decomposition at $40°\text{C}$ by catalase 2.5U/mL for different time instants t_i, $i \in \{1, 2, \ldots, 6\}$, in hours. Source [11].

In order to apply results about the 1-PDFs determined in Sect. 2, it is necessary to establish the joint distribution of the random vector $(k_D(\omega), k_R^*(\omega))$. For the sake of clarity and simplification in our subsequent computations, we will assume that both parameters are independent random variables, therefore, as it has been indicated in the introduction, the joint PDF can be calculated as the product of their corresponding marginal PDFs. To obtain the PDF of each random input parameter, $(k_D(\omega), k_R^*(\omega))$, we will apply the Principle of Maximum Entropy (PME) [10]. Let $Y(\omega)$ be an absolutely continuous random variable, then according to PME, we seek for a function $g_Y(y)$, which represents the PDF of $Y(\omega)$, by maximizing the Shannon functional $S(g_Y)$, which represents the entropy,

$$\max \ S(g_Y) = -\int_{a_1}^{a_2} g_Y(y) \log(g_Y(y)) \, \mathrm{d}y, \tag{21}$$

subject to certain restrictions, as the integrability condition for $g_Y(y)$ so that it represents a PDF, and further information on statistics of the random variable, $Y(\omega)$, such as its mean and higher moments.

$$\int_{a_1}^{a_2} g_Y(y) \, \mathrm{d}y = 1, \quad \mathbb{E}\left[(Y(\omega))^k\right] = \int_{a_1}^{a_2} y^k g_Y(y) \, \mathrm{d}y = m_k, \quad k = 1, 2, \ldots, K. \tag{22}$$

In practice, the values m_k as well as the domain, $\mathcal{D}(Y(\omega)) = (a_1, a_2)$, $-\infty \leq a_1 < a_2 \leq \infty$, of random variable $Y(\omega)$ are obtained taking into account all the available information about the statistical problem and/or the sampling process. In our example, we will apply the PME with $K = 1$. Solving the optimization functional programme (21) and (22), by means of the Lagrange multiplier technique, it is easy to check that

$$g_Y(y) = \mathbb{1}_{[a_1,a_2]}\, e^{-1-\lambda_0-\lambda_1 y}, \qquad \mathbb{1}_{[a_1,a_2]}(y) = \begin{cases} 1 & a_1 \leq y \leq a_2, \\ 0 & \text{otherwise,} \end{cases}$$

where the so called Lagrange multipliers, λ_0, λ_1 and λ_2, are calculated by solving the following non-linear system

$$\int_{a_1}^{a_2} e^{-1-\lambda_0-\lambda_1 y}\, \mathrm{d}y = 1, \qquad \int_{a_1}^{a_2} y\, e^{-1-\lambda_0-\lambda_1 y}\, \mathrm{d}y = m_1. \qquad (23)$$

Let us assume that m_1 is known (later, we will show how to calculate it). Observe that system (23) has then four unknowns, a_1, a_2, λ_0 and λ_1. However, computing the two integrals appearing on the left-hand side in (23), we can express λ_0 and a_2, in terms of a_1 and λ_1

$$\lambda_0(a_1, \lambda_1) = -1 + \log\left(\frac{e^{-a_1\lambda_1} - e^{-a_2(a_1,\lambda_1)\lambda_1}}{\lambda_1}\right), \qquad (24)$$

$$a_2(a_1, \lambda_1) = \frac{-1 + m_1\lambda_1 - W_{-1}(e^{-1-a_1\lambda_1+m_1\lambda_1}(-1+a_1\lambda_1+m_1\lambda_1))}{\lambda_1}, \quad (25)$$

where $W_k(x)$ denotes the Lambert function, which is a multivalued function, namely the branches of the inverse relation of the function $w\, e^w$ [2]. That is, for each integer k, there is one branch, $W_k(z)$, with the following property: if z and w are any complex numbers, then

$$w\, e^w = z \text{ holds if and only if } w = W_k(z), \text{ for some integer } k.$$

W_0 is known as the principal branch, and it gives the principal solution for w in $z = w\, e^w$. In the set of real numbers, two branches W_0 and W_{-1} are sufficient. Equation $x = y\, e^y$ can be solved only if $x \geq -1/\,e$, in addition if $x \geq 0$ the solution is $y = W_0(x)$, but if $-1/\,e \leq x < 0$ the equation has two solutions, $W_0(x)$ and $W_{-1}(x)$. In this example, to ensure that $a_2(a_1, \lambda_1) > a_1$, so that the domain (a_1, a_2) makes sense, we select the solution W_{-1}.

Now, we compute the value of m_1 for each random variable, $k_D(\omega)$ and $k_R^*(\omega)$. For the sake of clarity, hereinafter these values will be denoted by $m_{1,D}$ and $m_{1,R}$, respectively. As m_1 represents an expectation (see (23)), so $m_{1,D}$ and $m_{1,R}$ are deterministic, and then we approximate them by minimizing the normalized mean square error between the data and the deterministic solution in each time instant

$$\min_{k_D, k_R^* > 0} \quad \sum_{i=1}^{6} \left(\frac{X_i - X(t_i; k_D, k_R^*)}{X_i}\right)^2, \qquad (26)$$

where $X(t_i; k_D, k_R^*)$ is obtained by evaluating the first expression in (6) at $t_1 = 0.24$, $t_2 = 0.49$, $t_3 = 0.74$, $t_4 = 0.99$, $t_5 = 1.24$ and $t_6 = 1.48$ (see Table 1). We must point out that other objective error functions are also plausible, like the mean square error, however, for the sake of consistency, we here consider its normalized value as in reference [11]. Solving the optimization programme (26), we obtain $m_{1,D} = k_D = 96.3324$ and $m_{1,R} = k_R^* = 1.75125$.

Finally, to completely determine the PDFs of each random input parameter, we calculate $\{a_{1,D}, \lambda_{1,D}\}$ and $\{a_{1,R}, \lambda_{1,R}\}$ for each random variable, $k_D(\omega)$ and $k_R^*(\omega)$, respectively. To this aim, and motivated by the deterministic fitting, we minimize the normalized mean square error between the data and the expectation of the solution stochastic process, $X(t_i; a_{1,D}, \lambda_{1,D}, a_{1,R}, \lambda_{1,R})$ (where for convenience in the notation with have highlighted the parameters to be determined and hidden the ω-notation). That is, we solve the following optimization programme

$$\min_{a_{1,D}, \lambda_{1,D}, a_{1,R}, \lambda_{1,R} > 0} \sum_{i=1}^{6} \left(\frac{X_i - \mathbb{E}\left[X(t_i; a_{1,D}, \lambda_{1,D}, a_{1,R}, \lambda_{1,R}) \right]}{X_i} \right)^2 .$$

Utilizing the Nelder Mead algorithm, implemented in Mathematica© Software, we have obtained $a_{1,D} = 62.552840$, $\lambda_{1,D} = 0.029604$, $a_{1,R} = 1.565847$ and $\lambda_{1,R} = 0.004471$. The rest of parameters are calculated by substituting these values in expressions (24) and (25), this yields $a_{2,D} = 574.657$, $\lambda_{0,D} = 0.66807$, $a_{2,R} = 1.93675$ and $\lambda_{0,R} = -0.000362$. Summarizing, the PDFs of the random variables, $k_D(\omega)$ and $k_R^*(\omega)$, are

$$f_{k_D}(k_D) = \begin{cases} e^{-1.66807 - 0.029604 k_D} & 62.5528 \leq k_D \leq 574.657, \\ 0 & \text{otherwise}, \end{cases} \tag{27}$$

$$f_{k_R^*}(k_R^*) = \begin{cases} e^{-0.999638 - 0.004471 k_R^*} & 1.56585 \leq k_R^* \leq 1.93675, \\ 0 & \text{otherwise}. \end{cases} \tag{28}$$

In agreement with the general theory of PME, these PDFs correspond to truncated exponential distributions since $k_D(\omega)$ and $k_R^*(\omega)$, are positive random variables defined on finite intervals. In the case of $k_R^*(\omega)$, we observe that it approximately distributes as a uniform distribution since $\lambda_{1,R} \approx 0$. In Fig. 1, we have plotted both PDFs.

Fig. 2 shows the 1-PDF, $f_{X(t)}(x)$, of the fractional conversion of hydrogen peroxide, $X(t, \omega)$, given in expression (12). This density has been calculated from the PDF of the random inputs parameters indicated in formulas (27) and (28). This graphical representation has been calculated at the time instants t_i, $i \in \{1, 2, \ldots, 6\}$, indicated in Table 1. From this 3-D graphical representation, we observe that rate $X(t, \omega)$ and its variability increase over the time. This behaviour is better observed in Fig. 3 where the expectation, $\mu_X(t)$, and 95% confidence intervals are plotted together with the real data collected in Table 1. The expectation function has been computed via (8) while 95% confidence intervals have been computed using expression (9) with $\alpha = 0.05$ at $\hat{t} = t_i$, $i \in \{1, 2, \ldots, 6\}$, respectively. In both plots, we can see that the confidence
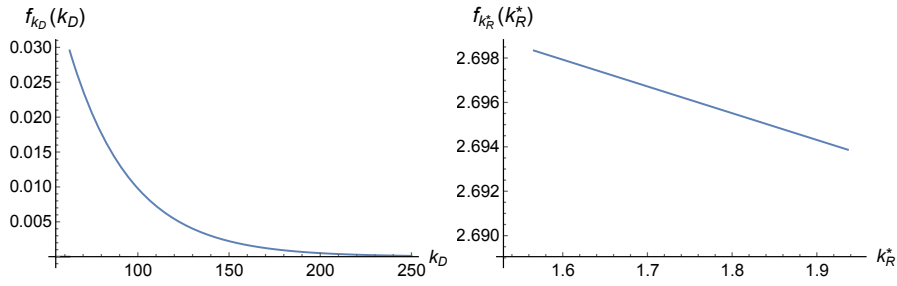
Fig. 1 PDFs of the random variables, $k_D(\omega)$ and $k_R(\omega)$, $f_{k_D}(k_D)$ (left) and $f_{k_R^*}(k_R^*)$ (right), given in (27) and (28), respectively. Both correspond to truncated exponential distributions.

intervals, built at every time instant t_i, are not symmetric, which clearly indicates that we are not dealing with a Gaussian distribution.
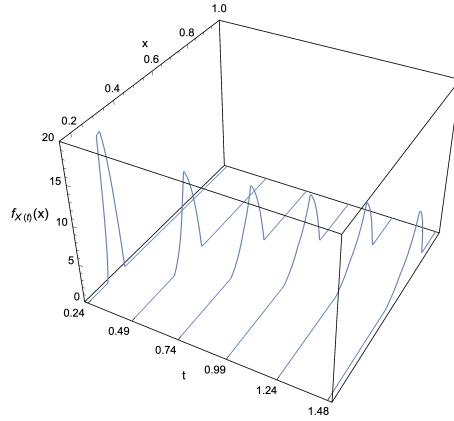

Fig. 2 Graphical representation of PDF, $f_{X(t)}(x)$, of the solution stochastic process $X(t,\omega)$ given in (12) for the different time instants t_i, $i \in \{1, 2, ..., 6\}$ (in hours) indicated in Table 1.

In Fig. 4, we show the PDF of the time, $T(\omega)$, until a given fractional conversion of hydrogen peroxide $\rho \in (0, 1)$ is reached. This plot has been done for the following values of $\rho \in \{0.3, 0.48, 0.61, 0.68, 0.73, 0.74\}$, that just correspond to the ones listed in Table 1. In this way we check the consistency of the numerical results. In this graphical representation we see that the mean and the variance increase when the fractional conversion of hydrogen peroxide does. For instance, we calculate the conditional expectation of $T(\omega)$ for $\rho = 0.68$, $\mathbb{E}[T(\omega)|C] = \int_0^\infty t f_T(t; 0.68) dt = 1.128431$. Therefore, it takes just over an hour to reach the fractional conversion of hydrogen peroxide level $\rho = 0.68$. In Table 2 we have computed $\mathbb{E}[T(\omega)|C]$ for different values of ρ. Table 2 also shows the probability of event $C = \{\omega \in \Omega : W(\omega) > 0\}$ being $W(\omega) =$
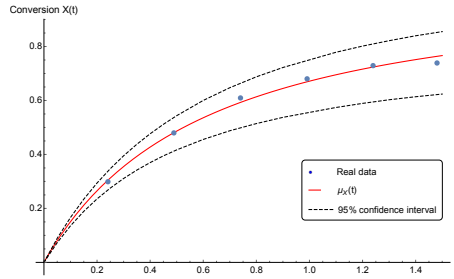
Fig. 3 Probabilistic fitting using real data collected in Table 1 (blue points). Expectation (red solid line) and 95% confidence interval (dashed black lines). Time is measured in hours.

$1 - C_{S_0} k_D \omega / k_R^*(\omega)\rho$, that is, we calculate

$$\mathbb{P}\left[C\right] = \mathbb{P}\left[\{\omega \in \Omega : W(\omega) > 0\}\right] = \mathbb{P}\left[\{\omega \in \Omega : 1 - C_{S_0} k_D(\omega)/k_R^*(\omega)\rho > 0\}\right],$$

for different values of ρ. We observe that for large values of ρ in the interval $(0,1)$ the probability of the event C is different of 1. Then, in these cases the mean of the RV $T(\omega)$ shall be computed as the quotient between $\mathbb{E}[T|C]$, calculated directly from the PDF $f_T(t;\rho)$, and $\mathbb{P}[C]$, i.e., $\mathbb{E}[T|C] = \mathbb{E}[T \cdot \mathbb{1}_C]/\mathbb{P}[C]$ where $\mathbb{1}_C$ is the characteristic function for event C.
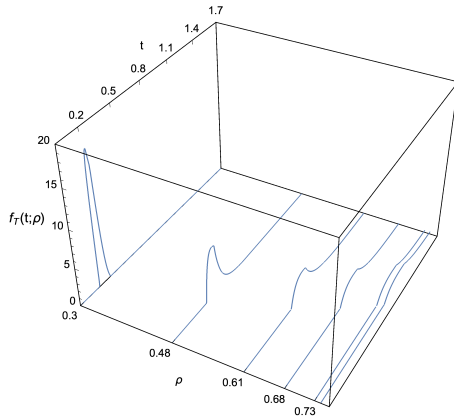
Fig. 4 PDF, $f_T(t;\rho)$, of the time $T(\omega)$ (in hours) for different fractional conversions fixed $\rho \in \{0.3, 0.48, 0.61, 0.68, 0.73, 0.74\}$.

Furthermore, in Fig. 5 we have represented the activity of the catalase, $a(t,\omega)$. As expected, we can observe that the activity tends to decrease as time increases. This is because as time goes on there is less hydrogen peroxide to be decomposed. The mean and the variance of the stochastic process $a(t\omega)$ have been plotted in Fig. 6.

ρ	0.3	0.48	0.61	0.68	0.73	0.74
$\mathbb{P}[C]$	≈ 1	≈ 1	≈ 1	0.995641	0.979157	0.974381
$\mathbb{E}[T|C]$	0.237878	0.498751	0.829759	1.128431	1.410168	1.474823

Table 2 Expectation of the time $T(\omega)$ (in hours) until a given fractional conversion of hydrogen peroxide level ρ is reached, for different values of ρ, on the conditional space $(\Omega, \mathcal{F}, \mathbb{P}[\cdot|C])$. $\mathbb{P}[C]$ is the probability of event C on the probability space $(\Omega, \mathcal{F}, \mathbb{P})$.
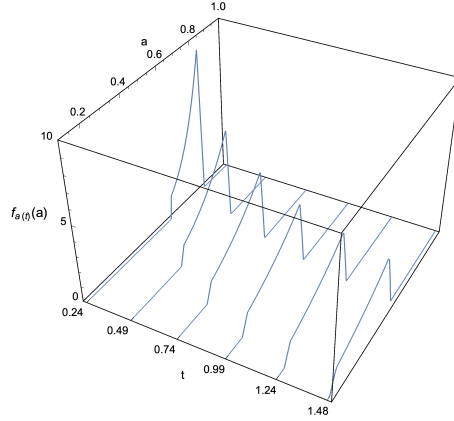
Fig. 5 PDF, $f_{a(t)}(a)$, of the activity of the catalase $a(t, \omega)$ given in expression (17) for different fixed time instants t_i, $i \in \{1, 2, ..., 6\}$ (in hours) indicated in Table 1.
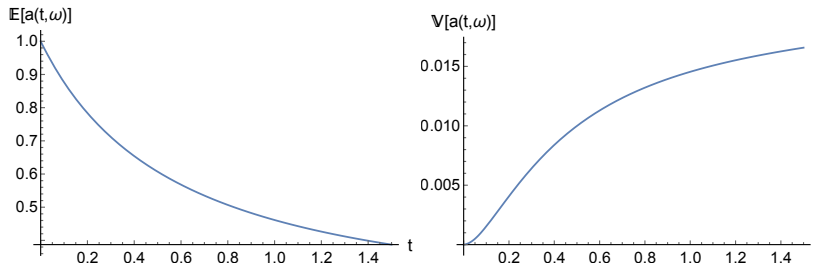

Fig. 6 Mean (left) and variance (right) of the activity of the catalase $a(t, \omega)$ in the time interval $[0, 1.5]$ (in hours).

To analyse the long-term behaviour of $X(t, \omega)$ and $a(t, \omega)$, according to findings developed in Subsect. 2.4, we first need to calculate, using (19), the probability $p_1 = \mathbb{P}[Y(\omega) > 0] = 0.794479$, associated to Case 1. This means that is more likely the randomized fractional conversion, $X(t, \omega)$, tends to its maximum value 1 (corresponding to Case 1) than converging to RV $L(\omega)$, defined in (18), whose probability of occurrence is $1 - p_1 = \mathbb{P}[Y(\omega) < 0] = 0.205522$ (corresponding to Case 2). We can observe in Fig. 3 that $\mathbb{E}[X(t, \omega)]$ tends approximately to 0.8, which is the mean of RV $L(\omega)|Y(\omega) < 0$. In

Fig. 7 (right) we have represented this RV. In Fig. 7, the PDFs of the RVs $Z(\omega)$ (left) and $L(\omega)$ (right) have been plotted. They represent the asymptotic distributions of $a(t,\omega)$ (Case 1) and $X(t,\omega)$ (Case 2), respectively. In both figures the conditional PDFs calculated in Subsect. 2.4 are plotted in red colour.
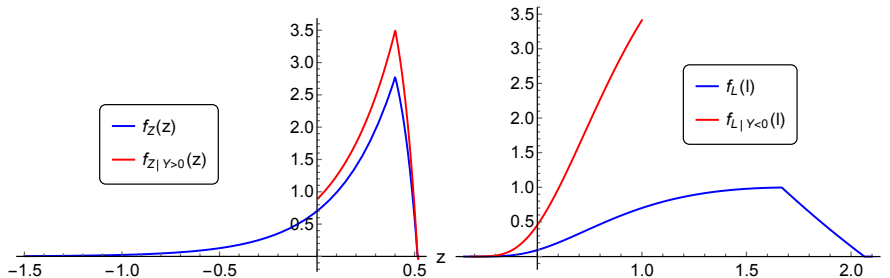

Fig. 7 Left: PDFs of RV $Z(\omega)$ (blue) and $Z(\omega)|Y(\omega) > 0$ (red). Right: PDFs of RV $L(\omega)$ (blue) and $L(\omega)|Y(\omega) < 0$ (red).

Finally, we point out that in the computation of all the PDFs shown throughout this example, we have checked that $\int_{\mathcal{D}_X} f_{X(t)}(x)\,\mathrm{d}x = 1$, for every time instants $t = t_i$, $i \in \{1, 2, \ldots, 6\}$ (see Table 1). In the case of RV $T(\omega)$, as it is defined on the conditional space $(\Omega, \mathcal{F}, \mathbb{P}[\cdot|C])$, the testing condition for each ρ fixed is $(\int_{\mathcal{D}(T)} f_T(t; \rho)\,\mathrm{d}t)/(\int_0^\infty f_W(w; \rho)\,\mathrm{d}w) = 1$, begin $f_W(w; \rho)$ the PDF of the RV $W(\omega) = 1 - C_{S_0} k_D \omega / k_R^*(\omega)\rho$.

4 Conclusions

In this paper we have proposed the randomization of a reaction-deactivation of hydrogen peroxide decomposition model based on the kinetic equation by treating the reaction and deactivation rates as random variables with known probability distributions. We have obtained closed-form expressions for the probability density functions of certain important quantities that describe the chemical process. Furthermore, we have shown how to apply the obtained theoretical results in order to provide a more complete and realistic description of the reaction-deactivation process, using real data excerpted from the recent literature. Indeed, our approach permits to calculate, not only reliable punctual and probabilistic predictions (via the expectation and confidence intervals, respectively), but also determining the probability density function of relevant chemistry quantities, which, to be best of our knowledge is rarely given in the mathematical studies. Our analysis may be extended to study other important chemical processes, and in this sense we think that can open new avenues in the realm of mathematical modelling in Chemistry.

Conflict of interest

The authors declare that they have no conflict of interest.

References

1. Berzelius, J.J.: Sur un force jusq'ici peu remarquée qui est probablement active dans la formation des composés organiques. Jahres-Bericht **14**, 237 (1835)
2. de Bruijn, N.G.: Asymptotic Methods in Analysis, *Dover Books on Mathematics*, vol. 27. Dover Publications Inc. (2003)
3. Casabán, M.C., Cortés, J.C., Navarro-Quiles, A., Romero, J.V., Roselló, M.D., Villanueva, R.J.: A comprehensive probabilistic solution of random SIS-type epidemiological models using the Random Variable Transformation technique. Communications in Nonlinear Science and Numerical Simulation **32**, 199–210 (2016). DOI 10.1016/j.cnsns.2014.12.016
4. Chelikani, P., Fita, I., Loewen, P.C.: Diversity of structures and properties among catalases. Cellular and Molecular Life Sciences **61**(2), 192–208 (2004)
5. Cortés, J.C., Navarro-Quiles, A., Romero, J.V., Roselló, M.D.: A probabilistic analysis of a Beverton-Holt–type discrete model: Theoretical and computing analysis. Computational and Mathematical Methods **1**(1), e1013 (2019). DOI 10.1002/cmm4.1013
6. Dorini, F.A., Cecconello, M.S., Dorini, L.B.: On the logistic equation subject to uncertainties in the environmental carrying capacity and initial population density. Communications in Nonlinear Science and Numerical Simulation **33**, 160–173 (2016). DOI 10.1016/j.cnsns.2014.12.016
7. Hussein, A., Selim, M.M.: A general probabilistic solution of randomized radioactive decay chain (RDC) model using RVT technique. European Physics Journal Plus **35**, 1–16 (2020). DOI 110.1140/epjp/s13360-020-00389-6
8. Kakaei, K., Esrafili, M.D., Ehsani, A.: Chapter 1 - Introduction to catalysis. In: K. Kakaei, M.D. Esrafili, A. Ehsani (eds.) Graphene Surfaces, *Interface Science and Technology*, vol. 27, pp. 1 – 21. Elsevier (2019). DOI https://doi.org/10.1016/B978-0-12-814523-4.00001-0
9. Leeuwen, P.W.: Homogeneous Catalysis: Understanding. Springer Science & Business Media (2006)
10. Michalowicz, J.V., Nichols, J.M., Bucholtz, F.: Handbook of Differential Entropy. CRC Press (2013)
11. Milek, J.: Estimation of the kinetic parameters for H_2O_2 enzymatic decomposition and for catalase deactivation. Brazilian Journal of Chemical Engineering **35**(3), 995–1004 (2018). DOI https://doi.org/10.1590/0104-6632.20180353s20160617
12. Soong, T.T.: Random Differential Equations in Science and Engineering. Academic Press, New York (1973)