DEVELOPMENT OF A STATISTICAL NON-ISOTHERMAL KINETIC MODEL USING THE MONTE-CARLO METHOD FOR MODELING CELLULOSE PYROLYSIS

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Dedicatoria

A mis padres y mi hermana, porque sin ellos nada de esto sería posible.

Mi abuelo, que me acompañó hasta donde pudo, sin su apoyo y la sazón de sus comidas este camino no hubiese sido el mismo.

Mis compañeros y ahora colegas, una parte de ustedes siempre estará presente en cada una de mis acciones, y lo mejor, las risas nunca faltaron.

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Resumen

Título: Desarrollo de un modelo cinético estadístico no isotérmico usando el método de Monte-Carlo para modelado de pirolisis de celulosa[*].

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Palabras clave: Pirolisis, modelado, estadística, celulosa, cinética

Descripción: Las enormes emisiones de gases de efecto invernadero están provocando el calentamiento global, esto se debe al uso de combustibles fósiles durante la generación de energía. Una alternativa a los combustibles fósiles es la biomasa, que puede proporcionar combustibles sólidos, líquidos y gaseosos que permiten la generación de energía térmica y eléctrica. La pirólisis es un proceso de degradación térmica que permite la transformación de la biomasa en biogás, biocombustible o biocarbón para producir energía. Los modelos cinéticos agrupados se centran en la cantidad de productos de pirólisis y requieren solo tres parámetros principales: energía de activación, factor preexponencial y modelo de reacción y estos pueden determinarse mediante análisis termogravimétrico (TGA). Sin embargo, la mayoría de los métodos tradicionales para resolver estos modelos son aproximaciones numéricas para sistemas no isotérmicos, mientras que los métodos estadísticos convierten la expresión en una función de densidad de probabilidad cuyo principal parámetro son los parámetros cinéticos, permitiendo la estimación de intervalos de confianza. El objetivo principal de este proyecto fue desarrollar un método cinético estadístico usando un modelo reaccional agrupado con el algoritmo Monte-Carlo usando parámetros cinéticos obtenidos por el método de iso-conversion usando información de pirólisis de biomasa de celulosa aislada obtenida de TGA a cuatro velocidades de calentamiento diferentes para calcular los parámetros cinéticos, se desarrolló el algoritmo en Matlab y se comparó el ajuste con los datos experimentales y se utilizó un método de ajuste para estimar los parámetros cinéticos que lo mejoran. Los resultados muestran que el modelo cinético elegido permite la implementación del algoritmo Monte-Carlo para estimar la conversión en valores de tiempo específicos y la relación con el requerimiento de números aleatorios y temperatura.

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Abstract

Title: Development of a statistical non-isothermal kinetic model using the Monte-Carlo method for modeling cellulose pyrolysis[*].

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Key words: Pyrolysis, modeling, statistical, cellulose, kinetic**.**

Description: The huge emissions of greenhouse gases are causing global warming, this is due to the use of fossil fuels during energy generation. An alternative to fossil fuels is biomass, it can provide solid, liquid and gases fuels allowing heat and electricity energy generation. Pyrolysis is a thermal degradation process which allows transformation of biomass into biogas, biofuel, or biochar to produce energy. Lumped kinetic models focus on the quantity of the pyrolysis products and just require three main parameters: energy activation, preexponential factor and reaction model and can be determined by thermogravimetric analysis (TGA). However, most of the traditional methods to solve these models are numerical approximations for non-isothermal systems, while statistical methods become the expression into a probability density function which main parameter are the kinetic parameters, allowing the estimation of confident intervals. The main objective of this project was developing a statistical kinetic method using a lumped reactional model with the Monte-Carlo algorithm using kinetic parameters obtained from iso-conversional methods using isolated cellulose biomass pyrolysis information obtained from TGA at four different heating rates to calculate the kinetic parameters, the algorithm was developed in Matlab and the adjustment was compared with the experimental data and a fitting method was used to estimate the kinetic parameters which improve the adjustment. The results show that the chosen kinetic model allows the implementation of the Monte-Carlo algorithm to estimate conversion at specific time values and the relation with the requirement of random numbers and temperature.

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Introduction

The use of fossil fuels in energy generation is one of the main causes of the global warming due to the emission of huge quantities of greenhouse gases. The emissions of these gases were reported over 500 billion tons in just 2016, about 76 % related to anthropogenic carbon emissions (IMF, 2019). As a preventive measure, the *Paris agreement* was created in the United Nations Framework Convention on Climate Change in 2015 (COP21), in which the signatory countries, including Colombia, seek to keep the increase of the global surface temperature below 2°C through the development of sustainable industrial and energy processes (United Nations, 2016).

The solar radiation incident on the earth is absorbed and transformed into other types of energy. This is the case of plants, which through the process of photosynthesis capture solar radiation, store it, and use it as a motor in their internal biochemical processes (Jenkins et al., 1998). This energy can be used in various ways, one of them, and one of the oldest, is through the combustion of biomass. However, combustion in traditional furnaces is not efficient and generates high greenhouse gas emissions (Jenkins et al., 1998). An alternative to combustion is pyrolysis, a thermochemical process in which the fast thermal degradation of biomass occurs in an inert atmosphere producing liquid fuels (bio-oil) mainly, gases and biochar (Rueda-Ordóñez et al., 2015).

Biomass is an alternative highly flexible and viable in energy generation: it can provide solid, liquid, and gases fuels allowing heat and electricity energy generation; it helps in poverty reduction in developing countries; it can meet energy needs without expensive conversion equipment and many more (Demirbas et al., 2009). Currently, about 13% of world energy demand is supplied by biomass (Demirbas et al., 2009) and in Colombia, around 0.77% of energy is generated from sugarcane bagasse combustion (PNUD, 2018). However, according to the Mining and Energy Planning Unit (UPME), the biomass from the residues of some representative species of the agricultural sector in the country is around 144 Mt/year (2006); with an energy potential of around 675,000 TJ/year (Unidad de Planeación Minero Energética UPME, 2005). This potential can be exploited through thermochemical degradation processes.

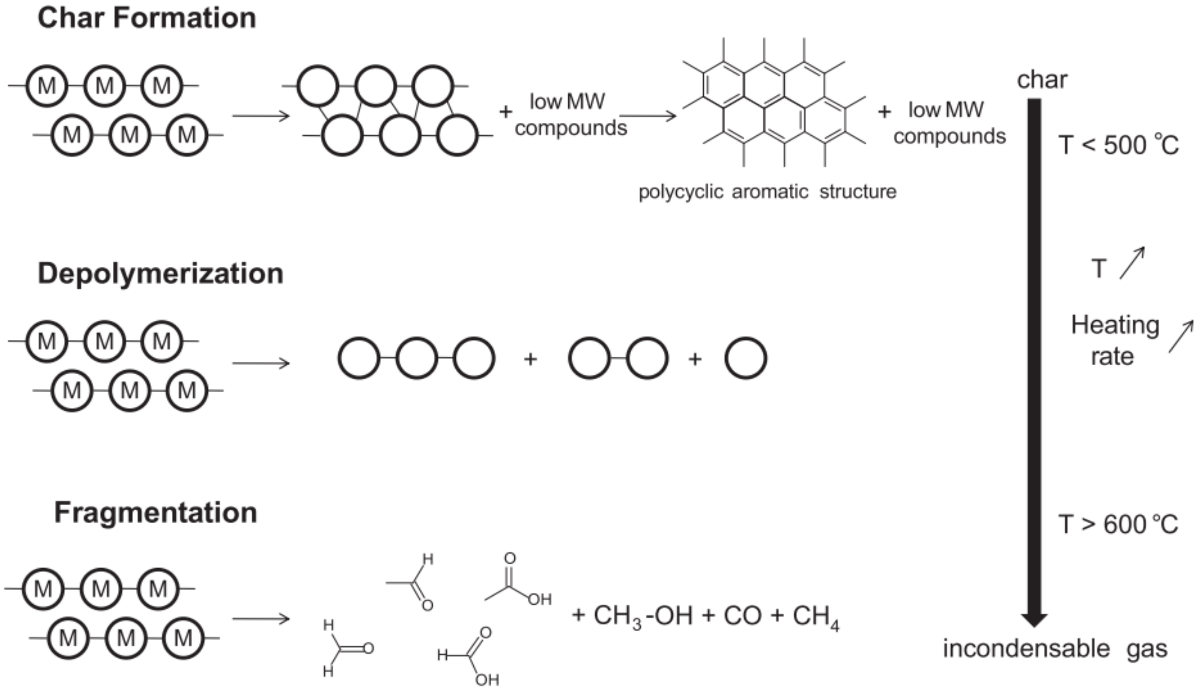
Pyrolysis is a thermal degradation process carried out in an inert atmosphere, normally using Nitrogen or Argon as an inert gas. Unlike other thermochemical methods, the temperature used in pyrolysis has the lowest operation range, normally between 573-973 K (Sharma et al., 2015), (di Blasi, 2008) while gasification and combustion are over 973 K and 1173 K, respectively (Sharma et al., 2015).

Lignocellulosic biomass is all the organic material, from stems to the whole plant, such as wood, herbaceous species, bagasse, agricultural residues, aquatic plants, bio-solids, etc., and that can be converted into useful fuel (di Blasi, 2008) (Yaman, 2004). In chemical terms, it is a mixture of Carbon, Hydrogen, and Oxygen with a low content of Sulphur, Nitrogen, and inorganics (Sharma et al., 2015); different from fossil fuels that produce significant amounts of greenhouse gases such as NO_x and SO_x (Jenkins et al., 1998). Generally, biomass consists of three main groups of natural polymeric materials: cellulose which constitutes about 50 wt.% on a dry basis, hemicelluloses between 10-30 wt.% in woods on a dry basis and lignin with a content of 20-40 wt.% composition on dry basis (Yaman, 2004). It also contains small organic molecules of proteins, acids, salts, and some inorganic compounds such as alkali and alkaline earth metals, which content can vary between less than 1 wt.% and up to 25 wt.% depending on the kind of biomass.

During pyrolysis, the biopolymers exhibit thermoplastic or thermosetting behavior, the solid biomass particles pass through a liquid phase as it decomposes or not. The reactions in this process are classified into two groups: primary and secondary reactions (Collard & Blin, 2014). In the first stage, the biopolymer bonds are broken, and volatile compounds are released while the residual matter passes through rearrangement reactions. This stage is also described by three main pathways: char formation, depolymerization, and fragmentation. In the secondary reactions, the unstable volatile compounds formed through primary mechanisms can undergo cracking or re-polymerization reactions depending on the reactor temperature. **Figure *1*** shows the common reaction pathways and their reaction intervals. The operation conditions such as temperature, reactor configuration, particle size, residence time, etc. define the yield and quality of pyrolysis products (Collard & Blin, 2014).

Figure 1

Primary mechanisms reactions pathways in pyrolysis processes



Nota. M: monomer; MW: molecular weight. Extracted from (Collard & Blin, 2014)

Pyrolysis process can be classified in two groups: fast pyrolysis and convention or slow pyrolysis. In fast pyrolysis process, the heating rate (~500°C/s) and heat transfers are fast; then favoring the devolatilization of solids. Residence time of products in the vapor phase should be short (<2 seconds) and they have to be rapidly condensed to maximize the yield of liquid products as biofuel. Otherwise, a long residence time of products in this phase allows the occurrence of repolymerization and cracking (e.i. secondary reactions) resulting in higher yield of solids or non-condensable gases products, respectively (Hoekstra et al., 2012). In the other hand, in conventional pyrolysis, the heating rate is slow (< ~0.15 °C/s) and the residence time of solid and volatiles long. To achieve a specific product yield is necessary to choose the correct type of reactor considering the mentioned conditions and other parameters. Fixed-bed reactors are used to carry out conventional pyrolysis, the heating particle rate is slow due to the indirect heating and residence time, which are very long. In this configuration, heat is transferred by convection (72-84%) and radiation (16-28%), conduction is negligible (Gouws et al., 2021). Slow heating of the solid matrix allows the weakest chemical bonds to break and the polymer is just slightly transformed into a more stable matrix through rearrangement reactions (Collard & Blin, 2014). Conversely, the entrained-flow reactor has a residence time very short (<1 s) and the heating rate is fast. Its configuration allows a heat transfer close to a pure convection regime (99%), with fast heating rate (>100°C/s). Under those conditions, many bonds are broken simultaneously releasing many volatile compounds and the short residence time prevents rearrangement reactions of happening. Besides those reactors, the Fluidized Bed Reactor is a configuration using intermediate heating rates and residence time that results in similar solid reaction time and volatile residence time and subsequently in different products yield compared to the other two reactors. **Table *1*** shows the yields of the three main pyrolysis products according to the reactor configuration, there can be noticed how the configuration maximizes these yields following the reactions described.

Table 1

Yield of pyrolysis products according to the operation conditions and heat transfers modes

Reactor type	Pyrolysis type	Product yield (%)			Estimated contribution of heat transfer mode (%)[a]		
		Liquid	Solid	Gas	Conduction	Convection	Radiation
Fluidized bed	Fast	40 - 75	10 - 22	8 - 34	77	17	6
Entrained	Flash	10 - 40	8 - 30	16 - 44	0	99	1
Fixed bed	Slow	18 - 35	25 - 43	11 - 38	0	79	21

Nota. [a.] Process carry out at 500°C. Adapted from (Gouws et al., 2021).

The variability in pyrolysis systems makes necessary the development of modeling tools to estimate optimized conditions for a targeted product. That is why the implementation of mathematical models and simulation becomes necessary to improve, optimize and design efficient pyrolysis plants at large, medium or laboratory scale. Furthermore, simulation and modelling along with the implementation of different strategies allow the control of yield and reactor performance predictions bringing a quantitative representation of the chemical and physical phenomena.

Objectives

General objective

Develop a statistical kinetic method using a lumped reactional model with the Monte-Carlo algorithm to predict yields of biomass pyrolysis. This first step is looking for lay the foundations of the model using cellulose to optimize and validate the results, obtaining the kinetic parameters using iso-conversional methods.

Specified objectives

- Define a kinetic model based on the Monte-Carlo method that allows modeling pyrolysis of biomass using iso-conversional methods to obtain the kinetic parameters.
- Develop an algorithm using the kinetic Monte-Carlo model to predict biomass pyrolysis and calculate conversion profiles.
- Validate the model developed using cellulose pyrolysis of biomass in a wide range of decomposition temperature using experimental data at different heating rates.

1. Kinetic, modeling and simulation

Modelling pyrolysis process helps understanding the mechanism of primary and secondary reactions; the heat and mass transfer phenomena that affect the reactions involved; predicting products according to the feedstock conditions or allowing the adjustment of operation conditions to drive an optimal operation and much more applications.

1.1. Modelling scale

Chemical reactions are affected by the velocity of physical and chemical processes, and pyrolysis reactions are not an exception. Physical processes are mass and heat transfer, and they could be described using transport phenomena, while chemical part is detailed by chemical kinetics models (Perry & Green, 2008). To understand the complexity of pyrolysis reactions those events are studied using mathematical models at different scales and with different approaches. Hameed et al. (Hameed et al., 2019) classified pyrolysis models according to three level scales: molecular, particle and reactor level; considering what the models can describe: the complexity and the required parameters.

1.1.1. Molecular level

At this level, models focus on explaining the primary and secondary reactions at a molecular scale seeking an understanding of the pyrolysis reaction mechanisms. Here can be found the mechanistic models, these models can explain the elementary reactions, including all the reactions pathways and the formed compounds. Normally, they are based on two methods: electronic structure calculation (or density functional theory) and molecular mechanism. It helps create a solid scheme reaction predicting products and the intermediate steps, and also calculating theorical kinetics parameters. However, Mechanistic models are mainly focus on the gas phase reactions and in the model compound (Hameed et al., 2019).

1.1.2. Particle level

During the pyrolysis process, depolymerization and repolymerization reactions take place. The network or structural models consider the rupture of bonds, the chain crosslinking and the diffusion and convection during this process (Hameed et al., 2019). These models explain the detailed structural change during reactions starting from macromolecular characterization of biomass (which basic constituents are cellulose, hemicelluloses, and lignin), allowing the determination of the molecular weight distribution of pyrolysis products. Furthermore, with the distribution results, kinetic parameters can be estimated depending on the reaction pathway, making it possible scaling up the results to large pyrolysis processes.

The common structural models for biomass devolatilization are Functional Group Depolymerization Vaporization Crosslinking (FG-DVC), FLASHCHAIN and Chemical Percolation Devolatilization (CDP). For predicting products distribution these models use statistical calculation methods, such us Monte-Carlo or percolation lattice theory; to estimate the probability of bonds being broken in the structure of the involved compounds (Hameed et al., 2019). However, the input data for the model is highly specific depending on the feedstock. Furthermore, it becomes very complex when physical transport phenomena are considered in the model (Hameed et al., 2019).

1.1.3. Reactor level

The models in the previous two scales are helpful to understand thoroughly the reaction mechanisms and the effect of heat and mass transfer processes on pyrolysis reactions, however scaling these models to large scale process is a complicated task. At reactor scale, kinetic, mass and heat transfers models must be integrated to develop economic and efficient pyrolysis reactors. Hameed et al. (Hameed et al., 2019) suggest the use of Computational Fluid Dynamics (CFD), along with lumped kinetic models to predict pyrolysis processes at this scale. Different from mechanistic models, lumped kinetic models group products in three different classes: gas, tar, and char.

The use of statistical methods in models at molecular and particle levels is very common due the number of interactions between each individual component, while kinetic lumped models at reactor level focus on the quantity of solid, liquid and gas product obtained. The model can be improved to predict the chemical compounds formed during pyrolysis process in each phase by increasing the complexity adding the kinetics related to each compound. Kinetic models required three main parameters: energy activation, pre-exponential factor and reaction model. Lumped kinetic models commonly use thermal analysis, more specifically, the Thermogravimetry Analysis (TGA), to estimate the kinetic parameters and validate the models developed. This is due to the lumped reaction scheme considered, in which biomass thermochemical conversion into gas products is measured by the weight loss of the solid material.

The existing methods to estimate kinetic parameters using TGA information are classified in model-fitting and model-free methods. Iso-conversional methods analysis are model-free because it does not require the specification of a reaction model, allowing calculated the Energy activation as a function of conversion at different heating rates, this is also called Friedman's method. Carrier et al. (Carrier et al., 2016) developed a procedure to obtain reliable energy activation values of the isolated biomass pseudo-compounds (cellulose, hemicelluloses and lignin) using Friedman's method.

1.2. Kinetic approaches

The theorical thermal degradation of biomass is calculated using the model with the estimated kinetic parameters, Caballero et al (Caballero & Conesa, 2005) classify kinetic methods to calculate the conversion according to differential and integral methods and Vyazovkin et al. (Vyazovkin & Wight, 1998) also introduced the statistical methods. Those latter are used to solve kinetic models, which are expressed as a differential equation, and are useful to estimate kinetic parameters and make corrections on it to improve the fitting of the experimental data with the theorical calculation.

1.2.1. Acquisition of data: Differential vs Integral

Differential methods are the most common way to calculate the conversion of biomass, in other words, a way to solve the differential equation. These are based on Euler method, showed in equation (1), where X_i is dependent variable that usually is the conversion, $f(t_{i-1}, X_{i-1})$ is the derivate evaluated at the latest time and conversion obtained and Δt is the size step defined for each calculation. More complex and accurate differential methods are modifications of it, as fourth order Runge Kutta method, which is one of the most used. The solution is obtained through the calculation of tiny straight lines using the slope at the last point.

$$X_i = X_{i-1} + f(t_{i-1}, X_{i-1})\Delta t \tag{1}$$

However, these differential approaches can introduce error on each calculation considering that the next approximation is calculated with the latest, the major problem is related with the flat zone at the final conversions on the curve (Caballero & Conesa, 2005), the mentioned methods are unable to model it. An alternative to solve this problem is to decrease the size step, nevertheless, a tiny size step is not practical from a numerical point of view. A solution presented by Caballero et. al (Caballero & Conesa, 2005) is the use of solver with correction step as the explicit ODE (Ordinary Differential Equations) solvers implemented in Matlab^{TM}. The software provides an ODE algorithm to estimate the solution of an ordinary differential equation or a system of it. The solver, “ode45”, is the most used and recommended by the software to use as a first approximation, it is based on an explicit Runge-Kutta (4,5) formula, the Dormand-Prince pair. It is a single-step solver – in computing $X(t_i)$, it needs only the solution at the immediately preceding time point, $X(t_{i-1})$ (Dormand & Prince, 1986; Shampine & Reichelt, 1997). However, when an ODE exhibits stiffness problems (such as those mentioned at the final conversion flat zone) it is necessary to use stiff solvers.

Integral methods looking for a solution through the integration of the differential kinetic equation. There are two ways to solve the equation according to Caballero et al. (Caballero & Conesa, 2005), analytical integration and numerical integration. Although it is not an exact analytical solution, it was the first option for researchers and many analytical approximations with good results were suggested. However, these numerical methods must be used with care (Vyazovkin & Wight, 1998). In the other hand, the numerical integrations lead with the same problems that differential methods, to obtain good results is necessary to use a suitable size step. Another way to solve the integral is using statistical methods.

1.2.2. Statistical methods

Statistical methods consider that the adequate kinetics parameters are the statistical description of the pyrolysis process. However, it is necessary to take into account the confident limits to discriminate the results (Vyazovkin & Wight, 1998). To estimate the conversion of biomass with this method the kinetic parameters are used into a density probability function (PDF). As mentioned, methods at particle and molecular levels use a statistical approach combined with Monte-Carlo algorithm in order to determine kinetic parameter and reaction mechanisms. However, the Monte-Carlo algorithm can be implemented in kinetic models at reactor scale, Dhaundiyal et al. (Dhaundiyal et al., 2019) implemented the algorithm to estimate the kinetic parameters of pine waste in a Distributed Activation Energy Model (DAEM), generating random numbers of temperature to predict conversion. Furthermore, these algorithms have been widely used in physics applications, radiation detectors, absorbed doses, etc.

1.2.3. Choice of models

The election of the most suitable model depends on many variables, such as the kind of reactor, the process parameters, the raw materials, etc. Focused on kinetics, the reaction rate is parameterized in terms of three variables: pressure, temperature, and the extent of conversion α, however, the majority of the kinetic methods used in the thermal analysis are a function of the latter two variables (Vyazovkin et al., 2011). The temperature dependance is usually described through the Arrhenius law, where two important kinetic parameters are introduced: the energy activation and the pre-exponential factor. On the other hand, the effect of the extent of conversion in the rate of the process is described using the reaction model $f(\alpha)$, which is a function of conversion. For solid-state reactions, the reaction models can be classified into three main groups: accelerating, decelerating, and autocatalytic or sigmoidal. Accelerating models refers to the processes in which rates increase continuously with the increase of conversion, the most common examples are the power-law models; decelerating models are the opposite, the rates decrease with the extent of conversion, and the rate rises his maximum at the beginning of the process; finally, sigmoidal models represent an accelerating behavior at the beginning and a decelerating behavior at the end of the process, which means that the maximum rate will be placed on an intermediate moment of the reaction (Vyazovkin et al., 2011).

However, under non-isothermal conditions, the changes on these two variables give place to a sigmoidal behavior on the reaction profile, which makes it difficult to identify the appropriate reaction model.

1.3. Conclusions on literature review

Modeling biomass pyrolysis remains a considerable challenge considering the heterogeneity of the chemical structures, the multitude of chemical reactions involved, and the wide number of available reactors and operating conditions. It requires establishing a clear and comprehensive experimental strategy to first collect an adequate dataset obtained in an intrinsic regime. Reactor-scale models usually group the products according to their physical state, facilitating the study and obtaining of the reaction parameters by thermogravimetric analysis, following the changes in temperature and the extent of the conversion. On the other hand, the computational statistical models used at the molecular scale allow estimating the products obtained and their quantity, methods such as the Monte-Carlo method are versatile and have been used satisfactorily in various areas, which makes them stand out from more complex models that require a larger number of parameters.

The development of new and versatile pyrolysis models seeks to improve the process, seeking the optimal parameters to predict and control the formation of multiple products, to make it a highly viable alternative in the energy transition from fossil energies.

Considering the previous, the objective of this project is to develop a statistical kinetic method using a lumped reactional model with the Monte-Carlo algorithm to predict yields of biomass pyrolysis. This first step is looking for lay the foundations of the model using cellulose to optimize and validate the results, obtaining the kinetic parameters using iso-conversional methods.

2. Methodology

2.1. Data treatment

The experimental data used in this work were obtained using TGA equipment, and the procedures that will be described to obtain the kinetic parameters and data fitting were developed to use those data. Initially, the dehydration stage was removed following the ASTM E1131 procedure (Astm E1131 − 08, 2015) to determine T_0 and the beginning of the pyrolysis process was established at this point. After that, the loss weight measured through TGA was normalized using eq(2), where alpha is the extent of conversion and varies between 0 and 1, m_0, m_i and m_f represent the mass of the sample at the beginning, at the time t_i and at the end of the reaction, respectively. This allows a quantitative comparison of model results at different heating rates and the study of temperature and respectively mass loss ranges.

$$\alpha(t_i) = \frac{m_0 - m_i}{m_0 - m_f} \tag{2}$$

The derivate of conversion as a function of time was calculated using finite differences approximation, equation (3) for intermediate data, and equations (4) and (5) for initial and final data, respectively. These values were used to filter data, negative and zero values for the derivate were discarded. The remaining points are those that will be used in the estimation of kinetic parameters and model fitting.

$$\left(\frac{d\alpha}{dt}\right)_{t_i} = \frac{\alpha(t_{i+1}) - \alpha(t_{i-1})}{t_{i+1} - t_{i-1}} \tag{3}$$

$$\left(\frac{d\alpha}{dt}\right)_{t_i} = \frac{3\alpha(t_i) + 4\alpha(t_{i+1}) - \alpha(t_{i+2})}{t_{i+2} - t_i} \tag{4}$$

$$\left(\frac{d\alpha}{dt}\right)_{t_i} = \frac{-3\alpha(t_{i-2}) + 4\alpha(t_{i-1}) - \alpha(t_i)}{t_i - t_{i-2}} \tag{5}$$

2.2. Kinetic analysis and methods

In general, heterogeneous solid-state reactions are described using a global kinetic model by the equations below:

$$\left(\frac{d\alpha(t)}{dt}\right)_i = k_i\big(T(t)\big)\, f_i\big(\alpha(t)\big) \tag{6}$$

$$k_i\big(T(t)\big) = k_{0,i}\exp\left(-\frac{E_{\alpha,i}}{RT(t)}\right) \tag{7}$$

$$\frac{dT(t)}{dt} = \beta \tag{8}$$

Where $f_i\big(\alpha(t)\big)$ is the reaction model, $k_i\big(T(t)\big)$ is the kinetic constant and its temperature dependance for non-isothermal reactions is based on Arrhenius's law, shown in eq (7). $E_{\alpha,i}$ is the activation energy, $k_{0,i}$ is the pre-exponential or frequency factor, T is temperature and R is the universal gas constant. The most common approach to the non-isothermal pyrolysis process is using a constant heating rate, β, its relation between time and temperature is described in eq (8).

For this project, the reaction model will be the same for all the i pseudo-components, equation (9) shows the model selected. It is the first order Mampel's model (Vyazovkin & Wight, 1998) which is a common approach to describe the thermal transformation in solids. Furthermore, the model was selected considering the research of other authors, like Rueda-Ordónez et al. (Rueda-Ordóñez et al., 2015), to compare the results obtained. The equation describes that the conversion rate is based on the quantity of solid biomass at t_i.

$$f_i\big(\alpha(t)\big) = \big(1 - \alpha(t)\big) \tag{9}$$

Replacing those equations in equation (6) turns it into the next expression:

$$\left(\frac{d\alpha(t)}{dt}\right)_i = k_{0,i}\exp\left(-\frac{E_{\alpha,i}}{RT(t)}\right)\big(1 - \alpha(t)\big) \tag{10}$$

As already said, lignocellulosic biomass is mainly composed of three biopolymers and its thermal degradation is described by their conversion. This approach allows the modeling of different types of biomasses according to their composition. This reaction scheme has been widely used (Rueda-Ordóñez et al., 2015, 2019); and detailed in other works (Hameed et al., 2019; Papari & Hawboldt, 2015). The following equation represents the additive reaction scheme.

$$\left(\frac{d\alpha(t)}{dt}\right)_t = \sum_{i=HC,C,L} w_i \left(\frac{d\alpha(t)}{dt}\right)_i \tag{11}$$

In the equation, HC, $C,$ and L represent hemicelluloses, cellulose, and lignin, respectively; w_i is the mass fraction of each pseudo-component and $(d\alpha(t)/dt)_i$ represents their conversion while $(d\alpha(t)/dt)_t$ is the total conversion of biomass.

2.3. Determination of kinetic parameters

2.3.1. Energy Activation

The energy activation was calculated using the procedure detailed by Carrier et al. (Carrier et al., 2016), using the iso-conversional Friedman method. This approach helps to determine $E_{\alpha,i}$ by a linearization form of the equation (6). It is useful because it does not depend on the reaction model, and this is achieved assuming that it is constant. For this, data of the derivate of the conversion as a function of time at different temperatures for the same conversion are required, these can be obtained by carrying out experiments at different heating rates (Friedman, 1964). The linearization is between the $\ln(d\alpha(t)/dt)_i$ versus $1/T(t)$ and the slope of the equation results in energy activation as can be seen in equation (12).

$$\ln\left(\frac{d\alpha(t)}{dt}\right)_i = \ln\left(k_{0,i}\, f_i(\alpha(t))\right) - \frac{E_{\alpha,i}}{RT(t)} \tag{12}$$

2.3.2. Pre-exponential factor

The pre-exponential factor was calculated using the iso-conversional Friedman method as well. It can be estimated using the intercept of the straight line, $\ln\left(k_{0,i}\, f_i(\alpha)\right)$. The reported value is the average $k_{0,i}$ calculated in each one of the linear regressions. Applying properties of logarithms and substituting the expression for the conversion function, the next expression is obtained:

$$\ln\left(k_{0,i}\, f_i\left(\alpha(t)\right)\right) = \ln\left(k_{0,i}\right) + \ln\left(1 - \alpha(t)\right) \tag{13}$$

Equation (13) can be used to calculate the $\ln\left(k_{0,i}\right)$ for each intercept in the straight lines obtained using the Friedman method, the obtained value is the average of the results.

2.4. Theorical conversion calculation

To estimate the thermal degradation curves of biomass the calculation of α at a specific time, t_i, is necessary. This project focuses on the development of an algorithm to calculate the conversion using statistical and differential methods. To understand their differences and limitations all the calculations of conversion will be done with both methods to compare their accuracy and efficiency.

2.4.1. Differential methods

As already said, differential methods are the most common way to solve equation (6). In this work, two types of solvers were used to compare the results of the development model with traditional methods: the mentioned “ode45”, although it is used for non-stiff problems; and the “ode15s” which is preferred to solve stiff problems. Both were used to calculate the theoretical conversion data and plot the thermal degradation curves.

2.4.2. Integral methods

Equation (14) is the integrated form of equation (6), for a non-isothermal process, the integral does not have an explicit solution.

$$\int_{\alpha_0}^{\alpha_f} \frac{d\alpha}{f_i(\alpha(t))} = \int_{t_0}^{t} k_{0,i} \exp\left(-\frac{E_{\alpha,i}}{RT(t)}\right) dt \tag{14}$$

The develop of the model begin by looking for a solution for equation (14), although the final expression is also an integral, it is going to be solved using the Monte-Carlo algorithm, which is a statistical method. In the next section, the main functions and statistical concepts will be described to clearly explain the algorithm and understand it.

2.4.3. Statistical methods

The method uses the kinetic parameters as the parameters of a probability function, which are used to estimate the thermal degradation of the compound as a time function. The results in statistical methods are the probable value inside a defined confidence interval at specific conditions. The value is known as the mean or expected value and it can be obtained using an appropriate probability function. The developed model estimates the conversion, $\alpha(t_i)$, at time t_i through the generation of random numbers for time according to a probability function.

2.4.3.1. Random variable. Random variables are divided into two types: discrete and continuous. Discrete variables have a finite number of possible results, the most common example is the set of results of rolling a dice, which are the numbers from 1 to 6 and there is not any other possible result different from these. On the other hand, a continuous variable can take any value in a range, hence the number of possible values for the variable is uncountably infinite (Montgomery & Runger, 1994). Biomass conversion is a continuous random variable and the probability function to estimate the expected value must be according to this.

2.4.3.2. Probability Density Function (pdf). A probability density function describes the probability distribution of a continuous random variable X, a pdf, $p(x)$, is a function such that:

1) $p(x) \geq 0$

2) $\int_{-\infty}^{\infty} p(x)\, dx = 1$

3) $P(a \leq X \leq b) = \int_{a}^{b} p(x)\, dx$

The function provides a simple description of the probabilities associated with a random variable (Montgomery & Runger, 1994). In this project, the pdf is used to generate values for the random variable according to it. The function used is the exponential distribution.

2.4.3.2.1 Exponential probability density function. In the distribution the random variable, $X,$ is equal to the distance between successive counts of points on subintervals, considering these subintervals with the same length but independent of other subintervals. The functions have a parameter λ, which is the mean of counts per interval and with a mean equal to $\mu = 1/\lambda$. The next equation is the probability density function:

$$p(x) = \lambda \exp(-\lambda\, x) \tag{15}$$

In the further development of the model, this function and the parameter λ will be identified.

2.4.3.3. Expected value, variance, and confidence intervals.

The expected value or mean is a measure of the middle of the probability distribution, for a continuous random variable it is estimated through the equation below, where $p(x)$ is the pdf associated.

$$E(x) = \int x\, p(x)\, dx \tag{16}$$

For a function $f(X)$ of a continuous random variable, the expected value is defined with a similar expression:

$$E[f(X)] = \mu = \int f(x)\, p(x)\, dx \tag{17}$$

The variance is a measure of the dispersion or variability in the distribution, the equation below shows the expression to calculate it for a function $f(X)$ of a continuous random variable.

$$\sigma^2[f(x)] = \int (x - \mu)^2\, p(x) dx \tag{18}$$

The standard deviation is σ and is equal to the root of the variance, it is used to estimate the confidence intervals to the expected value.

$$\sigma[f(x)] = \sqrt{\sigma^2[f(x)]} \tag{19}$$

2.4.4. Monte-Carlo Method

The Monte-Carlo methods are used to simulate complex probabilistic events through simple random events. It is based on the repeated generation of random numbers, or in computing applications, a pseudo-random number generation.

The Monte-Carlo algorithm uses the generation of N values for a random variable following a pdf to calculate the expected value of a function of it. The following equations show how the expected value is calculated using the Monte-Carlo method, where x_i is each of the generated random values evaluated in the function, these pseudo-random values are generated following the probability function $p(x)$.

$$E[f(X)] = \int f(x)\, p(x)\, dx \approx \frac{1}{N} \sum_{i=1}^{N} f(x_i) \tag{20}$$

The expected value is calculated by the sum of the calculated values divided by the number of random numbers generated. However, the Monte-Carlo method is relevant because, using the random values, allows the calculation of the variance and the standard deviation of the expected value. Equations (21) and (22) show how these values can be obtained, respectively.

$$\sigma^2[f(x)] = \int (x-\mu)^2\, p(x)dx \approx \frac{1}{N}\left(\frac{1}{N}\sum_{i=1}^{N}\big(f(x_i)\big)^2 - \left(\frac{1}{N}\sum_{i=1}^{N} f(x_i)\right)^2\right) \tag{21}$$

$$\sigma\,[f(x)] \approx \sqrt{\frac{1}{N}\left(\frac{1}{N}\sum_{i=1}^{N}\big(f(x_i)\big)^2 - \left(\frac{1}{N}\sum_{i=1}^{N} f(x_i)\right)^2\right)} \tag{22}$$

Using the standard deviation, confidence intervals can be calculated for the expected values obtained, using the empirical rule $P(\mu - 3\sigma \ \leq\ E[f(X)] \leq\ \mu + 3\sigma\,) \approx 0.997$ allows obtaining an approximate confidence interval of 99.7%, this rule will be used to obtain the confidence intervals in subsequent calculations.

2.5. Model development

2.5.1. Isothermal process

As a first approach, the kinetic model was solved by considering a constant temperature during all pyrolysis processes. This condition becomes the equation (7) into a constant value denoted as k'. This allows to solve the equation and express it explicitly, equation (23) being the solution.

$$\alpha(t) = 1 - (1-\alpha_0)\exp(-\,k'\,t) \tag{23}$$

However, this project aims to model the thermal degradation of biomass using the Monte-Carlo method through the generation of random numbers. For this reason, equation (23) was expressed as an integral form that allows the use of the statistical method using the exponential pdf, resulting in equation (24).

$$\alpha(t) = \int_0^\infty \rho(t,\tau)\, P(\tau)\, d\tau \tag{24}$$

Where $\rho(t,\tau)$ is a piecewise function defined as follows:

$$\rho(t,\tau) = \begin{Bmatrix} 1 & , & \tau \leq t \\ \alpha_0 & , & \tau > t \end{Bmatrix} \tag{25}$$

And $P(\tau)$ is:

$$P(\tau) = k' \exp(-k' \tau) \tag{26}$$

When α_0 is settled in 0, the function turns into the Heaviside function. Equation (24) will be used to calculate the conversion of biomass as a function of time. Although the expression is not practical considering the explicit solution it is useful to identify each element for the Monte-Carlo algorithm. The equation is the same as equation (17), which is used to estimate the expected value of a function of a continuous random variable, which allows the use of the statistical method, therefore, equation (26) is the pdf and it has the form of an exponential PDF and the parameter of the function is k'.

2.5.2. Non-Isothermal process

Different from the isothermal process, the temperature changes induce changes in the kinetic constant (eq. (7)). This means that the expression will be different as time goes by. With this condition, the differential kinetic equation (eq. (6)) is not possible to solve explicitly. It is more difficult to express the conversion as a time function in an integral form (like eq. (24)) and makes possible the use of the Monte-Carlo algorithm.

This section introduces the mathematical work to give place to the non-isothermal conversion model. Starting from equation (10), the Arrhenius expression is replaced by $k(T(t))$, representing the change of the kinetic constant as a temperature function.

$$\frac{d\alpha(t)}{dt} = k(T(t))\,(1-\alpha(t)) \tag{27}$$

To remove the temperature dependence in the equation is necessary the addition of a parameter to replace the kinetic rate, adding $\bar{k}$, which is the highest value that the kinetic constant can reach during the conversion range, it also corresponds to the highest temperature value. The addition of this parameter and the mathematical treatment accomplished was presented in the research of Galtier, M (Galtier, 2014). In his work, a Monte-Carlo algorithm was developed to study the radiative transfers in gases and then applied to this study.

$$\bar{k} = k(T(t))_{max} \tag{28}$$

Adding it into equation (27):

$$\frac{d\alpha(t)}{dt} = (1-\alpha(t))\,k(T(t)) - \alpha(t)\,\bar{k} + \alpha(t)\,\bar{k} \tag{29}$$

The constant must be introduced along with the conversion $\alpha(t)$, this is looking for replacing the term that depends on temperature with the constant term. Rearranging the equation as follows:

$$\frac{d\alpha(t)}{dt} = k(T(t)) - \alpha(t)\,k(T(t)) + \alpha(t)\,\bar{k} - \alpha(t)\,\bar{k}$$

$$\frac{d\alpha(t)}{dt} = -\alpha(t)\,\bar{k} + k(T(t)) - \alpha(t)\,k(T(t)) + \alpha(t)\,\bar{k}$$

$$\frac{d\alpha(t)}{dt} = -\alpha(t)\,\bar{k} + k(T(t)) + \alpha(t)\,\left(\bar{k} - k(T(t))\right)$$

$$\frac{d\alpha(t)}{dt} = -\alpha(t)\,\bar{k} + \left[\frac{k\big(T(t)\big) + \alpha(t)\,\left(\bar{k} - k\big(T(t)\big)\right)}{\bar{k}}\right]\,\bar{k}$$

$$\frac{d\alpha(t)}{dt} = -\alpha(t)\,\bar{k} + \left[\frac{k\big(T(t)\big)}{\bar{k}} + \alpha(t)\left(1 - \frac{k\big(T(t)\big)}{\bar{k}}\right)\right]\,\bar{k} \qquad \textit{(29.a)}$$

From equation (29.a) a new variable is defined, denoted by $\alpha_s(t)$.

$$\alpha_s(t) = \frac{k\big(T(t)\big)}{\bar{k}} + \alpha(t)\left(1 - \frac{k\big(T(t)\big)}{\bar{k}}\right) \qquad \textit{(30)}$$

The main idea about the introduction of variable $\alpha_s(t)$ helps to overcome the problem related to the variable temperature and it is useful to obtain a Monte-Carlo expression to calculate biomass conversion. The final equation is below:

$$\frac{d\alpha(t)}{dt} + \alpha(t)\,\bar{k} = \alpha_s(t)\,\bar{k} \qquad \textit{(31)}$$

The solution of this differential equation can be expressed as the sum of two parts, the solution of the homogeneous equation and the solution of the particular equation (eq. (32), the terms on the left side correspond to the homogeneous part of the equation, while the term $\alpha_s(t)$ to the right side of equality forms the particular expression.

$$\alpha(t) = \alpha(t)_H + \alpha(t)_P \qquad \textit{(32)}$$

The homogeneous differential equation is shown below:

$$\frac{d\alpha(t)_H}{dt} + \alpha(t)_H\,\bar{k} = 0 \qquad \textit{(33)}$$

And its solution:

$$\alpha(t)_H = C_1 \exp\big(-\bar{k}\,t\big) \qquad \textit{(34)}$$

The solution of the equation arises from the solution of the homogeneous equation, supposing the integration constant as a function of time:

$$\alpha(t)_P = C_2(t)\ \exp\left(-\bar{k}\ t\right) \tag{35}$$

To determine $C_2(t)$, equation (35) is derivate.

$$\frac{d\alpha(t)_P}{dt} = \frac{dC_2(t)}{dt}\ \exp\left(-\bar{k}\ t\right) - C_2(t)\ \bar{k}\ \exp\left(-\bar{k}\ t\right) \tag{36}$$

And replaced those equations, eq. (35) and eq.(36), in equation (31).

$$\frac{dC_2(t)}{dt}\ \exp\left(-\bar{k}\ t\right) - C_2(t)\ \bar{k}\ \exp\left(-\bar{k}\ t\right) + C_2(t)\ \exp\left(-\bar{k}\ t\right)\ \bar{k} = \alpha_s(t)\ \bar{k}$$

$$\frac{dC_2(t)}{dt} = \alpha_s(t)\ \bar{k}\ \exp\left(\bar{k}\ t\right) \tag{37}$$

Solving the equation gives an expression for $C_2(t)$.

$$\int dC_2(t) = \int \alpha_s(t)\ \bar{k}\ \exp\left(\bar{k}\ t\right)\ dt$$

$$C_2(t) = \int_0^t \alpha_s(\gamma)\ \bar{k}\ \exp\left(\bar{k}\ \gamma\right)\ d\gamma + C_2 \tag{38}$$

At the right side of the equality, the integral remains because there is not an analytical solution for this expression, the next step is to replace equation (35) to finally obtain the particular solution of the differential equation.

$$\alpha(t)_P\ \exp\left(\bar{k}\ t\right) = \int_0^t \alpha_s(\gamma)\ \bar{k}\ \exp\left(\bar{k}\ \gamma\right)\ d\gamma + C_2$$

$$\alpha(t)_P = \exp\left(-\bar{k}\ t\right) \int_0^t \alpha_s(\gamma)\ \bar{k}\ \exp\left(\bar{k}\ \gamma\right)\ d\gamma + C_2\ \exp\left(-\bar{k}\ t\right) \tag{39}$$

With the particular and homogeneous solution defined, equation (32) can be rewritten by substituting each expression:

$$\alpha(t) = C_1 \exp\left(-\bar{k}\, t\right) + C_2\ \exp\left(-\bar{k}\, t\right) + \exp\left(-\bar{k}\, t\right) \int_0^t \alpha_s(\gamma)\, \bar{k}\ \exp\left(\bar{k}\, \gamma\right)\ d\gamma$$

$$\alpha(t) = (C_1 + C_2) \exp\left(-\bar{k}\, t\right) + \exp\left(-\bar{k}\, t\right) \int_0^t \alpha_s(\gamma)\, \bar{k}\ \exp\left(\bar{k}\, \gamma\right)\ d\gamma \qquad \textit{(40)}$$

Equation (40) describes the biomass conversion as a function of time, by replacing the initial condition, $\alpha(t=0) = \alpha_0$, the value of the integration constants $(C_1 + C_2)$ was determined, these being equal to α_0. Thus, the equation can finally be rewritten as:

$$\alpha(t) = \alpha_0 \exp\left(-\bar{k}\, t\right) + \exp\left(-\bar{k}\, t\right) \int_0^t \alpha_s(\gamma)\, \bar{k}\ \exp\left(\bar{k}\, \gamma\right)\ d\gamma \qquad \textit{(41)}$$

However, in this equation the Monte-Carlo method cannot yet be applied, it is necessary to express it completely in an integral form. Starting with the integral term, the exponential expression that multiplies it can be grouped within the same integral, considering that the time where the conversion is to be evaluated will be constant.

$$\alpha(t) = \alpha_0 \exp\left(-\bar{k}\, t\right) + \int_0^t \alpha_s(\gamma)\, \bar{k}\ \exp\left(-\bar{k}\, (t-\gamma)\right)\ d\gamma$$

Using the substitution "$\tau = t - \gamma$" and "$d\tau = -d\gamma$" in the integral:

$$\alpha(t) = \alpha_0 \exp\left(-\bar{k}\, t\right) + \int_0^t \alpha_s(t-\tau)\, \bar{k}\ \exp\left(-\bar{k}\, \tau\right)\ d\tau$$

Finally, the first term of the equation must be rewritten in integral form:

$$\alpha(t) = \int_t^\infty \alpha_0\, \bar{k} \exp\left(-\bar{k}\, \tau\right)\ d\tau + \int_0^t \alpha_s(t-\tau)\, \bar{k}\ \exp\left(-\bar{k}\, \tau\right)\ d\tau \qquad \textit{(41.a)}$$

The two integrals can be unified by defining a weight function called $\delta(t,\tau)$, showed below.

$$\delta(t,\tau) = \begin{cases} \alpha_s(t-\tau), & \tau \leq t \\ \alpha_0 \quad , & \tau > t \end{cases} \tag{42}$$

Substituting the function $\delta(t,\tau)$ into the conversion equation (41.a).

$$\alpha(t) = \int_0^{\infty} \delta(t,\tau)\, \bar{k}\ \exp\left(-\bar{k}\,\tau\right)\, d\tau \tag{43}$$

At this point, the exponential probability function can be identified in the conversion model, so the final expression of the model reduces to the following.

$$\alpha(t) = \int_0^{\infty} P(\tau)\, \delta(t,\tau)\, d\tau \tag{44}$$

$$\delta(t,\tau) = \begin{cases} \dfrac{k\big(T(t-\tau)\big)}{\bar{k}} + \alpha(t-\tau)\left(1 - \dfrac{k\big(T(t-\tau)\big)}{\bar{k}}\right) & , \quad \tau \leq t \\ \alpha_0 & , \quad \tau > t \end{cases} \tag{45}$$

$$P(\tau) = \bar{k}\exp\left(-\bar{k}\,\tau\right) \tag{46}$$

Equation (44) is the biomass conversion model for non-isothermal systems, this integral expression allows the use of the Monte-Carlo method to estimate changes in conversion over time. Note that the introduction of the parameter $\bar{k}$ is what allows to obtain the exponential probability function of equation (46), in which the main parameter is this constant and therefore it is what allows the implementation of the Monte-Carlo method.

Similar to equation (25), equation (45) is a piecewise function, and equation (46) is the same as equation (26), an exponential PDF that described the probability distribution of time as a random variable. The equation (44) is going to be used in the calculation of biomass conversion in a non-isothermal process. Furthermore, if it is supposed that $k\big(T(t)\big) = \bar{k}$ for all the time range, or in other words, the process is isothermal, the equation (44) becomes equation (24), this means that equation (44) is the general expression to calculate the thermal degradation of biomass, in an isothermal or non-isothermal process.

Should be highlighted that the integrals showed in equations (25) and (44) have to be solved to estimate conversion at a specific time. This means that to calculate a conversion profile the Monte-Carlo algorithm must be run each time depending on the number of points required.

2.6. Algorithm development

2.6.1. Monte-Carlo conversion algorithm

The derived equations for the non-isothermal process, specifically the last three equations (44) - (46), were used to develop the Monte-Carlo algorithm, it is necessary to generate a defined number (N) of random time values (τ) following the exponential pdf to calculate the conversion or expected value at a defined time (t_i). Notice that the result of function $\delta(t_i, \tau)$ depends on the generated random time value respect with the calculation time, when τ is higher than t_i there is just one possible result. However, when it is lower than t_i the function to evaluate depends on temperature and on the conversion, function evaluated at $t_i - \tau$. To get this value, it is necessary to generate a new random time value but, instead of using the same function $\delta(t_i, \tau)$, it will be used the function $\delta(t_i - \tau_1, \tau_2)$. The main difference is that now the new random value generated will be compared with $t_i - \tau_1$. If τ_2 result is lower than the condition, the described process must be repeated. **Figure *2*** and **Figure *3*** are the flowchart with the algorithm described; it was implemented in Matlab (MATLAB, 2022) to make the calculations.

Figure 2

Flowchart of the algorithm developed to estimate the conversion as a function of time using the Monte-Carlo method for non-isothermal processes.

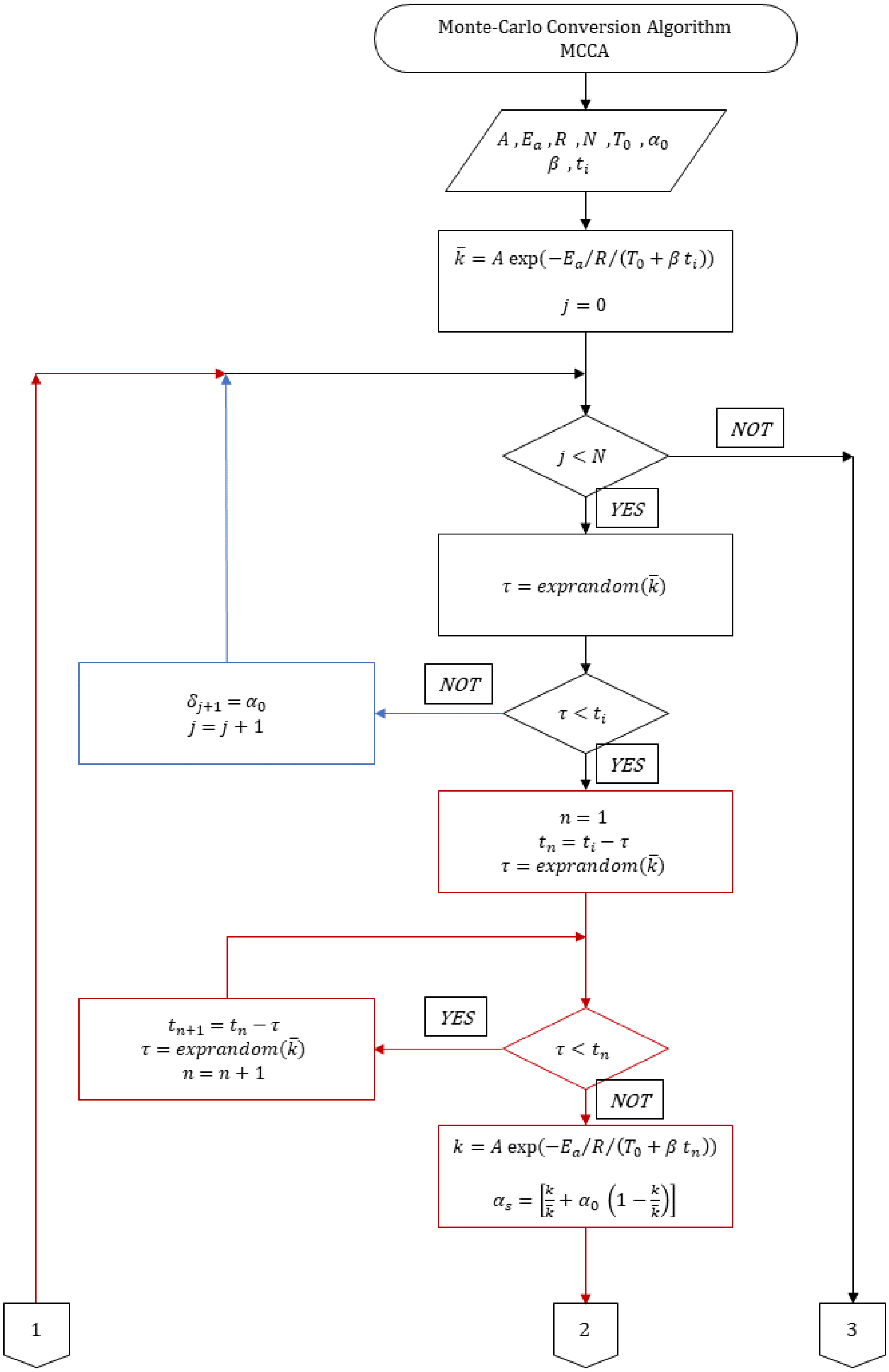
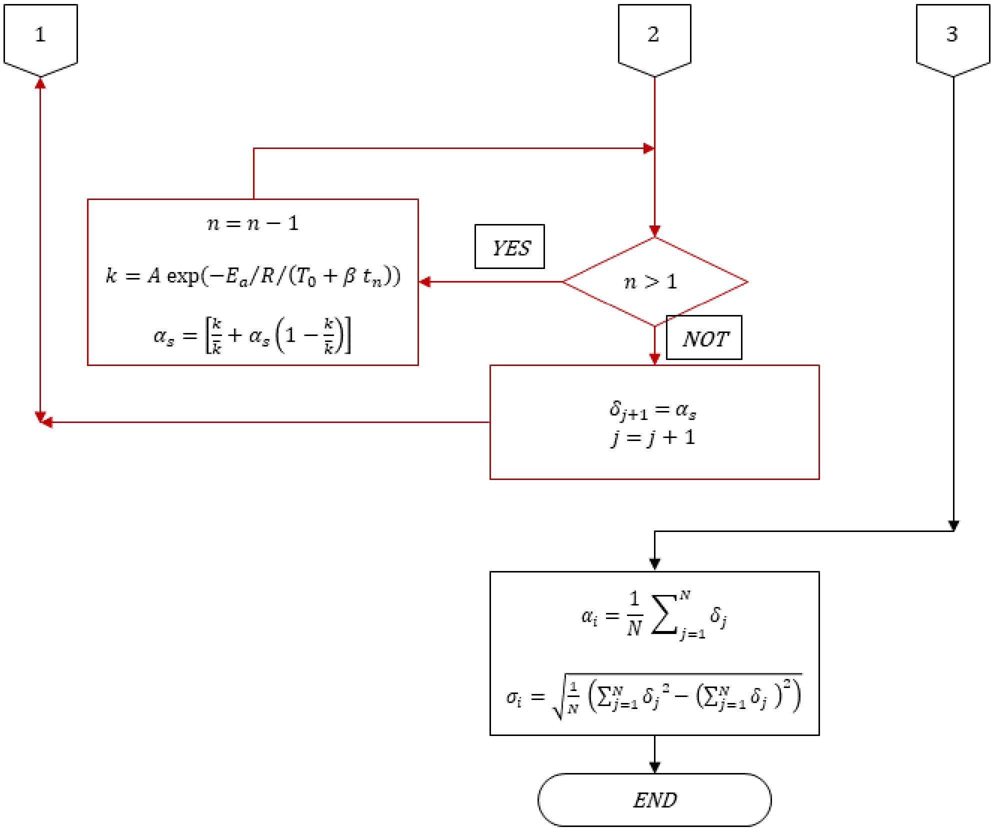


Figure 3

Continuation of the flowchart of the algorithm developed to estimate the conversion as a function of time using the Monte Carlo method for non-isothermal processes.



The function $exprandom(\bar{k})$ generates pseudo-random numbers following an exponential pdf, in this project the function "*exprnd*" implemented in Matlab was used, which generates the values using the mean of the distribution as the only parameter, as already mentioned in *2.4.3.2. Probability Density Function (pdf)* section, the mean of the exponential pdf of equation (46) would be $\mu = 1/\bar{k}$, so only this parameter is required in the function, as can be seen in the diagram.

On the other hand, two important options were highlighted in the diagram using the colors blue and red. The blue path is taken when the generated random time is greater than the calculation time, in this case only the initial conversion is assigned to the weight function. Otherwise, the red path requires a greater number of calculations, since when the generated time is less than the calculation time, the algorithm enters a loop, whose stop condition is only reached when the generated time is greater than the calculated times in each iteration, which translates into a greater calculation time and power required.

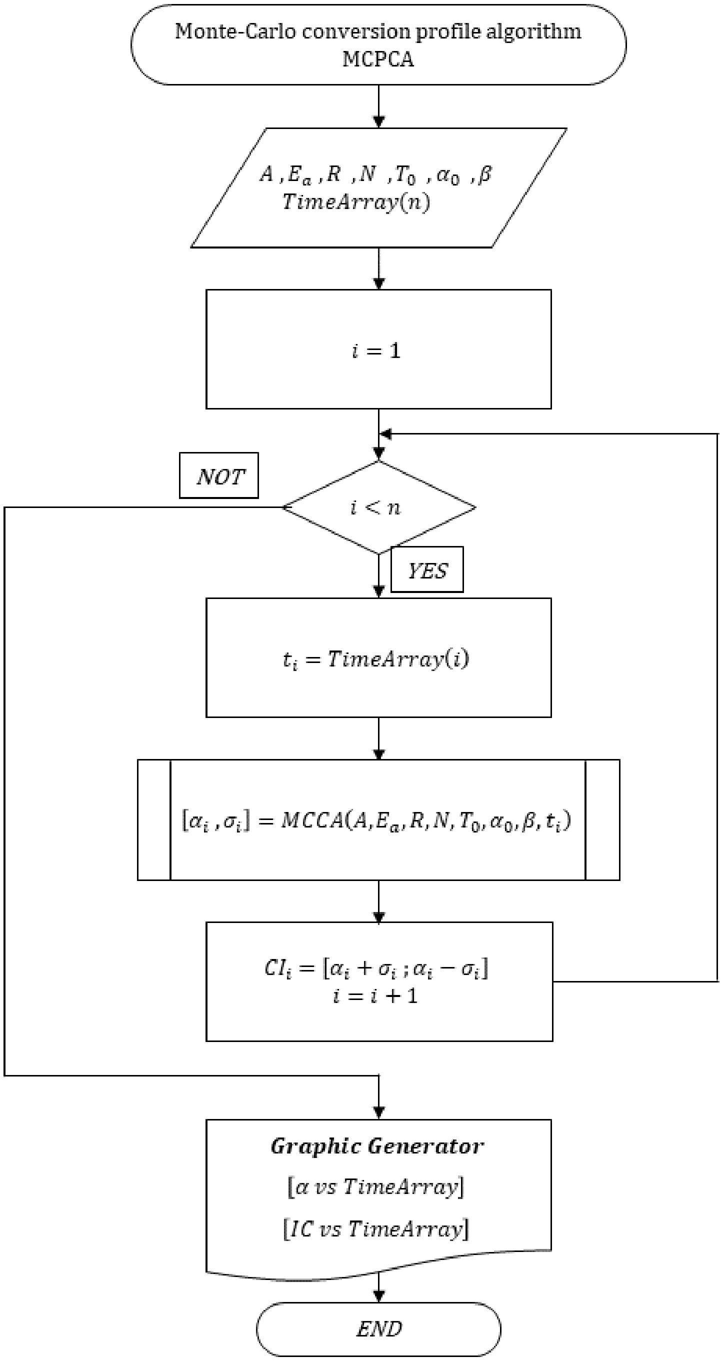
2.6.2. Monte-Carlo conversion profile algorithm

Considering that the Monte-Carlo conversion algorithm only works to estimate the conversion in a given specific time, to generate the conversion profile it is enough to define a time array that contains the range where the profile is to be generated. Therefore, this algorithm uses the same parameters as the previous one. **Figure *4*** shows the flowchart that describes it.

Additionally, using the standard deviation calculated for each point, the confidence interval was calculated, just after obtaining the conversion and the deviation, in the formula the interval used is three times the deviation above and 3 times below, as already mentioned, this results in a 99.73% confidence interval for the calculated conversion.

Figure 4

Flowchart of the algorithm developed to generate the conversion profile as a function of time using the Monte Carlo conversion algorithm (MCCA).



3. Results and discussion

3.1. Data treatment: dehydration stage

The data obtained through thermogravimetric analysis for alpha-cellulose were normalized and filtered, this process was carried out for the four heating rates used: 10°C/min, 20°C/min, 30°C/min, and 50°C/min. **Figure *5*** shows the conversion profile against time and temperature and the conversion derivate as a function of time against temperature. In addition, the curve smoothing method called *moving window average* is presented by (Caballero & Conesa, 2005), to reduce the noise in the image.

The procedure outlined in the ASTM E1131 was followed to identify the temperature where the dehydration stage finish. **Figure *6*** shows the region between 300 K and 600 K from curves b-c of **Figure *5***, these data were used to identify the temperature for each heating rate. **Table *2*** shows the temperature values found.

Table 2

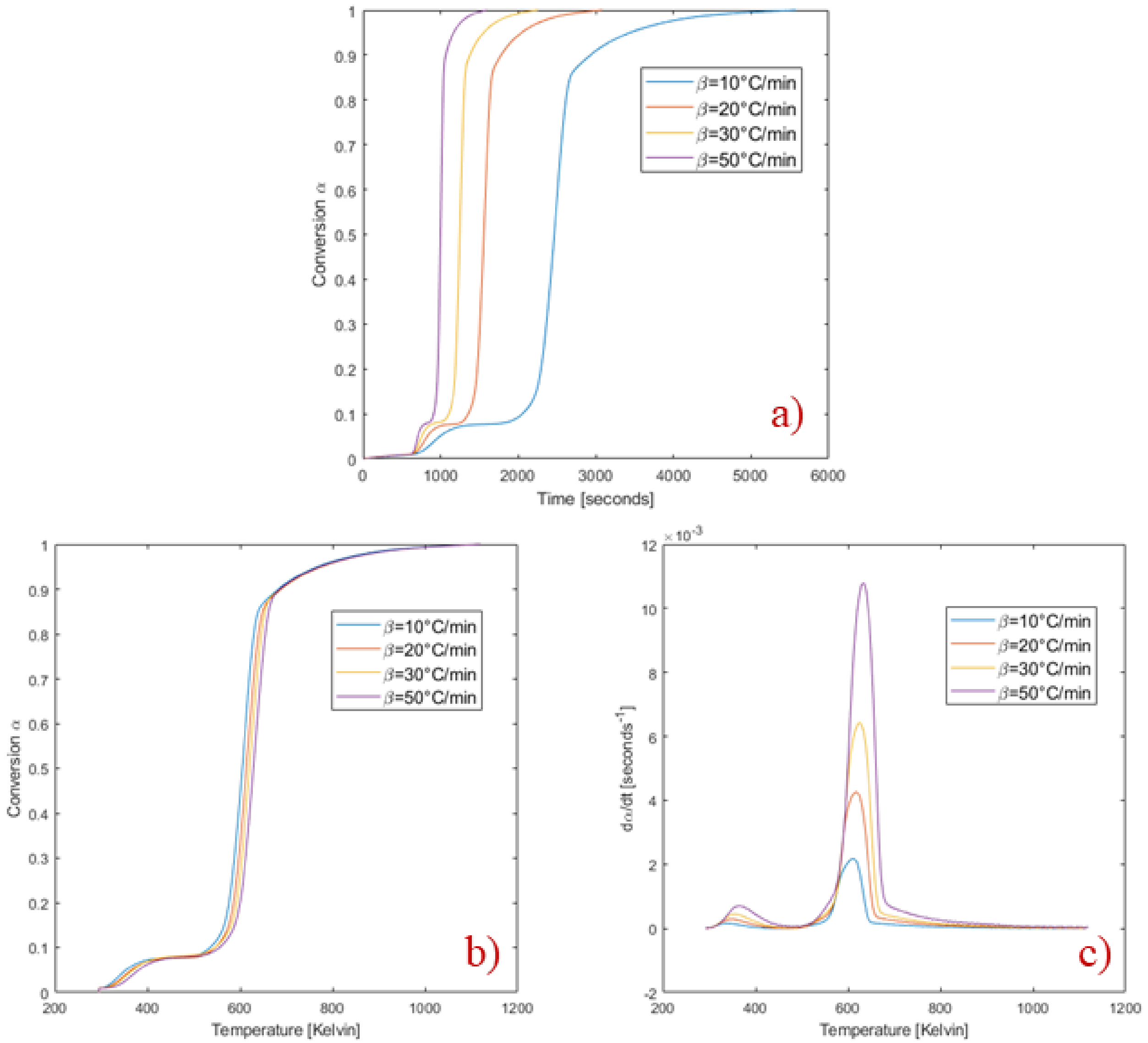
Dehydration stage temperature found for each heating rate.

Heating rate [°C/min]	Dehydration stage temperature [Kelvin]
10	453.15
20	463.15
30	473.15
50	483.15

Nota. Obtained using Figure 6.

Figure 5

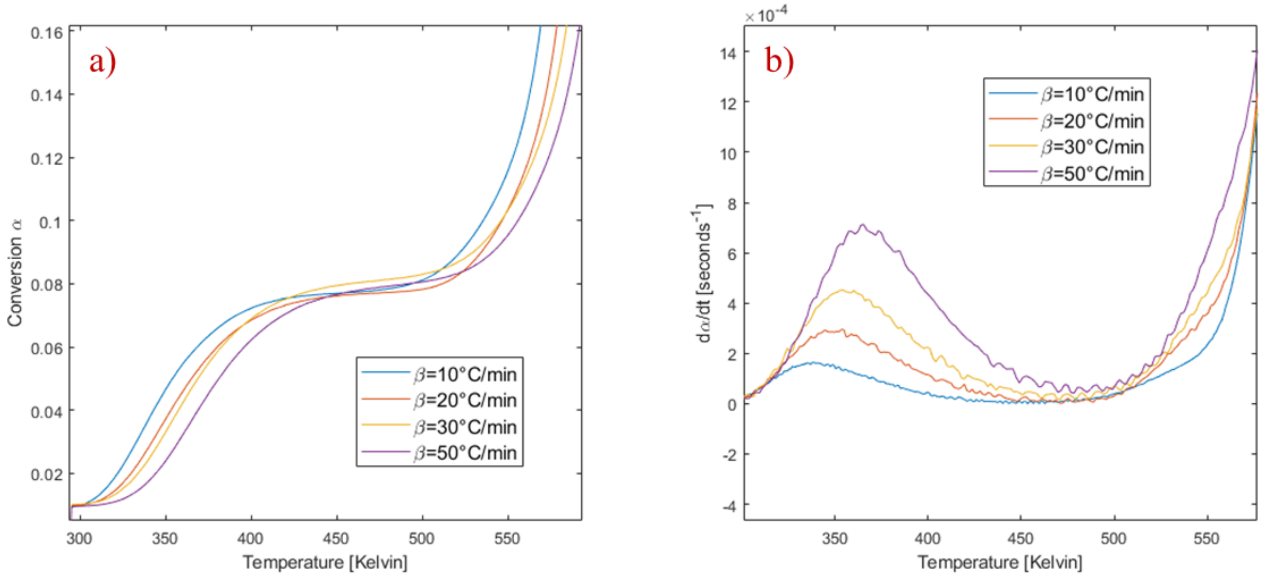
Conversion profile and its derivate as a time function for the complete extent of data normalized obtained by TGA.



Nota. a) Conversion versus time, b) Conversion versus temperature, c) Derivate of conversion as a function of time versus temperature.

Figure 6

Conversion profile and conversion derivate as a function of time focused on the dehydration stage identified.

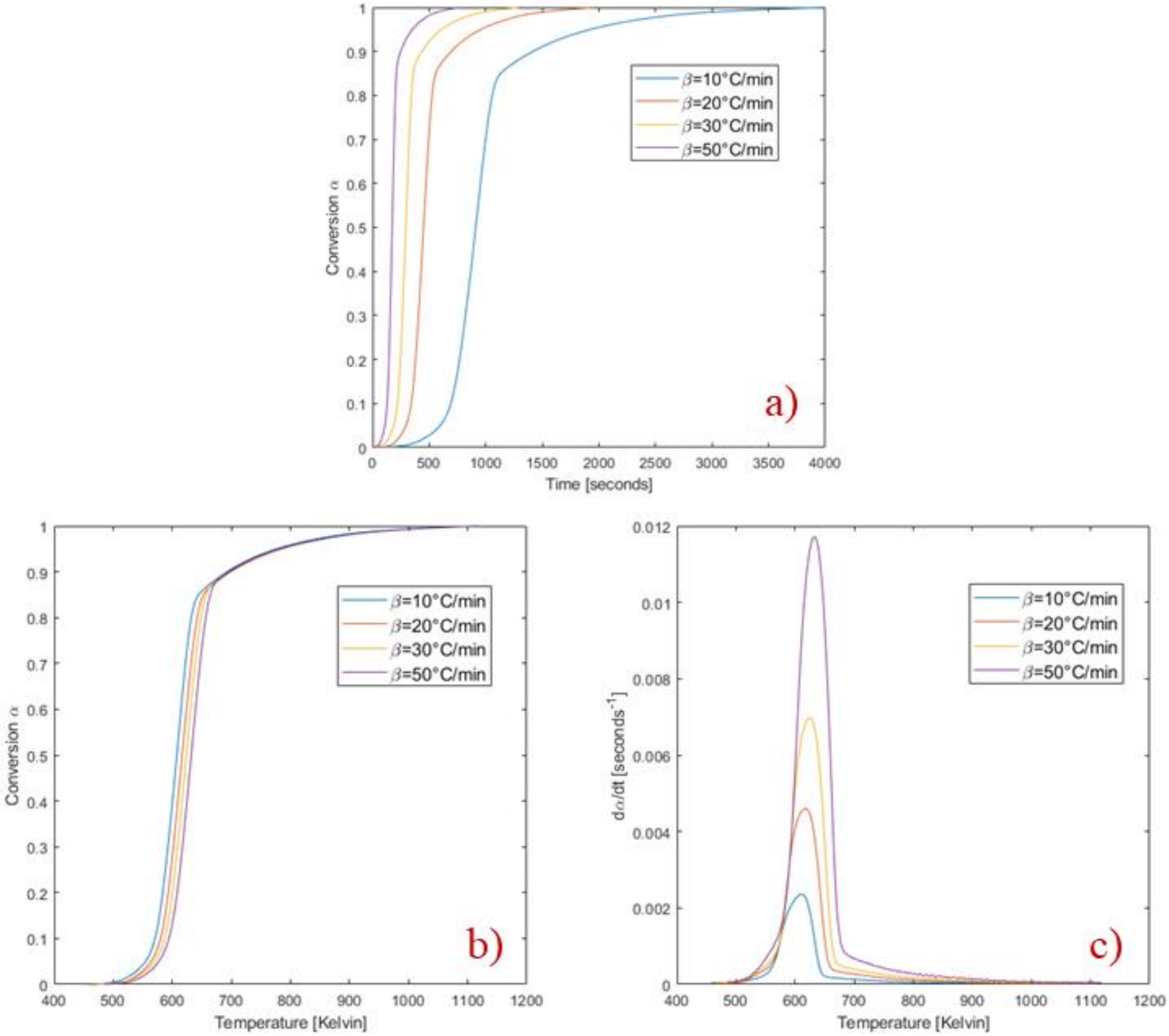


*Nota. a) C*onversion versus temperature, b) Derivate of conversion as a function of time versus temperature. The graphs allow identifying the temperature at which the dehydration stage ends, by identifying the values where the rate of change is equal to zero.

The dehydration stage was removed from the data set, considering that this stage of the process does not make part of the pyrolysis reactions, considering this, the conversion values were adjusted, making the time and conversion equal to zero at the found temperatures, which means that this is the point where the pyrolysis thermal decomposition process begins. With the data filtered and fixed, **Figure *7*** was created, now, it can be seen only one peak in the conversion derivate, which means that a single-step reaction is having place.

Figure 7

Conversion profile and its derivate as a time function for the data normalized and adjusted after removing the dehydration stage.



Nota. a) Conversion versus time, b) Conversion versus temperature, c) Derivate of conversion as a function of time versus temperature.

3.2. Kinetic parameter calculation

With the data set prepared obtained from TGA, the Friedman method was applied, following the methodology developed by (Carrier et al., 2016) to get the kinetic parameters using Friedman´s method. Through the linearization **Figure *8*** was created, a) shows the linearization of the differential equation for conversion values between 0 to 1, using 150 values equally spaced in conversion, the value of the slope presents considerable variations when passing the conversion of 0.85, this means that the energy activation values should be considerable different from those obtained at lower temperatures. In order to use only one set of kinetic parameters, the conversion values above 0.85 were removed, **Figure *8*** b) shows the linearization for the conversion values in the selected region, a clear pattern can be seen in the trend lines.

Table 3 shows the results obtained for the activation energy and the pre-exponential factor in the defined range. These parameters were used to test the Monte-Carlo Conversion Algorithm.

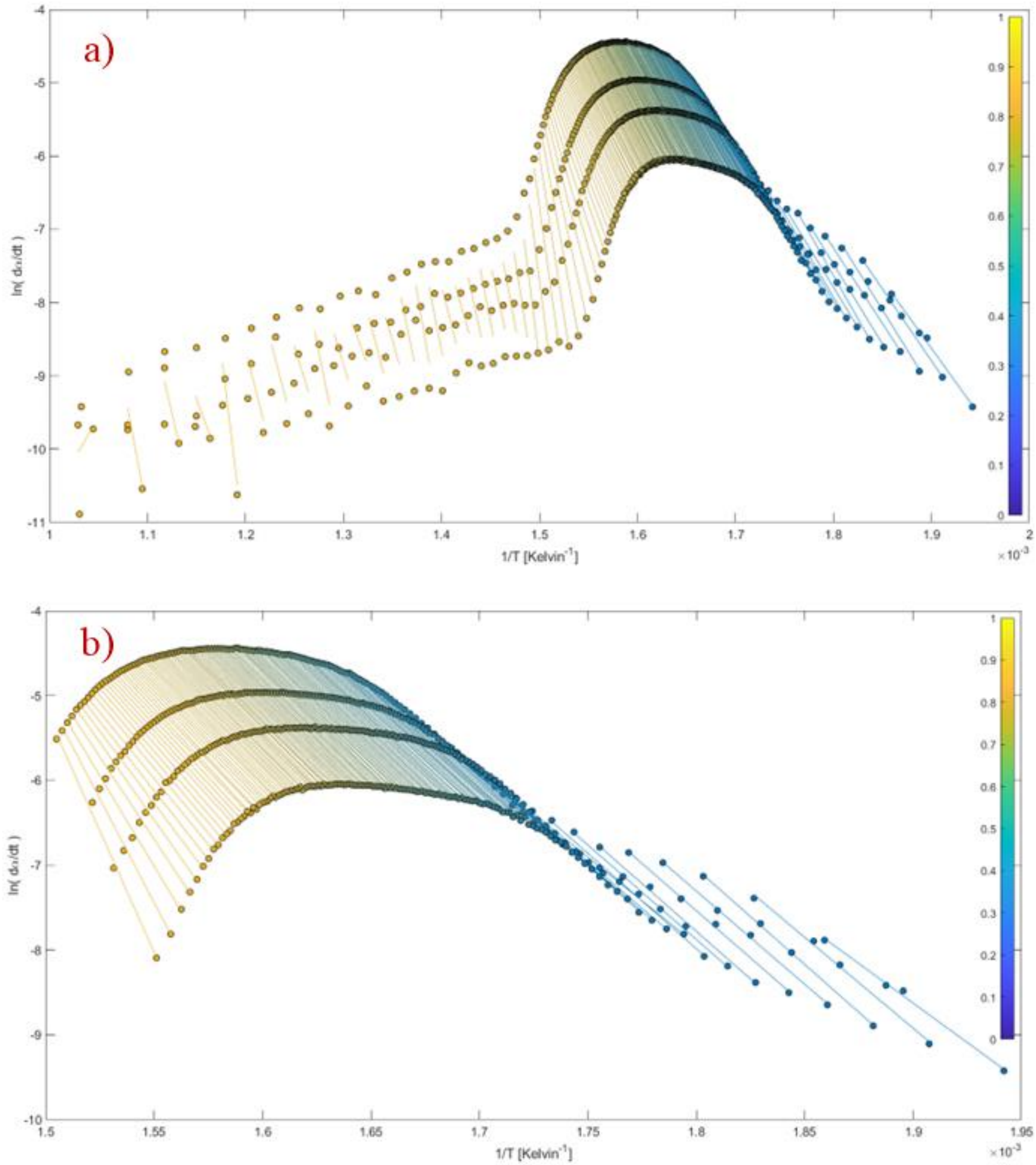
Table 3

Kinetic parameters calculated by the iso-conversional Friedman method and adjusted kinetic parameters.

	Iso-conversional Method Parameters		Adjusted Parameters	
	Energy Activation Ea $[kJ/mol]$	Pre-exponential factor $ln(k_0)$	Energy Activation Ea $[kJ/mol]$	Pre-exponential factor $ln(k_0)$
Cellulose	209.72	36.12	209.00	36.75

Figure 8

Iso-conversional method plot for the calculation of kinetic parameters



Nota. Graph generated by the application of the iso-conversional Friedman's method by linearizing the natural logarithm of the derivative of the conversion as a function of time versus the inverse of the temperature for a) the extent of conversion between 0 and 1, b) extent of conversion between 0 and 0.85.

3.3. Individual conversion calculations

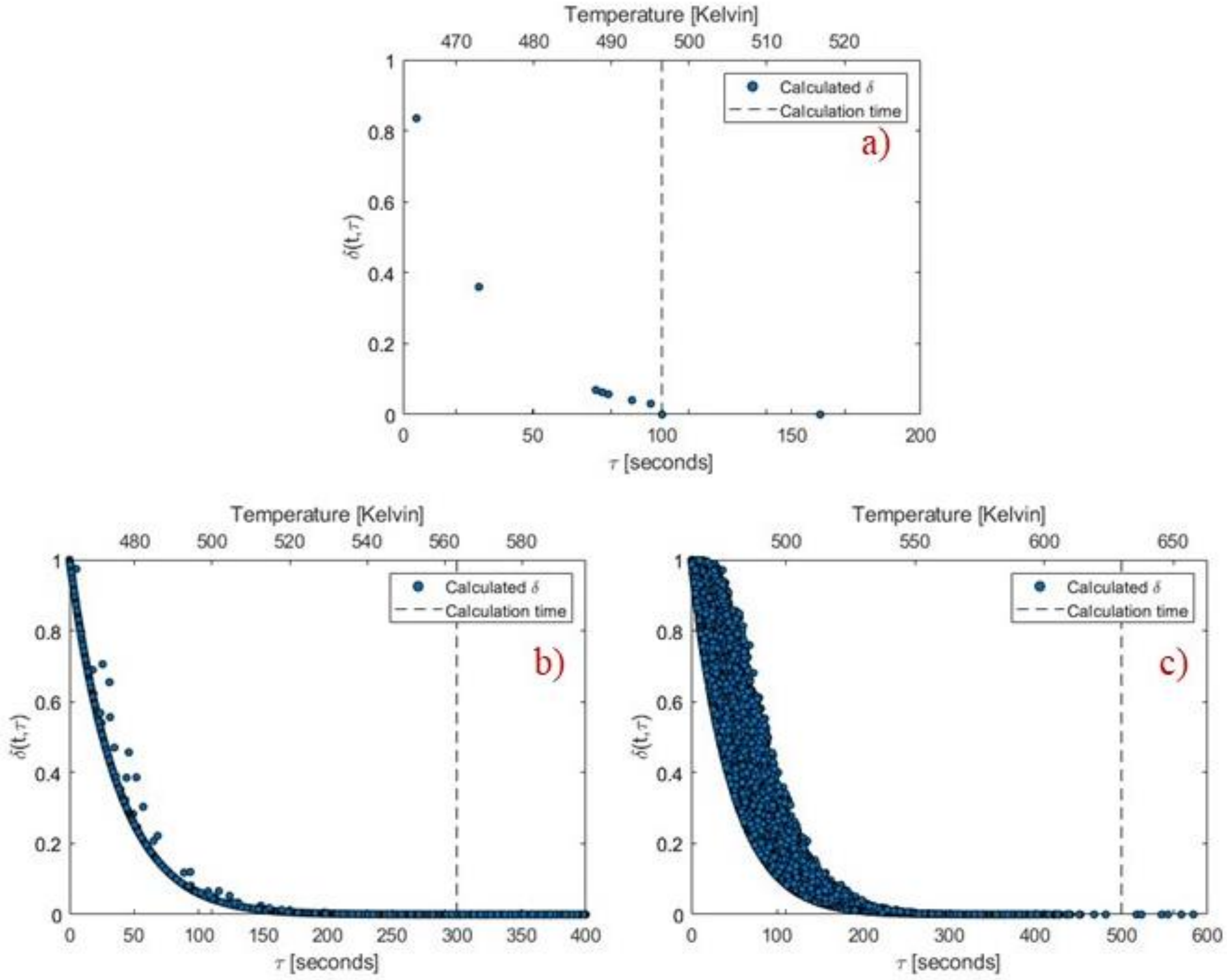
Before generating the pyrolysis conversion profile, it was decided to first study the performance of the model in obtaining individual conversion values using the MCCA, analyzing how it is affected by changes in the number of iterations (N) and the time of calculation (t_i) for the different heating rates. The tests carried out for the model are found in **Appendix *C.*** Calculation for individual conversion values.

The results show that increasing the number of iterations (N) decreases the standard deviation, which decreases the size of the confidence interval, this can be deduced when the equation to calculate the standard deviation is analyzed, however, at different time values, the algorithm presents performance variations. It was found that, at low times, which also means low temperatures, the performance of the model is better than that obtained at higher times. On the other hand, increasing the heating rate causes higher temperatures to be reached at lower times, so the time limit for which the performance remains constant is reduced.

So, what affects the performance of the model? The tests show that as the temperature increases, the performance decreases, so the analysis will be done around this variable. To estimate the conversion with the algorithm generating random time values, it is necessary to define the parameters of the pdf, in this case, the main parameter is the rate constant ($\bar{k}$). For the pdf, the mean (μ) is equal to the inverse of the rate constant, so the lower its value, the higher the mean will be, so the average of the times generated will be around it. Now, in the conversion algorithm, there are 2 paths, the choice depends on the generated time if this is greater or less than the calculation time; when the generated value is less than this, the path that the algorithm takes starts an iterative process in which it generates an additional amount of random numbers, which increases the calculation time. For this reason, the lower the mean value, the more likely the algorithm will follow this path a greater number of times. Since the temperature increases with time, the values of the rate constant will be greater at higher temperatures, which is normal in the Arrhenius model used, so the average of the random times generated will be around a low value of time and since the calculation time is high, the probabilities that the generated times will be less than the calculation time, will be high, causing the performance of the algorithm to be reduced due to a large number of random numbers additional generated.

Figure 9

Distribution of the weight function at different calculations times.



Nota. N equal to 10^5 generated random time values, HR 20 °C/min, for different calculation times: a) 100 seconds, b) 300 seconds, c) 500 seconds.

Figure *9* shows the distribution of the calculated values with the generated random numbers, it can be noticed how the amount of values lower than the calculus time increases when its increases along with the temperature. The percentage of values less than the calculus time is 0.002%, 1.567%, and 95.214% for graphs a), b) and c) respectively. The increase in these values means that the Monte-Carlo Conversion Algorithm must generate additional random numbers for each of these values, reducing the performance of the calculus process and increasing their complexity.

3.4. Conversion profile calculation

After analyzing the performance of the model to the general individual points, the generation of the conversion profile was started. Using the same kinetic parameters obtained through the iso-conversional method, these were loaded in the Monte-Carlo conversion profile algorithm with a specified time array that contained times related to the experimental conversion data between 0 and 0.85, the amount of random numbers (N) was set in 10^3.

Figure *10* a) shows the experimental data and the theoretical results, the error bars correspond to the confidence interval calculated with the Monte-Carlo Conversion algorithm. The shape of the experimental data is sigmoidal, and the theoretical results have a similar trend. However, they are shifted to the right, compared to the real ones, so the adjustment error can be attributed to the kinetic parameters obtained.

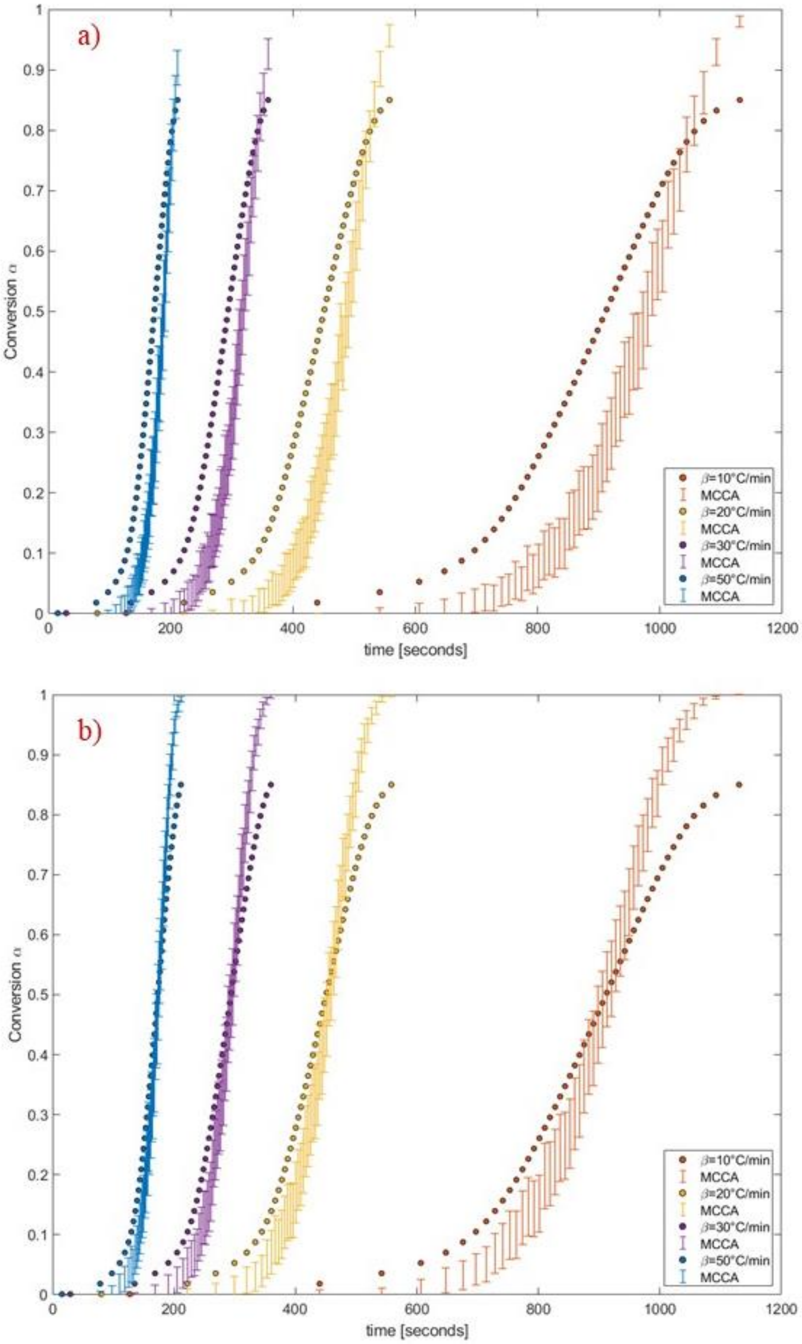
To fit the kinetic parameters to the experimental data, a fitting algorithm was created, whose objective is to reduce the relative error between the experimental and theoretical data using an optimization method. The objective of the adjustment method used is to find the kinetic parameters that reduce the sum of squares of the difference between the experimental value and the theoretical value calculated with the Monte-Carlo Conversion Algorithm, the adjustment was made using a minimization function implemented in Matlab that iterates both parameters.

Table 3 shows the results of the adjusted parameters. The optimized activation energy is slightly lower than the one obtained by the iso-conversional method, and the value found corresponds to those obtained by Carrier et. al (Carrier et al., 2016). Similarly, the pre-exponential factor slightly increased. With the adjusted kinetic parameters, **Figure *10*** b) was generated, where an improvement in the adjustment of the results can be seen, thus confirming that the problem was with the kinetic parameters. Now, the theoretical profile calculated with the Monte-Carlo Conversion Algorithm is superimposed on the experimental data profile.

The relative error calculated for the activation energy concerning the adjusted value is 0.344%, when calculating the relative error for the pre-exponential factor, using the adjusted parameter as a reference, this was calculated at 46.7%, the change when it is calculated using the natural logarithm for this parameter is 1.714%, considering that the iso-conversional method allows obtaining the logarithm of the pre-exponential factor, it means that small variations to this value cause significant differences in the calculation of the conversion profile; on the other hand, the change in activation energy is very low compared to the one initially obtained, so the method used can be adopted to obtain reliable activation energy values to be used in the Monte-Carlo Conversion model, while the pre-exponential factor requires fitting methods to estimate a value that allows calculating reliable results, it also has to be considered the use of alternatives methods to obtain this parameter. Another factor to take into account is that the result obtained for this value is linked to the reaction model used, which must be adjusted to the behavior of the pyrolysis reaction.

Figure 10

Experimental conversion and theoretical Monte-Carlo conversion error bars for Cellulose at 4 different heating rates.



Nota. Heating rates (10 / 20 / 30 / 50 °C/min) a) calculated using the energy activation and pre-exponential factor obtained by the iso-conversional Friedman method (Table 2), b) calculated using the adjusted kinetic parameters obtained with the optimization method.

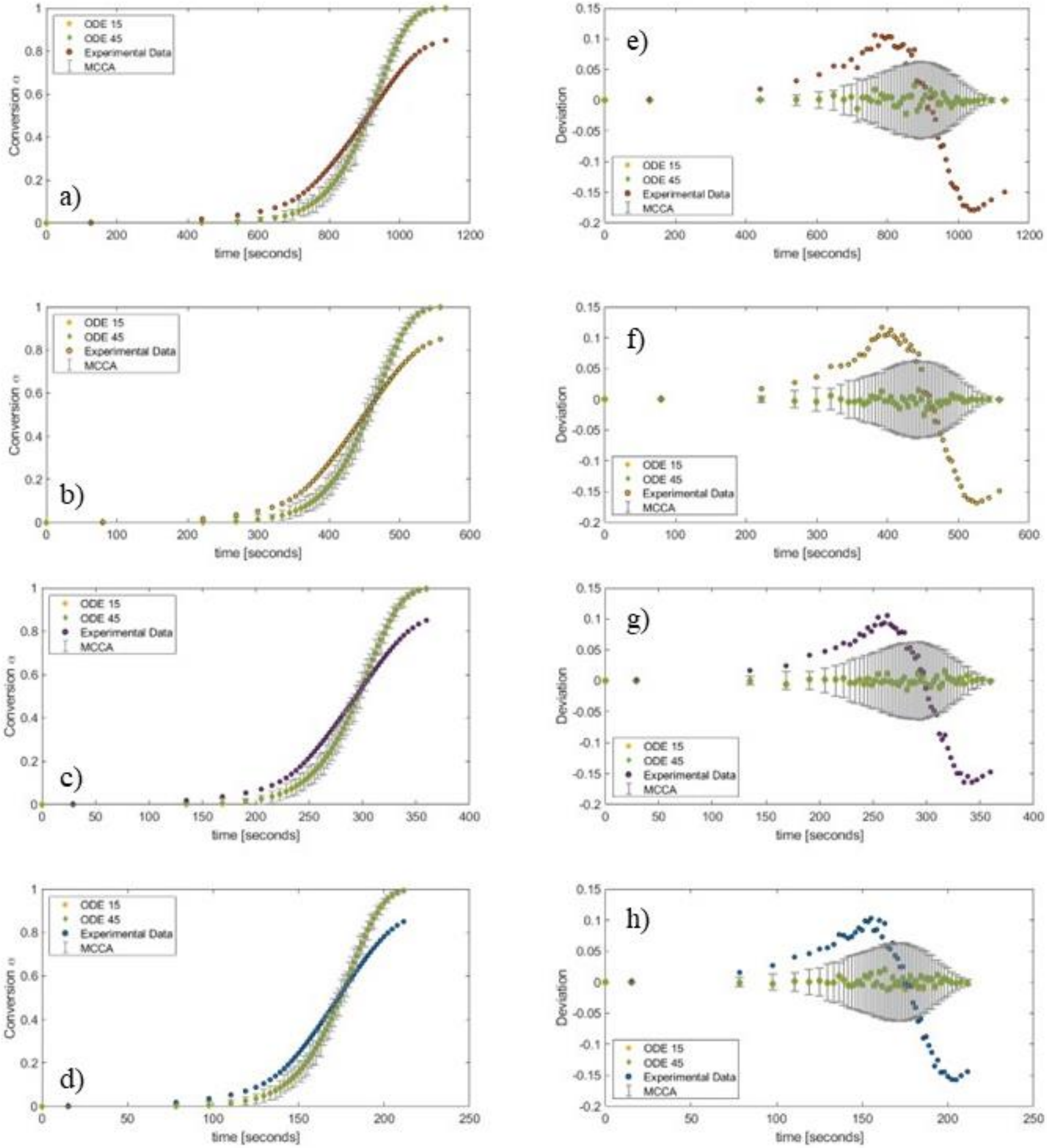
The curve generated by the model is superimposed on the profile of the experimental data, presenting adjustment problems at the beginning and the end of the profile. This adjustment problem can be attributed to the reaction function selected for the development of the model, as mentioned in 1.2.3. Choice of models, there are three categories for reactions models, (Vyazovkin et al., 2011) places the model used in this work as a decelerating model, on the other hand, many reactions models present additional parameters that can improve the adjustment of the conversion profile. While fixing the reaction order in one, which reduces the number of adjustment parameters only to the pre-exponential factor and the activation energy. However, this assumption was necessary to develop the Monte-Carlo Conversion model in another way, equation (44) would not have been obtained. The addition of additional parameters with different kinds of reaction models could solve the adjustment problems, for this, the development of new expressions of the weight function for the Monte-Carlo conversion model is required.

3.5. Model comparison

To compare the results obtained with the Monte-Carlo conversion model, the same conversion curves were generated using the ODE methods implemented in Matlab. The optimized kinetic parameters were loaded, and the profiles were generated, **Figure *11*** shows the curves generated by the two methods and the residual values compared with the error bars calculated with the Monte-Carlo Conversion Algorithm.

Figure 11

Conversion profile calculated using the differential solution methods "ODE45" and "ODE15" to compare with the experimental data and the MCCA.



Nota. MCCA using N=10^3. a/e) HR=10°C/min, b/f) HR=20°C/min, c/g) HR=30°C/min, d/h) HR=50°C/min.

Figure *11* a-d) shows the conversion profiles generated by the 3 methods and the experimental data, the profile calculated with the ODE methods overlaps the error bars of the Monte-Carlo Conversion model in all the cases, this can be better appreciated in the **Figure *11*** e-h), where the difference between the ODE methods and experimental data with the middle value of the error bars is shown, thus it confirms that the conversion profile calculated with the ODE methods have the same pattern that the model developed and all the values are within the confidence interval calculated. Therefore, the methods present the same adjustment errors already highlighted in the Monte-Carlo Conversion Algorithm. The graphs on the right side also show more clearly the fit problems at the beginning and the end of the calculated profile with respect to the experimental data.

Now, when comparing the traditional differential methods with the Monte-Carlo conversion algorithm developed there would be no notable difference between using one or the other, however, the advantage of the Monte-Carlo Conversion model lies in the confidence interval calculated for each point, instead of estimating a single conversion value as the ODE methods do. Furthermore, the developed model allows estimating biomass conversion at any time value without calculating the complete previous profile, thereby reducing the use of unnecessary computational resources.

On the other hand, the traditional differential methods allow an easiest implementation of additional parameters to the reaction models, like the reaction order, which supposes better adjustment of the conversion profile concerning the experimental data due to the implementation of fitting methods could be faster and less complex, this supposes an advantage over the Monte-Carlo conversion model since at the moment this can only be used in specific situations.

4. Conclusions

The selected first-order kinetic model allowed the implementation of the Monte-Carlo method, obtaining a biomass conversion model for isothermal and non-isothermal systems as a function of time, using as parameters the activation energy and the pre-exponential factor and specific values initials in time, if required.

An algorithm was developed that allows the implementation of the model, which through the generation of random numbers allows calculating individual conversion values at specific times, the analysis of the individual conversion calculations showed that as the temperature and time increase the obtaining of values requires a greater generation of random numbers, increasing the complexity and calculation times, in the same way, to reduce the confidence interval of the values it is necessary to increase the amount of random numbers generated.

The model was used to calculate the cellulose conversion profile, using the Friedman method to obtain the kinetic parameters through experimental thermogravimetry data. The superimposition of the profile and the experimental data showed differences in the adjustment, however, the parameter optimization algorithm created shows that the problem lies mainly in the pre-exponential factor, while the activation energy had minimal changes, to improve profile fitting, another method should be used to obtain the pre-exponential factor.

The model and algorithm developed for the calculation of the biomass conversion profile were compared with the traditional differential solution methods "ode45" and "ode15s" implemented in Matlab, the superposition of the obtained profiles showed that all the conversions calculated by these methods were within the confidence interval of the Monte-Carlo conversion model, this makes the developed model an alternative for calculating the biomass conversion profile for specific cases to which the first order reaction function used in its development is adjusted. However, in terms of performance and computation time, the traditional methods were considerably better, and allow adding more parameters to the kinetic model, such as the order for the reaction function, allowing better adjustments.

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Appendices

Appendix A. *Data normalization algorithm function implemented in Matlab.*

The function called “NormalizedData” was developed in Matlab (MATLAB, 2022), its aim is take the raw data obtained from TGA as a “.txt” file, and filter the information, remove the dehydration stage and normalize the data to obtain conversion information. The input information required are the name of the file with extension “.txt” (FileName) it must be in the same folder, the line number where headers are in the file (headerlinesIn), the algorithm also allow obtaining a range of conversion data by the specification of the initial conversion required (ic), the amount of conversion data to extract with the same size step (nd), the final conversion (fc) and the dehydration stage temperature in °C (T).

The output information is an array with the time in seconds, temperature in Kelvin, conversion and the derivate of conversion as a time function. The algorithm is shown below.

```
function data=NormalizedData(FileName,headerlinesIn,ic,nd,fc,T)
    %Importing data from TGA file
    A=importdata(FileName,' ',headerlinesIn);
    %Choosing relevant information: time, temperature and mass and removing the
    %dehydratation stage
    f=T-1;
    k=0;
    while f<T
        k=k+1;
        f=A.data(k,3);
    end
    [m,~]=size(A.data);
    B=zeros(m-k+1,4);
        %Time
    B(:,1)=A.data(k:end,2);
    B(:,1)=B(:,1)-B(1,1);
        %Temperature
    B(:,2)=A.data(k:end,3);
        %Mass
    B(:,3)=A.data(k:end,5);
    %Becoming the mass data into conversion
        InitialMass=B(1,3);
        FinalMass=B(end,3);
```

```
    B(:,3)=InitialMass-B(:,3);
    B(:,3)=B(:,3)*(1/(InitialMass-FinalMass));
%Changing units of temperature (°C--->K)
    B(:,2)=B(:,2)+273.15;

%Calculation of the derivate of conversion as time function
    %First data
    B(1,4)=(3*B(1,3)+4*B(2,3)-B(3,3))/(2*(B(2,1)-B(1,1)));
    %Intermediate data
    for j=2:m-k
        B(j,4)=(B(j+1,3)-B(j-1,3))/(2*(B(j+1,1)-B(j,1)));
    end
    %Final data
    B(m-k+1,4)=(-3*B(m-k-1,3)+4*B(m-k,3)-B(m-k+1,3))/(2*(B(m-k+1,1)-B(m-k,1)));
%DataFiltration discrimanating according to sign of derivate
j=0;
C=zeros(1,4);
for i=1:m-k+1
    if B(i,4) > 0
        j=j+1;
        C(j,1)=B(i,1);      %Time
        C(j,2)=B(i,2);      %Temperature
        C(j,3)=B(i,3);      %Conversion
        C(j,4)=B(i,4);      %Derivate of conversion
    else
    end
end
%Interpolated data to use the same conversion on Friedman method
dx=(fc-ic)/(nd-1);
x=(ic:dx:fc).';
%Matrix with the interpolated data
D=zeros(nd,4);
[n,~]=size(C);
k=0;
for i=ic:dx:fc
    par=i-1;
    j=0;
    while par<i
        if j~=n
            j=j+1;
            par=C(j,3);
        else
            par=i;
        end
    end
    k=k+1;
    if j~=1
        D(k,1)=C(j,1)+(C(j,1)-C(j-1,1))/(C(j,3)-C(j-1,3))*(i-C(j,3));
        D(k,2)=C(j,2)+(C(j,2)-C(j-1,2))/(C(j,3)-C(j-1,3))*(i-C(j,3));
        D(k,3)=i;
        D(k,4)=C(j,4)+(C(j,4)-C(j-1,4))/(C(j,3)-C(j-1,3))*(i-C(j,3));
    else
        D(k,1)=C(j,1);
        D(k,2)=C(j,2);
        D(k,3)=i;
```

```
            D(k,4)=C(j,4);
        end
    end
    data=D;
end
```

Appendix B. *Monte-Carlo Conversion Algorithm function implemented in Matlab*

The function called “MCCA” was developed in Matlab (MATLAB, 2022), the input information is pre-exponential factor (A), energy activation (Ea), universal gas constant (R), amount of random numbers (N), Initial temperature (which corresponds to the end of the dehydration stage) (T0), initial conversion (a0), the heating rate (B) in °C/min units, and the calculus time (time) which is the time where the conversion wants to be estimated. All the units in the international system, with the exception of the heating rate.

The output information is an array with the conversion and the standard deviation calculated. The algorithm is shown below.

```
function alpha=MCCA(A,Ea,R,N,T0,a0,B,time)
    alpha=zeros(1,3);
    t=time;
    disp(T0+B/60*t)
    %Function to calculate K depending on temperature
    k=@(t) A*exp(-Ea/R/(T0+B/60*t));
    kr=k(t);
    delta=0;
    delta2=0;
    for i=1:N
        tao=exprnd(1/kr);
        if tao<t    %More resources way (RED WAY)
            n=1;
            tc(n)=t-tao;
            tao=exprnd(1/kr);
            while tao<tc(n)     %Start the generation of additional random numbers
                n=n+1;
                tc(n)=tc(n-1)-tao;
                tao=exprnd(1/kr);
            end
            as=k(tc(n))/kr+a0*(1-k(tc(n))/kr);
            for j=n-1:-1:1
                as=k(tc(j))/kr+as*(1-k(tc(j))/kr);
            end
            clear tc
            delta=delta+as;
            delta2=delta2+as^2;
        else    %Easy way (BLUE WAY)
            delta=delta+a0;
            delta2=delta2+a0^2;
        end
    end
alpha(1,1)=delta/N;
```

```
alpha(1,2)=sqrt(1/N*(1/N*delta2-(1/N*delta)^2));
end
```

Appendix C. *Calculation for individual conversion values.*

The parameters for cellulose were introduced in the model at three different times (300 / 600 / 1100 seconds for HR 10°C/min and 100 / 300 / 500 seconds for the rest) and three different numbers of iterations N (10^3 / 10^5 / 10^7) were selected to study the variation and the effect of those variables on the estimation of individual values of conversion. The results are shown in Table A1.

Increasing temperature increases the rate constant, $\bar{k}$. This is a quite common result that is described by the Arrhenius law. For the exponential pdf, the mean μ is $1/\bar{k}$, this means that most of the random data time generated will be around this value. A decrease in $\bar{k}$ increases the mean of time, μ. Considering that the rate constant is low for low time values, most of the generated random numbers will be to the right side of the calculation time, making the calculated conversion for that point equal to 0. For this reason, when both the calculation time and $\bar{k}$ increase the average percentage of points to the left side also increases, which can be seen in Table A1.

Looking at the expression to estimate the expected value with the Monte-Carlo algorithm (eq. (20)) the conversions calculated to the right side of the calculation time do not contribute to the weight of the expected value because they will be equal to the initial condition α_0 (commonly equal to 0). This means that the important values of time are to the left side of the calculation time, however, when a generated time is at this side, the algorithm goes into a loop generating additional time values until the exit condition is met (see section *2.6.1. Monte-Carlo conversion* algorithm); making the algorithm heavy and increasing the operation time. For high $\bar{k}$ values, several random time numbers must be generated to rise the exit condition.

Table A1. *Calculated conversion and standard deviation at different times, HR and number of iterations N for Cellulose using the energy activation and pre-exponential factor obtained by the iso-conversional Friedman method.*

Heating Rate [°C/min]	**Time** [s]	**Temperature** [K]	$\bar{k}$ [s^{-1}]	**Generated random times** N	**Average percentage of generated times to the left of the calculation time**	**Performance** [s]	**Standard deviation** σ	**Fig.**
10	300	503.15	2.54E-07	10^3	0.0000%	7.358E-03	0	Fig. 1 a)
				10^5	0.0100%	4.731E-01	7.6970E-06	Fig. 1 b)
				10^7	0.0072%	46.0928	8.1276E-07	Fig. 1 c)
	600	553.15	2.35E-05	10^3	1.0000%	7.700E-03	5.0157E-04	Fig. 2 a)
				10^5	1.3900%	5.103E-01	8.6898E-05	Fig. 2 b)
				10^7	1.3526%	49.3625	9.1871E-06	Fig. 2 c)
	1100	636.48	9.20E-03	10^3	100.000%	9.998E-02	9.6615E-03	Fig. 3 a)
				10^5	99.9970%	8.5185	9.9828E-04	Fig. 3 b)
				10^7	99.9939%	850.58	9.9941E-05	Fig. 3 c)
20	100	496.48	4.18E-07	10^5	0.0070%	1.274E-01	9.1751E-06	Fig. 4 a)
	300	563.15	1.71E-04		4.8470%	1.765E-01	1.7171E-04	Fig. 4 b)
	500	629.82	1.96E-02		99.9930%	2.650	9.8811E-04	Fig. 4 c)
30	100	523.15	1.72E-06	10^5	0.0150%	4.566E-01	1.0102E-05	Fig. 5 a)
	300	623.15	3.93E-03		69.2070%	2.8739	6.9441E-04	Fig. 5 b)
	500	723.15	1.06E+00		100.000%	279.71	0	Fig. 5 c)
50	100	566.48	6.87E-05	10^5	0.7030%	4.792E-01	7.0827E-05	Fig. 6 a)
	150	608.15	1.45E-03		19.4450%	1.281	3.5135E-04	Fig. 6 b)
	200	649.82	2.07E-02		98.4300%	5.4224	1.0112E-03	Fig. 6 c)

Therefore, the Monte-Carlo conversion model can estimate the thermal degradation of biomass at a given specific time using the respectively parameters and initial conditions. However, for high values of time and $\bar{k}$, the quantity of random time numbers generated increases and the algorithm takes more time to complete the iterations. In the other hand, the number of iterations N also affects the time required for the algorithm. In first place, it affects the precision of the result, the confident interval depends on the number of random data generated, bigger quantity of values means a bigger precision. To reduce the confidence interval in a 10^{-1} order is necessary to increase N by 10^2 times (it can be seen in eq. (22)), requiring more resources and iterations in the algorithm.

When the rate constant, $\bar{k}$, and time are low, which means that the mean of the generated random times is high and this is far from the calculation time, the use of a bigger N increases the chance to obtain random time to the left side of the given time, and these values are the ones that actually lead to the conversion with highest precision. The above can be seen in Figures (2), (3) and (4). On each figure, the only parameter change was the N value, in all graphs only the points to the left or the calculation time is shown, higher values are zero for all cases. In Figure (2) it can be seen how increasing this value also increases the change of get points in the left zone, passing from not showing any point to giving rise to a curve formed by the points. The opposite case is Figure (4), where most of the data is generated on the left side of the calculation time, giving rise to a large accumulation of points in this area.

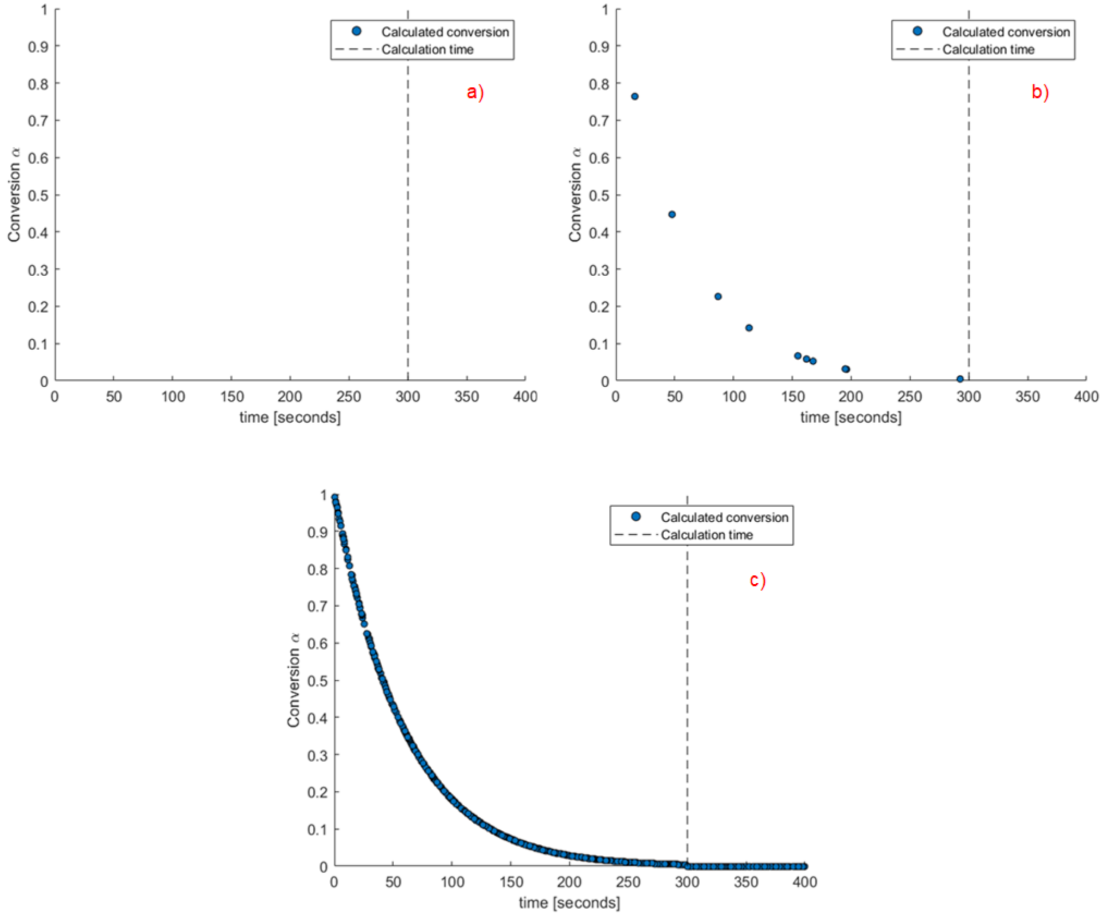

***Fig. 1** Calculated conversion at generated random time values at 300 seconds, HR 10 °C/min, for different quantity of random number: a) N 10^3, b) N 10^5, c) N 10^7.*

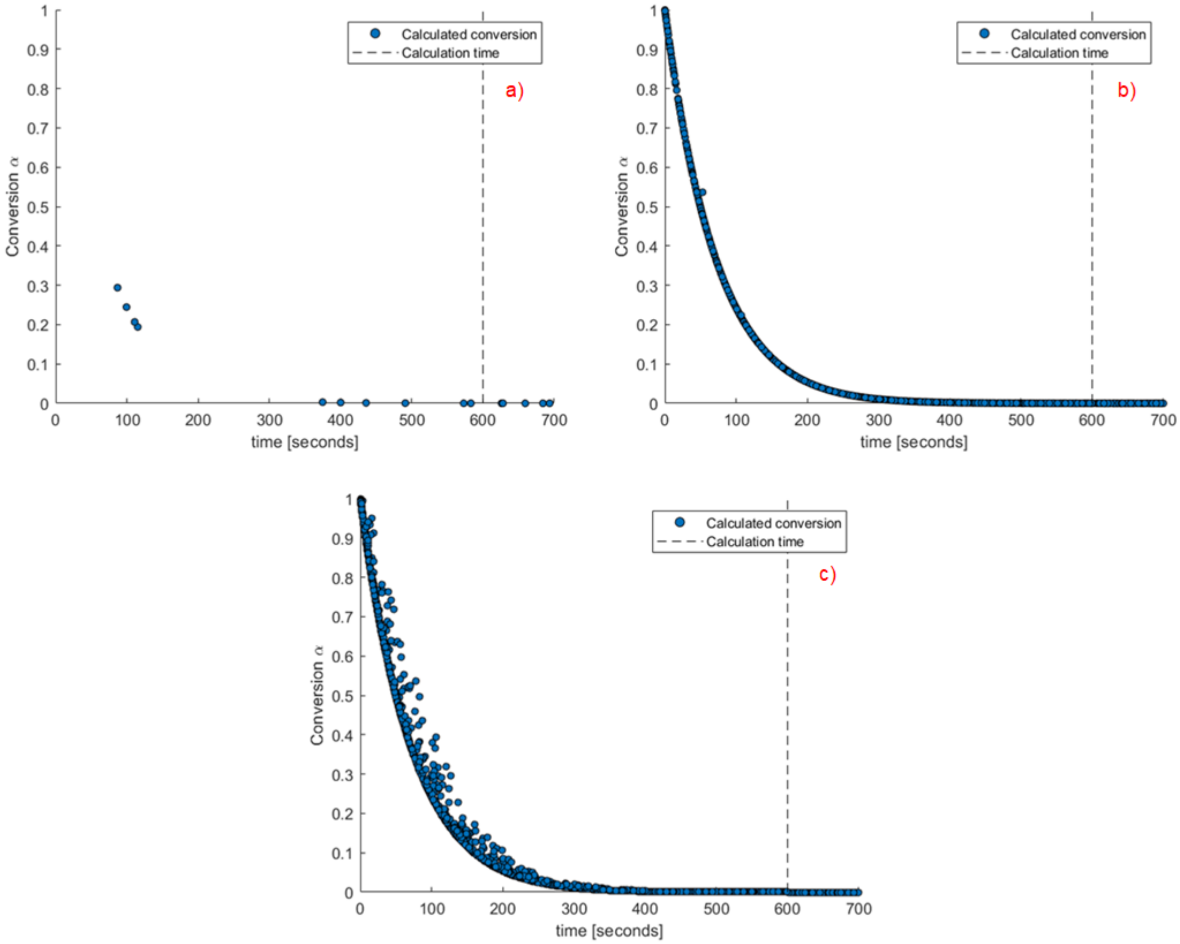

Fig. 2 *Calculated conversion at generated random time values at 600 seconds, HR 10 °C/min, for different quantity of random number: a) N 10^3, b) N 10^5, c) N 10^7.*

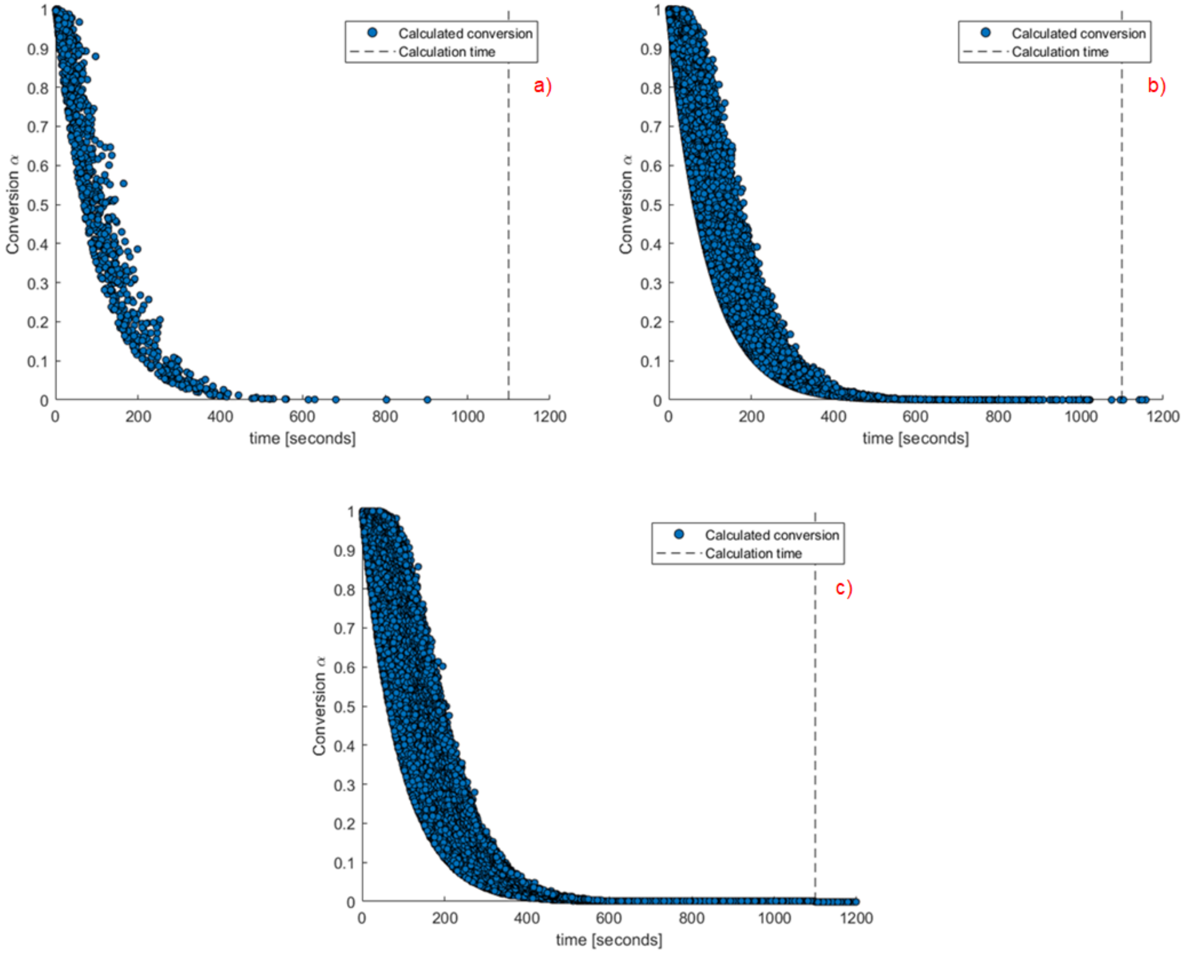

Fig. 3 *Calculated conversion at generated random time values at 1100 seconds, HR 10 °C/min, for different quantity of random number: a) N 10^3, b) N 10^5, c) N 10^7.*

The Figures Fig**. 4**, Fig**. 5** and Fig**. 6** show how the distribution of the generated data changes at three different times, using the same *N* for all of them. Each figure corresponds to a different HR. In the graphs, it can be seen the changes in the points distribution while time increases, the slope of the lower limit becomes steeper and as already was said, the density of points increases in this area. In the Figure Fig**. 5** c) is shown what happens when the model is evaluated in a large time, when the conversion is almost completed, the conversion values are equal to 1, there is not any curve distribution and all the random times generated are small and far from the calculation time.

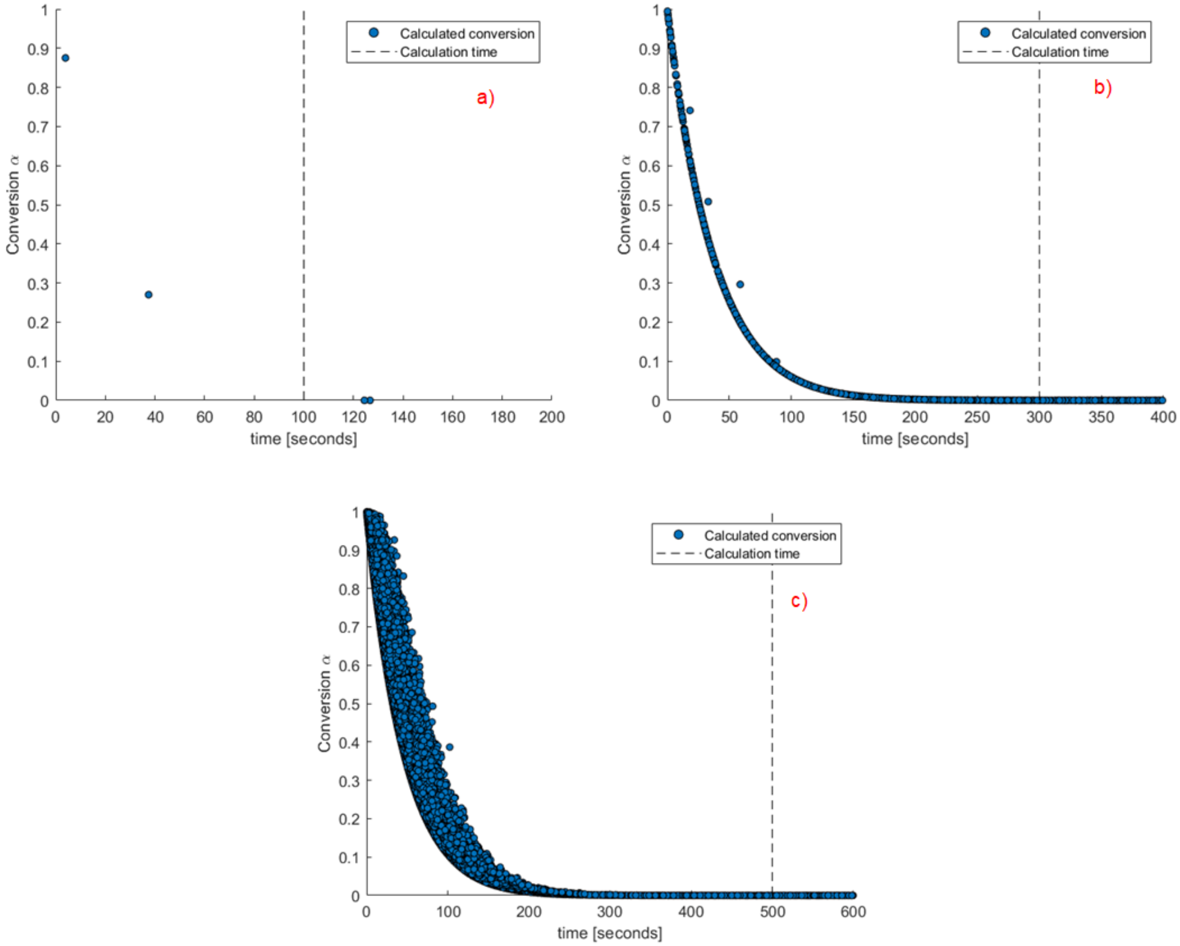

Fig. 4 *Calculated conversion at N equal to* 10^5 *generated random time values, HR 20 °C/min, for different calculation times: a) 100 seconds, b) 300 seconds, c) 500 seconds.*

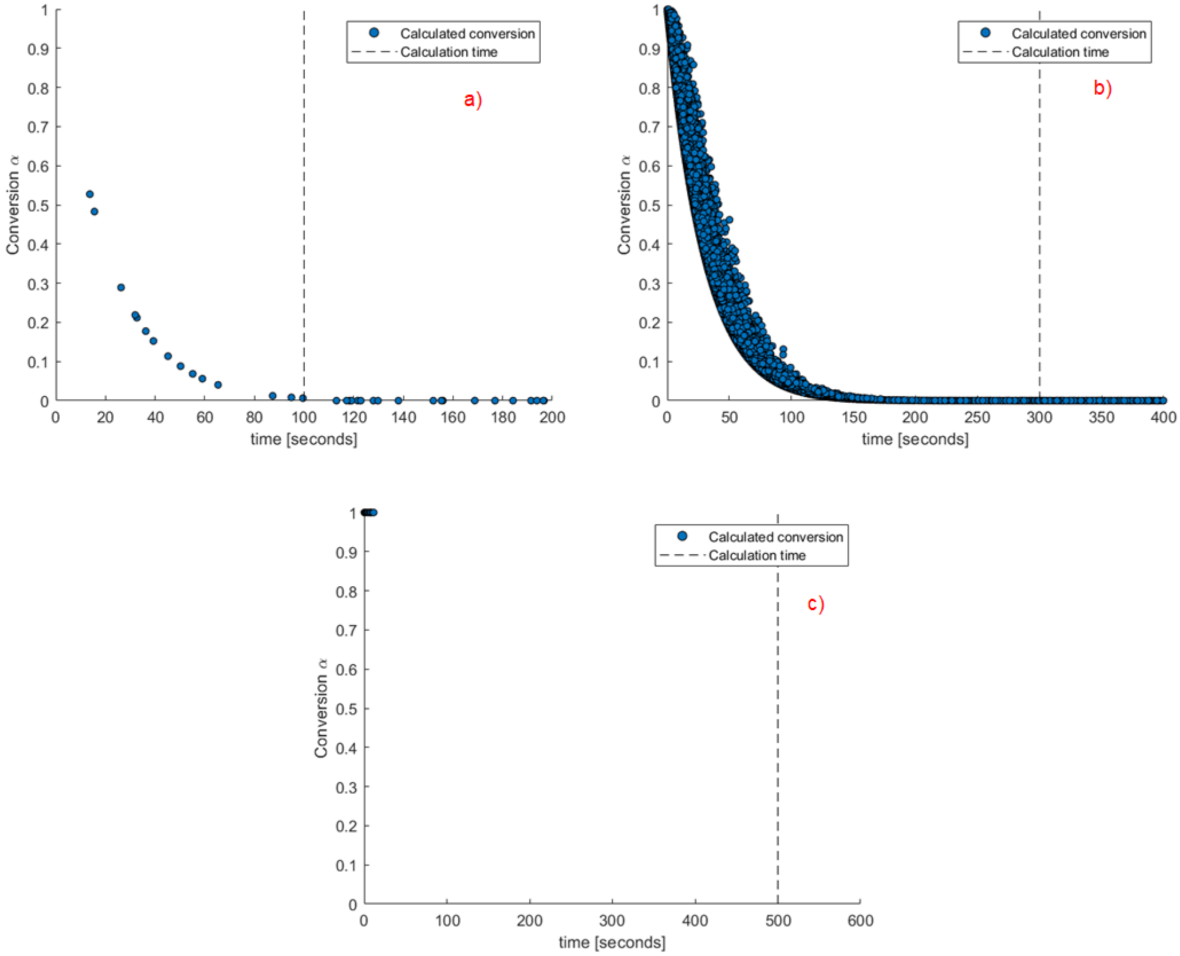

Fig. 5 *Calculated conversion at N equal to 10^5 generated random time values, HR 30 °C/min, for different calculation times: a) 100 seconds, b) 300 seconds, c) 500 seconds.*

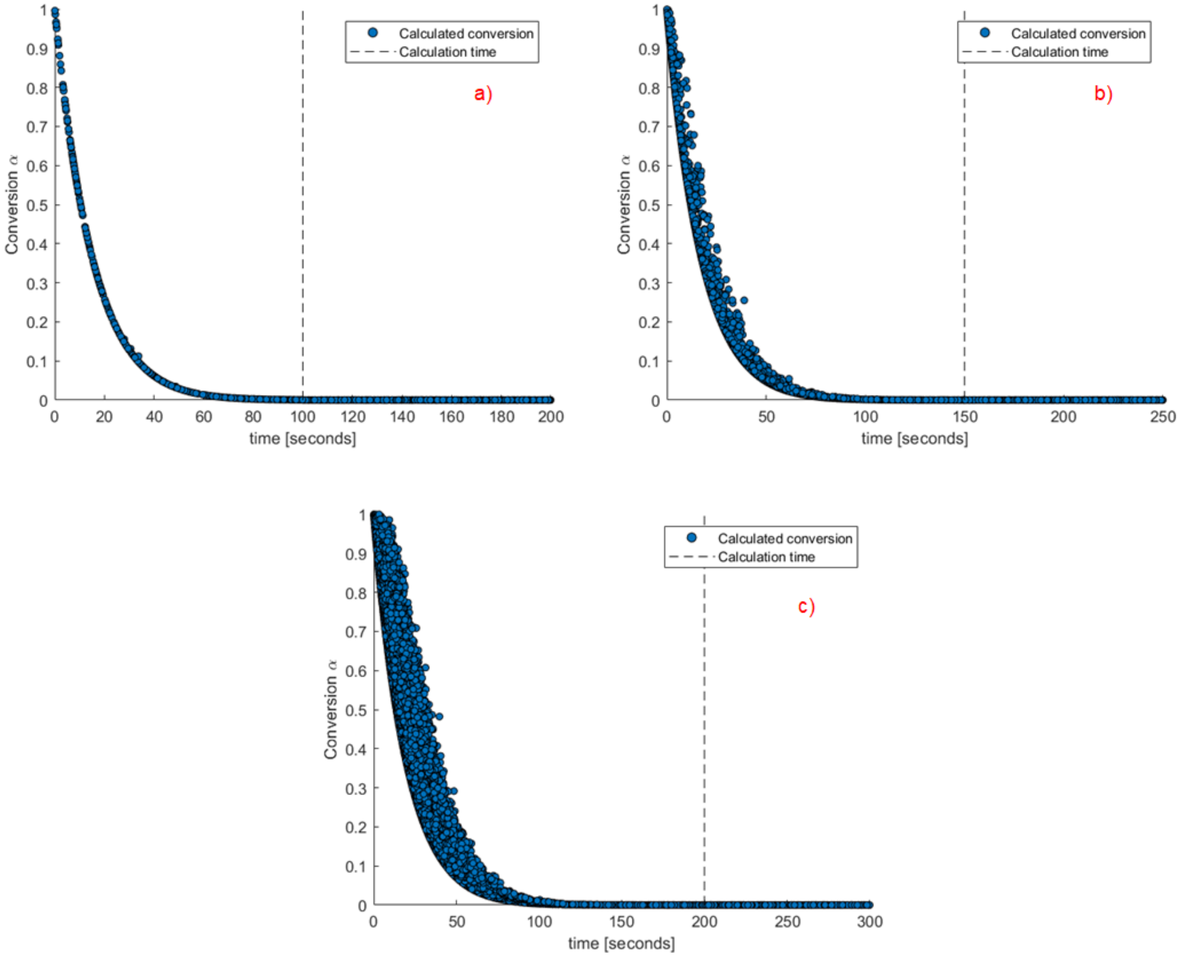

Fig. 6 *Calculated conversion at N equal to* 10^5 *generated random time values, HR 50 °C/min, for different calculation times: a) 100 seconds, b) 150 seconds, c) 200 seconds.*