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## ORIGINAL RESEARCH ARTICLE

# Catalytic effect of ferric sulfate and zinc sulfate on lignin pyrolysis

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## ABSTRACT

The effect of zinc sulfate and ferric sulfate on the pyrolysis process of lignin was studied at three different heating rates by using the thermogravimetric analysis technique. It was found that the pyrolysis of pure lignin is barely affected with the change of heating rates between 10 to 100 °C/min, which is unexpected because of the kinetic nature of pyrolysis. The pyrolysis kinetics of this major component of biomass was studied by using three fitting methods: the differential method with reaction order model n, the isoconversional method, and the distribution of activation energies model, DAEM. The best fit, which allowed calculating acceptable kinetic parameters, was obtained using the last method. The results show the influence of the catalysts and the heating rate on the lignin pyrolysis processes in the presence of the sulfates under study, which is confirmed by obtaining different kinetic parameters. The results suggest that zinc sulfate and ferric sulfate change the kinetic mechanism of lignin pyrolysis.

***Keywords:*** Catalysis; Lignin; Thermogravimetric Analysis; Pyrolysis

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## 1. Introduction

Among the new alternatives that have been implemented to try to reduce the amount of $CO_2$ and $NO_x$ emissions (substances produced during internal combustion processes[1]), biomass emerges as a renewable energy source that not only allows to partially replace fossil fuels[2], but also to reduce the concentrations of these polluting gases in the atmosphere[3]. The thermochemical transformation of biomass usually generates solid, liquid and gaseous fuels, which, in addition to partially replacing fossil fuels, generate heat, electricity and chemical products[4]. Pyrolysis and gasification are the most commercially used thermochemical transformation processes[5].

Biomass of lignocellulosic origin is the most abundant organic material on earth; its sources are forests, agricultural crops, crop residues and other industrial wastes[6]. It consists mainly of cellulose, hemicellulose and lignin[6,7]. To systematically characterize the pyrolysis behavior of biomass, it has been chosen to initially investigate the pyrolysis of each of these three components, using characterization techniques such as thermogravimetric analysis (TG), simultaneous analysis of thermogravimetry and gas chromatography (TG–GC) and simultaneous analysis of thermogravimetry and Fourier transform infrared spectroscopy

(TG–FTIR)[8,9]. Usually in more advanced stages of research (using these same techniques) the interactions that occur between the indicated components have been studied, as well as the interactions that take place between each of them with some alkaline minerals, alkaline earth minerals[10] and metallic salts such as zinc and nickel chlorides[11].

The transition metals, Fe and Zn, are elements that are naturally present in lignocellulosic biomass, however, their concentrations present variations that may depend on environmental factors as well as on the species under study. On the other hand, it is to be expected that the electronic properties of these metals play a fundamental role in the thermal decomposition processes in each of the biomass components. In order to analyze the influence of Fe and Zn (minority components), which can act as catalysts in thermal conversion processes, it is essential to study their effects on cellulose, hemicellulose and lignin (majority components). Fe and Zn added in higher proportions than those naturally present, could favor the thermal conversion process or improve the quality of the products (liquid or gaseous fuels). Therefore, this work aims to evaluate whether Fe and Zn have catalytic effects on the pyrolysis of lignin, for which the kinetics of devolatilization of this major component was investigated in the presence and absence of ferric sulfate $Fe_2(SO_4)_3$ and zinc sulfate $ZnSO_4$, by applying the Friedman differential method with a reaction order model n, the Ozawa, Flynn and Wall (OFW) or isoconversional method, and the distribution of activation energies model, DAEM. In the implementation of this work, the TG technique was used as the experimental analysis method.

## 2. Methodology

### 2.1 Kinetic models

#### *2.1.1 Reaction order model n*

Under isothermal conditions, the solid biomass decomposition rate equation can be expressed as[12]:

$$\frac{d\alpha}{dt} = Ae^{\frac{-E_a}{RT}} f(\alpha) \tag{1}$$

Where $A$ is the pre-exponential or frequency factor, $E_a$ the activation energy, $R$ the universal gas constant, $T$ the absolute temperature, $f(a)$ is the kinetic function representing the kinetic model and is the conversion. Introducing the heating rate $\beta = \frac{dT}{dt}$ for the case of non-isothermal tests, equation (1) becomes[13]:

$$\frac{d\alpha}{dt} = \frac{A}{\beta} e^{\frac{-E_a}{RT}} f(\alpha) \quad \frac{d\alpha}{dt} = \beta \left(\frac{d\alpha}{dT}\right) = Ae^{\frac{-E_a}{RT}} f(\alpha) \tag{2}$$

Equation (2) is the fundamental expression commonly used in the calculation methods of kinetic fitting models with thermogravimetric data. Applying logarithm to the above expression, one has:

$$\ln\left(\frac{d\alpha/dT}{f(\alpha)}\right) = \ln\left(\frac{A}{\beta}\right) - \frac{E_a}{RT} \tag{3}$$

Assuming a reaction model $f(\alpha) = (1-\alpha)^n$, typically used in this type of analysis[14], the modification of equation (3) is obtained:

$$\ln\left(\frac{d\alpha}{dT}\right) - n\ln(1-\alpha) = \ln\left(\frac{A}{\beta}\right) - \frac{E_a}{RT} \tag{4}$$

#### *2.1.2 Isoconversional method*

The isoconversional method does not require knowledge of the reaction mechanism to calculate the activation energy. For this reason, it is called model-free method[15] and constitutes an integral isoconversional technique, in which the activation energy is related to the heating rate and temperature at constant conversion[15,16]. The respective equation is:

$$\ln\beta = C_1 - \frac{E_a}{RT} \tag{5}$$

Where $C_1$ is a constant.

#### *2.1.3 Activation energy distribution model, DAEM*

The activation energy distribution model, DAEM, assumes a series of irreversible parallel first order reactions, characterized by a continuous distribution of activation energies that can be represented by the distribution function $D_j(E)$[17,18]. This model describes pyrolysis processes, in which the fraction of unreacted material $x_j(t)$, at this time $t$ is[19]:

$$x_j(t) = \int_0^\infty D_j(E) X_j(t,E)\, dE \tag{6}$$

Where $Xj(t, E)$ is the solution of the first order kinetic equation for a specific activation energy[15], and is represented by the following equation:

$$-\frac{dX_j(t,E)}{dt} = A_j \exp\left(\frac{-E}{RT(t)}\right) x_j(t,E) \tag{7}$$

For each pseudocomponent a kinetic equation is assumed as equation (1). The weight loss rate curve (DTG) is the weighted sum of the individual reaction rates[17], which is calculated using the following equation:

$$Y^{calc}(t) = -\sum_{j=1}^{M} c_j \frac{dx_j}{dt} \tag{8}$$

Where $x_j$ is the unreacted fraction of the material represented by the $j$-th kinetic equation, $C_j$ corresponds to the contribution of the $j$-th partial reaction of the measured quantity and $M$ is the number of pseudocomponents used for the fit[16]. Each curve of equation (8), can be obtained from equation (6) as follows:

$$\frac{dx_j(t)}{dt} = \int_0^{\infty} D_j(E) \frac{dX_j}{dt}(t,E) dE \tag{9}$$

To make possible the use of available numerical integration techniques, it is required to change the lower limit of integration of the right-hand member of this equation $E = 0$ to $E = -\infty$. Assuming usual pre-exponential factor values, obtaining results of $E = 0$ or $E < 0$ would correspond to events that would take place below ambient temperature. Given this analysis, changing the integration limit does not result in any significant change in the value of the integral[20]. Assuming a Gaussian distribution function $D_j(E)$, normally used for this type of processes[18,21] with an average apparent activation energy $E_0$ and a standard deviation $\sigma$, it is obtained that:

$$x_j(t) = \int_{-\infty}^{\infty} \frac{1}{\sqrt{2\pi}\,\sigma} \exp\left[-\frac{(E-E_{0j})^2}{2\sigma^2}\right] \tag{10}$$

Introducing the change of variable proposed by[21], the Gauss-Hermite quadrature rule and the rescaling proposed by [22] (consisting of a factor between 0.3 and 0.5) to increase the efficiency of the formula, we have

$$x_j(t) = \frac{1}{2\sqrt{\pi}} \sum_{i=1}^{N} w_i \exp[0.75\mu_j^{2}] X_j(t,\mu_j) d\mu_j \tag{11}$$

Where $w_i$ represents the weighting values. In this case, the rescaling factor 0.5, suggested by [20], has been chosen. Furthermore, in this equation 80 has been used as the number of partitions $N$ of the Gauss-Hermite quadrature formula[24].

To perform the least squares curve fitting, a nonlinear method of the same type (least squares) was used, where for the set of experimental curves, $Y_k^{obs}$ and calculated curves, $Y_k^{calc}$, the value of the following expression is minimized:

$$S = \sum_{i=1}^{N_k} [Y^{obs}(t_i) - Y^{calc}(t_i)]^2 \tag{12}$$

Where $N_k$ represents the number of points of the $i$-th evaluated curve[23].

## 2.2 Materials

Alkaline lignin, with low sulfonate content, (96%) was purchased from Sigma-Aldrich and used without further purification. The catalysts zinc sulfate (99%) and ferric sulfate (75%) were obtained from PanReac. Lignin/catalyst mixtures containing 3% by weight of catalyst were prepared by weighing, using appropriate masses of each of the components. The prepared samples, which were shaken until uniformity was achieved, were isothermally dried at 105 °C for 24 h and then stored in a desiccator.

## 2.3 Thermogravimetric analysis

Thermogravimetric analysis of pure components and lignin/catalyst mixtures were carried out on a TGA 2950 thermogravimetric balance (TA instruments). Three heating rates were used: 10, 30 and 100 °C/min. Helium (purity grade 5) with a constant flow rate of 100 mL/min was used as purge gas. In order to reduce heat and mass transfer effects[16], the mass of the samples loaded on the thermobalance was adjusted to the range 2–15 mg. The effect of heating rate and catalyst type on the DTG peak temperature of lignin pyrolysis was studied.

## 2.4 Fitting to kinetic models

The experimental results were analyzed with several widely recognized methods[14–16]. Specifically, to determine the kinetic parameters of the decomposition of lignin and its mixtures with the study catalysts, the reaction order n model, the isoconversional method and the activation energy distribution model, DAEM, were used.

### *2.4.1 Reaction order n model*

To obtain the kinetic parameters, the left–hand side of equation (4) is plotted as a function of 1/*T*; this allows the activation energy ($E_a$) to be obtained from the slope and the pre-exponential factor (*A*) from the intercept with the ordinate. To find the best fit, the order n of the reaction of equation (4) that gives the value closest to unity for the coefficient of determination $R^2$ is sought. To make this calculation we used the Find Target tool and the functions included by default in the MS Excel® software.

### *2.4.2 Isoconversional method*

According to equation (5), the activation energy can be calculated from the slope of 1nβ as a function of 1/*T*. The temperature measurements were obtained for fixed conversions at the different heating rates. Then, the activation energy for the pyrolysis process was calculated from the slopes ($-E_a/R$) of the graphs for different conversion values.

### *2.4.3 Activation energy distribution model, DAEM*

The construction of the necessary codes for the implementation of the DAEM model was coded in the Matlab® programming language. In this model, the sum of equation (11) is evaluated having as acceptance criterion the minimization of the value of equation (12).

## 3. Results and discussion

Subfigures (a), (b) and (c) of **Figure 1** show the TG curves of lignin and lignin with each catalyst (ferric sulfate and zinc sulfate) at the respective heating rates 10, 30 and 100 °C/min. These curves present a behavior similar to that reported in previous studies[24]. When comparing these results for lignin, with those reported in literature for the other components of lignocellulosic biomass[25], lignin exhibits a slow degradation rate, even up to temperatures as high as 540 °C. In these results, it is possible to appreciate that the addition of the catalysts does not affect the percentage of carbonization at the heating rates 10 and 30 °C/min. However, when the samples are heated at 100 °C/min, the percentage charring is higher with both catalysts when compared to the pyrolysis of pure lignin.

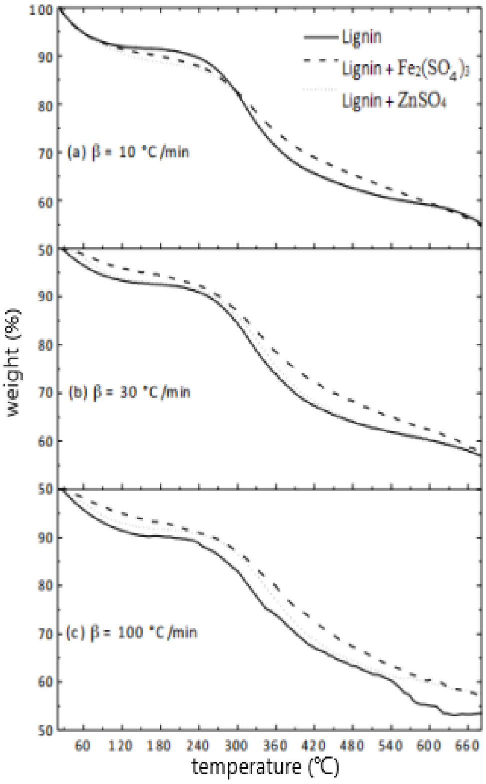

**Figure 1.** Thermograms of lignin pyrolysis with and without catalysts at three heating rates.

Subfigures (a), (b) and (c) of **Figure 2** present the DTG thermograms obtained for lignin with and without catalysts at the respective heating rates 10, 30 and 100 °C/min. These show a first event corresponding to the release or detachment of water[26], followed by a second event corresponding to the first thermal degradation event. Depending on the heating rate and the catalyst used, such event presents different retarding effects.

A comparative analysis of the DTG curves obtained at the different heating rates, specifically for the first thermal degradation event (after water release), shows that the lignin without catalyst has the lowest peak temperature regardless of the heating rate. In the thermogram of the lignin sample with zinc sulfate heated at 100 °C/min, the aforementioned retarding effect is seen in greater proportion, observing that the maximum peak temperature is shifted 32 °C towards higher temperatures with respect to the peak of pure lignin. This contrasts with the 18 and 19 °C shift obtained at the lower heating rates of 10 and 30 °C/min, respectively. Upon addition of ferric sulfate, it is observed that when

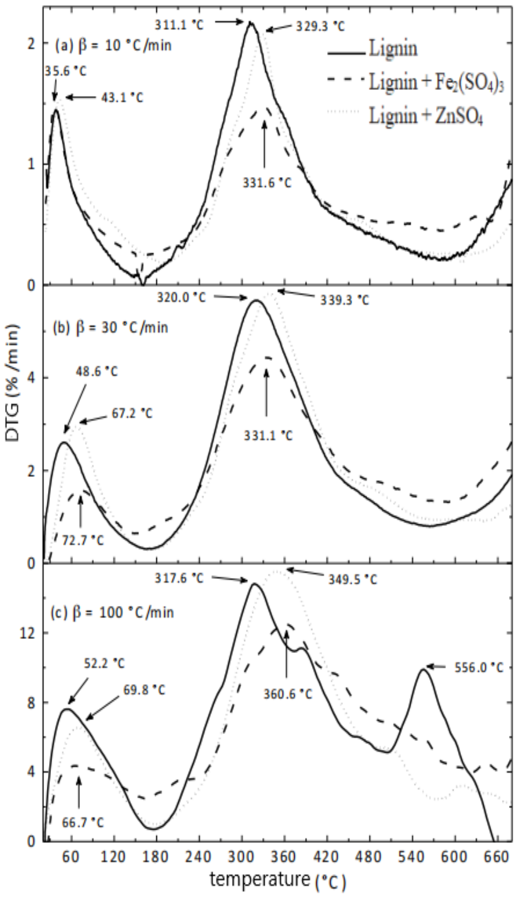

**Figure 2.** DTG thermograms of lignin pyrolysis with and without catalysts at three heating rates.

the sample is heated at 10 and 30 °C/min, the peak temperature remains virtually constant at 331 °C. However, by increasing the heating rate to 100 °C/min, the maximum rate of weight loss occurs at 360 °C.

This indicates that rapidly heating a lignin sample with ferric sulfate magnifies the retarding effect of the iron catalyst.

The addition of ferric sulfate, regardless of the heating rate, produced a significant reduction in the maximum degradation rate. An opposite behavior was obtained when zinc sulfate was added, since this catalyst slightly increased the maximum degradation rate of lignin. On the other hand, according to **Figure 2**, when lignin is heated at 100 °C/min, at 556 °C a third event occurs that is not observed at the other heating rates. This suggests that at this particular heating rate a change of mechanism in the chemical kinetics takes place. This event disappears under the presence of the two catalysts involved in the present investigation, evidencing that they affect the pyrolysis of lignin.

## 3.1 Effect of the heating rate and the catalysts studied

Using analysis of variance, the influence of catalysts and heating rates on the DTG peak temperature of the most significant event in lignin pyrolysis was analyzed. This task was performed using Statgraphics Centurion XVII statistical software. The values of the statistical analysis for lignin are presented in **Table 1**. The results show that the presence of the catalysts significantly affects the DTG peak temperature of the main pyrolysis event, while the effect of heating rate is statistically not significant. This is surprising since it is well known that pyrolysis is a kinetic phenomenon. Precisely for this reason the experiment was repeated multiple times in order to examine if any systematic error could take place, however, the results confirm that this is the thermal response of the samples.

## 3.2 Kinetic analysis

### *3.2.1 Reaction order model n*

The coefficient of determination $R^2$ obtained using the reaction order n model for all the trials was greater than 0.9, indicating a good fit of the data (in **Figure 3**). However, as noted in **Table** 2, the reaction orders obtained in several trials are very high from a kinetic point of view.

This demonstrates low reliability in the relationships established by the model, and therefore, it prevents obtaining solid conclusions. Although the model offers little reliability, it should be noted that a change in the reaction orders can be seen when catalysts are added. For example, for lignin without the addition of any catalyst, the order is

**Table 1.** ANOVA for lignin

| Source | Sum of squares | GL | Middle square | Ratio–F | Value–p |
|---|---|---|---|---|---|
| Main effects | | | | | |
| A: Catalyst | 1,192.86 | 2 | 596.431 | 9.54 | 0.0301 |
| B: Speed (β) of heating | 529.416 | 2 | 264.708 | 4.23 | 0.103 |
| Residuals | 250.184 | 4 | 625.461 | – | – |
| Total (Corrected) | 1,972.46 | 8 | – | – | – |

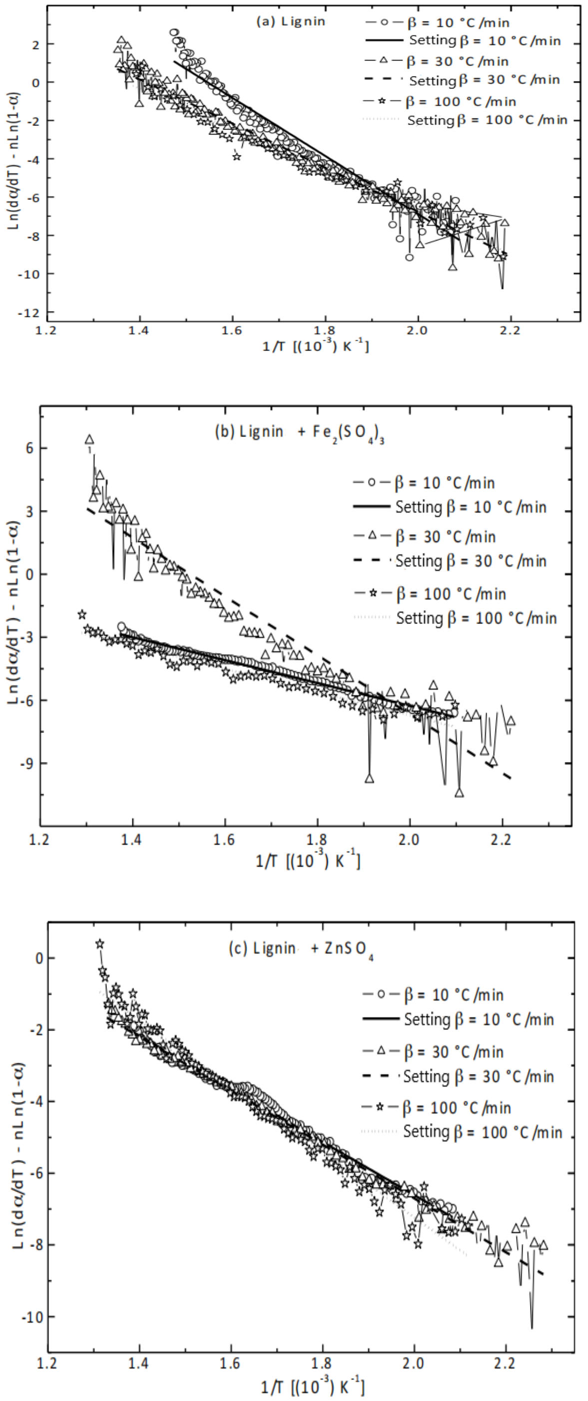

**Figure 3.** Fit to the n reaction order model for lignin with and without catalysts.

approximately 3; however, with the addition of ferric sulfate the reaction order is 5, 1.5 and 1.7 when the samples are heated at 30, 10 and 100 °C/min, respectively. The addition of zinc sulfate to lignin results in a change in reaction order from 3 to approximately 2 regardless of the heating rate, which represents an interesting result when applying this model. This suggests a change in the mechanism of the reaction kinetics of lignin pyrolysis in the presence of the catalysts involved in this work.

**Table 2.** Fit of experimental data to the n reaction order model

| Samples | β (°C/min) | n | $R^2$ | f(α ) |
|---|---|---|---|---|
| Lignin | 10 | 3 | 0.972 | $(1-\alpha)^{3.0}$ |
| | 30 | 3.5 | 0.959 | $(1-\alpha)^{3.5}$ |
| | 100 | 3 | 0.959 | $(1-\alpha)^{3.0}$ |
| Lignin + $Fe_2(SO_4)_3$ | 10 | 1.5 | 0.99 | $(1-\alpha)^{1.5}$ |
| | 30 | 5 | 0.904 | $(1-\alpha)^{5.0}$ |
| | 100 | 1.7 | 0.957 | $(1-\alpha)^{1.7}$ |
| Lignin + $ZnSO_4$ | 10 | 1.8 | 0.989 | $(1-\alpha)^{1.8}$ |
| | 30 | 2.2 | 0.986 | $(1-\alpha)^{2.2}$ |
| | 100 | 2.3 | 0.974 | $(1-\alpha)^{2.3}$ |

### *3.2.2 Isoconversional method*

**Figure 4**, which plots lnβ as a function of 1/*T*, represents the application of this method to DTG thermogram data for lignin with and without catalyst. For the lignin sample there is a slight shift to the right of the points measured at the highest heating rate. Such a shift is evident, as the expected linear behavior is altered[27]. Indeed, the coefficients of determination $R^2$ correspond even to values as low as 0.8. This suggests that at high heating rates a change of kinetic mechanism takes place. On the other hand, the samples with catalyst exhibit a good fit for conversions higher than 30%, presenting $R^2$ values very close to 1; this suggests that the reaction mechanism in the presence of the catalysts is independent of the heating rate within the range studied; which contrasts with the case of pure lignin. An average activation energy of 328 kJ/mol was obtained for lignin with zinc sulfate and 240 kJ/mol when ferric sulfate was added. These values correspond to the average of the results that present a fit with $R^2$ of at least 0.9. The values obtained are higher than those reported by other authors for lignin (207 kJ/mol[28–30]).

## 3.3 Activation energy distribution model, DAEM

Taking into account that during the pyrolysis of the studied systems numerous species are produced (polycyclic aromatic hydrocarbons, phenolic compounds and oxygenated organic species[31]), it was

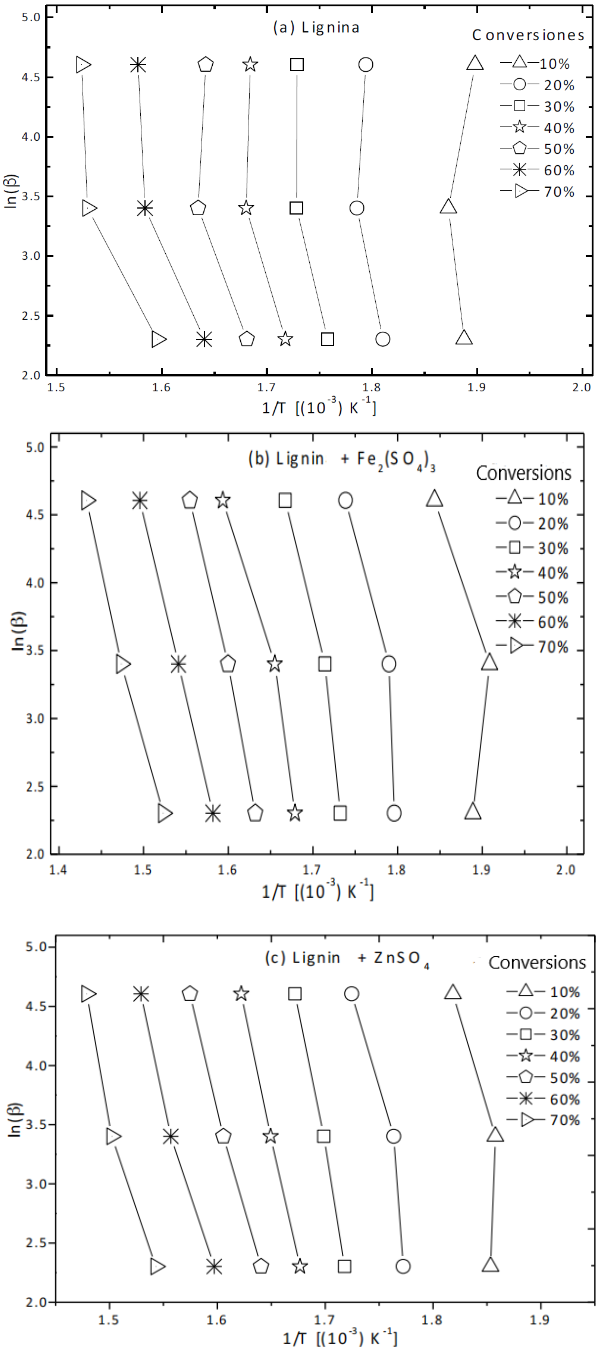

**Figure 4.** Isoconversional method for lignin with and without catalysts

decided to choose the number of reaction sets or pseudocomponents that offered the best fit. In most cases, this was achieved when selecting 3 pseudocomponents, which is atypical because lignin is a pure component. In the case of lignin samples with and without catalyst heated at 30 °C/min, the best fit was obtained using 2 pseudocomponents. Also in this case it was necessary to use more than one pseudocomponent to describe the lignin pyrolysis process.

The obtained settings are shown in subfigures (a), (b) and (c) of **Figure 5**, corresponding respectively to heating rates 10, 30 and 100 °C/min.

The results of the kinetic parameters obtained with this model for lignin without catalyst at the different heating rates (see **Table 3**) show activation energies that are within the ranges reported by the literature (35–361 kJ/mol)[32,33].

The curves that were fitted for the lignin samples with catalysts, at the different heating rates, are presented in **Figure 6**.

The data in **Table 3** show that the addition of sulfates affects the kinetic parameters of one or more of the reaction sets, mainly on the pre-exponential parameter, which in most cases decreases, causing the partial DAEM curve to shift towards higher temperatures. These results reiterate a change

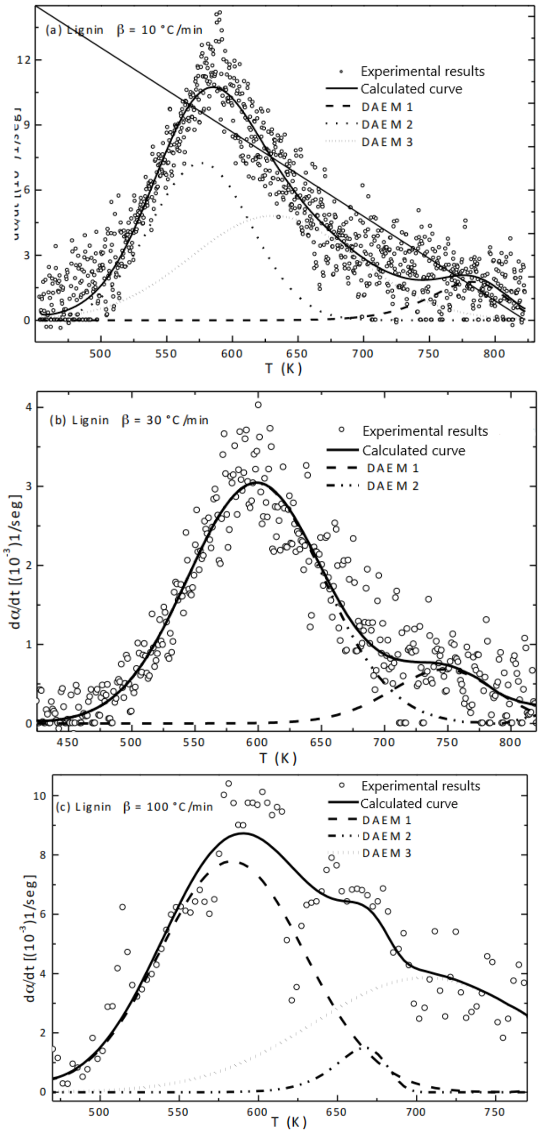

**Figure 5.** Fit to DAEM using several numbers of reaction sets for lignin pyrolysis.

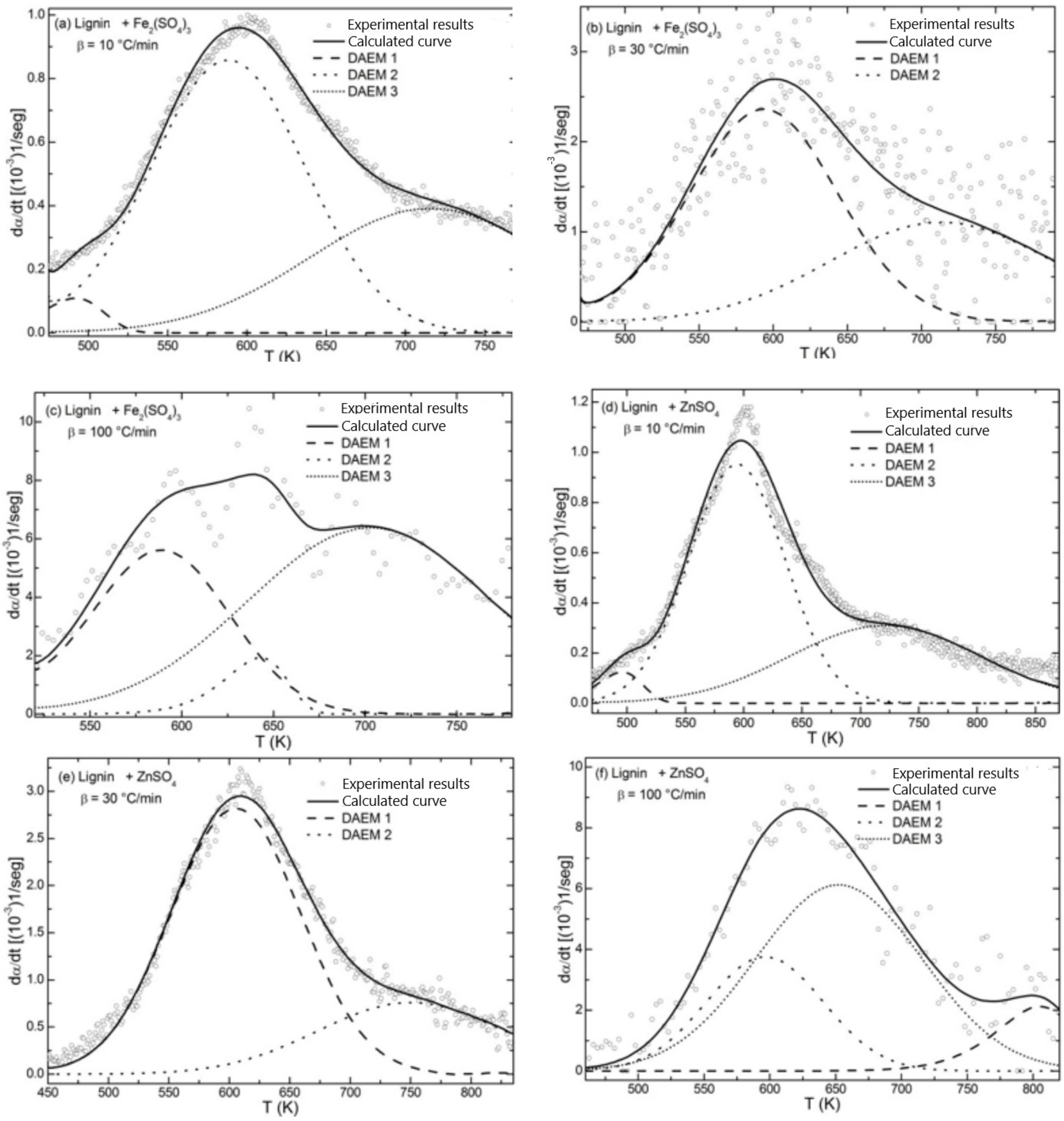

**Figure 6.** Fit of DAEM to lignin DTG curves with $Fe_2(SO_4)_3$ and $ZnSO_4$, at three heating rates.

in the reaction mechanism of lignin pyrolysis in the presence of the catalysts under study in the present investigation.

## 4. Conclusions

In this work, the thermal decomposition process of one of the main components of lignocellulosic biomass, lignin, was studied in the presence of ferric sulfate and zinc sulfate. The analysis of variance showed a significant effect of the presence of sulfates on the maximum decomposition rate temperature of the main pyrolysis event. In contrast, pyrolysis of pure lignin was found to be affected very little by changing heating rates between 10 and 100 °C/min, which is unexpected because of the kinetic nature of pyrolysis. In general terms, zinc and ferric sulfates retard the lignin pyrolysis process. This retarding effect is more pronounced in the case of ferric sulfate and is magnified at high heating rates (100 °C/min). These suggest that the effect of zinc and ferric sulfates is more pronounced on the pyrolysis mechanism at high heating rates than on the dominant mechanism at low heating rates.

The reaction order model n, showed a good fit

**Table 3.** Parameters of DAEM for lignin with and without catalysts

| Parameters | Lignin | Lignin + $Fe_2(SO_4)_3$ | Lignin + $ZnSO_4$ | Lignin | Lignin + $Fe_2(SO_4)_3$ | Lignin + $ZnSO_4$ | Lignin | Lignin + $Fe_2(SO_4)_3$ | Lignin + $ZnSO_4$ |
|---|---|---|---|---|---|---|---|---|---|
| | β = 10 °C/min | | | β = 30 °C/min | | | β = 100 °C/min | | |
| $c_1$ | 0.079 | 0.0245 | 0.0328 | 0.1436 | 0.5825 | 0.7463 | 0.5834 | 0.3485 | 0.0979 |
| $A_1$ ($s^{-1}$) | 9.08E+09 | 6.66E+09 | 5.64E+09 | 7.83E+10 | 5.95E+15 | 2.59E+15 | 3.75E+16 | 2.67E+16 | 5.72E+10 |
| $E_{01}$ (kJ/mol) | 182.7 | 112.2 | 112.3 | 182.3 | 198.3 | 198.3 | 198.3 | 198.4 | 185.1 |
| $\sigma_1$ (kJ/mol) | 1.758 | 1.758 | 1.719 | 7.83 | 16.09 | 17.01 | 14.4 | 11.3 | 1.8 |
| $c_2$ | 0.4219 | 0.6329 | 0.5936 | 0.8073 | 0.4169 | 0.2931 | 0.0403 | 0.0562 | 0.275 |
| $A_2$ ($s^{-1}$) | 2.64E+14 | 1.10E+14 | 7.70E+13 | 4.36E+15 | 4.60E+12 | 8.09E+11 | 6.97E+16 | 1.65E+15 | 6.37E+14 |
| $E_{02}$ (kJ/mol) | 182.8 | 182.8 | 182.8 | 198.3 | 198.3 | 198.3 | 228.9 | 200.1 | 182.8 |
| $\sigma_2$ (kJ/mol) | 11.1 | 14.3 | 11.6 | 17.3 | 20.3 | 19.5 | 0.001 | 0.001 | 12.4 |
| $c_3$ | 0.4593 | 0.451 | 0.3834 | – | – | – | 0.426 | 0.6658 | 0.6178 |
| $A_3$ ($s^{-1}$) | 1.54E+14 | 1.41E+12 | 1.07E+12 | – | – | – | 2.52E+13 | 2.96E+13 | 4.57E+14 |
| $E_{03}$ (kJ/mol) | 198.3 | 198.3 | 198.3 | – | – | – | 198.3 | 198.3 | 198.3 |
| $\sigma_3$ (kJ/mol) | 19.2 | 20.4 | 21.9 | – | – | – | 19.1 | 17.9 | 18.3 |

to the experimental data, but in some cases, very high and therefore unrealistic reaction order values. The isoconversional method did not fit the data for lignin pyrolysis without catalyst, but it did fit the data for lignin in the presence of zinc and ferric sulfates, which made it difficult to interpret the results of the effect of catalysts on lignin pyrolysis. To describe the kinetics of lignin pyrolysis with and without catalysts, with the DAEM model, it was necessary to use three pseudocomponents, which shows that it is a complex process and can hardly be modeled as a single decomposition reaction. This has strong implications for lignocellulosic biomass decomposition models. The three kinetic models used to analyze the thermogravimetric data showed that the kinetic parameters of the pyrolysis of pure lignin change if it is mixed with zinc sulfate or ferric sulfate, which in turn suggests a change of reaction mechanism.

## Conflict of interest

The authors declare that they have no conflict of interest.

## Acknowledgements

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## References

1. Rodríguez RP, Sierens R, Verhelst S, *et al.* Evaluation of the performance of internal combustion engines working with biodiesel (in Spanish). Mechanical Engineering 2008; 3: 33–38.
2. Perdices MB. Biomass as an energy resource. In: Castellanos PR (editors). Climate change, a challenge within our reach? (in Spanish) University of Salamanca Editions. Salamanca. 2009. p. 167–180.
3. Montiel JLR. Sugarcane biomass is an alternative to increase energy efficiency and reduce environmental pollution (in Spanish). Sugar Center 2003; 30(2): 14–21.
4. Camps Michelena M, Marcos Martín F. Biofuels (in Spanish). Madrid Editions Mundi Press; 2008. p. 20–40.
5. Soto NA, Machado WR, López DL. Determi-

nation of kinetic parameters in the pyrolysis of cypress pine (in Spanish). Quim. Nova 2010; 33(7): 1500–1505.

6. Abril A, Navarro EA. Ethanol from lignocellulosic biomass (in Spanish). Valencia: Aleta Editions; 2012. p. 11–41.
7. Caballero JA. Kinetic study of lignin pyrolysis: Design of a reactor for the study of secondary reactions (in Spanish). Doctor in Chemical Engineering. University of Alicante; 1995.
8. Gani A, Naruse I. Effect of cellulose and lignin content on pyrolysis and combustion characteristics for several types of biomass. Renewable Energy 2007; 32(4): 649–661.
9. Yang H, Yan R, Chen H, *et al.* Characteristics of hemicellulose, cellulose and lignin pyrolysis. Fuel 2007; 86(12): 1781–1788.
10. Lv D, Xu M, Liu X, *et al.* Effect of cellulose, lignin, alkali and alkaline earth metallic species on biomass pyrolysis and gasification. Fuel Processing Technology 2010; 91(8): 903–909.
11. Khelfa A, Bensakhria A, Weber J. Investigations into the pyrolytic behaviour of birch wood and its main components: primary degradation mechanisms, additivity and metallic salt effects. Journal of Analytical and Applied Pyrolysis 2013; 101: 111–121.
12. Hurley MJ, Gottuk DT, Hall Jr JR, *et al.* SFPE handbook of fire protection engineering. Springer 2015.
13. Çepelioğullar Ö, Haykırı-Açma H, Yaman S. Kinetic modelling of RDF pyrolysis: Model-fitting and model-free approaches. Waste Management 2016; 48: 275–284.
14. Martín-Lara M, Blázquez G, Zamora M, *et al.* Kinetic modelling of torrefaction of olive tree pruning. Applied Thermal Engineering 2017; 113: 1410–1418.
15. Açıkalın K. Pyrolytic characteristics and kinetics of pistachio shell by thermogravimetric analysis. Journal of Thermal Analysis and Calorimetry 2011; 109(1): 227–235.
16. Albis A, Ortiz E, Suárez A, *et al.* TG/MS study of the thermal devolatization of Copoazú peels (Theobroma grandiflorum). Journal of Thermal Analysis and Calorimetry 2013; 1–9.
17. Chen N, Ren J, Ye Z, *et al.* Kinetics of coffee industrial residue pyrolysis using distributed activation energy model and components separation of bio-oil by sequencing temperature—Raising pyrolysis. Bioresource Technology 2016; 221, 534–540.
18. Cheng Z, Wu W, Ji P, *et al.* Applicability of Fraser-Suzuki function in kinetic analysis of DAEM processes and lignocellulosic biomass pyrolysis processes. Journal of Thermal Analysis and Calorimetry 2015; 119(2): 1429–1438.
19. Várhegyi G. Aims and methods in non-isothermal reaction kinetics. Journal of Analytical and Applied Pyrolysis 2007; 79(1): 278–288.
20. Várhegyi G, Szabó P, Antal MJ. Kinetics of charcoal devolatilization. Energy & Fuels 2002; 16(3): 724–731.
21. Janković B. The pyrolysis process of wood biomass samples under isothermal experimental conditions—Energy density considerations: Application of the distributed apparent activation energy model with a mixture of distribution functions. Cellulose 2014; 21(4): 2285–2314.
22. Donskoi E, McElwain D. Optimization of coal pyrolysis modeling. Combustion and Flame 2000; 122(3): 359–367.
23. Abdelouahed L, Leveneur S, Vernieres-Hassimi L, *et al.* Comparative investigation for the determination of kinetic parameters for biomass pyrolysis by thermogravimetric analysis. Journal of Thermal Analysis and Calorimetry 2017; 129(2): 1201–1213.
24. Yu J, Paterson N, Blamey J, *et al.* Cellulose, xylan and lignin interactions during pyrolysis of lignocellulosic biomass. Fuel 2017; 191: 140–149.
25. Collard FX, Blin J. A review on pyrolysis of biomass constituents: Mechanisms and composition of the products obtained from the conversion of cellulose, hemicelluloses and lignin. Renewable and Sustainable Energy Reviews 2014; 38: 594–608.
26. Gottipati R, Mishra S. A kinetic study on pyrolysis and combustion characteristics of oil cakes: Effect of cellulose and lignin content. Journal of Fuel Chemistry and Technology 2011; 39(4): 265–270.
27. Ma Z, Sun Q, Ye J, *et al.* Study on the thermal

degradation behaviors and kinetics of alkali lignin for production of phenolic—Rich bio-oil using TGA-FTIR and Py-GC/MS. Journal of Analytical and Applied Pyrolysis 2016; 117: 116–124.

28. Caprariis BD, Santarelli ML, Scarsella M, *et al.* Kinetic analysis of biomass pyrolysis using a double distributed activation energy model. Journal of Thermal Analysis and Calorimetry 2015; 121(3): 1403–1410.
29. Cai J, Wu W, Liu R. An overview of distributed activation energy model and its application in the pyrolysis of lignocellulosic biomass. Renewable and Sustainable Energy Reviews 2014; 36: 236–246.
30. Chayaporn S, Sungsuk P, Sunphorka S, *et al.* Evaluation of biomass component effect on kinetic values for biomass pyrolysis using simplex lattice design. Korean Journal of Chemical Engineering 2015; 32(6): 1081–1093.
31. Qu T, Guo W, Shen L, *et al.* Experimental study of biomass pyrolysis based on three major components: Hemicellulose, cellulose, and lignin. Industrial & Engineering Chemistry Research 2011; 50(18): 10424–10433.
32. Murugan P, Mahinpey N, Johnson KE, *et al.* Kinetics of the pyrolysis of lignin using thermogravimetric and differential scanning calorimetry methods. Energy & Fuels 2008; 22(4): 2720–2724.
33. Ferdous D, Dalai A, Bej S, *et al.* Pyrolysis of lignins: Experimental and kinetics studies. Energy & Fuels 2002; 16(6): 1405–1412.