



Research article

A new approach to obtain kinetic parameters of corn cob pyrolysis catalyzed with CaO and CaCO₃



Erika Arenas Castiblanco^a, Juan Henao Montoya^b, Gabriela Valencia Rincón^b, Zulamita Zapata-Benabithé^{a,*}, Rafael Gómez-Vásquez^c, Diego A. Camargo-Trillos^c

^a Grupo de Energía y Termodinámica, Facultad de Ingeniería Química, Escuela de Ingenierías, Universidad Pontificia Bolivariana, Circular 1 No. 70-01, Medellín, 050031, Antioquia, Colombia

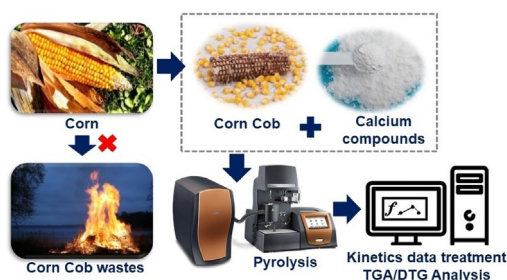
^b Semillero de Termodinámica y Conversión de La Energía, Facultad de Ingeniería Química, Escuela de Ingenierías, Universidad Pontificia Bolivariana, Circular 1 No. 70-01, Medellín, 050031, Antioquia, Colombia

^c Facultad de Ingeniería Mecánica, Universidad Pontificia Bolivariana, Carrera 6 No. 97A-99, Montería, 230003, Córdoba, Colombia

HIGHLIGHTS

- LS regression is a simple method to obtain kinetic parameters from pyrolysis of corn cob.
- Calcium compounds mixed with corn cob reduce thermal degradation in pyrolysis.
- The addition of CaO or CaCO₃ to corn cob pyrolysis showed a second-order reaction.

GRAPHICAL ABSTRACT



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ABSTRACT

A new approach is proposed to obtain the kinetic parameters of biomass pyrolysis mixed with calcium catalyst. This approach involves the optimization of least squares (LS) with the Coats-Redfern integral method to avoid mathematical biases that may appear when applying the linear regression approach. The method was applied to the TGA data of pyrolysis of corn cob and corn cob mixed with 20 or 40 % by weight of CaO or CaCO₃ under N₂ atmosphere at temperatures between 25 and 700 °C. For raw cob, r^2 reaches 0.997. For corn cob mixed with 20 % by weight of CaO or CaCO₃, r^2 reached 0.996–0.998, and for 40 % by weight, r^2 reached 0.836–0.957. Applying this method, the activation energy (EA) value of the raw cob pyrolysis is 58.35 kJ mol⁻¹, while the addition of CaO or CaCO₃ increases the EA to 69.33 and 66.07 kJ mol⁻¹, respectively. The method is simple to use and allows reliable values of kinetic parameters.

1. Introduction

Currently, non-renewable fuels, such as coal and those derived from oil, represent an increase in the emission of carbon dioxide (CO₂), methane

(CH₄), and among other, also called greenhouse gases (GHG) which raise the urgency to diversify the energy market with alternative sources other than fossils. Previous studies have focused on the development of renewable energy system models as sustainable planning strategies to promote

* Corresponding author.

E-mail address: zulamita.zapata@upb.edu.co (Z. Zapata-Benabithé).

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alternative sources of biofuels. Biomass is the only abundant and renewable source, capable of producing electricity, heat, fuels, and even chemicals. Due to its biodegradability, low cost, carbon neutrality, and low GHG emissions, Colombia has a high potential for the agricultural development of biomass as a renewable energy source. In Córdoba, a department located in the north of Colombia, one of the main economic activities is agriculture, mainly because it has 103,007 ha of land, of which 43,979 are used for growing corn with an approximate annual production of 154,273 tons, which corresponds to 30 % of the total national production [1]. Corn cob is the main crop residue and since its disposal is usually open burning it represents a contamination source that produces particulate material, soot, and GHG. However, due to its energetic properties, it is possible to subject it into thermochemical treatments and used it as a resource to produce green fuel [2]. Chemical thermal conversion processes including combustion, gasification, and pyrolysis are utilized to obtain energy through the production of new fuels or the generation of heat. Pyrolysis, in addition to being the first stage of gasification and combustion, is known for the variety of products obtained from different operating conditions [3] and is characterized by being an endothermic degradation process in an inert oxygen-free atmosphere carried out between approximately 250 °C and 600 °C. Adding a catalyst to the pyrolysis of biomass could reduce the pyrolysis temperature, increases the yield of the products, and improves their quality [4]. Ca-based additives could increase the concentrations of hydrogen and carbon monoxide and decrease the concentrations of methane and carbon dioxide [5, 6]. The kinetic study of the thermal degradation of biomass during pyrolysis, in the presence of calcium compounds, provides valuable information on the behavior of the process that allows the design of reactors and the realization of predictive simulations of the process evaluating different scenarios. Scientific studies regarding the evaluation of the calcium additives effects on pyrolysis kinetics and final product properties have been conducted by several researchers such as Zhang et al. [5], Veses et al. [7], and others. One of the widely recognized methods for analyzing thermogravimetric data is the Coats-Redfern (CR) integral method. This method assumes that the activation energy and the reaction order is constant during the degradation process, but it is subject to a function that varies according to the assumed reaction mechanism and depends solely on its conversion [8]. Wang et al. [9] or Mian et al. [10], among other authors use the CR model for the analysis of kinetic and highlight the practicality and simplicity in the development of the calculations because of the linearization by logarithms to solve the equation. However, these approximations do not apply optimization tools that allow a reliable adjustment of parameters such as the activation energy and the frequency factor.

2. Materials and methods

2.1. Materials and thermogravimetric analysis

Corn Cob from Córdoba was crushed up to a particle size of 125 μm . The proximate analysis and the high heating value (HHV) of the raw material were carried out in accordance with ASTM International Standards. The thermogravimetric assays were carried out using a thermobalance from TA Instruments (TGA-Q50TGA). For each test, 15 mg of the mixture were heated, applying a heating rate of 30 °C min^{-1} , between 25 °C and 700 °C under nitrogen flow (100 mL min^{-1}). Reproducibility of all thermogravimetric analyses was carried out in triplicate.

Corn cob was mixed with CaO or CaCO_3 at 20 wt.% and 40 wt.% The samples were coded as CC (corn cob) and CC-CaX-Y%, where X is the catalyst and Y is the percentage of catalyst in the mixture (CC-CaO-20%, CC-CaO-40%, CC- CaCO_3 -20%, and CC- CaCO_3 -40%). These values are in the range of biomass-calcium compounds mass ratios used by different researchers in previous studies such as [11,12].

2.2. Kinetic models for pyrolysis

Chemical non-isothermal kinetics of the solid-state reactions, it is common to assume a heating program at a constant heating rate. The

dependence of rate reaction on the temperature and conversion can be described by Eq. (1) [13].

$$\frac{dX}{dT} = \frac{k}{\beta} \cdot f(X) \quad (1)$$

Where $f(X)$ is the conversion of the raw material decomposition at time t [14], β is the heating rate, T is the absolute temperature, $f(X)$ is a function that depends on thermal decomposition mechanism, and k is the temperature-dependent rate constant described by Arrhenius and Van't Hoff in Eq. (2).

$$k = A \cdot \exp\left(-\frac{E}{RT}\right) \quad (2)$$

where A is the pre-exponential factor, R is the gas constant, and E is the activation energy. The general expression of the thermal decomposition is given by Eq. (3), which comes from the combination of Eqs. (1) and (2).

$$\frac{dX}{dT} = \frac{A}{\beta} \cdot \exp\left(-\frac{E}{RT}\right) \cdot f(X) \quad (3)$$

However, it is necessary to distinguish that the variability of the phenomena occurred due to the different characteristics between solids. Therefore, several functions have been developed based on assumptions related to the reaction mechanism that takes place on the surface of the solid, including the nucleation and random growth model defined by Avrami (equation 4) [15].

$$f(X) = (1 - X)^n \quad (4)$$

where n is the reaction order. Avrami considered that reactive germ nuclei are converted into growth nuclei in a single activated step [15]. Also, it is possible to obtain different mathematical formulations by treating Eq. (3) in several ways [16].

2.3. Coats-Redfern integral method

The Coats-Redfern Integral Method resolves the differential Eq. (5), which depends on the reaction order, through separation of variables, integration, and approximations [16].

$$\frac{dX}{dT} = \frac{A}{\beta} \cdot \exp\left(-\frac{E}{RT}\right) \cdot (1 - X)^n \quad (5)$$

Obtaining:

$$\frac{F(X)}{T^2} = \frac{AR}{E\beta} \left(1 - \frac{2RT}{E}\right) \exp\left(-\frac{E}{RT}\right) \quad (6)$$

Function $F(X)$ can be expressed as Eq. (7) when $n = 1$ and Eq. (8) when $n \neq 1$:

$$F(X) = -\text{Ln}(1 - X) \quad (7)$$

$$F(X) = \frac{1 - (1 - X)^{1-n}}{1 - n} \quad (8)$$

If $2RT/E \ll 1$ for general reaction interval and most E values, Eq. (6) could be rewritten as Eq. (9) [16]:

$$\frac{F(X)}{T^2} = \frac{AR}{E\beta} \cdot \exp\left(-\frac{E}{RT}\right) \quad (9)$$

According to Di Blasi [17], the reaction orders of multi-component devolatilization reactions range between 0.8 and 1.8, depending on the biomass. Moreover, Albis et al. [18] found that reaction order during pyrolysis of pure hemicellulose is 2, but they revealed that adding a catalyst could increase or decrease it. Several studies carried out by Koufopoulos et al. [19] among other authors [20, 21, 22, 23] evaluated

reaction orders between zero and two for different lignocellulosic materials (sugar cane, rice husk, wood) degradation processes to conclude which order better represents the experimental data. The reaction orders used in this paper are 0.5, 1, and 2.

2.4. Linear regression

Eq. (6) could be rewritten as Eq. (10):

$$Y = b \cdot e^{aX} \quad (10)$$

The range where pyrolysis occurs corresponds to conversion values between 10 % and 80 %. The constants a and b can be determined by Eqs. (11) and (12):

$$b = \exp\left(\frac{\sum X_i^2 \sum \ln(Y_i) - \sum X_i \ln(Y_i) \sum X_i}{n \sum X_i^2 - (\sum X_i)^2}\right) \quad (11)$$

$$a = \frac{n \sum X_i \ln(Y_i) - \sum X_i \sum \ln(Y_i)}{n \sum X_i^2 - (\sum X_i)^2} \quad (12)$$

The pre-exponential factor and activation energy can be obtained by solving Eqs. (6) and (10) simultaneously.

This method is useful to convert exponential functions of medium complexity into linear expressions. However, McCuen et al. [23] found that fitting an exponential model using the logarithmic transformation leads to an equation with partial regression coefficients biased and thus provides based estimates of the value of the independent variable. Furthermore, the regression coefficient (r^2) in the logarithmic scale does not show the precision of the prediction from the original equation (see equation 6) [23]. Therefore, the linear regression results would only allow knowing the initial values of the iterative routine of least squares regression.

2.5. Least-Squares Regression

Least-Squares Regression is an alternative to find the kinetic parameters without linear regression. The minimization of residuals was carried out between experimental data and those calculated from Eq. (6) for each reaction order. The objective function (equation 13) is defined as the square of the difference between the experimental results and the values calculated from Eq. (10).

$$F = \sum (Y_{i,exp} - Y_{i,calc})^2 \quad (13)$$

The Least-Squares Regression was performed from TGA results using the generalized reduced gradient (GRG) Nonlinear method, using forward derivatives at different experimental conditions. The results obtained from this method do not give biased results with minor variance concerning linear regression results. However, the sensibility of the method is lower due to the initial values for activation energy and pre-exponential factor and gives an unsatisfactory solution. Occasionally, the order of magnitude of the variable Y hinders the convergence of the method since the relative error with arbitrary initial values satisfies a local minimum of the function $F(X)$. Therefore, using linear regression results with variations lower than 20 % as initial values for least squares regression is appropriate. Setting the frequency factor with specific criteria is necessary due to it having a considerable impact on the final solution.

3. Results and discussion

3.1. Proximate analysis and high heating value

Table 1 shows the proximate analysis and high heating value (HHV) of the raw material. The proximate analysis is similar to the analysis

Table 1. Corn Cob proximate analysis and High Heating Value (HHV).

| Component | Value | Unit | Standard |
|-----------------|-------|---------------------|----------------------|
| Moisture | 9.29 | wt. % | ASTM D3173/3173M-17a |
| Ash | 1.67 | wt. % | ASTM D3174 - 12 |
| Volatile matter | 71.83 | wt. % | ISO 562 - 10 |
| Fixed carbon | 17.21 | wt. % | ASTM D3172 - 13 |
| HHV | 17.35 | MJ kg ⁻¹ | ASTM D5865 - 13 |

reported by other authors [24]. Corn cob may have potential as an energy source due to its high HHV and low ash content compared to other biomass sources [25].

3.2. Kinetic parameters

Figure 1 shows the TGA-DTG curves for pyrolysis of biomass with CaO (Fig. 1a and Fig. 1c) and biomass with CaCO₃ (Fig. 1b and Fig. 1d). The DTG curve for raw biomass shows three peaks. A first peak around 100 °C related to moisture loss. A second peak between 220 °C and 315 °C is related to the thermal degradation of hemicellulose and a third peak between 315 °C and 400 °C is related to the thermal degradation of cellulose [26]. When CaO is used (Figure 1c), the hemicellulose and cellulose peaks overlap due to the reaction between biomass and CaO and the DTG curve shows a Gaussian bell shape. As the amount of CaO increases, the size of the peak decreases because the reactions between biomass and CaO produce compounds of higher molecular weight and thermal stability [5]. Between 400 °C and 500 °C CaO also exhibits greater catalytic activity, producing higher weight loss compared to biomass without CaO [5]. Furthermore, in this temperature range, CO₂ is absorbed by CaO in the carbonation reaction [27]. Above 600 °C, an additional peak appears due to the calcination reaction where CO₂ is released. This reaction is endothermic and is favored when the temperature increases [28].

For biomass with CaCO₃ (Figure 1d) up to 400 °C the trend in the thermal decomposition of hemicellulose and cellulose is similar to that of CaO. The rate of weight loss decreases as the amount of CaCO₃ increases. Between 400 °C and 500 °C there is not peak because there is not carbonation reaction. Above 600 °C, there is a peak similar to CaO, but more pronounced because the amount of CaCO₃ is higher, and possibly more CO₂ is released. This peak is higher for CaCO₃ 40 wt.% than for CaCO₃ 20 wt.%, which supports the release of CO₂ due to calcination.

Table 2 shows the activation energy (E_{GRG}), the pre-exponential factor, the reaction order for pyrolysis, and the regression coefficient obtained by the proposed numerical method. Furthermore, the E_{GRG} is compared with the linear regression method (E_{Linear}). Although some authors such as Han and Yusan et al. developed their kinetic studies using first-order reaction models even for catalytic processes [29, 30], the addition of calcium compounds affects the structure of the solid, and the behavior of the reaction order should be evaluated. In Table 2, for the raw material, the pyrolysis corresponds to a first-order reaction, and for the biomass with CaO or CaCO₃ it corresponds to a second-order reaction. These results agree with those reported by Zhan et al. [5] in their study of pine sawdust pyrolysis with different calcium compounds. Zhan et al. [5] found that pyrolysis is a second-order reaction, and the reaction order does not change as the calcium concentration varies. Although López [31] indicates that the reaction order has no physical significance in thermal degradation processes, it is a parameter that must be reported considering the modeling by data fit and the effects of the experimental conditions. It is observed that although the thermal degradation curve of biomass-CaO20-% shows a behavior like that of the other samples if linear regression is applied the activation energy calculation for this sample reports a value of 79.86 kJ mol⁻¹, a different value compared to the other samples. But when the numerical method proposed in this research is applied, the activation energy value is 68.60 kJ mol⁻¹, a value

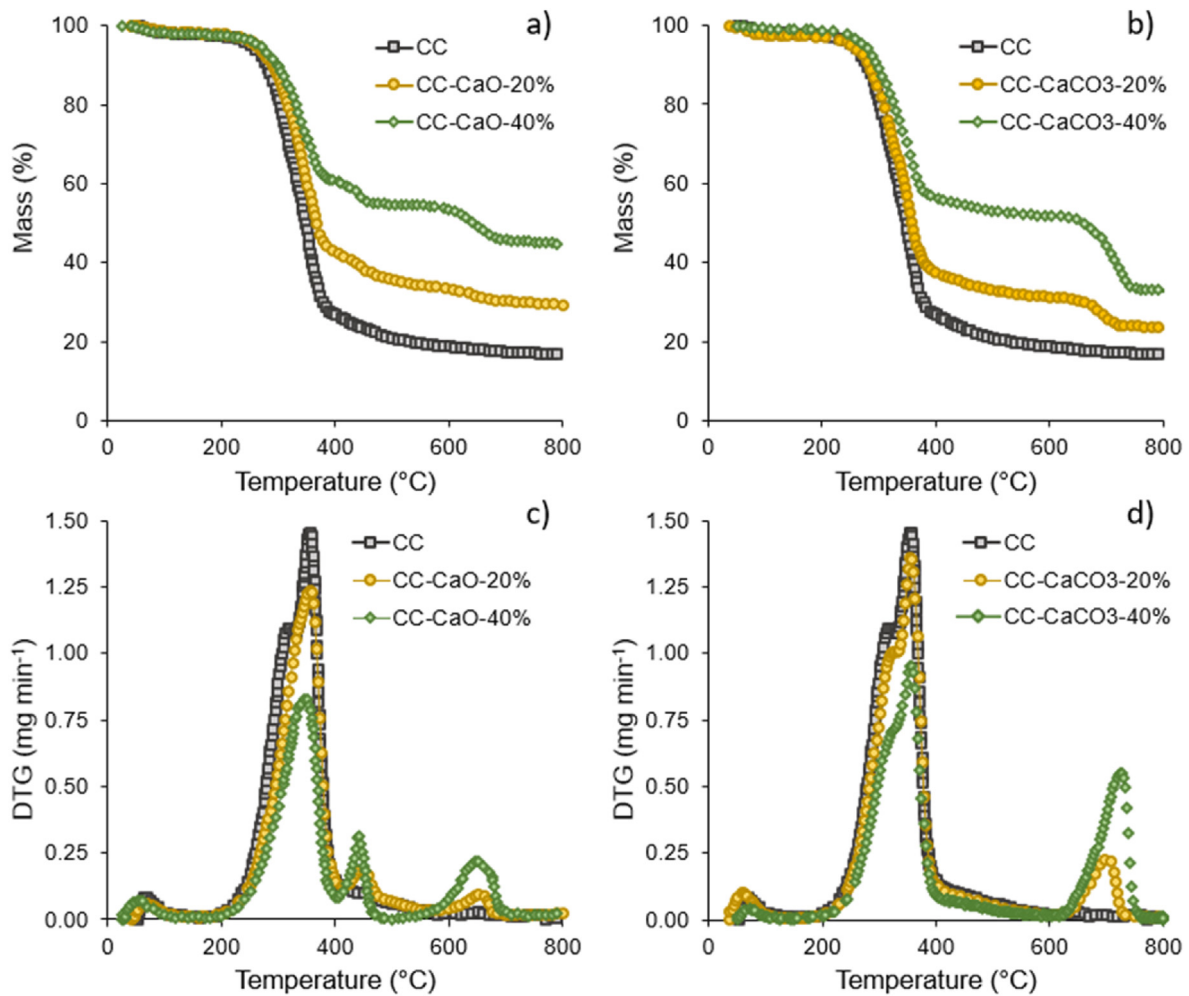


Figure 1. TGA-DTG curves for Corn Cob at different weight percentages of the catalyst (0 wt.%, 20 wt.%, 40 wt.%). Corn Cob and CaO a)-c), and Corn Cob and CaCO₃ b)-d).

very similar to the others, and it agrees with the behavior exhibited by TGA curves. The method presented in this study reduces statistical bias compared to the linear regression method. These values are like those obtained by other authors [32].

In Table 2, the results show that the activation energy for crude biomass pyrolysis is lower, compared to pyrolysis using calcium compounds. However, for CaO our results show that the activation energy increases slightly as the amount of CaO increases, but for CaCO₃ it decreases as the amount of CaCO₃ increases. There is no consensus on the effect of calcium compounds on the behavior of pyrolysis kinetic parameters. Zhang et al. [5] report that activation energy increases when calcium compounds are added to biomass pyrolysis, in agreement with the results found in our research. However, Han et al. [30], when studying the pyrolysis of wheat straw, found that the addition of calcium compounds in the pyrolysis reduces the activation energy of the process.

Table 2. Kinetic parameters values for Corn Cob Pyrolysis.

| Sample | E_{GRG} (kJ mol ⁻¹) | A (1 min ⁻¹) | n | r ² | E_{Linear} (kJ mol ⁻¹) |
|---------------------------|--------------------------------------|-----------------------------|---|----------------|---|
| CC | 58.35 | 2.40×10^5 | 1 | 0.997 | 56.69 |
| CC-CaO-20% | 68.60 | 3.46×10^5 | 2 | 0.996 | 79.86 |
| CC-CaO-40% | 69.33 | 9.83×10^5 | 2 | 0.957 | 69.94 |
| CC-CaCO ₃ -20% | 66.07 | 4.17×10^5 | 2 | 0.998 | 68.08 |
| CC-CaCO ₃ -40% | 62.79 | 3.00×10^5 | 2 | 0.836 | 65.30 |

Hui Lia et al. [11], in their study about the effect of lime mud (LM) on biomass pyrolysis, using different feedstock and biomass:LM ratios concluded that the effect of LM on activation energy (E) is diverse with different LM mass ratio and feedstock. In their study, the addition of LM increases E in pyrolysis of woody aspen sawdust, but in mixtures of LM-herbaceous corn cob, the addition of LM decreases E. Thus, there is no established trend in the behavior of E as calcium compounds are used in biomass pyrolysis.

For the pyrolysis of biomass-CaO, the increase in activation energy can be explained by the reaction of CaO with water (humidity) and the release of CO₂ at temperatures close to 300 °C producing Ca(OH)₂ and CaCO₃ by the adsorption and reaction of CO₂. CaCO₃ degrades at temperatures above 650 °C, leading to sustained weight loss, as seen in the TGA curves. The thermal stability of CaCO₃ reduces the cracking reaction of celluloses and hemicelluloses at low temperatures because CaCO₃ can

Table 3. Factors and levels used for the activation energy as the independent variable.

| Factor | Level | Factor | Level |
|----------|-------|---------------|------------------------|
| Reaction | 0.5 | Catalyzer-Cob | No Catalyzer |
| Order | 1 | mixture | CaO-20% |
| | 2 | | CaO-40% |
| | | | CaCO ₃ -20% |
| | | | CaCO ₃ -40% |

Table 4. Test of equality of Variances for the activation energy vs the order and catalyzer.

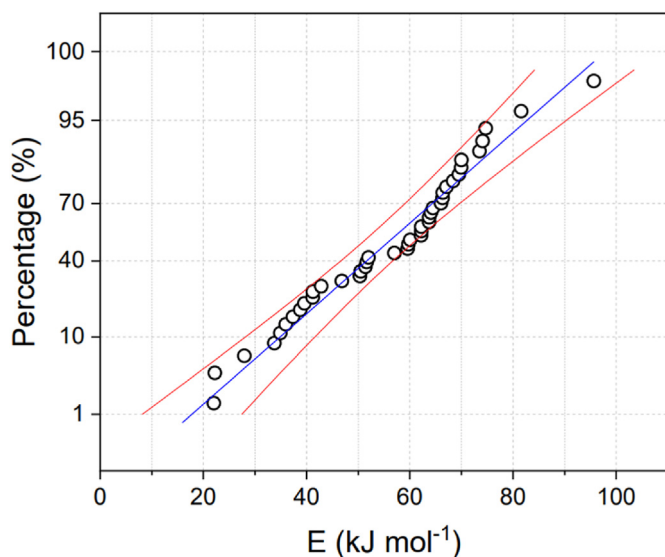
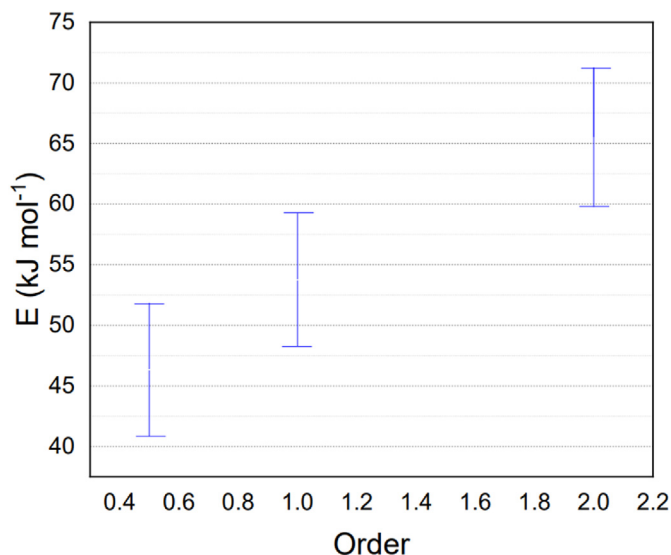
| Bartlett's test | |
|--------------------------------|-------|
| Activation energy vs Order n | 0.058 |
| Activation energy vs Catalyzer | 6.21 |

form a layer that limits heat and mass transfer and reduces pyrolysis [33]. This implies a higher energy requirement and increased activation energy. For the pyrolysis of biomass-CaCO₃, as the carbonate is already present in the sample, the explained effect of the thermal stability of CaCO₃ and the formation of the layer demand higher temperature and more time for the pyrolysis process, producing an increase in the activation energy. The above-mentioned effects can reduce the formation of tars in the use of corn cob as raw material in obtaining energy and gas in a gasification process, allowing the possibility of exploiting this material as a renewable energy source [2].

3.3. Statistic analysis

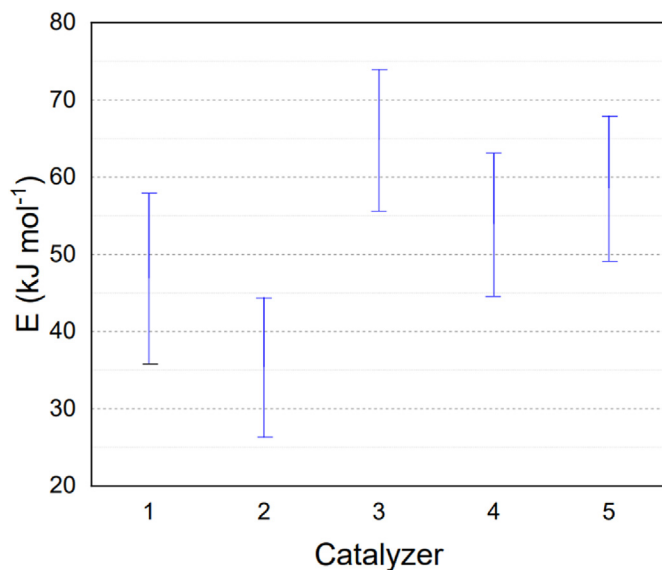
To avoid biases in the non-linear coefficients of the exponential model, least squares optimization models supported by the initial values of the linear regression can be used. By applying a numerical algorithm, kinetic parameters can be determined to contribute to a better understanding of thermochemical processes to use raw biomass or biomass mixed with calcium additives, as an alternative source of Energy the Statgraphics Centurion software was used as a tool for the statistical analysis of the process behavior of catalyzed samples and raw biomass respecting the effect on activation energy. Table 3 establishes the homoscedasticity levels and factors used in the montage.

For the reliability of the results of the analysis, it was necessary to corroborate the assumptions of normality and homoscedasticity in a multifactorial ANOVA. Table 4 presents the data obtained by verification of variances of the simple ANOVA of each factor for the assumption of homoscedasticity, which is accepted since the P values are higher than the significance level (0.05). Figure 2 is the verification of the assumption of normality with the nonparametric statistical test of "Shapiro-Wilk" that requires a P value higher than the significance level in which this case is fulfilled by stating that the data came from a normal distribution

**Figure 2.** Energy activation probability plot of Corn Cob pyrolysis catalyzed with CaO and CaCO₃.**Figure 3.** Mean plot for the activation energy vs reaction order pyrolysis catalyzed with CaO and CaCO₃.

of activation energies. This is associated with the fact that first-order irreversible parallel reactions occur simultaneously. This distribution obeys a Gaussian distribution with mean and standard deviation [34] as it is shown in the figure.

The mean plots determine which means are significantly different from each other using Fisher's intervals with a confidence level of 95%. Figure 3 shows that the interval for reaction order 2 does not overlap any other interval since there is not a horizontal line that crosses a pair of intervals (vertical lines) and therefore its mean differs significantly from the other two samples. In the case of the catalyst, Figure 4 explains that the only two non-superimposed pairs, using the same discrimination method mentioned, are CaCO₃-20% - CaO-20% and CaCO₃-40% - CaO-20%, the other levels in this factor do not have significant differences on the independent variable. This means that under the same experimental conditions the reaction orders 0.5 and 1 have the same effect on the activation energy.

**Figure 4.** Mean plot for the activation energy vs Catalyzer.1: CaCO₃-20%, 2: CaCO₃- 40%, 3: CaO-20%, 4: CaO-40%, 5: No Cat.

4. Conclusions

The least-squares method enables to obtain more reliable values of the kinetic parameters based on experimental data by avoiding the use of the linear regression model. The activation energy and the pre-exponential factor increase as calcium compounds are used in pyrolysis of the corn cob. The raw corn cob pyrolysis is a first-order reaction, while the addition of CaO or CaCO₃ shows a second-order reaction. The use of calcium compounds reduces thermal degradation by slowing down the pyrolysis process and this effect could be favorable to avoid the formation of tars in a process of biomass gasification.

Declarations

Author contribution statement

Erika Arenas Castiblanco: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.

Juan Henao Montoya, Gabriela Valencia Rincón: Performed the experiments; Analyzed and interpreted the data.

Zulamita Zapata-Benabithé: Conceived and designed the experiments; Wrote the paper.

Rafael Gómez-Vásquez, Diego A. Camargo-Trillos: Contributed reagents, materials, analysis tools or data.

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Data availability statement

Data included in article/supplementary material/referenced in article.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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