



Pyrolysis Kinetics of European Hazelnut Husk Grown in Chile

Christian Edward Seal Mery^{1*}, Sebastian Alejandro Correa Espinoza²⁾

^{1*)} Universidad de Santiago de Chile, Avenida Libertador Bernardo O'Higgins N° 3363, Santiago, Chile, christian.seal@usach.cl;

ORCID: 000-0003-4076-2352

²⁾ Universidad de Santiago de Chile, Avenida Libertador Bernardo O'Higgins N° 3363, Santiago, Chile, sace36@gmail.com, ORCID: 0009-0003-5511-6772

<https://doi.org/10.29227/IM-2025-02-02-036>

Submission date: 2025-04-04 | Review date: 2025-05-15

Abstract

*This study focuses in determining the pyrolysis kinetics for the husk of the *Corylus avellana* grown in Chile as a first step for determining the energy and chemical potential, and as an alternative of the disposal method of this biowaste in Chile. Thermogravimetric analysis (TGA) was performed on hazelnut husk sample at heating rates of 10, 20, 30, and 40 °C/min under nitrogen atmosphere (50 mL/min). The results were analyzed using three different kinetic models to determine the activation energy (E_a) and pre-exponential factor (A): the isoconversional methods of Kissinger-Akahira-Sonose (KAS), Ozawa-Flynn-Wall (OFW), and the Coats-Redfern method. The TGA results revealed a multi-stage pyrolysis process, beginning with dehydration and followed by the decomposition of hemicellulose and cellulose, culminating the formation of char (lignin content). The analysis demonstrated a clear dependence of the decomposition rate on heating rate, with faster heating rates resulting in higher peak temperatures. This effect is attributed to variations in heat transfer efficiency within the biomass particles. Applying the KAS and OFW isoconversional methods yielded an average activation energies of 121 kJ/mol and 126 kJ/mol. The Coats-Redfern method provided the corresponding pre-exponential factors. A detailed analysis of the activation energy and pre-exponential factor as a function of conversion degree was performed, revealing a non-linear relationship and providing insights into the reaction mechanism of the hazelnut husk. A comparative analysis with existing literature on the pyrolysis of similar biomass showed good agreement between the results obtained in this study and previously published data. Understanding the thermal behavior of the hazelnut husk offers a key information for the design and optimization of bioenergy and bio-chemical processes utilizing this underutilized resource.*

Keywords: Pyrolysis, Thermogravimetry, Kinetics, Biomass, hazelnut husk

1. Introduction

Fossil fuel play a key factor in the economy and everyday aspect of life; however, an increase of the environmental concern over its effects on the environment has created the need for the search of renewable energy sources [1]. With the global increase in population and economical demands, the use of fossil fuel has increased, which has led to an alarming rise of greenhouse emissions [2]. Among the possible alternatives is biomass, which is cleaner option, is renewable, and sustainable [3,4]. The use of biomass can reduce the dependence of fossil fuels and has a positive environmental impact, such as the reduction of carbon dioxide emissions [5,6].

Chile has made significant advancements in renewable energy, especially in solar and wind power, which have rapidly increased their percentage in the energy mix of the country [7]. In recent years, biomass use has remained practically stable; in fact, in 2021 it decreased only by 0.5% [7]. In this regard crude oil and carbon consumption, has been declining over time, largely due to the rise in renewable energy sources [7]. Notably, between 2016 and 2021, biomass usage in Chile decreased by percentage from 23% to 19% of total energy consumption, due to the increase of other cleaner energy source [7,8].

Chile is the largest producer of hazelnuts in the Southern Hemisphere and the fifth largest in the world [9]. In terms of cultivation area, hazelnuts are the third most widely planted crop and occupy 9.77% of Chile's total cultivated land [10]. The husks generated during hazelnut production are typically disposed of through combustion, landfill, or composting [11,12]. It's important to note that only the kernel is consumed, which can make up 25% to 67% of the hazelnut, the rest is the husk [13].

Pyrolysis is a widely utilized method for converting waste biomass into valuable chemicals and fuels [13]. This crucial thermochemical conversion process effectively transforms biomass—such as wood, agricultural residues, and other organic materials—into both gaseous and liquid fuels [14]. During pyrolysis, these organic materials are subjected to high temperatures in the absence of oxygen, which prevents combustion and allows the biomass to decompose into simpler compounds.

A key factor in efficiently converting biomass into energy is understanding the thermal decomposition kinetics involved in the process [15]. To explore this, a thermogravimetric analysis was conducted to determine the kinetics of hazelnut husk cultivated in Chile.

2. Material and Methods

2.1 Materials and Sample preparation

This study focused on local produced hazelnut husk. The hazelnut husk was initially grinded and left drying in an oven at 70°C for 24 hours, afterwards the samples were could in a desiccator until they reached room temperature. The husks were grinded with a household coffee grinder and sieved with a 40 and 200 ASTM mesh.

2.2 Thermogravimetric analysis

The pyrolysis kinetic analysis was conducted using a TA Q600 SDT Simultaneous Thermal Analyzer, which measures both weight (TGA) and differential heat flow (DSC). The analysis was performed under a nitrogen atmosphere at a constant flow rate of 50 mL/min.

Samples were studied at four heating rates: 10, 20, 30, and 40 °C/min, corresponding to weights of 23.46 mg, 1.31 mg, 11.15 mg, and 10.60 mg, respectively. The temperature range for heating was from 30 to 1000 °C.

2.3 Kinetic analysis

The kinetics of the pyrolysis reaction were carried out using the data obtained from the thermogravimetric analysis. Three different kinetic models were applied: the isoconversional model Kissinger-Akahira-Sunose (KAS), Ozawa-Flynn-Wall (OFW), and the Coats-Redfern (CR) method. The isoconversional methods allows for the determination of the kinetic parameters without the knowledge of the reaction mechanism [12]. In these methods, for a constant extent of conversion (α), the rate depends only on the temperature, and the reaction kinetics are not related to the heating rate [12,14,16]. Additionally, it is assumed that the conversion of raw materials into products is a one-step process [12,16].

The normalized conversion of the raw material decomposition can be defined as [17]:

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

where m_0 correspond to the initial mass of the sample, m_t is the mass at time t and m_f is the mass at time infinite.

The rate of the reaction can be described by the following equation

$$\frac{d\alpha}{dt} = K(T)f(\alpha) \quad (2)$$

Where $f(\alpha)$ represents the reaction model, while $K(T)$ is the rate constant expressed by the Arrhenius law as:

$$K(T) = Ae^{\left(-\frac{E_a}{RT}\right)} \quad (3)$$

Where E_a is the activation energy and A is the pre-exponential factor. By substituting equation 3 into equation 2:

$$\frac{d\alpha}{dt} = Ae^{\left(-\frac{E_a}{RT}\right)}f(\alpha) \quad (4)$$

Considering that temperature is a function of time and that it increases with a heating rate β , then β can be written as:

$$\beta = \frac{dT}{dt} = \frac{dT}{d\alpha} \frac{d\alpha}{dt} \quad (5)$$

Combining equation 5 with equation 4, and rearranging, we have:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \int_0^T \frac{A}{\beta} e^{\left(-\frac{E_a}{RT}\right)} dT = \frac{AE_a}{\beta R} \int_x^\infty u^{-2} e^{-u} du = \frac{AE_a}{\beta R} P(x) \quad (6)$$

Where X is $\frac{E_a}{RT}$. Because the function $P(x)$ has no exact solution, equation 6 can be solved by numerical methods or approximations. The name of isoconversional methods differs depending on the type of approximation method used.

2.3.1 KAS method

The Kissinger-Akahira-Sunose (KAS) method uses the approximation $P(x) = x^{-2}e^{-x}$ from equation 6. After rearranging the equation 6, it can be expressed as:

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left[\frac{AE_a}{Rg\alpha}\right] - \frac{E_a}{RT} \quad (7)$$

In the graph of $\ln(\beta/T^2)$ versus $1/T$, the slope is given by $-E_a/R$, where $R = 8.314$ J/mol K. By varying the conversion range from 0 to 1, the activation energy E_a can be determined for different progressive conversion values.

2.3.2 OFW method

The Ozawa-Flynn-Wall (OFW) method utilizes the Doyle approximation [18], which can be expressed as $\log(P(x)) \approx -2.315 - 0.457x$. By rearranging the equation 6, it can be expressed as:

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left[\frac{AE_a}{Rg\alpha}\right] - 2.315 - 0.457\frac{E_a}{RT} \quad (8)$$

In the graph of $\ln(\beta/T^2)$ versus $1/T$, the slope is given by $-0.457 E_a/R$, where $R = 8.314$ J/mol K. As mentioned above in the KAS method, by performing calculations for conversion values from 0 to 1, the activation energy can be calculated for progressive conversion values.

2.3.3 Coats-Redfern method

This method does not provide an approximation based on the Arrhenius equation. While the KAS and OFW methods are adequate for calculating activation energy, the Coats-Redfern method is suitable for determining the pre-exponential factor. The rate of the reaction can be express as:

$$\frac{d\alpha}{dt} = K(T)(1 - \alpha)^n \quad (9)$$

By rearranging equation 9:

$$\frac{d\alpha}{1-\alpha^n} = \frac{A}{\beta} e^{\left(-\frac{E_a}{RT}\right)} dT \quad (10)$$

By integrating the equation 10 and using the method given by Wang et al [19]. It is possible to set the integrating the limits between $\alpha = 0$ at $T = 0$ and $\alpha = \alpha$ at $T = T_0$ gives:

$$\int_0^\alpha \frac{1}{1-(1-\alpha)^n} = \int_{T_0}^T \frac{A}{\beta} e^{\left(-\frac{E_a}{RT}\right)} dT \quad (11)$$

By integrating $(1-\alpha)$ and the $e(-E_a/R)$ in equation 11, the following expression can be obtained:

$$\frac{1-(1-\alpha)^{1-n}}{1-n} = \frac{ART^2}{\beta E_a} \left(1 - \frac{2RT}{E_a}\right) e^{\left(-\frac{E_a}{RT}\right)} \quad (11)$$

By multiplying by a logarithm, expression 11 can be expressed as:

$$\ln\left(\frac{1-(1-\alpha)^{1-n}}{T^2}\right) = \ln\left(\frac{ART^2}{\beta E_a} \left(1 - \frac{2RT}{E_a}\right)\right) - \frac{E_a}{RT} \quad (12)$$

Assuming $(1-2RT/E_a) = 1$ and the reaction order of $n = 1$, equation 12:

$$\ln\left(\frac{\ln(1-\alpha)}{T^2}\right) = \ln\left(\frac{AR}{\beta E_a} \left(1 - \frac{2RT}{E_a}\right)\right) - \frac{E_a}{R} \frac{1}{T} \quad (12)$$

A linear regression can be employed where the slope is E_a/R and the intercept is $\ln(AR/\beta E_a)$

3. Results and discussion

3.1 Thermogravimetric analysis

The thermogravimetric analysis shows the percentage of mass loss as the temperature rises. If multiple weight loss is present, it indicates different decomposition process. Typically, this process are moisture removal, organic compound decomposition, and ash formation. The curve's shape helps identify thermal stability and the temperatures at which various components oxidize or decompose. Fig 1 shows the TGA and DTG of the pyrolysis of the four different heating rates. From Fig 1. the shapes of the TGA and DTG curves for the different heating rates follow the same form but differ when the moisture is removed and the organic compounds for the rate 40 °C/min.

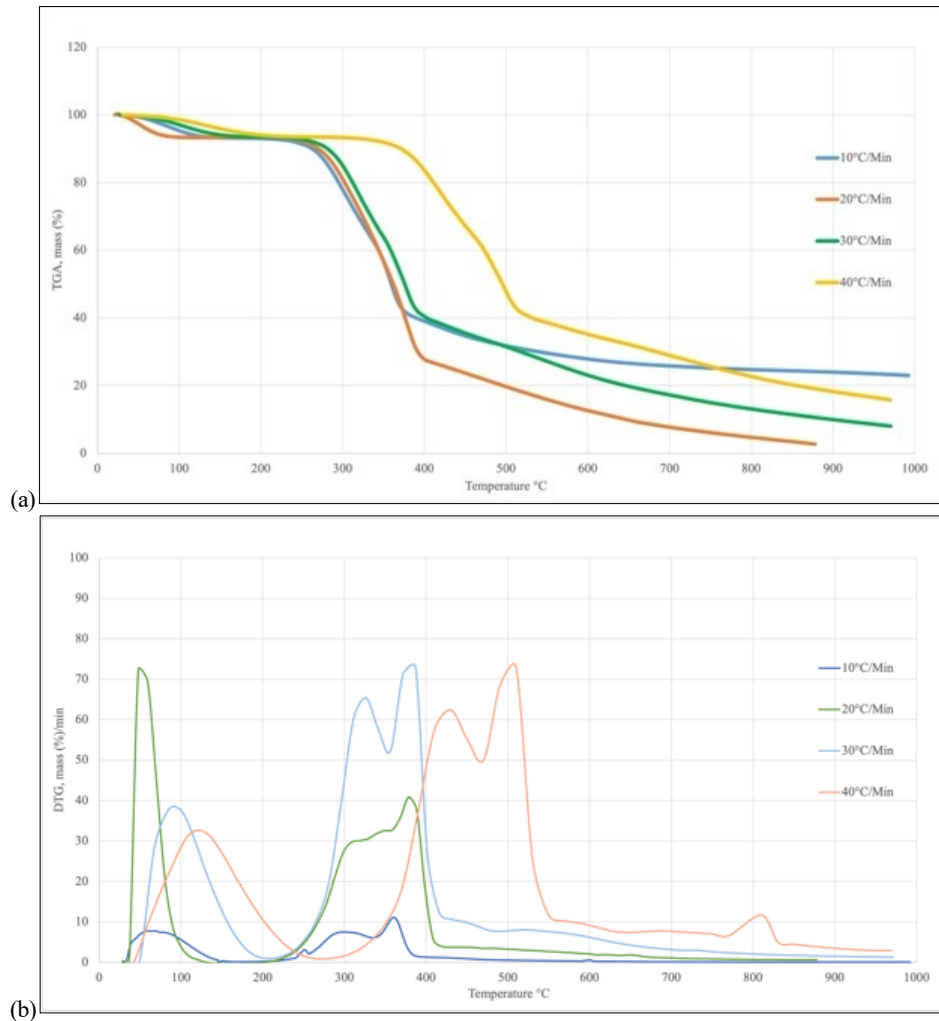


Fig. 1 (a) TGA and (b) DTG curves for the hazelnut husk at different heating rates.

The initial mass loss occurs between 42°C and 188°C, resulting in a mass reduction of 7% to 9% across four heating rates. This loss primarily reflects the evaporation of moisture and mainly the intracellular water from the husk. The subsequent mass loss associated with organic decomposition starts at 249°C and continues until 510°C, with a percentage reduction of 52.58% to 65.17%. Finally, the ash content ranges from 2.7% to 23.01%. From Fig. 1 (b), it is possible observe that the increase in heating rates merely raises the maximum temperature without altering the thermal decomposition profile. However, for the 40°C/min ramp, there is a noticeable rightward shift, which can be attributed to a change in composition. Due to the shift the three models were analysed with and without the 40 °C/min ramp.

3.2 Decomposition kinetics

The activation energy (E_a) for the hazelnut husk was determine by using isoconversional models KAS and, while the Coats-Redfern method was used to obtain the pre-exponential factor.

For the KAS model, the activation energy can be estimated based on the equation 7, and can be determine from the linear transformation of $\ln(\beta/T^2)$ versus $1/T$. The activation energies for each conversion rate are plotted in Fig. 2, and the calculated activation energies along with the regression coefficients for each rate are listed in Table 1.

Table 1 shows that correlation at conversion rates above 0.8 is low, leading to their exclusion from the analysis. Additionally, both graphs reveal low correlation at conversion rates of 0.1, 0.7, and 0.8. Thus, the study focuses on conversion rates between 0.2 and 0.6. For this interval, the estimated activation energies were close to each other and the average for all the ramps was 121,52 kJ/mol and without the 40°C/min ramp 105,65 kJ/mol.

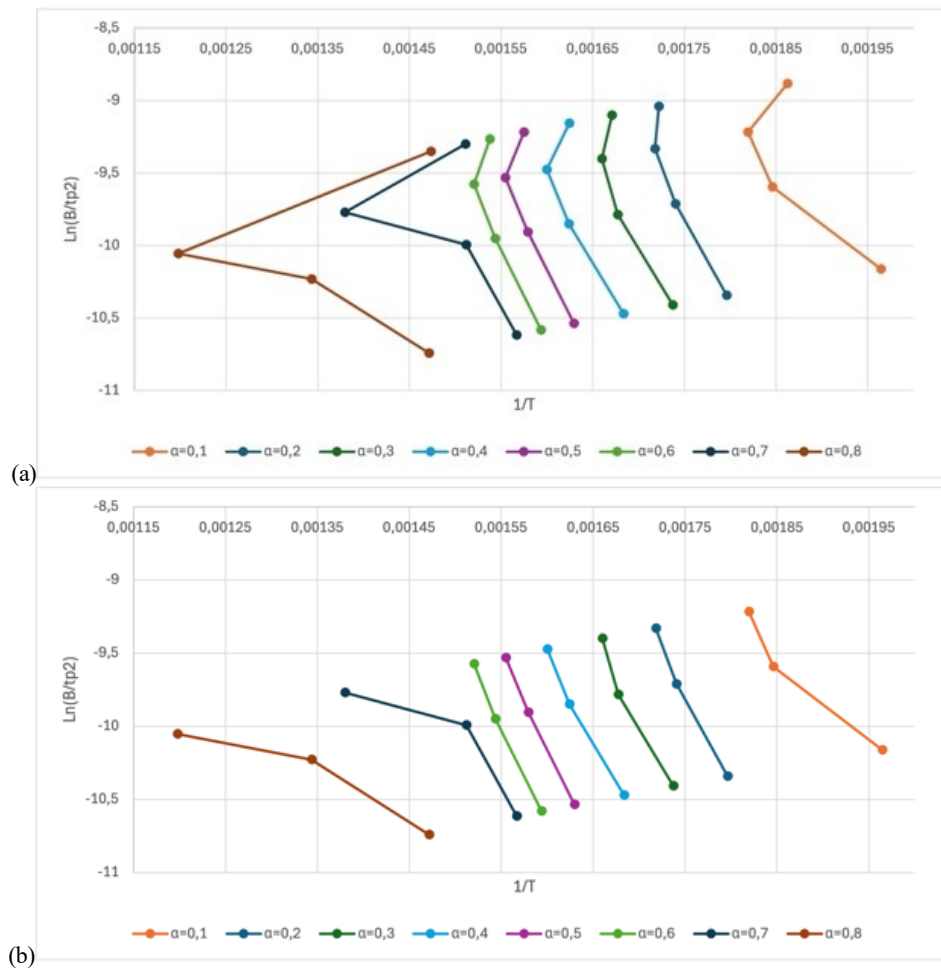


Fig. 2 Kinetic analysis with KAS model (a) All ramps and (b) not considering ramp 40°C/min

Tab. 1. Activation energy and R^2 for KAS model.

α	All the Ramps		Without the 40 °C/min ramp	
	E_a (kJ/mol)	R^2	E_a (kJ/mol)	R^2
0,1	54,75	0,582	49,74	0,946
0,2	120,41	0,897	105,20	0,990
0,3	120,83	0,797	102,67	0,971
0,4	108,70	0,681	96,64	0,991
0,5	127,04	0,731	110,93	0,998
0,6	130,63	0,760	112,79	0,996
0,7	25,52	0,200	33,20	0,770
0,8	-1,31	0,001	20,61	0,905

For the OFW model, the activation energy can be estimated based on the equation 8, and can be determine from the linear transformation of $\ln(\beta)$ versus $1/T$. The activation energies for each conversion rate are plotted in Fig. 3, and the calculated activation energies along with the regression coefficients for each rate are listed in Table 2.

From Table 2 is possible to observe the same correlation as in KAS model, therefore the conversion rates that are gone to be analyses are between 0.2 and 0.6. For this interval, the estimated activation energies were close to each other and the average for all the ramps was 125,63 kJ/mol and without the 40°C/min ramp 109,99 kJ/mol.

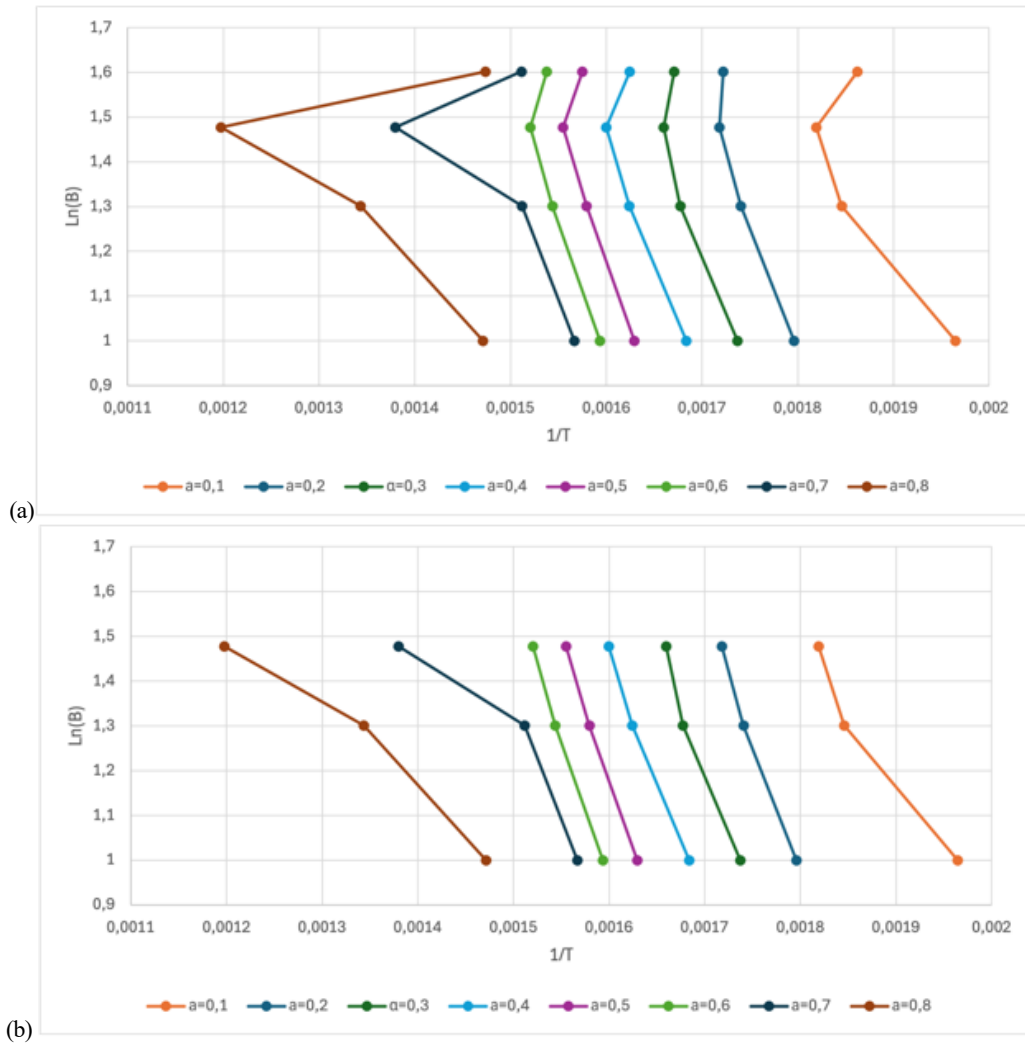


Fig. 3 Kinetic analysis with OFW model (a) All ramps and (b) not considering ramp 40°C/min

Tab. 2. Activation energy and R^2 for OFW model.

α	All the Ramps		Without the 40 °C/min ramp	
	E_a (kJ/mol)	R^2	E_a (kJ/mol)	R^2
0,1	60,3	0,652	55,61	0,960
0,2	126,3	0,910	108,96	0,992
0,3	124,1	0,821	106,86	0,975
0,4	112,9	0,718	101,45	0,993
0,5	130,6	0,761	115,33	0,998
0,6	134,3	0,787	117,33	0,997
0,7	35,1	0,344	42,33	0,860
0,8	10,6	0,009	31,49	0,965

From the analysis of KAS and OFW models, the activation energies in relation to the conversion rates ranges are between 0,2 and 0,6. The resulting activation energies are close in average for the each of the ramps set use.

The activation energy versus the conversion rate for the two data set can be seen in Fig. 4. The estimated activation energy for pyrolysis increases for the husk between α 0,1 to 0,2 and then decreases for α higher that 0,7. Comparing Figures 4a and 4b, it is evident that excluding the 40 °C/min ramp results in lower activation energy.

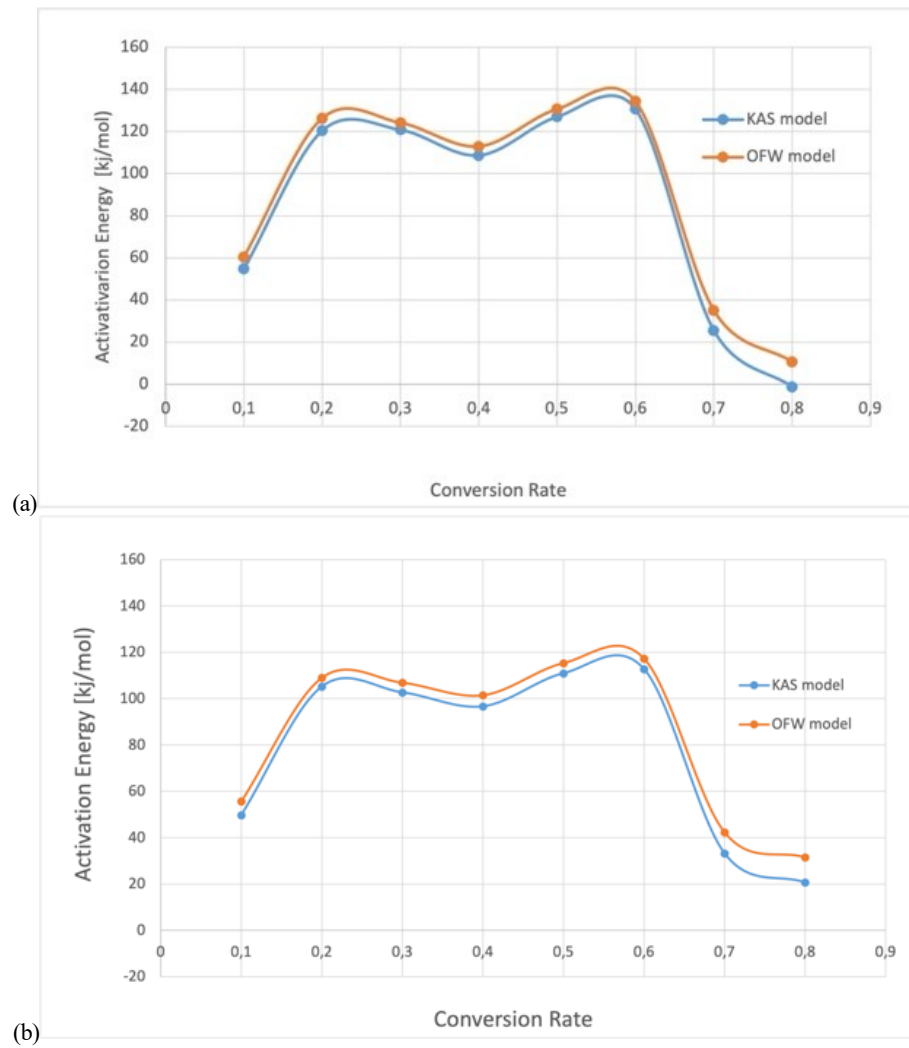


Fig. 4. activation energy versus the conversion rate (a) All ramps and (b) not considering ramp 40°C/min

To validate the kinetic parameters, the pre-exponential factors based on conversion were determined using the Coats-Redfern method. The activation energies obtained from the more reliable KAS and OFW methods were then used to calculate the pre-exponential factor, as shown in Table 3 (all the ramps) and Table 4 (without ramp 40°C/min). Note that the reaction order was not assessed in this investigation.

Tab. 3. Pre-exponential factor (A , min^{-1}) calculated from Coats-Redfern.

Conversion α	$\beta = 10^\circ\text{C/min}$		$\beta = 20^\circ\text{C/min}$		$\beta = 30^\circ\text{C/min}$		$\beta = 40^\circ\text{C/min}$	
	KAS	OFW	KAS	OFW	KAS	OFW	KAS	OFW
0,1	1,16E+06	1,39E+08	2,32E+06	2,79E+08	3,49E+06	4,18E+08	4,65E+06	5,57E+08
0,2	1,71E+12	1,05E+11	3,41E+12	2,11E+11	5,12E+12	3,16E+11	6,82E+12	4,21E+11
0,3	4,02E+11	5,68E+10	8,03E+11	1,14E+11	1,20E+12	1,70E+11	1,61E+12	2,27E+11
0,4	1,44E+10	1,31E+10	2,88E+10	2,63E+10	4,32E+10	3,94E+10	5,76E+10	5,25E+10
0,5	2,78E+11	5,27E+10	5,56E+11	1,05E+11	8,34E+11	1,58E+11	1,11E+12	2,11E+11
0,6	3,09E+11	5,71E+10	6,18E+11	1,14E+11	9,27E+11	1,71E+11	1,24E+12	2,28E+11
0,7	1,47E+02	2,87E+06	2,95E+02	5,74E+06	4,42E+02	8,61E+06	5,90E+02	1,15E+07
0,8	-5,26E-02	1,09E+05	-1,05E-01	2,17E+05	-1,6E-01	3,26E+05	-2,10E-01	4,34E+05

Tab. 4. pre-exponential factor (A , min^{-1}) calculated from Coats-Redfern.

Conversion α	$\beta = 10^\circ\text{C/min}$		$\beta = 20^\circ\text{C/min}$		$\beta = 30^\circ\text{C/min}$	
	KAS	OFW	KAS	OFW	KAS	OFW
0,1	2,87E+05	7,30E+07	2,32E+06	2,79E+08	3,49E+06	4,18E+08
0,2	2,98E+10	1,66E+10	3,41E+12	2,11E+11	5,12E+12	3,16E+11
0,3	7,56E+09	9,34E+09	8,03E+11	1,14E+11	1,20E+12	1,70E+11
0,4	1,02E+09	3,94E+09	2,88E+10	2,63E+10	4,32E+10	3,94E+10
0,5	9,70E+09	1,15E+10	5,56E+11	1,05E+11	8,34E+11	1,58E+11
0,6	8,34E+09	1,11E+10	6,18E+11	1,14E+11	9,27E+11	1,71E+11
0,7	6,04E+02	5,70E+06	2,95E+02	5,74E+06	4,42E+02	8,61E+06
0,8	2,20E+01	1,35E+06	-1,05E-01	2,17E+05	-1,6E-01	3,26E+05

When comparing the pre-exponential factors from this analysis with previous research (Selim & Topcu, 2014), it is observed that the

heating rates of 10 and 20 °C/min are significantly higher than those reported before. This discrepancy may be attributed to the inaccuracy of the Coats-Redfern model when $n=1$ [12].

4. Conclusion

Thermogravimetric analysis of the hazelnut shell from Chile enabled the determination of activation energy. The average activation energies calculated using the KAS and OFW models, with and without the 40°C/min ramp, differed by 3.3% and 3.9%, respectively, indicating that both models yield similar results. Specifically, the activation energy for the KAS model was 121.52 kJ/mol with the ramp and 105.65 kJ/mol without it, while for the OFW model it was 125.63 kJ/mol with the ramp and 109.99 kJ/mol without it. Additionally, any change in composition can influence the results, as shown by the comparison of activation energy outcomes between all ramps and shown in the case of excluding the ramp for 40°C/min.

References

1. F. Alipour, S. Z. Lak, and M. R. Rahimpour, "Economic challenges of moving beyond fossil fuels", *Encyclopedia of Renewable Energy, Sustainability and the Environment*, Vol 1, pp 131-142 (2024).
2. J. Wang, and W. Azam, "Natural resource scarcity, fossil fuel energy consumption, and total green gas emissions un top emitting countries", *Geoscience Frontiers* 15, 101757 (2024).
3. L. J. R. Nunes, M. Casau, M. F. Dias, J. C. O. Matias, and L. C. Teixeira, "Agroforest wood residual biomass to energy supply chain analysis: Feasible and sustainable renewable resource exploitation for an alternative to fossil fuels", *Results in Engineering* 17, 101010 (2023).
4. M. Melikoglu, M. Ozdemir, and M. Ates, "Pyrolysis kinetics, physicochemical characteristics and thermal decomposition behavior of agricultural wastes using thermogravimetric analysis", *Energy Nexus* 11, 100231 (2023).
5. A. R. Aghamiri, and P. Lahijani, "Catalytic conversion of biomass and plant waste to alternative aviation fuels: A review", *Biomass and Bioenergy* 182, 107120 (2024).
6. H. Stancin, V. Strezov, and H. Mikulcic, "Life cycle assessment of alternative fuel production by co-pyrolysis of biomass and plastics",
7. CNE. Anuario Estadístico de Energía 2023, Pp. 158-168. Accessed: April 3, 2025, [Online]. Available from <https://www.cne.cl/nuestros-servicios/reportes/informacion-y-estadisticas/>.
8. S. Rocha, O. Candia, F. Valdebenito, J. F. Espinoza-Monje, and L. Azócar, "Biomass quality index: Searching for suitable biomass as an energy source in Chile", *Fuel* 264, 116820 (2020).
9. E. M. Sandoval, P. Gonzalez, A. Jequier, M. Contreras, and P. G. Berretta, "Chilean Hazelnut Situation and Perspectives" *Acta Hort.* 1052, pp. 329-342 (2014).
10. CIREM, *Catastro Frutícola 2024* (ODEPA and CIREN, 2024), pp 11.
11. N. Söyler, and S. Ceylan, "Thermokinetic analysis and product characterization of waste tire-hazelnut shell co-pyrolysis: TG-FTIR and fixed bed reactor study", *Journal of Environmental Chemical Engineering* 9, 106165 (2021).
12. S. Ceylan, and Y. Topcu, "Pyrolysis kinetics of hazelnut husk using thermogravimetric analysis", *Bioresource Technology* 156, pp. 182-188 (2014)
13. A. Borkowska, K. Klimek, G. Maj, and M. Kaplan, "Analysis of the energy potential of hazelnut husk depending of the variety" *Energy* 17, 2933 (2024).
14. Th. Damartizis, D. Vamvuka, S. Sfakiotakis, and A. Zabaniotou, "Thermal degradation studies and kinetic modeling of cardoon (*Cynara cardunculus*) pyrolysis using thermogravimetric analysis (TGA)", *Bioresource Technology* 102, PP. 6230-6238 (2011).
15. A. Fernandez, A. Saffe, R. Pereya, G. Mazza, and R. Rodriguez, "Kinetic study of regional agro-industrial wastes pyrolysis using non-isothermal TGA analysis" *Applied Thermal Engineering* 106, pp. 1157-1164 (2016).
16. S. S. Idris, N. A. Rahman, K. Ismail, A. B. Alias, Z. A. Rashid, and M. J. Aris, "Investigation on the thermochemical behavior of low rank Malaysian coal, oil palm biomass and their blends during pyrolysis via thermogravimetric analysis (TGA)", *Bioresource Technology* 101, pp. 4584-4592 (2010).
17. E. Kantarelis, W. Yang, Z. Blasiak, C. Forsgen, and A. Zabaniotou, "Thermochemical treatment of E-waste from small household appliances using highly pre-heated nitrogen-thermogravimetric investigation and pyrolysis kinetics", *Applied Energy* 88, pp. 922-929 (2011).}
18. C. D. Doyle, "Kinetic analysis of thermogravimetric data" *J. Appl Polym Sci*, 5 (1961)
19. L. Wang, H. Lei, J. Liu, and Q. Bu, "Thermal decomposition behavior and kinetics for pyrolysis and catalytic pyrolysis of Douglas fir" *RSC Adv* 8, pp. 2196-2202 (2018).