

Kinetic analysis of Wood residues and Gorse (*Ulex europaeus*) pyrolysis under non-isothermal conditions: A case of study in Bogotá, Colombia

Vivian Beltrán¹, Laura V. Martínez¹, Andrés López², and María F. Gómez^{1,*}

¹ Energy, Materials and Environment Group, Department of Chemical Engineering, Universidad de La Sabana, Campus Universitario Puente del Común, Km 7 Autopista Norte, Bogotá, Colombia

² Department of Chemical Engineering, Universidad Nacional de Colombia, Faculty of Engineering and Architecture, Manizales, Colombia

Abstract. Thermal degradation and kinetic for biomass materials wood residues and Gorse (*Ulex europaeus*) have been evaluated under pyrolysis (N₂) conditions, using a non-isothermal thermogravimetric method (TGA) from 25°C to 900°C at different heating rates of 10, 20, 30 and 40°C min⁻¹. In DTG curves the temperature peaks at maximum weight loss rate changed with increasing heating rate. The maximum rate of weight loss (%s⁻¹) was obtained at a heating rate of 40°C/min of 0,38 and 0,46 (%s⁻¹) for wood residues and Gorse, respectively. Activation energy calculations were based on selected non-isothermal methods (Kissinger, FWO, KAS, and Starink). For Gorse, the energy activation was 195.41, 194.44, 214.39 and 179.42 kJmol⁻¹ by Kissinger, FWO, KAS, and Starink methods, respectively. In the other hand, the energy activation for wood residues was 176.03, 221.75, 243.08 and 198.26 kJmol⁻¹ by Kissinger, FWO, KAS, and Starink methods, respectively. The results showed that Gorse has a lower activation energy than wood residues, which represents a great potential to be used as a feedstock in thermochemical technologies. The Levelized Cost of Electricity (LCOE) was calculated for gasification of wood residues and Gorse, which was 186 and 169 USD/MWh, respectively.

1. INTRODUCTION

Nowadays, the need for new renewable energy sources to supply growing demands of energy, diversifying the energy matrix and reducing the use of fossil fuels is widely recognized. The environmental impact of the greenhouse gases (air pollution, global warming and acid rains), which are emitted by fossil fuels, are of great concern in different contexts [1, 2].

One of the most promising renewable energy sources is lignocellulosic residual biomass, not only because of its availability worldwide but also because of remarkable advantages such as being CO₂ neutral and promoting a large annual generation rate [3]. An example of this type of biomass is residual wood, which is produced during tree pruning activities.

In Bogotá, Colombia, approximately 5.856 t of trimming residues are disposed annually into the landfill [4]. This value excludes residues of Gorse (*Ulex europaeus*), which is an exotic species and it is listed as one of the most invasive species in the world, because of its high reproduction rate, rapid growth, high germination potential, high ability to disperse its seeds, resistance to different environmental factors and it burns easily.

For all these reasons, Gorse outcompetes native species and is a fire hazard.

Approximately, 15.000 hectares are invaded by Gorse in Bogotá and there are about 72.000 ha with a high probability of being invaded by this lignocellulosic material [5]. Local Authorities have been looking for an effective way to eradicate it but have not succeeded yet. At the moment, Gorse expansion is being limited putting underground the gorse into plastic bags to ensure its degradation [6]. This situation represents an opportunity to study and evaluate the conversion of energy of the Gorse and the wood residues for power generation in the capital district.

Biomass can be transformed into other forms of energy by different ways such as biological, chemical and thermochemical conversions. The latter is used for electricity and heat generation using heat and pressure. It is appropriate for dried biomass. In contrast, the biological route which is known as bio-digestion, uses microorganisms to produce gas and it is suitable for moist biomass.

* Corresponding author: maria.gomez@unisabana.edu.co, Tel: +57 1 861 5555 Ext 25217

The chemical route is used to produce biofuels such as ethanol and other chemical products using enzymes [7, 8].

Thermochemical conversion includes transformations such as pyrolysis, direct combustion and gasification. As a separate technology and the preliminary stage of combustion and gasification, pyrolysis involves complicated chemical processes and complex physical processes such as heat and mass transfer. It has a significant effect on the gasification process. As a result, a deep understanding of pyrolysis kinetics is key to provide guidance on the design, feasibility of industrial gasification reactors and optimizing the operating conditions [9].

In this work, pyrolysis of wood residues and Gorse (*Ulex europaeus*) has been studied with the goal of evaluating their thermal decomposition kinetics and estimate their energy potential.

2. Experimental

2.1 Samples

Gorse (*Ulex europaeus*) and wood residues samples were supplied by the Botanical garden José Celestino Mutis of Bogotá. The material included trunks and branches without leaves. The samples were ground and sieved into a particle size less than 250 µm in preparation for the thermogravimetric analysis.

2.2 Material characteristics

Proximate analysis was performed after a drying process at 40°C for 60 h, according to ASTM D7582-12. The ultimate analysis was conducted using a CHNS/O analyzer (TruSpec micro, LECO) according to ASTM-5373-08. The high calorific value (HHV) was carried out in a calorimetric pump (plain jacket calorimeter 1341, Paar™) according to ASTM D-2015. The biochemical analysis was performed using a fibre analysis system FiberCap™ according AOAC methods 962.09 and 978.10.

The proximate, ultimate and biochemical analysis results, as well as the high calorific value (HHV) of the lignocellulosic samples are listed in Table 1.

Table 1. Proximate, ultimate, Biochemical and HHV analyses of Wood residues and Gorse analysis.

	Proximate analysis (wt% ^a)		Ultimate analysis (wt% ^a)		Biochemical analysis ^b		Calorific power				
	Wood residues	Gorse	Wood residues	Gorse	Wood residues	Gorse	Wood residues	Gorse			
Volatile matter	91,11	85,73	C	53,60	52,20	Cellulose	17,39	6,35	HHV (kCal/kg)	4099	4177
Fixed carbon	8,55	13,04	H	4,80	5,30	Hemicellulose	15,00	21,85			
Moisture ^b	10,70	8,13	O	40,50	39,30	Lignin	41,11	51,50			
Ash	0,35	1,70	N	0,35	1,10						
			S	0,40	0,40						

^a Dry basis, ^b As received basis

2.3 Method

2.3.1 Thermogravimetric analysis

Thermogravimetric tests were performed in a thermogravimetric analyser (TGA/DSC1, Mettler Toledo), where the weight loss of a sample was measured continuously at atmospheric pressure, under a constant volume flow rate of nitrogen at 50mL/min, at different heating rates.

First, the sample was heated to 105°C for 30 min. Then, the pyrolysis process was carried out from 25°C at four different constant rates of 10, 20, 30 and 40 °C/min to 900°C. A sample of 10±2 mg was used, and all the experiments were made in duplicate.

2.3.2 Theory

The primary pyrolysis process of biomass is represented by the following reaction scheme: Biomass → char + (volatiles + gases). The global kinetics of the reaction can be described as:

$$d\alpha/dt = k(T)f(\alpha) \quad (1)$$

where α is the fraction of conversion, $\alpha = (W_0 - W_t)/(W_0 - W_\infty)$. W_0 and W_∞ are sample masses at the beginning and at the end of the mass loss reaction, respectively. W_t is the sample mass at time t /temperature T .

$f(\alpha)$ is the differential function of conversion. T is temperature, $k(T)$ is the rate constant which is described by Arrhenius equation, $k(T) = A e^{(-E/RT)}$, where A is the pre-exponential factor, E is the apparent activation energy, R is the gas constant (8.314J/mol K). Eq. (1) can be converted into Eq. (2) expressed as:

$$d\alpha/dt = A f(\alpha) e^{(-E/RT)} \quad (2)$$

Table 2. Model-free non-isothermal methods

Method	Model	Plot	Energy activation (kJmol ⁻¹)	Ref
Kissinger	$Ln(\beta/T_m^2) = ln(AR/E) - (E/RT_m)$ T _m denote the temperature peak of DTG curve	Ln(β/T _m ²) against 1000/T _m at different heating rates	E= -slope·R	
FWO	$Ln(\beta_i) = ln(A_\alpha \cdot E_\alpha/R \cdot g(\alpha)) - 5.331 - 1.052(E_\alpha/RT_{\alpha i})$ i and α denote heating rate and conversion, respectively.	Ln(β _i) against 1000/T _{αi}	E= slope · R/-1.052	[10]
KAS	$Ln(\beta_i/T_{\alpha i}) = ln(A_\alpha \cdot R/E_\alpha \cdot g(\alpha)) - E_\alpha/RT_{\alpha i}$	Ln(β _i /T _{αi} ²) against 1000/T _{αi}	E= -slope·R	
Starink	$Ln(\beta/T^{1.8}) = C_s - 1.0037 E/RT$	Ln(β/T ^{1.8}) against 1/T at different heating rates	E= slope · R/-1.0037	[9]

For no isothermal TGA experiments at linear heating rate (β=dT/dt), equation (3) can be written as:

$$d\alpha/dT = (A/\beta) f(\alpha) e^{(-E/RT)} \quad (3)$$

This equation expresses the fraction of material consumed per unit of time. The activation energy was obtained from non-isothermal TGA. The methods used to calculate kinetic parameters are called model-free non-isothermal methods and require a set of experimental tests at different heating rates [9, 10].

2.3.3 Model-free methods

Activation energy was obtained from non-isothermal TGA through the following model-free non-isothermal methods: Kissinger, Flynn-Wall-Ozawa (FWO) and Kissinger-Akahira-Sunose (KAS) and Starink. These methods allow to obtain the kinetic parameters such as activation energy (E) of a solid state reaction without knowing the reaction mechanism [10]. A summary of used methods is given in table 2.

2.3.4 Levelized Cost of Energy (LCOE)

The Levelized Cost of Electricity (USD/MWh) was calculated for gasification technology using as a feedstock wood residues and Gorse according to equation (4).

$$LCOE = (I - D + C - S) / P \quad (4)$$

Where the parameters represent:

I= Initial investment (USD)

D= Depreciation costs (USD)

C= annual costs (USD)

S= value of assets at the end of the life cycle (USD)

P= total power generation (MWh).

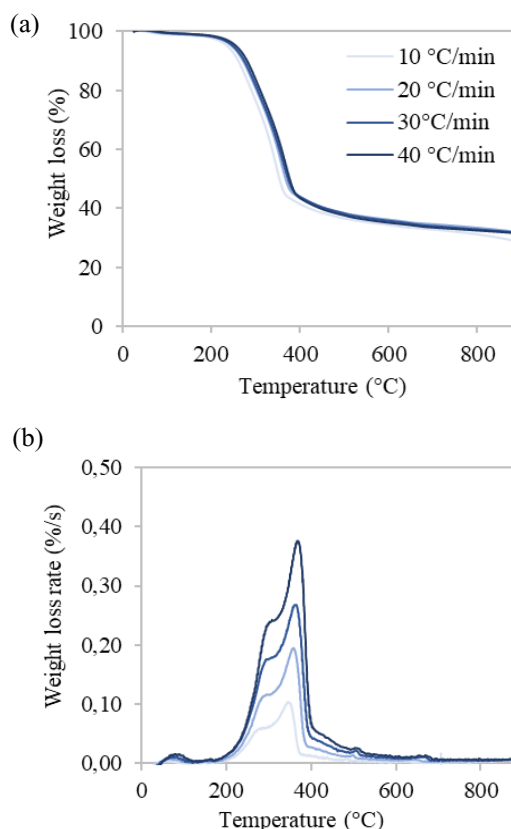


Fig. 1 (a) TG and (b) DTG profiles of Wood residues at different heating rates.

3. Results and analysis

3.1 characterization of fuels

According to the proximate analysis results of the samples, it can be observed a low moisture content (8,13% and 10,70) and a high amount of volatiles ranging from 85,73% to 91,11% of these lignocellulosic biomasses.

* Corresponding author: maria.gomez@unisabana.edu.co, Tel: +57 1 861 5555 Ext 25217

This indicates that wood residues and Gorse can be considered as desirable feedstocks for thermochemical processes. Furthermore, the lower ash content of both samples represents an advantage for the pyrolysis process because a high ash content will result in fouling production on the reactor [11].

3.2 Thermal degradation characteristics

The TG and DTG profiles of Wood residues and Gorse (*Ulex europaeus*) at different heating rates of 10-40 °C/min under nitrogen atmosphere are illustrated in Fig. 1 and 2, respectively. As can be seen from the plots, the devolatilization process started at approximately 235°C and proceeded rapidly with increasing temperature and then the weight loss decreased slowly to the final temperature. The residue at the end of the process was between 25-31% of the initial weight for both samples.

The pyrolysis processes can be divided into three different zones from DTG curves. While zone (I) corresponds to the mass loss due to evaporation of water and light volatiles, zone (II) shows the main pyrolysis stage caused by devolatilization and zone (III) illustrates degradation of carbonaceous in the residue. In this last zone, little mass loss is observed [11, 12].

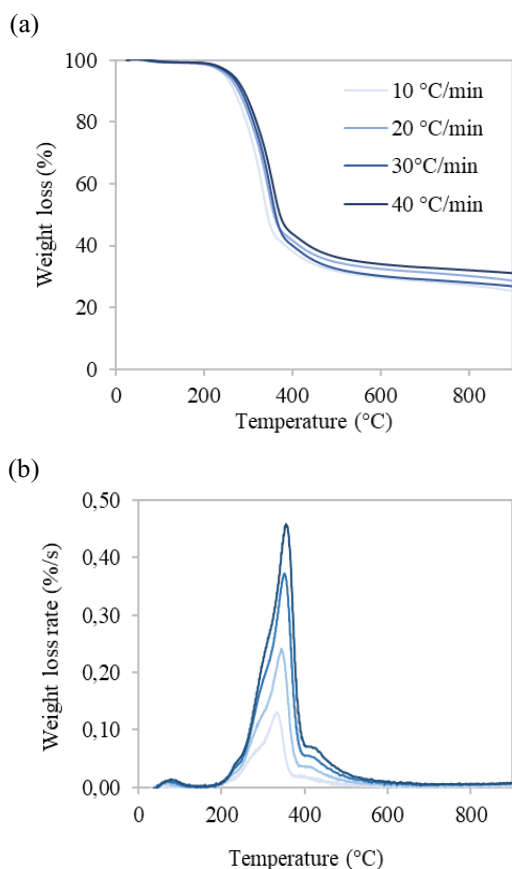


Fig. 2 (a) TG and (b) DTG profile of Gorse (*Ulex europaeus*) at different heating rates.

In the main pyrolysis zone, it can be observed one peak, one shoulder and one long tailing for each DTG curve.

The shoulder represents the fastest conversion of hemicellulose, the peak corresponds to the decomposition of cellulose and the tailing mainly corresponds to the lignin degradation [11].

It can be seen from the DTG curves that Gorse had a higher hemicellulose and lignin content than Wood residues, which is supported by the biochemical analysis results (Table 1). This experimental results are in good agreement with the reported results of the pyrolysis of Cellulose, hemicellulose and lignin [12].

In order to describe the properties of the pyrolysis process of these samples under the effect of varied heating rates, some characteristic parameters were calculated from the TG-DTG curves and are listed in Table 3. The highest degradation was obtained at a heating rate of 10°C/min and the obtained solid residues were of 25,31% and 28,47% for wood residues and Gorse, respectively. This occurred because of the lower ash content and higher volatile matter of Gorse [13].

On the other hand, the Figs. 1(b) and 2(b) show that a higher heating rate, the weight loss rate is greater. Biomass had some resistance to the reaction, so peaks in DTG curves moved to the right (table 3). These results have been reported by other authors with lignocellulosic materials such as [10, 14]. However, the highest weight loss rate, 0,46 %/s and 0,38% for Gorse and wood residues correspondingly, was obtained at 40°C/min.

Table 3. Characteristic parameters of Wood residues and Gorse during pyrolysis process.

Sample	Heating rate (°C/min)	T _v (°C)	T _p (°C)	DTG _{max} (% s ⁻¹)	Residue (%)
Wood residues	10	236,17	344,67	0,10	28,47
	20	246,67	358,33	0,20	31,83
	30	249,00	364,50	0,27	31,65
	40	255,67	369,00	0,38	31,53
Gorse	10	247,33	333,83	0,13	25,31
	20	253,33	344,33	0,24	28,64
	30	260,50	351,00	0,37	26,85
	40	265,67	355,00	0,46	31,09

T_v - the devolatilization temperature (°C), T_p - the corresponding of the peak rate of weight loss (°C), DTG_{max} - the maximum weight loss rate (% s⁻¹) and the residue % (compared to the initial sample weight) of each sample and heating rate

3.3 Kinetic parameters

The TGA data were analysed using model-free methods for determination of apparent activation energies of the pyrolysis. The Kissinger, FWO, KAS and Starink methods were used to calculate the activation energy as a function of the conversion ($\alpha = 0,1 - 0,7$).

Table 4. Apparent energy activation (E) and correlation coefficient (R²) deduced from FWO, KAS, Kissinger and Starink methods for Wood residues and Gorse.

Sample	Wood residues						Gorse					
	FWO		KAS		Starink		FWO		KAS		Starink	
	E (kJmol ⁻¹)	R ²	E (kJmol ⁻¹)	R ²	E (kJmol ⁻¹)	R ²	E (kJmol ⁻¹)	R ²	E (kJmol ⁻¹)	R ²	E (kJmol ⁻¹)	R ²
α												
0,1	176,97	0,974	195,00	0,976	166,59	0,951	173,38	0,976	191,40	0,979	149,62	0,998
0,2	195,79	0,984	215,22	0,985	181,00	0,984	182,25	0,995	201,12	0,995	163,68	0,999
0,3	218,10	0,983	239,01	0,984	197,01	0,986	195,73	0,999	215,60	0,999	178,97	0,999
0,4	243,81	0,985	266,37	0,986	209,86	0,989	198,73	0,998	219,00	0,998	187,48	0,998
0,5	243,47	0,992	266,28	0,993	211,73	0,991	200,16	0,999	220,70	0,999	189,90	0,998
0,6	237,06	0,996	259,77	0,996	213,51	0,997	198,70	1,000	219,32	1,000	192,89	0,997
0,7	237,05	1,000	259,94	1,000	208,08	1,000	212,12	1,000	233,62	1,000	193,37	0,999
Average	221,75	0,988	243,08	0,989	198,26	0,987	194,44	0,995	214,39	0,996	179,42	0,998
Kissinger	176,03	0,993					195,41	0,999				

Table 4 illustrates the kinetic parameters and the R² fitted from the plots of each method. The correlation coefficient (R²) was in range from 0,951 to 1,000 for all cases. The Figure 3 shows the apparent energy activation for (a) wood residues and (b) Gorse against the conversion obtained by the four methods. It can be observed that the apparent activation energy for KAS and FWO and Starink methods was not similar for all conversions, which indicates the existence of a complex multi-step mechanism that occurs in solid state.

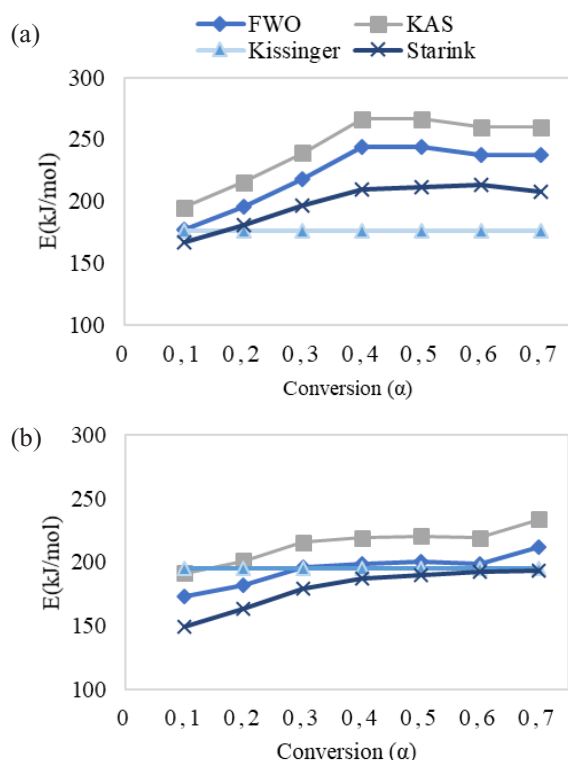


Fig. 3 Activation energy as a function of conversion for (a) Wood residues and (b) Gorse.

The average of the energy activation from Kissinger, FWO, KAS and Starink methods was 195.41, 194.44, 214.39 and 179.42 kJ/mol, respectively for Gorse and

176.03, 221.75, 243.08 and 198.26 kJ/mol, respectively for wood residues. It can be observed that activation energy is lower for Gorse than for wood residues. These results show the ability of Gorse to be transformed by a thermochemical process. It needs lower energy to be transformed compared with wood residues. Additionally, the high calorific value of Gorse is greater than that of wood residues. This characteristic could increase the conversion through a thermochemical route such as gasification.

It has been reported many studies of wood gasification. However, there are few studies about thermochemical conversion of Gorse. A study of power generation using Gorse gasification was carried out in a downdraft reactor with a coupled system of power generation in which a peak of 13.8 kW was obtained [5].

3.4 Levelized Cost of Electricity (LCOE)

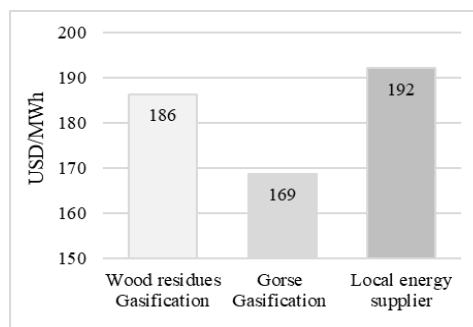


Fig. 4 Levelized Cost of Electricity in Bogotá, Colombia

The levelized cost of electricity of gasification of wood residues and Gorse is illustrated in Fig. 4. The LCOE for Gorse gasification was 169 USD/MWh which was lower as compared to LCOE for wood residues gasification, which was 186 USD/MWh. For the purpose of comparison, the cost of electricity from the local supplier of 192 USD/MWh [15].

In the same way, a study of power generation from gasification of corncobs reported a LCOE of 170

* Corresponding author: maria.gomez@unisabana.edu.co, Tel: +57 1 861 5555 Ext 25217

USD/MWh, which indicates that using residual biomass for power generation in Bogotá is a viable option to supply part of the local energy demand [16]. These results showed that gasification of Gorse and wood residues represent an opportunity to promote eradication and control processes of this invasive species and take advantage of the energy potential of these lignocellulosic biomasses to supply part of the increasing energy demand.

4 Conclusions

In this work, thermal characteristics of wood residues and Gorse (*Ulex europaeus*) have been studied. Experiments were performed under inert atmosphere, revealing that pyrolysis of analyzed lignocellulosic biomasses has a complex multi-step mechanism that occurs in solid state. This is due to different structural and elemental characteristics. Also, activation energy was determined and compared with four different methods and It was found that activation energy for pyrolysis of gorse is lower than required energy for pyrolysis of wood residues, which implies a great potential to be transformed through thermochemical technologies.

The LCOE for gasification of wood residues and Gorse were calculated. Using lignocellulosic biomass for power generation could be cheaper than the cost of energy from the local supplier if residues are gasified in-situ. The effect of blends of Wood residues and Gorse over the gasification and LCOE will be studied in a future analysis.

The authors wish to express their gratitude to University of La Sabana, specially to Master's in Design and Process Management for providing funding to conduct the experimental analysis in the frame of the project ING. 185/2016. To the Botanical Garden of Bogotá, José Celestino Mutis for supplying wood residues. Also, the authors are grateful to Universidad Nacional de Manizales for providing valuable technical support.

References

- [1] L. Ding, Y. Zhang, Z. Wang, J. Huang, and Y. Fang, "Interaction and its induced inhibiting or synergistic effects during co-gasification of coal char and biomass char," *Bioresour. Technol.*, vol. **173**, pp. 11–20, (2014).
- [2] B. B. Krishna, B. Biswas, P. Ohri, J. Kumar, R. Singh, and T. Bhaskar, "Pyrolysis of Cedrus deodara saw mill shavings in hydrogen and nitrogen atmosphere for the production of bio-oil," *Renew. Energy*, vol. **98**, pp. 238–244, (2016).
- [3] H. Aldana, F. J. Lozano, J. Acevedo, and A. Mendoza, "Thermogravimetric characterization and gasification of pecan nut shells," *Bioresour. Technol.*, vol. **198**, pp. 634–641, (2015).
- [4] U. A. E. de S. P. (UAESP), "Documento técnico de soporte del plan de gestión integral de residuos sólidos para Bogotá D.C.," (2016).
- [5] Y. Niño, L. T. Vega, and B. Ruiz, "Evaluation of the energy potential of the gorse (*ulex europaeus*) in the generation of electrical energy by gasification," *Chem. Eng. Trans.*, vol. **64**, no. 2008, pp. 481–486, (2018).
- [6] Jardín Botánico de Bogotá, "Descripción de las acciones realizadas en el proceso de intervención y recuperación de áreas invadidas de retamo como medida de mitigación de incendios forestales," (2014).
- [7] A. González, J. R. Riba, R. Puig, and P. Navarro, "Review of micro- and small-scale technologies to produce electricity and heat from Mediterranean forests' wood chips," *Renew. Sustain. Energy Rev.*, vol. **43**, pp. 143–155, (2015).
- [8] V. Dhyani and T. Bhaskar, "A comprehensive review on the pyrolysis of lignocellulosic biomass," *Renew. Energy*, vol. **129**, pp. 695–716, (2018).
- [9] C. Gai, Y. Dong, and T. Zhang, "The kinetic analysis of the pyrolysis of agricultural residue under non-isothermal conditions," *Bioresour. Technol.*, vol. **127**, pp. 298–305, (2013).
- [10] K. Słopiecka, P. Bartocci, and F. Fantozzi, "Thermogravimetric analysis and kinetic study of poplar wood pyrolysis," *Appl. Energy*, vol. **97**, pp. 491–497, (2012).
- [11] Z. Chen, M. Hu, X. Zhu, D. Guo, S. Liu, Z. Hu, B. Xiao, J. Wang, and M. Laghari, "Characteristics and kinetic study on pyrolysis of five lignocellulosic biomass via thermogravimetric analysis," *Bioresour. Technol.*, vol. **192**, pp. 441–450, (2015).
- [12] C. Quan, N. Gao, and Q. Song, "Pyrolysis of biomass components in a TGA and a fixed-bed reactor: Thermochemical behaviors, kinetics, and product characterization," *J. Anal. Appl. Pyrolysis*, vol. **121**, pp. 84–92, (2016).
- [13] S. Munir, S. S. Daood, W. Nimmo, A. M. Cunliffe, and B. M. Gibbs, "Thermal analysis and devolatilization kinetics of cotton stalk, sugar cane bagasse and shea meal under nitrogen and air atmospheres," *Bioresour. Technol.*, vol. **100**, no. 3, pp. 1413–1418, (2009).
- [14] J. Cai, D. Xu, Z. Dong, X. Yu, Y. Yang, S. W. Banks, and A. V. Bridgwater, "Processing thermogravimetric analysis data for isoconversional kinetic analysis of lignocellulosic biomass pyrolysis: Case study of corn stalk," *Renew. Sustain. Energy Rev.*, vol. **82**, no. April 2017, pp. 2705–2715, (2018).
- [15] Codensa, "Tarifas energía Eléctrica.pdf,"(2019). [Online]. Available: <https://www.enel.com.co/es/personas/tarifas-energia-enel-codensa.html>.
- [16] L. V. Martínez, "Producción de energía eléctrica a partir de la gasificación de raquis de maíz blanco (*Zea mays*) producidos en la Central de abastos de Bogotá – Corabastos," (2017).