

Thermogravimetric Study of Solid Residues from the 1G and 2G Ethanol Production Chain from *Agave sisalana* for Energy Applications

Emile dos Santos Araujo^{1*}, Roberto Batista da Silva Jr¹, Luis Gabriel Gomes Pereira¹, Daniel Freire Almeida¹, Danilo Silva Ferreira¹, Otanea Brito de Oliveira¹, Fernando Luiz Pellegrini Pessoa²

¹ SENAI CIMATEC University, Chemical, Petrochemical, and Refining Processes, Salvador, Bahia, Brazil

² SENAI CIMATEC University, Computational Modeling, Salvador, Bahia, Brazil

*Corresponding author: SENAI CIMATEC University; Salvador-BA; emile.araujo72@gmail.com

Abstract: The cultivation of *Agave sisalana* represents a significant socio-economic activity in the Brazilian semi-arid region, with the country accounting for approximately 40.3% of global sisal fiber production. The fiber processing generates large volumes of solid and liquid residues that remain underutilized. Although historically overlooked, these residues present high sugar content, making them attractive for energy recovery. The conversion of such materials through integrated biorefineries, combining biochemical and thermochemical routes, has been identified as a viable strategy to maximize biomass utilization efficiency, diversify product output, and reduce environmental impacts. Among thermochemical routes, pyrolysis stands out for its ability to simultaneously produce biochar, bio-oil, and pyrogas. However, industrial-scale implementation still faces operational challenges, particularly regarding thermal control and the process's sensitivity to variables such as heating rate. This study evaluated the thermal behavior of three residues from agave processing, leaves bagasse (LB), pine bagasse (PB), and 2G residue (2GR), through physicochemical characterization and thermogravimetric analyses (TG/DTG) at different heating rates (10, 50, and 90 °C.min⁻¹). The resulting curves revealed three main stages of thermal decomposition and showed that lower heating rates promote more complete reactions and higher biochar yields, while higher rates enhance volatile release. The results reinforce the potential of *Agave sisalana* residues as viable feedstocks for energy applications, with the choice of technological route depending on the specific characteristics of each fraction and the intended conversion objectives.

Keywords: Lignocellulosic biomass. Thermal degradation. Pyrolysis. Biochar.

Abbreviations: LB, leaves bagasse. PB, pine bagasse. 2GR, 2G residue.

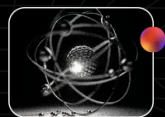
1. Introduction

The growing demand for renewable energy sources has driven the development of technologies aimed at the valorization of agro-industrial residues. These resources, often wasted or underutilized, can be converted into energy or high-value bioproducts within integrated biorefineries [1]. In such systems, the combination of biochemical and thermochemical pathways enables the efficient utilization of residual biomass, promoting sustainability, product diversification, and the reduction of environmental impacts [2].

Brazil is currently the world's largest producer of *Agave sisalana*, a plant traditionally

cultivated for fiber extraction. In the first half of 2025 alone, Brazil exported 35.8 thousand tons of sisal fibers, generating a revenue of US\$ 49.1 million [3]. However, the processing of agave results in significant quantities of liquid and solid residues rich in carbohydrates. The liquid fraction is particularly attractive for biochemical conversion processes such as fermentation and anaerobic digestion [4], while the solid fraction can be exploited through both biochemical routes (e.g., 2G ethanol production) and thermochemical processes, including pyrolysis, combustion, and gasification [5].

Among thermochemical technologies, pyrolysis has been widely studied. It involves the thermal



decomposition of biomass under an inert atmosphere, resulting in the production of biochar, bio-oil, and pyrolysis gases [6]. Biochar is a carbon-rich material, characterized by high porosity and the presence of aromatic and oxygenated functional groups on its surface, properties that enable its use in various fields such as soil quality improvement, climate change mitigation, and other applications [7].

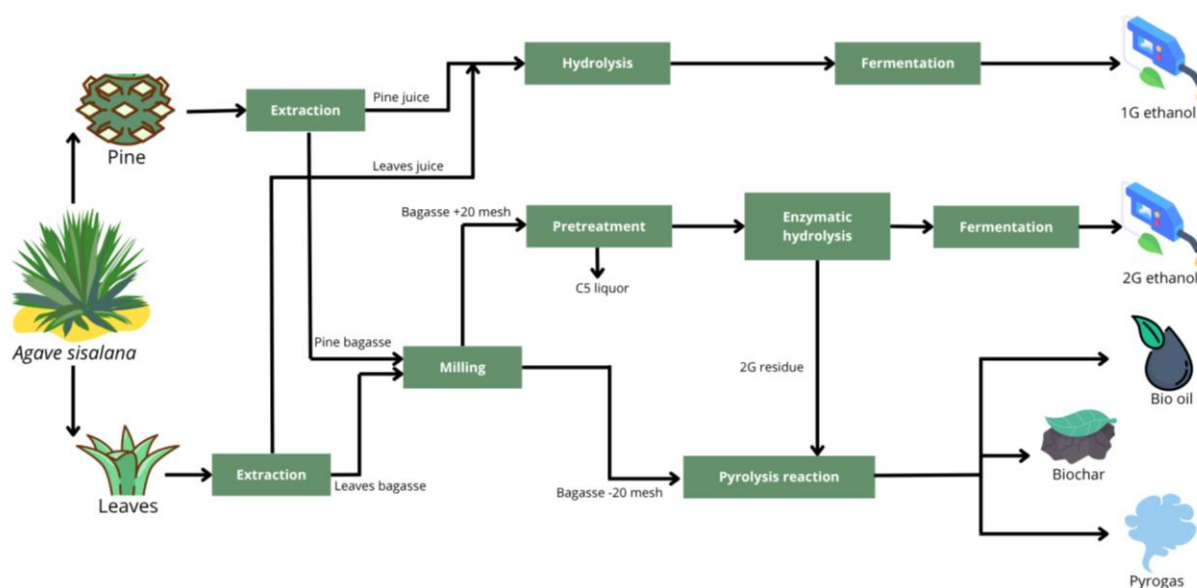
Despite the abundant availability of raw material, the scale-up of pyrolytic systems still faces several challenges, ranging from process control and the establishment of a consumer market to ensuring product quality and reliability, which are largely influenced by the feedstock characteristics [8]. Therefore, this study aims to investigate the thermal behavior of different residues from the 1G and 2G ethanol production chain derived from *Agave sisalana*, through thermogravimetric analysis at different heating rates, with a focus on sustainable energy applications.

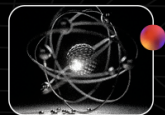
2. Methodology

2.1. Biomass Preparation

For this study, *Agave sisalana* cultivated in the municipality of Conceição do Coité (Bahia, Brazil), aged between 5 and 6 years, was used. The leaves and the pine underwent separate juice extraction steps, and the combined juice was directed to first-generation ethanol (1G) production. The resulting bagasse was air-dried for 24 hours over a period of three days, then milled using a Tramontina TRE 25 forage shredder and sieved. Fractions smaller than 0.84 mm were collected for this study, while fractions between 0.84 mm and 2 mm were mixed in a 1:1 ratio (leaves:pine) and processed for second-generation (2G) ethanol production. The solid residue from the enzymatic hydrolysis step was also collected and included in this study. Figure 1 presents a schematic representation of the *Agave sisalana* processing workflow.

Figure 1. Flow diagram of the processing stages of *Agave sisalana*.





2.2. Proximate Analysis

The proximate analysis was carried out to determine the moisture content, volatile matter, fixed carbon, and ash content of the biomass. The methodology described by Karatepe and Sadriye (1993) [9] was adopted, using a Netzsch Simultaneous Thermogravimetric Analyzer, model STA 2500 Regulus (TG/DTA). Moisture content was quantified under an inert nitrogen atmosphere (40 mL.min^{-1}), with the sample heated from 30°C to 110°C at a heating rate of $20^\circ\text{C.min}^{-1}$. Once 110°C was reached, the temperature was held constant for 30 minutes to ensure the complete removal of free moisture. Subsequently, the temperature was increased to 950°C at a heating rate of $40^\circ\text{C.min}^{-1}$ and held for 7 minutes for the determination of volatile matter. The system was then cooled to 750°C at a rate of $20^\circ\text{C.min}^{-1}$. Upon reaching this temperature, the furnace atmosphere was switched to synthetic air and maintained for 30 minutes to enable the determination of ash content and fixed carbon.

2.3. Higher Heating Value

The Higher Heating Value (HHV) is defined as the amount of energy released during the complete combustion of a fuel, with all water formed remaining in the liquid state. The HHV of the agave processing residues was determined using an IKA C200 Bomb Calorimeter, following the DIN 51 900 standard method. The

samples were combusted in a high-pressure oxygen atmosphere saturated with water vapor, to ensure the complete oxidation of organic material and the condensation of the water produced.

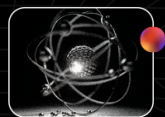
2.4. Thermogravimetric Analysis

The thermal decomposition reaction was investigated using a Netzsch Simultaneous Thermogravimetric Analyzer, model STA 2500 Regulus (TG/DTA). Approximately 10 mg of each sample was heated under a nitrogen atmosphere (flow rate of 40 mL.min^{-1}) up to a final temperature of 900°C , with heating rates set at 10, 50, and $90^\circ\text{C.min}^{-1}$.

3. Results and Discussion

The results of the physicochemical characterization of the biomass samples studied are presented in Table 1. For comparison purposes, the table also includes literature data on the characterization of sugarcane bagasse, a residue currently valorized through thermochemical conversion routes.

The nature of the residues from the *Agave sisalana* production chain influences the physicochemical properties of the biomass and should be considered when selecting the appropriate technological route for energy conversion. All the samples analyzed exhibited characteristics similar to those of sugarcane bagasse, which is widely referenced in the



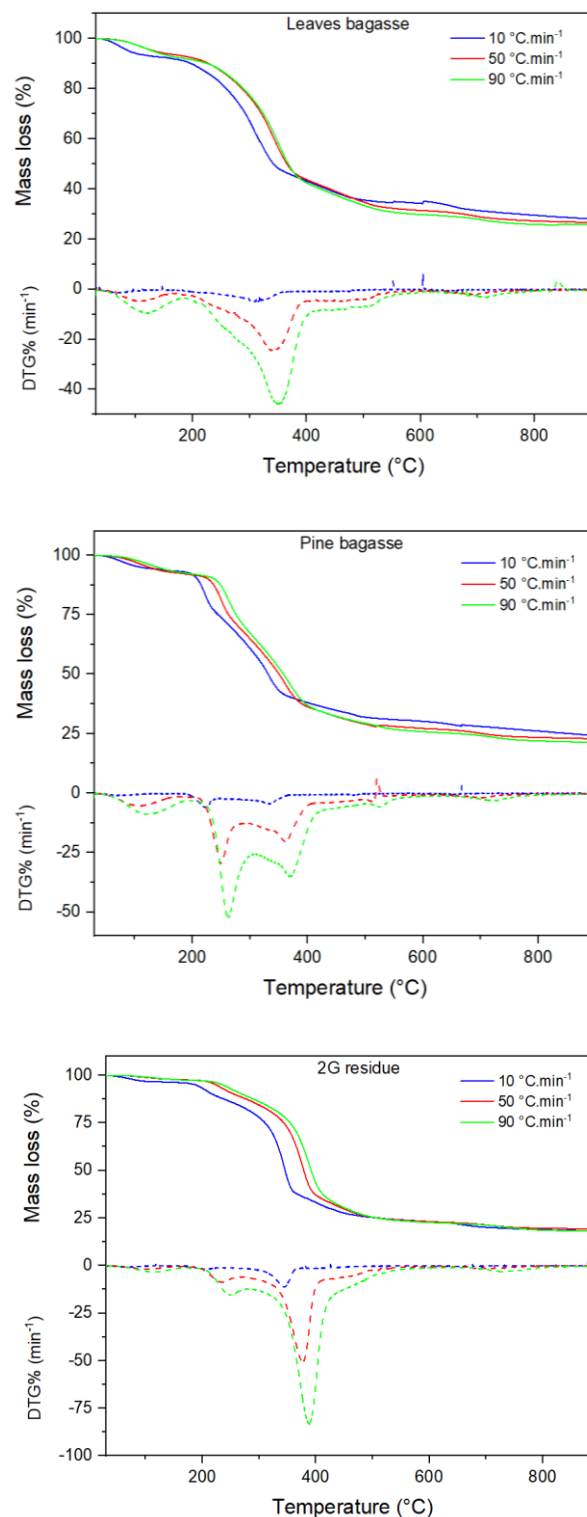
literature due to its high energy potential. Among the evaluated materials, the 2GR stood out for having the highest higher heating value ($20.545 \text{ MJ.kg}^{-1}$) and the lowest moisture content (2.65%), attributes that make it particularly promising for thermochemical applications requiring high energy efficiency. In general, low HHV and fixed carbon content can limit the performance of biomass in certain thermal applications [11]. Additionally, the high ash content (8.5–10.3%) may pose operational disadvantages, such as slag formation, fouling, and equipment wear, negatively impacting both process efficiency and product quality [10,11].

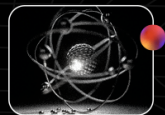
Table 1. Physical and chemical characteristics of biomasses.

Characteristics	Leaves bagasse	Pine bagasse	2G Residue	Sugarcane bagasse Carrier et al. [10]
Physical property				
Particle size (mm)	<0,84	<0,84	0,84 – 2,00	0,25 – 2,00
Bulk density (kg.m^{-3})	312,42	226,45	242,40	170,00
High Heating Value (MJ.kg^{-1})	15,210	15,013	20,545	17,600
Proximate analysis (wt %)				
Water	5,02	10,66	2,65	6,7
Volatile	71,54	71,01	75,80	76,1
Fixed carbon	14,88	8,28	11,24	6,9
Ash	8,5	10,04	10,31	9,1

Thermogravimetric analysis (TGA) tests were essential for evaluating the behavior of these biomasses under conditions similar to pyrolysis. The thermal decomposition and derivative (DTG) curves are presented in Figure 2 below.

Figure 2. Thermal decomposition curves of residues from the *Agave sisalana* production chain at different heating rates.





The analysis of the TG/DTG curves of residues derived from the processing of *Agave sisalana* allowed the identification of three main mass loss events, whose occurrence is influenced by the applied heating rates (10, 50, and 90 °C.min⁻¹). The DTG curve profiles exhibited similar features among the different residues, reflecting the common lignocellulosic nature of the biomasses. However, significant variations were observed in the intensity of the degradation peaks, indicating differences in the relative composition of organic constituents and in the thermal reactivity of each material.

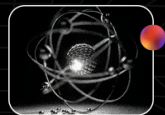
The first event occurs up to approximately 150 °C and corresponds to the removal of free and adsorbed water present in the sample. This mass loss was similar across all heating rates, indicating that the dehydration process occurs relatively independently of the thermal rate applied.

The second event, occurring between 200 and 400 °C, represents the main thermal degradation zone (40–50%) of the biomass organic components, hemicellulose, cellulose, and part of the lignin [12,13]. During this stage, intense release of volatile compounds such as light gases (CO, CO₂, CH₄, H₂O) and bio-oil is observed. Typically, hemicellulose degrades first (between 200–300 °C), followed by cellulose, which degrades more intensely between 300–400 °C [14,15]. Between 400 and 600 °C, moderate mass loss (~10–15%) is observed, related to the slow degradation of

lignin and carbonaceous residues, which usually occur over a broad temperature range.

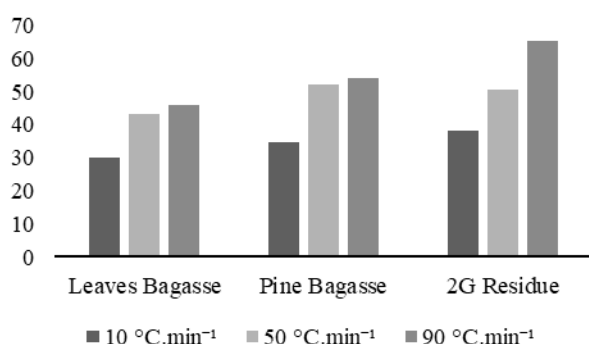
The curve obtained with the lowest heating rate (10 °C.min⁻¹) showed a shift in mass loss to lower temperatures, suggesting more efficient and complete thermal decomposition due to the longer thermal residence time. In contrast, the curves obtained at 50 and 90 °C.min⁻¹ exhibited a shift of the degradation events toward higher temperatures, a phenomenon known as thermal lag, caused by the rapid temperature increase that limits the reaction time of the pyrolysis steps [16–18].

In the third event, above 600 °C, mass loss is minimal, since at this point the biomass has already been largely converted into solid charcoal (biochar). The remaining mass variation is attributed to the slow and gradual degradation of residual fixed carbon and highly aromatic and thermally resistant compounds [11]. When comparing the final residual mass of biochar across different heating rates for the same biomass, a variation of up to 31% was observed. For the 10 °C.min⁻¹ condition, slightly higher residual mass was found for all biomass types. Rueda-Ordóñez and Tannous (2015) [18] concluded in their studies that heating rates below 10 °C.min⁻¹ result in more efficient thermal conversion of biomass, favored by longer reaction times. However, for heating rates above 10 °C.min⁻¹, the reaction behavior is affected by transport phenomena, leading to lower residual masses.



It was observed that the *Agave sisalana* residues begin their thermal decomposition at approximately 200 °C, completing around 570 °C under the highest heating rate conditions. The 2GR showed higher-intensity peaks in the DTG curve around 400 °C, which may be associated with its composition, characterized by higher lignin content and lower structural carbohydrate content. This feature is expected in materials subjected to pretreatment and enzymatic hydrolysis steps, which selectively remove cellulose and hemicellulose fractions, concentrating more recalcitrant compounds in the remaining solid residue. The resulting biochars were evaluated using the same proximate analysis method, and the fixed carbon values are presented in Figure 3.

Figure 3. Fixed carbon content in the biochar produced in the thermal degradation experiments.



It was observed that biochars produced under higher heating rates generally exhibited higher fixed carbon content. However, studies by Jayaraman *et al.* (2018) [16], using thermogravimetric analysis, indicated that for

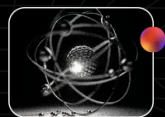
heating rates exceeding 100 °C.min⁻¹, there is a decrease in carbon content and an increase in the ash fraction in the solid residue. The authors attribute this behavior to the rapid release of volatiles during pyrolysis at high heating rates, which reduces carbon retention in the solid matrix and intensifies the relative concentration of inorganic materials.

From an energy perspective, the higher mass loss rate observed between 200 and 400 °C indicates a significant energetic potential of the evaluated biomasses, since this temperature range corresponds to the degradation of cellulosic fractions, responsible for the highest energy release during combustion or pyrolysis.

4. Conclusion

The physicochemical characterization of the residues from the *Agave sisalana* production chain revealed properties favorable to thermochemical conversion, with the 2G residue standing out due to its highest higher heating value (20.545 MJ.kg⁻¹) and lowest moisture content, attributes that make it particularly promising for applications requiring high energy efficiency, such as the production of high-performance solid biofuels. The 1G residue (PB e LB), with intermediate fixed carbon content and good thermal stability, shows potential for biochar production aimed at improving soil quality and carbon sequestration.

Thermogravimetric analyses demonstrated the significant influence of the heating rate on the



thermal decomposition dynamics of the biomasses. The results suggest that the proper adjustment of this parameter is crucial for optimizing the pyrolysis process, as it can directly impact both the yield and quality of the resulting products.

Acknowledgement

The authors would like to acknowledge Shell Brasil and ANP (Agência Nacional do Petróleo, Gás Natural e Biocombustíveis) for the strategic support provided through regulatory incentives for Research, Development & Innovation. We also acknowledge EMBRAPPII and Senai CIMATEC for the encouragement and funding.

References

- [1] Rajesh Banu J., Preethi, S.K., Tyagi V.K., Gunasekaran M., Karthikeyan O.P., *et al.* Lignocellulosic biomass based biorefinery: A successful platform towards circular bioeconomy. *Fuel*. 2021; 302:121086.
- [2] Rios-Del Toro E.E., Chi H., González-Álvarez V., Méndez-Acosta H.O., Arreola-Vargas J., Liu H. Coupling the biochemical and thermochemical biorefinery platforms to enhance energy and product recovery from *Agave tequilana* bagasse. *Appl Energy*. 2021; 299:117293.
- [3] Companhia Nacional de Abastecimento - CONAB. Sisal - Análise Mensal: junho de 2025. Brasília; 2025.
- [4] de Paula M.S., Adarme O.F.H., Volpi M.P.C., Flores-Rodriguez C.I., Carazzolle M.F., Mockaitis G., *et al.* Unveiling the biogas potential of raw Agave leaf juice: Exploring a novel biomass source. *Biomass Bioenergy*. 2025;193:107522.
- [5] Jambeiro T.A., Silva M.F.S., Pereira L.G.G., da Silva Vasconcelos D., Batalha Silva G., Figueirêdo M.B., *et al.* Fast Pyrolysis of Sisal Residue in a Pilot Fluidized Bed Reactor. *Energy & Fuels*. 2018; 32(9):9478–9492.
- [6] Glushkov D., Nyashina G., Shvets A., Pereira A., Ramanathan A. Current Status of the Pyrolysis and Gasification Mechanism of Biomass. *Energies (Basel)*. 2021; 14(22):7541.
- [7] Supraja K.V., Kachroo H., Viswanathan G., Verma V.K., Behera B., Doddapaneni T.R.K.C., *et al.* Biochar production and its environmental applications: Recent developments and machine learning insights. *Bioresour Technol*. 2023; 387:129634.
- [8] Garcia-Nunez J.A., Pelaez-Samaniego M.R., Garcia-Perez M.E., Fonts I., Abrego J., Westerhof R.J.M., *et al.* Historical Developments of Pyrolysis Reactors: A Review. *Energy & Fuels*. 2017; 31(6):5751–5775.
- [9] Karatepe N., Kuçukbayrak S. Proximate analysis of some Turkish lignites by thermogravimetry. *Thermochim Acta*. 1993; 213:147–150.
- [10] Carrier M., Joubert JE, Danje S, Hugo T, Görgens J, Knoetze J (Hansie). Impact of the lignocellulosic material on fast pyrolysis yields and product quality. *Bioresour Technol*. 2013; 150:129–138.
- [11] da Silva J.C.G., Arias S., Pacheco J.G.A., Raya F.T., Pereira G.A.G., Mockaitis G. Exploring the pyrolysis of Agave species as a novel bioenergy source: Thermo-kinetics, modeling, and product composition insights. *J Anal Appl Pyrolysis*. 2025; 188:107053.
- [12] Mortari D.A., Ávila I., Dos Santos A.M., Crnkovic P.M. Study of Thermal Decomposition and Ignition Temperature of Bagasse, *Coal and Their Blends*. Thermal Engineering. 2010; 9:81–88.
- [13] Guimarães J.L., Frollini E., da Silva C.G., Wypych F., Satyanarayana K.G. Characterization of banana, sugarcane bagasse and sponge gourd fibers of Brazil. *Ind Crops Prod*. 2009; 30(3):407–415.
- [14] Piazza V., da Silva Junior R. B., Frassoldati A., Lietti L., Gambaro C., Rajendran K., *et al.* Unravelling the complexity of hemicellulose pyrolysis: Quantitative and detailed product speciation for xylan and glucomannan in TGA and fixed bed reactor. *Chemical Engineering Journal*. 2024; 497:154579.
- [15] Piazza V., da Silva Junior R.B., Frassoldati A., Lietti L., Chiaberge S., Gambaro C., *et al.* Detailed speciation of biomass pyrolysis products with a novel TGA-based methodology: the case-study of cellulose. *J Anal Appl Pyrolysis*. 2024; 178:106413.
- [16] Jayaraman K., Gokalp I., Petrus S., Beldandria V., Bostyn S. Energy recovery analysis from sugar cane bagasse pyrolysis and gasification using thermogravimetry, mass spectrometry and kinetic models. *J Anal Appl Pyrolysis*. 2018; 132:225–236.
- [17] Seo D.K., Park S.S., Hwang J., Yu T.U. Study of the pyrolysis of biomass using thermo-gravimetric analysis (TGA) and concentration measurements of the evolved species. *J Anal Appl Pyrolysis*. 2010 Sep;89(1):66–73.
- [18] Rueda-Ordóñez Y.J., Tannous K. Isoconversional kinetic study of the thermal decomposition of sugarcane straw for thermal conversion processes. *Bioresour Technol*. 2015; 196:136–144.