

Kinetic and thermogravimetric analysis of millet cob or water hyacinth pyrolysis to produce bio sources carbon materials

Wend-Waoga Anthelme Zemané¹, Oumarou Savadogo^{2*}

¹ 2500 Chemin de Polytechnique, Montréal, H3T 1J4, QC, Canada

² 2500 Chemin de Polytechnique, Montréal, H3T 1J4, QC, Canada

Corresponding Author Email: oumarou.savadogo@polymtl.ca

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ABSTRACT

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This study investigates the potential of producing carbon materials from millet cob and water hyacinth through the analysis of their pyrolysis behavior. Thermogravimetric experiments were performed from 35 °C to 700 °C under nitrogen to characterize mass-loss profiles and identify decomposition stages. Kinetic parameters were determined at heating rates of 5, 10, 15, and 20 °C/min using Kissinger, Kissinger–Akahira–Sunose, and Flynn–Wall–Ozawa methods. Carbon contents obtained by combustion analysis were 44.9 % for millet cob and 40.6 % for water hyacinth. Both precursors exhibited three main transitions: moisture evaporation, hemicellulose and cellulose decomposition, and major lignin degradation. Proximate analysis showed distinct compositions, with millet cob containing 72.1 % volatile matter and 5.5 % ash, while water hyacinth presented 68.9 % volatile matter and 8.7 % ash. XPS results revealed differences in surface chemistry: millet cob displayed a higher proportion of sp² carbon and a less oxidized surface, whereas water hyacinth contained more oxygenated functional groups and mineral species. These findings indicate that both biomass sources can serve as viable precursors for producing raw carbon materials, with their structural and chemical characteristics offering potential advantages for various electrochemical applications.

NOMENCLATURE

BET	Brunauer, Emmett et Teller
C	Carbon
E _a	Activation energy
EDS	Energy Dispersive Spectroscopy
EIS	Electrochemical Impedance Spectroscopy
FWO	Flynn-Wall-Ozawa
HCl	Hydrogen chloride
H ₃ PO ₄	Phosphoric acid
KAS	Kissinger-Akahira-Sunose
KOH	Potassium hydroxide
Li ⁺	Lithium Ion
N ₂	Nitrogen
R _{ct}	Charge transfer resistance
R _e	Electrolyte resistance
SEM	Scanning Electron Microscopy
TGA	Thermogravimetric analysis
XRD	X-ray diffraction

Subscripts

CM	Carbonous materials
DTG	Derivative thermogravimetric
MC	Millet cob
NLDFT	Non-Local Density Functional Theory
WH	Water Hyacinth

1. INTRODUCTION

The depletion of fossil resources, combined with the challenges of climate change, is driving humanity toward the adoption of so-called clean energy sources. Among these, biomass emerges as a promising alternative due to its abundance and its multiple economic and energetic advantages. Biomass can be converted into various forms of energy, fuels, or chemicals through biochemical and thermochemical processes. The latter include combustion, pyrolysis, gasification, and hydrothermal liquefaction [1].

Numerous proximate analysis studies have been conducted on various types of biomass, including fibrous wood fragments [2], *Miscanthus giganteus* [3], coconut fibers, and eucalyptus dead leaves [4]. These studies provide critical insights into the composition of biomass precursors, highlighting key fractions such as moisture content, volatile matter, ash content, and fixed carbon. This characterization plays a fundamental role in assessing the energy potential of biomass, guiding its optimization for renewable energy applications.

X-ray photoelectron spectroscopy (XPS) is a powerful characterization method for analyzing the surface chemistry of solid materials. It provides qualitative and quantitative data on the elemental composition, except for hydrogen and helium, as well as the nature of chemical functional groups, thus providing a deep understanding of surface interactions [5], [6].

Pyrolysis is an efficient method used for biomass molecules' decomposition into gaseous or volatile matter, liquid or tar and solid carbonized matter or char or carbon [7]. It is possible now to synthesize an active carbon use as the electro catalyst support for electric vehicle batteries applications. However, the synthesis of natural activated carbon is a complex process that requires a thorough understanding of thermal and kinetic behaviors. To use biomass waste such as millet cob and water hyacinth as raw materials for activated carbon production, it is essential to conduct thermal and kinetic analyses of their thermal decomposition. Millet cob and water hyacinth have the advantage of being abundantly available in many parts of the world and are often considered low-value or waste materials. Millet alone accounts for nearly half of global production and is widely cultivated in arid and semi-arid regions of Africa and Asia. [8]. Millet is also cultivated and used as a fern plant in the United States, in the Caribbean countries as Haiti and Australia [9].

According to the International Union for Conservation of Nature (IUCN), water hyacinth is considered one of the most dangerously invasive aquatic plants due to its rapid propagation [10]. Native to the Amazon region of Brazil, it has since spread extensively across tropical areas of Africa and Asia [8]. Within a few days, it can cover large portions of water surfaces with thick, dense mats supported by its bulbous submerged stems. These mats enable the plant to float, often obstructing sunlight from reaching the water below. As a result, aquatic ecosystems can be severely affected, with reduced light penetration potentially leading to the death of underwater fauna due to lack of photosynthesis [8]. Water hyacinth also disrupts human activities by blocking ponds and canals, thereby interfering with water supply, fishing, irrigation, and tourism services [8].

It has been shown that its minimum temperature growth is 12°C, the optimum is in the range of 25-33°C and the maximum temperature is 33-35°C. If the water hyacinth lives

in this last range of temperature, its leaves and stems lose their water under high sunlight which may stop the plant growth [11], [12], [13], [14].

Based on the above data of discussion on the plant, it is not very useful in its environment and for human activities. It can also be produced easily at high volume in a short time, and it is a renewable carbon source. Accordingly, its utilization as carbon support as active materials for Li-ions battery applications.

Thermogravimetric analysis (TGA) is a widely recognized and reliable technique used to accurately assess mass loss during the thermal decomposition of biomass samples through pyrolysis [15]. This thermal analysis method is essential for understanding the degradation behavior of materials by monitoring changes in mass as a function of temperature or relative to reference temperature. Depending on the nature of the sample and the objectives of the study, TGA can be performed in various modes: (i) dynamic mode, where the sample is heated at a constant rate; (ii) isothermal mode, where it is maintained at a fixed temperature; or (iii) under a non-linear temperature profile. All measurements are conducted under a controlled atmosphere to ensure reproducibility and relevance of the results [16].

Many biomass resources have already been studied by pyrolysis to get carbon support for battery applications. These studies include the characteristics and kinetics analysis of the thermal decomposition process of rice straw [17], corn cob quantitative analysis of the thermal degradation characteristics [18], sorghum straw decomposition using thermogravimetric analysis [19], jute sticks characterization by pyrolysis and kinetic analysis [20], coconut shell waste kinetic study by pyrolysis [21], bioenergetic potential study of pearl millet by kinetic analysis under pyrolysis and combustion [22], water hyacinth roots, stems and leaves pyrolytic bioenergy potential quantification [23], Tunisian tomato waste as biomass fuel potential study by thermogravimetric analysis and kinetic study [24], carbonization process and model mechanism study for bamboo pyrolysis [25], apple waste thermal and kinetic characterization by pyrolysis [26], microalgal residues pyrolysis kinetic analysis [27].

Most biomass waste can be used to synthesize activated carbon for battery electrodes; however, determining the appropriate heating rate and optimal activation temperature remains challenging. Thermogravimetric analysis of pyrolysis is a valuable tool that addresses this issue by providing insight into the thermal behavior and kinetic parameters of the samples.

In this study, following the compositional analysis of millet cob and water hyacinth samples, their thermal and kinetic behaviors were investigated using thermogravimetric analysis. To determine the kinetic parameters governing their thermal decomposition, iso-conversional models such as Kissinger, Kissinger-Akahira-Sunose (KAS), and Flynn-Wall-Ozawa (FWO) were applied. TGA and its derivative curves were used to identify the temperatures corresponding to each stage of the decomposition process, including the release of volatiles, formation of char, fixed carbon, and residual ash. Activation energy and pre-exponential factors were estimated as a function of the conversion rate using the kinetic models. Lastly, a kinetic investigation was carried out by varying the heating rate to determine the optimal conditions for both chemical and physical activation of the resulting carbon materials.

Although millet cob and water hyacinth waste are abundant, there are no studies on the valorization of its wastes into active support carbon for Li-ion batteries electrodes for electric vehicle applications. Only one has addressed thermal and kinetic analyses on pearl millet [22]. Two research papers have focused on water hyacinth, including a study of its bioenergetic potential [23] and a description of its thermal degradation kinetics [28]. However, this study focused on the bioenergetic potentiality of the entire millet plant, but here we are only interested in the millet cob, which may present a morphological aspect favorable to the synthesis of active carbon. On the other hand, advances in the development of novel carbon materials encourage the evaluation of the bioenergetic potential of plants such as water hyacinth. Accordingly, for water hyacinth as well as millet cob, we are mainly interested in temperature determination during their phase transitions and the optimal heating rate to be used for the synthesis of active carbon as effective support materials for active electrodes for electrochemical energy storage applications as Li-ion batteries.

2. Materials and methods

2.1 Materials

For the proximate analysis, millet cob and water hyacinth samples were weighed using an analytical balance and placed in refractory crucibles. A furnace operating under an argon atmosphere was used both for drying and for determining the volatile matter and ash content. X-ray photoelectron spectroscopy (XPS) was carried out on the precursors using a Thermo Scientific ESCALAB 250Xi system equipped with a monochromatic Al K α source (1486.7 eV). The morphological characteristics of the precursors were examined using a JEOL JSM-7600F scanning electron microscope.

Thermogravimetric analysis was performed to assess the pyrolysis behavior of the samples. The analyses were conducted using a TGA 8000 thermobalance from Perkin-Elmer, which allows for both TGA and differential scanning calorimetry (DSC) measurements. Nitrogen was used as purge gas throughout the experiments. The dried biomass samples were collected from various regions of Burkina Faso. Prior to analysis, the samples were disinfected with 10% hydrochloric acid, rinsed with deionized water, and dried at 80 °C for 48 hours, then ground into powder form.

2.2. Proximate analysis method

The moisture content of millet cob and water hyacinth samples is determined using ASTM E871-82 [29]. The crucibles are conditioned in an oven at 105°C for thirty minutes. The millet cob and water hyacinth samples are removed, reduced to a uniform size and placed in the sealed crucibles. After an initial weighing of approximately 1 g of each sample, they are heated at 105°C for 16 hours, then cooled and weighed again. The percentage of moisture present in the biomass is determined using equation (1) [29] :

$\% \text{ Moisture} = (W_i - W_f) / (W_i - W_c) * 100$	(1)
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Where: W_c = Weight of empty crucible (g)
 W_i = Initial Weight of crucible and sample (g)

W_f = Final Weight of crucible and dry sample (g)

The ash content is determined according to the ASTM E1755-01 method, the procedure of which consists of first heating the empty crucibles to 600 °C before cooling them and weighing them with an accuracy of 0.1 mg [30]. Each sample of millet cob and water hyacinth with a mass of 2 g is then placed in the crucible, weighed, and then dried at 105 °C until its weight is stabilized. Once the sample is dry, it is heated in a muffle furnace at 600 °C for 4 h, to eliminate the carbon by combustion without generating mechanical losses. The crucibles are cooled and then weighed immediately [30]. The percentage of ash present in the biomass is determined from equation (2) [30]:

$\% \text{ Ash} = W_{\text{ash}} / W_{\text{dry sample}}$	(2)
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Where: W_{ash} = Weight of ash (g)
 $W_{\text{dry sample}}$ = Weight of dried sample (g)

The determination of volatile matter (VM) follows the ASTM E872-82 method, where 1 g of sample previously dried at 105°C is heated to 950°C for 7 minutes, with a heating rate of 50°C/min under a neutral argon atmosphere [31]. Before the experiment, the empty crucible is weighed, followed by the weighing of the sample placed inside, and then the hole is taken to the furnace. After the heat treatment, the sample is rapidly cooled and immediately weighed to measure the mass loss due to the evaporation of volatile matter. The final quantity is calculated according to equation (3) of the standard [31]:

$\% \text{ VM} = (W_{\text{id}} - W_{\text{f}}) / (W_{\text{id}} - W_{\text{c}}) * 100$	(3)
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Where: W_c = Mass of empty crucible (g),
 W_{id} = Initial mass of crucible and dry sample (g),
 W_f = Final mass of crucible and sample (g)

The amount of fixed carbon (FC) is calculated by subtracting the constituent fractions of the material, namely moisture, volatile matter and ash. This approach makes it possible to estimate the proportion of residual carbon after removal of volatile and inorganic components. The mathematical relationship used is given by equation (4) [32]:

$\% \text{ FC} = 100 - (\% \text{ Moisture} + \% \text{ VM} + \% \text{ ash})$	(4)
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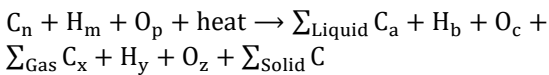
2.3. X-ray photoelectron spectroscopy (XPS) Analysis method

For the analysis, powdered samples were affixed to adhesive tape and positioned directly on the sample holder. To ensure measurement accuracy, standard charge compensation was applied using low-energy electrons and Ar⁺ ions. Spectral data were processed with Avantage v6.5, and relative atomic percentages were derived from peak areas, utilizing manufacturer sensitivity factors. The Powell algorithm was employed for peak fitting, integrating a Gaussian-Lorentzian mix. Specific constraints were implemented: while the Lorentzian/Gaussian ratio was not fixed, it was kept consistent across all component peaks of a given element and orbital, yet allowed to vary between samples. Additionally, the relative

areas of the fitted $2p3/2$ - $2p1/2$ and $3d5/2$ - $3d3/2$ doublets were constrained to ratios of 2:1 and 3:2, respectively.

2.4. Thermogravimetry experiments in pyrolysis conditions

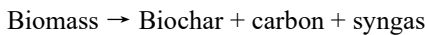
Pyrolysis is a thermal decomposition process in which biomass samples are heated to a target temperature at a controlled heating rate in the absence of oxygen or air. The primary products of pyrolysis include condensable vapors and solid coke. These vapors can undergo further transformation into non-condensable gases such as CO, CO₂, H₂ or CH₄, as well as into liquids or tars [33]. The pyrolysis process and its associated products can be represented by the following generalized equation: [33]:



For the pyrolysis, millet cob and water hyacinth samples were placed in the thermobalance chamber under a nitrogen atmosphere. Thermogravimetric analysis was conducted to monitor the mass variation of the samples as a function of temperature and time. The carbon content of both biomass types was determined by combustion using a Perkin-Elmer A200 carbon analyzer. For TGA, the dynamic mode was employed, in which samples were heated at a constant rate of 20 °C/min in a nitrogen-purged environment. The nitrogen flow rate was set to 40 mL/min to ensure a consistent inert atmosphere throughout the process. Each sample was heated from 35 °C to 700 °C. For the kinetic analysis, additional tests were conducted at four different heating rates: 5 °C/min, 10 °C/min, 15 °C/min, and 20 °C/min, all under the same inert conditions. The initial mass of millet cob samples ranged from 10.50 mg to 15.60 mg, while that of water hyacinth samples varied between 7.90 mg and 10.40 mg.

2.5. Description of the kinetic models

The possibility and rates of biomass transformation into syngas, biochar or carbon depend on the kinetic parameters used during pyrolysis. Hence an accurate kinetic model must be used to obtain the desired optimized product from biomass like carbon [34]. As for other types of biomasses, the thermochemical conversion process can be represented by the generalized reaction:



To describe the thermal decomposition kinetics, a single-step reaction model can be applied, using the conversion rate as a function of temperature and time. This model is usually governed by the Arrhenius equation, which allows calculating the activation energy required for pyrolysis and the reaction rate constants essential for predicting the decomposition behavior of biomass. The classic kinetic equation describing the thermal decomposition by a single reaction conversion rate can be written as [35]:

$\frac{d\alpha}{dt} = k(T) \cdot f(\alpha)$	(5)
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With α is the conversion degree, $f(\alpha)$ is the conversion degree function, t is the decomposition time and $k(T)$ is the Arrhenius classic function given by:

$k(T) = A \exp\left(-\frac{E_a}{RT}\right)$	(6)
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Where $R = 8.314 \times 10^{-3}$ kJ/K/mol is the gas constant, E_a (J/mol) is the activation energy, A is the Arrhenius equation pre-exponential factor (/min) and T (K) the absolute temperature.

The degree of conversion α is defined as:

$\alpha = \frac{m_i - m_t}{m_i - m_f}$	(7)
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With m_i is the initial mass, m_t is the mass at the decomposition time t and m_f is the final mass of the sample.

By combining equations (5) and (6), we obtain the following relation:

$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right) \cdot f(\alpha)$	(8)
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The heating rate can be expressed as follows:

$\beta = \frac{dT}{dt}$, where β is the heating rate, dT the change in temperature, and dt the change in time.

By applying the necessary transformations, equation (8) becomes:

$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E_a}{RT}\right) \cdot f(\alpha)$	(9)
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Given that $T = \beta dt + T_0$, integrating equation (9) results in:

$g(\alpha) = \int_0^\alpha \frac{1}{f(\alpha)} \cdot d\alpha = \frac{A}{\beta} \int_{T_0}^T \exp\left(-\frac{E_a}{RT}\right) \cdot dT$	(10)
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where $g(\alpha)$ is a function representing the decomposition mechanism. It typically denotes the limiting stage of the reaction, which can be classified as: chemical reaction, phase boundary reaction, random nucleation and nuclei growth, or diffusion.

To determine the different parameters and kinetic mechanisms, the most well-known non-isothermal methods have been employed. These include Kissinger, Kissinger-Akahira-Sunose (KAS), Flynn-Wall-Ozawa (FWO) and the Coats-Redfern method have been used, respectively [36], [37], [38], [39], [40].

The Kissinger method is basically given by [39] :

$\ln\left(\frac{\beta}{T_m^2}\right) = \ln\left(\frac{AR}{E_a}\right) - \frac{E_a}{R \cdot T_m}$	(11)
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Here, T_m denotes the maximum temperature.

The KAS method developed in [39] and in [40] consists of pyrolysis of the sample following at least three different heating rates. The KAS method expression is defined as:

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AE_a}{R \cdot g(c)}\right) - \frac{E_a}{R \cdot T} \quad (12)$$

Utilizing equation (12), we can plot the $\ln\left(\frac{\beta}{T^2}\right)$ curve as a function of $\left(\frac{1}{T}\right)$. This plot results in a straight line, allowing us to determine the activation energy E_a from the slope. This method provides a clear and straightforward way to derive kinetic parameters from the experimental data.

The FWO method, as developed in references [35] and [41], closely parallels the KAS method. By pyrolyzing the sample at multiple heating rates, this method facilitates the determination of key parameters and the kinetic mechanism. The expression for the FWO method is as follows:

$$\ln\beta = \ln\left(\frac{AE_a}{R \cdot g(c)}\right) - 5.331 - 1.052\left(\frac{E_a}{R \cdot T}\right) \quad (13)$$

Like the KAS method, plotting $\ln\beta$ against $\left(\frac{1}{T}\right)$ yields a straight line from which the slope can be used to determine the activation energy E_a . By applying this technique to the thermogravimetric data of millet cob and water hyacinth, it is possible to determine and analyze the kinetic parameters governing their thermal decomposition. These results offer valuable insights into the decomposition behavior of these biomasses and highlight their potential for use in bioenergy production.

3. Results and discussion

3.1. Proximate analysis of millet cob and water hyacinth

Proximate analysis reveals that millet cob contains a higher percentage of volatile matter and a lower ash content compared to water hyacinth. The results are detailed in the table 1 below.

Table 1: Proximate analysis of millet cob and water hyacinth

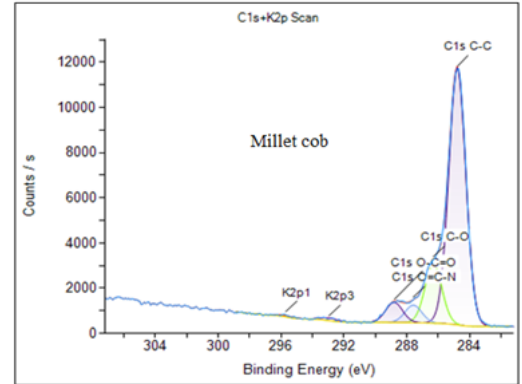
Samples	Moisture (%)	Volatile Matter (%)	Ash (%)	Fixed Carbon (%)
Millet cob	4.4	72.1	5.5	18.0
Water hyacinthe	6.0	68.8	8.7	16.5

The lower moisture content in millet cob, naturally drier than water hyacinth, could reduce drying costs before pyrolysis or carbonization. Additionally, its slightly higher volatility promotes pore formation, which is beneficial for chemical or physical activation of carbon. The higher ash content in water hyacinth is attributed to its aquatic origin, which involves increased mineral content. Finally, the fixed carbon content in both samples indicates a good residual carbon yield after pyrolysis, making them suitable for energy valorization.

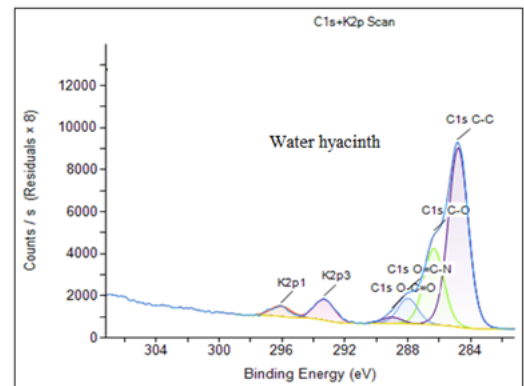
3.2. XPS Analysis of millet cob and water hyacinth

The XPS analysis of both Sample JE and Sample EM indicates the absence of a $\pi \rightarrow \pi^*$ shake-up transition in the C1s photoelectron peak, suggesting a low concentration of sp^2 -hybridized carbon. Further investigation of the CKLL Auger electron region reveals a D-parameter of 13.5 eV for the water hyacinth Sample, corresponding to an sp^2 -carbon content of 5 %, while millet cob sample presents a D-parameter of 14.0 eV, indicating a slightly higher sp^2 -carbon fraction of 10 %. The precision of these estimations, based on the D-parameter, is evaluated at approximately 5 % for both samples.

Figure 1 below shows the high-resolution C1s peak decomposition curves for millet cob and water hyacinth samples. These spectra distinguish the different forms of carbon bonds present on the surface of the two materials. For millet cob, the peak decomposition reveals a predominance of the C-C/C=C signal (at ~284.8 eV), characteristic of a predominantly aliphatic or amorphous carbon, accompanied by significant contributions from C-O, C=O, and O-C=O bonds, indicating the presence of oxygenated functional groups. As for water hyacinth, although the C-C signal is also dominant, the relative proportions of the C-O, O=C-N, and O-C=O components are higher, reflecting a more oxidized and functionalized surface, consistent with its aquatic origin. This suggests a greater richness in polar groups, which may improve the chemical interaction of the material with other active components or electrolytes.



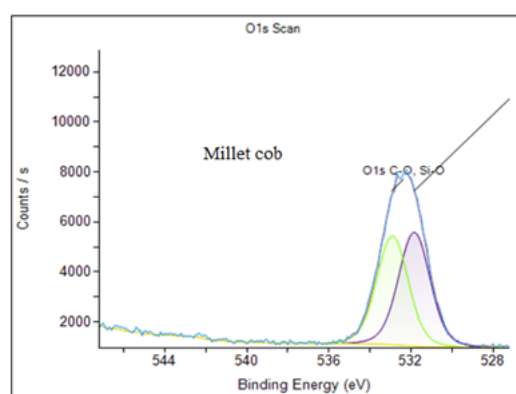
(a) Millet cob



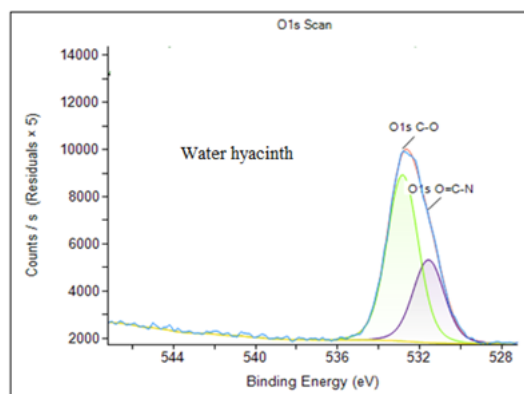
(b) Water hyacinth

Figure 1: C1s peak decay curves (high resolution)

Figure 2 below shows the high-resolution XPS spectra of the O1s band for millet cob (left) and water hyacinth (right). These spectra highlight the chemical nature of the oxygenated groups present on the surface of both biomasses. For millet cob, the splitting of the O1s peak reveals two main contributions: one at ~ 531.8 eV, attributed to C=O bonds (carbonyls or carboxyls), and a second at ~ 532.9 eV, corresponding to C–O bonds (alcohols, ethers) or Si–O bonds, which is consistent with the presence of silica detected in the elemental analysis. For water hyacinth, the two components observed at ~ 531.6 eV and ~ 532.8 eV are respectively attributed to O=C–N (amides or urea) and C–O bonds, indicating a surface more enriched in nitrogenous and oxygenated functional groups. This chemical signature testifies to a stronger surface functionalization, which could improve the wettability and chemical interaction capacity of the material, for adsorption or electrochemistry applications.



(a) Millet cob



(b) Water hyacinth

Figure 2: O1s spectra

The histogram below illustrates the surface atomic composition of millet cob and water hyacinth samples obtained by XPS analysis. It highlights the relative percentages of the main elements detected on the surface of the materials.

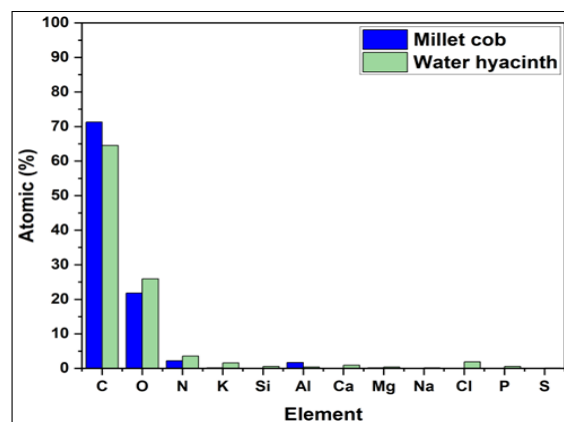


Figure 3: Atomic Percentage Bar Chart of millet cob and water hyacinth

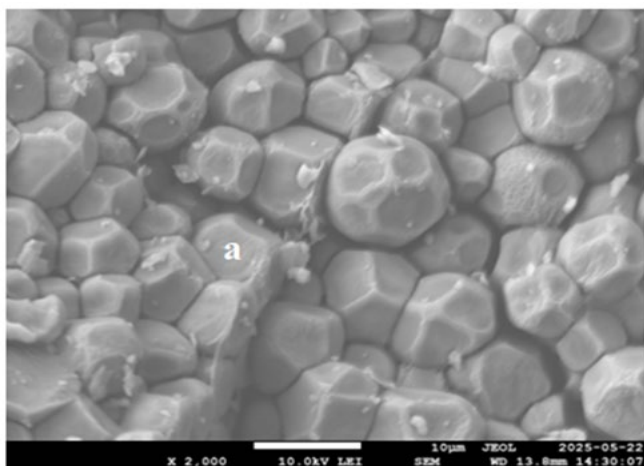
It is observed that millet cob has a significantly higher carbon content (71.3%) than water hyacinth (64.5%), reflecting a more carbonaceous and potentially more thermally stable surface. Conversely, water hyacinth exhibits a higher oxygen concentration (25.9% versus 21.8%), reflecting more pronounced surface oxidation, likely related to the presence of numerous oxygenated functional groups (C–O, O=C–N) identified in the C1s and O1s spectra.

Additionally, water hyacinth has higher amounts of inorganic elements such as potassium, chlorine, calcium, and nitrogen, due to its aquatic environment rich in minerals and nitrogenous organic matter. In contrast, millet cob has a more homogeneous surface and are less loaded with mineral elements. However, this entire composition is subject to change when carbon is chemically activated at high temperatures.

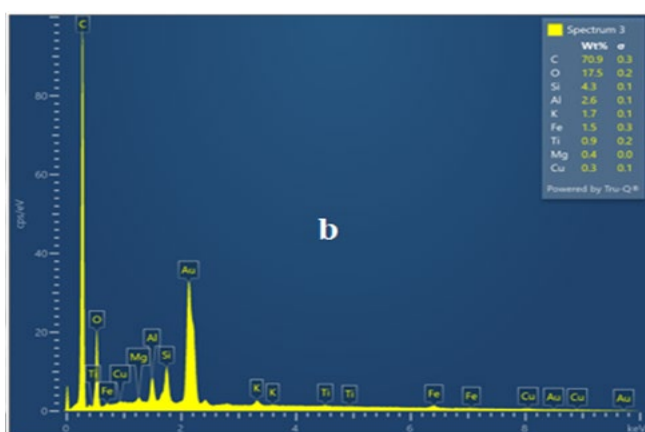
The XPS analysis results are consistent with the ultimate analysis, which revealed a higher volatile matter content in millet cob compared to water hyacinth. The majority conversion of carbon to CO, CO₂ (volatile matter) confirms that millet cob contains more carbon, in line with the conclusions of the XPS analysis.

3.3 Surface morphology by SEM of millet cob and water hyacinth

The SEM images of millet cob and water hyacinth precursors reveal distinct morphological differences between the two materials. The millet cob precursor exhibits circular hexagonal-shaped particles, a structural characteristic that could promote pore formation during carbon activation. This feature may enhance the material's porosity, improving its adsorption capabilities for various applications. Figure 4 below presents the SEM image (a) and the chemical composition (b) analyzed by EDS for millet cob.



(a) SEM



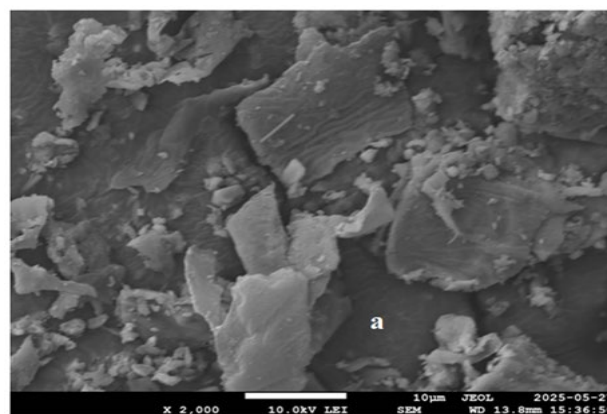
(b) EDS

Figure 4: Morphology and chemical composition of millet cob

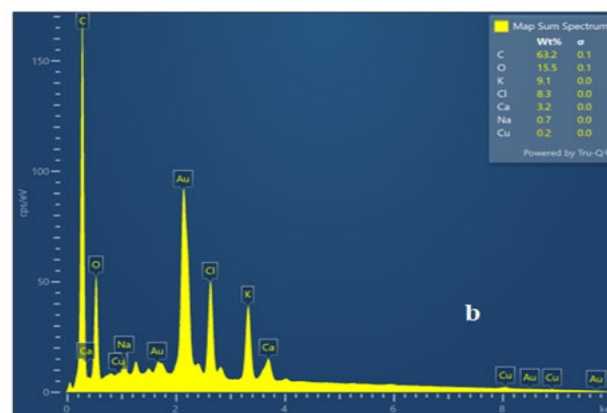
The SEM image reveals a regular and compact hexagonal morphology of millet cob particles, a key advantage for activated carbon synthesis. This structure provides a highly organized surface, promoting the formation of a well-developed porous network after activation. The EDS analysis indicates a high carbon content (70.9 %), which is beneficial for optimal activated carbon yield. The presence of oxygen (17.5 %) suggests the existence of oxygenated functional groups (-OH, -COOH), influencing the material's adsorption properties. The gold detected in the EDS corresponds to a metallic coating applied to enhance electrical conductivity and achieve better SEM imaging resolution and is not an intrinsic component of the material. Lastly, the absence of significant metallic catalysts limits graphitic crystallization, indicating that activated carbon derived from millet cob via chemical activation would be predominantly amorphous.

The SEM analysis of the water hyacinth precursor is presented in Figure 5. Unlike the millet cob precursor, whose morphology reveals particles of a predominantly hexagonal shape, that of the water hyacinth is characterized by particles with a lamellar morphology, evoking platelet or sheet structure. Figure 5 indicates that the water hyacinth precursor exhibits a lamellar and fibrous morphology, characterized by plates, stacked layers and flat surfaces, revealing a presence of

lignin and oriented natural fibers. This structural organization favors the formation of ordered domains during heat treatment, thanks to the presence of initial planes that facilitate reorganization into more regular stacks. In addition, the observation of agglomerated microparticles on the surface highlights a natural porosity of the material, which optimizes the development of pores during activation. This SEM analysis confirms that the precursor has an intrinsically organized architecture and a morphology conducive to partial graphitization, thus offering remarkable potential for applications in carbon materials.



(a) SEM



(b) EDS

Figure 5: Morphology and chemical composition of water hyacinth

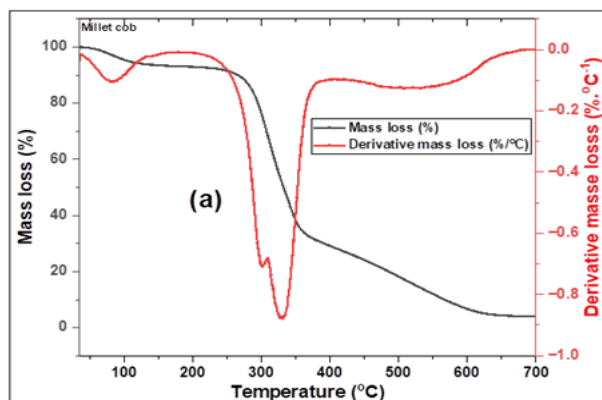
The results of the SEM analysis corroborate those of the XPS analysis, confirming that the millet cob has a higher carbon content, while the water hyacinth contains a significant proportion of mineral salts.

3.4. Thermogravimetric (TG) and derivative Thermogravimetric (DTG) curves analysis

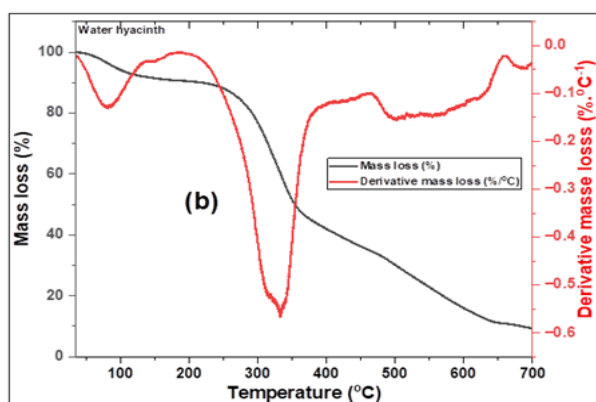
The thermal degradation through the study of their mass variations with temperature of the millet cob and the water hyacinth was achieved over a range of 35°C to 700°C for a heating rate of 20°C/min.

Figure 6.a and Figure 6.b show, both the TG and DTG curves for millet cob and water hyacinth, respectively.

The TG curves of these figures show the mass loss (%) variation as a function of temperature for millet cob and water hyacinth, respectively. This is an indication that these biomass sources can produce active carbon.



(a) Millet cob



(b) Water hyacinth

Figure 6: TG and DTG curves at 20°C/min heating rate for (a) Millet cob; (b) Water hyacinth

Three transitions are observed on the TG curves of the respective thermal decomposition of both millet cob and water hyacinth. For millet cob (Figure 6.a), the first transition corresponds to a mass loss of about 6.60 % between 44°C to 200°C and a 0.32 mg/min maximum loss rate. For water hyacinth the same trend is observed and a 9.30 % mass loss between the temperature range of 45°C to 190°C corresponding to a 0.26 mg/min maximum loss rate. This initial mass loss could be attributed to water evaporation from the millet cob and water hyacinth samples. This is in agreement with some results obtained elsewhere on the kinetics of pyrolysis which have shown that the elephant grass exhibited a dehydration phase over the temperature range from 30°C to 100°C [42]. Since the mass loss in this range of temperature, corresponding to the moisture content in both samples, is less than 10 %, it can be concluded that millet cob and water hyacinth are suitable for the pyrolysis reaction and the carbon production. Both samples were pretreated under the same conditions, and their mass loss is 6.60 % for millet cob and 9.30 % for water hyacinth. Accordingly, water hyacinth has a greater capacity for surface moisture retention than millet because the mass loss of water hyacinth is higher than that of

millet, but the maximum water loss rate of millet cob (0.32 mg/min) is higher than that of water hyacinth (0.26 mg/min). Accordingly, millet cob losses more easily its surface water than water hyacinth. This might influence the physical and chemical properties of carbon produced from these two biomass sources.

The millet cob second transition corresponds to 63 % mass loss in the temperature range of 200°C to 400°C. This transition takes place in two stages, the first stage in the temperature range of 200°C to 320°C with 37 % mass loss and a 2.74 mg/min maximum mass loss rate. The second stage occurs from 320°C to 400°C following 26 % mass loss with 2.22 mg/min maximum loss rate. For water hyacinth, the second transition corresponds to a 55.40 % mass loss in the temperature range of 190°C to 455°C. Like for millet cob, this transition also occurs in two stages, the first in 190°C to 330°C range with a 23.90% mass loss with 1.07 mg/min maximum mass loss rate and the second part from 330°C to 385°C following 31.50 % mass loss with 1.16 mg/min maximum loss rate. In the range of 200°C to 400°C, the maximum mass loss rate of millet cob (4.96 mg/min) is higher than that of water hyacinth (2.23 mg/min). The decomposition peaks of hemicellulose and cellulose of biomass are in this range of temperature e.g. 200 °C-400°C [43]. These results are in agreement with other results which show that the second transient phase is at the temperature range 200°C to 365°C [7]. This is also in agreement with another study of the pyrolysis of date palm biomass which obtained this second transition over the temperature range of 200°C to 400°C [43]. This is also confirmed by this other study of the pyrolysis characteristics of hemicellulose, cellulose and lignin which indicated that the decomposition peak of hemicellulose is 275°C and that of cellulose is 355°C [44]. On the other hand, the results obtained in our work indicate that for this second transition, the maximum decomposition rate of the hemicellulose and cellulose of millet cob is higher than that of water hyacinth. This agrees with the first transition between 30°C and 200°C where the mass loss was 0.32 mg/min for millet cob which is higher than 0.26 mg/min for water hyacinth.

In the second transition, mass loss for these two samples is likely due to the formation of significant volatile materials such as carbon monoxide (CO) and carbon dioxide (CO₂), resulting from the decomposition of hemicellulose, cellulose, or parts of lignin. Previous studies have shown that hemicellulose decomposes easily into volatiles like CO and CO₂. Other research indicates that hemicellulose decomposes between 220 °C and 315 °C, cellulose between 315°C and 400 °C, and lignin between 180°C and 900°C [38]. The second transition results reveal that millet cob is primarily hemicellulosic, while water hyacinth is predominantly cellulosic. This is further supported by the fact that the water hyacinth sample has a harder appearance compared to the millet cob. Carbon formation begins at around 400°C for millet cob and at 455°C for water hyacinth. Consequently, carbon yields decrease beyond 400°C for millet cob and beyond 455°C for water hyacinth. It has been shown that millet cob has a porous structure [44]. Its porosity increases from 50 % to 70 % when the moisture increases from 5 % to 22.5 % and its surface area increases from 20 mm² to 35 mm² when the moisture increases from 5% to 22.5 %. This porous structure and low density of millet cob allow it to be more easily exposed to high temperatures, thus accelerating its decomposition. In contrast,

water hyacinth with its denser, more compact structure undergoes thermal degradation at a slower rate. This variation in thermal behavior likely affects the physical and chemical characteristics of the carbon derived from these two biomass sources.

The third transition occurs over a 400°C to 650°C temperature range for millet cob with 26 % mass loss and 0.37 mg/min maximum mass loss rate and over a 455°C to 690°C range, 24.85 % mass loss with a 0.27 mg/min maximum mass loss rate for water hyacinth. The latter transition could correspond essentially to the lignin decomposition. This agrees with the that lignin degrades over a wide temperature range (100 – 900°C) [44].

Great differences were found among the pyrolysis behaviors of the three components. Hemicellulose started its decomposition easily, with the weight loss mainly happened at 220 – 315 °C. It got the maximum mass loss rate (0.95 wt.%/°C) at 268°C, and there was still 20 % solid residue left even at 900°C. Cellulose pyrolysis was focused on a higher temperature range (315–400°C) with the maximum weight loss rate (2.84 wt.%/°C) attained at 355°C. When the temperature was higher than 400 °C, almost all cellulose was pyrolyzed with a very low solid residue (6.5 wt.%/C) left. Among the three components, the lignin was the most difficult one to decompose. Its decomposition happened slowly under the whole temperature range from ambient to 900 °C, but at a very low mass loss rate (less than 0.14 Wt%/°C). The solid residue left from lignin pyrolysis (45.7 wt.%) was the highest. The differences in the inherent structures and chemical nature of the three components possibly account for the different behaviors observed [45], [46], [47].

The presence of these three transitions for both samples align with the various products typically obtained within similar temperature ranges during biomass pyrolysis, as noted in [44]. In the pyrolysis, biomass undergoes thermal decomposition into smaller organic components: solid biochar, condensable vapors (tars and bio-oils), and gases, usually within the 350°C to 800°C range. The specific temperature range and decomposition rate depends on several pyrolysis conditions, including feedstock type, temperature, heating rate, and pressure [44].

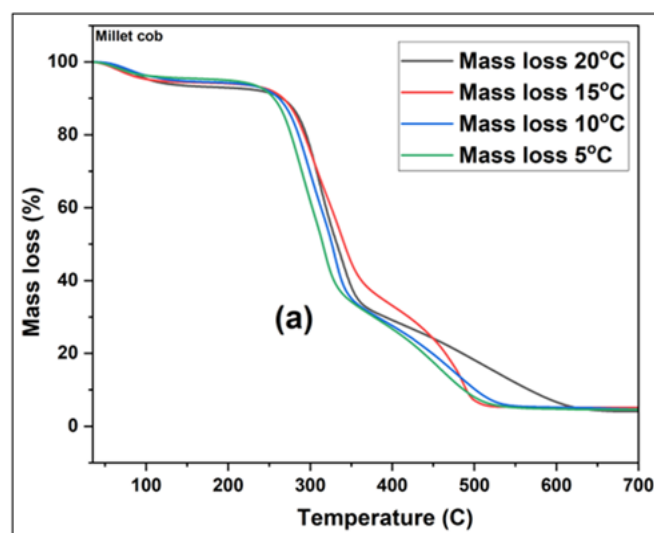
The maximum mass loss rate for millet cob was 17.64 %/min at 310°C, compared to 11.23 %/min at 333°C for water hyacinth. Overall, the mass loss rate of millet cob is higher than that of water hyacinth, with the peak rate occurring at a lower temperature for millet cob. This suggests that the high density of water hyacinth acts as a retarding factor in its thermal decomposition, requiring additional energy to evaporate the water before actual decomposition begins. This likely explains why millet cob waste decomposes faster, as TG analysis shows it has less moisture compared to water hyacinth. Consequently, carbon from millet cob could be activated at lower temperatures compared to water hyacinth. Given that millet cob decomposes more rapidly, it might offer better energy potential in terms of heat release during pyrolysis. A faster maximum decomposition rate may indicate higher conversion efficiency to end products such as activated carbon.

3.5. KINETIC ANALYSIS OF THE PYROLYSIS OF THE SAMPLES

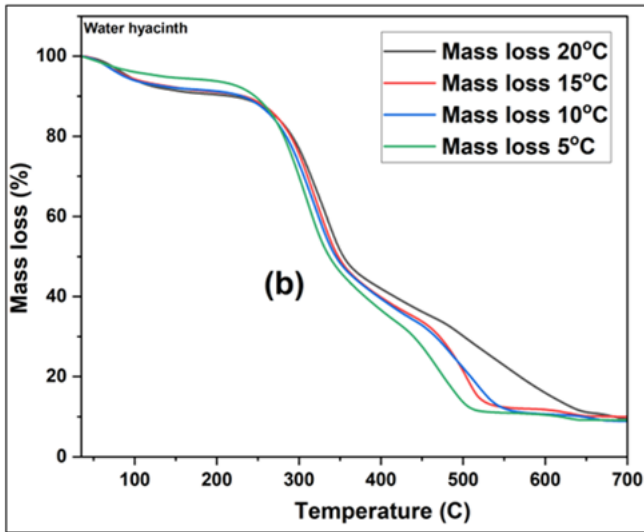
3.5.1. Effect of heating rate on the samples

The influence of heating rate on the pyrolysis behavior of millet cob and water hyacinth samples was investigated by applying four different rates: 5 °C/min, 10 °C/min, 15 °C/min, and 20 °C/min. The TG curves in Figure 7 obtained for these four rates have the same shape, however, they shift to the right. This is an indication that for a given temperature in the second and the third transitions, the mass loss increases when the heating rates increases. As an example, for the millet cob, at 320°C, the mass loss is around 60 % for 5°C/min and this mass loss is more than 70 % at 20°C/min. For the same temperature, the water hyacinth mass loss is around 45 % and 55 % for the heating rate of 5 °C/min and 20 °C/min, respectively.

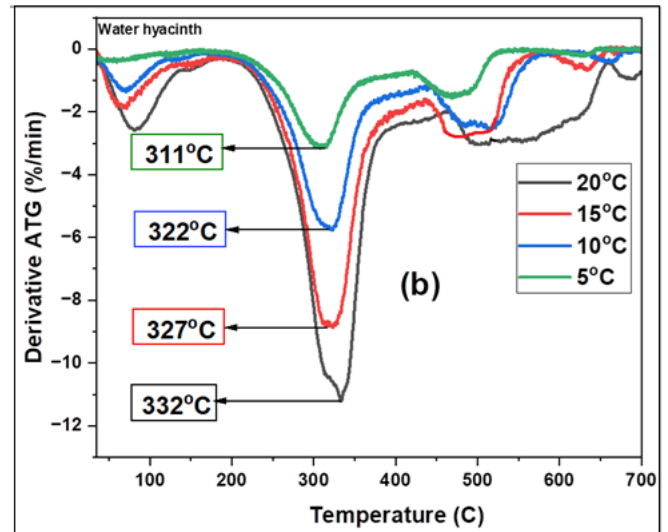
This behavior can likely be attributed to the increased thermal energy imparted to the sample at higher heating rates. However, elevated heating rates result in shorter residence times within the pyrolysis chamber, which hinders uniform heat distribution across the biomass particles. Previous studies have reported that such conditions lead to thermal gradients and uneven decomposition within the sample [36]. Consequently, concerns may arise regarding the homogeneity of the pyrolysis process at high heating rates. One major drawback is the difficulty in precisely controlling the sequential release of volatiles, char formation, and ash content during the three transitional stages of pyrolysis. In contrast, lower heating rates (5°C/min, 10°C/min) allow for a more gradual temperature rise, promoting better thermal penetration and uniform conversion throughout the sample matrix.



(a) Millet cob



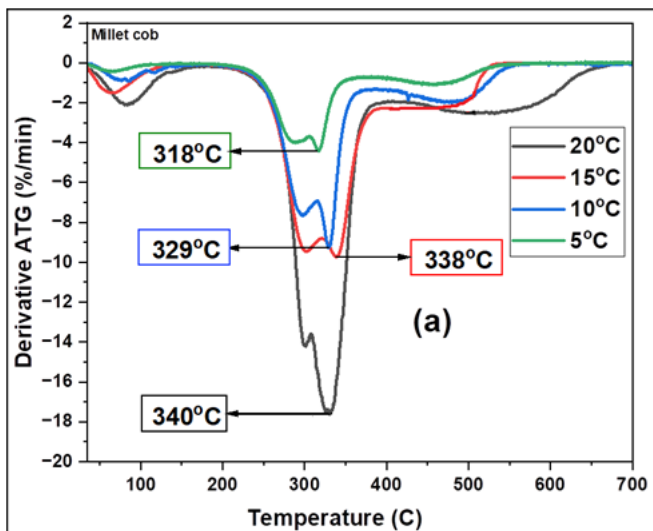
(b) Water hyacinth

Figure 7: TG curves at four heating rates for (a) millet cob and (b) Water hyacinth.

(b) Water hyacinth

Figure 8: Differential TG (DTG) curves at the heating rates of 5oC/min, 10oC/min, 15oC/min and 20oC/min for (a) millet cob and (b) water hyacinth.

Figure 8 represents the millet cob and water hyacinth Differential TG (DTG) curves. show that the temperature peak increases with the heating rate. This method gave a quantification of the moisture, volatile matter (hemicellulose, cellulose, ...), fixed carbon, and ash by constant weight lines. The rate of mass loss as indicated by the DTG curves is an indication of the temperature on the decomposition reactivity of each material. The maximum weight loss was observed for millet cob at temperatures 318 °C, 329°C, 338°C and 340°C respectively at heating rates of 5°C/min, 10°C/min, 15°C/min, and 20 °C/min. For water hyacinth the peak maximum weight loss is at 311°C, 322°C, 327°C and 332°C respectively at heating rates of 5°C/min, 10°C/min, 15°C/min, and 20°C/min.



(a) Millet cob and

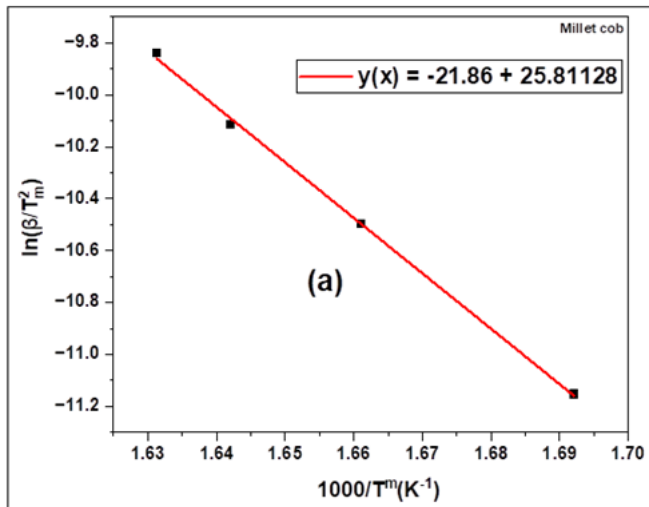
Accordingly, the temperature peak of the thermal decomposition or the thermal degradation increases with the heating rate. This suggests that the peak temperature obtained is, of course, highly dependent on the heating rate applied to the sample, and the type of the sample, during pyrolysis. Also, the TG curves of the millet cob and the water hyacinth show a difference at the second transition. At this transition, the TG curve of the millet cob contains two peaks corresponding to the degradation of hemicellulose and cellulose respectively. However, water hyacinth TG curve has only one peak, which means that there is a superimposed decomposition of hemicellulose and cellulose. This difference could be explained by the fact that millet cob contains more lignin compared to water hyacinth [48]. This is an advantage for millet cob because lignin contributes to the formation of most of the solid residues such as carbon during pyrolysis [48].

3.5.2. Kinetic analysis

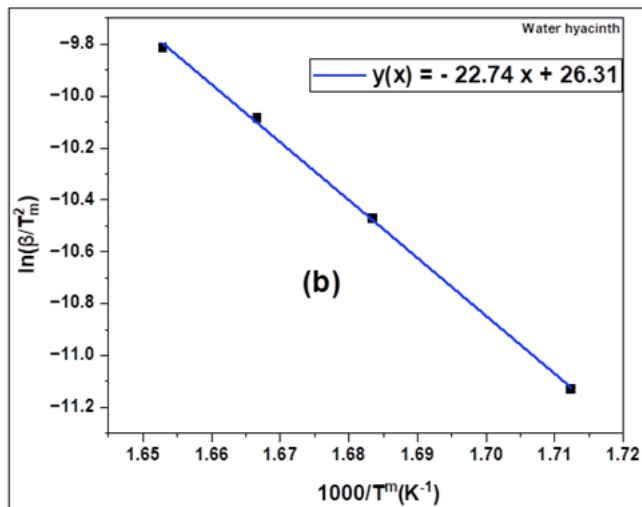
The kinetic analysis of the millet cob and water hyacinth pyrolysis was studied from the derivative thermogravimetric analysis results. DTG curves displayed three peaks corresponding to three distinct transition phases, with their maximum temperatures (T_m) illustrated in Figure 8. From the three maximum temperatures corresponding to the four heating rates and using above equation (11) and rewritten below, we obtain Kissinger plot of millet cob and water hyacinth (Figure 9).

$$\ln\left(\frac{\beta}{T_m^2}\right) = \ln\left(\frac{AR}{E_a}\right) - \frac{E_a}{R \cdot T_m} \quad (11)$$

Where: $\beta = \frac{dT}{dt}$ (T and t are the decomposition temperature and decomposition time respectively)



(a) Millet cob

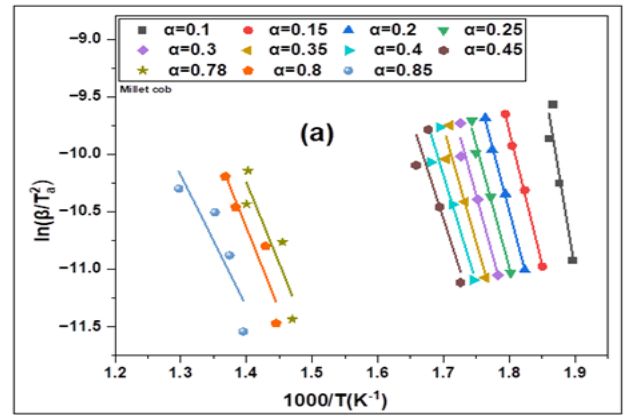


(b) Water hyacinth

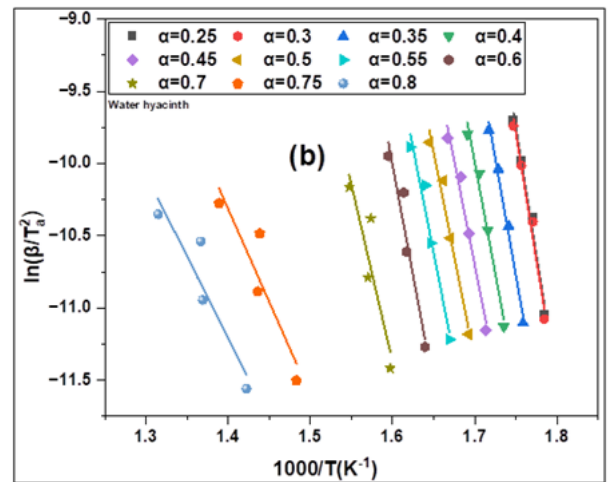
Figure 9: Kissinger plot ($\ln(\beta/T_m^2)$ vs. $1000/T$) for (a) millet cob and (b) water hyacinth.

To determine the Activation Energy (E_a), one must calculate the slope of the linear fit to this plot, denoted as $-E/R$. Multiply this slope by $-R$ to obtain the activation energy, expressed as: $E_a = -(\text{slope}) \times R$.

To determine the activation energy using the KAS method, we construct the $\ln(\beta/T_a^2)$ curve as a function of $1000/T_a$ (Figure 10). The slope of the resulting linear regression line, which is equal to $-E/R$, provides the activation energy (E_a) when multiplied by the gas constant (R). This graphical approach enables an accurate determination of activation energy, which is crucial for understanding the thermal decomposition kinetics of the biomass samples.



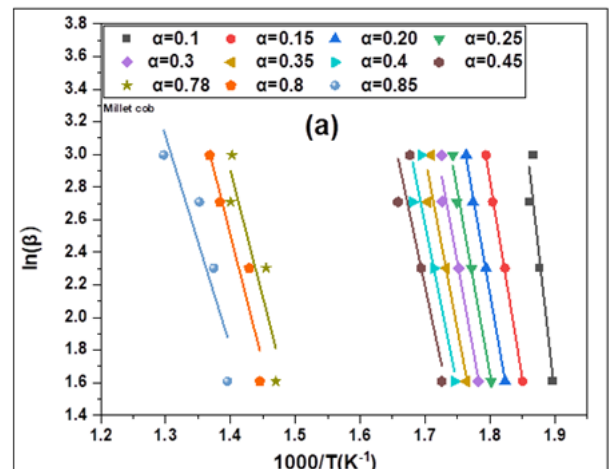
(a) Millet cob



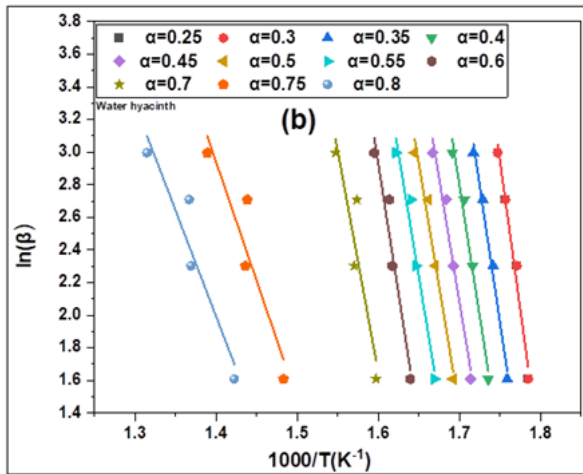
(b) Water hyacinth

Figure 10: KAS Plot ($\ln(\beta/T_a^2)$ vs. $1000/T_a$) for (a) millet cob; (b) water hyacinth

Similarly, to determine the activation energy using the FWO method, we construct the $\ln(\beta)$ curve as a function of $1000/T_a$ (Figure 11). The fitting line for this curve will have a slope of $-1.052 (E/R)$, which also facilitates the deduction of the activation energy.



(a) Millet cob



(b) Water hyacinth

Figure 11: FWO plot ($\ln(\beta)$ vs. $1000/T_\alpha$) for (a) millet cob and (b) water hyacinth

Table 2 presents the activation energy values obtained by the Kissinger, KAS and FWO methods, these values are respectively close for each sample. For millet cob sample, according to Kissinger, KAS and FWO methods we obtain an average activation energy of 181 kJ/mol, 198 kJ/mol and 208 kJ/mol respectively. For water hyacinth, Kissinger, KAS, and FWO methods yielded 179 kJ/mol, 203 kJ/mol, and 210 kJ/mol, respectively. In the literature, the error of the activation energy is 2.5 % for cotton stalk, 3.2 % for sugarcane bagasse, 1.6 % for wheat straw [49]. The same range of errors can be applied in the present studies. The authors [50] in their study of activation energy by thermogravimetric analysis in an approach to using agricultural waste fibres in bio-composites application found an average active energy value of 132.6 kJ/mol for sugarcane bagasse, 200.50 kJ/mol for coconut husks, 157.1 kJ/mol for pineapple leaf, and 136.7 kJ/mol for banana pseudo stem. Also, authors [26] in their study on the pyrolysis kinetics of apple pomace as waste biomass from thermogravimetric found a mean value of active energy from FWO and KAS methods respectively 213.0 and 201.7 kJ/mol.

To determine the pre-exponential factor A in kinetic studies, methods such as Kissinger, KAS, and FWO are commonly applied. Each method involves plotting specific temperature-related terms against the inverse temperature at different heating rates. For all the three methods, by obtaining E_a from the slope and using the intercept, the pre-exponential factor A is calculated for each method, giving insights into the frequency of successful collisions that lead to decomposition. The pre-exponential factor A is calculated using the following relation: $A = e^{\text{intercept}}$.

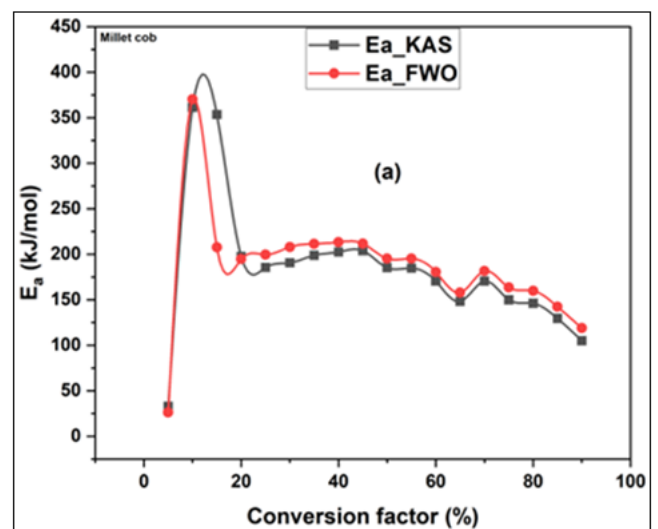
Accordingly, the activation energy values obtained by the KAS method are close to those obtained for the FWO method. These activation energies values are slightly higher than the values obtained by the Kissinger method. For a given method, the activation energy obtained from the pyrolysis of millet cob is like that obtained for the water hyacinth. This might be an indication that the decomposition kinetics of both samples are

similar. This is supported by the pre-exponential factor values which are similar for both samples for the same method of analysis. The pre-exponential factor values increase from Kissinger method (1015) to KAS method (1023) and to FWO method (1030). This indicates that the successful collisions that lead to decomposition is obtained using the FWO method. We may argue that FWO method followed by the KAS method might be the best methods to characterise the decomposition mechanism of a such complex system. This agrees with the results obtained elsewhere on the kinetic studies of the decomposition of other biomass samples based on rice straw [46]. We also notice an average regression coefficient (R^2) value close to 1, which indicates fitting lines good accuracy.

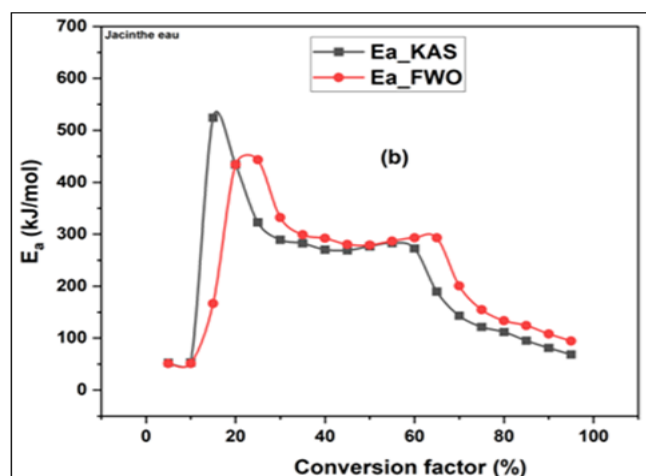
Table 2: Activation energy, pre-exponential factor and regression coefficient (R^2) by Kissinger, KAS and FWO for millet cob and water hyacinth

Sample	Method	E_a (kJ mol ⁻¹)	A (min ⁻¹)	R^2
MC	Kissinger	181	1.8×10^{15}	0.98
	KAS	198	3.7×10^{23}	0.85
	FWO	208	9.6×10^{29}	0.87
WH	Kissinger	178	6.0×10^{15}	0.97
	KAS	203	3.4×10^{23}	0.91
	FWO	210	1.0×10^{30}	0.92

Figure 12 shows the variation of activation energy (E_a) as a function of conversion for millet cob (a) and water hyacinth (b) during pyrolysis, as calculated by the KAS and FWO methods. The curves for both samples exhibit a similar pattern, although a slight stability is observed in the case of millet cob. This indicates a more consistent kinetic behavior for millet cob compared to water hyacinth during pyrolysis. Such insights are crucial for optimizing pyrolysis processes and improving the efficiency of bioenergy production from these biomass sources.



(a) Millet cob



(b) Water hyacinth

Figure 12: Variation of E_a with conversion factor for (a) millet cob and (b) water hyacinth.

The plots reveal that the activation energy strongly depends on the conversion factor, suggesting that pyrolysis for both samples is a multi-step process involving several overlapping reactions.

At the early stages of conversion ($5\% < \alpha < 15\%$), both samples exhibit a pronounced peak in activation energy, indicating the onset of volatile release as the biomass begins to thermally decompose. This initial peak corresponds to the formation of large amounts of volatile compounds, which requires significant energy. After this peak, a notable decrease and stabilization of activation energy values is observed, reflecting the breakdown of weaker molecular bonds and the progressive degradation of volatile compounds.

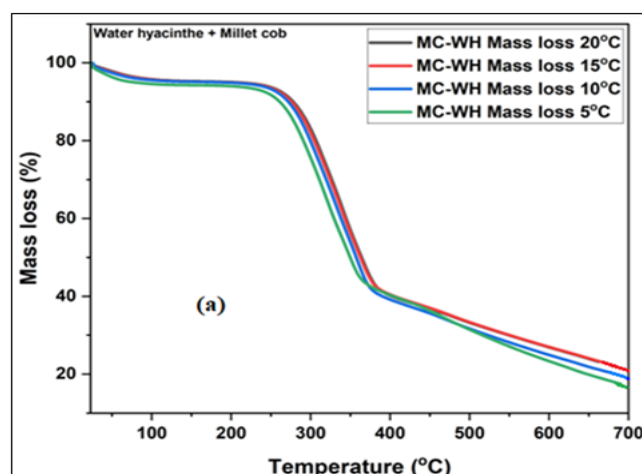
A second peak in activation energy is observed between 55 and 75 % conversion, which corresponds to the primary degradation phase of lignin, a biomass component that decomposes at higher temperatures and requires more energy to decompose. This peak reflects the increased energy demand associated with lignin's complex structure and resistance to thermal decomposition. After 75 % conversion, the activation energy gradually decreases and stabilizes, indicating the final stages of pyrolysis. In this phase, most of the volatile compounds have been released and the reaction progresses toward the formation of a stable carbonaceous residue (biochar). This stabilization suggests minimal further reaction as the remaining material undergoes char formation with a lower energy demand.

Overall, the distinct activation energy peaks and patterns reflect the complex thermal behavior of biomass pyrolysis, with different components decomposing at different stages and requiring varying energy levels for bond dissociation and mass loss.

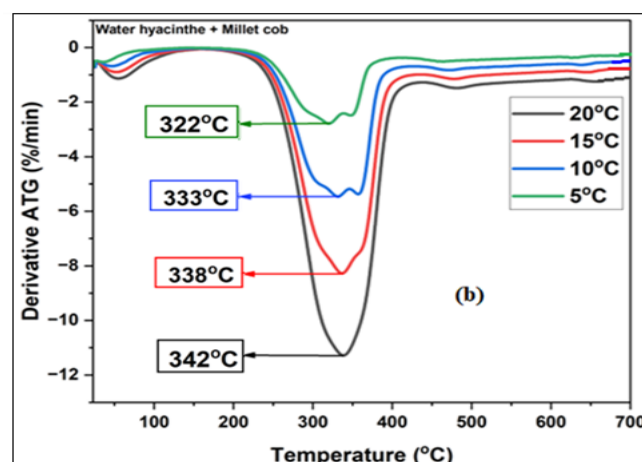
3.6. TG and kinetic analysis of the mixture of millet cob and water hyacinth

To better understand the thermal behavior and degradation kinetics of millet cob and water hyacinth, a mixture was prepared with equal parts (50 % by mass) of the two biomasses. The same tests as those carried out previously were applied to this mixture to evaluate its decomposition profile.

The figure below illustrates the curves corresponding to the mass loss (a) as well as the derivative of the mass loss (b).



(a) Mass loss

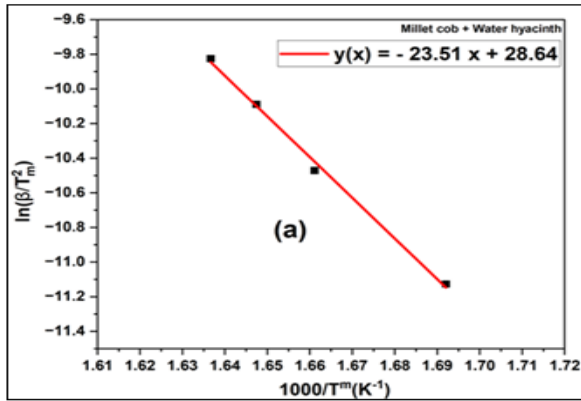


(b) Differential TG

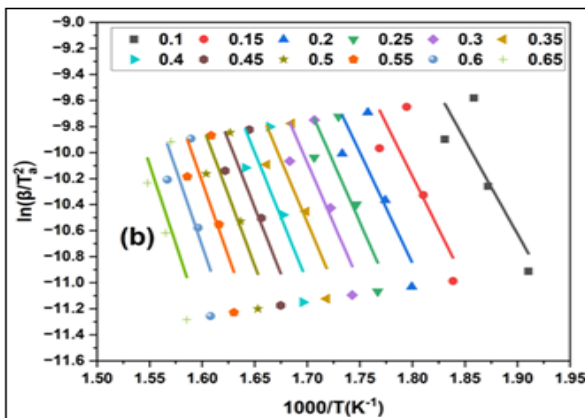
Figure 13: Curves at the heating rates of 5 °C/min, 10 °C/min, 15 °C/min and 20 °C/min for mixture of millet cob and water hyacinth

Just like millet cob and water hyacinth individually, the thermogravimetric analysis (TGA) curve of their mixture displays three distinct transitions. The first transition, corresponding to water evaporation, results in a mass loss of approximately 6 % over a temperature range from 25 °C to 192 °C. The second transition, associated with the main decomposition phase, leads to a total mass loss of 59 % between 192 °C and 410 °C. This phase is divided into two stages, as is the case for the individual materials: from 192 °C to 336 °C, with a 26 % mass loss, and from 336 °C to 438 °C, with a further 33 % loss. The third transition, linked to the final degradation stage, causes a 15 % mass loss between 438 °C and 665 °C. The maximum decomposition temperatures of the millet cob–water hyacinth mixture are slightly higher than those of the materials analyzed separately, suggesting a thermal interaction that influences their degradation behavior. Furthermore, the presence of a significant amount of residual matter (ash) indicates a transformation process that may affect the stability and final composition of the residues.

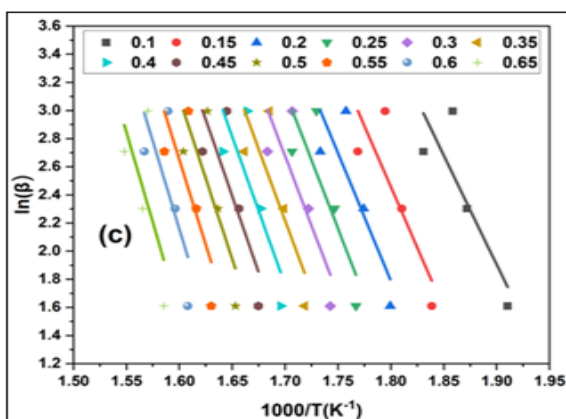
The kinetic study of the millet cob and water hyacinth mixture was conducted under the same experimental conditions as those applied to the individual samples. The fitting curves were established using the Kissinger, KAS, and FWO methods, allowing for the determination of the kinetic parameters of the mixture. The figure below shows the fitted lines obtained respectively using the Kissinger method (a), the FWO method (b), and the KAS method (c).



(a) Kissinger ($\ln(\beta/T_m^2)$ vs. $1000/T$)



(b) KAS ($\ln(\beta/T\alpha^2)$ vs. $1000/T\alpha$)



(c) FWO ($\ln(\beta)$ vs. $1000/T\alpha$)

Figure 14: Plots of $\ln(\beta)$ vs. $1000/T\alpha$ for (a) Kissinger, (b) KAS and (c) FWO models. for the mixture of millet cob–water hyacinth

The activation energy and pre-exponential factor values for the millet cob–water hyacinth mixture were determined using three kinetic methods: Kissinger, KAS, and FWO. The results obtained show a high degree of similarity across all three approaches, with slightly higher values compared to those calculated for millet cob and water hyacinth when analyzed individually. The table below presents the activation energy and pre-exponential factor values corresponding to the studied mixture.

Table 3: Activation energy, and pre-exponential factor of millet cob and water hyacinth mixture

Sample	Kissinger method			KAS method			FWO method		
	E (kJ/mol)	A (/min)	R ²	E (kJ/mol)	A (/min)	R ²	E (kJ/mol)	A (/min)	R ²
MC + WH	195	6.4×10^{16}	0.99	211	4.6×10^{32}	0.70	214	8.7×10^{35}	0.73

These findings highlight the complexity of the thermal reactions within the mixture, suggesting specific interactions between its components that influence the kinetics degradation. The blend combines two distinct biomasses: millet cob, which is rich in lignin and cellulose, and water hyacinth, which contains higher levels of hemicellulose and mineral substances. As a result, the mixture forms a more heterogeneous and intricate network, characterized by less uniform molecular interactions. This behavior indicates that the degradation of the millet cob–water hyacinth mixture does not simply reflect the additive behavior of its individual components. Instead, synergistic effects appear to alter the thermal degradation pathways, making the mixed system more resistant to pyrolysis. This may explain the slight increase observed in both the activation energy and the pre-exponential factor.

4. DISCUSSION

The results obtained from the various thermal, kinetic, and morphological analyses of water hyacinth and millet cob precursors provide insights into the mechanisms leading to the formation of amorphous or crystalline carbon structures upon activation.

The proximate analysis reveals that millet cob has a higher volatile matter content (72.1 %) and lower ash content (5.5 %) compared to water hyacinth (68.9 % volatile, 8.9 % ash). This difference suggests a more intense decomposition and an abundant release of volatile gases during pyrolysis, enabling more aggressive activation of the material. The high gas release enhances pore formation, but may also disrupt atomic order, limiting crystalline domain formation. In contrast, the higher ash content in water hyacinth, due to its aquatic nature rich in mineral salts, may act as a catalyst for structural reorganization, promoting some degree of crystallinity.

XPS analysis indicates that activated carbon from millet cob has a slightly more graphitic surface (10 % sp^2) with less surface oxidation compared to water hyacinth (5% sp^2). However, water hyacinth contains more oxygenated

functional groups and mineral elements (K, N, Cl), enhancing its chemical reactivity. These structural and chemical differences influence the conductivity, adsorption, and functionalization properties of the carbon materials during synthesis.

Thermogravimetric curves reveal that carbon formation begins at lower temperatures for millet cob ($\sim 400^\circ\text{C}$) compared to water hyacinth ($\sim 455^\circ\text{C}$), indicating a faster decomposition of organic components such as hemicellulose and cellulose in millet cob. However, this rapid decomposition often leads to a disordered atomic structure, contributing to the formation of amorphous carbon after activation. Conversely, the gradual thermal degradation of water hyacinth (volatile formation from 190°C to 455°C , followed by lignin decomposition up to 690°C) promotes slow and orderly carbonization, allowing partial graphitic domain development. Additionally, the presence of lignin, suggested by the lamellar morphology observed via SEM, supports the formation of rigid and more ordered carbon structures. Since the lignin of water hyacinth is thermally stable, its slow transformation at high temperatures facilitates carbon crystallization during activation.

The thermogravimetric curves indicate that carbon formation starts at 400°C for millet cob and 455°C for water hyacinth, with degradation stabilizing at 650°C for millet cob and 690°C for water hyacinth. Therefore, for activated carbon synthesis following chemical method, the heating rate should be selected between $5^\circ\text{C}/\text{min}$ and $10^\circ\text{C}/\text{min}$, with carbonization temperatures reaching up to 700°C . The slightly higher activation energies observed for water hyacinth (up to 210 kJ/mol using the FWO method, compared to 208 kJ/mol for millet cob) indicate greater thermal resistance, which could also contribute to the formation of more ordered carbon structures under prolonged activation conditions.

The heterogeneous network formed by blending millet cob and water hyacinth requires greater energy input to initiate the thermal degradation of the combined system, resulting in a higher activation energy. During heating, the intermediate products generated from the decomposition of water hyacinth may interact with the more stable carbon chains of millet cob. These interactions can delay certain reactions or induce transient stabilization effects, thereby requiring additional energy to sustain decomposition. Furthermore, the mixture exhibits a wider variety of chemical bonds, which increases the number of possible reaction pathways. This leads to a greater number of potential effective collisions, ultimately contributing to a higher pre-exponential factor.

SEM images further support these findings. The millet cob precursor exhibits regularly shaped particles, sometimes hexagonal, with a compact structure. This compactness may limit structural rearrangements during carbonization, reinforcing the formation of amorphous carbon, despite the development of porosity. In contrast, water hyacinth presents a lamellar morphology, with sheet-like structures and flat surfaces, characteristic of lignin-rich plant fibers. This spatial arrangement facilitates carbon sheet stacking during pyrolysis and activation, aiding in the formation of ordered domains like graphite. EDS analysis further confirms these distinctions. Although both materials have high carbon content, the presence of minerals in water hyacinth (Na, Ca, K) may act as a catalyst, facilitating the formation of crystalline structures at high temperatures.

Overall, findings from thermal, morphological, chemical, and spectroscopic analyses clearly demonstrate that the structural properties of synthesized activated carbon depend significantly on the nature of the plant precursor. Activated carbon derived from water hyacinth is likely to exhibit partially crystalline characteristics, driven by slow thermal degradation, a lamellar morphology conducive to ordered stacking, and surface minerals acting as graphitization catalysts. Conversely, activated carbon from millet cob is expected to display a predominantly amorphous structure, resulting from rapid carbonization, a less functionalized surface, and a compact morphology unfavorable to crystalline organization.

5. CONCLUSIONS

This study investigated millet cob and water hyacinth as potential precursors for activated carbon for utilization as lithium-ion battery electrodes. Comprehensive characterization through thermogravimetric, pyrolysis, decomposition kinetics, SEM, EDS, and XPS analyses revealed distinct properties for each biomass.

Millet cob demonstrated high volatile matter and fixed carbon content, along with low moisture and ash levels, suggesting favorable activated carbon yield and porosity developed with reduced pre-drying energy requirements. XPS analysis indicated a carbon-rich, slightly graphitic ($\sim 10\%$ sp^2) surface with limited functionalization. In contrast, water hyacinth exhibited a more functionalized and oxidized surface, despite its low sp^2 carbon content ($\sim 5\%$), enhancing its surface adsorption and electrochemical doping potential. Chemical activation with KOH at 700°C could further improve water hyacinth's graphitization due to its inherent mineral content, acting as a catalyst for carbon structural ordering. SEM revealed key morphological differences: millet cob displayed a compact, granular structure, while water hyacinth exhibited a fibrous, lamellar morphology, influencing porosity and graphitic structure formation upon activation.

Thermogravimetric analysis of a millet cob–water hyacinth mixture showed altered thermal behavior compared to individual biomasses, with higher decomposition temperatures, broader mass loss profiles, and increased residual ash. These findings suggest synergistic interactions that enhance thermal stability and modify degradation kinetics, making the mixture more resistant to pyrolysis. The higher activation energy and pre-exponential factor indicate complex reaction kinetics, highlighting that the mixture behaves as an integrated system rather than a simple combination of individual components.

Activated carbon from millet cob is expected to be predominantly amorphous due to rapid decomposition and compact morphology, whereas water hyacinth-derived carbon may develop a partially crystalline structure, aided by slower carbonization, sheet-like morphology promoting stacking, and catalytic mineral content. These insights provide valuable guidance for optimizing biomass selection and processing conditions for high-performance electrode materials.

The kinetic studies also showed the consistency of the Kissinger, KAS and FWO methods whose activation energies are respectively 181 kJ/mol , 198 kJ/mol and 208 kJ/mol for millet cob and 189 kJ/mol , 203 kJ/mol and 210 kJ/mol for water hyacinth.; and 195 kJ/mole for the mixture of millet cob and water hyacinth.

The high value of the preexponential factor of the pyrolysis of the mixture of Millet cob-water hyacinth compare to those of millet cob and water hyacinth, respectively, is an indication of the resistance of the mixture to thermal decomposition.

All thermogravimetric results and the carbon composition of millet cob and water hyacinth show that these samples have a good potential for the synthesis of active carbon used as active materials support for Li-ion batteries applications

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