



Feasibility Assessment of Coconut Shell for Biographite Production and Thermo-Catalytic Graphitization Reactor Design

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Abstract:

Recently the safe disposal of the biomass is gaining more attention due to the increase air pollution due to waste burning. In this paper the characterisation studies of coconut shell were done to assess the feasibility of the- agriculture waste to be utilize for the biographiteproduction and design of the thermo catalytic graphitization unit.in this study the basic characterisation of biomass such as proximate and ultimate analysis was done. The thermogravimetric analysis was done to study the degradation temperature of the coconut shell with different heating rate viz. 10, 20, 30,40 °C/min. This study shows that the good quality biographite can be prepared by using the low to medium temperature pyrolysis technique from the coconut shell. The maximum degradation temperature for the coconut shell was found to be around 450 °C.

Key Words: Coconut shell, Characterisation, Graphitization, Biographite, TGA.

1. Introduction

India is the world's largest coconut producer, accounting for 31.45% of the world's total production in 2021-22. In 2023, India produced an estimated 13.5 million metric tons of

coconuts. This is an increase from the previous fiscal year. The top coconut-producing states in India are: Karnataka, Tamil Nadu, Andhra Pradesh, Kerala. These states account for more than 90% of India's total coconut production. Karnataka produces 4,210.87 metric tonnes annually, which is 30.83% of the country's total coconut output.(Aliyev et al., 2019)

The burning of coconut shells not only contributes to the release of greenhouse gases but also emits pollutants and particulate matter into the air, thereby posing environmental and health risks. To address this challenge, the production of biographite from coconut shells offers a potential solution.(Obeng et al., 2020)

This study is done to assess the feasibility of coconut shells for biographite production and design of thermo-catalytic biomass graphitization reactor. In this study the physiochemical characterisation of the coconut shell is done, also the analysis of the coconut shells done with the Thermogravimetric analysis, to study the suitability of the coconut shells for the biographite production.



Fig. 1 Coconut shell

2. Materials and Method

2.1. Characterization of Coconut shell

The physical parameters, proximal analysis, ultimate analysis, calorific value, and thermal gravimetric analysis of the coconut shell were evaluated using the conventional protocols outlined below.

2.2. Physical Properties

Knowledge of physical properties of biomass, such as bulk density, true density, and porosity, is critical for proper design of reactor systems, production and operation.

2.3. Bulk density

The bulk density of the coconut shell was calculated using ASTM E-873-06. The following formula was used to calculate the bulk density (Nath et al., 2023).

$$\text{Bulk density (kg m}^{-3}\text{)} = \frac{(W_2 - W_1)}{V} \quad (3.1)$$

where,

W1 = Empty mass of the container, kg

W2 = Mass of the container along with sample, kg

V = Volume of the container, m³

Proximate analysis

The approximate composition of the selected feedstock, such as moisture, volatile matter, ash content, and fixed carbon content, was estimated using an American Society for Testing and Materials (ASTM) protocol, and the procedure for each analysis is as follows. (Volborth, 1979).

2.4. Moisture Content

A hot air oven was used to determine the moisture content of the sample (ASTM, E-871-82). 5 g of powdered material (ground in a grinding machine) was placed in a petri dish and baked at 105°C until the constant weight was achieved. Using the formula below, the moisture content was estimated by measuring the initial weight (WI) and end weight of the sample (WF). (Bhavsar et al., 2018).

$$\text{Moisture content, \%} = \frac{(W_I - W_F)}{W_I} \quad (3.4)$$

Where,

WI = Initial mass of the sample, g

WF = Final mass of the sample, g

2.5. Volatile Matter

To determine the volatile content, a known weight of dried sample was placed in a closed crucible and placed into the muffle furnace for six minutes at 650°C and another six minutes at 750°C (ASTM D-3175-07). The percentage of volatile matter in the material is calculated by dividing the volatile escaped by the sample weight. The formula is as follows:

$$\text{Volatile matter, \%} = \frac{\text{Loss in mass of the sample, g}}{\text{Mass of moisture free sample, g}} \times 100 \quad (3.5)$$

2.6. Ash Content

The ash content of the feedstock represents the non-organic mineral component. The ash content of the selected biomass was determined (ASTM D-3174-04) by placing a specified amount of dried sample in an open crucible and heating it to 750°C in a muffle furnace until it reached a constant weight. The fraction of ash content of the tested material was calculated as the ratio of the remaining weight of materials in the crucible to the sample taken. (Airton et al., n.d.).

$$\text{Ash content, \%} = \frac{\text{Mass of ash formed, g}}{\text{Mass of dried sample, g}} \times 100 \quad (3.6)$$

2.7. Fixed Carbon

The fixed carbon content of the samples was estimated by subtracting the total of the ash content (percentage) and volatile matter (percentage) from 100. The residue left after eliminating the volatile stuff and ash from the material is the fixed carbon. (Bhavsar et al., 2018).

$$\text{Fixed carbon, \%} = 100 - [(\text{volatile matter (\%)} + \text{ash content (\%)})] \quad (3.7)$$

2.8. Thermo-gravimetric analysis

Thermo gravimetric analysis (TGA) of samples is performed using a thermo gravimetric analyser (TGA/DTG-EXSTAR/6300) to determine variations in the mass of feedstock in response to temperature changes. The accuracy of the three measures, mass, temperature, and temperature change, is critical to this investigation. A temperature vs.

derivative of mass loss curve can be used to determine the point at which mass loss is most visible. Plotting mass (percentage) versus temperature allowed for analysis as the temperature gradually increased. (Sumaila et al., 2022)

Table 1 Technical specifications of TGA

Temperature Range	25° C to 1000 °C
Scan Range	Variable 0.1 °C / min to 100 °C / min
Sample Size	Up to 1500 mg
Temperature Accuracy	1 ° C
Micro balance Sensitivity	0.1 mg
Selectable Atmosphere	Nitrogen
Gas Flow rate Control	Through built in mass flow controller and software

At the selected feedstocks, thermogravimetric analysis was performed at heating rates of 10, 20, 30, 40°C min⁻¹ for degradation temperatures up to 1000°C. As the purge gas, nitrogen was employed.

3. Result and Discussion

This section discusses the results of physiochemical characterisation and thermogravimetric analysis of the coconut shell.

3.1. Physiochemical properties of coconut shell

The physiochemical characterisation of the coconut shell was carried out in order to determine parameters such as bulk density, moisture content, volatile matter, ash content, fixed carbon, calorific value. The results of physical characterization of coconut shell are summarised in Table 1.

From the results of this study and the references, the bulk density of coconut shell is varying from 435–650 kg/m³. The moisture content varies from 4.20-9.30 percent. The volatile matter ranges from 47 to 70 percent, the fixed carbon in the coconut shell varied from 17-42 percent.

Table 2. Physical and Biochemical characterisation of coconut shell

Parameter	This Study	(Haruna &Lakshmipathy, 2014)	(Kabir Ahmad et al., 2022)	(Irawan et al., 2017)
Bulk density (kg/m ³)	435	650		
Moisture Content (%)	9.30	4.20	5.56	7.40
Volatile Matter (%)	58	60	70.82	47.27
Ash Content (%)	1.33	0.63	1.80	0.73
Fixed Carbon (%)	40.67	42.30	21.80	17.7

3.2.TGA analysis of coconut shell

The thermo-gravimetric analysis of the coconut shell is done to analyse the degradation pattern of the coconut shell, to design the thermo catalytic graphitization reactor and to calculate its parameters such as heating rate, pyrolysis temperature and retention time it is very important to analyse the TGA of the coconut shell.

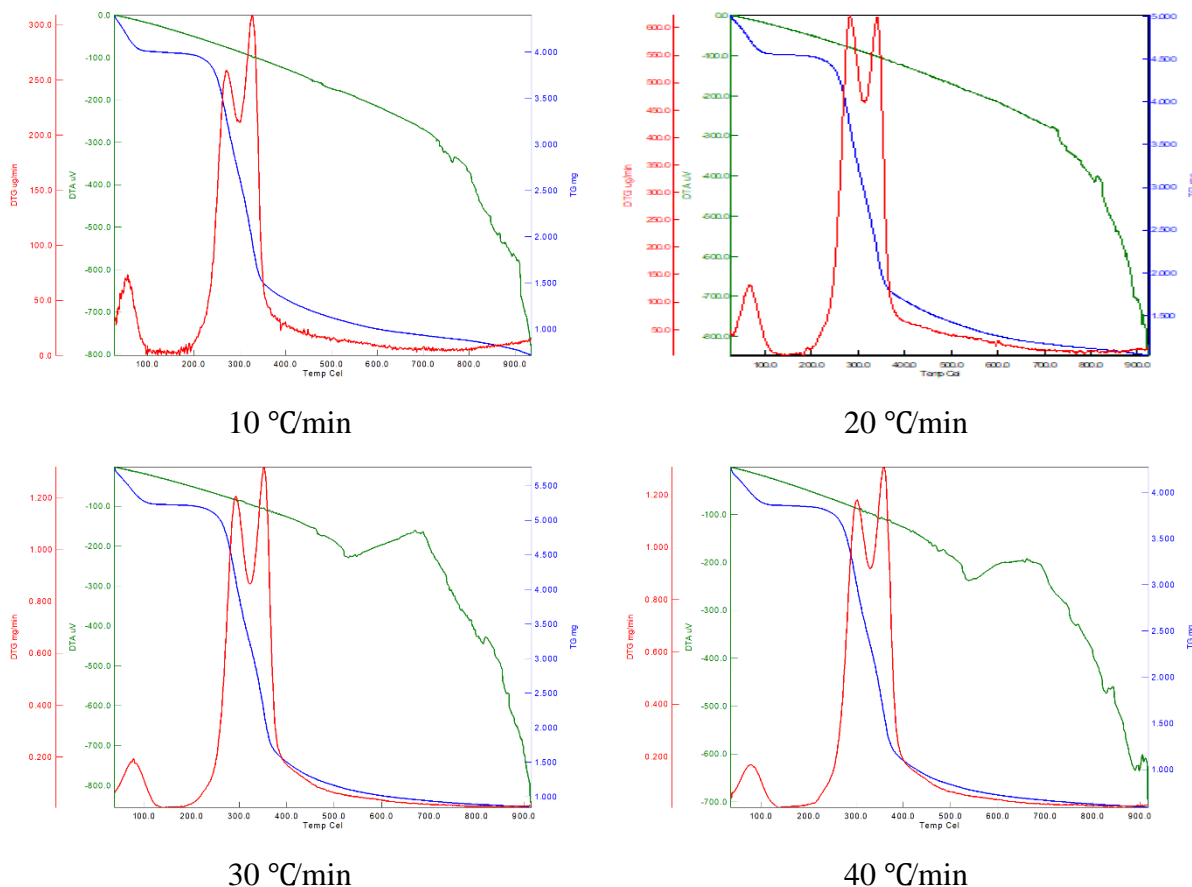


Fig. 2 TGA of Coconut shell at 10, 20, 30,40 °C/min

Figure 2 depicts the TGA of the coconut shell at various heating rates of 10, 20, 30, and 40 °C/min. The graph depicts the degradation temperatures of the various biomass components as well as the thermal degradation behaviour of the biomass.

The first graph of TGA at 10 °C/min reveals that 4.409 milligramme of coconut shell sample weight was maintained for TGA. The initial weight loss is detected up to 150 °C, implying moisture evaporation from the material. At 59.5°C, the maximum rate of weight loss for moisture removal was 147 g/min. The steady weight loss continues as the temperature rises until it achieves the activation energy required to begin active pyrolysis, which lasted from 195 to 600 °C. At 350 °C, the maximum rate of weight loss was reported during the pyrolysis stage, which was 578 g/min. The rapid weight loss was continued until the temperature reached 500°C and the rate of weight loss stabilised. It denotes the end of the active pyrolysis stage and the start of the passive pyrolysis stage. The passive pyrolysis stage is continued until the rate of weight loss stabilises at 650 °C.

TGA at 20 °C/min, a coconut shell sample weight of 5.018 milligramme is used for TGA. The initial weight loss is recorded up to 159 °C, implying moisture evaporation from the material. At 99.09°C, the maximum rate of weight loss for moisture removal was 160 g/min. Further increasing the temperature results in steady weight loss until it achieves the activation energy to begin active pyrolysis, which lasted from 205 to 600 °C. At 367 °C, the maximum rate of weight loss was reported during the pyrolysis stage, which was 697 g/min. The rapid weight loss was maintained until the temperature reached 424°C and the rate of weight loss stabilised. It denotes the end of the active pyrolysis stage and the start of the passive pyrolysis stage. The passive pyrolysis step is continued until the weight loss rate reaches a constant, which occurs at 610 °C.

TGA graph at 30 °C/min reveals that a coconut shell sample weight of 5.777 milligramme was used for TGA. The initial weight loss is detected up to 170 °C, implying moisture evaporation from the material. At 94 °C, the maximum rate of weight loss for moisture removal was 186 g/min. The steady weight loss continues as the temperature rises until it achieves the activation energy required to begin active pyrolysis, which lasted from 190 to 600 °C. At 363 °C, the maximum rate of weight loss was reported during the pyrolysis stage, which was 1249.29 g/min. The rapid weight loss was maintained until the temperature

reached 400°C and the rate of weight loss stabilised. It denotes the end of the active pyrolysis stage and the start of the passive pyrolysis stage. The passive pyrolysis stage is maintained until the rate of weight loss is constant, which occurs at 580°C.

TGA at 40 °C/min, 4.276 milligramme of coconut shell sample weight was used for TGA. The initial weight loss is recorded up to 189.55 °C, implying moisture evaporation from the sample. At 89.84 °C, the maximum rate of weight loss for moisture removal was 269.6 g/min. Further increases in temperature result in steady weight loss until it achieves the activation energy to begin active pyrolysis, which lasted from 190 to 500 °C. At 326 °C, the maximum rate of weight loss was reported during the pyrolysis stage, which was 2477.221 g/min. The rapid weight loss was maintained until the temperature reached 400°C and the rate of weight loss stabilised. It denotes the end of the active pyrolysis stage and the start of the passive pyrolysis stage. The passive pyrolysis stage is continued until the rate of weight loss stabilises at 550 °C.

The graph also indicates the commencement of the thermal degradation of the coconut shell by moisture and volatile removal maximum up to 190°C, followed by the thermal degradation of the hemicellulose maximum up to 300°C. The weight loss between 190 and 400°C indicates cellulose degradation in the coconut shell. The lignin in the coconut shell was degraded up to 600 °C with cellulose co-degradation.

According to the TGA investigation, the maximum pyrolysis temperature for biographite formation from coconut shell at heating rates of 10, 20, 30, 40 °C/min would not exceed 600°C.

Conclusion:

The coconut shell biomass is the abundant biomass available in India. Its safe disposal without burning in the field is a concern to be addressed. The biomass material is major source of Carbone which was captured from atmosphere and stored during the process of photosynthesis.

This study confirms that utilising the low to medium temperature graphitization process, can produce high grade biographite from coconut shells. The coconut shell contains high fixed carbon and less ash content which is feasible for high grade graphite production. The coconut shell's maximal deterioration temperature was discovered to be about 600 °C.

The existence of hemicellulose, cellulose, and lignin in the coconut shell, which can be the primary precursor of biographite.

References:

- Airton, J., Carneiro-Junior, M., Felix De Oliveira, G., Alves, C. T., Angel, M., Duro, I., & Torres, E. A. (n.d.). *Termogravimetric Characterization of Biomass Impregnated with Biodegradable Ionic Liquids*. <https://doi.org/10.1590/2179-8087.043418>
- Aliyev, E., Filiz, V., Khan, M. M., Lee, Y. J., Abetz, C., & Abetz, V. (2019). Structural Characterization of Graphene Oxide: Surface Functional Groups and Fractionated Oxidative Debris. *Nanomaterials*, 9(8). <https://doi.org/10.3390/NANO9081180>
- Bhavsar, P. A., Jagadale, M. H., Khandetod, Y. P., & Mohod, A. G. (2018). Proximate Analysis of Selected NonWoody Biomass. *Int.J.Curr.Microbiol.App.Sci*, 7(9), 2846–2849. <https://doi.org/10.20546/ijcmas.2018.709.353>
- Haruna, S., & Lakshmipathy, M. (2014). *Licensed Under Creative Commons Attribution CC BY Ductility Behaviour of Bamboo Reinforced Coconut Shell Concrete Beams* (Vol. 3). <https://www.researchgate.net/publication/315155255>
- Irawan, A., Latifah Upe, S., & MeityDwi, I. P. (2017). Effect of torrefaction process on the coconut shell energy content for solid fuel. *AIP Conference Proceedings*, 1826. <https://doi.org/10.1063/1.4979226>
- Kabir Ahmad, R., Anwar Sulaiman, S., Yusup, S., Sham Dol, S., Inayat, M., & Aminu Umar, H. (2022). Exploring the potential of coconut shell biomass for charcoal production. *Ain Shams Engineering Journal*, 13(1), 101499. <https://doi.org/10.1016/J.ASEJ.2021.05.013>
- Nath, B., Chen, G., Bowtell, L., & Mahmood, R. A. (2023). Assessment of densified fuel quality parameters: A case study for wheat straw pellet. *Journal of Bioresources and Bioproducts*, 8(1), 45–58. <https://doi.org/10.1016/J.JOBAB.2022.10.001>
- Obeng, G. Y., Amoah, D. Y., Opoku, R., Sekyere, C. K. K., Adjei, E. A., & Mensah, E. (2020). Coconut Wastes as Bioresource for Sustainable Energy: Quantifying Wastes, Calorific Values and Emissions in Ghana. *Energies 2020*, Vol. 13, Page 2178, 13(9), 2178. <https://doi.org/10.3390/EN13092178>
- Sumaila, A., Sumaila, A. O., Usman, A. O., Abdullahi, A. S., & Abdullahi, Z. (2022). Thermal Degradation and Particle Size Distribution Studies of Activated Carbon obtained from Coconut Shells. *J. Mater. Environ. Sci*, 2022(7), 7. <http://www.jmaterenvirosci.com>
- Volborth, A. (1979). Problems of Oxygen Stoichiometry in Analyses of Coal and Related Materials. *Analytical Methods for Coal and Coal Products*, 543–583. <https://doi.org/10.1016/B978-0-12-399903-0.50024-6>