Torrefaction: Transforming Sugarcane Biomass into High-Quality Carbon for Supercapacitor

Shaikh Shaista Sharmuddin[1], Nainika Rajesh Dedhia[2], Rounak R. Atram[3]
[1,2,3] *Department of Physics, M. M. College of Arts, N.M. Institute of Science and H. R. J College of Commerce, Bhavan's College (Autonomous), Andheri West, Mumbai (M.S), India, 400058*

***Abstract*—India is one of the largest sugarcane cultivators, with an estimated production of 419.25 million tonnes. With more than 500 sugar mills, India generates 91 million tons of sugarcane bagasse (SB) annually. Therefore, sugarcane waste can be recycled as valuable products. It is rich in organic carbon, making it a potential raw material for carbon production. Biomass-derived carbon has a wide range of applications in energy storage devices. In our research, sugarcane bagasse was procured from vendors, cleaned, and dried to remove any moisture. At higher temperatures, the material was torrefied in a controlled oxygen environment, resulting in the formation of carbon in the form of Sugarcane Bagasse Carbon (SBC). The torrefied carbon was further subjected to polymerization processes to form a binary composite of Sugarcane Bagasse Carbon/PANI (SBC/PANI), which increased its specific capacitance and energy density, making it more suitable for wide applications such as supercapacitors, photodegradation, metal adsorbents, and solar cells. The morphology of the composite material was studied by SEM. Electrochemical results revealed SBC/PANI achieved highest specific capacitance of 188 Fg^{-1} at current density of 0.5 Ag^{-1} resulting in higher energy density of 7.89 Wh Kg^{-1} at power density of 69 W kg^{-1}.**

***Index Terms*—Biomass, Carbonization, Lignocellulosic, Polymerization, Sugarcane, Torrefaction.**

I. INTRODUCTION

India is the largest producer of sugarcane in Asia, and its sugar sector ranks second among all agro-based industries [1]. In addition, sugarcane (Saccharum officinarum) is grown in large quantities in different tropical nations. Sugarcane bagasse (SB) is produced by extracting water from sugarcane stems [2]. The sugarcane stalk can be divided into two portions: the outside rind and the inner pith. Longer and finer bundles of fibers were found in the outer part of the rind, whereas shorter fibers were found in the inner part. Both types of fibers are present in bagasse [3]. Bagasse from sugarcane has traditionally been used as a raw material for fertilizers, animal feed, pulp, and paper particleboard. However, the economic value of this is minimal and of low economic significance. Biomass-derived carbon from sugarcane is a key material for energy storage devices such as batteries, supercapacitors, and fuel cells [4]. Supercapacitors are energy storage devices that can be classified into two types, EDLC and pseudocapacitors, depending on their charge storage mechanism. EDLC have carbon materials as the main electrode materials, whereas pseudocapacitors have metal oxides and conducting polymers. [5]

In this work, we have focused on the use of Sugarcane Bagasse Carbon (SBC) as an electrode material for supercapacitors and a composite material of SBC with the conducting polymer PANI to derive the synergistic electrochemical results of both materials.

II. METHODOLOGY

2.1 Preparation of SBC by Torrefaction

Sugarcane bagasse (SB) was procured from local vendors, cleaned, and dried in a hot air oven at 120 °C for 12 h to remove moisture. The dried SB was then chopped into small pieces (> 4–5 cm) and ground into a fine powder in a mixer. Crushed fine powder of biomass was then filled into crucibles and covered with seven layers of aluminium foil to reduce contact with oxygen. Oxidative stabilization was performed at 220°C for 8 h in a muffle furnace under controlled oxygen conditions [6]. During this process, the complex organic molecules disintegrate into simpler molecules that are rich in carbon. Therefore, the carbon concentration of biomass increases while its

oxygen content decreases. This carbon was again heated in a muffle furnace at a higher temperature of 400°C. Hence, the material was torrefied in a controlled oxygen environment, resulting in the formation of carbon[7]. The torrefied carbon was further grinded by mortar and pestle for 4-5 hours to obtain ultra-light weight carbon particles. The synthesis process of SBC is shown in Fig. 1 and Table-1 represents the temperatures at which different chemical components of sugarcane bagasse decompose [2].

Chemical components	Temperature of decomposition in °C
Hemicellulose	220°C-315°C
Cellulose	315°C-400°C
Lignin	160°C-900°C

Table 1: Temperature of decomposition of the chemical components of sugarcane bagasse (°C).

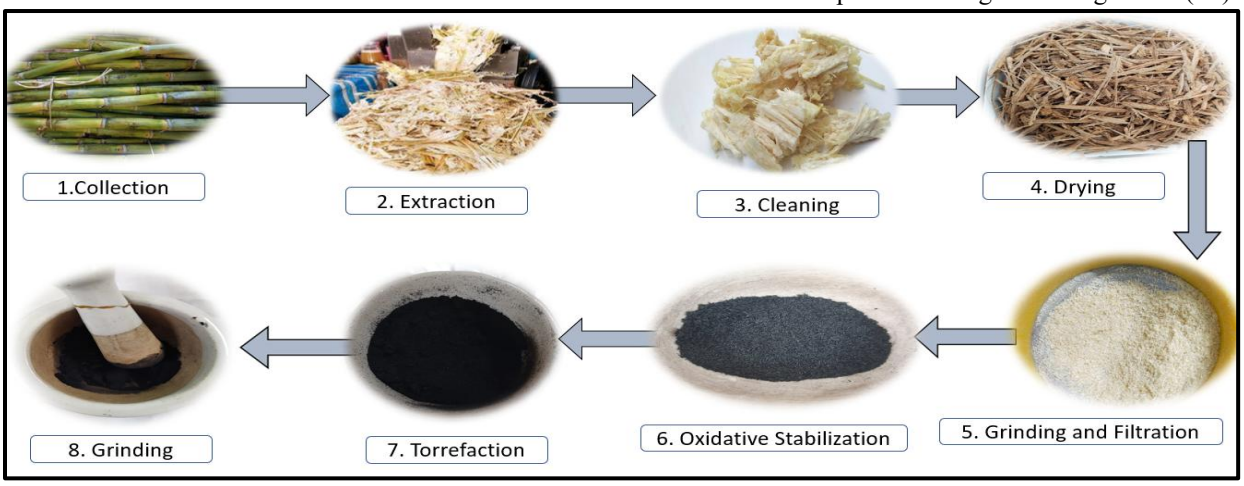

Fig 1: Torrefaction process

2.2 Preparation of SBC/PANI binary composite: -

To prepare the SBC/PANI binary composites, two different solutions were prepared and mixed. In the first solution 1M HCL and 0.25M APS were added to 25 ml distilled water and magnetically stirred for 30 min. In the second solution 1M HCL and 0.25 M aniline were added to 25 ml distilled water and magnetically stirred for 30 min. SBC (50 mg) was then added to the second solution and ultrasonicated for 30 min. The first solution was filled in a burette and added dropwise to the second solution with continuous stirring at low temperature. The mixture was further stirred for 6 h at low temperature (>4 °C) to complete the polymerization process [8]. The mixture was then kept at rest in a refrigerator for 12 h and further filtered by vacuum filtration. The mixture was filtered, washed, and dried in a vacuum oven at 80 °C for 12 h, resulting in an SBC/PANI binary composite [9]. The detailed polymerization process is illustrated in Fig. 2.

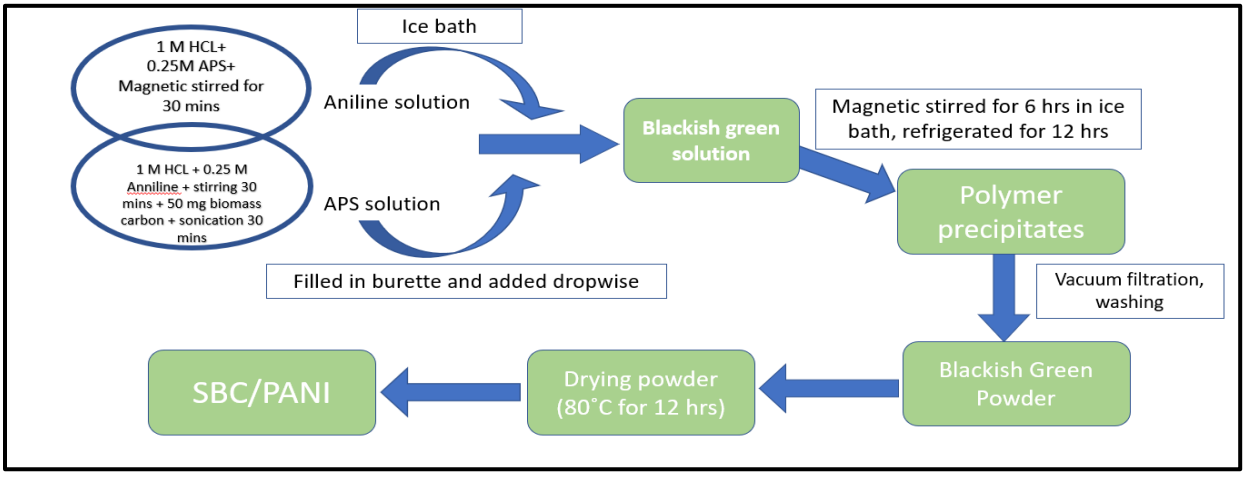

Fig 2: Polymerization process for the synthesis of SBC/PANI.

III. RESULTS AND DISCUSSIONS

3.1 Mass Yield

The first characterization of the biomass observed in the laboratory was the loss in mass using the yield factor. The mass Yield can be defined as the temperature rise during the torrefaction process, and the mass is lost. The cellulose content loses the most mass, and the lignin content loses the least mass [2]. Table-2 gives the details of the mass yield for various masses observed for the same process.

$$\% \text{ Yield of SBC} = \left[\frac{\text{Mass of SB (grams)}}{\text{Mass of SBC (grams)}}\right] \times 100\ \% \quad (1)$$

$$\% \text{ Loss of SBC} = 100 - \left[\frac{\text{Mass of SB (grams)}}{\text{Mass of SBC (grams)}}\right] \times 100\% \quad (2)$$

Mass SB (grams)	Mass of SBC (grams)	% Yield	% Loss
5.002	1.359	27.18	72.82
5.006	1.498	29.94	70.06
5.012	1.447	28.88	71.12
5.023	1.349	26.87	73.13
5.028	1.464	29.12	70.88
5.065	1.416	27.96	72.04

Table 2: % yield of SBC

Average yield % = 28.28% (3)

Average lost % = 71.675% (4)

3.2 Scanning Electron Microscope (SEM)

The morphology of the synthesized SBC and SBC/PANI was determined using SEM, which proved to be of great importance in the study of the structure and versatility of biomass. An SEM image of the SBC is shown in Fig. 3 (a), which reveals the fiber surface [10]. The torrefied SBC exhibited a rigid fibrous and very compact morphology. After torrefaction, SBC provide tremendous accessibility for hydrolytic enzymes. This provides for the hydrolysis of lignocellulosic biomass. Fig 3 (b) shows the SEM image of SBC/PANI, which shows the growth of PANI fibers with a wide interconnected network structure all over the surface of the SBC. This network provides wide accessibility for the flow of ions, resulting in a higher conductivity and lower resistance. This unique structure of SBC/PANI allowed the composite to achieve superior electrochemical results.

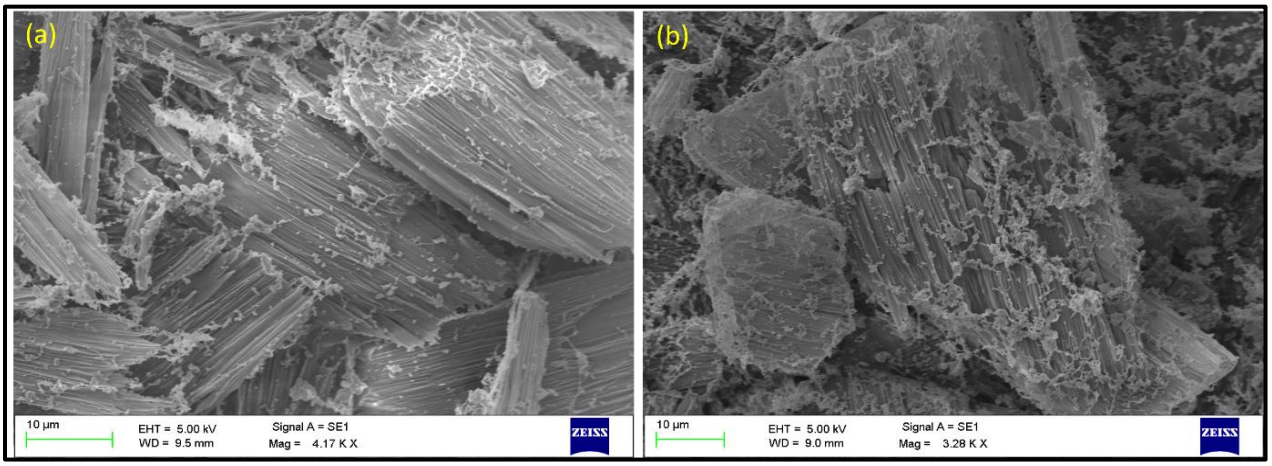

Fig. 3 SEM images of (a) SBC and (b) SBC/PANI

3.3 Electrochemical Performance

The electrochemical performance of the composite material was studied using cyclic voltammetry (CV) and galvanostatic charge discharge in a 1M H_2SO_4 electrolyte with platinum as the counter electrode and Ag/AgCl as the reference electrode. Fig. 4 (a) shows the CV curve for SBC at various scan rates ranging from 5 to 75 mV/s. The CV curve revealed the perfect EDLC behavior of the SBC. The closed-loop quasi-rectangular shape of the SBC is clearly visible in the CV curve. This revealed the perfectly reversible nature

of the sample. This also results in higher cycling stability

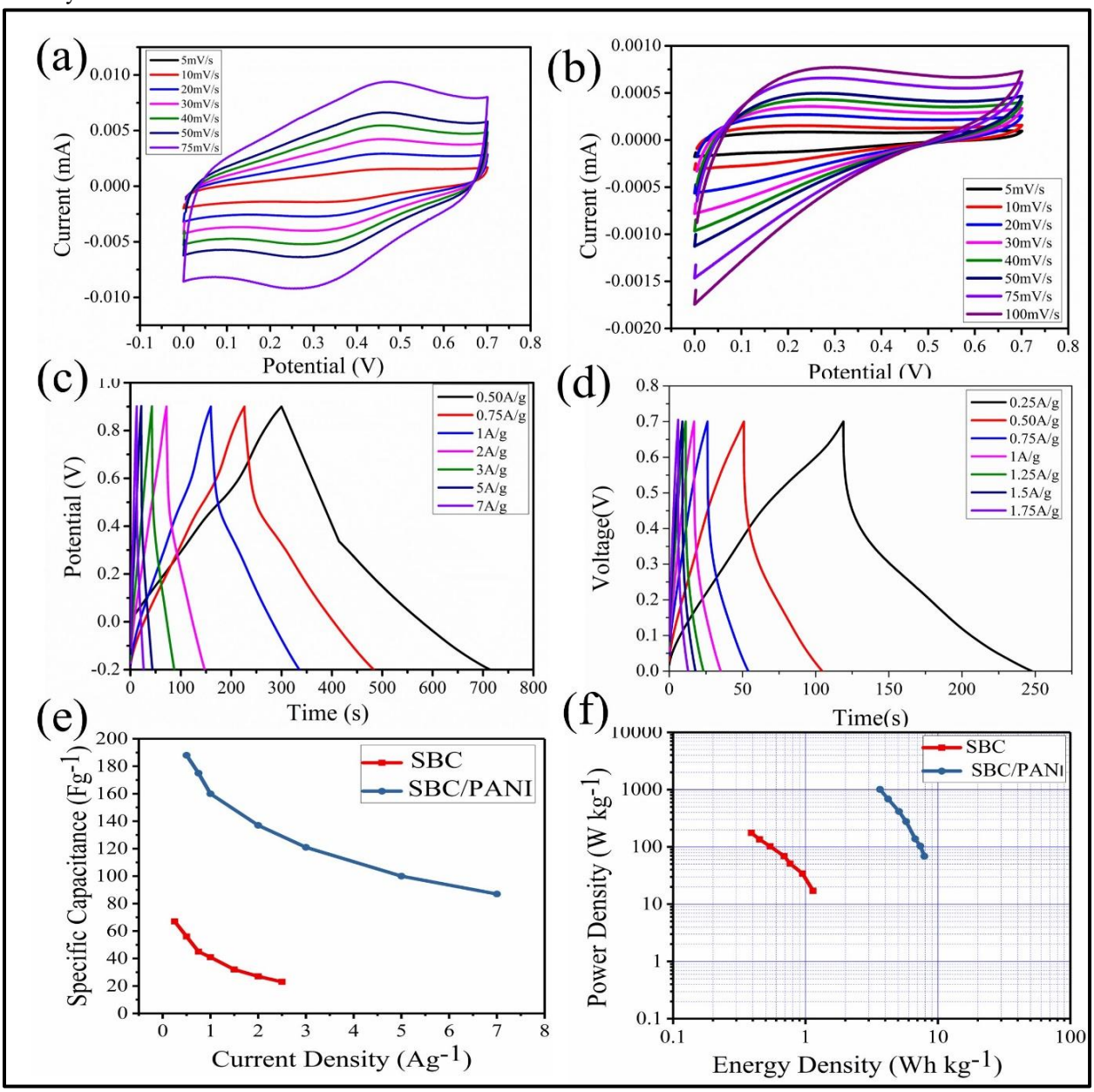

Fig. 4 Cyclic Voltammetry of (a) SBC, (b) SBC/PANI; and Galvanostatic Charge Discharge (c) SBC, (d) SBC/PANI; (e) Capacitive curve of SBC and SBC/PANI; (f) Ragone plot of SBC and SBC/PANI

of the sample. The CV curve remained unchanged for higher scan rates, indicating the stability of the SBC. Fig. 4 (b) shows the CV curve for SBC/PANI at scan rates ranging from 5 to 100 mV/s. The CV curve reveals the effect of PANI on the SBC with a large area under the curve during the sweep at different scan rates. PANI allows for a higher exchange of ions between the electrode and the electrolyte. Hence, SBC/PANI had a higher conductivity than SBC and achieved a higher current density during CV. The CV curves remained unchanged with increasing scan rate, which suggests the stability of the material in the electrolyte. One redox peak was visible at a low scan rate of 5mV/s at 0.2 V and 0.3 V.

The electrochemical properties of SBC and SBC/PANI were studied using galvanostatic charge–

discharge, as shown in Fig. 4 (c) and (d). Fig. 4 (c) shows the GCD curve for SBC with a perfectly triangular shape related to the EDLC-type material for the SBC composite. The specific capacitance of the SBC was calculated from the GCD curve, which revealed the highest specific capacitance of 67 Fg^{-1} at a lower current density of 0.25 Ag^{-1}. The GCD curve for SBC/PANI is shown in Fig. 4 (d), which reveals the highest specific capacitance of 189 Fg^{-1} at a lower current density 0.5 Ag^{-1}. IR drop was not observed in either of the GCD curves, which indicates that no degradation of the material occurred during GCD testing.

The capacitive curve in Fig. 4 (e) shows the relationship between the specific capacitance and current density. SBC exhibited specific capacitances of 67, 56, 45, 41, 32, 27 and 23 Fg^{-1} at current densities of 0.25, 0.5, 0.75, 1, 1.5, 2 and 2.5 Ag^{-1} respectively. SBC/PANI showed specific capacitances of 189, 175, 160, 137, 121, 100, and 87 at current densities of 0.5, 0.75, 1, 2, 3, 5, 7 Ag^{-1} respectively. A gradual decrease in the specific capacitance was observed in both composite materials with increasing current density.
The relationship between the energy density and power density is given with the help of a Ragone plot. Fig. 4 (f) shows Ragone plots for SBC and SBC/PANI. Here it can be seen that SBC/PANI has higher energy densities of 7.89, 7.35, 6.72 5.75 5.08, 4.20 and 3.65 Wh kg^{-1} at power density of 68.60, 103.35, 138.25, 276.00, 475.63, 687.27 and 1010.76 W kg^{-1} respectively.

IV. CONCLUSION

All the electrochemical results of SBC and SBC/PANI showed that SBC/PANI possesses more enhanced results than SBC. SBC/PANI has higher specific capacitance of 189 Fg^{-1} at current density of 0.5 Ag^{-1} with energy density of 7.89 Wh kg^{-1} at power density of 68.60 W kg^{-1}.

V. ACKNOWLEDGMENT

Authors would like to thank Bhavan's College for their infrastructural support.

REFERENCES

[1] D. Agarwal, V. Kumar, Recent progress on sugarcane-bagasse based lactic acid production: Technical advancements, potential and limitations, Volume 193, March 2023, 116132, https://doi.org/10.1016/j.indcrop.2022.116132

[2] M. Dwiyaniti, A. Barruna, R. Naufal, I. Subiyanto, R. Setiabudy, C. Hudaya, extremely high surface area of activated carbon originated from sugarcane bagasse, *IOP Conf. Ser.: Mater. Sci. Eng.* **909** 012018, 10.1088/1757-899X/909/1/012018

[3] M. Kabeyi, O. Olanrewaju, Smart grid technologies and application in the sustainable energy transition: a review, International Journal of Sustainable Energy Volume 42, 2023 - Issue 1, https://doi.org/10.1080/14786451.2023.2222298.

[4] Md. Mahmud, and F. Anannya, Sugarcane bagasse - A source of cellulosic fiber for diverse applications, Heliyon, Volume 7, Issue 8, August 2021, e07771, https://doi.org/10.1016/j.heliyon.2021.e07771

[5] W. Chen, H. Wang, W. Lan, D. Li, A. Zhang, C. Liu, Construction of sugarcane bagasse-derived porous and flexible carbon nanofibers by electrospinning for supercapacitors, Industrial Crops and Products Volume 170, 15 October 2021, 113700, *https://doi.org/10.1016/j.indcrop.2021.113700*

[6] D. Supramono, Y. Devina, D. Tristantini, Effect of heating rate of torrefaction of sugarcane bagasse on its physical characteristics, International Journal of Technology (2015) 7: 1084-1093, http://dx.doi.org/10.14716/ijtech.v6i7.1771

[7] S. Kanwal, N. Chaudhry, S. Munir, H. Sana, Effect of torrefaction conditions on the physicochemical characterization of agricultural waste (sugarcane bagasse), Waste Management Volume 88, 1 April 2019, Pages 280-290, https://doi.org/10.1016/j.wasman.2019.03.053

[8] S. Siwal, Q. Zhang, N. Devi, V. Thakur, *Polymers* 12, no. 3 (2020): 505, https://doi.org/10.3390/polym12030505

[9] Yim, Yoon-Ji, Byung-Joo Kim. *Polymers* 15, no. 16 (2023): 3472.

[10] Lima, Marisa A. et al. "Evaluating the composition and processing potential of novel

sources of Brazilian biomass for sustainable biorenewables production." *Biotechnology for biofuels* 7 (2014): 1-19.