ISSN No:-2456-2165

Experimental Investigation and Optimization of Municipal Waste Biomass for Applicative Approach in Electrochemical Energy Storage

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Abstract:- Biochar acts as a promising material in energy storage applications due to its porous structures. In this study, Coconut shells (CS) and Assam lemon peel (ALP) are studied and optimized based on the required properties for electrochemical energy storage systems. The biomass are collected and the fine powder is prepared using powder mettalurgy route. Then the raw biomass was converted to biochar by slow pyrolysis using a fixed bed reactor in different parameters to find the best optimum biochar for further experimental process designed for energy storage systems. The best-optimized biochar obtained is the lemon peel biochar at 500 ^{0}C with heating rate of 15 ^{0}C (ALPB500/15). The maximum solid char yield attained for both the coconut shell and Assam lemon peel biochar is 46% and 27% respectively at 500 ^{0}C at 15 ^{0}C/min. According to Brunauer-Emmett-Teller (BET) analysis the pore volume, pore size and surface area acquired for the Assam lemon peel biochar (ALPB) sample increases with an augment in pyrolytic temperature whereas in coconut shell biochar (CSB) the BET surface area shows no significant rise. Thus, the best optimized sample according to BET analysis is found to be LPB500/15. Thermo Gravimetric analysis (TGA) displays that the obtained sample is thermally stable with LPB500/15 showing type II isotherm and H3 hysteresis.

Keywords:- *Coconut Shell Biochar, Assam Lemon Peel Biochar, Pyrolysis, Pore Size Distribution, Optimization.*

I. INTRODUCTION

The demand for clean and green energy with ever-alarmingly rise in climate change is growing at a faster rate. Fossil fuels is an alternate energy sources that has led to uncontrollable depletion. Thus, an alternate renewable energy which is also easily available at low cost is the need of the hour. Also, the climate change, air pollution are the major concern in today's world that requires urgent attention to be tackled soon and in a wise manner. The biomass in such case is very suitable candidate as an alternate renewable energy source and also can be used for energy production, conversion and storage[1]. Carbon is the most abundant material on the earth and it provides the basis for the storage of renewable energy in various forms. Carbon-based materials play an important role in energy storage system like in Li-ion battery, hydrogen storage, electrodes in supercapacitors, solar drying applications, and much more.

Demand for high performance energy storage devices is increasing day by day with the enhancement in the price of the fossil fuels. Electric Vehicles also needs energy in the form of kinetic energy when vehicles accelerate. Capacitors have a property of instant charging and discharging, however due[2] to its poor energy density as compared to Li-ion batteries it is still in the hold. Moreover, supercapacitors can be the most potential replacement for batteries with improved performance. Electrodes is a important part in improving the performance of a capacitor as the material in the electrode can be develop using biochars or biochar based composites. Activation of biochar in the form of physical or chemical may lead to more porosity and surface area which can be more useful for energy storage systems and also lignin content of biomass excels thermal conductivity as reported by some literatures[3].

Dissimilar thermal treatment of biomass like pyrolysis leads to biochar production that is useful for energy storage applications due to its porous nature. Activated biochar of peanut shell is used in zinc-air batteries and super capacitance[4]. Bardalai et al[5] illustrate the production of areca catechu dust biochar manufacture through pyrolysis. Bamboo, Betel Nutshell, and Rice straw were taken for investigation on pyrolysis kinetics and thermal properties in the N_2 atmosphere[6]. Agricultural residues and municipal wastes in the form of biochar are being studied in the utilization of electrochemical energy storage devices[7]. The biochar based materials are also sources for hydrogen production along with hydrogen storage[2]. Citrus peels of orange was studied by converting to biochar with varying pyrolytic temperatures to 300 ^{0}C to 700 ^{0}C and found that on increasing pyrolytic temperature the char yield decreased, oxygen content reduced whereas carbon and energy content increased[8]. Thus, different biomass-derived biochar has energy storage applications that need to be studied more precisely with diverse absorbent materials to trap the energy increasing the sustainability potential of the biochar. Biochar with some phase change materials (PCMs) such as metal alloys, alcohols, fatty acids, paraffin, etc., is proved to be most potential composites for energy storage [9]–[11] which proves that biochar has a bigger role to play in energy storage. Thus, in this paper an optimized biochar material in the form of additive is studied precisely to boost the energy storage capacity in the form of heat or electricity in order to achieve a better form of energy management storage system.

II. MATERIALS AND METHODS

The coconut shell and the Assamese lemons are collected from local sources. The Assamese lemon is found only in the state of Assam and has a physical characteristic difference from other lemons (C. Mukhim*, A. Nath, 2015). The biomass were washed thoroughly with tap water and then with distilled water. The coconut shell and the Assam lemon peel after peeling off were sun-dried for 8 and 3 days respectively, to remove the moisture content. It is dried in oven at 105 ^{0}C for 10 hours to remove the moisture from the shell and the peels. It is then motor grinded and sieved through 300 microns to lessen the particle size as displayed in *Fig.*The prepared biomass of 10 g per batch is taken in a fixed bed reactor for pyrolysis to convert it into biochar. Two dissimilar parameters were taken for the pyrolysis at 400 ^{0}C and 500 ^{0}C at 15 ^{0}C/min. After cooling the weight of the obtained char is noted and then it is kept for oven drying. The prepared biochars are further taken for characterization and analysis.

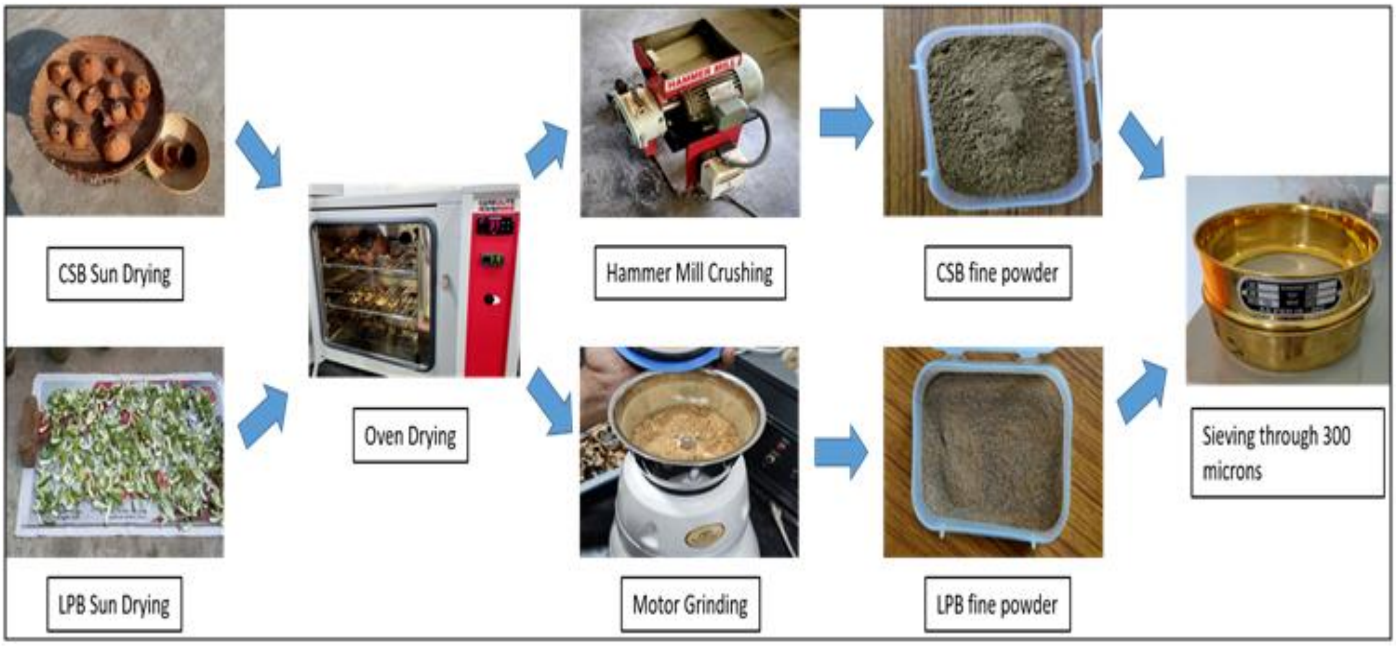

Fig 1 Biomass Particle Size Reduction Route

A. *Pyrolysis Conditions of the CSB and LPB and Char Yield Calculation*:

The Coconut shell biochar (CSB) and Assam lemon peel biochar (LPB) were pyrolyzed in a furnace using a fixed bed reactor in two different temperatures at 400 ^{0}C and 500 ^{0}C at the same heating rate of 15 ^{0}C/min to find the optimal sample for energy storage with maximum solid char yield for further processes. The solid char yield will be calculated using the below mentioned equation (1).

$$\text{Char yield of biochar} = (\text{Weight after pyrolysis})/(\text{Weight before pyrolysis}) \times 100 \qquad (1)$$

B. *Characterization:*

The BET analysis and experimental protocol is derived from a assorted experiment carried out by Das.et.al and is being modified in this work according to the requirements.

➢ *Brunauer-Emmett-Teller (BET) Analysis:*

The BET analysis provides the surface area, pore volume, and pore size of the prepared coconut shell and Assam lemon peel biochar samples. The surface area was measured by the adsorption of liquid Nitrogen as a function of relative pressure. The 300 micron fine particle biochar sample was dried in oven at 103 ± 2 °C for 24 hour before the experiment was carried out. About 15 mg of the sample was taken in the glass tube and degassing was done at 180 °C for 4 hour with the purging of N_2 gas. The adsorbed gases and vapors needs to be removed through outgassing of the biochar samples. The BET experiment provides the data and analysis of the surface area, pore size or volume and the pore dia is being carried out by studying the adsorption isotherm obtained from the experimental data[13].

➢ *Field Emission Scanning Electron Microscope (FESEM) Analysis:*

The Field Emission Scanning Electron Microscope is a morphological analysis of samples that gives the picture of the material surface and morphology. A variety of magnification can be adjusted in this particular analysis. The magnification considered for the analysis is 5000 X, 7500 X, 10000 X and 15000 X. The material is coated and then kept for charging and when the electrons start flowing it provides a clear view of the image. Here the focus was kept on the pores of the sample. The instrument used for this analysis is (Make:Zeiss, Model:Sigma)

➢ *Thermo Gravimetric Analysis (TGA):*

In TGA analysis, the weight loss is calculated as a function of temperature and hence determine the thermal stability. The temperature range set for the analysis of coconut shell and Assam lemon peel biochars is 30 ^{0}C to 800 ^{0}C at a heating rate of 15 ^{0}C/min. As the samples get heated in due course of time the weight loss is measured which provides us how the material behaves in thermal differential conditions. The TGA analyzer used in this experiment was (Make:Mettler Toledo, Model:TGA 2/SF/1100).

III. RESULTS AND DISCUSSIONS

The two biochars have been tested separately to check the feasibility of acting with different materials for energy storage. The porous nature of biochar is the prime focus to be worked on as the pores will trap the energy effectively and will thus provide a timeline for change in properties required for energy storage. For thermal applications, the heating and cooling effect can be studied using the porous nature of biochar materials.

In this study, pyrolysis was done for both CSB and LPB at 400 ^{0}C and 500 ^{0}Cat a heating rate of 15 0C/min. Maximum char yield is calculated for both the biochars. The maximum char yield obtained as per equation (1) for CSB and LPB at 500 0C at 15 ^{0}C/min is 40% and 27% respectively. The Thermo Gravimetric analysis (TGA) and Brunauer-Emmett-Teller (BET) analysis for CSB and LPB is also carried out. Further morphological study Field Emission Scanning Electron Microscope (FESEM) analysis for both the CSB and LPB is performed.

➢ *Calculation of Solid Char Yield of CSB and LPB at Various Pyrolytic Temperatures:*

CSB has more solid char yield than LPB for all pyrolytic temperatures at the same heating rate of 15 ^{0}C/min as shown in *Table.*

Table 1 Char Yield

Sample Name	**Initial Weight (g)**	**Final Weight (g)**	**Char Yield (%)**
CSB400/15	10	4.5903	45.90
CSB500/15	10	4.0016	40.01
LPB400/15	5	1.6509	33.01
LPB500/15	5	1.3486	26.97

➢ *Morphological and BET Analysis of the Biochars:*

The morphological FESEM images of CSB500/15 and LPB500/15 are shown in **Error! Reference source not found.** and **Error! Reference source not found.** and it displays with unstructured irregular surfaces with more meso and macro pores present along the surface of the LPB than the CSB. When the pyrolysis temperature augmented more definite pores are visible with decrease in surface area. The BET analysis of CSB500/15 and LPB500/15 gives the pore size in nanometers averaging about 6.71321 nm and 7.85535 nm respectively that indicates presence of more meso pores (⩾2 nm – 50 nm) on the biochar surface of the Assam lemon peel biochar than coconut shell biochar. The meso porous structures helps in adsorption of different liquid or semi liquid components which may be considered as an energy storage capability. The CSB500/15 as displayed in *Fig*, shows type II isotherm and no hysteresis occurs as the desorption follows the adsorption isotherm which means that it is non-porous or less porous material. In other hand the LPB500/15 demonstrate type II isotherm and H3 hysteresis according to IUPAC nomenclature (Thommes et al., 2015). It means that it is a meso porous material and the process is having a multilayer adsorption followed by the capillary condensation (p/p0>>2). Also, the desorption isotherm closer to the adsorption isotherm is due to the cavitation. This may be due to the uneven porosity on the sample flat surface and this can be minimized by chemical activation process of the biochar. LPB500/15 possess more BET surface area of 2.6550 m^2/g as compared to LPB400/15 that possess 1.8696 m^2/g making it the more potential candidate for energy storage.

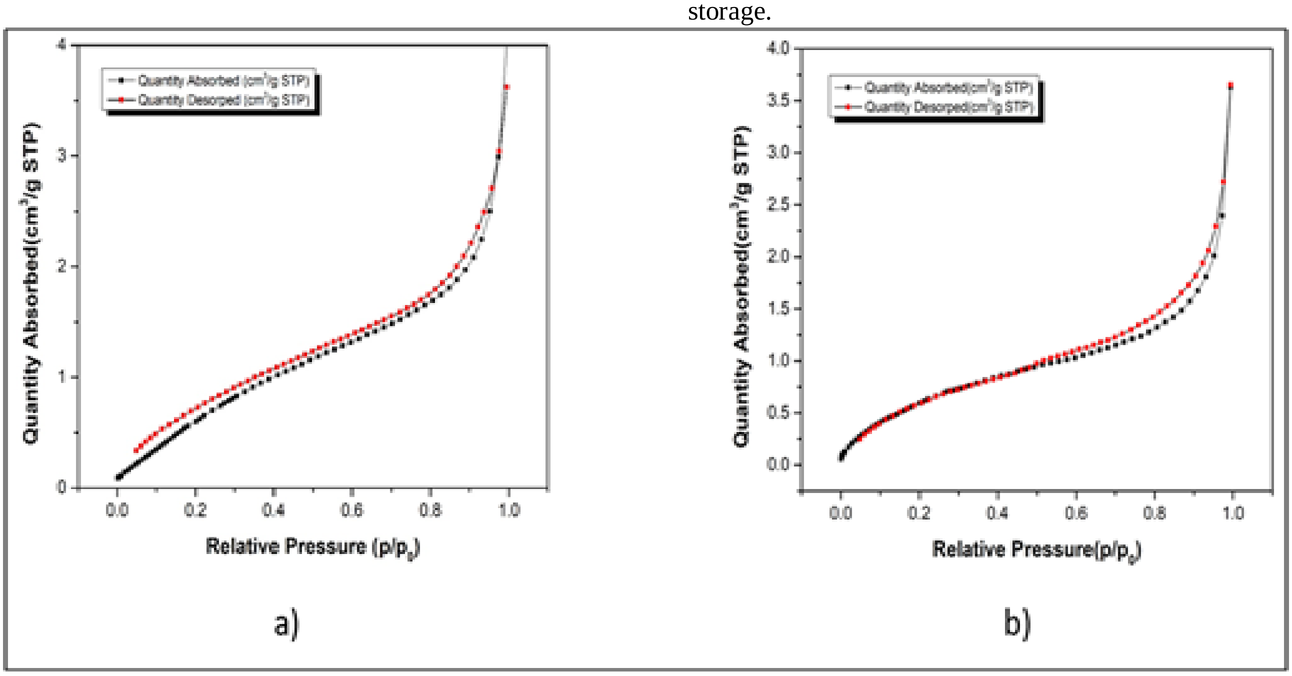

Fig 2 Adsorbtion-Desorption Isotherm of a) CSB 500/15 and b) LPB 500/15

ISSN No:-2456-2165

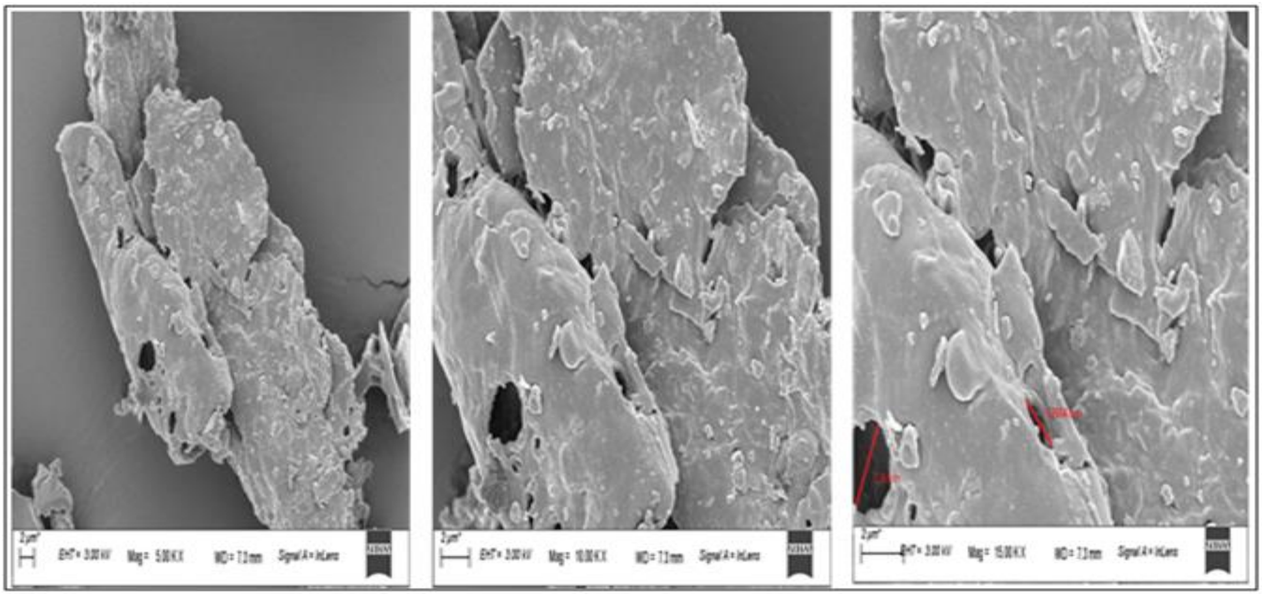

Fig 3 CSB 500/15 at Different Magnification

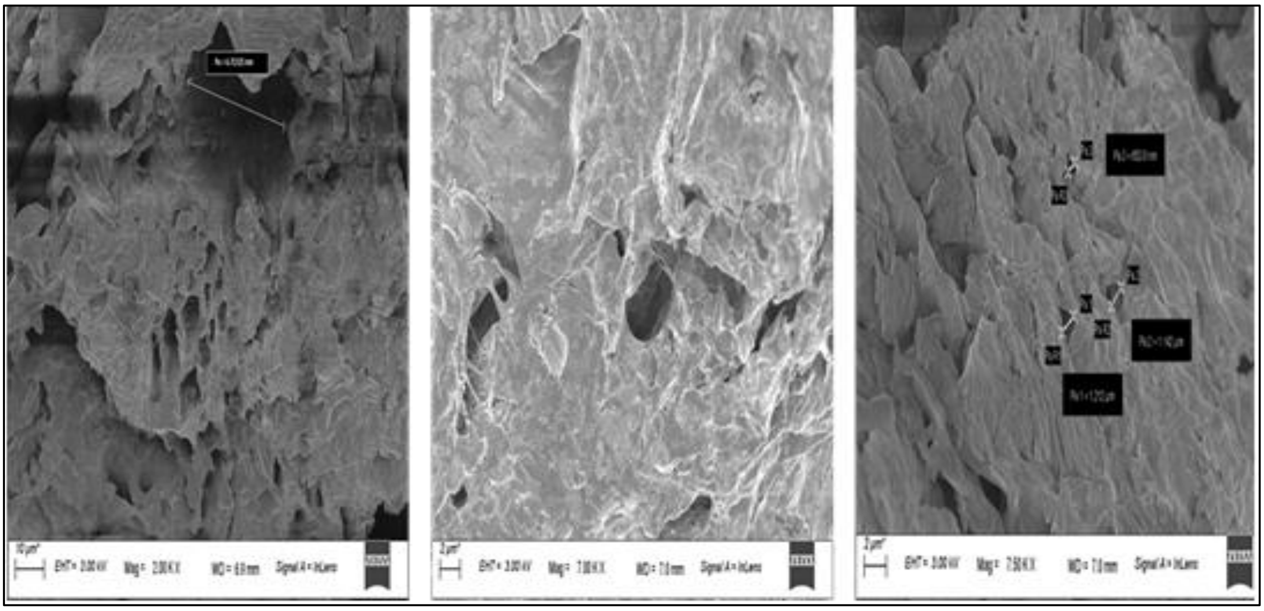

Fig 4 LPB 500/15 at Three Magnification Range

- *Thermo Gravimetric Analysis of CSB and LPB:*

The Thermo Gravimetric analysis of the coconut shell biochar and Assam lemon peel pyrolyzed at 400 ^{0}C and 500 ^{0}C at 15 ^{0}C/min is carried out and found that Assam lemon peel biochar is more thermally stable than coconut shell biochar. The thermal degradation of the CSB happened in three stages at a unlike weight-to-temperature ratio as shown in *Fig*.a) and the DTG curve is also demonstrated in *Fig*.b). The CSB500/15 first step degradation had a weight loss of ~3% at approx. temperature range of 60 ^{0}C – 220 ^{0}C, the second step degradation of ~15% at approx. 410 ^{0}C and the final step degradation of ~8% at above 575 ^{0}C. Thus, the mass loss is gradual at the start, maximum at the mid-stage where pyrolysis temperature was set and then again it gradually decreases for CSB500/15. The first peak is due to the evaporation of the moisture, the second peak is due to the pyrolytic decomposition of the hemicellulose in the temperature range of 200 ^{0}C - 270 ^{0}C and the third peak is due to the presence of cellulose degrades at high-temperature ranges. Elkhalifa et al, (Elkhalifa et al., 2022) also reported the TGA analysis of carrot biochar and blended carrot with cucumber biochar and found that the thermal degradation occurs in three stages due to the presence of moisture, hemicellulose, and cellulose in three various pyrolytic temperature ranges. The LPB500/15 is more thermally stable as the temperature increases the mass loss enhances at a constant rate where as in CSB500/15 the rate of weight loss to temperature is not constant. As displayed in Figure.5c) and Figure.5d) the LPB500/15 has its first step degradation at a weight loss of approx. 8% in the temperature range of 60 ^{0}C – 110 ^{0}C. The second step degradation occurs at a weight loss of approx. 25% at temperature range of 110 ^{0}C - 450 ^{0}C and the final thermal degradation occurs above 550 ^{0}C nearing the pyrolytic temperature range at a weight loss of 30% after which it becomes constant till it reaches 800 ^{0}C at a heating rate of 15 ^{0}C/min.

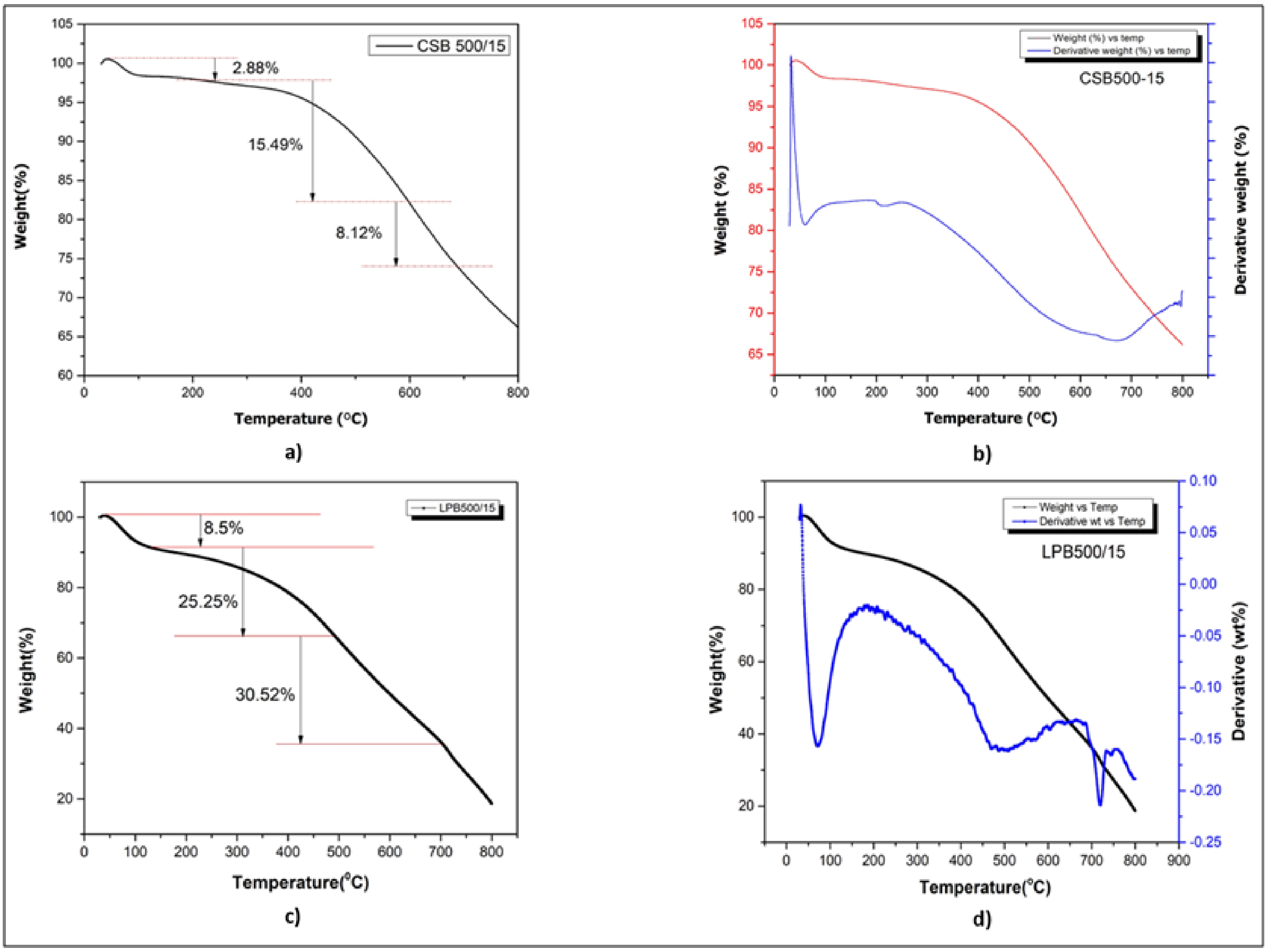

Fig 5 a) CSB 500/15 Weight Loss vs Temperature, b) CSB 500/15 DTG Curve, c) LPB 500/15 Weight Loss vs Temperature, d) LPB 500/15 DTG Curve.

IV. CONCLUSIONS

The Coconut shell biochar and the Assam lemon peel biochar are both characterized to study the pores size distribution, morphological changes and thermal stability to check the sample potential for energy storage. The obtained meso porous structures of Assam lemon peel biochar is found more suitable than the less porous structure of the coconut shell biochar through FESEM analysis. Even the BET analysis shows H3 hysteresis in the Assam lemon peel biochar indicating the presence of more meso pores on the material surface becoming the most beneficial for energy storage compared to CSB. The thermal degradation of the CSB500/15 dsiplays that the mass loss is gradual at the start, maximum at the mid-stage where pyrolysis temperature was set and then again it gradually decreases. In LPB500/15 the constant mass loss indicates that it is more thermally stable. Thus, the porous nature of the Assam lemon peel biochar makes it a more optimal candidate than the coconut shell biochar for energy storage applications.

ACKNOWLEDGEMENT

I want to acknowledge Assam Science and Technology University, Assam Engineering College, IIT Guwahati for providing support and sample testing facilities for carrying out the research work in a smooth manner.

➢ *Conflict of Interest*
There is no probable conflict of interest.

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