



# Agro-Industrial Waste Valorization for Energy and High-Valued Sustainable Materials: A Circular Economy Approach



**Neelam Bora\***

Research Scholar, Biofuel Laboratory



**Dr. Manika D Kataki\*\***

Assistant Professor & Head



**Dr. Subhash Maheshwari\*\*\***

Ex Technical Advisor



**Dr. Rupam Kataki\***

Professor & Head,  
Department of Energy

\*Biofuel Laboratory, Department of Energy, Tezpur University,

\*\*Department of Biotechnology,

Darrang College (Autonomous), Tezpur

\*\*\*Ex Technical Advisor, Tanjungenim Lestari Pulp and Paper Company,

**Abstract:** The efficient management of agro-industrial wastes and their processing into valuable bio-energy and sustainable materials are important for the growth of the circular bio-economy. A massive amount of waste is generated from various industries and agriculture, resulting in environmental pollution because of their unmanaged disposal methods. The conversion of these wastes into biofuels and carbonaceous materials not only reduces environmental burdens, but also enhances resource efficiency and economic sustainability. Thermochemical and hydrothermal conversion methods have been recognized as potential technologies for the agro-industrial wastes valorization. In the present investigation, black liquor (a paper industry waste), sugarcane bagasse, and wheat waste (wheat straw and husk) were considered to be potential candidates for the processing of energy materials and high-valued products. Pyrolysis experiments were carried out on dried black liquor solids to evaluate the influence of temperature on the overall yield products, as well as characterization of the obtained bio-oil and biochar. The highest bio-oil yield was found at a temperature of 500°C with heating rate of 40°C/min, with calorific values of 29.86 MJ/kg. Biochar exhibited basic properties, which are useful as soil-correcting agent materials required for the reduction of soil acidity. In addition, hydrothermal processing of wheat straw and wheat husk was also investigated for the integrated synthesis of biofuel and carbon quantum dots (CQDs). Water-soluble CQDs of average size between 4.67 nm and 4.71 nm were successfully prepared, and the obtained hydrochars showed calorific value between 18.71 to 25.94 MJ/kg. Pyrolysis of sugarcane bagasse biomass was carried out to obtain biochar, which was further activated using potassium hydroxide (KOH) to synthesize activated carbon. The activated carbon displayed high specific surface area of 2336.45 m<sup>2</sup>/g. When applied as supercapacitor electrode material, the activated carbon showed excellent electrochemical characteristics, with specific capacitance of 197.33 F/g at scan rate of 1 mV/s in 1.5 M KOH electrolyte. The findings of the presented research work clearly indicate the immense potential of agro-industrial wastes to synthesize renewable energy material as well as an advanced functional material, thus helping to sustain environmentally beneficial waste management and develop effective circular economy principles.

**Keywords:** Pyrolysis, Hydrothermal conversion, Agro-industrial waste, Biochar, Hydrochar.

## Introduction

The increased rate of population growth, along with the accelerated pace of industrialization and urbanization, has led to an enhanced demand for energy with a substantial burden on the available sources of energy. Although fossil fuels are abundant and contribute significantly to the global energy supply, their finite nature, along with the adverse environmental impacts associated with their extraction and combustion, has intensified the search for cleaner and environmentally benign alternative fuel sources with minimal greenhouse gas emissions. On the other hand, the increased importance of agricultural and industrial operations has led to the creation of massive amounts of wastes in the form of solids and liquids. The disposal of agro-industrial wastes, as well as various industrial by-products, is generally done in inefficient manner, thereby contaminating the soil, water, as well as posing potential risks to the public. The rising generation of wastes is, thus, responsible for the rising concerns about the need for efficient waste management practices [1, 2]. For efficient utilization of these varying bio-waste resources,

numerous conversion technologies have been developed. Among them, thermochemical and hydrothermal routes of conversion have emerged as two promising approaches for biomass, agro-industrial residues, and industrial wastes valorization. Pyrolysis is one of the significant thermochemical methods, where biomass or organic wastes undergo thermal decomposition in absence of oxygen, producing bio-oil, biochar, and non-condensable gases. Hydrothermal conversion is a process through which hydrochar, biofuels, and high-performance carbon nanomaterials in the form of Carbon Quantum Dots (CQDs) are produced [3-6].

The current work focuses on the integrated valorization of agro-industrial and industrial wastes such as black liquor, sugarcane bagasse, and residues from wheat processing using thermochemical and hydrothermal processing. The integrated production of sustainable energy and high-value carbon based materials presents high potential in the context of sustainable waste management and the development of the bio-circular economy.

## 2. Materials and methods

### 2.1 Materials

Black liquor utilized in this study was collected from a local paper mill at Jagiroad, Nagaon, Assam. Prior to use, it was solidified through lyophilization, where the sample was frozen at  $-20^{\circ}\text{C}$  and freeze-dried under high vacuum, resulting in about 92% total solids. Wheat straw and wheat husk were obtained from Lahkar Udyog Private Limited, Sonitpur, Assam. Sugarcane bagasse was obtained from a jaggery-making unit near Tezpur University. Both the bio-wastes were washed, sun-dried, followed by oven-drying at  $110^{\circ}\text{C}$ , ground, and sieved to a particle size of 2 mm before storage in desiccators.

### 2.2 Pyrolysis of black liquor and sugarcane bagasse

Dried black liquor solids (DBLS) were subjected to pyrolysis in a fixed-bed tubular reactor equipped with a Ni-Cr thermocouple for accurate temperature monitoring and control. Approximately 20 g of DBLS was loaded in the reactor and heated in a pyrolyser with a heating rate of  $40^{\circ}\text{C}/\text{min}$  to final temperatures of 300, 350, 400, 450, and  $500^{\circ}\text{C}$  under nitrogen ( $\text{N}_2$ ) flow.

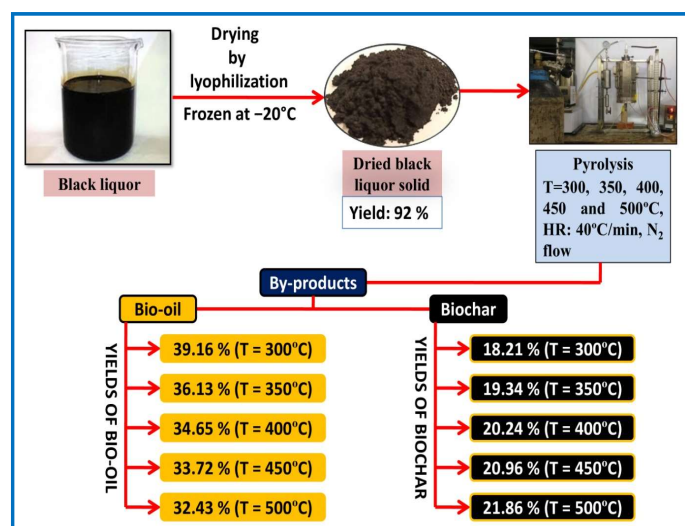


Fig 1: Schematic of pyrolysis of dried black liquor at different temperatures yielding biochar and bio-oil

Pyrolysis of sugarcane bagasse was performed in a fixed-bed pyrolyzer at  $800^{\circ}\text{C}$  for 2 hrs with a heating rate of  $5^{\circ}\text{C}/\text{min}$  under an inert  $\text{N}_2$  atmosphere. The obtained biochar was chemically activated using potassium hydroxide (KOH) at a biochar-to-KOH weight ratio of 1:3. The impregnated sample was further pyrolyzed at  $800^{\circ}\text{C}$  for 1 hr. After activation, the product was washed with hydrochloric acid (HCl) followed by repeated rinsing with double-deionized water until neutral pH was achieved. The resulting activated biochar was designated as ASB8.

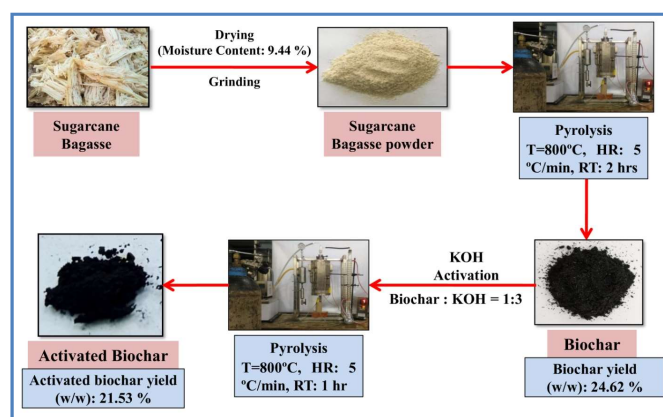


Fig 2: Flow chart of the pyrolysis process of sugarcane bagasse at  $800^{\circ}\text{C}$  for production of activated biochar

### 2.3 Hydrothermal carbonization of wheat straw and husk

Pre-treated wheat straw (WS) and wheat husk (WH) were processed through hydrothermal carbonization. For each experiment, 6 g of biomass was dispersed in 300 mL of double-distilled water and relocated into a 600 mL stainless-steel hydrothermal reactor. The reactions were performed at 180, 220, and  $260^{\circ}\text{C}$  for a constant residence time of 3 hrs. The resulting dark brown suspension was ultrasonicated, centrifuged, and filtered to obtain a clear aqueous dispersion of carbon quantum dots (CQDs), which was freeze-dried and kept for further characterization. The separated hydrochar was dried and preserved for physicochemical analysis.

### 2.4 Characterization Methods

#### 2.4.1 Physicochemical properties of biomass and their thermochemical and hydrothermal derivatives

Proximate analysis for waste biomass samples was conducted according to ASTM D3172-07a standards. Ultimate analysis for waste biomass samples and derived materials from pyrolysis and hydrothermal carbonization processes was conducted using Euro EA elemental analyzer and CHNS analyzer (Perkin Elmer 2400 Series 2). The calorific value for biomass samples and derived materials was conducted according to ASTM D2015 using automatic bomb calorimeter (5E-1AC/ML model). Functional groups for produced materials were analyzed using Fourier transform infrared spectrophotometer (Nicolet Impact I-410). The pH for byproducts was analyzed by dispersing it in deionized water (1:20 ratio), using pH meter. Surface morphology was evaluated using scanning electron microscopy (SEM, JEOL JSM-6390 LV), and functional groups were identified using Fourier transform infrared (FT-IR) spectroscopy (Nicolet Impact I-410). The specific surface area of the byproducts was determined by Brunauer-Emmett-Teller (BET) analysis using a surface area analyzer (NOVA 1000E).

#### 2.4.2 Properties of Carbon Quantum Dots (CQDs)

The CQDs synthesized from WS and WH was characterized using transmission electron microscopy (TEM) to assess morphology and particle size. Particle size distribution was determined using ImageJ software. Optical properties and surface functional groups were analyzed using UV-visible spectroscopy and FT-IR spectroscopy.

#### 2.4.3 Electrochemical evaluation of SB-activated biochar

Activated biochar derived from sugarcane bagasse was used to fabricate supercapacitor working electrode with 0.5 % Nafion as a binder and Flourine-doped tin oxide (FTO) glass as the current collector. Electrochemical measurements were conducted in 1.5 M KOH electrolyte using a Bio-Logic SP-150 Potentiostat, employing cyclic voltammetry to evaluate specific capacitance. The specific capacitance was evaluated using the equation (1):

$$C \text{ (Fg}^{-1}\text{)} = \frac{\int_{V_1}^{V_2} Idv}{mv(V_2 - V_1)} \quad (1)$$

where, I (A) is the current, m (g) is the mass of biochar, v (V/s) is the scan rate, V1 and V2 (in V) are the potential limits.

### 3. Results and Discussion

#### 3.1 Properties of biomass/bio-waste

The physicochemical properties of DBLS, sugarcane bagasse, wheat straw (WS), and wheat husk (WH) were evaluated through proximate and ultimate analyses. DBLS exhibited a low moisture content (MC) of 5.76%, indicating its fitness for thermochemical conversion. Elemental analysis on a dry ash-free basis showed carbon, hydrogen, nitrogen, and oxygen contents of 34.12%, 4.21%, 0.41%, and 32.99%, respectively. Sugarcane bagasse showed a higher MC of 9.44%, with elemental compositions of 38.58% C, 4.72% H, 2.88% N, and 53.82% O.

For WS and WH, proximate analysis revealed a higher MC in WS (11.88%) compared to WH (9.51%). Both feedstocks exhibited comparable volatile matter and fixed carbon contents, although WH showed relatively higher ash content. Ultimate analysis indicated that WS possessed higher carbon and lower oxygen content than WH. Hydrogen and sulfur contents were low and similar for both samples, while nitrogen in WH was below the detection limit. The detailed results are shown in Table 1.

Table 1: Properties of biomass/bio-waste

Properties	Dried Black Liquor (DBLS)	Sugarcane Bagasse (SB)	Wheat Straw (WS)	Wheat Husk (WH)
<b>Proximate Analysis (wt. %)</b>				
MC	5.76	9.44	11.88	9.51
Ash	3.12	3.46	5.32	13.24
VM	53.92	65.32	77.14	73.53
FC	37.20	21.78	5.66	3.72
<b>Ultimate Analysis (wt. %)</b>				
C	34.12	38.58	40.23	35.08
H	4.21	4.72	6.47	5.49
N	0.41	2.88	1.44	-
O	61.26	53.82	51.66	59.14
S	-	-	0.20	0.29
H/C ratio	1.48	1.47	1.93	1.88
O/C ratio	0.73	1.05	0.96	1.26
Calorific ratio (MJ/kg)	-	17.33	14.08	13.03

#### 3.2 Pyrolysis and hydrothermal carbonization product yields

DBLS was pyrolyzed at heating rates of 40°C/min over temperatures ranging from 300 to 500°C under a nitrogen atmosphere. Increasing temperature led to reduction in biochar yield and corresponding rise in bio-oil yield. The biochar yield declined from 39.16 to 32.43%, and bio-oil increased from 18.21 to 21.86%. The highest bio-oil yield was found at 500°C and 40°C/min, which was selected for further studies. Sugarcane bagasse pyrolyzed at 800°C produced 24.62% biochar, reflecting extensive thermal degradation at high temperatures (Table 2).

Hydrothermal carbonization of WS and WH showed maximum hydrochar yields at 220°C, corresponding to the onset of cellulose decomposition. The increase in yield from 180 to 220°C was more pronounced for WH, whereas further temperature increase to 260°C resulted in reduced hydrochar yield due to lignin degradation. Consequently, 220°C was selected as the optimal temperature, and the hydrochars were designated as WSH and WHH (Table 2).

Table 2: Yields of biochar, hydrochar and bio-oil from different biomass/waste

Temperature (°C)	Biochar (%)	Bio-oil (%)
<b>Dried Black Liquor (DBLS)</b>		
300	39.16	18.21
350	36.13	19.34
400	34.65	20.24
450	33.72	20.96
500	32.43	21.86
<b>Wheat Straw (WS)</b>		
180	34.78	-
220	36.42	-
260	35.42	-
<b>Wheat Husk (WH)</b>		
180	42.17	-
220	49.33	-
260	41.55	-
<b>Sugarcane Bagasse (SB)</b>		
800	24.62	-

#### 3.3 Characterization of products obtained from pyrolysis and hydrothermal carbonization

##### 3.3.1 Properties of biochars derived from dried black liquor (DBLS)

The ultimate analysis of DBLS-derived biochars revealed increased carbon content and higher heating values with rising pyrolysis temperature. Biochar pH also increased due to the concentration of alkaline salts during thermal decomposition.[7].

Table 3: Different properties of biochars derived from dried black liquor (DBLS)

Properties	Temperature (°C)				
	300	350	400	450	500
<b>Ultimate analysis (wt. %)</b>					
C	38.44	43.12	47.86	49.54	52.16
H	3.87	3.65	3.34	3.08	2.86
N	0.37	0.34	0.29	0.27	0.24
O	57.32	52.89	48.51	47.11	44.74
Calorific value (MJ/kg)	24.97	25.73	26.68	26.92	27.18
pH	8.02	9.59	9.87	10.03	10.41

Fig. 1 presents SEM images of DBLS derived biochars produced at 350, 400, and 500 °C with heating rate of 40°C/min. The SEM analysis revealed porous, amorphous, and heterogeneous surface morphologies for all biochars, consistent with observations reported by Bordoloi et al. [8].

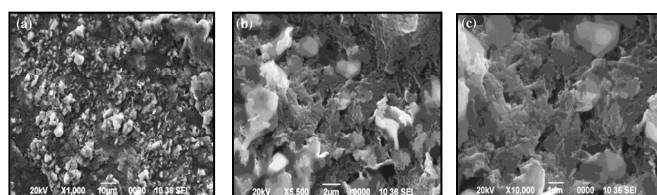


Fig 1: SEM images of DBLS biochar at (a) 350°C (b) 400°C and (c) 500°C

##### 3.3.2 Properties of bio-oil derived from dried black liquor (DBLS)

Table 4 depicts the elemental composition, calorific value, and atomic H/C and O/C ratios of the bio-oil produced at the optimal pyrolysis temperature,

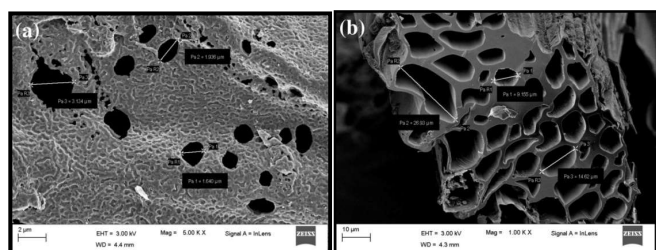
with heating rate of 40°C/min. Compared to the original DBLS feedstock, the bio-oil shows a marked reduction in oxygen content, leading to an enhanced calorific value of 29.86 MJ/kg. The H/C molar ratio of 1.56 falls within the range of conventional petroleum fuels (1.5–2.0), indicating an improvement in fuel quality and energy density.

**Table 4: Different properties of DBLS bio-oil**

Parameter	DBLS Bio-oil
C	67.69
H	8.87
N	5.98
O	17.46
H/C	1.56
O/C	0.19
Calorific value (MJ/kg)	29.86
pH	3.7

### 3.3.3 Properties of raw biochar and activated biochar derived from sugarcane bagasse (SB)

The raw sugarcane bagasse (SB) biochar produced at 800°C contained 54.33 % of C, 5.11 % of H, 2.04 % of N, and 38.52 % of O, and exhibited a high calorific value of 29.88 MJ/kg. The biochar was alkaline in nature, with a pH of 10.34. After chemical activation, the elemental analysis of the biochar revealed the presence of 73.24 % of C, 2.80 % of H, 1.86 % of N, and 22.10 % of O. The obtained activated biochar (ASB8) was washed with deionized water until its pH became neutral. The SEM analysis as shown in Fig. 2(a-b) and BET analyses confirmed enhanced pore development, with the surface area increasing from 333.20 to 2336.45 m<sup>2</sup>/g after activation.



**Fig. 2: SEM images of (a) raw biochar and (b) activated biochar derived from sugarcane bagasse**

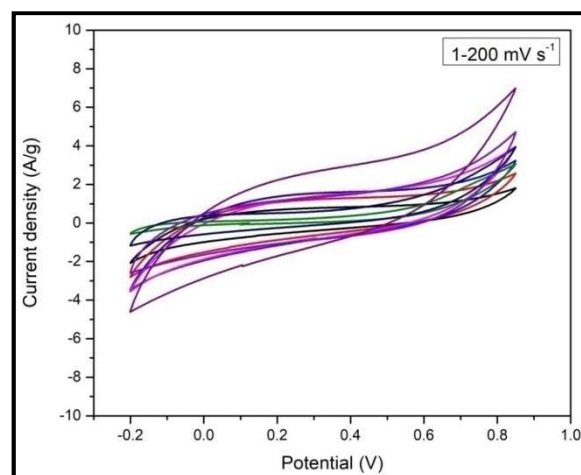
### 3.3.4 Electrochemical performance of activated SB-biochar as supercapacitor electrode material

Cyclic voltammetry (CV) was performed in the potential window of -0.2 to 0.85 V to evaluate the specific capacitance of the working electrode prepared from activated biochar (ASB8). The ASB8 electrode exhibited good electrical conductivity and a typical electric double-layer capacitive behavior. A maximum specific capacitance of 197.33 F/g was achieved at the scan rate of 1 mV/s, which is comparable to previously reported biochar-based supercapacitor electrodes.

**Table 5: Specific capacitances of activated biochar (ASB8) electrode**

Scan rate (mV/s)	ASB8 (F/g)
1	197.33
10	109.20
25	78.68
50	41.75
75	35.43
100	31.44
150	25.79
200	22.98

Table 5 summarizes the specific capacitance values at different applied scan rates for the ASB8 electrode. Figure 3 illustrates the variation of capacitance of ASB8 electrode with scan rate.



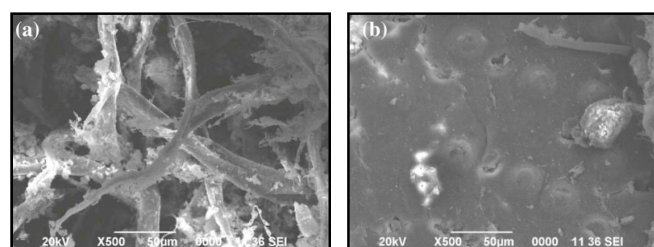
**Fig. 3: CV curves of the activated biochar (ASB8) in the range 1-200 mV s<sup>-1</sup>**

Table 6 summarizes the ultimate analysis of hydrochars prepared at 220°C. Hydrothermal conversion increased the carbon content of WS- and WH-derived hydrochars, with a corresponding reduction in oxygen content, while H, N, and S contents showed minimal change. As a result, both O/C and H/C atomic ratios decreased compared to the raw feedstocks, attributed to the conversion of carbon and hydrogen into CO<sub>2</sub>, CO, and H<sub>2</sub>O through exothermic reactions at elevated temperatures. The WS-derived hydrochar exhibited the highest calorific value, followed by WH-derived hydrochar, and both were slightly acidic.

**Table 6: Characteristics of hydrochar generated at 220°C**

Properties	Hydrochars	
	WSH	WHH
<b>Ultimate analysis (wt. %)</b>		
C	43.02	40.78
H	6.86	5.97
N	0.96	0.65
S	0.19	0.11
O	48.97	52.49
H/C ratio	0.85	0.97
O/C ratio	1.91	1.76
Calorific ratio (MJ/kg)	25.94	18.71
pH	6.28	6.12

The SEM images (Fig. 4a-b) reveal rough, irregular, and degraded surfaces with fragmentation and pore formation, more pronounced in WS due to higher hemicellulose and lignin content.



**Fig. 4: SEM images of (a) WSH, and (b) WHH**

### 3.3.6 Properties of CQDs derived from wheat straw and husk

The CQDs were synthesized from WS and WH, designated as WSC and WHC. Yield analysis showed higher mass yield and CQD concentration for WH, likely due to its greater cellulose content [9]. The concentration of CQD solutions for WS and WH were found to be 3.85 and 4.75 mg/mL respectively, whereas their corresponding mass yields were obtained as 19.25 and 23.75% respectively.

TEM analysis was applied to examine the morphology and size of the CQDs as depicted by Fig. 5. TEM analysis revealed spherical CQDs with nanoscale dimensions, and size distribution measurements of 105 particles indicated good uniformity and monodispersity. CQD sizes ranged from 1.87 to 8.48 nm, consistent with lignocellulosic biomass-derived CQDs. The CQDs were highly monodispersed with an average diameter of 4.77 nm. The CQDs derived from both feedstocks exhibited comparable size distributions. As the size of CQDs is strongly influenced by the conversion operating conditions, the similar reaction conditions employed for both feedstocks likely resulted in CQDs with comparable average diameters.

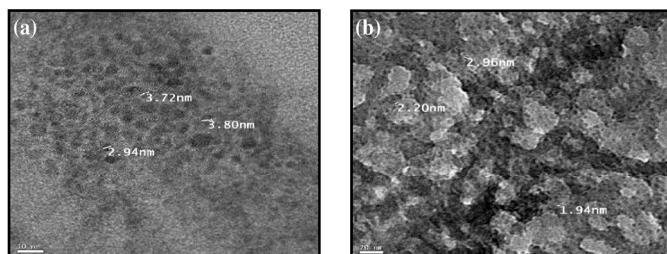


Fig. 5: TEM images of CQDs (a) WSC, and (b) WHC

#### 4. Opportunities, Challenges, and Cost–Benefit Perspective for Commercial-Scale Implementation

The above proposed process of this study demonstrates strong potential for commercial-scale implementation, owing to the abundant availability of low-cost biomass feedstocks and its ability to simultaneously generate value-added products alongside energy co-products. The environmental advantages of waste reduction, carbon sequestration, and sustainability also add to the commercial viability of the process. However, there are still challenges in the commercial-scale implementation of the process, such as high capital costs, energy-intensive process steps, variability in feedstocks, and the need for product quality and emission control.

Economic viability of the process in this study from a cost-benefit point of view would thus depend on keeping the operating costs low through process integration and internal energy recycling, and maximizing economic returns from the high-value application of char, as well as any possible economic incentives. With proper optimization and quality management, it should be possible to achieve a good economic and environmental balance.

#### 5. Conclusion

The findings of the current study exhibited that for the pyrolysis of DBLS, the highest yield of bio-oil was obtained at the temperature of 500°C with

heating rate of 40°C/min. The chemical composition of the derived bio-oil was proved to be favorable with high H/C atom ratio of 1.57 and calorific value of 29.86 MJ/kg. The significance of the temperature in affecting the yield of the products was proved since a rise in temperature amplified the yield of liquid products, with the decrease in the yield of biochar. The C content and calorific value of the DBLS-derived biochar were high, which depicted enormous potential as a solid fuel. The high basicity of the DBLS-derived biochar showed significant potential as a soil-liming material for the acidic soil of north-east India. The high surface area of activated biochar derived from SB via pyrolysis and KOH activation showed moderately mesoporous structure and excellent electrochemical characteristics suitable for a supercapacitor. The biomass composition exhibited significant effect on the yield of hydrochar and CQDs in the hydrothermal conversion of WS and WH. The hydrochar yield decreased with increased temperature that showed the temperature dependency of the process. The highest yield of hydrochar from WH was observed at 220°C, due to its higher cellulose content. TEM confirmed the nanoscale dimensions of CQDs, while SEM and BET analyses highlighted the suitability of wheat straw-derived hydrochar for soil amendment applications.

#### Acknowledgement

The authors acknowledge Tezpur University for granting access to laboratory and analytical facilities essential for carrying out this work. The authors also gratefully acknowledge the PURSE grant from the DST, Government of India (DST File no. SR/PURSE/2024/240 dated 14 October 2024).

#### References

- [1] Wu, L., Adebayo, T. S., Yue, X. G., Umut, A., *International Journal of Sustainable Development & World Ecology*, 30, 21–36 (2023).
- [2] Wang, J., Azam, W., *Geoscience Frontiers*, 15, 101757 (2024).
- [3] Zhang, J., Xia, A., Zhu, X., Huang, Y., Zhu, X., Liao, Q., *Fuel Processing Technology*, 232, 107276 (2022).
- [4] Masoumi, S., Borugadda, V. B., Nanda, S., Dalai, A. K., *Catalysts*, 11, 939 (2021).
- [5] Tambe, P., Mane, S., Chaudhari, B. P., Kulabhusan, P. K., *Fundamentals of Bionanomaterials*, 293–325 (2022).
- [6] Kumar, M., Upadhyay, S. N., Mishra, P. K., *ACS omega*, 7, 32, 28052–28064 (2022).
- [7] Yuan, J. H., Xu, R. K., Zhang, H., *Bioresource technology*, 102, 3, 3488–3497 (2011).
- [8] Püttin, A. E., Özbay, N., Önal, E. P., Püttin, E., *Fuel Processing Technology*, 86, 11, 1207–1219 (2005).
- [9] Sevilla, M., Fuertes, A. B., *Carbon*, 47, 9, 2281–2289 (2009).