ABSTRACT: The present work addresses the transformation of bio-oil into valuable biocarbon through slow pyrolysis. The biocarbons produced at three different temperatures (400, 600, and 900 °C), 10 °C min⁻¹ heating rate, and 30 min holding time were tested for their surface morphology, thermal stability, elemental composition, functionality, particle size, and thermal and electrical conductivity. The physicochemical study of bio-oil showed substantial carbon content, higher heating value, and lower nitrogen content. Also, the Thermogravimetric analyzer–Fourier Transform Infrared Spectroscopy (TGA-FTIR) study of bio-oil confirmed that the majority of gases released were hydrocarbons, carbonyl products, ethers, CO, and CO₂, with a minor percentage of water and alcohol. Overall, it was found that the pyrolysis temperature has the dominant role in the yield and properties of biocarbon. The physicochemical characterization of biocarbon showed that the higher temperature based pyrolyzed biocarbon (600 and 900 °C) improved the properties in terms of thermal stability, thermal conductivity, graphitic content, ash content, and carbon content. Furthermore, the elemental and Energy-Dispersive Spectroscopy study of biocarbon confirmed the substantial depletion in oxygen and hydrogen at a higher temperature (600 and 900 °C) than the lower temperature based pyrolyzed biocarbon (400 °C). Additionally, the purest form of the biocarbon is found at a higher temperature (600 and 900 °C) with higher thermal stability and carbon content. The study of the surface morphology of biocarbon revealed that the higher temperature based pyrolyzed biocarbon (600 and 900 °C) showed larger and harder particles than the lower temperature biocarbon (400 °C); however, the electrical conductivity of biocarbon decreased, whereas thermal conductivity increased, with an increase in the pyrolysis temperatures. Moreover, the particle size analysis of biocarbon confirmed that most of the particles were found in the range of 1 μm. The increased thermal stability, carbon content, and graphitic content and the lower ash content endorse biocarbon as an excellent feedstock for carbon-based energy storage materials.

INTRODUCTION

The rapid increase in population, urbanization, and change in lifestyle has led to the depletion of nonrenewable energy reserves and deterioration of our environment. The depletion of fossil resources (coal, fossil fuel, and fossil gas) forces the exploration of renewable fuels that are sustainable and eco-friendly. In this context, bio-oil plays an essential role in reducing our dependence on petroleum products. Bio-oil can be derived through the thermochemical conversion of biomass, usually through pyrolysis. Pyrolysis has gained good attention in recent times due to its very positive properties, being that it can deliver three forms of energy parallelly (solid, liquid, and gaseous). The pyrolysis refers to biomass burning in the non-
attendance or partial incidence of air/O\textsubscript{2} at medium temperatures (400–700 °C).\textsuperscript{1} Pyrolysis is a relatively new and emerging technology that converts dry biomass into a different form of energy, such as liquid (bio-oil), solid (biocarbon), and gases.\textsuperscript{1–5} The yield of pyrolytic products strongly depends on the operational process, mainly slow or fast pyrolysis.\textsuperscript{1} Also, the applied pyrolysis process substantially alters the yield and characteristics of products.\textsuperscript{2} The pyrolytic end products, such as gaseous products (hydrogen, CO, and CO\textsubscript{2}); however, liquid products (bio-oil) are either black or brown in color and derived from the condensation of condensable gases with different physicochemical characteristics. Generally, bio-oil is used either as a transportation fuel or for power/heat production; however, the advanced use of bio-oil is still under investigation.\textsuperscript{1} Also, bio-oil is used as a transportation fuel by blending with conventional fuel or directly in furnaces and turbines to produce heat and electricity.\textsuperscript{7} The bio-oil from biomass pyrolysis is used in boilers, gas turbines, and diesel engines for the generation of heat and power. The upgradation of bio-oil for transportation fuel is described by Czernik and Bridgewater\textsuperscript{4} and by Bridgewater.\textsuperscript{7} Bio-oil is also used as a binder material for the preparation of charcoal ore pellets.\textsuperscript{6} Results displayed that the use of bio-oil as a binder material in charcoal–bio-oil blends is found to be more reactive than fossil-based coke.\textsuperscript{7} Toth et al. (2018) explored the structure of carbon black obtained from the bio-oil pyrolysis through a high-temperature spray process.\textsuperscript{7} They stated that the structural properties of carbon black were highly dependent on the operating temperature and were matched with those of commercial carbon black. Elliott et al. (2013) explored the pyrolysis of bio-oil into low-sulfur electrode carbon through catalytic hydropyrolysis and stated that carbonous products produced from the bio-oil pyrolysis have a low residual oxygen content.\textsuperscript{8} Moreover, Mohan et al. (2006) explored the pyrolysis of biomass (especially wood) into bio-oil and demonstrated the application of bio-oil into heat production, electricity production, synthesis gas production, and different types of chemicals.\textsuperscript{8} They also studied how the properties of bio-oil varied with different feedstocks, operating conditions, types of reactors, etc. Additionally, bio-oil is used for the extraction of various beneficial chemicals (resins, fertilizers, food flavoring, and soap making\textsuperscript{9}) and adhesives.\textsuperscript{10} The physicochemical characteristics of bio-oil, such as higher viscosity, density, moisture, lower calorific value, lower acidity, extreme corrosiveness, and highly unstable nature compared with conventional fuel, limit its application for direct burning or using as transportation fuel.\textsuperscript{2–7} Thus, this study brings renewed attention to the research using waste bio-oil as pyrolysis feedstock for the generation of valuable biocarbon. The biocarbon found at the end of the pyrolysis has an enormous effect in satisfying energy supply in the form of heat and currently displays maximal real-world applications to reduce global warming by capturing and saving atmospheric carbon. Biocarbon is mainly used in soil amendment, CO\textsubscript{2} capturing, catalysts, bio-adsorbents, fuel cells, supercapacitors,\textsuperscript{12–15} biofertilizers,\textsuperscript{16} and biocomposite materials.\textsuperscript{16}

The biocarbon gained from the pyrolysis of waste and low-value biomass has been highlighted for various technological applications as such as sensors, catalysts, energy storage, and conversion devices.\textsuperscript{16,17} The physicochemical properties of biocarbon are subject to the biochemical composition of feedstocks and pyrolysis operating conditions (temperature, particle size, residence time, and heating rate).\textsuperscript{1} Among them, temperature, heating rate, feedstock particle size, and holding time alter the yield and quality of biocarbon. The sequestration of atmospheric carbon is essential to tackle the issue of climate change. However, with an augmented propensity in the utilization of thermal mode (pyrolysis) to capture the carbon as a solid substance (biocarbon), the generation of bio-oil and syngas would increase rapidly.\textsuperscript{18} Thus, it has become essential to deliver parallel investigations for converting the pyrolysis co-products, like bio-oil. In this direction, the turning of bio-oil into carbon, in the form of biocarbon (solid state), boosts carbon sequestration without the threat of inappropriate dumping and pricey storage of bio-oil. Also, similar research has the potential to deliver a novel form of biocarbon with enhanced characteristics.

Although the application of biocarbon gained new heights within a limited time span, the production of biochar from the pyrolysis of low-value-waste biomass has increased substantially. However, to the best knowledge of the authors and based on a thorough literature survey, the production of biocarbon from bio-oil through slow pyrolysis has not yet been studied substantially. Thus, the current investigation is focused on the pyrolysis of crude bio-oil to produce new valuable biocarbon through the slow pyrolysis technique. Further, the properties of biocarbon produced at multiple temperatures were tested with different characterization tools such as a thermogravimetric analyzer, FTIR, Raman Spectroscopy, SEM, particle size analyzer, EDS, TGA-FTIR analyzer, and CHNS analyzer.

### RESULTS AND DISCUSSION

#### Physicochemical Study of Bio-oil

The physicochemical study of bio-oil is demonstrated in Table 1. The bio-oil yield was found to be 33 and 32.12 wt % for CF and SCG, respectively, which is very close to the bio-oil yield of pine sawdust (39.39 wt %) and Gulmohar seeds (36.68 wt %).\textsuperscript{19} However, a slight variation in the bio-oil yield was caused by the compositional difference in feedstocks and pyrolysis operating conditions. Further, the elemental study of bio-oil confirmed the presence of a higher carbon content (64.70 and 69.27% for CF and SCG, respectively) than the miscanthus bio-oil (43.6%).\textsuperscript{16} The bio-oil pyrolyzed in this study is found to be clean, with a lower viscosity than the miscanthus bio-oil and a difference in biochemical composition, thus resulting in a higher carbon content. Further, the amount of nitrogen content (9.45 and 5.72% for CF and SCG, respectively) was detected to be greater than that of miscanthus bio-oil (0.8%).\textsuperscript{20}

| Parameters                      | CF          | Bio-oil     |
|---------------------------------|-------------|-------------|
| Temperature (°C)                | 600         | 600         |
| Yield (wt %)                    | 33.00%      | 32.12 wt.%  |
| C (%)                           | 64.70 ± 0.20 | 69.27 ± 0.18 |
| H (%)                           | 8.97 ± 0.12  | 7.92 ± 0.10  |
| O (%)                           | 16.86 ± 0.16 | 14.38 ± 0.16 |
| N (%)                           | 9.45 ± 0.15  | 5.72 ± 0.13  |
| S (%)                           | 0.02 ± 0.001 | 0.06 ± 0.001 |
| HHV (MJ/kg)                     | 27.77 ± 1.1  | 30.57 ± 0.4  |
| pH                              | 9.11 ± 0.12  | 7.11 ± 0.20  |
| ash content (wt %)              | 1.47 ± 1.10  | 1.30 ± 0.86  |
mainly due to biochemical compositional differences. Among CF and SCG, CF demonstrated a higher nitrogen content than SCG. CF is derived from the proteinous feedstock, whereas SCG is derived from lignocellulosic feedstock; thus, CF demonstrated a higher nitrogen content.\textsuperscript{21,22} The oxygen content in bio-oil was found to be lower (16.86 and 14.38\% for CF and SCG) than that in miscanthus bio-oil (21.6\%),\textsuperscript{20} probably due to the elimination of oxygen-bounded groups in the form of water. Although CF and SCG have a lower oxygen content than miscanthus bio-oil, they limit the direct feed of bio-oil in engine application due to decreased flame temperature and also damage the automation of the engine.\textsuperscript{19} Further, the higher heating value (HHV) of CF and SCG was detected to be 27.77 and 30.57 MJ kg\textsuperscript{-1}, respectively, which is close to that of other studied bio-oil such as the sawdust of sal (28.36 MJ kg\textsuperscript{-1}).\textsuperscript{23} The pH of CF and SCG was found to be 9.11 and 7.11, respectively, which demonstrated the alkalinity of bio-oil. The bio-oil has an alkali nature and improved heating value due to the lower presence of proton ions.\textsuperscript{9,24} The bio-oil enriched with a higher acidity produced a lower moisture content during the determination of the heating value of fuel.\textsuperscript{23} Moreover, the lower amount of proton ions significantly reduced the formation of water molecules during pyrolysis. Also, the pH study of bio-oil revealed that CF has a lower pH than SCG, which means that SCG is associated with a higher amount of acidic content. The ash content of CF and SCG was found to be (1.47 and 1.30 wt \%) well-matched with that of liquid tar (1.1 wt \%) but lower than that of miscanthus bio-oil (4.65\%).\textsuperscript{20} Moreover, the higher viscosity of miscanthus derived bio-oil is the consequence of the higher ash content.\textsuperscript{25}

**TGA-FTIR Analysis of Bio-oil.** TGA-FTIR is an analytical tool that determines the produced hot volatiles during the heating of materials. Also, the information gained from TGA-FTIR for the pyrolysis of materials can be used for the estimation of the nature of various gases such as hydrogen, methane, carbon dioxide, and carbon monoxide that substantially had ample environmental effects.\textsuperscript{26} The 3D surface plot of CF and SCG generated from the TGA-FTIR analyzer is shown in Figure 1a,c; however, the relative amount of volatile gases generated from heating of materials is presented in Figure 1b,d. It was found that most of the volatile products vanished within 18\textasciitilde44 min. The TGA-FTIR analysis of CF and SCG showed substantial differences in generated volatiles due to the difference in the chemical composition of bio-oil (Figure 1b,d). It is imperative to mention that SCG was generated from lignocellulosic feedstock;\textsuperscript{27} however, CF was generated from proteinous feedstock; thus, bio-oil has compositional differences.\textsuperscript{26} The 3D surface plot (Figure 1a,c) of CF and SCG showed an almost similar pattern except for CO and CO\textsubscript{2} peaks in SCG.
The differences arose due to the formation of decarboxylation chemical reactions during pyrolysis. The decarboxylation reaction favored the formation of CO2 by eliminating a carbon atom from a carbon chain. Overall, the peaks 3485 and 3573 cm⁻¹ were attributed to the existence of moisture and alcohol; 2932 and 2930 cm⁻¹ confirmed releases of hydrocarbons; 1768, 1721,1725, and 1769 cm⁻¹ confirmed the release of carbonyl compounds; and 2362 and 2366 cm⁻¹ were attributed to asymmetric vibrations and confirmed the existence of carbon dioxide. The peaks 1113 and 1129 cm⁻¹ connected to the C–O stretching documented the release of ethers during pyrolysis. Moreover, the variations in CO2 amounts may have arisen due to the decarboxylation reaction. Decarbonylation is an organic reaction in which one or two carbonyl groups are removed from the molecules. The removal of moisture/alcohol was found to be 5.96 and 7.37% for SCG and CF, respectively, mainly due to the formation of the dehydration reaction. Finally, the release of ether products was found to be 2.62 and 10.48% for CF and SCG caused by the attendance of an oxygen-bounded compound in the bio-oil. Overall, the TGA-FTIR results of bio-oil are well-matched with the FTIR findings of bio-oil, as discussed in the results and discussion section. Also, it was noticed that the majority of gases released during pyrolysis involved hydrocarbons, carbonyl products, ether, CO, and CO2, along with a minor percentage of water and alcohol. It was stated that the gas evolved during pyrolysis, exposed to TGA-FTIR, was substantially influenced by the particle size of the material. Pyrolysis occurred at the lower heating rate; the weight loss of the samples was lower for larger particles (1 mm) compared to the lower particle size (27 μm). Thus, it was concluded that samples with a bigger particle size (1 mm) produced a higher amount of CO2 at the time of pyrolysis than the smaller particle size of biomass (100 μm).

Thermal Stability Analysis of Bio-oil. The thermal stability profile of CF and SCG is displayed in Figure 2. The thermal decomposition profile of CF and SCG established a three-stage decomposition profile. The first stage confirmed the elimination of moisture and very light volatile compounds up to 100 °C. However, the second stage (100–450 °C) allowed the maximum decomposition of bio-oil; thus, it is identified as an active pyrolytic stage. The moistureless bio-oil mainly contains relatively lower molecular weight products such as carbohydrates, furans, phenols, guaiacols, and syringols. In this stage, the mass-loss rate reached was at its highest value at 218 and 230 °C for SCG and CF, respectively. Also, the maximum decomposition (formation of maximum hot volatiles) of bio-oil occurred in the same stage, typically due to the volatilization of lower molecular weight products. Similar thermal stability results of bio-oil were also reported by many authors that originated from miscellaneous compounds and fragmented at dynamic temperatures. It was also noticed that the temperature beyond 500 °C had only a minimal effect on the weight loss profile of both the bio-oils. Generally, bio-oil is a rich mixture of hydrocarbons, phenolic compounds, acidic products, and oxygenated compounds (ketones, esters, and ethers). Apart from water, bio-oil contains acetic hydroxypropanone, hydroxyacetalddehyde, and levoglucosan. Also, the pyrolysis of lignin produced mainly hydroxy-phenolics, guaiacols, and syringols that decomposed at slightly higher temperatures. The majority of compounds in bio-oil (especially hydrocarbons, acids, and oxygenated
compounds) decomposed below 500 °C; only a few compounds linked with lignin derivatives get converted into biocarbon at temperatures beyond 500 °C.\(^{(35,37)}\) Moreover, the specific types of the products formed from the degradation of cellulose heavily subsidized the generation of secondary char.\(^{(35)}\) However, the higher yield of biocarbon was gained from the decomposition of phenolic rich products and possible extractives and higher molecular weight compounds.\(^{(35)}\) The DTG thermograph confirmed that the maximum decomposition of bio-oil occurred in the wide temperature range from 100 to 350 °C, while the maximum decomposition peak was found at 218 °C for SCG and 230 °C for CF. The wide peak mostly corresponds to the presence of lighter and higher molecular weight compounds such as light aromatics and lower isoeugenol (267 °C), syringol (205 °C), catechol (246 °C), syringol (261 °C), and cresol (200 °C).\(^{(20,37)}\) It was also noticed that the bio-oil comprises around 5–10 wt % organic acids obtained from slow pyrolysis like formic acid, hexadecenoic acid, propionic acid, and acetic acid.\(^{(2,31,36,37)}\) The decomposition of bio-oil arose between 100 and 140 °C, demonstrating the decomposition of typical acids, such as acetic acids (118 °C), formic acid (101 °C), and propionic acid (141 °C). In addition, benzene and toluene also decomposed in the same temperature range.\(^{(20)}\) Further, the bio-oil decomposed in the temperature range 400–500 °C or higher temperatures, indicating the degradation of lignin-based oligomer products in the bio-oil\(^{(38)}\) that ultimately yields biocarbon.

**FTIR Analysis of Bio-oil.** FTIR spectra of CF and SCG are presented in Figure 3. Overall, the FTIR study showed that both the bio-oils have almost similar functional groups; thus, a specific description of bio-oil becomes complex. The band peaks greater than 3000 cm\(^{-1}\) (3192) was ascribed to the −OH stretching vibration and confirmed the water, phenol, and aromatics in the bio-oil.\(^{(39)}\) Further, the peak 1262 cm\(^{-1}\) corresponded to the C–O stretching vibration and endorsed the occurrence of phenol and alcohol.\(^{(20)}\) The band peaks 2920 and 2856 cm\(^{-1}\) were credited to the aliphatic C–H stretching vibration, and peaks 1405 and 1452 cm\(^{-1}\) connected with the C–H bending vibration established the occurrence of alkanes.\(^{(20)}\) The peak 1652 cm\(^{-1}\) allotted to the C=O stretching vibration indicated the occurrence of acid, ketones, aldehyde, and esters.\(^{(20)}\) Finally, the peaks found in the range of 600–900 cm\(^{-1}\) allotted to aromatic the C–H stretching vibration established the occurrence of poly- and monoaromatics in the bio-oil.\(^{(38)}\) Overall, the FTIR findings of CF and SCG confirmed the presence of phenols, aromatics, alcohol, acids, ketones, esters, and aldehyde which which aligns with other findings in the available literature.\(^{(20,25,34)}\)

**Physicochemical Characterization of Biocarbon.** The physicochemical properties of chicken feather bio-oil biocarbon (CFB) and spent coffee ground bio-oil biocarbon (SCGB) obtained at multiple temperatures (400, 600, and 900 °C) are listed in Table 2. It was detected that with an upsurge in temperature from 400 to 900 °C, the yield of biocarbon decreased. The yield of CFB and SCGB was found to be higher (11.27 and 11.64 wt %) at a lower temperature (400 °C) due to the mainly fractional pyrolysis (lower heat and mass transfer between bio-oil).\(^{(19)}\) The term “fractional pyrolysis” refers to the presence of uncooked hydrocarbons in the biocarbon at a lower temperature. However, the yield of biocarbon was found to be lower (9.46 and 7.89 wt % for CFB; 10.11 and 9.26 wt % for SCGB) at higher temperatures (600 and 900 °C), attributed to the complete pyrolysis of bio-oil (higher heat and mass exchange between bio-oil molecules).\(^{(19)}\) The term “complete pyrolysis” refers to the absence of uncooked materials in the biocarbon at a greater temperature. Titiladunayo et al. (2012) pyrolyzed different categories of biomass in a fixed-bed reactor at dynamic temperatures (400, 500, 600, 700, and 800 °C). They stated that with an increase in temperature from 400 to 800 °C, the yield of biocarbon decreased from 37 to 29% due to complete pyrolysis.\(^{(31)}\) The elemental analysis of CFB and SCGB established that the carbon content improved with an upsurge in temperature by the deletion of oxygen molecules from the biocarbon (Table 2).\(^{(31)}\) A similar result was also documented by Arnold et al. (2018) for the pyrolysis of miscanthus bio-oil into biocarbon.\(^{(20)}\) It was also found that the biocarbon gained at a lower temperature (400 °C) had a lower carbon purity as compared with the higher-temperature (600 and 900 °C) biocarbon due to the attendance of unprocessed materials in biocarbon. Also, the elemental analysis of CFB and SCGB results confirmed that the biocarbon has a lower nitrogen content than the bio-oils (CF and SCG) mainly due to the disintegration of proteins leading to the formation of NH\(_3\) and hydrogen cyanide (HCN) by deamination and cyclization reactions.\(^{(42)}\) The ash content of CFB and SCGB confirmed that with an increase in temperature from 400 to 900 °C, the amount of ash content decreased (Table 2) due to the elimination of uncooked materials (possible inorganics like potassium, calcium, sodium, etc.).\(^{(31)}\) It was established that biocarbon has a lower ash content and a higher carbon content and was considered to be a more promising candidate for material applications such as fuel cell, supercapacitor, and biocomposite applications.\(^{(17)}\) Finally, the higher heating value (HHV) of biocarbon was found to be higher than that of other reported biocarbons such as oil palm empty fruit bunch (23 MJ kg\(^{-1}\)) due to the difference in the elemental composition of biocarbon\(^{(31)}\) since the heating value of biocarbon is directly linked to its elemental composition (C, H, N, O, Mg, Si, and S).\(^{(45)}\) More specifically, the biocarbon obtained from the present study is also known as secondary char, formed by the repolymerization reactions of bio-oils. However, the biocarbon gained from the direct
Table 2. Physicochemical Characterization of the Biocarbon (CFB and SCGB) Obtained at Three Different Temperatures and Compared with the Biocarbon Gained from the Pyrolysis of Chicken Feathers and Spent Coffee Ground

| parameters | CFB | SCGB | "chicken feather biocarbon" | "spent coffee ground biocarbon" |
|------------|-----|------|-----------------------------|-------------------------------|
| Temperature (°C) |  |  |  |  |
| 400 |  |  |  |  |
| 600 |  |  |  |  |
| 900 |  |  |  |  |
| Yield (wt %) | 11.27 ± 0.60 | 7.89 ± 0.60 | 9.26 ± 0.80 | 55.50 |
| C (%) | 83.34 ± 0.50 | 87.19 ± 0.34 | 90.14 ± 0.40 | 84.20 ± 0.60 |
| H (%) | 5.18 ± 0.13 | 4.86 ± 0.12 | 3.89 ± 0.12 | 3.14 ± 0.12 |
| O (%) | 7.90 ± 0.82 | 2.13 ± 0.12 | 1.59 ± 0.11 | 2.42 ± 0.40 |
| N (%) | 3.58 ± 0.01 | 5.82 ± 0.80 | 4.38 ± 0.20 | 3.14 ± 0.12 |
| S (%) | 1.47 ± 0.12 | 1.30 ± 0.08 | 1.25 ± 0.03 | 0.66 ± 0.59 |
| HHV (MJ/kg) | 35.75 ± 1.2 | 37.08 ± 1.4 | 36.88 ± 1.2 | 0.19 ± 0.26 |
| ash content (wt %) | 37.37 ± 1.1 | 35.49 ± 1.4 | 36.38 ± 1.4 | 0.19 ± 0.26 |

*Biocarbon is derived from the slow pyrolysis of chicken feathers and spent coffee ground.*
the present study recognized the occurrence of a higher carbon content (90−92%) than reported for other biocarbon, such as miscanthus bio-oil derived biocarbon (79%)\textsuperscript{20} and perennial grass derived biocarbon (78%).\textsuperscript{52} Thermal Stability of Biocarbon. The thermal stability profile of CFB and SCGB at different temperatures (400, 600, and 900 °C) is presented in Figure 4a,b. Figure 4a,b displays that the biocarbon obtained at a higher temperature, such as 900 and 600 °C, has a higher thermal stability than the 400 °C biocarbon. The biocarbon gained at higher temperatures (900 and 600 °C) pyrolyzed completely (removal of oxygen and hydrogen); thus, the thermal stability increased. However, the biocarbon gained at a lower temperature (400 °C) comprised some uncooked impurities that reduced the thermal stability of the biocarbon. Further, it was noticed that the biocarbon obtained at 400 °C possesses thermal stability up to 350 °C with a mass loss of around 3.17 and 3.07% for SCGB and CFB. Similarly, the biocarbon obtained at 600 °C possesses thermal stability up to 590 °C with a mass loss of around 4.67 and 7.85% for SCGB and CFB; however, the biocarbon obtained at 900 °C possesses thermal stability up to 900 °C with a mass loss of around 2 and 3.43% for SCGB and CFB. The overall thermal decomposition profile of biocarbon from 30–900 °C confirmed that the lower-temperature biocarbon (400 °C) showed the highest decomposition of around 34.69 and 36.45% followed by 600 °C (8.83 and 13.89%) and 900 °C (2 and 3.43%) for SCGB and CFB. The lower-temperature biocarbon contains some uncooked impurities (such as hydrocarbons) due to the partial pyrolysis (lower heat and mass transfer) and thus showed a higher decomposition compared to the higher-temperature biocarbon. The DTG analysis of biocarbon showed that the maximum mass loss peak of the 400 and 600 °C biocarbon was found at ∼450 and ∼700 °C for CFB and SCGB, while the 900 °C biocarbon did not show any decomposition peak. A similar decomposition profile of biocarbon was also reported by Arnold et al. (2018)\textsuperscript{20} for miscanthus bio-oil derived biocarbon. It was assumed that pyrolysis causes the development of biocarbon subjected to C=C bonds, extremely opposing at higher temperatures since pyrolysis occurred in the inert environment. The attendance of C=C bonds is usually spotted in biocarbon gained from biomass at a temperature higher than 300 °C.\textsuperscript{20} Moreover, the
agglomeration of biocarbon started after the elimination of O\textsubscript{2} or its related functional groups.\textsuperscript{53} The higher thermal stability of biocarbon was found at the higher-temperature biocarbon (600 and 900 °C) due to the complete pyrolysis (maximum heat and mass transfer), which ultimately confirmed the purest form of carbon that can be seen in the SEM analysis of biocarbon. Similar findings of the decomposition of biocarbon derived at different temperatures were also reported by Mimmo et al. (2014)\textsuperscript{54} and Arnold et al. (2018).\textsuperscript{20} Overall, the biocarbon derived at higher temperature showed a lower mass loss with respect to temperature, which possess more than the stable biocarbon due to the elimination of most of the impurities in the biocarbon.

**FTIR Analysis of Biocarbon.** FTIR spectra of CFB and SCGB are depicted in Figure 5a,b. It was observed that the biocarbon peaks were very different from the FTIR spectra of the bio-oils due to the elimination of most of the functional groups. It was found that the biocarbon has a similar functional group as CF and SCG due to the partial pyrolysis of bio-oil at a lower temperature (400 °C). In this case, most of the compounds in biocarbon remain uncooked, resulting in various functional groups being present. More specifically, the band peaks in the range of 2900–2850 cm\textsuperscript{-1} credited to the aliphatic C–H stretching vibration established the existence of alkanes.\textsuperscript{20} Further, the peak 1225 cm\textsuperscript{-1} related to the C–O stretching vibration endorsed the occurrence of phenol impurities.\textsuperscript{20} The band peaks 1431 and 1437 cm\textsuperscript{-1} connected
fl to the C–H bending vibration established the occurrence of alkanes.20 Finally, the peaks found below 900 cm\(^{-1}\) allotted to the aromatic C–H stretching vibration recognized the existence of poly- and monoaromatic products in the biocarbon.20,47 Also, the biocarbon derived at 600 and 900 °C showed evidence of no peak except for the aliphatic C–H stretching vibration at 2923 cm\(^{-1}\) and the C–H bending vibration at 1437 cm\(^{-1}\), which confirmed the existence of alkanes (hydrocarbon).47 Overall, FTIR spectra of CFB and SCGB have a good agreement with other reports in the literature.20,47 The FTIR investigation of biocarbon demonstrated that the higher temperature based biocarbon engaged with less functional groups.

**Thermal Conductivity (TC), Thermal Conductivity (TD), and Specific Heat (SH) of Biocarbon.** The thermal and electrical conductivity, thermal diffusivity, and specific heat of CFB and SCGB derived at 400, 600, and 900 °C are listed in Table 4. From the results (Table 4), it was noticed that the electrical conductivity of the biocarbon decreased with an increase in temperature from 400 to 900 °C. The alteration appeared due to a disturbance in the interparticle contact between the carbon atoms with an increase in temperature from 400 to 900 °C that resisted the flow of electricity and ultimately reduced the electrical conductivity of biocarbon.55 Similar results were also studied by Arnold et al. (2018) for miscanthus bio-oil derived biocarbon.20 The electrical conductivities were found in the range of 0.00282–0.00412 S m\(^{-1}\) for CFB and 0.00301–0.00432 S m\(^{-1}\) for SCGB. As per the literature, the values reported for these biocarbon are lower compared with those for elemental carbon derived from lignin (0.2 S m\(^{-1}\)) and carbon blacks (4.3 S m\(^{-1}\)), as stated by Snowdon et al. (2014).56 EC of the material is highly reliant on the functional weight; this may be noteworthy for materials experienced at moderately low pressures during the examination and with a wide particle size distribution.57 The materials free from the oxygen-containing functional groups showed better carbon purity; however, biocarbon obtained at the higher temperature favors aggregation. Marinho et al. (2012) established that the functional weight has a positive impact on the graphene; however, the surface area has a better impact on the carbon blacks.58 They also confirmed that the electrical conductivity declines with an increase in temperature. EC of the biocarbon greatly relied on the degree of the carbonization, with a small percentage increase in the content of carbon can lead to many orders of magnitude growth in EC. Also, the EC of the biocarbon mainly depends on the sp\(^2\) electron configuration (e.g., graphite and graphene). The biocarbon has an sp\(^2\) electron configuration and showed an increased EC, whereas the biocarbon that was not enriched with an sp\(^2\) electron configuration showed a reduced EC.59 However, the presence of a higher amount of carbon content or sp\(^2\) electron configuration alone cannot improve the EC of biocarbon, as proven by Gabhi et al. (2017); there are some other important factors such as porosity, particle size, ash content, and aromatization degree that also control the EC of biocarbon.60

The thermal conductivity (TC), thermal diffusivity (TD), and specific heat (SH) of CFB and SCGB, obtained at three temperatures is 0.231 ± 0.001147 W m\(^{-1}\) K\(^{-1}\) for CFB and 0.2621 ± 0.001724 W m\(^{-1}\) K\(^{-1}\) for SCGB. The obtained results for biocarbon are very close to those for amorphous carbon (0.01–2 W m\(^{-1}\) K\(^{-1}\)) and carbon black (0.492 W m\(^{-1}\) K\(^{-1}\)).62 Table 4 data showed that the thermal diffusivity of biocarbon increased with an increase in temperature as the thermal diffusivity of biocarbon is directly linked with TC, implying that if TC of the biocarbon increased, thermal diffusivity of biocarbon would also increase. The specific heat of the biocarbon decreased with an increase in temperature from 400 to 900 °C because of the presence of ash content in the individual biocarbon.63 The ash content comprised a considerably lower specific heat than that of charcoal, thus decreasing the specific heat of the biocarbon.

### Table 4. Thermal Conductivity, Electrical Conductivity, Thermal Diffusivity, and Specific Heat of CFB and SCGB

| Temperature (°C) | Electrical conductivity (S m\(^{-1}\)) | Thermal conductivity (W m\(^{-1}\) K\(^{-1}\)) | Thermal diffusivity (mm\(^2\) s\(^{-1}\)) | Specific heat (MJ m\(^{-3}\) K\(^{-1}\)) | References |
|-----------------|--------------------------------------|---------------------------------------------|--------------------------------------|----------------------------------------|------------|
| 400             | 0.00412 ± 8.445E-05                  | 0.2311 ± 0.001147                          | 0.0915 ± 0.002010                    | 3.142 ± 0.002214                      | present work |
| 600             | 0.00325 ± 3.840E-05                  | 0.2621 ± 0.001724                          | 0.0927 ± 0.002042                    | 2.521 ± 0.049984                      | present work |
| 900             | 0.00282 ± 5.695E-05                  | 0.2912 ± 0.002614                          | 0.0954 ± 0.001517                    | 2.314 ± 0.091054                      | present work |
| CFB             |                                       |                                              |                                      |                                        |            |
| 400             | 0.00432 ± 6.334E-05                  | 0.2176 ± 0.001132                          | 0.0879 ± 0.001654                    | 3.658 ± 0.002214                      | present work |
| 600             | 0.00346 ± 5.225E-05                  | 0.2865 ± 0.001654                          | 0.0901 ± 0.001125                    | 2.836 ± 0.004024                      | present work |
| 900             | 0.00301 ± 5.256E-05                  | 0.3122 ± 0.002242                          | 0.0915 ± 0.005147                    | 2.705 ± 0.072315                      | present work |
| coal            | 0.26                                 | 0.15                                       | 1.70                                 |                                        |            |
| carbon black    | 4.30                                 | 0.49                                       | 2.94                                 | 0.16                                   | Snowdon et al. (2014) |

Raman Analysis of Biocarbon. Raman spectra of CFB and SCGB biocarbon are demonstrated in Figure 6a,b. Raman spectra were examined from 800 to 2000 cm\(^{-1}\) to estimate the content of graphitization in both biocarbon samples; the ratio of \(I_D/I_G\) is presented in Table 5. For the analysis of graphitization content in both biocarbons, two peaks were nominated. The maximum peaks 1354–1357 cm\(^{-1}\) and 1568–1575 cm\(^{-1}\) for the D and G bands were observed in biocarbons. Similar outcomes were also stated by Li et al. (2020) for the chicken feather biocarbon.67 Reports from the literature were reflected in the sample, as the band peak D is attributed to the sp\(^2\) orbital and displayed a disturbed content, while the band peak G is attributed to the sp\(^2\) orbital of the graphitic content. The band peak I_D is linked with C–C bonds.
Figure 6. Raman spectroscopy analysis of (a) CFB and (b) SCGB at 400, 600, and 900 °C.
Table 5. Raman Spectra of CFB and SCGB at 400, 600, and 900 °C

| Sample name | Temperature | \(I_D/I_G\) |
|-------------|-------------|-------------|
|              | 400 °C      | 600 °C      | 900 °C      |
| CFB          | 0.852       | 0.861       | 0.868       |
| SCGB         | 0.857       | 0.861       | 0.864       |

established in the aromatic rings. The peak \(I_D\)’s indicate that the relative strength is associated with the higher content of carbon in the biocarbon, as supported by the well-known study of biocarbon. Further, peak \(I_G\) demonstrated a \(\text{C}=\text{C}\) bond attributed to the link of the aromatic structure, which is also supported by the FTIR study of biocarbon. The \(I_D/I_G\) ratio has been presented to designate the massive aromatic groups in amorphous carbon. The higher value of the \(I_D/I_G\) ratio demonstrated that the sample is enriched with a greater amount of aromatic groups. The ratios of \(I_D/I_G\) for CFB and SCGB were found to be 0.852, 0.861, and 0.868 and 0.857, 0.861, and 0.864, respectively, at 400, 600, and 900 °C, which were lower than the \(I_D/I_G\) ratios of chicken feather biocarbon (1.06 and 1.07 at 300 and 600 °C, respectively). The lower value of the \(I_D/I_G\) ratio demonstrated the higher graphitization of biocarbon (greater order of the carbon structure). Although the graphitic content of biocarbon was found to be greater than that of the chicken feather biocarbon, it needs further upgradation to meet the standards of commercially available graphitic carbon.

Scanning Electron Microscopy (SEM) and Particle Size Analysis of Biocarbon. The morphological characteristics of CFB and SCGB gained at three different temperatures (400, 600, and 900 °C) are shown in Figure 7a.b. The morphology study of biocarbon becomes multifaceted by the clustering of innumerable minerals. At the same time, different types of multifaceted chemical reactions such as dehydration (removal of moisture), decarbonylation (removal of CO), decarboxylation (loss of carboxyl group) are formed, which altered the biocarbon morphology. The SEM analysis of CFB and SCGB showed a usual surface design and some small pores due to the release of various hot volatiles during pyrolysis. Additionally, the pores and surface structure of biocarbon were changed by fluctuating the operating conditions of pyrolysis, especially temperatures. The SEM image showed that the biocarbon obtained at a higher temperature, such as 900 °C compared with 600 °C, showed bigger and harder particles with a smooth structure for CFB and SCGB. Similarly, the biocarbon gained from 600 °C showed better and bigger particles with a harder and smoother surface than the 400 °C biocarbon. The SEM image of the biocarbon obtained at 400 °C showed usually rough surface structure, small active pores, and slightly soft particles. This alteration appeared probably due to the pyrolysis of bio-oil at elevated temperatures. It yielded a purer and much more thermally stable carbon due to the elimination of hydrogen and oxidized products (TGA and FTIR results also lent support). Additionally, the interaction of molecules among all the carbon particles in the non-attendance of oxygen and hydrogen will boost the alignment and shape of the biocarbon.

The particle size study of CFB and SCGB at temperatures of 400, 600, and 900 °C is listed in Table 6. It is imperative to declare that the particle size of biocarbon was achieved with an image analysis tool like SEM due to the irregular shapes of biocarbon. The particle size of biocarbon was analyzed with 2 h ball milling. The ball mill was used in this study to reduce the size of biocarbon particles. It was found that the biocarbon produced at a lower temperature (400 °C) is easy to break into smaller particles due to the lower thermal stability (carbon bond associated with a weaker bond); however, the biocarbons produced at higher temperatures (600 and 900 °C) are slightly tough to break due to the higher thermal stability (carbon bond associated with a strong bond interaction). From the results (Table 6), it was noted that the average particle size of biocarbon was found to be 2.18 and 2.17 μm at 400 °C, 2.18 and 1.74 μm at 600 °C, and 2.34 and 1.66 μm at 900 °C for CFB and SCGB, respectively. However, the median particle size of biocarbon was found to be 1.72 and 1.77 μm at 400 °C, 1.75 and 1.39 μm at 600 °C, and 1.65 and 1.31 μm at 900 °C for CFB and SCGB, respectively. The maximum size of the particle was found to be 12.58 and 11.33 μm at 400 °C, 17.55 and 11.74 μm at 600 °C, and 17.47 and 13.40 μm at 900 °C for CFB and SCGB, respectively. Among all the tested biocarbons, the biocarbon gained at 400 °C provided a higher percentage of nanocarbons (<500 nm) due to the increased breaking of bigger particles into smaller particles as compared with the higher-temperature biocarbon (Table 6). It was also noticed that the maximum number of the particles was found to be in the 1 μm range (<2 μm) followed by 2 μm (<3 μm) and 3 μm (<4 μm). Overall, the particle size analysis of the CFB and SCGB biocarbon confirmed that the majority of the particles lie within the 1 μm range.

## CONCLUSIONS

The present study established the production of value-added biocarbon through the slow pyrolysis of waste bio-oil that can be used for different industrial applications such as fuel cells, supercapacitors, catalysts, and biocomposite materials. Although the pyrolysis of bio-oil is still not a fully recognized technology yet, the recovery of valuable products (biocarbon) from the bio-oil offers a decent alternative to manage the bio-oil waste. Overall, the pyrolysis results confirmed that the properties and yield of biocarbon are directly influenced by pyrolysis temperatures. The yield of biocarbon decreased (11.27 to 789 wt % for CFB and 12.64 to 9.26 wt % for SCGB) with an increase in temperature from 400 to 900 °C due to the higher heat and mass transfer during pyrolysis. Further, the elemental study of biocarbon confirmed the significant enhancement in carbon content (83.34 to 91.20 wt % for CFB and 84.20 to 91.20 wt % for SCGB) and substantial reduction in hydrogen content (5.18 to 3.89 wt % and 5.77 to 3.14 wt % for CFB and SCGB) with an increase in temperature from 400 to 900 °C. The thermal stability study of biocarbon confirmed that maximum decomposition occurred at the lower-temperature biocarbon (400 °C) followed by 600 and 900 °C. The FTIR study of biocarbon established the occurrence of alkanes and aromatic products, whereas a high graphitic content was found in the high-temperature biocarbon (900 °C) as confirmed by the Raman spectroscopy analysis. The surface morphology of biocarbon established that the higher-temperature biocarbons (600 and 900 °C) showed smooth surface properties, with a larger particle size than the lower-temperature biocarbon (400 °C), due to the removal of most of the impurities from the biocarbon. The electrical conductivity of biocarbon decreased, whereas the thermal conductivity increased, with an increase in pyrolysis temperatures. Finally, the majority of the particle sizes of biocarbon were in the range of 1 μm, as confirmed by the particle size.
Figure 7. SEM image of (a) CFB and (b) SCGB at 400, 600, and 900 °C.
analysis. The overall characterization results of bio-oil based biocarbon showed enhanced properties compared to biocarbon produced from biomass, demonstrating an outstanding material to be used for different applications.

## MATERIALS AND METHODS

### Sample Collection and Preparations

The crude bio-oil of spent coffee ground (SCG) and chicken feathers (CF) was collected from our laboratory (Bioproducts Discovery and Development Centre) for further pyrolysis to find their value-added uses. The phase separation of bio-oil was done individually for both the bio-oils. For that, the collected bio-oil was placed in a separating funnel overnight. The organic phase (bio-oil) was converted into biocarbon through slow pyrolysis.

**Physicochemical Characterization.** The elemental composition of bio-oil and biocarbon was estimated via an organic elemental analyzer (FLASH 2000, Thermo Fisher Scientific Inc., USA) using ASTM D5373. However, the oxygen content was figured out by the difference. Further, the ash content of bio-oil (SCG and CF) and biocarbon (SCGB and CFB) was determined using the ASTM D1762-84 method in a thermogravimetric analyzer (TGA), whereas the acidity was quantified with a pH meter (Eutech waterproof, pH Spear). The higher heating value (HHV) of bio-oil and biocarbon was figured out with the Dulong formula (eq 1) based on the elemental composition of samples.

\[
HHV (\text{MJ/kg}) = 32.7934 + 0.5321 C^2 - 0.5321 C - 2.8769 H + 0.608 CH - 0.2401 N
\]

where HHV = higher heating value, \( C \) = carbon, \( H \) = hydrogen, and \( N \) = nitrogen.

**Thermal Stability Analysis of Bio-oil and Biocarbon.** The thermal stability examination of bio-oil (SCG and CF) and biocarbon (SCGB and CFB) was achieved in a thermogravimetric analyzer (Q500, TA-Instruments, New Castle, Delaware, USA). The desired quantity of the sample was fed into the platinum crucible and heated from 30 to 900 °C at 20 °C min⁻¹ heating rate with 50 mL min⁻¹ flow rate of nitrogen. Further, the relative absorbance of the individual volatiles was estimated by using the Gram-Schmidt software.

**Pyrolysis Experiment.** The pyrolysis of bio-oil was conducted in a horizontal tube furnace (Carbolite 1200 °C G-range). The experimental setup comprises a control panel (to control the heating rate, temperature, and holding time), ceramic boat, stopper, quartz tube, nitrogen cylinder, and rotameter to measure the flow rate of gas. For each pyrolysis experiment, 8 ± 0.10 g of bio-oil was placed in the ceramic boats and placed in the ceramic tube. One end of the tube furnace was coupled with nitrogen gas, and the other end was used as an outlet of nitrogen and hot volatiles. The flow rate of nitrogen gas was held constant (~1.5 standard liter per minute (SLPM)) throughout the experiment; however, nitrogen gas was purged 10 min before starting the experiment to evacuate the unwanted gases from the reactor. The PID controller was connected to the furnace. The furnace is designed to distribute heat across the tube uniformly, with the assumption of no heat loss. The pyrolysis experiment of both bio-oils was achieved at three temperatures (400, 600, and 900 °C) and 10 °C min⁻¹ heating rate, while the holding time was kept at 30 min. The temperature selection of the pyrolysis experiment was optimized as per the thermal stability profile of bio-oil (Figure 2) and existing literature. Arnold et al. (2018) studied the effect of temperature and heating rate on the yield and properties of biocarbon at two temperatures (600 and 900 °C). They were not able to draw any conclusions about the properties of biocarbon at a lower temperature (less than 600 °C); thus, this study was carried out at 400, 600, and 900 °C. The holding time is the time in which the pyrolysis temperature attains equilibrium (complete pyrolysis of bio-oil). To ensure the accuracy of biocarbon yield, the pyrolysis experiment was performed twice at each temperature. At the completion of the test, the reactor was cooled up to room temperature (25–30 °C); thereafter, the biocarbon was removed and stored in an airtight glass jar. A complete

### Table 6. The Particle Size Distribution of CFB and SCGB at 400, 600, and 900 °C

| sample | average particle size (μm) | median particle size (μm) | aspect ratio | <500 nm | <800 nm | <1 μm | <2 μm | <3 μm | <4 μm | <5 μm | <6 μm | <7 μm | <8 μm | <9 μm | cumulative percentage (%) | max. size particle detected (μm) |
|--------|--------------------------|--------------------------|--------------|--------|--------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-----------------------------|---------------------------|
| SCGB   | 400                      | 2.18                      | 1.72         | 0.657  | 0.557  | 1.23  | 7.265 | 57.23 | 20.256 | 4.856  | 3.345 | 1.86  | 1.356 | 1.89  | 12.58 μm                     |
|        | 600                      | 2.27                      | 1.75         | 0.659  | 0.415  | 0.839 | 6.327 | 52.643| 20.731 | 8.153  | 4.634 | 2.509 | 1.489 | 2.225 | 17.55 μm                     |
|        | 900                      | 2.34                      | 1.65         | 0.670  | 0.208  | 5.234 | 9.146 | 45.635| 18.316 | 7.954  | 5.224 | 2.751 | 1.544 | 3.788 | 17.97 μm                     |
| CFB    | 400                      | 1.77                      | 0.667        | 0.623  | 0.261  | 6.521 | 11.926| 55.118| 14.116 | 6.588  | 2.015 | 1.023 | 0.259 | 2.056 | 11.33 μm                     |
|        | 600                      | 1.39                      | 0.681        | 0.531  | 0.825  | 14.313| 49.375| 16.192| 6.219  | 2.328  | 1.356 | 0.452 | 1.008 | 11.74 μm                    |
|        | 900                      | 1.31                      | 0.659        | 0.427  | 13.406 | 16.731| 45.859| 13.924| 5.278  | 1.962  | 0.873 | 0.599 | 0.845 | 13.40 μm                    |
schematic outline of the experimental setup is demonstrated in Figure 8.

![Experimental Setup Diagram](https://pubs.acs.org/10.1021/acsomega.1c01743)

Figure 8. Schematic arrangement of the pyrolysis experimental setup.

Finally, the yield of biocarbon was calculated using eq 2.

\[
\% \text{Yield of biocarbon} = \left( \frac{\text{solid material left after the pyrolysis}}{\text{weight of bio-oil}} \right) \times 100
\]  

(2)

Furthermore, the biocarbon was placed in the ball mill (Retsch Planetary Ball Mill PM 100, Retsch Co., Germany) for 2 h at 200 rpm using grinding balls to reduce the particle size of biocarbon.69 The milled samples were collected and stored in the glass vials to stop moisture absorption for further analysis.

Raman Analysis. The Raman spectra of biocarbon (CFB and SCGB) were recorded by a Raman spectrometer (Thermo Scientific, USA). For the analysis of each spectrum, a 785 nm laser was employed at 200 mW. A Raman study was applied to compute the relative quantity of graphitic against disordered carbon in the materials. A Raman instrument was used at 10 times zoom via a 50 μm slit. The exported data in Excel format from the Raman study were used in the Originlab software to study the graphitic content of biocarbon using two-peak fitting. The two-peak fitting of biocarbon yielded a correction coefficient \( R^2 \) value greater than 0.97 in each case; thus, we have chosen only two-peak fitting.

Electrical Conductivity (TC), Thermal Conductivity (TC), and Specific Heat (SH) Analysis of Biocarbon. The electrical conductivity of biocarbon (CFB and SCGB) was determined with an Autolab PGSTAT302N (Netherlands). The powder sample of biocarbon (2-h ball mill) was filled in the clear hollow cylinder (10 mm diameter). The piston had a 1 kg weight placed on top of the cylinder without pressing down and allowed 30–40 s for compressing the biocarbon. The device was connected to the electrodes, while the electrodes were connected to the machine. The thermal conductivity, diffusivity, and specific heat were estimated through the ThermTest Hot Disk TPS 500 Thermal Constants Analyzer. For the analysis, power of heating, frequency, time, and sensor radius were selected as 120 mW, 60 Hz, 80 s and 6 mm, respectively.

Scanning Electron Microscopy/Energy-Dispersive Spectroscopy (SEM-EDS) and Particle Size Analysis of Biocarbon. The particle size and morphology study of biocarbon (SCGB and CFB) at three temperatures (400, 600, and 900 °C) was performed in a scanning electron microscope (SEM, Phenom ProX electron microscope scanner, Phenom-World BV, Eindhoven, Netherlands) attached to an energy-dispersive spectroscopy (EDS). The SEM analysis of biocarbon was done without any surface coating. The SEM image was captured at 10 kV accelerating voltage. Further, EDS was used for the elemental analysis of biocarbon at 10 kV with a gathering time of 90 s. For particle size analysis, the number of images (maximum 4) was recorded with varying magnifications to capture different sizes of particles; the average value is reported in this study. The recorded images were analyzed with the particle size analysis application (version 1.0.346.44124) of Phenom-World B.V. to capture the shape and particle size of each image. The number of particles in the image was usually recorded as more than 1000 particles.

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Notes

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■ NOMENCLATURE

CF chicken feather bio-oil
SCG spent coffee ground bio-oil
REFERENCES

(1) Akhtar, J.; Amin, N. S. A review on operating parameters for optimum liquid oil yield in biomass pyrolysis. Renew. Sustain. Energy Rev. 2012, 16, 5101−5109.
(2) Mohan, D.; Pittman, C. U., Jr.; Steele, P. H. Pyrolysis of wood/biomass for bio-oil: a critical review. Energy Fuels 2006, 20, 848−889.
(3) Beran, M.; Axelson, L. Application of pyrolysis oil in the OP16 gas turbine—development of a low caloric fuel combustor. PyNe News 2014, 35, 16−17.
(4) Czernek, S.; Bridgwater, A. V. Overview of applications of biomass fast pyrolysis oil. Energy Fuels 2004, 18, 590−598.
(5) Bridgwater, A. V. Biomass fast pyrolysis. Therm. Sci. 2004, 8, 21−50.
(6) Surup, G. R.; Nielsen, H. K.; Grosof, M.; Deike, R.; Van den Bulcke, J.; Kibler, P.; Müller, M.; Ziegner, M.; Yazhenshik, E.; Beloshapkin, S. Effect of operating conditions and feedstock composition on the properties of manganese oxide or quartz charcoal pellets for the use in ferroalloy industries. Energy 2020, 193, 116736.
(7) Toth, P.; Vikström, T.; Molinder, R.; Wiimikk, H. Structure of carbon black continuously produced from biomass pyrolysis oil. Green Chem. 2018, 20, 3981−3992.
(8) Elliott, D. C.; Neuenschwander, G. G.; Hart, T. R. Hydro-processing bio-oil and products separation for coke production. ACS Sustainable Chem. Eng. 2013, 1, 389−392.
(9) Mishra, R. K.; Mohanty, K. Thermocatalytic conversion of non-edible Neem seeds towards clean fuel and chemicals. ACS Chem. Energy Convers. Manage. 2018, 598, 1228−5.
(10) Boland, M.; Ziegner, M.; Yazhenshik, E.; Eibl, M.; Fassbender, F.; Schillinger, U.; Zschenderlein, P. A technique for monitoring volatile organic compound emissions from wood−plastic composites. Indoor Built Environ. 2018, 27, 194−204.
(11) Scully, D.; Jaiswal, A.; Abu-Ghannam, N. An investigation into spent coffee waste as a sustainable source of bio-composites and industrially important sugars. Bioeng. 2016, 3, 33.
(12) Zhang, S.; Yang, X.; Zhang, H.; Chu, C.; Zheng, K.; Ju, M.; Liu, L. Liquefaction of biomass and upgrading of bio-oil: a review. Molecules 2019, 24, 2250.
(13) Mishra, R. K.; Mohanty, K.; Wang, X. Pyrolysis kinetic behavior and Py-GC−MS analysis of waste tea flowers into renewable fuel and value-added chemicals. Fuel 2020, 260, 116338.
(14) Watt, E.; Abdelwahab, M. A.; Snowden, M. R.; Mohanty, A. K.; Khalil, H.; Misra, M. Hybrid biocomposites from polypropylene, sustainable biocarbon and graphene nanoplatelets. Sci. Rep. 2020, 10, 1−13.
(15) Mishra, R. K.; Kumar, V.; Mohanty, K. Pyrolysis kinetics behaviour and thermal pyrolysis of Samanea saman seeds towards the production of renewable fuel. J. Energy Inst. 2020, 93, 1148−1162.
(16) Gautam, R.; Vinu, R.; Vaitlyathanan, P. Analytical fast pyrolysis of nutrient-rich mosquito species via pyrolysis−FTIR and pyrolysis−GC/MS. J. Anal Appl Pyroly. 2020, 146, 104766.
(17) Surippaarao, D. V.; Vinu, R. Effects of biomass particle size on slow pyrolysis kinetics and fast pyrolysis product distribution. Waste Biomass Valor. 2018, 9, 465−477.
(18) Xiu, S.; Rojanala, H. K.; Shahbazi, A.; Fini, E. H.; Wang, L. Pyrolysis and combustion characteristics of Bio-oil from swine manure. 2012, 102 (7), 823−829.
(19) Branca, C.; Di Blasi, C.; Elefante, R. Devolatilization of conventional pyrolysis oils generated from biomass and cellulose. Energy Fuels 2006, 20, 2253−2261.
(20) Branca, C.; Blasi, C. D.; Elefante, R. Devolatilization and heterogeneous combustion of wood fast pyrolysis oils. Ind. Eng. Chem. Res. 2005, 44, 799−810.
(21) Asadullah, M.; Rahman, M. A.; Ali, M. M.; Rahman, M. S.; Motin, M. A.; Sultan, M. B.; Alam, M. R. Production of bio-oil from fixed bed pyrolysis of bagasse. Fuel 2007, 86, 2514−2520.
(22) Xiu, S.; Shahbazi, A. Bio-oil production and upgrading research: A review. Renew. Sustain. Energy Rev. 2012, 16, 4406−4414.
(23) Mishra, A.; Kumari, U.; Turlapati, V. Y.; Siddiqi, H.; Meikap, B. C. Extensive thermogravimetric and thermo-kinetic study of waste motor oil based on iso-conversional methods. Energy Convers. Manage. 2020, 221, 113194.
(40) Trubetskaya, A.; Johnson, R.; Monaghan, R. F. D.; Ramos, A. S.; Brunsvik, A.; Wittgens, B.; Han, Y.; Pisano, L.; Leahy, J. J.; Budarin, V. Combined analytical strategies for chemical and physical characterization of tar from torrefaction of olive stone. Fuel 2021, 291, 120086.

(41) Titiladunayo, I. F.; McDonald, A. G.; Fapetu, O. P. Effect of temperature on biochar product yield from selected lignocellulosic biomass in a pyrolysis process. Waste Biomass Valori. 2012, 3, 311–318.

(42) Debiagi, P. E. A.; Trinchera, M.; Frassoldati, A.; Faravelli, T.; Vinu, R.; Ranzi, E. Algae characterization and multistep pyrolysis mechanism. J. Anal. Appl. Pyrol. 2017, 128, 423–436.

(43) Zhao, S.-X.; Da, N.; Wang, X.-D. Effect of temperature on the structural and physicochemical properties of biochar with apple tree branches as feedstock material. Energies 2017, 10, 1293.

(44) Idiris, J.; Shirai, Y.; Anduo, Y.; Ali, A. A. M.; Othman, M. R.; Ibrahim, I.; Husen, R.; Hassan, M. A. Improved yield and higher heating value of biochar from oil palm biomass at low retention time under self-sustained carbonization. J. Cleaner Prod. 2015, 104, 475–479.

(45) Phounglamcheik, A.; Wang, L.; Romar, H.; Kienzl, N.; Broström, M.; Ramser, K.; Skeirepig, O.; Umeki, K. Effects of Pyrolysis conditions and feedstocks on the properties and gasification reactivity of charcoal from woodchips. Energy Fuels 2020, 34, 8353–8365.

(46) Paulsen, A. D., Primary and secondary reactions of cellulose melt pyrolysis. 2014.

(47) Li, Z.; Reimer, C.; Picard, M.; Mohanty, A. K.; Misra, M. Characterization of chicken feather biochar for use in sustainable biocomposites. Front. Mater. Sci. 2020, 7, 3.

(48) Zarrinbaksh, N.; Wang, T.; Rodriguez-Uribe, A.; Misra, M.; Mohanty, A. K. Characterization of wastes and coproducts from the coffee industry for composite material production. BioResources 2016, 11, 7637–7653.

(49) Edreis, E. M. A.; Yao, H. Kinetic thermal behaviour and evaluation of physical structure of sugar cane bagasse char during non-isothermal steam gasification. J. Mater. Res. Technol. 2016, 5, 317–326.

(50) Fu, P.; Yi, W.; Bai, X.; Li, Z.; Hu, S.; Xiang, J. Effect of temperature on gas composition and char structural features of pyrolyzed agricultural residues. Bioresour. Technol. 2011, 102, 8211–8219.

(51) Rafiq, M. K.; Bachmann, R. T.; Rafiq, M. T.; Shang, Z.; Joseph, S.; Long, R. Influence of pyrolysis temperature on physico-chemical properties of corn stover (Zea mays L.) biochar and feasibility for carbon capture and energy balance. PLoS One 2016, 11, No. e0156894.

(52) Behazin, E.; Misra, M.; Mohanty, A. K. Sustainable biochar from pyrolyzed perennial grasses and their effects on impact modified polypropylene biocomposites. Compos. B. Eng. 2017, 118, 116–124.

(53) Kelluweit, M.; Nico, P. S.; Johnson, M. G.; Kleber, M. Dynamic molecular structure of plant biomass-derived black carbon (biochar). Environ. Sci. Technol. 2010, 44, 1247–1253.

(54) Mimmo, T.; Panzacchi, P.; Baratieri, M.; Davies, C. A.; Tonon, G. Effect of pyrolysis temperature on miscanthus (Miscanthus giganteus) biochar physical, chemical and functional properties. Biomass Bioenergy 2014, 62, 149–157.

(55) Kwon, J. H.; Park, S. B.; Ayrimlis, N.; Oh, S. W.; Kim, N. H. Effect of carbonization temperature on electrical resistivity and physical properties of wood and wood-based composites. Compos. B. Eng. 2013, 46, 102–107.

(56) Snowdon, M. R.; Mohanty, A. K.; Misra, M. A study of carbonized lignin as an alternative to carbon black. ACS Sustainable Chem. Eng. 2014, 2, 1257–1263.

(57) Celzard, A.; Marelle, J. F.; Payot, F.; Furdin, G. Electrical conductivity of carbonaceous powders. Carbon 2002, 40, 2801–2815.

(58) Marinho, B.; Ghislandi, M.; Tkalya, E.; Koning, C. E.; de With, G. Electrical conductivity of composites of graphene, multi-wall carbon nanotubes, carbon black, and graphite powder. Powder Technol. 2012, 221, 351–358.

(59) Gabhi, R. S.; Kirk, D. W.; Jia, C. Q. Preliminary investigation of electrical conductivity of monolithic biochar. Carbon 2017, 116, 435–442.

(60) Gabhi, R.; Basile, L.; Kirk, D. W.; Giorgelli, M.; Tagliaferro, A.; Jia, C. Q. Electrical conductivity of wood biochar monoliths and its dependence on pyrolysis temperature. Biochar 2020, 2, 369–378.

(61) Smith, W. R.; Wilkes, G. B. Thermal conductivity of carbon blacks. Ind. Eng. Chem. Res. 1944, 36, 1111–1112.

(62) Balandin, A. A. Thermal properties of graphene and nanostructured carbon materials. Nat. Mater. 2011, 10, 569–581.

(63) Quosai, P.; Anstey, A.; Mohanty, A. K.; Misra, M. Characterization of biocarbon generated by high-and low-temperature pyrolysis of soy hulls and coffee chaff: For polymer composite applications. R. Soc. Open Sci. 2018, 5, 171970.

(64) Li, X.; Hayashi, J.-I.; Li, C.-Z. FT-Raman spectroscopic study of the evolution of char structure during the pyrolysis of Victorian brown coal. Fuel 2006, 85, 1700–1707.

(65) Zhang, J.; Huang, Z.-H.; Lv, R.; Yang, Q.-H.; Kang, F. Effect of growing CNTs onto bamboo charcoals on adsorption of copper ions in aqueous solution. Langmuir 2009, 25, 269–274.

(66) Yargicoglu, E. N.; Sadasivam, B. Y.; Reddy, K. R.; Spokas, K. Physical and chemical characterization of waste wood derived biochars. Waste Manage. 2015, 36, 256–268.

(67) Mishra, R. K.; Mohanty, K. Fuel properties and compositional analysis of Areca catechu sawdust over MgO and ZSM-5 catalysts. J. Energy Inst. 2021, 94, 252–262.

(68) Nhuchhen, D.; Afzal, M. HHV predicting correlations for torrefied biomass using proximate and ultimate analyses. Bioengineering 2017, 4, 7.

(69) Peterson, S. C.; Jackson, M. A.; Kim, S.; Palmquist, D. E. Increasing biochar surface area: Optimization of ball milling parameters. Powder Technol. 2012, 228, 115–120.