

Influence of Thermal and Morphological Behaviour on Biomass Waste Materials during Pyrolysis

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Abstract. Aim of this study to investigate the thermal and morphological behaviour of different types of biomass feedstock. For investigation of thermal behaviour we used thermo-gravimetric (TG) analysis and derivative thermo-gravimetric (DTG) analysis. The biomass feedstocks were conceded out under vigorous conditions using nitrogen gas at specific heating rates to gradient the temperature from 25°C to 1000°C. The derivative thermo-gravimetric (DTG) results show that thermal decomposition on these feedstocks. First-order reaction model were used to determine the kinetics parameters for the pyrolysis of biomass wastes. This study used Field Emission Scanning Electron Microscopy (FE-SEM) to observe surface morphology properties of the different biomass wastes. The FE-SEM images showed that clearly retained the fibrous structures in the biomass wastes and were rich in macro-pores.

1 Introduction

The raising the energy demand secured with the necessity to minimise the GHG radiation and the threat of reducing fossils fuel reserves has carried into emphasis on the alternative renewable source of energy. Among the various renewable energy sources, biomass has the potential to be used as alternative source of energy with zero emissions.

Developed and developing countries have already encompassed the exceptional idea of usage of biomass [1] and are quiet depending on accessibility of natural resources including coal gas and oil.

Biomass can be transformed into the various forms of energy using different treatments [2]. The knowledge on thermal properties of the different biomass gives better support to comprehend on thermochemical processes at industrial scale [3]. Other investigators have estimated these properties including motile parameters on biomass under ideal conditions [2, 4-7]. Utilization of biomass wastes in energy production is very important because the depletion of fossil fuels. It would also be a very effective way for the removal of bio-waste, which occupies humongous volumes when disposed to a landfill [8] and direct burning of these wastes emits GHG emissions into the environment.

Pyrolysis is one of the thermo-chemical processes that are conducted at high temperatures in the absence of air (oxygen). Throughout the pyrolysis process,

biomass is converted into solid, liquid and gaseous products based on heating rates, time and temperature [9]. Hence we can say that energy generated from biomass has a high capacity to bridge the global energy shortage gap caused by the depletion of fossil fuel resources while keeping environmental sustainability.

‘Thermo-gravimetric’ (TG) and ‘derivative thermo-gravimetric’ (DTG) analysis is the most operational method to compare the thermal kinetics and trials during the thermochemical process such as combustion and pyrolysis [10-14]. It determines the weight loss percentage of sample as a function between time and temperature. The decomposition reactions can takes place in the testing sample start by TGA at given temperature [15-18].

It is important to comprehend that how the morphological characteristics are influenced by different biomass feedstocks with different pyrolysis conditions. Field Emission Scanning Electron Microscopy (FE-SEM) provides a shortest way to detect the surface structure and mineral distribution of biomass and their corresponding char [19-21].

This study demonstrates the comparative effects of heating temperature (400, 600, 800 and 1000°C) on the physiognomies of bio-chars Thermo-gravimetric and morphological analysis were used for this study.

2 MATERIALS AND METHODOLOGY

2.1 Biomass materials and Preparation of Biochar

Figures Biomass samples mainly used for this study are Tea Wastes (TW), Coconut Shell (CS) and Eucalyptus Shell (ES). The parameters like feedstock type and heating profile (i.e. pyrolysis temperature) have been frequently recognised as important variables for determining the composition and characteristics of produced bio-char [22-25]. Besides, the significance of pyrolysis time during biochar production is less conclusive due to a limited number of studies varying these conditions. Therefore detailed investigations would aid in reaching a definitive conclusion on the importance and preferred value for these variables. The heating temperature range studied throughout the experimental work covered a range from 400°C to 1000°C. This temperature choice covered the main regions of biomass degradation as well as the respective upper and lower limits of temperatures associated with slow pyrolysis at slow heating rate (15-25°C/min) [26]. A low heating rate was selected to provide longer heating time in an attempt to provide tolerable time for sufficient heat transfer and heat penetration into the biomass particles. Based on realistic times seen in industrial sized units to generate fast conversion of feedstock to biochar, the residence times chosen were therefore 60 minutes.

2.2 Methodology

2.2.1 Proximate and ultimate analyses and higher heating value (HHV)

“Proximate analysis” was employed on selected and prepared materials for the estimation of physiochemical properties with ensuing standards “(ASTM E871-82, E1755-01, and E872-82)” [27]. And the proximate analysis for obtained biochar from studied samples was evaluated according to “ASTM D1762-84” standard method [28].

“ASTM E777, E778 and E775” standard method was ensued for “ultimate analysis” [29] to calculate the elemental components of the selected samples and their corresponding biochar using “CHNS analyser” (Vario EL III). In the ultimate analysis we determine the Carbon, Hydrogen, Nitrogen and Sulphur in weight percentage.

Higher Heating Value (HHV) of all samples were estimated by “bomb calorimeter” (Model: AC-350 LECO) according to “ASTM D4809” standard [30].

2.2.2 Thermo-gravimetric analysis (TGA) and differential thermal gravimetric analysis (DTG)

The experimental work was carried out using a NETZSCH SAT 449F3 thermo-gravimetry analyser. The TGA/DTA facilitated the attainment of weight loss, and mass range data as a function of heating rate, time and temperature. The complete explanation of the

experiment is provided by Suman and Gautam [31]. The process starts at room temperature to 105°C.

5-15 mg of sample was taken and heated up to a final temperature of 700°C at an increment rate of 36/10°C/min with 20 ml/min flow rate of nitrogen. It gives an assortment of temperature in which maximum thermal degradation of samples takes place.

2.2.3 FE-SEM (Field Emission Scanning Electron Microscope)

FE-SEM is an excellent technique for analysing the morphological behaviour of solid particles. The samples were coated in conductive tapes and examined using an SUPRA’55 MonoCL4 field emission scanning electron microscope (FE-SEM). The magnifications of the FE-SEM images were selected as 100X to 15000X.

3 RESULTS AND DISCUSSION

3.1 Proximate, ultimate analyses and heating values of studied biomass samples

The proximate, ultimate analyses and heating values of the studied biomass samples are summarized in Table 1(a) and (b). As per the various literature [32], the parametric values of samples vary in the range: ash (5.06-10.04%), VM (66.54-73.68%), FC (14.71-15.19%), C (39.17-45.55%), O (48.52-55.65%), H (4.73-5.41%), N (0.31-0.67%), and S (0.14-0.19%). Their ash depends on the feedstock types with their terrestrial region.

Table 1(a)

Proximate analysis (dry basis), Ultimate analysis and higher heating value of studied biomass samples

Samples	M %	Ash %	VM %	FC %
Tea Waste (TW)	8.20±0.27	5.66±0.16	71.43±0.33	14.71±0.11
Coconut Shell (CS)	6.07±0.15	5.06±0.22	73.68±0.36	15.19±0.09
Eucalyptus Shell (ES)	8.59±0.44	10.04±0.43	66.54±0.60	14.83±0.32

Table 1(b)

Ultimate analysis and higher heating value of studied biomass samples

Samples	C %	H %	N %	S %	O %	GCV (MJ/kg)
Tea Waste (TW)	42.19	5.01	0.67	0.19	51.94	15.09
Coconut Shell (CS)	45.55	5.41	0.37	0.15	48.52	18.10
Eucalyptus Shell (ES)	39.17	4.73	0.31	0.14	55.65	15.24

The HHV of selected biomass vary in the range of 15.09-18.10 MJ/Kg. These values are also within the range of literature value [33] and that is comparable with primary and other renewable energy source.

Heating value directly affected by ash, its high or less weight percentage depends on the calorific value which shows their heating energy.

From above result and data, it can be decided that less ash containing samples makes it more desirable as a ‘fuel’ [34-35].

In particular, the fast growing crops mostly have higher content of ash Cl, K, Mg, S, Na, and Si [36-37]. The higher HHV of coconut shell is because of lower content of ash i.e. an incombustible component and higher amount of combustible components such as volatile matter, fixed carbon, carbon and hydrogen than in other biomass materials.

3.2 Compositional analysis of studied biomass samples

The composition of biomass can be characterized by some major components like cellulose, hemicellulose, lignin and extractives. The concentration of each component depending on types of feedstocks, but there is also a lot of variation within a single feedstock. This variation depends on their terrestrial and geological area. Table 2 compiles the data on the composition of different biomass samples. Determining the composition of studied biomass is detailed and complex undertaking when all of the constituents are individually measured. These compositional components were calculated by analytical method [38].

Table 2

Compositional analysis of studied biomass Samples

Samples	Extractives (%)	Hemicellulose (%)	Lignin (%)	Cellulose (%)
TW	11.39	28.21	21.00	27.96
CS	9.50	20.50	26.80	42.17
ES	22.31	21.50	24.00	11.96

As a fuel, heating value is plays an important role for any biomass material, is pretentious by the amount of extractives (a combustible organic constituents). The gross calorific values or heating values of the extractive-free were found to be lower than those of the extracted part indicates a likely positive influence of extractives towards the increase of heating values. High extractive content of agricultural biomass part makes it predictable as fuel [32]. The heating value narrates to the oxygen contents required for complete combustion. Typically, 30 - 60 wt% of the dry matter in biomass is oxygen, from which lignin has higher degree of oxidation than cellulose and hemicellulose [39]. After analysing the extractive content and GCV of biomass, it was found that lignin found to contribute to GCV followed by cellulose and hemicellulose. That means, there is no direct relation between GCV, cellulose and hemicellulose of the agricultural biomass samples, but lignin content directly affects the gross calorific value of the agricultural biomass [32]. Lignin has contains higher energy (about 30-40%) than cellulose and hemicellulose. GCV of all agricultural

biomass increases with increase in lignin contents [40], because of its greater amount of oxidation.

3.3 TG/DTG analysis of the studied biomass samples

TG/DTG tests were carried out to conclude the imperative evidence such as stage change with temperatures and weight losses occurs during combustion process for studied agricultural biomass samples. DTG entails of the derivative of the TG curve, giving mainly the same information, but in a much more visual and clear way. They both are presented in Figures 1 (a)-(c). TG analysis exemplifies the rate of change of mass with respect to temperature at specified heating and its possibility towards pyrolytic process [41]. This is worth mentioning that the biomass basically consists of hemicelluloses, cellulose and lignin, where the content of the individual component varies depending on the type of the biomass. According to the TGA curves, between 65% and 95% of the samples were decomposed at temperature below 700°C, wherein the weight loss mostly occurred at the temperature between 150°C and 450°C. The behaviour reflects in less mass loss in the sample due to the higher mineral content, which acts as a barrier that prevents the diffusion of heat, and hence the less release of the volatile component during the carbonising process [42].

The DTG curves for the different agricultural biomass samples are shown in Figures 1 (a)-(c). Generally, two distinct peaks can be seen for the temperature action of biomass in a passive atmosphere [43], where the first peak is dispensed to the thermal breakdown of hemicelluloses and another one is for the cellulose and then lignin breakdown, which covers a longer range.

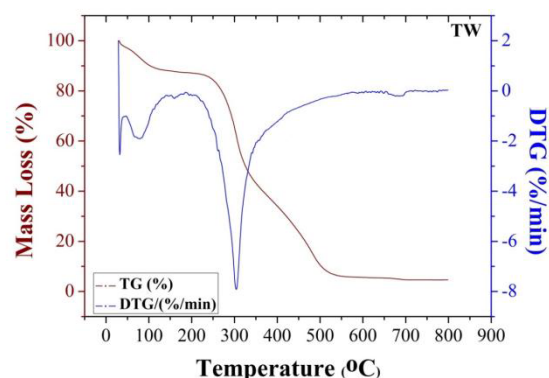


Fig. 1 (a). TG-DTG analysis of TW

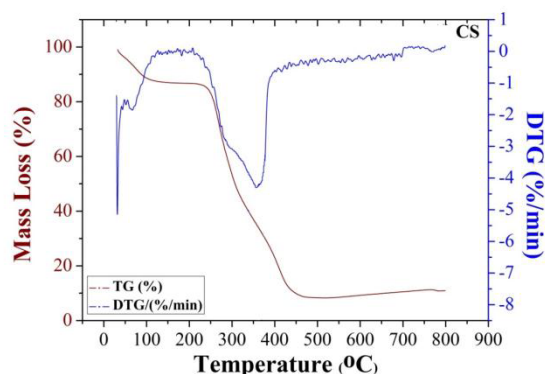


Fig. 1(b). TG-DTG analysis of CS

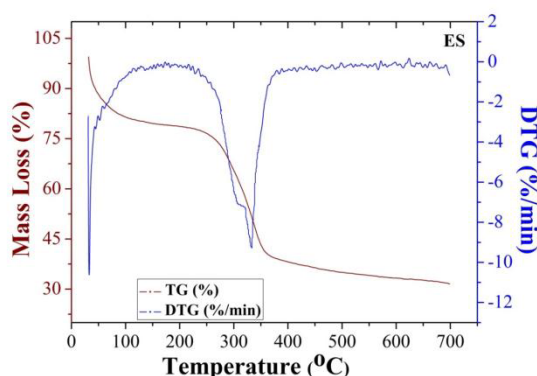


Fig. 1(c). TG-DTG analysis of ES

From the DTG (first derivative) profile for the rate of weight loss, the behaviour of all the different samples shows three distinct peaks, indicating that the degradation can be explained by dividing the curve into three stages, as shown in Figure 1 (a)-(c), the initial mass loss starts at 70°C, its mass loss occurs due to the presence of moisture in the sample. In the second stage from 290-305°C the maximum weight loss achieved at 300°C is attributable to the hemicelluloses deprivation. The third stage appeared from 335-395°C with maximum breakdown rate at 365°C. Compared with cellulose and hemicellulose components, lignin was the most difficult one to crumble even at higher temperature. The highest mass losses in the shortest residence time are indicative short combustion time, which is depicted from figures. Those biomass samples have longer combustion time for its mass loss is interesting for fuel.

3.4 FE-SEM image analysis of studied biomass samples

FE-SEM images of all the biomass samples were analysed at magnifications ranging from 50X to 15000X which are shown in Figures 2 (a)-(c). Photographic examination of these images demonstrates the transformations in microstructure between the studied samples. FE-SEM images were examined from different point sections of the samples presented that internal parts of these passages are also packed and

initially raw forerunners are not porous. The studied biochar samples have typical lingo-cellulosic structure and are made of solid cells in the form of openings on the surface [44]. The morphological structure of the TW, CS and ES showed uniform short fibrous and coarser structure with masses of loose spongy lingo-cellulosic structures [45].

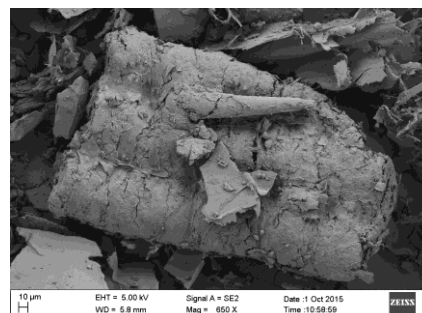


Fig. 2(a). FE-SEM image analysis of TW

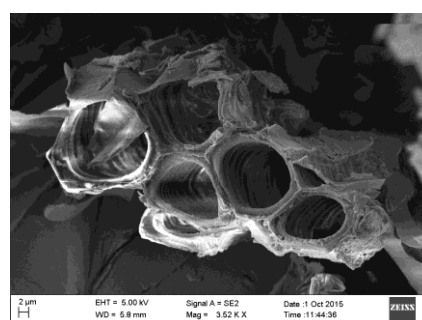


Fig. 2(b). FE-SEM image analysis of CS

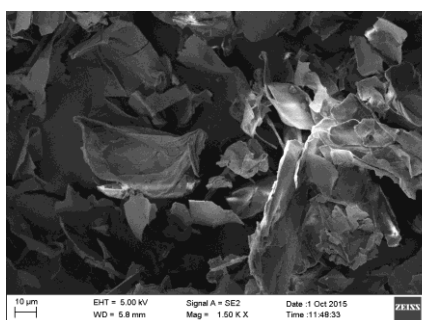


Fig. 2(c). FE-SEM image analysis of ES

Some uneven long and fibrous fragments are observed on the surface of tea waste. Among the all studied samples, CS showed more integral and stable arrangement as of its shell strong nature. On the other hand, TW and ES biomass had a more porous and crumbled arrangement. These biomass samples have flat and long fibres that are mostly composed of tracheid cells and hence give good penetrability. The fibres in CS samples, which consist of true fibres and hardwood tracheids, are shorter and smaller. Their cracks and voids inside were less open and the surface of the fibre wall sustained the adjacent veracity among fibres for making the xylem tissue [45]. In coconut shell image like spongy structure with small granulated dense channel structures are shown.

3.5 Proximate and ultimate analyses of prepared biochar samples at different temperature

The proximate and ultimate analyses of the carbonized products of different biomass samples at different temperature are incorporated in Table 3 (a) and (b). As per the literature, the parametric values in case of a variety of studied biochar vary in the range: ash (3.44 – 23.49%), VM (5.42 – 57.76%), FC (38.66-84.68%), C (33.26-79.46%), O (16.91-58.22%), H (1.10-6.34%), N (0.32-2.11%), and S (0.02-0.18%) [47]. Here the values from proximate and ultimate analysis (Table 3 a & b) of each of the biochar samples differ from each other and are well within these literature values. Biochar is mainly formed from the thermal breakdown of lignin and extractives of samples; while the VM content is converted into the gas stage and minerals presents in the samples are left as ashes [48].

Table 3 (a)

Proximate analysis (dry basis), and Ultimate analysis of the prepared biochars at different temperatures

Biomass Feedstock	Temperature	VM%	Ash%	FC%
TWC	400	54.76	6.58	38.66
	600	14.45	21.08	64.47
	800	5.46	22.81	71.73
	1000	4.44	23.49	72.07
CSC	400	40.63	3.44	55.93
	600	21.21	5.65	73.14
	800	13.49	6.08	79.43
	1000	9.02	6.30	84.68
ESC	400	45.45	16.81	37.74
	600	14.63	19.44	65.93
	800	6.67	21.65	71.68
	1000	5.42	22.36	72.22

Table 3 (b)

Ultimate analysis of the prepared biochars at different temperatures

Sampl es	Temper ature	C%	H%	N%	S%	O%
TWC	400	49.64	4.91	2.00	0.02	43.43
	600	58.45	3.54	1.97	0.10	35.94
	800	69.26	2.34	1.21	0.11	27.08
	1000	71.82	1.73	0.45	0.15	25.85

CSC	400	52.39	4.68	1.99	0.13	40.81
	600	69.98	3.74	1.06	0.03	25.19
	800	77.45	3.54	0.97	0.03	18.01
	1000	79.46	3.12	0.32	0.19	16.91
ESC	400	33.26	6.34	2.11	0.07	58.22
	600	59.20	4.76	1.56	0.02	34.46
	800	68.98	2.74	1.06	0.12	28.10
	1000	71.05	1.10	0.87	0.18	26.80

From the Table 3(a), it can be seen that volatile matter content of all the biochars gradually decreases with rise in temperature from 400 to 1000°C. The related figures for TWC, CSC and ESC are in the range (54.76 – 4.44), (40.63 – 9.02), and (45.45 – 5.52) wt.%, respectively. The high VM of biochars derived from agricultural biomass at comparatively low temperatures is ascribable to the existence of lignin in the biomass material, which can moderately resist pyrolytic breakdown at 360-395°C, but not at temperatures as high as 1000°C [42]. The increase in temperature from 350 to 800°C is also associated with speedy loss of volatile matter [49]; because of the formation of aromatic molecules.

The ash content in the corresponding biochars varies as (6.58-23.49), (3.44-6.30) and (16.81-22.36) %, respectively. The observation of higher contents of ash in the ESC than TWC and CSC are similar to the observations of others [49-50]. Additionally, partial change in the configuration supported by a likely interaction between organic and inorganic constituents [42] may be another reason for the higher ash content of the biochars of tea waste and eucalyptus shell materials. Fixed carbon in TWC, CSC and ESC, all biochar sample increases with increase in temperature, the related range values being (38.66-72.07), (53.93-84.68) and (37.74-72.22) wt.%, respectively. Thus biochars with high ash have the lower values of fixed carbon and vice versa.

Volatile Matter decreases with increase in the pyrolysis temperature, presenting a comparable trend with the yield of biochar, whereas dissimilar trend was seen for the Fixed Carbon. This influence is owed by the increase in pyrolysis heat results in further cracking of the volatile segments into small and low molecular weights of liquid and gases instead of biochar [51]. For now, the desiccation of ‘hydroxyl groups’ and thermal deprivation of cellulose and lignin influence also occur with the increasing the heating temperature [48]. Mentioned facts and data established that the increase in temperature improved the immovability of biochar for the loss of volatile [52]. It was quite fascinating that the ash content unusually increased with the increase in heating temperature from 400 to 1000°C. The increase in ash caused from lenient concentration of inorganic components [53]. In some cases when pyrolysis temperature increased from 800 to 1000°C, some

inorganic matter might have volatilized (as gas or liquid), thus, reducing the ash content at higher temperature (1000°C).

3.6 TG/DTG analysis of prepared biochars at different temperature

TG data analysis demonstrates the rate of change of mass with respect to heating temperature and its viability to pyrolytic process [42]. The weight loss of derived biochar of different agricultural biomass at different temperatures is shown in Figure 3(a)-(c), respectively. This is worth mentioning that the biomass basically consists of hemicelluloses, cellulose and lignin, where the content of the individual component varies depending on the type of the biomass.

During pyrolysis, the decomposition regions of hemicelluloses and cellulose usually occurs in the range of around 220-315°C and 315-400°C, respectively with the maximum mass losses at 268-355°C, whereas in case of lignin decomposition takes place in a wide range of 180-900°C [54]. According to the TGA curves Figure 3(a)-(c), between 70% and 90% of the samples were decomposed at temperature below 700°C, wherein the weight loss mostly occurred at the temperature between 150°C and 450°C. This is a good indication that these wastes are easily decomposed via thermal processing and would be an excellent feedstock for pyrolysis reactions. In particular, the weight loss of coconut shell and others wastes was 70-90% and 40-50% of the total weight, respectively [42]. Thus these feedstocks are realised as potential sources for pyrolysis.

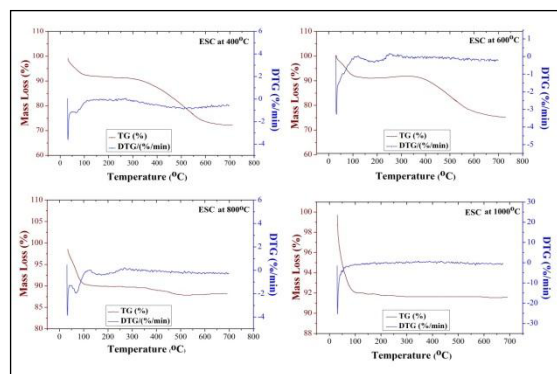


Fig. 3(c). TG/DTG analysis of ESC at different temperature

The DTG curves for biochars are included in Figure 3(a)-(c). From the DTG curve of CSC at 400°C it can be seen that the deprivation of cellulose and hemicellulose is complete and the dilapidation of lignin occurred at temperature 350°C and beyond. But the DTG profile of the CSC at 600°C and 800°C indicates that the decomposition of lignin is complete, and attains steady state at 1000°C. The DTG profile of CSC at studied heating temperatures is also pertinent to that of the other feedstocks and resultant biochars at studied heating temperatures.

3.7 FE-SEM image of prepared biochar

The heating temperature has substantial influence on the pore structure and morphology of biochar [55]. This is because for thermal modification; large amounts of VM drifts from the solid material in a short period of time, that variations the surface, shrinking, and excruciating of the particles [42]. At 800°C of temperature, the discharge of volatile matter entirely separates the particles, which initiate a hole-like arrangements and constructions full of passages that might have frolicked the role of stacks during gas release, as can be seen in most of the figures, especially in TWC and ESC. Through this study we found that every sample shows a homogeneous morphological structure. The image of TWC shows amalgam of tiny particles, which is possibly because of cluster, due to the melting of alkali compounds [56].

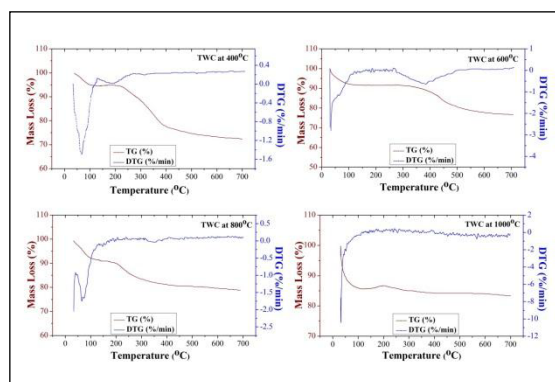


Fig. 3(a). TG/DTG analysis of TWC at different temperature

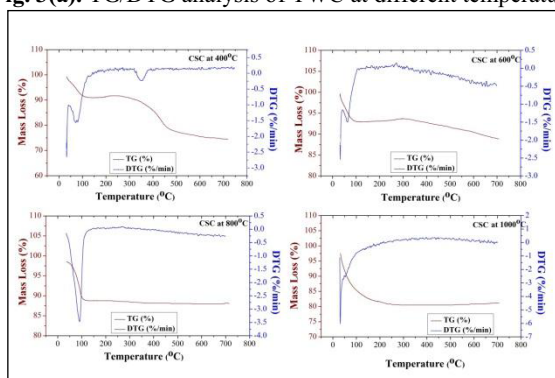


Fig. 3(b). TG/DTG analysis of CSC at different temperature

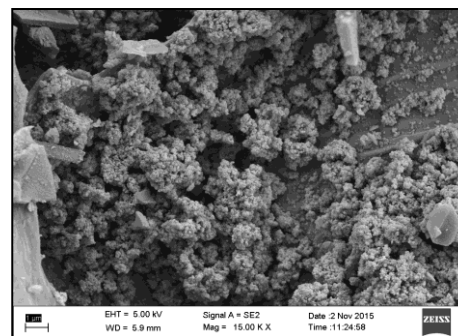


Fig. 4(a). FE-SEM image analysis of TW biochar prepared at 800°C temperature

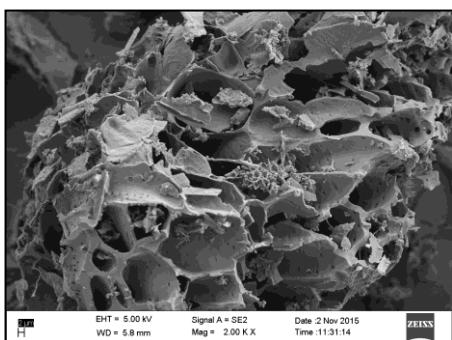


Fig. 4(b). FE-SEM image analysis of CS biochar prepared at 800°C temperature

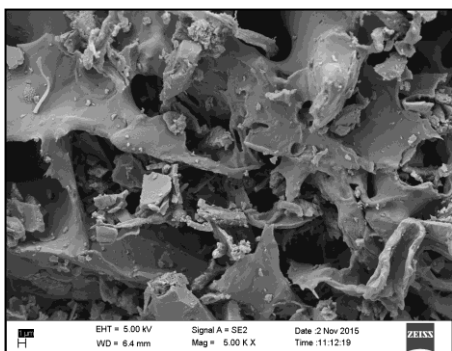


Fig. 4(c). FE-SEM image analysis of ES biochar prepared at 800°C temperature

However, there is a large morphological changes occur in the conversion of biomass to biochar. The removal of a substantial amount of volatiles produces pore opening and also it create channel like structure. Thermal breakdown of ‘chemical bonds’ and the melting of some compounds give more pores. Hence FE-SEM analysis recommends that the surface area of the biochar can be improved with heating temperature, and this observation is consistent with others’ findings [57]. With high pyrolysis temperature, the bio-char surfaces were found to rupture significantly and it had a more split construction instigated by thermal cracking of their raw biomass at 800°C temperatures. CSC retained moderately less dissociated surfaces which were due to the fibrous nature of their biomass. However, as it is reported by others [58].

Conclusions

In this study the pyrolysis of waste like tea waste, coconut shell and eucalyptus shell biomass has been investigated at different temperatures by means of thermo-gravimetric and morphological analysis. This study validates that the type of samples and heating temperature strongly influence the characteristics of the bio-char. Coconut shell has higher content of volatile matter, fixed carbon, C, H, and higher heating value (HHV) than the others; reverse is true in case of ash, O, N, and S content. With increase in heating temperature, VM, and H of all the bio-chars decrease; but ash, FC, C, aromaticity, degree of carbonisation, HHV. Higher the heating temperatures endorse condensation reactions and aromaticity. TG/DTG analysis showed good covenant with experimental

data. However, the use of an FE-SEM established a relatively high temperature the tested samples showed signs of softening and enlargement. The results of this study are vital as it provides an insight for future application of biomass as a resource of energy

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