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Biochar Derived from Agricultural Waste Biomass Act as a Clean and Alternative Energy Source of Fossil Fuel Inputs

Swapan Suman and Shalini Gautam

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Abstract

In this study, pyrolysis was used to upgrade the agricultural biomass waste (ABW) and increase its energy at pyrolysis temperatures ranging from 350 to 950°C and a residence time of 60 minutes. The produced biochars were characterized and their fuel qualities (such as, fixed carbon & carbon percentage, gross calorific value, pH and surface area) were evaluated. Physiochemical analysis showed that the biochar has improved fuel qualities compared to the raw biomass, such as decreased volatile matter, increased carbon content, pH and its gross calorific value with lower ash content. The evolution of derived biochar, as determined by TG-DTG and FT-IR, showed that most hemicellulose and cellulose were decomposed at below 350°C while the decomposition of lignin only occurs at higher pyrolysis temperatures. The biochars had increased ignition temperatures and higher combustion temperature regions compared to raw biomass feedstock. The present study showed that pyrolysis pointed the differences in fuel qualities among different agricultural biomass feedstocks. It also compromises with a promising conversion process for the production of biochar which has an alternative, clean and environment friendly energy source.

Keywords: biomass, pyrolysis, biochar, heating value, physiochemical properties

1. Introduction

The increasing demand of energy tied with the need to minimize the greenhouse gas emission and the menace of reducing oil reserves has brought into focus on the potential use of biomass as a renewable energy source [1, 2]. Most of the developed countries have already comprised this ideal concept of biomass use and application and their inexorable potential for development [3, 4].

Biomass energy is widely used in the third world principally in rural regions where it is frequently the main energy source for domestic purpose [5]. Most developing countries are still depending largely on availability of natural resources including coal, mineral mining etc. There are many alternative renewable energy sources which can be used in place of fossil and conventional fuels. Renewable energy resources are also often called alternative sources of energy. Renewable energy resources that use domestic resources have the potential to provide energy services with zero or almost zero emissions of both air pollutants and greenhouse gases [6].

Biomass can be converted into liquid, solid and gaseous fuels with the help of some physical, chemical and biological conversion processes [7, 8]. The conversion of biomass materials has a precise objective to transform a carbonaceous solid material [9]. The uses of agricultural by-products (like, coconut coir, rice husk, sugarcane bagasse, ground nut shell etc) are as fuel for cooking, cattle-feed and raw materials for paper and pulp industries. However, a large amount of this is wasted and creates disposal problem.

Pyrolysis is a new and green technology where these biomass wastes are converted into biochars [10]. Pyrolysis is a multi-product process which has shown the potential of recovering hydrocarbon liquid from carbonaceous solid waste, besides the char and the gas products. These carbonaceous solid wastes are renewable energy sources and therefore, the potential of converting them into useful energy [11].

Biochar is a value added product, which can be used for many purposes. It is highly carbonaceous and hence contains high energy content, comparable to high rank coals [12]. In addition, the heterogeneous reaction of solid carbon with oxygen is slower than homogeneous oxidation, which is relatively safe and easy to control. Biochar also has a large microscopic surface area due to the microspores developed during pyrolysis, and can be used for the filtration and adsorption of pollutants [12].

This study investigates the properties of biochar by slow pyrolysis [13] for coconut coir (CC) and ground nut shell (GNS) at different temperature at 350, 550, 750 and 950°C. Detailed properties of biochar from the samples were compared for the mass yield, elemental composition, pH, ash content and its functional group. Based on the results, the utilization of the biomass residues for biochar production was discussed.

2. Experimental

2.1. Selection of materials and biochar preparation

Coconut coir (CC) and ground nut shell (GNS) were selected as the representative agricultural waste biomass due to their high consumption potential in Jharkhand. The agricultural biomass was crushed to less than 5 mm and then dried at 105 ± 3°C for 24 h for pyrolysis study. These samples were air dried and undertaken for slow pyrolysis [14]. The pyrolysis was carried out

at varying temperature (350, 550, 750 and 950°C) for 1 hour, after attaining these temperatures on heating @ 5–15°C/min.

3. Characterization

Proximate analysis was performed on agricultural waste biomass samples for the determination of ash, moisture, volatile matter and fixed carbon contents following the (ASTM E871-82, E1755-01, and E872-82) [9]. The fixed carbon (FC) content was calculated by difference.

ASTM D1762–84 standard method was followed for proximate analysis [15] for derived biochar in order to determine ash, moisture, volatile matter and fixed carbon contents presents in the biochar.

ASTM E777, 778 and 775 standard test method was followed for ultimate analysis [16] using (Vario EL III) CHNS analyzer.

The heating values of the samples were determined by bomb calorimeter (TESTMASTER T-451). A bomb calorimeter was used according to the (ASTM D4809-00) standard test method [17].

For pH determination, biochar slurry was prepared in (1.20, w/v) ratio of biochar and water [12]. PCS Testr™ 35 pH meter was used for pH determination.

ASTM E1131-03 standard method was followed for TGA/DTG by using a computerized NETZSCH SAT 449F3 thermogravimetry analyzer.

FT-IR spectroscopy was analyzed by a Perkin Elmer Spectra 2, USA, in which the pellet was prepared by mixing 1 mg of dried biochar with 200 mg of pre-dried and pulverized spectroscopic-grade KBr (potassium bromide).

4. Results and discussions

4.1. Proximate and ultimate analysis of CC and GNS samples

The proximate and ultimate analysis of the CC and GNS are shown in **Table 1**. From table, it is observed that the both the agricultural biomass have relatively less ash (0.94 and 1.79%, respectively); higher content of VM (80.73 and 79.54%, respectively) with FC (14.97 and 14.13%, respectively), and GCV (14.74 and 14.03 MJ/kg).

The contents of carbon, oxygen and hydrogen in all the feedstocks are (C, 47.78 and 45.50%; O, 46.14 and 48.45%; H, 5.87 and 5.44%, respectively). Further the lower content of hetero elements (N, 0.19 and 0.46% and S, 0.11 and 0.15%, respectively) in CC and GNS are advantageous for environmental disquiets. Also agricultural biomass at thermo-chemical treatment releases less toxic gases (such as, SOx and NOx gases) comparable with fossil fuels. Than which we can say biomass are environment friendly and clean energy source.

ABW samples	Proximate analysis				Ultimate analysis					GCV(MJ/kg)
	M %	VM %	Ash %	FC %	C %	N %	H %	S %	O %	
Coconut coir (CC	3.36	80.73	0.94	14.97	47.78	0.19	5.87	0.11	46.14	14.74
Ground nut shell (GNS)	4.54	79.54	1.79	14.13	45.50	0.46	5.44	0.15	48.45	14.03

Table 1. Proximate and Ultimate analysis (as received basis) of CC and GNS.

Biochar samples	Temperature (°C)	Biochar energy yield (%)	pH	GCV (MJ/Kg)
CCC$_h$	350	30.60	8.04	16.40
	550	28.34	9.49	19.73
	750	25.65	10.11	22.26
	950	22.04	11.08	23.12
GNSC$_h$	350	48.50	7.70	17.58
	550	41.39	8.83	20.51
	750	38.53	9.50	22.46
	950	35.35	10.41	23.50

Table 2. Physiochemical characteristics of CCC$_h$ and GNSC$_h$ at different temperatures.

4.2. Yield, pH, and GCV of the biochars

Physiochemical characteristics like, Yield%, pH, and GCV of the derived biochars at different temperatures from CC and GNS are shown in **Table 2**. From this table it is observed that there is relatively higher percentage of yield at 350°C of pyrolysis, which further decreases with increase in temperature up to 950°C. From this table, it is observed that there is relatively higher yield of chars at lower temperature of pyrolysis, which further decreases progressively with increase in temperature. Reduction in the bio-char yield at high temperatures is attributable to undergoing the secondary reactions of the bio-char formed during the primary pyrolysis, which lead to the formation of liquid and gaseous products at the cost of solid char [18]. The energy given to the biomass at high temperature may exceed the bond breaking energy which supports the release of the volatile components of the biomass in the form of gases resulting in less char yield [19]. The reduction in the bio-char yield with increase in pyrolysis temperature is also reported by other workers [20, 21]. As with the biomass feedstocks, the char products have energy values roughly related to their carbon contents. Release of this energy by combustion can again be considered as renewable and is largely carbon neutral; the carbon returned to the atmosphere as carbon dioxide is the same as would otherwise have resulted from biomass decomposition. If the char product is not burnt, but retained in a way that the carbon in it is stable, then that carbon can be equated to carbon dioxide removed from the atmosphere and sequestered.

The pH values of coconut coir char (CCC_h) and ground nut shell char ($GNSC_h$) varies from (8.04–11.08) and (7.70–10.41) respectively are also increase with increase in pyrolysis temperature. Biochars with higher pH and significant surface area are suggestive for their better application potential in reducing the soil acidity and treating the soil and water contaminated with toxic elements and organic pollutants [22–24]. Similarly the heating value (GCV) for these biochars also varies in the range 16.40–23.12 MJ/kg and 17.58–23.50 MJ/kg respectively [25]. The increase in the GCV of the biochars is attributable to the heat endorsing components (like FC, C, and H) present in these agricultural wastes biomass.

4.3. Proximate and ultimate analyses of CCC_h and $GNSC_h$ at different pyrolysis temperature

Proximate and Ultimate analysis of CCC_h and $GNSC_h$ are shown in **Table 3**. volatile matter (VM) content of biochar decreases with increase in pyrolysis temperature i.e., 32.48–5.56% and 30.80–6.48% in case of CCC_h and $GNSC_h$ respectively. The presence of lignin in the agricultural biomass waste material can partially resist pyrolytic decomposition at lower temperature but not in case at temperatures as high as 950°C [26]. The CCC_h and $GNSC_h$ showed a high ash content, and this may be because of the partial change in the composition promoted by a possible relation between organic and inorganic constituents [26]. It can be seen that biochars with higher content of ash generally have the lower values of fixed carbon and vice versa. Similarly fixed carbon (FC) in CCC_h and $GNSC_h$ varies from 45.25–84.32% and 49.91–85.06%, respectively.

Further the ultimate analysis of CCC_h and $GNSC_h$ varies significantly in respect of C, H, N, S, and O contents, which is tabulated in **Table 3**.

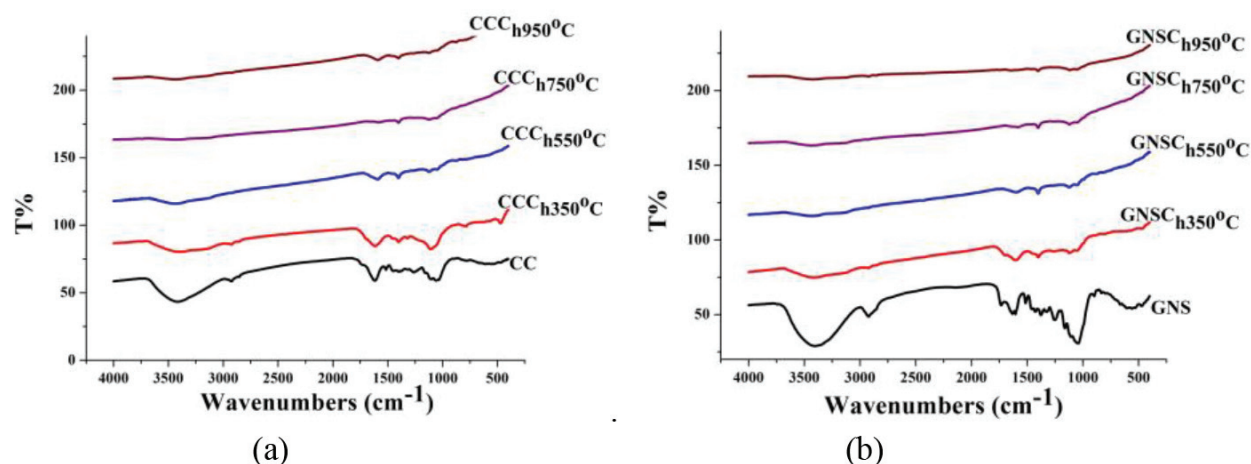FT-IR Analysis of the CC, GNS, and their derived char at different pyrolysis temperature.

Figure 1 (a) and **(b)** shows the FTIR spectra of CC, GNS, and their derived char at different pyrolysis temperatures. These graphs are plotted against wave numbers and transmittance

Biochars	Pyrolysis temperature (°C)	VM%	Ash%	FC %	C %	N %	H %	S %	O %
CCC_h	350	32.48	22.27	45.25	49.73	1.14	4.50	0.18	44.45
	550	21.80	19.78	58.42	64.40	1.01	3.78	0.16	30.65
	750	6.38	15.62	78.05	80.69	0.79	2.55	0.16	15.81
	950	5.56	10.12	84.32	87.45	0.47	2.02	0.17	9.89
$GNSC_h$	350	30.80	19.29	49.91	56.20	0.86	5.61	0.09	37.24
	550	19.56	15.34	65.10	71.78	0.79	3.46	0.09	23.88
	750	8.67	10.21	81.12	83.49	0.58	2.39	0.07	13.47
	950	6.48	8.46	85.06	87.78	0.43	2.11	0.06	9.62

*Air dried basis.

**Table 3.** Proximate* and ultimate analysis of CCC_h and $GNSC_h$ at different pyrolysis temperature.

Figure 1. FTIR analysis of (a) coconut coir (CC) and (b) ground nut shell (GNS) and their derived char at different temperatures.

percentage, which show the aliphatic loss in their functional group. The AWB samples (CC and GNS) have bands at 3401-3420 cm^{-1} (O-H stretching), 2940-2955 cm^{-1} (CH, CH$_2$ stretching), 1600-1645 cm^{-1} (C=C stretching), 1510-1520 cm^{-1} (benzene ring), 1420-1470 cm^{-1} (aromatic skeletal vibrations; asymmetric in -CH$_3$ and -CH$_2$-), 1310-1380 cm^{-1}(Phenolic OH; aliphatic C-H deformation vibrations in cellulose and hemicelluloses), 1210-1245 cm^{-1}(C-O-C stretching in alkyl aromatic), (1140-1161 cm^{-1} (C-O-C asymmetry stretching), 1030-1060 cm^{-1} (C-O stretching).

From the FTIR spectra of CHC$_h$ and SBC$_h$, it is seen from **Figure 1 (a)** and **(b)**, that the aliphatic losses are represented by the C-H stretching (2800-2950 cm^{-1}) with increasing in pyrolysis temperature [27]. The representative peaks seemed for aromatic carbon C-H stretching (3050-3000 cm^{-1}), C=C (1350-1450 cm^{-1}), C-C, and C-O stretching (1580-1730 cm^{-1}) [28–30]. This is obviously because the pyrolysis temperature amends the functional group. It can be seen from result aliphatic C group decreases but aromatic C group increases [31]. But, when the pyrolysis temperature becomes high, the intensity of the bands such as that of the hydroxyl groups (3210-3450 cm^{-1}) and aromatic groups (1550-1650 and 3050-3250 cm^{-1}) [27, 32], gradually diminishes.

5. Combustion behavior of biochar

Figures 2 and **3** shows the TG/DTG curves for the CC, GNS and their derived biochars, with the combustion parameters summarized in **Table 4**. From the curves, it can be seen that the combustion behavior of the agricultural biomass changed significantly after pyrolysis. For CC and GNS, a sharp DTG peak was observed centered at about 296°C and a weight loss of 75–85% was occurred at 350°C. The combustion of CC involves mainly volatile matter combustion, which was ignited at a low temperature of 283°C due to the high reactivity of volatile matter. The rapid weight loss in CC and GNS within a short time at the lower temperature
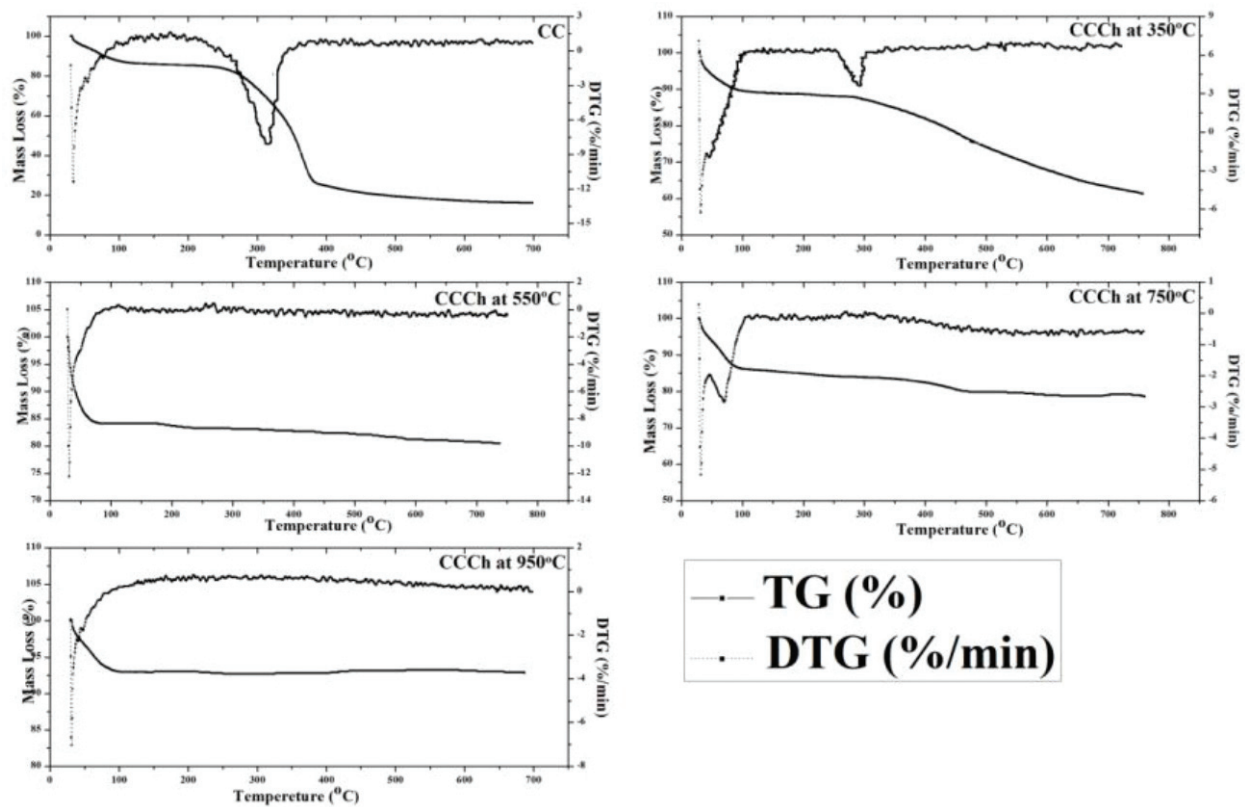
Figure 2. TG and DTG curve of coconut coir (CC) its derived char at different temperatures.

range implies that there was incomplete combustion with low efficiency and high pollutant emissions [33].

Compared to raw biomass, the reactivity of the biochar decreased, resulting in a higher ignition temperature and combustion in a wider temperature range. The elevated combustion temperature with high weight loss rate implies improved combustion safety, increased combustion efficiency and decreased pollutant emission. These combustion characteristics of biochar are significant improvements over raw biomass feedstock as a fuel [33, 34]. Generally, two separate peaks can be seen for all derived biochars in an inert atmosphere [35], where the first one is assigned to the thermal decomposition of hemicelluloses and the second one is for the cellulose and lignin decomposition, which covers a longer range. From the DTG profile, the initial mass loss at about 70°C is due to the moisture present in the sample. In the second stage from 295 to 308°C with maximum weight loss rate obtained at 310°C is attributable to the hemicelluloses degradation. The third stage appeared from 355 to 405°C with maximum decomposition rate at 355°C. Compared with these three components, lignin was the most difficult one to decompose even at higher temperature.

From the DTG curve of $CCC_{h(350°C)}$ and $GNSC_{h(350°C)}$, it can be seen that the degradation of cellulose and hemi-cellulose is complete. But the DTG profile of the $CCC_{h(550-750°C)}$ and $GNSC_{h(550-750°C)}$ indicates that the decomposition of lignin is complete, and attains steady state at $CCC_{h(950°C)}$ and $GNSC_{h(950°C)}$.
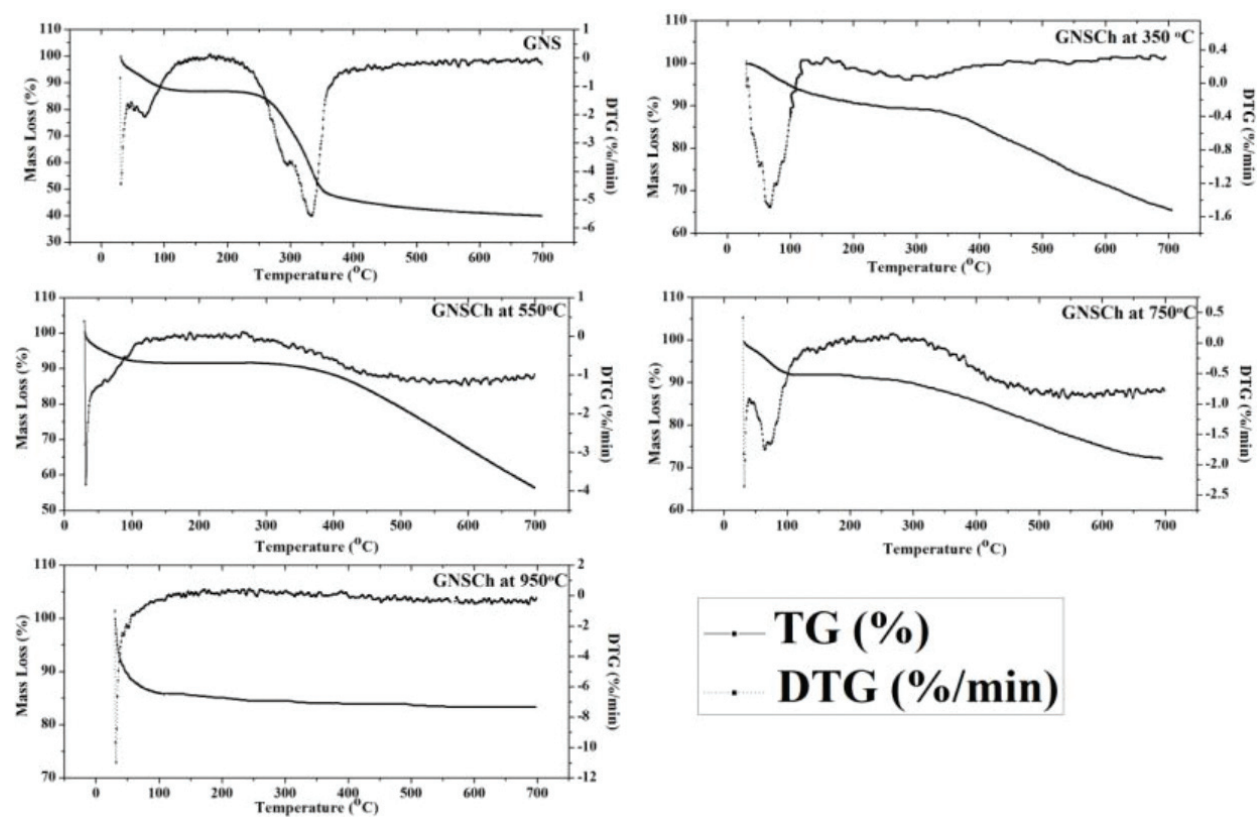
Figure 3. TG and DTG curve of ground nut shell (GNS) its derived char at different temperatures.

Sample	T_i	T_m	T_b	R_{max}	D_i ($\times 10^{-3}$)
CC	195	300	375	1.09	0.57
$CCC_{h(350°C)}$	295	395	490	0.55	0.29
$CCC_{h(550°C)}$	—	—	—	0.51	0.27
$CCC_{h(750°C)}$	375	530	696	0.38	0.20
$CCC_{h(950°C)}$	—	—	—	0.19	0.09
GNS	240	310	375	1.12	0.65
$GNSC_{h(350°C)}$	298	355	400	0.7	0.37
$GNSC_{h(550°C)}$	375	525	695	0.51	0.27
$GNSC_{h(750°C)}$	400	505	698	0.4	0.21
$GNSC_{h(950°C)}$	—	—	—	0.14	0.07

Table 4. Combustion parameters of agricultural waste biomass samples and their derived biochar.

For evaluation of the ignition performance, ignition index (Di) of the biomass and biochar was calculated with the following equation [36]:

$$D_i = R_{max}/(t_{max} \times t_i),$$

where R_{max} is the maximum weight loss rate,

t_{max} and t_i are corresponding to the time of the maximum weight loss rate and ignition temperature, respectively.

Higher values of ignition index (D_i) are indicative of better ignition performance [37]. As shown in **Table 4**, the coconut coir and ground nut shell derived biochars have lower D_i values than its corresponding raw samples, and the D_i values decreases with increase in temperature.

5.1. Environmental implications of biochar production processes

Pyrolysis produces high energy-density fuels, such as biochar. Biochars are non-polluting and reliable, and also contain oxygen levels of 10–45% [38]. Biochars have efficient as eco-friendly media for removal of organic and inorganic contaminant in aqueous environment such as polluted soil, water, waste effluents among others. Application of biochars to soils has been examined at the field scale as an in-situ remediation strategy for both organic and inorganic contaminants to determine their ability to increase the sorption capacity of varying soils and sediments [39]. Biochars may also help in mitigating some negative environmental effects by addressing the climate changes which in-turn may lead to economic as well as environmental benefits. Thus the inimitable characteristics of biochar in C-sequestration as well as their biodegradability make them dynamic role in this field. Thus the usage of biochars in various applications will prove absolutely beneficial in the near future.

Pyrolysis processes can be used as part of renewable energy systems based on biomass in a number of ways. Such systems can offset use of fossil fuels and so avoid associated emissions of greenhouse gases. The gas product through pyrolysis process is termed synthesis gas, shortened to syngas. It is generally composed of carbon dioxide (9–55% by volume), carbon monoxide (16–51%), methane (4–11%), hydrogen (2–43%) and hydrocarbons in varying proportions. The gases are usually present with nitrogen introduced to inert the pyrolysis process, this can be treated as a diluent and discounted for material balancing. The carbon dioxide and nitrogen provide no energy value in combustion; the other gases are flammable and provide energy value in proportion to their individual properties. The use of energy in the gas can be considered as renewable and largely carbon neutral. No special consideration of the carbon dioxide in the pyrolysis gas is required as it is not additional to what would result from biomass decomposition.

6. Conclusion

Biochars with upgraded fuel qualities were successfully produced from pyrolysis of agricultural biomass waste (ABW). This study demonstrates the type of feedstocks and pyrolysis temperature strongly stimulus the characteristics of the biochar. Increase in pyrolysis temperature, percentage of yield, VM and H, of all the bio-chars decrease; but FC, C, degree of carbonization, GCV, and pH increase. The combustion behaviors of biochars were distinct from raw agricultural biomass, with increased maximum weight loss, raised the ignition temperature and wide combustion ranges at higher pyrolysis temperatures. The conversion

of agricultural biomass wastes by pyrolysis to biochar can be a potential option to utilize these wastes for various sustainable purposes like as a as a substitute of renewable energy sources and which we used as a clean and environment friendly energy source.

Symbols and nomenclature

VM%	Volatile Matter Content (weight %),
FC%	Fixed Carbon Content (weight %),
C%	Carbon Content (weight %),
N%	Nitrogen Content (weight %),
H%	Hydrogen Content (weight %),
S%	Sulfur Content (weight %),
O%	Oxygen Content (weight %),
GCV	Gross Calorific Value,
MJ/kg	Mega joule per kilogram,
CC	Corn Cob,
$CCC_{h(350°C)}$	Corn Cob Char at 350°C,
$CCC_{h(550°C)}$	Corn Cob Char at 550°C,
$CCC_{h(750°C)}$	Corn Cob Char at 750°C,
$CCC_{h(950°C)}$	Corn Cob Char at 950°C,
GNS	Ground Nut shell,
$GNSC_{h(350°C)}$	Ground Nut Shell Char at 350°C,
$GNSC_{h(550°C)}$	Ground Nut Shell Char at 550°C,
$GNSC_{h(750°C)}$	Ground Nut Shell Char at 750°C,
$GNSC_{h(950°C)}$	Ground Nut Shell Char at 950°C,
t_{max}	time of the maximum weight loss rate,
t_i	ignition temperature,
Di	ignition index,
R_{max}	maximum weight loss rate

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