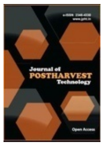

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RESEARCH ARTICLE

Experimental investigations on feasibility of corn cob as a potential feed stalk for biochar production

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ABSTRACT

Burning of agricultural waste is nowadays practiced predominantly to eradicate the unutilized waste material. It pollutes the atmosphere with massive amounts of particulate and gaseous contaminants. Corn cob is one of such material remains unutilized, that can be used for potential applications. Biochar is black colored porous carbon material obtained by slow pyrolysis in absence of oxygen. It has many applications such as soil ameliorant, composting, pharmaceutical and industrial usage. This paper is compiled with the aim to check feasibility of corn cob as a feedstock for biochar production. The characteristics of corn cob such as elemental composition, proximate analysis, and thermo-gravimetric analysis have been presented in this article. The results revealed good amount of carbon in biomass i.e., 45 % which is good for biochar production. The low content of nitrogen and sulphur suggests environmentally friendly utilization of biomass. This conversion of corn cob into biochar offers advantages of utilization of waste residues for holistic purpose.

Keywords: Agricultural waste, biochar, burning, corn cob, waste management.

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INTRODUCTION

Agricultural waste is emerging as global problem due to its improper method of disposal. The field burning of unutilized residue causes release of harmful gases in the atmosphere, which affects the environment and human health. These agro-residues can be processed to get energy and other value-added products. It could be one of the sources of renewable energy in the present context of energy crises and environmental pollution. Biomass is an important source of renewable energy in India, providing energy mainly for cooking and process heat in residential and industrial sectors. As biomass is carbon neutral, there is increasing interest in using biomass to replace fossil fuel, and thereby reducing the impact of climate change. Conversion of biomass to biofuel can be achieved by process such as thermal, chemical and biochemical

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methods. Biochar is black coloured porous carbon material obtained by thermochemical method in absence of oxygen. Thisbiochar serves as a tool for soil conditioning and for carbon sequestration to combat climate change. At present, the use of bio-char for improving the soil health is getting attention world- wide. Application of bio-char in soil, results in good fertility and significant increase in crop yielddue to different characteristics of it.

Maize (Zea mays L) also known as corn is one of the top grown crops worldwide due to its wider adaptability under varied agro-climatic conditions. Its global production was estimated 1.06million thousand tonnes in 2020 (World Data Atlas, 2020). United State, China and Brazil are among the top three countries producing corn and India ranks 6th in it, producing 31.5 million tonnes in the year 2022 (www.statistica.com). In national food basket of country, its contributionis about 9%. The predominant maize growing states that contributes more than 80 % of the total maize production are Andhra Pradesh (20.9%), Karnataka (16.5%), Rajasthan (9.9%),Maharashtra (9.1%), Bihar (8.9%), Uttar Pradesh (6.1%), Madhya Pradesh (5.7%), Himachal Pradesh (4.4%). The huge number of corn production ultimately provides huge amount of corn wastes in the form of stalk, leaves, and cob (Parsimehr and Ehsani 2020). In maize field, about 1 tha^{-1}cob is produced and 12-13 t ha^{-1} straw is generated. From one of kg of grain about 0.15-0.20 kg of cob is generated. Considering the lower CR Ratio, at a global level 0.16 million thousand tonnes cob will be produced. It is mainly considered as waste agricultural residues, which can be used for production of green technologies for further potential applications. Corn cob residues provide an excellent opportunity to produce green fuel as an alternative to fossil fuels (Klaas *et al.*2020). In addition to this, as the corn cobs have high carbon content (45-50%), it has great potentialto be used as a precursor for biochar production.

In India maize is third most important crop after rice and wheat and its production in 2018-19was about 27 Million tonnes. Corn cob is one of the such material remains unutilized, that can beused for potential applications. This corn cob can be used as a raw feedstock for the production ofbiochar. Considering the availability and characteristics of corn cob as a precursor for biochar production, many authors studied the pyrolysis of corn cob. It will also provide insights into further possible application of biochar produced from corn cob.

MATERIALS AND METHODS

The corn cob samples were collected from farm section and dried in the sun for a few days to remove the moisture content so as to avoid the growth of orange fungus and grey mould. The CHNS analyser was used for determination for elemental composition and TGA analyzer was usedfor thermogravimetric analysis. Proximate analysis was carried out using standard ASTM methodas listed below.

Moisture content

The moisture content of a biomass is one of the most important properties of the biomass,over which it's heating value or calorific depends. The oven dry method was used determination of the moisture content of biomass. Initially, the sample of known weight is kept in an oven at 105 °C for 24 hours and final weight of the oven-dried sample was noted down. The difference betweenthe initial and final weights is taken as moisture content of the material.

Volatile matter

Volatile matter is determined by keeping dried sample in the muffle furnace with closed crucible at 900 $\pm$ 5 °C for six minutes. The crucible is allowed to cooled fit in the air and weighed again. The difference in weight due to the loss of volatiles is taken as the total volatile matter present in the biomass.

Ash content

The residual material obtained in the crucible is then again heated in a muffle furnace at 700 ± 50 °C for an hour without the lid. The crucible is then taken out, it was first cooled in the airand then in desiccators and weighed. The residue is reported as ash on percent basis.

Fixed carbon

The fixed carbon was calculated on percentage basis by subtracting the sum of percentage of moisture content, volatile matter and ash content from the hundred percent. The carbon contentdetermined by applying this method is not the actual carbon content present in the biomass but only the non-volatile part of carbon content, as some of the carbon present in biomass also escapesalong with the volatiles.

Ultimate analysis

The ultimate analysis gives carbon, hydrogen, oxygen, nitrogen and sulphur content of the material. The nitrogen and sulphur are normally negligible in the biomass material. The carbon, hydrogen, nitrogen, and oxygen in corn cob biomass samples was determined by using elementalanalyzer.

TGA Analysis

The thermo-gravimetric analysis (TGA) was carried out to study the thermal behavior of the corn cob sample. The TGA analyser (STA 7300 Hitachi, Germany) installed at departmental laboratory was used for the study. The temperature range was maintained from 30- 1000 ℃ at various heating rate (10, 20 and 30 ℃/min) and at a nitrogen flow rate of 50 mL/minute.

METHODS OF PYROLYSIS

Pyrolysis is broadly categorized into two types i.e., slow pyrolysis and fast pyrolysis depending upon operating condition. It is described in following sub-section. The conversion of biomass intobiochar is shown in Figure 1.

Slow pyrolysis

Slow pyrolysis is the conventional method of pyrolysis used for the production of biochar from ancient time. It is characterized by longer heating time and lower heating rate. This lower heating rate and longer vapor residence time provides a suitable ambience and sufficient time for the secondary reactions to complete during the process. In slow pyrolysis, biomass is subjected to heating at a rate of 0.1 to 1 ℃/s for a long duration varies from 5 to 30 min to the temperature to the order of 400-500 °C (Tripathi et al., 2016). The yield of all biochar made up of rice hull, peanut hull, cornstalk, and tobacco stalk ranged from 30 to 99 wt. % dry basis (db) and it is negatively correlated with temperature and residence time (Cao et al*.,* 2018). The longer vapor residence timeallows vapours to secondary thermal cracking reaction which ultimately results in the formation of more char.

Fast pyrolysis

Fast pyrolysis process is the preferred method for the purpose of maximize the yield of liquid products resulting from biomass pyrolysis. In this a low temperature, high heating rate, short gas residence time are employed in this technology so that thermal cracking can take place as well asminimize the exposure time which otherwise favors the char formation. Typically, on a weight basis, fast pyrolysis produces 60%–75% of liquid products, 15%–25% of solids (mainly biochar)and 10%–20% of gaseous products. The basic characteristics of the fast pyrolysis process includesits high heat transfer and heating rate, very short vapour residence time, rapid cooling of vapours for high bio-oil yield (Demirbas A. 2004).

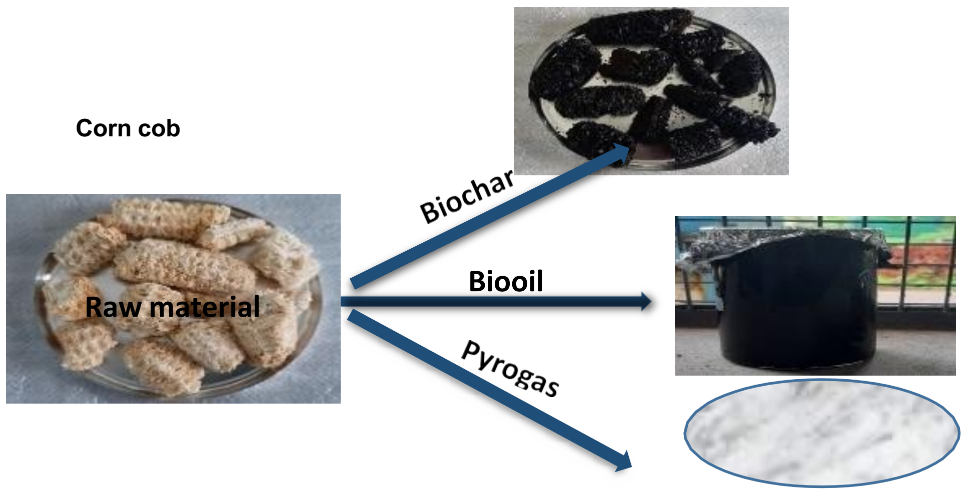

Figure 1: Conversion of corn cob to biochar via slow pyrolysis

RESULTS AND DISCUSSION

The pyrolysis process mainly affected by the process parameters and characteristics of biomaterial. Different kinds of biomaterials behave differently at same operating conditions due to their inherent composition. These compositions are cellulose, hemicellulose and lignin which affects biochar yield and characteristics of biochar produced. Each of above components behave differently in their thermal degradation behaviour. The results obtained for proximate, ultimate and TGA are expressed in following sub-sections.

Proximate and ultimate analysis

The proximate analysis refers to quantitative analysis of moisture content, volatile matter, ash content and fixed carbon content of the material. The ultimate analysis includes C, H, O, N and S.These characteristics of material affects the yield and properties of final product during pyrolysis.Table 1 depicts the proximate analysis of corn cob. The low moisture content of biomass is advocated for thermal pyrolysis process for maximizing the solid yield and to ensure the economical pyrolysis. At the same time, heat transfer during pyrolysis significantly affected by moisture content of biomaterial and it also influences the product distribution. Therefore, drying of high moisture content biomass is essential before pyrolysis, otherwise more energy will be required during pyrolysis. The high fixed carbon content of biomass is preferred for biochar production. The percentage of carbon content and ash content in the feedstock also could influencethe heating value of the biomass feedstock.

The volatile matter, ash content was found to be 73 and 3%, respectively. The quantum of volatile matter in corn cob encourages that corn cob can be easily put forward as a raw material inthe pyrolysis process. During the pyrolysis process, the volatile matter present in biomass can increase the biochar formation (10-20%) by secondary thermal decomposition (Ferrara et al. 2014). It could be observed that the ash content of the corn cob is quite low which ranges from 1.0to 4.0%. Rafiq et. al. (2016) reported that with the progressing pyrolysis temperature the ash content increases. The observed ash content (3%) in the corn cob in the study indicates its feasibility to be used in the furnace as it minimised the slagging and fouling problems in the reactor during pyrolysis. The higher ash content resulted in lowering the biomass conversion efficiency and increased the process economics. The results obtained were in accordance with (Shariff et al.,2016). Table 1 compares the results obtained for proximate analysis of this study with reports of other studies.

Table 1: Proximate analysis of selected biomass feedstocks and other parameters

Analysis	**Results of the study**	**(Ogunjobi an Lajide 2013) (mf wt %)**	**(Demirbas 2004) (wt %)**	**(Liu *et a* 2014) (wt %)**	**(Tippayawonga *et al.,* 2018) (wt %)**	**(Ceranic *et al.* ,2016)(wt %)**	**(Lyu *et al.* 2015)**
Moisture content	5	7.14	-	11.7	9.6	8.55	-
Ash conten	3	1.05	1.1	2.9	1.6	1.14	3.15
Volatile Matter	73	87.76	84.6	69.5	71.6	70.95	80.98
Fixed Carbon	19	11.19	15.4	15.9	17.2	19.34	15.87

As it can be seen from Table 1, the recorded highest fixed carbon content was 19.00%. The high percentage of fixed carbon in biomass suggested its potential for maximum biochar production. While, the low percentage of fixed carbon in biomass feedstock indicated the lower lignin composition. The higher heating value of biomass was estimated by using correlation given by using proximate analysis. The higher heating value of about 16.43 MJ kg-1 was recorded and was found very close or slightly higher than other biomass materials (Santos et al. 2020; Bai et al.2017).

The ultimate analysis (C, H, N, S, and O) of the raw material are listed in Table 2. Three experimental trials were performed in triplicate for getting the average value of biomass. The average value of observed moisture content was 5%. A low moisture content biomass was advocated for thermal pyrolysis process to ensure the economical pyrolysis. In contrast, if the moisture content is more than 10%, excess amount of energy will be required for biomass pyrolysis. It is suggested that, for thermochemical conversion, a low moisture level (<10%) in biomass should be preferred. The increase in moisture content resulted into increased liquid product yield and decreased solid and gas yields. This was due to the water vapour favoured quickremoval of the volatile compounds from the fuel and from the reactor.

Table 2: Ultimate analysis of corn cob biomass

Analysis	Results of the study	(Ogunjobi and Lajide 2013) (mf wt %)	(Demirbas 2004) (wt %)	(Liu *et al.*, 2014)(wt %)	(Tippayawonga *et al.,* 2018) (wt %)	(Ceranic *et al.* ,2016) (wt %)	(Lyu *et al.,*2015)
Carbon	45.92	43.81	49.0	48.12	44.4	46.74	47.23
Hydrogen	5.93	6.54	5.6	6.48	6.5	5.46	5.95
Oxygen	47.88	48.19	43.8	43.5	48.8	38.16	46.34
Nitrogen	0.15	0.77	0.5	1.89	0.3	3.83	0.47
Sulfur	0.19	0.69	-	-	0.0	0.12	0.01

The ultimate composition of the corn cob indicated that it was suitable for biochar production. It contained 45.92% C, 5.92% H_2 and 47.88% O_2. The quantum of carbon content in raw feedstock denoted its suitability towards biochar production. The higher percentage of oxygen in all biomass feedstock indicated its quality of surface hydrophilicity and polar nature.It did not emit nitrous oxide (N_2O) or sulphur dioxide (SO_2) in the environment due to lesser amount of nitrogen (N) and sulphur (S) in the biomaterial. These parameters all together have integrated effect on characteristics of end products of pyrolysis. Thus, it is crucial to study the proximate and ultimate data of feed stock for biochar production.

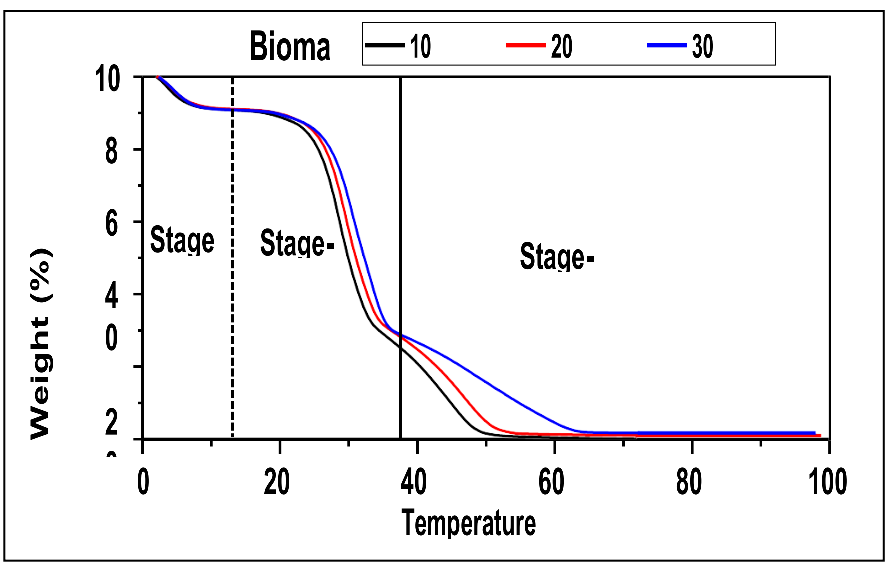

Figure 2: Thermogravimetric analysis of corn cob

Thermo-gravimetric analysis (TGA)

Thermogravimetric analysis is useful in determining material deformation changes under controlled conditions of force, atmosphere, time, and temperature. In the present study, the thermogravimetric analysis was also carried out to study the thermal behavior of the material. The result of TG analysis of the corn cob was shown in Figure 2. TG analysis suggests relationbetween mass loss rate with temperature and time. In the present study, thermogram of corn cob have been studied at different heating rate. The temperature value was maintained from 30- 900 ℃ at various heating rate (10, 20 and 30

℃/min) and at a nitrogen flow rate of 50 mL/min. In the temperature range of 100℃–200℃, no obvious weight loss was observed. The TG analysis showed that the corn cob samples started to degrade at 250℃ and the weight loss was prominent in between 250℃ and 350℃. The curve consists of two distinct peaks between this temperature range, which correspond to the thermal decomposition of hemicelluloses and cellulose respectively. Similar results on corn cob TGA were also reported by (Piash et al.,2016) that TG analysis showed that the corn cob samples started to degrade at 250°C. Gupta et al. (2017) reported that pyrolysis process of corn cob is divided into three different stages namely, drying, decomposition and carbonization. The first stage is drying stage, which occursbetween the temperature 50 and 150 °C. The second stage is decomposition stage where main mass loss occurred. And this mass loss started at around 210 °C and ended up at approximately600 °C (Zhang et al., 2009). Mullen et al. (2018) reported recovery of biochar as 18.9 % using corn cob at 500 °C pyrolysis temperature.

CONCLUSIONS

The abundance of corn waste in India lead to the utilisation of corn cob as the feedstock for pyrolysis process. Corn cobs can be successfully converted to biochar via pyrolysis conversion method for its further application. The inherent characteristics of biomass significantly affect the yield and properties of biochar produced along with the process parameters. The higher fixed caron content of corn cob was observed 19% whereas the total carbon content was in the range of 45- 50%. The low value of moisture and ash content was observed in biomass indicating its suitability for biochar production. This biochar production technology via slow pyrolysis offers advantages of utilization of waste residues for holistic purpose.

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