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Assessment of agro-residues as biochar feedstock: Cotton stalk, soybean straw, and pigeon pea stalk

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Abstract
Agro residue generation is increasing globally due to the increase in agricultural crop area and cropping intensity. The increasing agricultural activities and modernization produces a lot of food processing waste, bio-waste and solid waste to meet the demands of food and energy for the growing population in the world. Improper disposal of biomass produced by the agricultural sector is a major challenge worldwide. conversion of agro residue into biochar helps to offset global warming gases emission and improve the soil health under changing climate. Converting agro residue into environmentally acceptable, low-cost biochar is not only a sensible recycling method, but also a cure for pollution control. Characterizing agro-residues involves detailed analysis of their physical, chemical and thermal properties to ensure they are suitable for biochar production. In India, the availability of diverse agro-residues presents a significant opportunity for sustainable biochar production, which can enhance soil health, sequester carbon, and provide an additional revenue stream for farmers. Biochar production from agricultural residues offers a sustainable solution for waste management and soil enhancement. This study assesses the potential of cotton stalk, soybean straw, and pigeon pea stalk as feedstock for biochar production. Comprehensive characterization was conducted through proximate and ultimate analysis, energy content evaluation. The findings indicate that each feedstock exhibits unique properties, influencing biochar yield and quality. The study highlights the comparative advantages and challenges of using these residues for biochar, aiming to optimize biochar production processes in agricultural systems.

Keywords: Agro residue, cotton stalk, soybean straw, pigeon pea stalk, proximate analysis, ultimate analysis, thermal properties, biochar

1. Introduction
Biomass is any type of living or recently living organic material that comes from plants and animals (Danso-Boateng and Achaw 2022) [3]. Biomass is referred as an indirect source of solar energy and considered a source of stored energy. Negi *et al*. (2023) [8] stated that India is an agricultural powerhouse, having a net sown area of about 139.3 Mha (42.4%) from a total geographical area of 328.7 million hectares (Mha). Further, 54.6% of the total workforce of India is reported to be engaged in agricultural and allied sectors and accounts for 17.8% of the country's Gross Value Added. The agricultural production system is the main source of livelihood for one third of population of an India (Phadtare *et al*., 2023) [10]. Agro residue generation is increasing globally due to the increase in agricultural crop area and cropping intensity. The increasing agricultural activities and modernization produces a lot of food processing waste, bio-waste and solid waste to meet the demands of food and energy for the growing population in the world. Improper disposal of biomass produced by the agricultural sector is a major challenge worldwide. While agriculture produces food, it also produces waste known as agriculture residue or crop waste. Crop residue term is used for the biomass produced as by-products from harvesting and processing of agricultural crops (Yadav *et al*. 2017) [16]. Crop residue is classified as field-based residues and processing-based residues. Field based residues are generated in the field at the time of harvest. Processing based residue are co-produced during processing of agriculture produce. The total amount of agricultural waste generated annually in India is much greater than that in other countries.

According to the Ministry of New and Renewable Energy (MNRE) estimates, an average of 500 Mt of crop residue is generated in India each year, a majority portion of which is used as fuel for industrial and domestic purposes (Saxena *et al*. 2021) [12]. India produces more than 686 million tonnes (Mt) of crop residue every year, of which 368 Mt comes from cereal crops. Among cereal crops, rice and wheat are the dominating crops, contributing about 154 and 131 Mt, respectively, in the total crop residue production (Kumar *et al*. 2023) [6]. Table 1. represent the estimates potential amounts of gross residue and surplus residue of the crop residue (Deka *et al*. 2023) [4].

Table 1: Estimates potential amounts of gross residue, surplus residue of the crop residues

Crop group	Crop residue	Gross residue potential (MT)	Surplus residue potential (MT)
Cereals	Rice straw	169.14	40.59
	Rice husk	22.55	16.01
	Wheat straw	149.80	22.47
	Bajra stalk	18.42	13.48
	Barley stalk	2.32	0.23
Pulses	Tur stalk	10.73	1.72
	Moong stalk	2.23	0.22
	Urad stalk	3.84	0.42
Oilseeds	Soybean stalk	18.59	6.13
	Mustard stalk	15.17	14.42
	Sunflower stalk	0.67	0.11
	Groundnut stalk	11.10	1.67
	Castor stalk	2.67	1.17
	Safflower stalk	0.17	0.13
Horticulture	Banana waste	94.95	33.23
	Coconut fond	19.86	9.93
	Arecanut fond	2.50	0.88
Others	Cotton stalk	17.86	9.46
	Sugarcane tops and leaves	19.00	3.61
	Jute stalk	3.61	0.36

In developing countries farmers commonly use crop residue burning to rapidly clean arable land in order to boost production. The burning of crop residue produces in a waste incinerator harmful emission that result in climate change. Burning of crop residue potentially has adverse effects on soil health including huge loss of nutrients carbon, nitrogen, Sulphur etc (Shan *et al*., 2008) [13]. Farmers in the Vidarbha area of Maharashtra mostly cultivate cotton, pigeon pea and soybean crop. Farmers in Vidarbha region primarily burn cotton and pigeon pea residue. Also, many farmers are presently using soybean straw to feed cattle, with leftovers being burnt on the farm. Cotton stalk soybean straw and pigeon pea stalk agro residue, an abundant agricultural waste, is a promising feedstock for pyrolytic conversion to biochar. Cotton stalks are the residues remaining after cotton production, which are estimated to amount to 3.5-5 tons per ton of cotton crop. Global cotton production amounted to 25.8 million tons in 2018 and is expected to reach approximately 29.2 million tons by 2028. A study from the Maharashtra Energy Development Agency states that India generates 4 Mt of pigeon pea stalk and per year. All the researchers are now a days advocating the sustainable development and use of renewable energy. (Phadtare *et al*., 2019) [11] So, conversion of agro residue into biochar helps to offset global warming gases emission and improve the soil health under changing climate. Converting agro residue into environmentally acceptable, low-cost biochar is not only a sensible recycling method, but also a cure for pollution control. Biochar achieved significant advances in lowering greenhouse gas emissions, soil nutrient management, sequestering atmospheric carbon into the soil, enhancing agricultural output, and reducing environmental pollutants (Phadtare and Kalbande 2023) [10]. Characterizing agro-residues involves detailed analysis of their physical, chemical and thermal properties to ensure they are suitable for biochar production. In India, the availability of diverse agro-residues presents a significant opportunity for sustainable biochar production, which can enhance soil health, sequester carbon, and provide an additional revenue stream for farmers. Biochar production from agricultural residues offers a sustainable solution for waste management and soil enhancement. This study assesses the potential of cotton stalk, soybean straw, and pigeon pea stalk as feedstock for biochar production. Comprehensive characterization was conducted through proximate analysis, energy content evaluation.

2. Materials and Methods

The experiment work was undertaken at the Department of Unconventional Energy Sources and Electrical Engineering, College of Agricultural Engineering and Technology, Dr. PDKV, Akola.

2.1 Biomass collection and sample preparation

The agro residues cotton stalk, soybean straw and pigeon pea stalk were collected from field of Dr. PDKV Akola.The samples were air-dried, ground to a uniform particle size, and stored in airtight containers for further analysis. Plate 1 shows the raw cotton stalk, soybean straw and pigeon pea stalk.

a. b. c.

Plate 1: a. Cotton stalk b. soybean straw c. pigeon pea stalk

2.2 Characterization of agro-residue
The physiochemical properties of cotton stalk, soybean straw and pigeon pea stalk including bulk density, angle of repose, moisture content, volatile matter, ash content, fixed carbon and calorific value and TGA were determined using standard procedures as follows

2.2.1 Physical Properties
The knowledge of physical properties such as bulk density of the biomass is of fundamental importance for proper design, manufacturing and operation of the pyrolizer.

2.2.2 Bulk density
It was determined by weighing the agro residues sample filled in a vessel of known volume and calculating the ratio of the weight of the agro residues sample to the volume of the vessel. The average of five trials was reported as the volume of the bulk density of the agro residues (Makavana *et al.*, 2018) [7].

$$\text{Bulk density } (\rho),\ kg/m^3 = \frac{w}{v}$$

Where,
W=weight of the agro residues sample, kg
V= volume of the vessel, m^3

2.2.3 Angle of repose
The angle of repose was measured with the help of cylinder arrangement. The cylinder was filled up to the top with the sample and then slowly lifted, thus a conical shape of the material resulted. By measuring the height of the cone angle of repose was calculated using following equation 3.1 (Sidhu and Sadhya 2015) [14].

$$\alpha = \tan^{-1}\left(\frac{2H}{B}\right)$$

Where,
α = Angle of repose, degree
H = Height of cone, mm
B = Base of the cone, mm

2.2.4 Proximate analysis
The proximate composition such as moisture, volatile matter, ash content and fixed carbon content of the agro-residue were calculated by American Society for Testing and Materials standards ASTM-D-3173-3175.

2.2.4.1 Moisture Content
Using hot air oven moisture content of the sample was determined. By oven drying method (ASTM D-3173). The sample was kept in electric oven at 105 °C for an hour and noted weight was obtained. Moisture content will be calculated as,

$$M.C.\ (\%) = \frac{W_2 - W_3}{W_2 - W_1} \times 100$$

Where,
W_1 = Weight of crucible, g
W_2 = Weight of crucible, g + Initial weight of sample, g
W_3 = Weight of crucible, g + Weight of dried sample, g

2.2.4.2 Volatile Matter
The volatile matter was determined using (ASTM D-3175) muffle furnace. It was determined by sample left in crucible by heating uo it 950 °C ± 25 °Cin a muffle furnace for 7 minutes. After removing from muffle furnace, it was cooled first in air and then inside a desiccator and weighed again. The loss in weight was reported as percent of volatile matter and calculated as

$$V.M.\ (\%) = \frac{W_3 - W_4}{W_2 - W_1} \times 100$$

Where,
W_1 = Weight of crucible, g
W_2 = Weight of crucible, g + Initial weight of sample, g
W_3 = Weight of crucible, g + Weight of dried sample, g
W_4 = Weight of crucible, g + Weight of sample after heating in muffle furnace, g

2.2.4.3 Ash Content
The quantity of ash was determined by warming the moisture free sample in muffle furnace without lid at temperature of 750 °C for half hour as per ASTM D – 3174. After removing from muffle furnace, it was cooled first in air and then inside a desiccator. Heating -cooling was repeated till constant weight noted. Ash content was calculated as

$$A.C.\ (\%) = \frac{W_4 - W_1}{W_2 - W_1} \times 100$$

Where,
W_1 = Weight of crucible, g
W_2 = Weight of crucible, g + Initial weight of sample, g
W_3 = Weight of crucible, g + Weight of dried sample, g
W_4 = Weight of crucible, g + Weight of sample after heating in muffle furnace, g

2.2.4.4 Fixed Carbon
The fixed carbon is the residue left after removing the volatile matter and the ash from the substance. The fixed carbon of agro residues sample was calculated by subtracting the sum of volatiles and ash content (%) from 100.

F. C. % = 100 - % of (MC+ VM + AC)

2.2.5 Calorific Value
Calorific value, also known as heating value, is one of the most important properties to consider when evaluating biochar for use as a fuel. Biochar has excellent potential for application in the energy. Calorific value measures the energy content of the agro residue. Calorific value is normally expressed as energy per kilogram of dry agro residues (kcal/kg) and it is dependent on the presence of moisture in the agro residues. A higher moisture content in the agro residues implies a decrease of the heating value because part of the energy is used to evaporate the water. The calorific value of sample was determined by using bomb calorimeter. Bomb Calorimeter consists of a stainless-steel bomb, inside which the agro residues sample is burnt in rich oxygen environment. The bomb is provided with an oxygen inlet valve and two stainless steel electrodes. To one of the electrodes, a small ring is attached. In this ring, the stainless-steel crucible is placed. The bomb is placed in a calorimeter which contains three fourth of water. The calorimeter is provided with a Beckmann thermometer and a stirrer. The calorimeter is surrounded by an air jacket and water jacket

2.2.6 Working of bomb calorimeter

The calorific value of sample was determined by using bomb calorimeter with ASTME – 711 test code. A fine magnesium wire, touching the fuel sample, was stretched across the electrodes and then setup is kept inside the bomb. The bomb lid was tightly sealed and was filled with oxygen up to 25 atmospheric pressures of oxygen. The bomb was kept in the calorimeter. Initial temperature of water in the calorimeter was noted after thorough stirring. The electrodes were then connected to battery. The sample was fired electrically and the fuel sample in crucible burns with the evolution of heat. The heat evolved due to the combustion of the sample, raised the temperature of water in the calorimeter. The final temperature of water was noted. The heat evolved when unit mass of fuel is burnt is known as calorific value. The calorific value of sample using bomb calorimeter was determined by following formula

$$CV = \frac{(W+w)T-(E1+E2)}{X}$$

Where,
W = Weight of water, ml
w = Water equivalent of calorimeter assembly, cal/°C
T = Rise in temperature, °C
E_1 = Correction for nichrome wire, cal = wt of wire, g × calorific value
E_2 = Correction for cotton thread, cal = wt of thread, g × calorific value
X = Weight of sample, g

3. Results and Discussion

The results obtained from physiochemical characterisation of the cotton stalk, soybean straw and pigeon pea stalk were discussed in this section.

3.1 Physiochemical properties of cotton stalk

The physiochemical characterisation of the cotton stalk, soybean straw and pigeon pea stalk were done to analyse the parameters such as bulk density, moisture content, volatile matter, ash content, fixed carbon, calorific value. Table 2 summarise the results physiochemical characterisation of agro residue.

Table 2: Physiochemical characterisation of agro-residue

Sr. No.	Properties	Cotton stalk	Soybean straw	Pigeon pea stalk
1.	Bulk density (kg/m^3)	212.6	220.14	243.8
2.	Angle of repose (°)	42.61	44.12	40.15
2.	Moisture content (%)	09.56	08.21	9.43
3.	Volatile matter (%)	68.15	69.41	67.08
4.	Ash content (%)	05.13	06.32	05.82
5.	Fixed carbon (%)	17.16	16.06	17.67
6.	Calorific value (kcal/kg)	3756	3638	3845

The bulk density of cotton stalk, soybean straw and pigeon pea stalk were found to be 215.80 kg/m^3, 220.18 kg/m^3 and 236.89 kg/m^3, respectively. Higher the density, more weight of biomass can be accommodated in same volume of reactor, higher the energy density and carbon content of biomass (Amer and Elwardany 2020) [2]. The average moisture content in cotton stalk, soybean straw and pigeon pea stalk were found to be 09.56 per cent, 8.21 per cent and 9.43 per cent, respectively which is below 15 per cent which is within desirable limit for agro residues to be used for pyrolysis (Fonseca *et al*., 2019) [5]. The average volatile matter in cotton stalk, soybean straw and pigeon pea stalk were found to be 68.15 per cent, 69.41 per cent and 67.08 per cent, respectively. The components of biomass that burn easily in the presence of oxygen; these usually consist of a mixture of short- and long-chain hydrocarbons, sulfur fumes, and aromatic hydrocarbons that develop during the thermal breakdown of biomass known as volatile matter. Condensable and non-condensable gases are created during the thermal decomposition of biomass to form volatile matter (Suárez-Ruiz and Ward 2008) [15]. The average ash content in cotton stalk, soybean straw and pigeon pea stalk were found to be 05.13 per cent, 06.62 per cent and 05.82 per cent, respectively. The average fixed carbon in cotton stalk, soybean straw and pigeon pea stalk were found to be 17.16 per cent, 16.06 per cent and 17.67 per cent, respectively. Fixed carbon content is an important factor in biomass as it affects combustion properties. Carbonization of raw materials can increase the fixed carbon content, resulting in improved calorific value (Ajimotokan *et al*., 2019) [1]. The average calorific value in cotton stalk, soybean straw and pigeon pea stalk were found to be 3756 kcal/kg, 3638 kcal/kg and 3845 kcal/kg, respectively. The physiochemical properties of agro residues used for pyrolysis process affect the yield and properties of biochar. The calorific value of biomass, also known as its heating value or heat of combustion, is the amount of energy stored in a unit mass of biomass. It's an important property of biomass that determines its energy value and the amount of heat energy generated from a given quantity of fuel.

4. Conclusion

Cotton stalk, soybean straw, and pigeon pea stalk in the Vidarbha region are promising feedstocks for biochar production due to their favourable moisture content, fixed carbon content, and calorific value. Utilizing these residues for pyrolytic conversion to biochar not only provides a renewable energy source but also offers an environmentally friendly alternative to burning agricultural waste. This practice can enhance soil fertility, sequester carbon, and contribute to sustainable agricultural practices in the region. It was discovered that the average moisture level of the stalks from cotton, soybeans, and pigeon peas was less than 15%, which is within the ideal range for using agricultural leftovers for pyrolysis. It was discovered that the average fixed carbon content of pigeon pea, soybean, and cotton stalks was 17.67%, 16.06 percent, and 17.16 percent, respectively. Fixed carbon content has a significant impact on the properties of combustion in biomass. Increased fixed carbon content from carbonisation of raw materials can lead to higher calorific value. It was discovered that the average calorific value of pigeon pea, soybean, and cotton stalks were 3845 kcal/kg, 3638 kcal/kg, and 3756 kcal/kg, respectively. The physiochemical properties of agro residues used for pyrolysis process affect the yield and properties of biochar. From the study it can be concluded that the cotton stalk, soybean straw and pigeon pea stalk can be used for the production of the biochar.

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