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CHARACTERIZATION OF PHYSICAL AND CHEMICAL PROPERTIES OF COTTON STALK AND ITS DERIVED BIO-CHAR

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ABSTRACT

Cotton stalks and other agricultural crop residues are available in plenty and are potential as an energy source in Saurashtra region. Overall, India produces 686 MT gross crop residue biomass on annual basis. These residues are sometimes, burnt in the field itself which creates an adverse condition to soil health. Conversion of this residue into bio-char will be a good option to be used as fuel. Physical properties of whole cotton stalk were determined in terms of average length, diameter and bulk density. Physical properties of shredded cotton stalk were also determined in terms of average length, diameter and bulk density. Proximate analysis in terms of ash content, volatile matter and fixed carbon were also determined for cotton stalk biomass and its bio-char. Calorific value of cotton stalk and its bio-char, considered as most important thermal property of the fuel was also determined. Chemical analysis in terms of pH, EC and CEC, considered as soil amendment. Average bulk density of whole cotton stalk and shredded cotton stalk was found as 29.90 kg/m^3 and 147.02 kg/m^3, respectively.

Key words : Agricultural crop residues, Bio-char, Biomass energy, Bulk density, Cotton stalks.

Introduction

Energy extraction from biomass is one of the best options to manage the increasing energy demand at global level. The biomass utilization will also unload the pressure on limited reserve of commercial fuels. Biomass pyrolysis is one the establishing and proven process for harnessing the biomass energy. Results on the physical properties, proximate analysis, chemical analysis, elemental analysis of cotton stalk and its bio-char, development of small capacity (5 kg) batch type pyrolyser; bio-char, bio-oil and pyro-gas yield from the pyrolysis of shredded cotton stalk at different temperature and residence time.

Physical properties of whole cotton stalk were determined in terms of average length, diameter and bulk density. The whole cotton stalk biomass is difficult to use directly in the pyrolyser reactor so the shredded cotton stalk was prepared using cotton stalk shredder and used in the study as feed material. Physical properties of shredded cotton stalk and its bio-char were determined in terms of average length, diameter and bulk density. Proximate analysis in terms of ash content, volatile matter and fixed carbon were also determined for cotton stalk biomass and its bio-char. Calorific value of cotton stalk and its bio-char, considered as most important thermal property of the fuel was also determined. Chemical analysis in terms of pH, EC and CEC, considered as soil amendment were also determined. Elemental analysis (N, C, H, O and S) of cotton stalk and its bio-char were also carried out.

Methodology

Physical Properties of Whole Cotton Stalk

Physical properties of whole and shredded cotton stalk were determined in terms of average length, diameter and bulk density. Average length of 15 pieces of randomly selected whole cotton plant stalks were measured with the help of measure tape. Average diameter of 15 pieces of randomly selected whole cotton plant stalks were measured with the help of verni caliper. The bulk density of whole cotton stalk plant was also measured. The bulk density of whole cotton stalk plant was determined by tying the plant with the help of ropes with gentle rolling and pressing, so as to consider the bunch as cylinder. Weight of the bunch was measured with the help of spring balance. The bulk density is the weight of biomass bunch divided by the volume occupied by cotton stalk bunch (Makavana and Sarsavadiya, 2018.).

Physical Properties of Shredded Cotton Stalk Biomass and Its Bio-Char

Different size fractions of shredded cotton stalk were analysed in terms of weight and length. Three samples of randomly selected, 2 kg shredded cotton stalk biomass were considered for the analyses. Each sample was divided into seven fractions *i.e.* (1) thick, having diameter ranging from 13-20 mm, (2) medium, having diameter 9-12 mm, (3) thin, having diameter 4-8 mm, (4) very thin, having diameter 2-3 mm, (5) very fine having diameter less than 2 mm, material passed through 2 mm sieve, (6) cotton burrs (woody cover of cotton bolls) and, (7) bark. The diameter of each fraction of cotton stalk was measured with the help of verni caliper. The maximum and minimum length of each fraction of shredded material was also measured with the help of scale. Five fractions i.e. thick, medium, thin, cotton burrs and bark were separated manually. Remaining samples were sieved through 2 mm sieve. The material retained in the sieve was considered as thin material and passed through, it was considered as very fine thin material. Each sample of the shredding material was weighed using a weighing balance (Metler pe-3600) having capacity and least count of 3.6 kg and 0.01g, respectively. The bulk density of shredded cotton stalk was determined by the weight of biomass placed in a container & divided by the analysis occupied. Development of batch type biomass pyrolysis for agricultural residue (Makavana and Sarsavadiya, 2018).

Proximate analysis

Proximate analysis of the fuel defines its volatility and burning properties. ASTM standard (ASTM E870-82, 2013) methods. Calorific value measured with the help of Bomb calorimeter and find out the bulk density with help of standard methods.

Results and Discussion

Physical properties of Whole Cotton Stalk Biomass

Physical properties of whole cotton stalk plant in terms of length, diameter and bulk density were measured. The randomly selected 15 plant was considered in three sections as lower, middle and upper part. The lower part was considered up to 500 mm, middle part was considered from 500 mm to 1000 mm and the remaining part considered as upper part. The diameter of each part of the randomly selected plants was measured at the middle of these sections. The length and diameter of all the randomly selected plants are given in Appendix-A. The average diameter of each section is given in Table 1. The average diameter of whole cotton plant i.e. lower section, middle section and upper section was found as 15.7 mm, 11.9 mm and 8.0 mm respectively. The average length, average diameter and bulk density of the whole cotton stalk plant is shown in Table 2. It can be seen from the Table 2 that the average length, average diameter and bulk density were found as 1488.7 mm, 11.9 mm and 29.9 kg/m^3, respectively. Pyrolysis requires relatively dry feedstock (usually moisture content < 30 wt. %, but moisture contents of ~10 wt. % are preferred), and grinded to around 2 mm particle sizes (Makavana *et al.,* 2020b).

Physical properties of shredded cotton stalk biomass

As the shredded cotton stalk was used as feed stalk instead of whole cotton stalk, physical properties of shredded cotton stalk were also measured. Table 3 the different size fractions of shredded cotton stalk biomass in terms average weight, per cent weight and minimum-maximum length of shredded cotton stalk. The values of different size fractions of randomly selected three samples of 2000 g shredded cotton stalk biomass sample. The fractions of shredded mass were divided into seven different size fractions as thick, having diameter ranged from 13 to 20 mm, medium having diameter from 9 to 12 mm, thin having diameter from 4 to 8 mm, very thin having diameter 2 to 3 mm, very fine having diameter less than 2 mm, cotton burrs and bark. It can be seen from table 4.3 that the average weight of thick, medium, thin, very thin, very fine, cotton burrs and bark fractions of shredded cotton stalk were found as 476.13 g, 267.33 g, 389.57 g, 224.36 g, 50.60 g, 245.55 g and 346.47 g respectively. The percent weight of thick, medium, thin, very thin, very fine, cotton burrs and bark fractions were found as 23.80 %, 13.37 %, and 19.48 %, 11.21 %, 2.53 %, 12.28 % and 17.32 % respectively. It can also be seen from the table that maximum and minimum per cent weight fractions were found as 23.80 % and 2.53 % having diameter ranged from 13 to 20 mm and less than 2 mm diameter respectively. It can also be seen from the table that the minimum and maximum length of different size fractions of thick, medium, thin, very thin, very fine, cotton burrs

Table 1 : Average diameter of each section of whole cotton stalk plant.

S. no.	Average diameter of lower section up to 500 mm	Average diameter of middle section 500 mm-1000 mm	Average diameter of upper section 1000 mm-1500 mm
1	15.7 mm	11.9 mm	8.0 mm

Table 2 : Average length, diameter and bulk density of whole cotton stalk.

S. no.	Average length (mm)	Average diameter (mm)	Bulk density (kg/m^3)
1	1488.7	11.9	29.9

Table 3 : Different size fractions of shredded cotton stalk biomass.

S. no.	Size fractions	Average weight		Length (mm)	
		g	%	Minimum	Maximum
1	Thick,13-20 mm dia.	476.13	23.80	19	180
2	Medium,9-12 mm dia.	267.33	13.37	14	160
3	Thin,4-8 mm dia.	389.57	19.48	23	139
4	Very thin,2 mm-3 mm dia.	224.36	11.21	10	58
5	Very fine,less than 2 mm dia.	50.60	02.53	2	7
6	Cotton burrs	245.55	12.28	8	38
7	Bark	346.47	17.32	32	290
	Total	2000	100.00		

and bark were ranged from 19-180 mm, 14-160 mm, 23-139 mm, 10-58 mm, 2-7 mm, 8-38 mm and 32-290 mm, respectively.

The bulk density of shredded cotton stalk biomass was found as147.02 kg/m^3. This bulk density and different size fractions represented the suitability of shredded cotton stalk as compared to whole cotton stalk for pyrolysis process because biomass with high density is advantageous for combustion systems as it represents a high energy value for smaller volumes and needs less storage space. Dubey and Gangil (2009) reported the bulk density of cotton sticks 160 kg/m^3.

Physical Properties of Shredded Cotton Stalk Bio-char

The fractions of shredded cotton stalk bio-char were divided into five different size fractions as the material retained in 3 x 3 screen opening sieve, material retained in 4 x 4 screen opening sieve, material retained in 6 x 6 screen opening sieve, material retained in 10 x 10 screen opening sieve and powder (< 1.5 mm) as the material passed through 10 x 10 screen opening sieve. Different size fractions of shredded cotton stalk bio-char in terms of average weight in g and per cent as well as minimum and maximum length. These values of shredded cotton stalk bio-char at different residence time of 60, 120, 180 and 240 min are given in Tables 4 to 7 respectively for 200, 300, 400 and 500°C.

Table 4 shows the values of different size fractions of shredded cotton stalk bio-char at different residence time of 60, 120, 180 and 240 min for 200 °C. It can be seen from the Table 4 that average weight of the different size fraction was ranged from a minimum of 103.00 g (10.30%) to a maximum of 473.00 g (47.30%) for 10 × 10 screen opening and 3 x 3 screen opening respectively for 60 min residence time. The powder fractions (< 1.5 mm size) were found as 177.00 g (17.70 %). Different size fraction of bio-char of shredded cotton stalk were also analysed in terms of weight and length (Makavana *et al.*, 2022).

The length of bio-char was ranged from 5 mm to 94 mm among these fractions. It can be seen from the table that average weight of the different size fractions were ranged from 119.33 g (11.93%) to 483.34 g (48.34%) for 4 × 4 screen opening and 3 × 3 screen opening, from 119.33 g (11.93 %) to 495.34 g (49.53 %) for 4 × 4 screen opening and 3 x 3 screen opening, from 106.33 g (10.60%) to 426.00 g (42.60%) for 4 x 4 screen opening and 3 × 3 screen opening for 120 min, 180 min and 240 min residence time respectively. The powder fractions (< 1.5 mm size) were obtained as 133.67 g (13.37%), 118.33 g (11.83%) and 151.67 g (15.20%) for 120 min, 180 min and 240 min residence time, respectively.

Table 5 shows the different size fractions of shredded cotton stalk bio-char at different residence time of 60, 120, 180 and 240 min for 300 °C. It can be seen from the table that average weight of the different size fractions were ranged from a minimum of 109.67 g (10.97%) to a maximum of 348.00 g (34.80 %) for 6 × 6 screen opening and 3 × 3 screen opening, 117.67 g (11.77%) to 354.00 g (35.40%) for 6 x 6 screen opening and 3 × 3 screen opening, from 121.33 g (12.13 %) to 334.00 g (33.40%) for 10 × 10 screen opening and 3 x 3 screen opening, from 118.00 g (11.80 %) to 339.00 g (33.90%) for 6 x 6 screen opening and 3 x 3 screen opening for 60 min, 120 min, 180 min and 240 min residence time, respectively. The powder fractions (< 1.5 mm size) were found as 280.66 g (28.00%), 276.33 g (27.63%), 251.00 g (25.10%)

Table 4 : Different size fractions of shredded cotton stalk bio-char at different residence time for 200°C temperature.

S. no.	Size fraction	Residence time, min											
		60			120			180			240		
		Avg. weight	Length, mm		Avg. weight	Length, mm		Avg. weight	Length, mm		Avg. weight	Length, mm	
		g(%)	min	max	g(%)	min	max	g (%)	min	max	g(%)	min	max
1	Retained in 3 × 3 screen opening	473 (47.30)	70	94	483.34 (48.34)	69	89	495.34 (49.53)	68	90	426 (42.60)	67	78
2	Retained in 4×4 screen opening	114 (11.40)	32	61	119.33 (11.93)	30	67	119.33 (11.93)	29	66	106.33 (10.60)	33	68
3	Retained in 6 × 6 screen opening	133 (13.30)	10	40	141.33 (14.13)	6	58	144 (14.40)	10	64	157 (15.70)	6	60
4	Retained in 10 × 10 screen opening	103 (10.30)	5	21	122.33 (12.23)	5	10	123.1 (12.31)	6	30	159 (15.90)	5	30
5	Powder <1.5 mm	177 (17.70)	-	-	133.67 (13.37)	-	-	118.33 (11.83)	-	-	151.67 (15.20)	-	-
	Total	1000 (100.00)			1000 (100.00)			1000 (100.00)			1000 (100.00)		

Table 5 : Different size fractions of shredded cotton stalk bio-char at different residence time for 300 °C temperature.

S. no.	Size fraction	Residence time, min											
		60			120			180			240		
		Avg. weight	Length, mm		Avg. weight	Length, mm		Avg. weight	Length, mm		Avg. weight	Length, mm	
		g(%)	min	max	g(%)	min	max	g (%)	min	max	g(%)	min	max
1	Retained in 3 × 3 screen opening	348 (34.80)	19	81	354 (35.40)	10	73	334 (33.40)	10	78	339 (33.90)	30	84
2	Retained in 4 × 4 screen opening	141.67 (14.17)	17	20	131.67 (13.17)	8	81	163.33 (16.34)	18	67	150 (15.00)	10	58
3	Retained in 6 × 6 screen opening	109.67 (10.97)	10	15	117.67 (11.77)	7	59	130.34 (13.03)	10	83	118 (11.80)	8	42
4	Retained in 10 × 10 screen opening	120 (12.00)	4	8	120.33 (12.03)	3	10	121.33 (12.13)	3	10	121.67 (12.17)	3	10
5	Powder <1.5 mm	280.66 (28.00)	-	-	276.33 (27.63)	-	-	251 (25.10)	-	-	271.33 (27.13)	-	-
	Total	1000 (100.00)			1000 (100.00)			1000 (100.00)			1000 (100.00)		

The length of bio-char was ranged from 4 mm to 81 mm, 3 mm to 73 mm, 3 mm to 78 mm and 3 mm to 84 mm for 60 min, 120 min, 180 min and 240 min residence time, respectively.

and 271.33 g (27.13%) for 60 min, 120 min, 180 min and 240 min residence time, respectively.

Likewise, Table 6 shows the different size fractions of shredded cotton stalk bio-char at different residence time of 60, 120, 180 and 240 min for 400°C. It can be seen from the Table 6 that average weight of the different size fraction were ranged from a minimum of 128.33 g (12.83%) to a maximum of 341.67 g (34.67 %) for 10 x 10 screen opening and 3 x 3 screen opening, 125.00 g (12.50%) to 336.33 g (33.63 %) for 6 x 6 screen opening and 3 x 3 screen opening, from 123.00 g (12.30%) to 362.33 g (36.23%) for 10 x 10 screen opening and 3 x 3 screen opening, from 121.00 g (12.10 %) to 345.00 g (34.50%) for 10 x 10 screen opening and 3 x 3 screen opening for 60 min, 120 min, 180 min and 240 min residence time respectively. The powder fractions (< 1.5 mm size) were found as 265.67 g (26.57%), 161.67 g (26.17%), 256.00 g (25.60%) and 265.33 g (26.53 %) for 60 min, 120 min, 180 min and 240 min residence time, respectively. The length of bio-char was ranged from 3 mm to 98 mm, 4 mm to 100 mm, 4 mm to 47 mm and 4 mm to 84 mm for 60 min, 120 min, 180 min and 240 min residence time, respectively.

The values of bulk density of shredded cotton stalk bio-char for all the experimental run at different temperature and residence time is shown in Table 8. It can be seen from the table the bulk density of bio-char was ranged from 173.86 – 184.09 kg/m^3, 161.36 – 177.27 kg/m^3, 156.81 – 163.18 kg/m^3 and 150.90 – 154.54 kg/m^3 at 200, 300, 400 and 500°C temperature respectively, at different experimental residence time. It can be seen from the table that the bulk density of bio-char is reduced with temperature. This may be perhaps due to the reason that more volatile matter losses occur at higher temperature. However, it can be seen from the table that the density of bio-char is not significantly changed with residence time (Makavana *et al*., 2020). Density was increased by 3.91 times and calorific value was increased by 1.19 times. Bulk density of rice husk and rice straw was 331.59 kg/m^3 and 380.54 kg/m^3, respectively. For sugarcane bagasse and cotton stalk it was 723.2 and 206.14kg/m^3 respectively (Makavana *et al*., 2018). The paper may examine the physical characteristics such as porosity, particle size and density of the bio-char, which influence its suitability for applications like soil amendment or pollution control. The broader environmental and economic implications of converting agricultural residues like cotton stalks into bio-char could also be addressed, especially regarding sustainability, reducing waste, and contributing to the circular bio-economy.

Proximate analysis of shredded cotton stalk bio-char

Proximate analysis ASTM E870-82, (2013) of cotton stalk bio-char in terms of ash content, volatile matter and fixed carbon were determined for all the experimental runs.

Ash content

The values of ash content of shredded cotton stalk bio-char for all the experimental run at different temperature and residence time is shown in Table 9. The value of ash content of bio-char was ranged from a minimum of 5.5% (d.b.) at 200 °C with 60 min residence time to a maximum of 15.56 % (d.b.) at 500 °C with 240 min residence time. Yang and Sheng (2012) also found similar results. They reported that ash content of cedar wood; pinewood and cotton stalk bio-char increased from 1.5 to 2.1%, 2.5 to 4.7 % and 6.0 to 10.1%, respectively as the temperature increased from 300 to 600°C. Novak *et al.* (2009) was also found the similar behaviour for bio-char obtained from different feedstocks like peanut hull, pecan shell, poultry litter and switch grass. They reported that ash content of peanut hull, pecan shell, poultry litter and switch grass bio-char was increased from 8.2- 9.3%, 2.4 to 5.2 %, 35.9 to 52.4% and 2.6 to 7.8 % as the temperature increased from 400 to 500°C, 350 to 700°C, 350 to 700°C and 250 to 500°C, respectively. Perhaps the reason behind that as the temperature increased, more volatiles are driven off which reduced the mass but the mineral components are retained in the solid fraction and therefore the percentage of ash increased. Makavana *et al*. (2024) reported the values of ash content (12.30%), volatile matter (65.90%), and fixed carbon (21.80%) for pigeon pea wood.

Volatile matter

The average values of volatile matter of shredded cotton stalk bio-char for all the experimental run at different temperature and residence time is shown in Table 9. The value of volatile matter of bio-char was ranged from a minimum of 48.02% (d.b) at 500 °C with 240 min residence time to a maximum of 79.48 % (d.b) at 200 °C with 60 min residence time. Similar results were also found by Yang and Sheng (2012). They reported that volatile matter of cedar wood, pine wood and cotton stalk bio-char decreased from 37.5 to 18.4 %, 37.3 to 17.2 % and 32.2 to 15.6% respectively as the temperature increased from 300 to 600°C. Jindo *et al.* (2014) also reported that the volatile matter of apple tree branch, oak tree, rice husk and rice straw bio-char decreased from 32.36 to 6.82%, 32.06 to 7.87 %, 22.00 to 3.17 % and 22.42 to 4.47% as the temperature increased from

400 to 800°C, 400 to 800 °C, 400 to 800 °C and 400 to 800°C, respectively. This may be perhaps due to the reason that as the pyrolysis temperature increases then the reaction of devolatilization occurs. This resulted in loss of volatile organic compounds hence volatile matter decreases.

Fixed carbon

The average values of fixed carbon of shredded cotton stalk bio-char for all the experimental run at different temperature and residence time is shown in Table 9. The value of fixed carbon of bio-char was ranged from a minimum of 15.02% (d.b) at 200°C with 60 min residence time to a maximum of 36.40% (d.b) at 500 °C with 240 min residence time. Similar results were also found by Yang and Sheng (2012). They reported that fixed carbon of cedar wood, pine wood and cotton stalk bio-char increased from 61.1 to 79.5%, 60.2 to 78.1 % and 61.8 to 74.2% respectively as the temperature increased from 300 to 600°C. Venkatesh *et al.* (2013) also reported that the fixed carbon of cotton stalk bio-char increased from 58.7 to 71.0% as the temperature increased from 350 to 500 °C. Perhaps the reason behind may be due to increasing in temperature the volatile matter being driven off during the pyrolysis process, resulting in the formation of more stable carbon known as fixed carbon. The feedstock and the method by which the bio-char is produced has a significant impact on bio-char characteristics, including concentrations of elemental constituents, density, porosity and pH, which collectively impact the ability of the bio-char for various applications (Makavana *et al*., 2020a).

Thermal property and Chemical Properties of Shredded Cotton Stalk and its Bio-Char

Thermal property (calorific value) and chemical properties in terms of pH, electrical conductivity and cation exchange capacity of shredded cotton stalk and its bio-char were determined for all each experiment run.

Calorific Value of Cotton Stalk Biomass

The calorific value of shredded cotton stalk is given in Table 10. The results of the energy equivalent of the calorimeter rise in temperature, correction factors for the chrome wire and thread as well as calorific value of the biomass is given in Table 10. That energy equivalent of the bomb calorimeter was found as 398.26 cal/°C. The temperature rise for burning of the 0.5077 g biomass sample was observed as 0.71 °C in the bomb calorimeter. Calorific value of the biomass was obtained after using the correction factor of nichrome wire and cotton thread as 3685.3 cal /g.

The calorific value of cotton stalk was found 15.42 MJ/kg. The results of calorific value of cotton stalk in the present study were in accordance with the results presented by Dubey and Gangil (2009) as LHV and HHV of cotton stick as 16 and 17.40 MJ/kg respectively. Vyas and Singh (2007) also determined the lower calorific value of jatropha seed husk as 16.92 MJ/kg. Erol *et al*. (2010) analysed 20 different biomass samples and determined net calorific value in the range of 15.41-19.52 MJ/kg.

Calorific Value of Shredded Cotton Stalk Bio-Char

The calorific value of bio-char along with temperature rise and sample weight of randomly selected samples of shredded cotton stalk bio-char for each run. The calorific values of shredded cotton stalk bio-char for all the experimental run at different temperature and residence time is shown in Table 11. The calorific value of bio-char was ranged from a minimum of 4622.0 cal /g (19.34 MJ/kg) at 200 °C with 60 min residence time to a maximum of 8101.3 cal /g (33.89 MJ/kg) at 500 °C with 240 min residence time. Similar results were also found by Yang and Sheng (2012). They reported that of cedar wood, pine wood and cotton stalk bio-char increased from 25.1 to 29.5MJ/ kg, 25.6 to 28.8 MJ/ kg and 25.7 to 27.6 MJ/kg respectively as the temperature increased from 300 to 600 °C. Lee *et al.* (2018) also reported that the calorific value of food waste containing grain, vegetables or meat ranged from 23.7 to 29.7 KJ/g as the temperature increased from 200 to 400°C. The calorific value of shredded cotton stalk bio-char is an indicator of its potential use as a renewable energy source and optimizing the pyrolysis process can enhance its energy output.

Chemical Properties of Shredded Cotton Stalk and its Bio-Char

Chemical properties of shredded cotton stalk and its bio-char in terms of pH, electrical conductivity (EC) and cation exchange capacity (CEC) is given in Table 12.

pH

The pH value of the shredded cotton stalk and its bio-char was determined with the help of pH meter. Table 12 that the pH of the cotton stalk was found as 5.59. It can also be seen from the table that the value of bio-char was ranged from a minimum of 5.88 at 200 °C with 60 min residence time to a maximum of 9.86 at 500 °C with 240 min residence time. The pH value of cotton stalk bio-char was increased with increase in temperature. The results are in accordance with the results presented by Venkatesh *et al.* (2013). They reported that the pH value of cotton stalk bio-char increased from 8.9 to 9.3 as the temperature increased from 350 to 500°C. Fuertes *et al.*

Table 6 : Different size fractions of shredded cotton stalk bio-char at different residence time for 400 °C temperature.

S. no.	Size fraction	Residence time, min											
		60			120			180			240		
		Avg. weight	Length, mm		Avg. weight	Length, mm		Avg. weight	Length, mm		Avg. weight	Length, mm	
		g(%)	min	max	g(%)	min	max	g (%)	min	max	g(%)	min	max
1	Retained in 3 × 3 screen opening	341.67 (34.67)	51	98	336.33 (33.63)	43	100	362.33 (36.23)	19	47	345 (34.50)	30	84
2	Retained in 4 × 4 screen opening	133 (13.30)	14	40	136.33 (13.63)	12	41	130.67 (13.07)	11	33	145 (14.50)	10	58
3	Retained in 6 × 6 screen opening	131.33 (13.13)	13	33	125 (12.50)	10	61	128 (12.80)	9	44	123.67 (12.37)	8	42
4	Retained in 10 × 10 screen opening	128.33 (12.83)	3	14	140.67 (14.07)	4	9	123 (12.30)	4	14	121 (12.10)	4	10
5	Powder < 1.5 mm	265.67 (26.57)	-	-	261.67 (26.17)	-	-	256 (25.60)	-	-	265.33 (26.53)	-	-
	Total	1000 (100.00)			1000 (100.00)			1000 (100.00)			1000 (100.00)		

Table 7 : Different size fractions of shredded cotton stalk bio-char at different residence time for 500 °C temperature.

S. no.	Size fraction	Residence time, min											
		60			120			180			240		
		Avg. weight	Length, mm		Avg. weight	Length, mm		Avg. weight	Length, mm		Avg. weight	Length, mm	
		g(%)	min	max	g(%)	min	max	g (%)	min	max	g(%)	min	max
1	Retained in 3 × 3 screen opening	156 -15.6	30	87	175 -17.53	19	98	153.67 -15.37	25	81	145.33 -14.53	26	73
2	Retained in 4 × 4 screen opening	195.33 -19.53	18	70	205 -20.5	10	88	200 -20	20	67	216.33 -21.63	21	46
3	Retained in 6 × 6 screen opening	170.67 -17.07	8	73	170.33 -17.03	8	73	159 -15.9	10	61	151 -15.1	15	23
4	Retained in 10 × 10 screen opening	188 -18.8	6	9	143.67 -14.37	4	19	165 -16.5	4	20	177.67 -17.77	4	18
5	Powder < 1.5 mm	290 -29	-	-	305.67 -30.57	-	-	322.33 -32.23	-	-	309.67 -30.97	-	-
	Total	1000 -100			1000 -100			1000 -100			1000 -100		

Table 8 : Bulk density of bio-char at different temperature and residence time.

Run No.	Temperature (°C)	Residence time (min)	Bulk density (kg / m^3)
1	200	60	184.09
2		120	178.4
3		180	179.54
4		240	173.86
1	300	60	177.27
2		120	165.9
3		180	161.36
4		240	168.18
1	400	60	160.22
2		120	156.81
3		180	163.18
4		240	163.18
1	500	60	151.54
2		120	151.13
3		180	150.9
4		240	151.59

Table 9 : Proximate analysis of shredded cotton stalk bio-char at different temperature & residence time.

Run No.	Temperature (°C)	Residence time (min)	Ash content (%, d.b)	Volatile matter (%, d.b)	Fixed carbon (%, d.b)
1	200	60	5.5	79.48	15.02
2		120	5.95	78.73	15.32
3		180	6.32	77.73	16.33
4		240	6.85	75.71	17.44
5	300	60	7.09	72.68	20.23
6		120	8.02	70.62	21.36
7		180	8.95	67.49	23.56
8		240	9.35	65.23	25.42
9	400	60	9.98	63.16	26.86
10		120	10.53	60.94	28.53
11		180	11.23	58.85	29.92
12		240	12.02	56.87	31.11
13	500	60	13.04	54.54	32.42
14		120	13.91	52.13	33.96
15		180	14.86	49.88	35.26
16		240	15.56	48.02	36.4

Table 10 : Energy equivalent of the calorimeter and calorific value of cotton stalk.

S. No.	Weight of water (ml)	Energy equivalent (cal / °C)	Weight of sample (g)	Temperature rise (°C)	Correction factor		CV of cotton stalk (cal /g)
					Nichrome wire(E_1) (cal)	Cotton thread (E_2) (cal)	
1	2000	398.26	0.5077	0.71	1.4	213.8	3685.3

(2010) also reported that the pH value of cotton stalk bio-char ranged from 8.9 to 9.0 as the temperature increased from 450 to 500°C. Jindo *et al.* (2014) also reported that the pH of apple tree branch, oak tree, rice husk and rice straw bio-char increased from 7.02 to 10.02, 6.43 to 9.68, 6.84 to 9.62 and 8.62 to 10.47 as the temperature increased from 400 to 800°C, 400 to 800°C, 400 to 800 °C and 400 to 800°C respectively. Novak *et al.* (2009) also found the similar behaviour for bio-char obtained from different feed stocks like peanut hull, pecan shell, poultry litter and switchgrass. They reported that pH of peanut hull, pecan shell, poultry litter and switchgrass bio-char was increased from 7.9 to 8.6, 5.9 to 7.2, 8.7 to 10.3 and 5.4 to 8.0 as the temperature increased from 400 to 500°C, 350 to 700 °C, 350 to 700°C and 250 to 500°C, respectively. However, no significant change or behaviour was observed with respect to increase in residence time.

Higher temperature during the conversion process had the strongest influence on the bio-char pH suggesting that higher temperature may have attributed to higher degree of volatilization, decomposition of surface oxygen groups and dihydroxylation. Substantial increases in pH occurred at the higher temperatures may be due to the concentration of non pyrolyzed inorganic elements in the bio-char.

Electrical Conductivity (EC)

The EC value of the shredded cotton stalk and its bio-char was determined with the help of pH/ conductivity meter. Table 12 that EC value of the cotton stalk was found as 0.03 dS/m. It can also be seen from the table that the salinity of all the cotton stalk bio-char had low EC value and from a minimum of 0.04 dS/m at 200°C with 60 min residence time to a maximum of 0.10 dS /m at 500°C with 240 min residence time. The EC value of

Table 11 : Calorific value of cotton stalk bio-char at different temp. and residence time.

Run No.	Temperature (°C)	Residence time (min)	Calorific value of cotton stalk bio-char (cal /g)
1	200	60	4622
2		120	4687
3		180	4738
4		240	5632.6
5	300	60	5473.1
6		120	5747.6
7		180	6093.4
8		240	6099.6
9	400	60	6463.5
10		120	6587.6
11		180	7974.3
12		240	7983.1
13	500	60	8013
14		120	8018.9
15		180	8042.1
16		240	8101.3

cotton stalk bio-char was increased with increase in temperature. Similar results were also found by Venkatesh *et al.* (2013) and reported that the EC value of cotton stalk bio-char increased from 0.05 to 0.11 dS/m as the temperature increased from 350 to 500 °C. Venkatesh *et al.* (2013a) also reported that the EC value of castor bean stalk bio-char increased from 0.01 to 0.05 dS/m as the temperature increased from 350 to 500°C. However, no significant change in EC values of the cotton stalk bio-char was observed at all the levels of experimental levels.

Cation exchange capacity (CEC)

The values of exchangeable Ca, Mg, Na, and K of cotton stalk and its bio-char obtained from each experimental run. The CEC value of the shredded cotton stalk and its bio-char for all the experimental run at different temperature and residence time is shown in Table 12. The CEC value of the cotton stalk was found as 38.84 cmol/ kg. Table 12 that the value of CEC of bio-char was ranged from a minimum of 24.39 cmol/ kg at 500 °C with 240 min residence time to a maximum of 38.02 cmol / kg at 200 °C with 60 min residence time. The CEC value of cotton stalk bio-char was decreased with increase in temperature. Similar results were also found by Venkatesh *et al.* (2013). They reported that the

Table 12 : pH, EC and CEC values different temperature and residence time for shredded cotton stalk and its bio-char.

Run No.	Temperature (°C)	Residence time (min)	pH	EC (dS/m)	CEC (cmol/kg)
1	Shredded cotton stalk	-	5.59	0.03	38.84
2	200	60	5.88	0.04	38.02
3		120	5.97	0.04	37.89
4		180	5.85	0.04	37.78
5		240	5.96	0.04	37.61
6	300	60	8.83	0.04	37.42
7		120	8.34	0.05	36.79
8		180	8.41	0.05	36.33
9		240	8.55	0.06	35.7
10	400	60	9.33	0.08	34.23
11		120	9.42	0.09	33.1
12		180	8.35	0.07	29.38
13		240	9.36	0.07	27.77
14	500	60	9.68	0.09	26.31
15		120	9.7	0.08	25.57
16		180	9.61	0.09	25.03
17		240	9.86	0.1	24.39

CEC value of cotton stalk bio-char increased from 51.3 to 11.7 cmol / kg as the temperature increased from 350 to 500°C. Venkatesh *et al.* (2013a) also reported that the CEC value of castor bean stalk bio-char decreased from 40.8 to 16.4 cmol / kg as the temperature increased from 350 to 500°C. The CEC values of bio-char were also decreased with residence time. However, the effect of residence time on CEC values of bio-char was less as compared to temperature. These may be perhaps due to the reason that trace element has more interaction with temperature as compared to residence time.

Conclusion

The study found that the bulk density of whole cotton stalk and shredded cotton stalk was 29.90 kg/m³ and 147.02 kg/m³, respectively, indicating a 3.91-fold increase in density upon shredding. The moisture content, ash content, volatile matter, and fixed carbon of shredded cotton stalk biomass were 12.5%, 5.27%, 80.22% and 14.51% (on a dry basis), respectively. The bio-char derived from this biomass showed ash content ranging from 5.5% to 15.56%, volatile matter from 48.02% to

79.48%, and fixed carbon from 15.02% to 36.40%. The calorific value of the cotton stalk biomass was 3685.3 cal/g, while the bio-char's calorific value ranged from 4622.0 cal/g to 8101.3 cal/g, indicating an increase of 1.19 times. Additionally, the pH, electrical conductivity (EC), and cation exchange capacity (CEC) of shredded cotton stalk biomass were 5.59, 0.03 dS/m, and 38.84 cmol/kg, respectively. The bio-char's pH ranged from 5.85 to 9.86, EC from 0.04 to 0.10 dS/m, and CEC from 38.02 to 24.39 cmol/kg, depending on the temperature and residence time. The highest quality bio-char was produced at 500°C and 240 minutes, with a calorific value of 8101.3 cal/g, nitrogen content of 1.56%, carbon content of 79.30%, and a C/N ratio of 50.83.

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