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Physicochemical properties and proximate analysis of cotton stalks biomass

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Abstract
Biomass gasification is a thermo-chemical process, which converts the solid biomass in oxygen deficient environment into combustible producer gas. The cotton stalk is abundantly available for converting solid biomass into useful form of energy. Gasifiers have promising potential for agriculture and agro industrial applications, which provided improved gas quality, particularly in terms of tar and particulate matter contents of the gas. Average bulk density of shredded cotton stalk was found as 146.58 kg/m^3 and increased 485.36% of whole cotton stalk. The proximate analysis of shredded cotton stalk biomass in terms of moisture content, fixed carbon, volatile matter and ash content were found as 11.46, 16.47, 78.12, and 5.41 (%, d.b), respectively. The values of pH, EC, O.C., available N, P_2O_5, K_2O and S of shredded cotton stalk were found as 5.41, 3.05 dS/m, 54.58%, 0.77%, 0.10%, 0.39% and 0.11%, respectively.

Keywords: Biomass, cotton stalks, agro residues

1. Introduction
Availability of huge amount of biomass in the form of agricultural, agro industrial residues in the agriculture sector have attracted the attention of scientists on developing biomass based renewable energy technologies, and alternate fuels**.** This huge amount of crop residue has economic value. In India, approximately 500-550 million tonnes (Mt) of crop residue is generated on-farm and off-farm annually from its production of 110 Mt of wheat, 122 Mt of rice, 71 Mt of maize, 26 Mt of millets, 141 Mt of sugarcane, 8 Mt of fiber crops (Jutemesta, cotton) and 28 Mt of pulses reported by Devi *et al.* (2017) [3]. In Gujarat, about 22.9 million tonnes of crop residue is generated annually. In Gujarat, crop residues of rice, wheat, coarse cereal, oilseed, sugarcane and cotton are generated in terms of 1.9, 4.0, 2.6, 4.3, 5.5 and 3.6 million tonnes respectively (Devi *et al*., 2017) [3].
It is realized that the fossil fuels are not going to last long, coupled with a steep increase in international/domestic prices of fossil fuels has compelled us to develop and exploit renewable sources of energy in the country. Crop production activity is the single largest and most important activity that harnesses solar energy in the form of seed, fruit, fodder, fuelwood and other biomass. If managed properly and exploited scientifically, the renewable source of energy available in the countryside can meet all requirements of energy/power for production, processing, transportation and domestic activity of rural people and also partly meet the energy requirements of urban people.
Biomass is possibly the most promising renewable energy source for rural development. Unlike wind it is widely distributed, it is also a means of energy storage. Biomass is like a partially oxygenated hydrocarbon. It has higher ash content than hydrocarbons but has much lower sulphur content. Biomass conversion and management technologies had a very important role in rural development in India. These technologies offer a great challenge to the conventional sources and put to the services of rural people development, especially improved cooking stoves, biogas and producer gas (Alam, 2000) [1]. Agriculture is highly dependent on fossil fuel energy and shortage of the latter will jeopardize world food security. The gasification crop residue will permit its use for thermal and mechanical/electrical energy generation in kW ranges. As a result of the recent change in diesel price, it was suggested that dual fuel mode of operation of gensets using 70 per cent producer gas from crop residue and 30 per cent diesel has become more economical than operation on diesel alone (Pathak, 2000) [9].

Biomass is the primary source of food, fodder, fibre, firewood, timber etc. and also discussed the factors that govern the energy synthesis and the available technologies for optimizing biomass production (Rai and Pathak, 2000) [10]. Assess the quantity of recoverable biomass from cropland, grassland, forest, roadsides and agroforestry. The total biomass availability per annum in 2001 was 1000 Mt and surplus was 249.9 Mt. They estimated total available crop residues in India as 523.4 Mt/year and surplus as 127.3 Mt/year. In certain regions where the production of the straw is high, demand for feed, fodder, and other uses is low and handling and transportation cost to deficit area is high, the straw is burned which creates a serious problem of environmental pollution and loss of valuable organic matter (Pathak and Srivastav, 2004) [8].

2. Material and Method

2.1. Physicochemical properties and proximate analysis of cotton stalk

Cotton stalk is considered as the gasification material. Cotton stalk was procured from the Cotton Research Farm, JAU, Junagadh and converted into shredded material with the help of shredder. The following properties were determined for cotton stalk biomass material.

2.1.1 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 measuring tap. Average diameter of 15 pieces of randomly selected whole cotton plant stalks were measured with the help of Verniercalliper. 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.

2.1.2 Physical properties of shredded cotton stalk

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 analysis. 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 2-3mm, (5) very very thin, 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 Vernier calliper. 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 very 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.

2.1.3 Proximate analysis

Proximate analysis characterizes the biomass feed stock for fuel moisture content, volatile matter, ash content and fixed carbon.

Proximate analysis of the fuel defines its volatility and burning properties. ASTM standard (ASTM, 1983) recommended for coal, sparky fuels, etc., which meets the demand of the biomass material largely, was used for these analysis.

2.1.3.1 Moisture content

Moisture content of most of the biomass fuel depends on the type of fuel, its origin and treatment before it is used. Moisture content of the fuel is usually referred to inherent moisture plus surface moisture. Fuel moisture content (FMC) of cotton stalk was determined by drying the known weight of sample in hot air oven at 105 ± 2 ºC while keeping the ground sample in petridish till constant weight. The ratio of weight of water to the initial weight of the sample was the moisture content of fuel on dry basis. For most of the biomass samples 2 h drying is sufficient.

$$\text{FMC, (\%, d.b.)} = \frac{(w_2 - w_3)}{(w_3 - w_1)} \times 100 \qquad (3.1)$$

Where, w_1= weight of the empty petridish, g
w_2= weight of the wet sample plus petridish, g
w_3= weight of dry sample plus petridish, g

2.1.3.2 Volatile matter

Oven-dried biomass sample was kept in the tarred crucible. Two drops of benzene was added in it to displace air in the environment surrounding the sample. The crucible was closed with lid and placed in the muffle furnace and heated at 600±10 °C for six minutes and 900±10 °C for another six minutes. The loss in weight divided by the initial weight of biomass is the volatile matter on dry basis of oven dried biomass fuel.

$$\text{Volatile matter (\%, d.b)} = \frac{(w_2 - w_3)}{(w_2 - w_1)} \times 100 \qquad (3.2)$$

Where,
w_1= weight of the empty crucible, g
w_2= initial weight of the sample plus crucible, g
w_3= final weight of sample plus crucible, g

2.1.3.3 Ash content

In this method, oven-dried biomass sample kept in the silica crucible was placed in the muffle furnace at 750 ± 25 °C till constant weight. The ratio of the final weight to the initial weight of the sample was the ash content of the moisture free biomass sample.

$$\text{Ash content (\%, d.b)} = \frac{(w_3 - w_1)}{((w_2 - w_1)} \times 100 \qquad (3.3)$$

Where,
w_1= weight of empty crucible, g
w_2= initial weight of the sample plus crucible, g
w_3= final weight of sample (ash) plus crucible, g

2.1.3.4 Fixed carbon

The fixed carbon represents the non-volatile combustible component of the fuel. After determining fuel moisture content (d.b.), volatile matter (d.b.) and fuel ash content (d.b.). The fixed carbon content was estimated from the material balance equation given below

FC (%, d.b.) = 100 – VM (%, d.b.) – ASH (%, d.b.) … (3.4)

Where,
FC (%, d.b.) = percentage of fixed carbon on dry basis
VM (%, d.b.) = percentage of volatile matter on dry basis
ASH (%, d.b.) = percentage of ash on dry basis

2.1.4 Chemical analysis of shredded cotton stalk biomass
Chemical analysis of shredded cotton stalk biomass were carried out in terms of pH, Electrical conductivity (EC), Organic Carbon, available N, available P_2O_5, available K_2O and available S for calculation method was used is given in Table 1.

Table 1: Chemical properties of shredded cotton stalk

Sr No.	Particular	Method followed
1	pH (1:10)	pH meter (Richards, 1954)
2	EC (1:10)(dS/m)	EC meter (Jackson, 1974)
3	Organic Carbon (%)	Ash method (Jackson, 1974)
4	Available N (%)	Alkaline $KMnO_4$ method (Subbiah and Asija, 1956)
5	Available P_2O_5 (%)	Vanado-Molybdo phosphoric acid (Jackson, 1974)
6	Available K_2O (%)	Flame photometric method (Jackson, 1974)
7	Available S (%)	Turbidity method (Chaudhary and Cornfield, 1966)

3. Results and discussion
3.1 Physical properties of whole cotton stalk biomass
Physical properties of whole cotton stalk plant in terms of length, diameter and bulk density were measured. Average length of 15 pieces of randomly selected whole cotton stalks were measured with the help of measure tap and the value is given in Table 2. It can be seen from the table that the average length of whole cotton stalk is 1456 mm. The length of these plants were considered in three sections as lower (0 mm to 500 mm), middle (500 mm to 1000 mm) and upper part (above 1000 mm) for obtaining the average diameter of the whole plant. The average diameter of these sections of randomly selected 15 plants was thus, obtained and given in Table 2. It can also be seen from the table that the average diameter of these sections i.e. lower section, middle section and upper section were found as 16.76 mm, 12.51 mm and 8.05 mm, respectively. The bulk density of the whole cotton stalk plant is also given in Table 4.1. It can also be seen from the Table 2 that average diameter and bulk density were found as 12.44 mm and 30.20 kg/m^3, respectively.

Table 2: Average length, average diameter of each section, average diameter and bulk density of whole cotton stalk

Sr. No.	Average length, mm	Average diameter of sections, mm			Average diameter of whole cotton stalk, mm	Bulk density, kg/m^3
		Lower section (0 - 500 mm)	Middle section (500 – 1000 mm)	Upper section (above 1000mm)		
1	1456	16.76	12.51	8.05	12.44	30.20

3.2 Physical properties of shredded cotton stalk biomass
Shredded cotton stalk was used as feed stalk instead of whole cotton stalk, physical properties of shredded cotton stalk were also measured. Table 3 shows the different size fractions of shredded cotton stalk biomass in terms of average weight, percent weight and minimum-maximum length of shredded cotton stalk. The fractions of shredded mass was divided into seven different size fractions as thick (13 - 20 mm diameter), medium (9 – 12.99 mm diameter), thin (4 – 8.99 mm diameter), very thin (2 - 3.99 mm diameter), fine (less than 2 mm diameter), cotton burrs and bark. It can be seen from table 4.2 that the average weight of thick, medium, thin, very thin, fine, cotton burrs and bark fractions of shredded cotton stalk were found as 483.013 g, 254.007 g, 365.399 g, 239.569 g, 50.919 g, 229.226 g and 376.868 g, respectively. The percent weight of thick, medium, thin, very thin, fine, cotton burrs and bark fractions were found as 24.2%, 12.7%, 18.27%, 11.98%, 2.55%, 11.46% and 18.84%, respectively. It can also be seen from the table that maximum and minimum percent weight fractions were found as 24.20% and 2.55% of the thick and fine fractions 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, fine, cotton burrs and bark were ranged from 18 - 192 mm, 14 - 158 mm, 22 - 142 mm, 11 - 57 mm, 2 - 8 mm, 7 - 34 mm and 33 - 280 mm, respectively.
The bulk density of shredded cotton stalk biomass was found as 146.58 kg/m^3. Dubey and Gangil (2009) [5] reported the bulk density of cotton sticks 160 kg/m^3.

Table 3: Different size fractions of shredded cotton stalk biomass

Sr. No.	Size fractions	Average weight		Length, mm	
		G	%	Minimum	Maximum
1	Thick, (13 - 20 mm diameter)	484.013	24.20	18	192
2	Medium, (9 – 12.99 mm diameter)	254.007	12.70	14	158
3	Thin, (4 – 8.99 mm diameter)	365.399	18.27	22	142
4	Very thin, (2 – 3.99 mm diameter)	239.569	11.98	11	57
5	Fine, (less than 2 mm diameter)	050.919	02.55	02	08
6	Cotton burrs	229.226	11.46	07	34
7	Bark	376.868	18.84	33	280
	Total	2000.000	100.00		

3.3 Proximate analysis of shredded cotton stalk biomass

Proximate analysis in terms moisture content, fixed carbon, volatile matter and ash content is determined and results of this analysis are presented below.

Table 4 shows the proximate analysis of cotton stalk biomass. Dogru *et al.* (2002) [4] reported the moisture content of hazelnut shell was around 12 (%, d.b) and reviewed that the moisture content of most of the biomass varies between 11 and 18 (%, d.b).

The fixed carbon, volatile matter and ash content were found as 16.47, 78.12, and 5.41 (%, d.b), respectively for cotton stalk as shown in Table 4. The results of proximate analysis of cotton stalk in the present study was in accordance with the results presented by Dubey and Gangil (2009) [5] as fixed carbon, volatile matter and ash content of 15.30, 81.40 and 3.30 (% d.b) respectively for cotton stick. Vyas and Singh (2007) [13] also found the fixed carbon, volatile matter and ash content as 24.99, 71.04 and 3.97 (%, d.b.), respectively for jatropha seed husk. Similarly, Jorapur and Rajvanshi (1997) [7] also reported that fixed carbon, volatile matter and ash content as 14.9, 77.4, and 7.7 (%, d.b.), respectively for sugarcane leaves.

Table 4: Proximate analysis of cotton stalk biomass

Sr. No.	Moisture Content, % d.b	Fixed carbon, % d.b	Volatile matter, % d.b	Ash content, %, d.b
1	11.46	16.47	78.12	5.41

3.4 Chemical properties of shredded cotton stalk biochar

Chemical analysis of shredded cotton stalk carried out in terms of pH, electrical conductivity (EC), O.C., available N, available P_2O_5, available K_2O, and available S. Table 5 shows the chemical properties of shredded cotton stalk.

It can be seen from the table that the values of pH, EC and O.C. of shredded cotton stalk were found as 5.41, 3.05 dS/m and 54.58%, respectively. It can also be seen from the table that the values of available N, available P_2O_5, available K_2O and available S of shredded cotton were found as 0.77, 0.10, 0.39 and 0.11%, respectively.

Table 4.4: Chemical properties of shredded cotton stalk

Sr No.	Particular	Shredded cotton stalk
1	pH (1:10)	5.41
2	EC (1:10), dS/m	3.05
3	Organic Carbon,%	54.58
4	Available N,%	0.77
5	Available P_2O_5,%	0.10
6	Available K_2O,%	0.39
7	Available S,%	0.11

5. Summary and conclusion

1. Average bulk density of shredded cotton stalk was found as 146.58 kg/m^3 and increased 485.36% of whole cotton stalk.
2. The proximate analysis of shredded cotton stalk biomass in terms of moisture content, fixed carbon, volatile matter and ash content were found as 11.46, 16.47, 78.12, and 5.41 (%, d.b), respectively.
3. The values of pH, EC, O.C., available N, P_2O_5, K_2O and S of shredded cotton stalk were found as 5.41, 3.05 dS/m, 54.58%, 0.77%, 0.10%, 0.39% and 0.11%, respectively.

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