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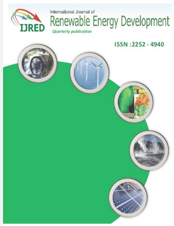

Research Article

Characterization of Agro-Waste and Weed Biomass to Assess Their Potential for Bioenergy Production

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ABSTRACT. Biomass resources are gaining increasing importance world over due to their ease of conversion to various energy product in the face of depleting fossil fuel store and increasing environmental concerns over their use. The present work elucidates different physico-chemical properties of three biomasses, paddy straw (PS)- an agricultural residue, spent paddy straw obtained after mushroom cultivation (SS), and a noxious weed (*Parthenium hysterophorus*; PR) to understand their properties and to explore the feasibility of using them as feedstocks in different biomass to bioenergy conversion routes. In addition to physico-chemical analysis, biochemical analysis of these biomasses along with XRD, thermogravimetric analysis, FTIR and SEM analysis have been carried out. Present study suggests that PS is a better choice as feedstock compared to both PR and SS. The calorific value to ash content ratio is more in PS (1.13) as compared to PR (1.06) and SS (0.84). Thus, it may be inferred that the biomasses in question are at par with commonly used bio-energy feedstocks like sugarcane bagasse and corn cob. ©2019. CBIORE-IJRED. All rights reserved

Keywords: Lignocellulosic biomass, parthenium, paddy straw, spent straw, physico-chemical characterization

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1. Introduction

Fossil fuels contribute more than 80% global energy requirement in the 20th century (IEA 2011). But with an ever increasing demand for more energy in current times, our fossil fuel reserves are depleting at a faster rate with estimated % fossil fuel reserve being 17.67 units, 64.99 units and 17.34 units for oil, coal and gas respectively (Singh & Singh 2012). Hence, alternative energy forms such as solar energy, geothermal energy and biomass energy are emerging as a viable alternative to the fossil fuel (Ahmadi et al. 2018a, Ahmadi et al. 2018b, Ojolo, Osheku & Sobamowo 2013). Biomass, a sole renewable energy source of carbon, can store solar energy and this energy can be converted to different forms of fuels as well as chemicals via successive conversion processes (Purbasari, Samadhi & Bindar 2016). The estimated globally available biomass per year is 220 billion oven-dry ton (ODT) or 4500 exa joule (EJ) (World Energy Council 2004). Countries like India, China, Brazil have a wide variety of vegetation thereby producing a plethora of biomasses that can be used as a feedstock to produce biofuel (Sasmal, Goud & Mohanty 2012). The biomass may originate from plants of agricultural origin (e.g. paddy straw, sugarcane bagasse etc.) or from unwanted weeds that grow on agricultural fields. There are a number of noxious and invasive weed species that not only competes with agricultural crops leading to its lesser production, low efficiency of costly agricultural inputs, but also many of a weed species causes harmful effects on humans and cattle. Utilization/valorization of such weed biomass could be a win-win situation for both farmers as well as for the energy sector, as physical de-weeding for feedstock purpose may be considered as a weed control measure. This will also curb application of chemical weed control agents, thereby increasing the quality and acceptability of the produced in the market. Agro-residue biomass which gets retained in the field and are not fit for human consumption may be either directly used or be processed to be used suitably for bio-energy production, instead of being burnt as a stubble.

Paddy straw is a common agro-residue having a wide variety of usage starting from fodder, thatching of roof, substrate for mushroom cultivation, etc. It is also widely used for gasification purpose thereby yielding gas, energy and other by-products like carbonized rice hull (soil conditioner), smoke vinegar (natural pesticide) and briquettes (for construction purpose) (Nidoy 2016, Ali *et al.*

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2016). Cultivation of oyster mushroom is picking up fast in India as the subtropical and tropical Indian climate is favorable for its fast and robust growth pattern (Mago *et al.* 2014). It has considerable organoleptic and nutritional appeal and is fast becoming a viable protein supplementation alternative for vegetarians, especially in urban regions of India (Garcha, Khanna & Dhanda 1997). Fresh oyster mushroom is priced in the range of Rs 100-150/kg in the retail market in India. Many types of biomasses being used for commercial cultivation of *Pleurotus* spp. in India, paddy straw has become the substrate of choice due to its abundance, easy availability and low cost (Rs 4-5/kg). Cultivation of *Pleurotus spp.* (namely *P. flabellatus*) on paddy straw was first reported in India by Bano and Srivastava (1962). Moreover, paddy straw is found to be the best substrate with respect to higher yield % and biological efficacy (BE) as compared to other biomass like wheat straw, sugarcane bagasse, sawdust etc. for the production of *Pleurotus* mushroom (Pokhrel & Ohga 2007, Sharma, Yadav & Pokhrel 2013). The increasing popularity of oyster mushroom cultivation over button mushroom is also due to the higher productivity of oyster (~ 500-700 kg/ton of dry paddy straw in 45-60 days) over button (~400-500 kg/ton of dry paddy straw in 80-100 days) (agridaksh.iasri.res.in). For determining the suitability for the energy sector, two types of paddy straws are taken; one is paddy straw (PS) collected directly from field as an agro-residue and another is paddy straw taken after being utilized as substrate (medium) for production of oyster mushrooms (*Pleurotus* spp.), which is termed as spent straw (SS) or as spent mushroom substrate (SMS). Stamets (2000) has elucidated the gross degradation profile of paddy straw by mushroom stating that ~ 50% of the biomass is liberated as carbon dioxide, 20% is lost as residual water, 20% remains as 'spent' biomass and only 10% of substrate mass is converted into mushrooms. The feasibility of using the 'spent' paddy straw, aka 'spent straw' (SS) remaining after mushroom harvesting *vis-a-vis* paddy straw (PS) collected directly from the field in the renewable energy sector will be investigated in this study.

Parthenium hysterophorus (PR) or "Congress Grass" (in local parlance) is an annual terrestrial weed that is ecologically harmful as well as being an aggressive colonizer [Kaur & Aggarwal 2016]. It has colonized the tropics intensely thereby causing huge loss to arable land (Safdar *et al.* 2016). To make things worse, *parthenium* hosts a number of crop pests and causes allergic respiratory problems, contact dermatitis and mutagenicity in human and livestock (Sharman, Persley & Thomas 2009, Patel 2011). Unfortunately, attempts to curb the spread of *parthenium* by several means (mechanical, chemical or biological) has been proved to be ineffective, but vermicomposting of *parthenium* biomass has proved to be a feasible method to convert the nutrients of the substrate into more bio-available form and transform its micro-flora so that it becomes more amicable for plant growth (Hussain, Abbasi & Abbasi 2016a, Hussain, Abbasi & Abbasi 2016b, Hussain, Abbasi & Abbasi 2016c). Other than composting, attempts have been made by Tavva et al. (2016) to generate bio-ethanol from *parthenium* biomass but achieving limited success and with almost no economic viability (Hussain, Abbasi & Abbasi 2016c). *Parthenium* biomass on pyrolysis in a fixed bed reactor produces a low quantity of bio-oil (6.3%) as compared to rice husk (31.87%) but the calorific value of *parthenium* bio-oil is more than that of rice husk derived bio-oil (Mythili *et al.* 2013). Pyrolysis of *parthenium* biomass leading to biochar formation is performed by Narzari *et al.*(2017) having a maximum yield at 350 °C (28.52%) with gradually decreasing yield with an increase in pyrolysis temperature. Since considerable work has been done on the bio-energy aspect of *parthenium*, it may be considered as a positive control in this study.

Studies featuring biochar and biooil preparation from *Parthenium* has been undertaken (Narzari et al, 2017 and Mythili et al. 2013), but a comparative assessment of weed biomass and agro-waste biomass for their potential for biofuel production has not been investigated. The present study elucidates for the first time the comparative potential of *Parthenium* and paddy straw for biofuel production. Thus, the objective of this study is to characterize the biomass samples of three different types i.e. paddy straw, an agricultural residue; spent paddy straw, a biowaste; and *Parthenium*, a noxious weed to understand the properties of these biomasses so as to highlight the feasible pathways for valorization of these wastes.

2. Materials and Methods

The biomass samples used in this study were collected from Sonitpur district of Assam. The air-dried samples of biomasses were chopped, ground and sieved (mesh size-BSS 30) to get a homogeneous powder that was used as the starting material for characterization.

2.1 Proximate analysis, CHN analysis, and calorific value determination

Proximate analysis appears to be a quick and practical way of evaluating the quality of fuel. Proximate analysis gives the information on moisture content (MC), ash content, volatile matter (VM) and fixed carbon (FC) content of the material and was conducted following the American Standard Test Method (ASTM) and TAPPI standard method.

Moisture content, the amount of water in the fuel, has a major effect on its conversion efficiency and heating value. The moisture content of the samples was determined by adopting the ASTM D3173 method. In this method, 2 gm samples were oven dried at 105±3 °C until a constant weight was reached. The dried samples were then placed in desiccators to cool down to room temperature. The sample was then re-weighed in order to calculate its moisture content.

Ash content is a measure of inorganic residue that remains after organic matters are removed. The ash content of biomass affects both the handling and processing costs of the overall biomass energy conversion cost. Dependent on the magnitude of the ash content, the available energy of the fuel is reduced proportionately. In a thermo-chemical conversion process, the chemical composition of the ash can present significant operational problems. Ash content of the samples was determined by burning 2 g of oven-dried ground sample in a muffle furnace at 575±25°C for 15 min as per the TAPPI standard method, T211 om-85 (Kataki & Konwer 2001).

Volatile matter is the percentage of volatile products, excluding the moisture, released from fuel during the heating under controlled conditions. It is derived as an important factor for evaluating burning characteristics. According to ASTM D3175 method, the volatile matter content of the samples was determined by heating 2 g of samples at 950 °C for 2 minutes.

The fixed carbon is a solid carbon residue that remains after the volatile products are driven off. It was determined by subtracting the sum of percentage composition of moisture content, volatile content and ash content from 100.

Ultimate analysis was performed to determine the elemental composition of the material. CHN analysis of the biomass samples was carried out by a Perkin Elmer Series II CHNS/O analyzer 2400 (accuracy: ≤0.3%), using approximately 1.0 mg of sample in a tin boat assortment and acetanilide as standard. The calorific value of samples was estimated in an auto bomb calorimeter (M/s Changsha Kaiyuan Instrument Co. Ltd, China; model no. 5E-1AC/ML, accuracy: ≤0.1%) as per ASTM manual (E711-87) using approximately 1.0 g of sample in the form of pellet put into pre-weighed crucibles.

2.2 Component analysis of the biomass samples

The three major biochemical components, i.e. cellulose, hemicellulose, and lignin content are determined using the gravimetric method in this paper. The methods are discussed as follows:

2.2.1 Determination of extractives

Non-structural material is often removed from biomass prior to chemical analysis due to its prominent interference on analysis of structural carbohydrates and lignin. These are comprised of solvent-soluble, non-volatile compounds such as fatty acids, resins, chlorophyll, tannins, etc., and usually comprise a minor proportion of biomass. However, for large-scale lignocellulosic biorefinery operations, extractives can be a potential source of value-added co-products (Sannigrahi et al. 2010).

For estimation of extractive content, 5 g of dried biomass sample was loaded into the cellulose thimble. With the soxhlet extractor set up, a mixture of benzene/ethanol (2:1 v/v) was used as a solvent for extraction and this operation was executed for 4 h. After extraction, the sample was air-dried for a few minutes followed by drying in an oven at 105±5 °C to a constant weight. Then the residue was allowed to cool to room temperature in desiccators and then weighted. The extractive wt% (E) is calculated from the difference in weight between the raw biomass and extractive-free biomass as mentioned elsewhere (Li et al. 2004).

2.2.2 Analysis of hemicellulose

1 g of residue from the extractive analysis was taken in a flask and then 150 ml 0.5 M NaOH solution was added to it. The mixture was boiled for 3.5 h. After cooling, the solution was subjected to vacuum filtration and washed, until neutral pH was obtained for the residue. The residue was then dried to room temperature in a desiccator and weighted. The difference between the sample weight, before and after this treatment is the hemicelluloses content (H, wt%) of dry biomass(Ayeni *et al* 2015).

2.2.3 Analysis of lignin

About 1 g of dried extracted biomass was taken in a flask. After slowly pouring about 10ml/g of 72% sulphuric acid (H_2SO_4), the mixture was kept at 8–15 °C for 24 h. Then 300 ml of distilled water was added and the sample was boiled for 1 h with distilled water. After cooling and filtration, the residue was washed until there was no more sulphate ion in the filtrate. The residue was then dried to a constant weight, cooled to room temperature in a desiccator and weighted and the lignin content (L, wt %) was determined (Li *et al.* 200).

2.2.4 Analysis of cellulose

The cellulose wt.% was calculated as:

$$\text{Cellulose, C (wt\%)} = 100-(\%E+\%H+\%L)$$

2.3 Thermogravimetric analysis

The thermogravimetric analysis (TGA) was done in a thermal analyzer (TGA-50, M/s Shimadzu Corp. Japan) under nitrogen atmosphere at a flow rate of 30 ml/min. The weight readability of the instrument is 0.1 µg. The sample of 3-5 mg was subjected to a temperature increment programme from room temperature to 700 °C at a heating rate of 10 °C/min. The TGA and DTG (1st differential of TGA against time) profiles along with T_{50} (temperature at the level of 50% weight loss) and R_{50} (rate of weight loss at T_{50}) values were determined for all the three samples. The TGA profile was plotted as % weight of organic faction volatilized (W) against temperature. Two parameters T_{50} (temperature at the level of 50% weight loss) and R_{50} (rate of weight loss at T_{50}) which are used to comprehend the gasification suitability of given biomass, are also compared between these three given biomasses (PS, PR, and SS).

2.4 FTIR analysis

Fourier transform infrared spectroscopy (FTIR) analysis of the biomass samples were carried out in a Perkin Elmer Frontier FTIR (wavenumber accuracy: 0.02 cm^{-1} at 2,000 cm^{-1}) by dispersing the dried powder samples with KBr (spectroscopic grade), homogenized in an agate mortar and pelletized at a pressure of about 1 MPa. The spectra were recorded over 400-4000 cm^{-1} range at a scan speed of 0.5 cm/s.

2.5 X-ray diffraction analysis

X-ray diffractometer (Brucker AXS, Germany D8Focus) is used to determine the crystallinity and structure of biomass. Crystallinity was calculated as a crystallinity index, determined by using equation (1)

$$CI(\%) = (I_{002}-I_{am})/I_{002}\times 100 \qquad (1)$$

Where I_{002} is the maximum intensity of the 002 diffraction peak near $2\theta = 22.8°$, and I_{am} is the minimum intensity of a peak near $2\theta = 16°$.

2.6 SEM-EDX

Scanning electron microscopy (SEM) images of the biomass were taken with a JEOL microscope (JSM-6390 LV, Jeol USA Inc.) with an acceleration voltage of 20 kV. SEM analysis was performed to find out the surface morphology of the biomass. Images of all the samples were taken at 1000× magnifications. SEM and EDX analyses of biomass were carried out by using JEOL (JSM-6390 LV) microscope.

3. Results and Discussion

3.1 Proximate analysis, CHN analysis and calorific value determination

The proximate analysis, CHN analysis and calorific value determination of the biomass samples are elicited in Table 1. The moisture content (in wet basis) is found to be maximum in SS (61.4%), with PR having comparable value (60.7%) but significantly less for PS (55.7%). The moisture content reached a maximum removal at 105 °C, but it is clear from the values that complete or near complete removal of moisture from biomass is very difficult. This may be due to the inherent hydrophilic nature of the lignocellulosic materials (Cruz *et al.* 2013). Volatile matter content of the three biomass are in a comparable range (11.4 for PR, 11.6 for PS and 12.7% for SS) while ash content is maximum in PR (14.67%) while decreasing to 12.49% for PS and 9.96% for SS. PS has the highest fixed carbon (20.21%) which decreases to 15.94% in SS sample and 13.23% in PR sample. The calorific value is the highest for PR (15.51 MJ/kg) while decreasing gradually to 14.1 MJ/kg for PS, indicating that PR and PS have a higher energy value per unit mass, which would make them preferable to SS (8.43 MJ/kg).

Table 1
Proximate data, CHN analysis and calorific value determination of biomass samples.

Sample	**Proximate analysis**				**CHN analysis**			**Calorific Value(MJ/kg)**
	Ash (%)	**VM(%)**	**FC(%)**	**MC(%)**	**C(%)**	**H(%)**	**N(%)**	
PS	12.49± 0.2	11.6± 0.3	20.21± 0.2	55.7± 0.5	39.76± 0.1	5.38± 0.2	0.84± 0.2	14.10± 0.2
PR	14.67± 0.1	11.4± 0.1	13.23± 0.3	60.7± 0.5	37.03± 0.2	4.61± 0.2	1.40± 0.1	15.51± 0.2
SS	9.96± 0.1	12.7± 0.1	15.94± 0.1	61.4± 0.3	27.82± 0.2	4.00± 0.1	0.87± 0.2	8.43± 0.1

As volatile matter content of a biomass increases, its calorific value decreases (Sasmal, Goud & Mohanty 2012). This thumb rule applies somewhat to these samples too, as SS has the least calorific value and the highest volatile matter content at the same time. According to Bin and Hongzhang (2010), high ash content slows down the chemical processing (e.g. saccharification or hydrolysis) rate of biomass and ash content has a negative correlation with the calorific value which is apparent for biomasses with a calorific value greater than or equal to 20 MJ/kg (Özyuguran & Yaman 2017). Thus all the biomass samples under consideration have calorific values way below 20 MJ/kg and hence do not correlate completely with the ash content data. A negative correlation exists between ash content and fixed carbon of PR and PS, but the corresponding values of SS do not comply with the above-mentioned correlation. This negative correlation between ash content and fixed carbon for PR and PS is in line with the observation by Crombie et al., (2013). The % of C and N of PR matches exactly with that reported by Narzari et al. (2017).

Table 2
Analysis results of the chemical components in biomass

Sample	**Cellulose (%)**	**Hemicellulose (%)**	**Lignin (%)**	**Extractive (%)**
PS	42± 1.65	23.5± 0.66	17.33±2.11	17.16± .98
PR	23.77±1.40	26.8±1.61	22.06±1.31	27.37±0.80
SS	40.83±0.76	19.3±1.11	15.67±1.11	24.2±2.83

3.2 Biochemical component analysis

Determination of biochemical components are very important criterion of biomass in determining the suitability for various conversion processes as well as their economic feasibility. Among the three components, cellulose is the most amenable to the production of biofuel like bio-ethanol by enzymatic hydrolysis followed by fermentation. Bioethanol can also be prepared from hemicelluloses part by using enzymes like xylanase followed by fermentation of pentose and hexose sugars by a suitable micro-organism. It is also possible to produce some important chemicals like furfural and acetic acid from hemicellulose. Similarly, the determination of the lignin content helps in the efficient utilization of biomass as bioenergy feedstock (Sannigrahi *et al.* 2010). Lignin also has various industrial applications as these can be converted to biodiesel or other liquid fuels. The information of the extractive content also helps to estimate the exact amount of fermentable sugars present in biomass. Basic compositions of the three biomasses were tabulated in Table 2. The chemical components, as analyzed in the samples, were distinctly different from each other. The highest cellulose content occurred with PS (42.00±1.65 %) followed by SS (40.83±0.76 %) and PR (23.77±1.40 %). This would make PS and SS are more desirable feedstock for the production of ethanol than PR. With the highest hemicelluloses content, PR (26.8±1.61%) would be the best candidate for the production of chemicals like furfural and acetic acid. Also, PR exhibited the highest lignin compared to the other two, which should be considered while designing pre-treatments and conversion strategies for the biomass.

3.3 Thermogravimetric analysis

The thermal decomposition pattern of the samples was evaluated using a constant isothermal ramp program under an inert atmosphere. The individual TGA and DTG patterns of PS, PR, and SS are listed in Fig. 1.

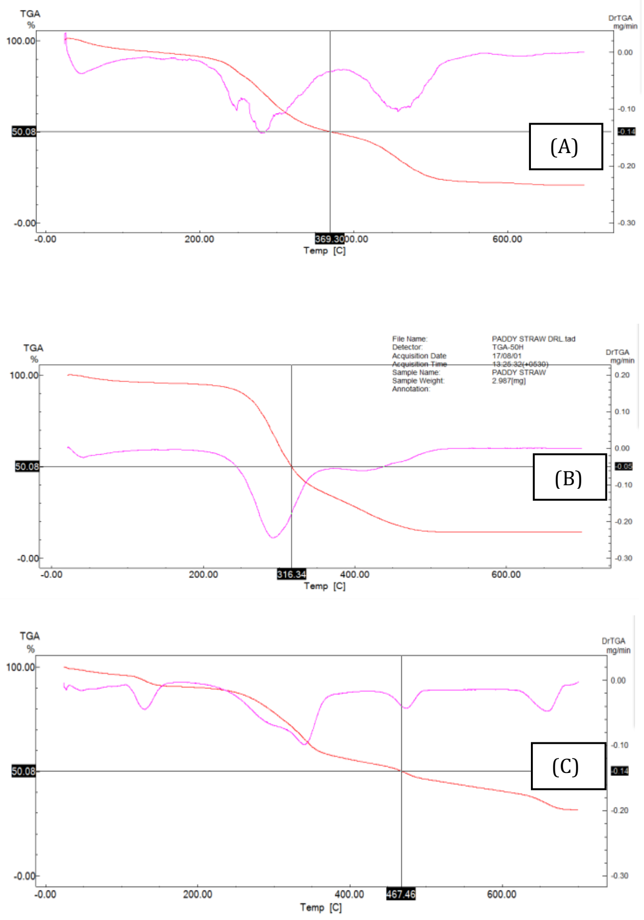

Fig. 1: TGA and DTG curves of (A) Parthenium, (B) Paddy Straw and (C) Spent Straw. The TGA curve is shown in red color while DTG curve is shown in pink color.

PS shows a major degradation at 310 °C (single major groove in DTG profile with 80% loss in weight). PR shows two major degradation grooves (one at 278 °C and another at 457 °C with 42% and 25% loss in weight respectively). SS exhibits one major degradation groove at 312 °C (32% weight loss) and three minor grooves at 130°C (5% weight loss), 468 °C (6% weight loss) and 652 °C (7% weight loss) respectively. In PR there is an initial weight loss of 6.5% at 57 °C which corresponds to the release of moisture as water vapour from the biomass. It is observed in all three samples that a major loss of weight is observed at the temperature range of 280 °C to 310 °C. This loss in weight is mainly due to the degradation of structural sugars namely cellulose and hemicelluloses (Yao et al. 2008, Wu & Dollimore 1998). As reported by Cruz et al. 2013, major grooves of PR and SS in the range of 280 °C to 310 °C exhibit shouldering pattern due to overlapping of degradation peaks of cellulose and hemicellulose. Another interesting observation in the DTG profile of PS and SS is that, PS shows one single distinct degradation groove at 310 °C (total weight loss is 80%) as opposed to SS in which the loss in weight is distributed over a range of temperatures (130 °C to 650 °C) with total weight loss being not more than 52%. This may be explained by the fact that the mushrooms have utilized the structural sugars of paddy straw by around 48% (Fig. 1C). This makes SS less suitable candidate for gasification as compared to the other two. Lignin degradation starts at around 500 °C and continues up to 800 °C [Yang *et al.* 2007], which may be observed for SS at 652 °C. The groove wise weight loss % values of PR and corresponding reported values of cellulose, hemicelluloses and lignin in PR are in unison with each other (Mythili *et al.* 2013). Mythili *et al.* (2013) also reported the values of cellulose, hemicellulose and lignin to be 19%, 24% and 22.1% respectively while the TGA data of PR in this study condition shows that weight loss at 280 °C is 42% (~ 19%+24%=43%) and that at 457 °C is 25%.

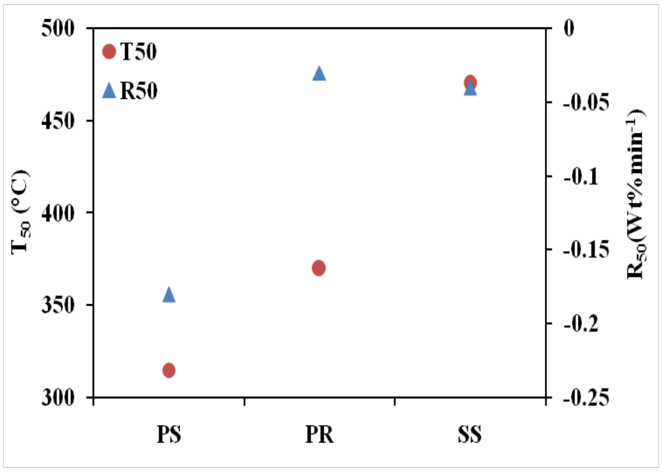

Fig. 2. Comparative analysis of T_{50} and R_{50} values of the three samples

The comparative analysis of the value of T_{50} and R_{50} values of the three samples are shown in Fig. 2. Higher value of R_{50} denotes higher thermal activity in the biomass at T_{50}. It is clearly observed that R_{50} value of paddy straw is 6 times and 4.5 times higher than that of PR and SS biomasses respectively (R_{50} of PS being -0.18 mg/min, while that of PR and SS being -0.03 mg/min and -0.04 mg/min respectively; -ve sign determines rate of decrease in weight).

3.4 FTIR analysis

Different types of chemical bonding environment, as well as surface functional groups of all biomass samples, were investigated with the help of different spectral peak performed in FTIR analysis. The FTIR spectra and band assignments of biomass samples are presented in Fig. 3.

The FTIR spectra of all the three samples were slightly different because of the differences in chemical composition. The lowest transmittance was shown by SS followed by PS and PR in the entire range. Broad bands centered at 3401, 3413 and 3436 cm^{-1} of PS, PR, and SS respectively attributed to the stretching vibrations of bonded and non-bonded hydroxyl groups from the glucoside linkages of cellulose or the hydroxyphenyl, guaiacyl and syringyl groups of lignin (Sasmal, Goud & Mohanty 2012). Bands at 2921-2915 cm^{-1} of PS, PR, and SS were due to the C-H symmetric and asymmetric stretching vibrations of methylene group.

Table 3
Assignment of FTIR bands of functional groups in lignocellulosic biomass samples.

Name of characteristics group	Wave number (cm^{-1})
Bonded and non-bonded -OH groups and water	3400-3600
C-H stretching of aliphatic structure	2960-2850
C=C stretching vibrations of aromatic rings of lignin	1640
CH_2 of cellulose and lignin	1462-1415
C-H deformation in cellulose, hemicellulose and lignin	1384-1346
C-H in plane bending of cellulose	1320
C-O-C vibration in cellulose and hemicellulose.	1158
C-O stretching in lignin and xylan	1266
C-O-C, C-O of polysaccharides	1200-900
C-OH stretching vibration of cellulose and hemicellulose	1060

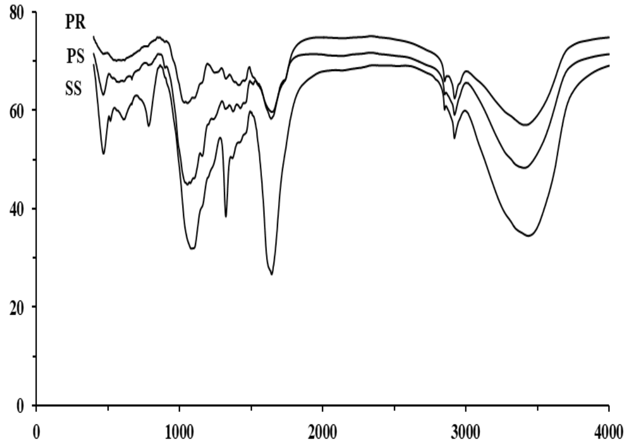

Fig. 3: FTIR spectra of PS, SS and PR

The sharp peaks obtained at 1639, 1647 and 1643 cm^{-1} for PS, PR and SS respectively correspond to the C=C stretching vibrations of the aromatic ring due to the presence of lignin in the samples (Pandey & Nagveni 2007). The fingerprint region is more complex due to the presence of cellulosic materials in biomass. This region was mainly dominated by C–H, N–O and O–H vibrations; and it was observed that PS and PR attribute more peaks in this region compared to SS. Due to the variation in the inorganic contents in all the three samples different small peaks were observed at the range of 1200-1750 cm^{-1}. The small absorbance at 1158 cm^{-1} for PS corresponds to C–O–C asymmetrical stretching of cellulose and hemicelluloses. Similarly, a slightly broadband at 1055-1060 cm^{-1} for all the samples attribute to the C–OH stretching vibration of cellulose and hemicellulose.

3.5 SEM-EDX

The elemental composition of the different biomass feedstocks was estimated by energy dispersive X-ray spectroscopy (EDX) which have been shown in the Fig. 4 and Table 4.

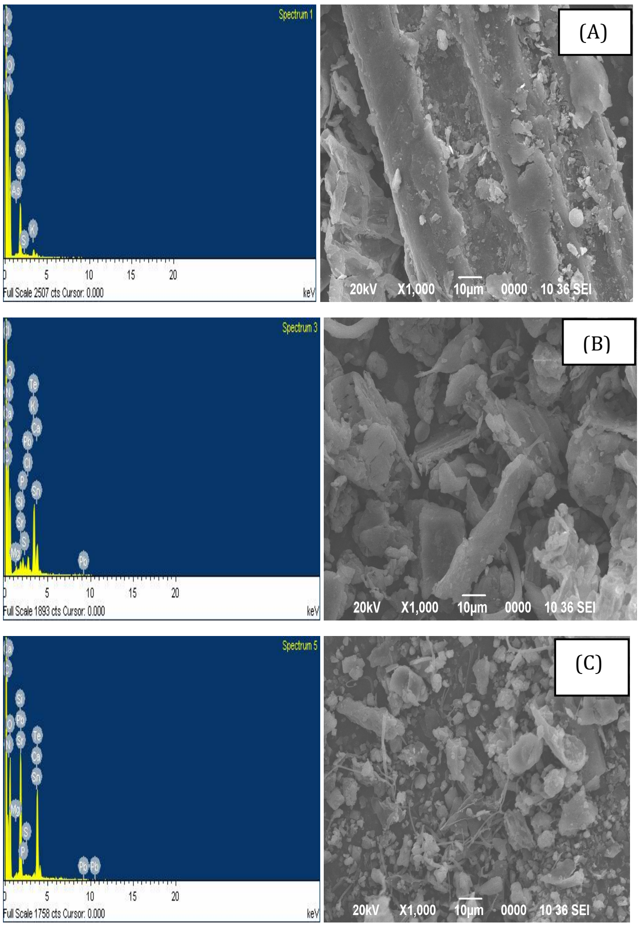

Fig. 4: SEM-EDX images of (A) PS, (B) PR and (C) SS

The EDX analysis revealed that carbon, oxygen and nitrogen were present abundantly in all the samples while Si, S, Pb and Sr were present as trace elements in all samples. Mg, Ca, Sn and Te were present as trace elements in PR and SS samples. As and Cl were present in trace amount only in PS and PR respectively.

The surface morphology of the samples was characterized by SEM technique as shown in the Fig. 4. On the basis of their morphology, the individual particles which were aggregation of some fine particles of irregular size were classified as mineral particles. This observation was also supported by EDX analysis.

Also, the surface for PS appears to be smooth compared to PR and SS. The more roughness of the surface of SS may be due to the presence of some microorganisms, extra cellular enzymes and also the presence of some elements as shown in EDX analysis (Fig. 4 C). This may be also a reason for the unusual behaviour of TG and DTG graph of SS samples compared to other two lignocellulosic biomasses.

3.6 XRD analysis

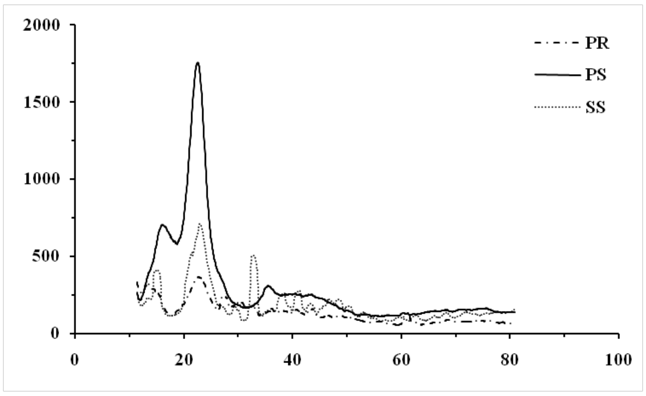

Fig. 5: XRD pattern of PS, PR, SS

Fig. 5 represents the XRD data of three biomasses, which were used to evaluate the crystallinity index values. Cellulose contributes to the strong crystalline arrangement, which hindered the enzymatic hydrolysis of sugar molecules, which leads to lower yield of fermentable sugar as well as ethanol (Rocha *et al.* 2011). In addition to cellulose content, wax content and the complex nature of bonding between the biochemical components also influence the overall crystallinity of the biomass (Naik *et al.* 2010). Two broad diffraction peaks at approximately 16 and 22.8 for the biomass were due to the 1 0 1 and 0 0 2 crystal planes, respectively. The intensity and sharpness of these peaks attributed to the crystalline region of cellulose in biomass. The higher value of crystallinity index means the higher degree of crystallinity which was equivalent to the higher crystalline area per unit volume in cellulose. The maximum crystallinity was observed in PS (59.26%) followed by SS (32.26%) and PR (17.53%). This result is consistent with the amount of biochemical components as included in Table 2.

Table 4
Elemental compositions of various samples

Sample	**Elemental Composition (atomic %)**														
	C	**O**	**N**	**Mg**	**Si**	**S**	**Ca**	**Cl**	**P**	**K**	**As**	**Sn**	**Pb**	**Te**	**Sr**
PS	51.02	30.11	17.76	-	0.87	0.01	-	-	-	0.09	0.02	-	0.01	-	0.13
PR	40.43	28.31	28.50	0.16	0.18	0.07	0.46	0.25	0.21	1.08	-	0.12	0.04	0.14	0.07
SS	22.76	41.75	29.37	0.16	2.94	0.03	1.81	-	0.11	-	-	0.02	0.01	0.59	0.47

4. Conclusion

The proper utilization of abundantly available waste biomass such as agricultural waste is an attractive option for recovering energy. The present investigation suggested that paddy straw, spent straw and *Parthenium* can be used as source for biofuel production. The thumb rule for a biomass to become suitable for bio-energy production is that it should have high calorific value and high cellulose and hemicellulose levels but low lignin and ash content. From the biochemical component analysis, it has been found that all the three biomass are quite comparable, which are also supported by FTIR analysis as well as TG and DTG analysis. The SEM and EDX analysis provided the morphological and mineral composition of the samples and it was observed that PS had good carbon percentage compared to other two biomasses. Other preliminary information on physicochemical characterization of these biomasses surely opens opportunity of selecting future biofuel candidates in the North-East region of India. Thus, paddy straw may be opted for a better bio-energy source as compared to both *Parthenium* and spent straw as calorific value to ash content ratio is more in PS (1.13) as compared to PR (1.06) and SS (0.84). Hence these above-mentioned lignocellulosic materials with the calorific values of 14.10 MJ/kg (PS), 15.51 MJ/kg (PR) and 8.43 MJ/kg (SS) may compete favorably with other conventional sources of biofuel production such as sugarcane bagasse (calorific value 9.50 MJ/kg) on the lower range to corn cob (calorific value 17.70-18.34 MJ/kg) at the higher range. The high-water content in all the biomasses (55-60%) is surely not very favorable factor for bio energy production, but if the process of bio energy production has to be scaled up, the plant materials are to be sundried under the open sky only, rather than in furnaces or ovens. Hence this high moisture content factor has to be compromised with. Otherwise gasification or fermentation processes may also be undertaken with the biomasses in question so that the production of second generation biofuels may be undertaken from PS, PR and SS.

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