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Characterization of South Asian agricultural residues for potential utilization in future 'energy mix'

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Abstract

This paper characterizes various locally available agricultural residues in South Asian region to evaluate their potential as feedstock for renewable energy production and contributing toward solving energy crisis and environmental issues. The thermo-chemical characterization has been performed in order to determine if the residues have potential to be used in biomass conversion technologies producing combined heat and power. The characterization methods for comparing different agricultural residues include proximate and ultimate analysis, heating value, ash content, thermo gravimetric analysis (TGA) and structural composition analysis (SCA). Widely available agricultural wastes in South Asian region were selected for the characterization i.e. bagasse, almond shell, corn cob, cotton stalks, wheat straw, sawdust, corn leaf, rice husk, rice straw, and corn straw. The analysis showed that the corn cob had the highest moisture content that will result in low energy efficiency of the thermal conversion technology due to energy requirement for drying. Whereas almond shell had the lowest moisture content. Ash and volatile contents were found to be highest in rice straw and almond shell respectively. The thermo gravimetric analysis showed that most of the agricultural residues can be easily decomposed and represent potential feedstock for biomass flexible combined heat and power systems through pyrolysis or gasification.

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Keywords: agriculture residue, future energy, characterization, pyrolysis, gasification

1. Introduction

1.1. Background

South Asian region (Pakistan, India, Bangladesh, and Sri Lanka) has one of the largest agriculture sector that plays a vital role in the region's economy. [1, 2] According to United Nations Environment Programme (UNEP), a single district in South Asia produces about 2.5 million tonnes of agriculture residues as wheat straw, rice straw, rice husk, bagasse, corn leaf, saw dust, cotton stalks etc. [3-5]. Currently, the agriculture residues are utilized for domestic heating and as food for domestic cattle [6, 7]. However, the energy content from the substantial amount of agriculture waste represents potential for bio-fuel or combined heat and power production [8, 9]. In Pakistan, about 30 million people lives in remote areas/villages and around 30,000 villages are not provided with natural gas and electricity that are major energy requirements [10]. Since the agriculture waste is widely distributed and locally available, each district or village can produce its own electricity together with heat. In addition, the distributed electricity production can contribute towards reducing severe energy crisis in the country [11].

Most of the developed countries are utilizing all waste streams in the energy system as feedstock for renewable energy production [12, 13]. However, South Asian countries still lagging behind the right methodology and execution of biomass and agricultural residues as alternative renewable energy resource [14, 15]. Efficient utilization of biomass

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and agricultural wastes to bio-energy can also contribute towards solving energy crisis and reducing complete dependency on fossil based resources [16, 17].

1.2. Objective of the study

A number of thermo-chemical technologies, e.g. pyrolysis, gasification etc., are available to convert various agriculture residues to produce energy products [18, 19]. For efficient utilization of the feedstock as renewable energy resource through thermal conversion methods requires detailed understanding of different properties of the locally available feedstock. This study characterizes widely available and distributed agriculture residues such as bagasse, cotton stalks, rice husk, corn cob, corn leaf, fruit shells, rice straw and corn straw that can be introduced in pyrolysis or gasification to produce flexible fuels like char, pyrolysis vapors, bio-oil or synthesis gas. The flexible fuels may then be utilized for combined heat and power production. The thermo-chemical characterization was performed and feedstocks are compared using proximate and ultimate analysis, heating values and thermo gravimetric analysis (TGA). Based on available residue properties, the efficient thermo-chemical conversion technology is identified for each resource. This research work will provide base for future studies on estimating potential biofuel or combined heat and power production at small scale that may be sufficient to meet local energy requirement of a single district or village.

2. Methodology

Following sub-sections describes the characterization methods used to compare biomass properties of various available agriculture residues in South Asia.

2.1. Agriculture residues

Agricultural residues such as bagasse, corn cob, corn leave, saw dust, almond shell, rice husk, cotton stalks, cotton straw, rice straw and wheat straw were used in the present study. It was estimated that production of these residues in south Asia is 898864388 metric tons [35]. The residues are the left over products obtained after harvesting. Most of the residue such as corn cob, corn leaves, saw dust, cotton straw and wheat straw were obtained from Kabirwala District in Pakistan. While almond shells and bagasse were collected from Faisalabad and Jhang districts. Rice husk and rice straw were collected from Gujranwala district. Each residue was analyzed in triplicate for characterization and average results are reported.

2.2. Methods used for biomass analysis

Proximate analysis was performed to determine fixed carbon, ash content, volatile content, and moisture content present in the desired amount of agriculture residue sample [20]. The standard test method for proximate analysis used i.e. D-3172 ASTM [21]. The moisture content was estimated by the weight loss of the biomass sample as a result of heating the sample at 115 ºC in a drying oven. To estimate the volatile contents, the weight loss was recorded after placing the sample in muffle furnace at 800 ºC for 10 minutes. Ash contents were calculated by the residue left after heating the sample at 650 ºC until the constant weight was achieved [22].

The elemental composition of the agriculture residues were determined through ultimate analysis of samples [23]. Leco CHN-600 analyzer was used to estimate the carbon, hydrogen and nitrogen contents of the dried agriculture residue samples. To estimate the sulfur content, Leco Sulfur Analyzer SC32 was used as per ASTM standards. It is significantly important to estimate the lignin, cellulose, and hemi-cellulose contents together with extractives for reliable characterization of biomass. Different techniques can be used for structural analysis based on qualitative and quantitative methods [24]. The structural analysis is done by using magnetic resonance techniques, as this technique has been proved to be most efficient analytical tool. More extraction was also done by using an acid detergent solution, containing 60% sulfuric acid solution. A large number of extraction processes are recommended for the hemicellulose, cellulose and lignin content [25].

The calorific values of the agriculture residue samples were determined by bomb calorimeters and also using empirical relationship obtained from the literature [26]. ASTM D2015 was used as standard analytical method to determine calorific values of biomass samples [27]. The empirical relation used for the determination of high heating values are extracted from basic analysis data, i.e. Ultimate analysis, proximate analysis and structural analysis for the specific sample of the biomass. The formula according to the composition of elements is as follow:

Higher heating value Dry (MJ/kg) = 0.3491C + 1.1783H + 0.1005S − 0.1034O − 0.0151N − 0.0211 ash [26].

Where C, N, S, H and O are the weight percentages of carbon, nitrogen, sulphur, hydrogen and oxygen on dry basis respectively.

2.3. Thermo-gravimetric Analysis (TGA)

LECO TGA-701 thermo-gravimetric analyzer was used in selectable atmosphere of N_2. The analyzer determine the weight loss as function of varying temperature in selectable atmosphere. The temperature used for the TGA start slowly from 80 °C at an incremental rate of 20 °C/min till the final temperature of 660 °C.

3. Results and Discussion

The proximate and ultimate analysis of the agriculture residue samples are reported in Table 1 and Table 2. Each estimated property is discussed in following sub-sections.

3.1. Moisture content

The moisture content plays a vital role in the selection of efficient thermal conversion technology. The biomass containing high moisture content represents significantly low new energy density by mass due to the mass of water. This results in utilization of energy-intensive drying operation to reduce the moisture content and to be able to operate conversion technology [28]. For efficient performance of the thermal conversion technology, gasification or pyrolysis, the biomass shall not represent more than 10-14% of moisture content. Biomass resources with higher moisture contents can be converted through bio-chemical processes such as anaerobic digestion for biogas production. The estimated moisture content in the obtained agriculture residue samples ranges between about 4.8 %wt. (almond shell) and about 11.8 %wt. (corn cob). It is important to note that the estimated moisture contents of available agriculture residues showed slightly different results for most of the agriculture residues when compared to values reported in the literature data previously published [29-31]. The marginal differences in reported values are mainly due to agriculture residues obtained from different locations, climate differences. In addition, the handling and storage also contributes towards moisture content.

Table 1 Proximate analysis of selected agricultural residues (% wt. as dry)

Samples	Moisture Contents	Volatile Matter	Ash Contents	Fix Carbon
Wheat straw	8.45	65.59	4.99	20.97
Rice Husk	7.88	54.39	14.02	23.71
Corn Cob	11.74	72.33	10.67	4.97
Corn Leaf	7.44	79.08	7.82	5.66
Saw Dust	8.52	73.68	2.91	14.89
Bagasse	8.77	79.39	8.02	3.82
Cotton Stalks	6.85	81.08	7.12	4.95
Corn straw	8.78	73.25	5.95	12.02
Rice straw	6.96	58.25	20.02	14.77
Almond shell	4.75	84.79	4.78	5.68

Table 2 Ultimate analysis of selected agricultural residues (% wt. as dry)

Sr. No	Samples	Carbon	Hydrogen	Nitrogen	Sulphur	Oxygen	HHV(MJ/Kg)
1	Saw Dust	47.14	5.59	0.37	0.06	46.03	19.22
2	Bagasse	46.96	5.81	0.28	0.23	46.72	17.54
3	Corn Cob	46.20	5.42	0.92	0.24	47.22	18.36
4	Rice Husk	44.13	5.01	0.39	0.07	50.40	15.45
5	Wheat Straw	47.25	5.28	0.61	0.18	46.68	17.25
6	Cotton Stalks	46.81	5.67	0.67	0.04	46.81	19.01
7	Corn Leaf	47.04	5.41	0.68	0.05	46.82	17.37
8	Corn straw	41.85	5.38	1.36	0.07	51.34	17.08
9	Rice straw	28.55	3.98	1.15	0.61	65.71	13.48
10	Almond shell	50.12	5.47	0.29	0.17	43.95	18.05

3.2. Volatile and ash contents

The volatile contents of the agriculture waste samples were determined on dry basis. The lowest volatile content was found in the rice husk i.e. 54 %wt. and the highest volatile content in the almond shell i.e. 84.79 %wt. The results regarding the ash contents determined in the study are considerably different from the data of literature due to the agriculture residues available in different regions and climate conditions.

The samples of wheat straw, corn leaf, saw dust, almond shell, cotton stalks and corn straws had low ash contents that were less than 8 % wt. The sugarcane bagasse and corn cob had medium ash contents that were less than 10 % wt. Among the selected biomass samples, rice straw and rice husk had substantially higher ash content i.e. greater than 15 % wt. Soil pollution (decay) is different for every biomass sample taken due to the difference origin of sources of samples. It is beneficial from another perspective that the inorganic compounds present in the agriculture waste resources with higher ash contents have potential to be used as catalysts in the thermal conversion technologies e.g. gasification and pyrolysis [32].

3.3. Elemental composition and Heating values

The calorific values of the samples are reported in the ultimate analysis (see Table 2). The heating/calorific values of the agriculture waste samples determined by Bomb Calorimeter showed nearly identical values as reported in the literature. Cotton stalks and saw dust showed the highest higher heating values (HHV) i.e. about 19 MJ/kg. Whereas, rice straw showed the lowest HHV among the available sample i.e. about 13 MJ/kg. The considerable heating values of the agriculture waste samples showed that these locally available renewable resources can potentially be converted to substantial amount of bio-energy products from effective conversion technologies.

From the elemental composition perspective, Sulfur and nitrogen were found to be in small amounts in all samples except corn straw that has highest nitrogen and rice straw that has highest sulfur content.

3.4. Chemical characterization

Chemical characterization of the agriculture residues will provide useful information for modeling of thermal conversion processes. Hemicellulose and cellulose contents present in agro-waste samples were found to be less than 50 %wt. Almond shell samples has highest cellulose content and corn leaf with the lowest cellulose content. The highest hemi-cellulose content was found in the corn cob samples.

Corn cob and cotton stalk samples represented lower lignin content, i.e. about 7 %wt. and 8 % wt. respectively. Since the biomass with low lignin contents are suitable for bio-oil production from pyrolysis, Corn cob and cotton stalk will be interesting option to be utilized in pyrolysis as compared to other selected samples. Whereas, rice husk and wheat straw samples could be gasified due to higher lignin content, i.e. about 40% wt. lignin content.

Table3: Structural analysis of agriculture waste samples (dry and free ash basis)

Sr. No	Samples	Cellulose	Hemicellulose	Lignin	Extractives
1	Saw Dust	42.58	18.54	11.21	27.67
2	Bagasse	43.87	21.49	17.02	17.62
3	Corn Cob	37.52	47.47	6.85	25.78
4	Rice Husk	38.35	11.14	40.16	10.35
5	Wheat Straw	45.12	9.16	37.41	8.31
6	Cotton Stalks	44.75	25.19	7.89	22.17
7	Corn Leaf	29.74	30.14	9.25	30.87
8	Corn straw	44.01	25.12	8.98	21.98
9	Rice straw	32.03	8.42	30.34	29.21
10	Almond shell	46.25	7.56	29.85	16.47

3.5. Thermal gravimetric analysis (TGA)

The thermal gravimetric analysis was used to study and analyze the degradation of selected samples. The TGA curves are shown in Figure 1. TGA combustion and pyrolysis techniques were adopted to found the molecular deterioration characteristics. TGA curves from 1-3 show that almost 60-75% of the weight of samples has been decomposed before 590°C. Major portion of the weight of the sample was decomposed in between 200-400 °C. The TGA curves are the best option to determine the optimum temperature for the gasification or pyrolysis reactions [33]. Easy decomposition of all the waste samples during thermal decomposition shows that these samples would be ideal feedstocks in combustion Processes [34].

The TGA curves indicates the optimum temperatures of the each of the biomass samples corresponding to their loss in weight .Sawdust, cotton stalks, Sugarcane bagasse, corn cobs and corn leaf have temperature range, ranging from 190 °C to 560 °C. The least value of the weight loss of the biomass samples is for corn leaf, i.e. 45%, while bagasse and almond shell indicate highest weight loss, i.e. 70%, at pyrolysis temperatures.

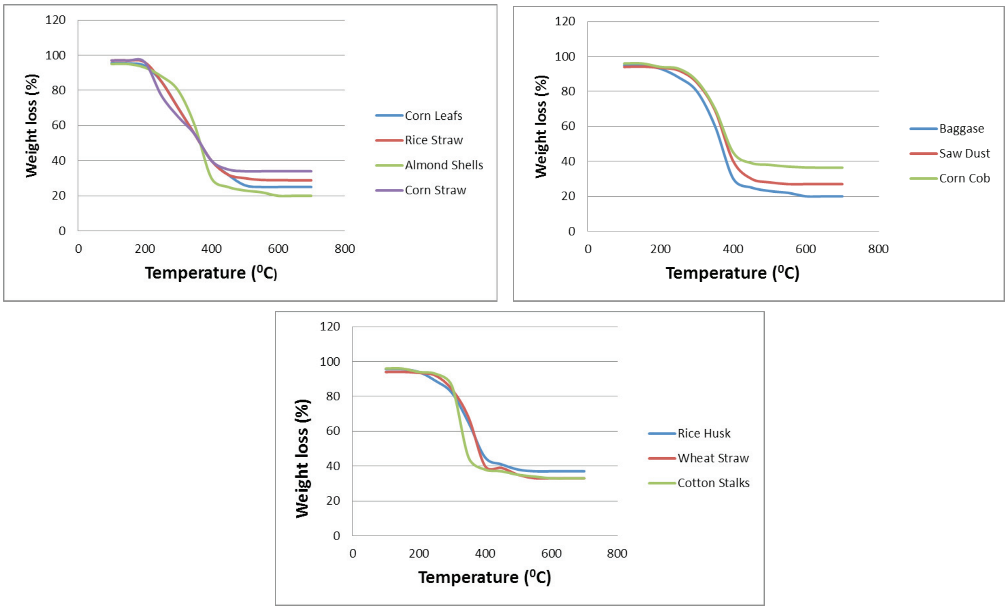

Figure 1 Thermo-gravimetric analysis curves of selected agriculture wastes

4. Conclusions

The study were conducted to determine the thermochemical properties of available agriculture residues in South Asian region to identify their potential to be used in thermal conversion processes for biofuel, heat or power production. The agriculture residues included bagasse, almond shell, corn cob, cotton stalks, wheat straw, sawdust, corn leaf, rice husk, rice straw, and corn straw. The estimated moisture contents of available agriculture residues showed slightly different results for most of the agriculture residues when compared to values reported in the literature. The marginal difference in reported values is mainly due to agriculture residues obtained from different locations, climate differences, handling and storage. The lowest volatile content was found in the rice husk i.e. 54 %wt. and the highest volatile content in the almond shell i.e. 84.79 %wt. Rice straw and rice husk had substantially higher ash content i.e. greater than 15 % wt. Cotton stalks and saw dust showed the highest higher heating values (HHV) i.e. about 19 MJ/kg. Based on available biomass in south Asia region, calculated amount of energy is 152, 806, 9459, 6MJ annually which can at least contribute to the basic needs of the countries. Hemicellulose and cellulose contents present in agro-waste samples were found to be less than 50 %wt. From the elemental composition perspective, Sulfur and nitrogen were in small amounts in all samples except corn straw that has highest nitrogen and rice straw that has highest sulfur content. TGA curves show that almost 60-75% of the weight of samples has been decomposed before 590°C. Major portion of the weight of the sample was decomposed in between 200-400 ^{o}C

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References

[1] Joshi, Pramod K., et al. "Agriculture diversification in South Asia: patterns, determinants and policy implications." *Economic and Political Weekly* (2004): 2457-2467.

[2] Alauddin, Mohammad, and John Quiggin. "Agricultural intensification, irrigation and the environment in South Asia: Issues and policy options." *Ecological Economics* 65.1 (2008): 111-124.

[3] Onchieku, J. M. *Quantification and characterisation of biomass residues for the formulation of charcoal briquettes for household use in Kenya*. Diss. Moi university, 2007.

[4] Mirza, Umar K., Nasir Ahmad, and Tariq Majeed. "An overview of biomass energy utilization in Pakistan." *Renewable and Sustainable Energy Reviews* 12.7 (2008): 1988-1996.

[5] Zaigham, Nayyer Alam, and Z. A. Nayyar. "Prospects of renewable energy sources in Pakistan." *Renewable Energy Technologies and Sustainable Development* (2005): 65-86.

[6] Demirbaş, Ayhan. "Biomass resource facilities and biomass conversion processing for fuels and chemicals." *Energy conversion and Management* 42.11 (2001): 1357-1378.

[7] Purohit, Pallav, Arun Kumar Tripathi, and Tara Chandra Kandpal. "Energetics of coal substitution by briquettes of agricultural residues." *Energy* 31.8 (2006): 1321-1331.

[8] Demirbas, Ayhan. "Potential applications of renewable energy sources, biomass combustion problems in boiler power systems and combustion related environmental issues." *Progress in energy and combustion science* 31.2 (2005): 171-192.

[9] Demirbas, M. Fatih, Mustafa Balat, and Havva Balat. "Potential contribution of biomass to the sustainable energy development." *Energy Conversion and Management* 50.7 (2009): 1746-1760.

[10] Loehr, Raymond. *Agricultural waste management: problems, processes, and approaches*. Elsevier, 2012.

[11] Dincer, Ibrahim. "Renewable energy and sustainable development: a crucial review." *Renewable and Sustainable Energy Reviews* 4.2 (2000): 157-175.

[12] Holm-Nielsen, Jens Bo, Theodorita Al Seadi, and Piotr Oleskowicz-Popiel. "The future of anaerobic digestion and biogas utilization." *Bioresource technology* 100.22 (2009): 5478-5484.

[13] Cherubini, Francesco. "The biorefinery concept: using biomass instead of oil for producing energy and chemicals." *Energy Conversion and Management* 51.7 (2010): 1412-1421.

[14] Omer, Abdeen Mustafa. "Green energies and the environment." *Renewable and Sustainable Energy Reviews* 12.7 (2008): 1789-1821.

[15] Omer, A. M. "Renewable energy technologies and sustainable development. The Agriculturist International Journal 1 (1): pp. 5-23." (2013).

[16] Koh, Lian Pin, and Jaboury Ghazoul. "Biofuels, biodiversity, and people: understanding the conflicts and finding opportunities." *Biological conservation* 141.10 (2008): 2450-2460.

[17] Faaij, Andre PC, and Julije Domac. "Emerging international bio-energy markets and opportunities for socio-economic development." *Energy for Sustainable Development* 10.1 (2006): 7-19.

[18] Goyal, H. B., Diptendu Seal, and R. C. Saxena. "Bio-fuels from thermochemical conversion of renewable resources: a review." *Renewable and Sustainable Energy Reviews* 12.2 (2008): 504-517.

[19] McKendry, Peter. "Energy production from biomass (part 2): conversion technologies." *Bioresource technology* 83.1 (2002): 47-54.

[20] Phanphanich, Manunya, and Sudhagar Mani. "Impact of torrefaction on the grindability and fuel characteristics of forest biomass." *Bioresource technology* 102.2 (2011): 1246-1253.

[21] Ahmaruzzaman, M. "Proximate analyses and predicting HHV of chars obtained from cocracking of petroleum vacuum residue with coal, plastics and biomass." *Bioresource technology* 99.11 (2008): 5043-5050.

[22] Cumming, John W., and Joseph McLaughlin. "The thermogravimetric behaviour of coal." *Thermochimica acta* 57.3 (1982): 253-272.
[23] Vamvuka, D., et al. "Pyrolysis characteristics and kinetics of biomass residuals mixtures with lignite< sup>☆</sup>." *Fuel* 82.15 (2003): 1949-1960.
[24] Bahng, Mi-Kyung, et al. "Current technologies for analysis of biomass thermochemical processing: a review." *Analytica Chimica Acta* 651.2 (2009): 117-138.
[25] Xiao, B., X. F. Sun, and RunCang Sun. "Chemical, structural, and thermal characterizations of alkali-soluble lignins and hemicelluloses, and cellulose from maize stems, rye straw, and rice straw." *Polymer Degradation and Stability* 74.2 (2001): 307-319.
[26] Sheng, Changdong, and J. L. T. Azevedo. "Estimating the higher heating value of biomass fuels from basic analysis data." *Biomass and Bioenergy* 28.5 (2005): 499-507.
[27] Parikh, Jigisha, S. A. Channiwala, and G. K. Ghosal. "A correlation for calculating HHV from proximate analysis of solid fuels." *Fuel* 84.5 (2005): 487-494.
[28] Saxena, R. C., et al. "Thermo-chemical routes for hydrogen rich gas from biomass: a review." *Renewable and Sustainable Energy Reviews* 12.7 (2008): 1909-1927.
[29] Raja, S.A., Kennedy, Z.R., Pillai, B.C., 2010. Flash pyrolysis of Jatropha oil cake in gas heated fluidized bed research reactor. Int. J. Chem. Eng. Res. 2, 1–12.
[30] Titiloye, J., Abu Bakar, M., Odetoye, T. 2013. Thermochemical characterisation of agricultural wastes from West Africa. Industrial Crops and Products 47, 199– 203
[31] Oladayo, A., 2010. Proximate composition of some agricultural wastes in Nigeria and their potential use in activated carbon production. J. Appl. Sci. Environ. Manage. 14, 55–58.
[32] Kenney, Kevin L., et al. "Understanding biomass feedstock variability." *Biofuels* 4.1 (2013): 111-127.
[33] Van de Velden, Manon, et al. "Fundamentals, kinetics and endothermicity of the biomass pyrolysis reaction." *Renewable energy* 35.1 (2010): 232-242.
[34] Skodras, George, et al. "Pyrolysis and combustion characteristics of biomass and waste-derived feedstock." *Industrial & engineering chemistry research* 45.11 (2006): 3791-3799.
[35] Electricity Generation from Agricultural Residues in Five South Asian Countries: Prospects and Potential Md. Mizanur Rahman and Jukka V. Paatero Department of Energy Technology, School of Engineering, Aalto University, Finland. 4th International Conference on Sustainable Energy and Environment (SEE 2011): A Paradigm Shift to Low Carbon Society 27-29 February 2012, Bangkok, Thailand.

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