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Feasibility test of agricultural residues through characterization for utilization in plasma gasification

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ABSTRACT

Agricultural residues were characterized to determine their feasibility as feedstock for plasma gasification. Husk, stalk, straw and shell were selected for the study and proximate analysis, elemental composition analysis, thermal value analysis were carried out using standard procedures. Producer gas generated from these bio-residues is well suited for plasma gasification process where the working temperature is between 1200-2000ºC. These substances have moisture content in the range of 5-12%, and volatile matter content of 58-70%, offering good burning characteristics and conversion to electricity. The fixed carbon content of 13 to 20% contributes significantly to its calorific value. The average calorific value of selected agricultural residues (18.27 MJ/kg) was higher than the calorific value of feedstock (12 to 16 MJ/kg) used in plasma gasification, thus reinforcing their suitability further. It was found that selected agricultural residues could be adopted and promising fuel for plasma generation and deserve further development as a sustainable and renewable alternative.

Key words: Agro residues, Biochemical characterization, Plasma gasification, TGA

Agricultural (agro) residues are used in several rural domestic applications. Heat derived from combustion of agro residues is an important alternative and promising renewable source for sustainable development in the rural sector (Huang and Tang 2007). Agro residues with high energy potential include stalk, shell, husk, straw and leaf litter. Agricultural residues in quantity accounted for 686 million tonnes (Gross weight on annual basis 2014) of which 34% (234 million tonnes of gross) is estimated as surplus for energy generation (Hiloidhari *et al.* 2014). Ministry of Statistics and Programme Implementation (MoSPI), 2014 reported that biomass power potential is estimated at 18.63% (17568 MW). Transformation of the residues into energy can be efficiently achieved by applying thermo-chemical methods such as combustion, pyrolysis, partial oxidation and gasification (Wen *et al.* 2009, Je Lueng *et al.* 2010). Gasification of agro residues is feasible to convert the biomass materials into a gaseous fuel (producer-gas). Producer-gas is a mixture of carbon monoxide, hydrogen, methane, carbon dioxide, nitrogen and water vapour. As compared to conventional biomass gasification, plasma gasification would be a better alternative to gasify agro residues without any pre-treatment (Spyridon *et al.* 2012).

Plasma Gasification involves thermo chemical conversion of biomass at high temperature through plasma torch, in presence of insufficient but controlled supply of air/oxygen, which generates producer gas (Capt and Bhasin 2009). The gas is made of combustible constituents, such as hydrogen, carbon monoxide and methane and can be used for direct combustion applications or as a fuel for internal combustion engines (Je *et al.* 2014). During plasma gasification, carbon-based materials break down into gases and inorganic materials melt into liquid slag which is poured off and cooled (Masoud *et al.*2010).

This study was conducted to determine the suitability of the agro residues for plasma gasification through the analysis of its thermal behaviour and physical characteristics of various agro residues (Demiral and Ayan 2011 and Hlina *et al.* 2014). In most developing countries, biomass meets a major portion of energy demand in rural areas.

MATERIALS AND METHODS

Bulk density: Bulk density was determined by weighing the feedstock filled in a vessel of known volume and calculating the ratio of the weight of the feedstock to the volume of the vessel (ASTM E-873-06). The average of five trials was reported as the volume of the bulk density

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of the feedstock.

Proximate composition: Proximate composition is the structural property such as moisture, volatile matter, ash content and fixed carbon content of the biomass species was calculated by ASTM standards (ASTM D3172-75).

(a) Moisture content: The moisture content of the samples was carried out in a hot air oven by oven method at 103±2 ºC up to the arrival of standard weight. The moisture content was calculated by measuring weight of moisture evaporated from the sample (W_2) and the original sample weight (W_1).

(b) Volatile matter: The volatile matter was found out using the dried biomass in a muffle furnace at 650 ºC for 10 min. The loss in weight of the sample was found out and the % of volatile matter was calculated as

Volatile matter (%) = (loss in weight of sample/weight of moisture free sample) ×100 (1)

(c) Ash content: The ash content of the material was determined in the muffle furnace at 750 ºC for 2 hr. The ratio between the remaining weight of materials in the crucible and the sample taken was the fraction of ash content of tested material. Dependent on the magnitude of the ash content, the available energy of the fuel is reduced proportionately.

Ash content (%) = (Weight of ash formed/Weight of dried sample) × 100 (2)

(d) Fixed carbon: The fixed carbon is the residue left after removing the volatile matter and the ash from the substance. The significance of the volatile matter and fixed carbon contents is that it provides a measure of the ease with which the biomass can be ignited and subsequently gasified, or oxidized, depending on how the biomass is to be utilized as an energy source.

Fixed carbon (%) = 100 – [volatile matter (%) + ash content (%)] (3)

Ultimate analysis: The ultimate analysis of the agro residues is to find the elemental composition was determined in the GS-MS (ASTM 5373-02). The elemental composition of agro residues consists of carbon, hydrogen and oxygen in major quantities. The chemical formula for the biomass is generally represented by $C_XH_YO_Z$.

Calorific value: The calorific value of the biomass was determined using bomb calorimeter (ASTM D-2015) and is the Higher Heating Value (HHV) or otherwise called as Gross Calorific Value (GCV). Lower Heating Value (LHV) can be calculated from Higher Heating Value (HHV). The calorific value (CV) of a material is an expression of the energy content, or heat value, released when burnt in air. The CV is usually measured in terms of the energy content per unit mass, or volume; hence MJ/kg for solids, MJ/l for liquids, or MJ/Nm^3 for gases.

Thermo gravimetric analysis: Thermo gravimetric analysis (TGA) is a testing method done on samples to determine the change in weight with respect to change in temperature. TGA relies on critical measurements such as weight, temperature and time. The rate of change in weight which is also a vital measurement is derived from temperature measurements. TGA curve alone may not be sufficient to interpret the weight loss of sample. Hence, a derivative thermo gravimetric curve along with TGA curve is needed to determine the apparent weight loss of samples. TGA apart from its useful application is also finding its claim in the study of characterization of agricultural residues. The degradation curves and the reaction rate subjected to combustion in the TGA at 40 ºC/min (40 ml N_2 flow rate). The maximum temperature was 1000 ºC. The rate of degradation of various carbonaceous materials subjected to TGA is an indication of the thermal behaviours of the particular material under gasification process. This technique is performed with a thermo gravimetric analyzer (TGA) as per procedure (ASTM-E1131).

RESULTS AND DISCUSSION

Bulk density

Bulk density of agricultural residues is considered in designing the capacity of the gasifier reactor. Size reduction of the selected agro residues was carried out in a shredder to less than 5 mm and the bulk density was found using the standard procedure. Bulk density of agricultural residues is given in Table 1. Higher bulk density of residues, higher the gas volume in gasifier since one charge results in power for longer time (Khardiwar *et al.* 2014). The average bulk density was found to be 273.80 kg/m^3. The lowest and highest value of bulk density is found in cashew nut shell and tamarind pod with 231.60 and 302.30 kg/m^3. The results are found to be on par with the results of Mamta and Karishma (2013). Bhavya *et al.* 2014, studied the bulk density of various feedstock such as coal, petroleum residue, biomass, and municipal solid waste (MSW) to produce synthetic gas. Bulk density, therefore, is one of the most important parameter to design the gasification reactor volume and to find the energy content of producer gas from single feed of feedstock.

Table 1 Bulk density of agro residues

Agro residues	Bulk density (kg/m^3)
Soya stalk	263.5
Sunflower stalk	286.2
Groundnut shell	246.3
Cashew nut shell	231.6
Arecanut husk	298.4
Date palm husk	293.8
Paddy straw	272.0
Wheat straw	287.4
Tamarind pod	302.3
Leaf litter	256.5

Proximate composition

Proximate compositions of agricultural residues were determined as per standard procedure and presented in Table 2. Calculations have been done in triplicate and the results were expressed on dry weight basis.

Table 2 Proximate composition of agro residues

Agro residues	Proximate composition (%)			
	Moisture	Volatile matter	Ash	Fixed carbon
Soya stalk	11.8	58.4	13.6	16.1
Sunflower stalk	10.4	62.3	10.4	16.9
Groundnut shell	5.2	68.3	6.3	20.2
Cashew nut shell	6.9	70.4	7.9	14.7
Arecanut husk	12.5	63.0	5.6	18.9
Date palm husk	10.5	63.4	8.9	17.3
Paddy straw	8.7	65.5	10.4	15.5
Wheat straw	7.9	67.5	10.2	14.4
Tamarind pod	8.4	68.6	9.6	13.4
Leaf litter	8.0	70.2	6.1	15.6

*(a) Moisture content: M*oisture content (%) was highest in arecanut husk and lowest in groundnut shell with 12.50 and 5.20% respectively. The average moisture content of feedstock was found to be 9.03% and it varies from 5.20 to 12.50%. Higher moisture content affects the gaseous compounds in producer-gas and gasification process which results in less temperature and low burning of gas in normal bio gasifiers. Isam *et al.* (2013) reports that for plasma gasification, the feedstock moisture content of about 20% is possible with process efficiency of gasifier around 22%. Besides impairing the bio gasifiers heat budget, high moisture content also puts load on cooling and filtering equipment by increasing the pressure drop across these units because of condensing liquid. In plasma gasification the moisture content in feedstock gets cracked in the plasma arc (>1200 °C) and helps in formation of more CO and CH_4 (Mountouris *et al. (*2008)). Dejtrakulwong and Patumsawad (2014) proved that moisture content influences the design of reactor and to decide the air fuel ratio in the gasification zone. They concluded that reactor height increases with the moisture content since moisture vapours have significant influence in the gasification reactions.

(b) Volatile matter: Volatile matter in agriculture residues is an important parameter which affects the producer gas composition on gasification process. The volatile content of feedstock falls in the range of 58.43 to 70.44%. The average volatile content in agricultural residue is found to be 65.75%. This indicates that agricultural residues are easier to ignite and burn and to ensure higher efficiency, complete combustion has to be maintained. During devolatization, the feedstock undergoes a thermal decomposition with subsequent release of the volatiles and formation of slag in plasma gasification. Shane *et al. (*2012) studied the detail review on biomass samples and concluded that biomass feedstock consists of 63.06% of volatile content. The sulphur pollutant from plasma gasifier with biomass is very less compared to other combustion process. The volatile content present in the agricultural residues follows the result of Qinglin *et al. (*2012).

(c) Ash: The ash content in different residues is studied to compare their suitability for gasification. The highest ash content (%) is found in soya stalk (13.59%) and lowest in arecanut husk (5.60%) in comparison to other feedstock. The average high ash content in agro residues is found to be 8.89% and indicates that it is suitable for thermo chemical conversion. However, the ash content of biomass affects both the handling and processing costs of overall biomass energy conversion cost. The ash yield from plasma gasification is very less due to higher temperature operations and ash removal system can be avoided compared with biomass gasifier. Xiu *et al.* (*2*005) states that ash content from agro residues comes under the range of 5.58 to 8. 90%, this coincides with the results of this study. Xiang Fang and Li Jia (2012) investigated with biomass ash and found that the ash melting temperatures of biomass is when the ashing temperature is higher and concluded that biomass should be ashed at lower ashing temperature when biomass are used in combustion process.

(d) Fixed carbon: The value of fixed carbon falls in the range of 13.44 to 20.20%. The lowest value and highest value found to be in tamarind pod and groundnut shell respectively. The average value of fixed carbon was found to be 16.30% and very much suitable for gasification process. Fixed carbon content mainly influences the calorific value of agro residues. Fixed carbon content also has direct influence on increasing the thermal value of producer-gas yield. The results of fixed carbon of feedstock are on par with the agricultural residue of rice and wheat straw studies by Xiu *et al. (*2005). Qinglin *et al.* (2013) also proved that plasma gasification is possible for feedstock with fixed carbon content of 10.70% with maximum energy efficiency of 58%.

Ultimate analysis

Elemental composition can vary across biomass types depending on the type of biomass and the region from which the biomass was acquired, but the typical elemental composition of biomass has four elements: carbon, hydrogen, oxygen, and nitrogen. It is important to know the composition in order to balance chemical equations to predict resulting products from a chemical reaction. The values of elemental composition such as carbon, hydrogen, oxygen and nitrogen are given in Table 3. The higher ratio of carbon and hydrogen percentage in biomass yields producer-gas with higher thermal value. The carbon, hydrogen and oxygen influence the yield of producer-gas with composition like carbon monoxide, hydrocarbons and carbon dioxide. The carbon, hydrogen, oxygen and nitrogen value falls in the range of 42.14 to 48.17, 5.10 to 6.48, 40.12 to 43.56 and 0.31 to 2.10% respectively. On an average, agro residues contains carbon, hydrogen, oxygen and nitrogen with 45.42, 5.68, 41.68 and 1.17% respectively. Kuang *et al.* (2014) found that the plasma pyrolysis/ gasification with C, H, O and N content of feed stock with 35.58, 5.03, 35.20 and 4.03% yielded good results. Je Lueng Shie (2014) reported that the lingo-cellulosic wastes contains C, H and N content of 53.13, 7.34 and 1.49%, this

Table 3 Ultimate analysis of agro residues

Agro residues	Elemental composition (%)			
	Carbon	Hydrogen	Oxygen	Nitrogen
Soya stalk	43.6	5.7	41.7	1.5
Sun flower stalk	46.6	5.4	40.1	1.9
Groundnut shell	47.0	5.6	41.6	0.6
Cashew nut shell	45.8	5.8	42.2	0.8
Arecanut husk	46.1	5.1	43.1	1.1
Date palm husk	48.2	6.0	40.1	1.3
Paddy straw	45.4	6.5	41.2	0.7
Wheat straw	42.1	5.9	43.6	1.5
Tamarind pod	44.6	5.1	42.1	2.1
Leaf litter	44.8	5.5	41.0	0.3

shows that selected agricultural residues have the same elemental composition and producer-gas yield would be around as same as 58%. Spyridon and Kapetanios (2013) stated that agro residues with this average elemental composition can be used in plasma process to convert materials into carbon monoxide and hydrogen using very high temperatures with oxygen and/or steam. Dutta *et al.* (2014) found that ultimate analysis was on par with the compositions of carbon, hydrogen, oxygen and nitrogen by weight (45.74%), (5.96%), (40.94%) and (1.72%) respectively. He also states that the experimental results of ultimate analysis with model that producer gas generated were fairly in good agreement with modeling results of producer gas production with higher hydrogen, carbon monoxide and methane content in composition leading to higher energy value.

Calorific value

The energy content (or heating value) of a material is the ratio of the enthalpy of complete combustion to the mass of the sample. The higher heating value (HHV) is the total amount of heat in a sample of fuel including the energy in the water vapour that is created during the combustion process. It is one of the most important parameters for a biomass sample and is used to design bioenergy systems and to know the characteristics of resultant producer-gas.

Table 4 Calorific value of agro residues

Agro residues	Calorific value (MJ/kg[1])	
	Higher heating value	Lower heating value
Soya stalk	19.4	17.2
Sun flower stalk	19.3	17.0
Groundnut shell	21.0	18.7
Cashew nut shell	19.3	17.1
Arecanut husk	17.4	15.2
Date palm husk	19.4	17.2
Paddy straw	17.8	15.6
Wheat straw	16.5	14.2
Tamarind pod	16.6	14.3
Leaf litter	15.9	13.6

The lower heating value (LHV) is the amount of heat in a sample of fuel minus the energy in the combustion water vapour.

Table 4 gives the calorific value of agro residues. The gross calorific value and lower heating value of agro residues falls in the range of 15.90 to 20.98 and 13.64 to 18.72 MJ/kg. Higher calorific value was found in groundnut shell sample which has high volatile content and fixed carbon content, as determined in proximate composition. The average calorific value of agricultural waste was found to be 18.27 MJ/kg and it can be used for plasma gasification to obtain producer-gas with heat content in the range of 12 to 14 MJ/kg (Sang and Jae 2012). Shane *et al.* (2014) reported that calorific value of municipal solid waste with 20% moisture content and 60% volatile content is 10.26 MJ/kg which is less than the average calorific value of agro residues, thus showing that agro residues could be well suited for plasma gasification. These results are on par with Keith *et al.* (2012) and Massimiliano *et al.* (2014).

Thermo gravimetric analysis

Thermo gravimetric analysis is a technique used to determine the weight loss of a material at a specific temperature or when it is subjected to a specific heating pattern. The degradation process has different phases like moisture evaporation, main devolatilization, and continuous devolatilization.

The TGA analysis continuously weighs a sample to the nearest millionth of a gram as it is heated to temperatures of up to 1000 °C. As the temperature is increased, various components of the sample burn off and the weight percentage of each can be measured. The initial loss in the decomposition curve corresponds to the release of moisture as vapour from the biomass in the temperature range of 50 to 100 °C. This loss of weight in 100 percent biomass lies in the range of 1.552 to 9.452%. Then the rate of weight reduction was higher in the temperature range of 100 to 600 °C, which may be due to the decomposition of cellulose and hemicellulose. The volatile reduction of weight at 600°C lies in the range of 52.13 to 75.23%. The reduction continued beyond 600 °C till 800 °C, but the rate of reaction was minimal which may be due to the degradation of lignin, which lies in the range of 2.594 to 13.19%. The rate of degradation becomes constant beyond 800 °C and it is due to the formation of ash and tar in the sample. The residue left at over 1000 °C is about 3.54%. From the TGA curve, it was observed that the process temperature was significant between 800 to 1200 °C, resulting in complete degradation of biomass.

Xiu *et al.* (2005) reported the char residue yields at the end of devolatilization decreased nearly linearly with temperature, from 75% at 700 °C to 58% at 1100 °C, which correspond to volatiles yields of 25 to 42%. This is on par with the results of agro residues. The results are also on par with the TGA results of Prakash *et al.* 2013. The TGA curves of agro residues follows the plasma gasification process simulation results of Talebi and Van Goethem (2014) in degrading residues into producer gas. Shen Chen (2014) carried out studies on TGA analysis on municipal solid waste for plasma gasification and found the decomposition characteristics of different 8 samples. The results showed degradation characteristics were less for gasification with the temperature less than 600 °C and more in the range of 700 to 900 °C was obvious because of the reaction between CO_2 and char. When pre-exponential factor was given as $2.2 \times 10^{13}(s^{-1})$, the activation energy of cellulose decomposed reaction was approximately 176 kJ/mol, while the activation energy of the reaction between CO_2 and char was 327 kJ/mol.

(a) Low moisture content (5.2 to 12.5%), high volatiles content (58.4 to 70.4%) and low ash content (maximum 13.6%) of agricultural residues selected offer greater efficiency in energy generation and increases burning velocity. The fixed carbon content was also favorable (13.4 to 20.2%) as it influences the energy value of produced gas.
(b) Higher carbon (45.4%) and oxygen (41.7%) content showed the possibility of complete gasification and meagre nitrogen content (1.2%), favouring in lesser impurity in producer-gas.
(c) The average calorific value of selected agricultural residues (18.27 MJ/kg) was higher than the calorific value of feedstock used in plasma gasification and hence the agro residues selected are suitable for plasma gasification.
(d) The weight loss of agricultural residues at a specific temperature of plasma gasification showed that the selected materials can be effectively used in plasma gasification for energy generation.
(e) The feasibility testing study showed that the agricultural residues selected are promising renewable fuel sources for plasma gasification sector for sustainable development.

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