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Assessment of Agro-Industrial Wastes Proximate, Ultimate, SEM and FTIR analysis for Feasibility of Solid Bio-Fuel Production

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Abstract:

Disposal of biomass wastes, produced in different agro-industrial activities, is normally an environmental problem. A key for such condition is the utilization of these residues for the production of energetic solid bio-fuel by increasing their proximate and ultimate properties of biomass. The aim of the present study agro-industrial wastes like press dug, saw mill dust, ground nut husk, jatropa seed cake, castor seed cake and tamarind fruit shell were analyzed for the feasibility for production of bio-briquettes. Agro-industrial wastes moisture content, bulk density, particle density, ash content, fixed carbon, calorific value, SEM and FTRI analysis were done by using standard procedures. The results concluded that combination of raw materials used during the production of bio-briquettes will give better mechanical and combustion properties than single raw material used. The final disposal of biomass wastes from agricultural activities is usually an environmental problem. Hence these agro-wastes utilized for production of briquettes turn out to be an environmental friendly fuel that is relatively simple to use and reduces environmental pollution.

Keywords: biomass, briquette, combustion, renewable energy, sustainable agriculture, sludge

1.0 Introduction:

Biomass as the solar energy stored in chemical form in plant and animal materials is among the most precious and versatile resources on earth. The solar energy, which is stored in plants and animals, or in the wastes that they produce, is called biomass energy. This energy can be recovered by burning biomass as a fuel (Tewfik, 2004). Biomass has considered as great potential renewable energy source, both for the richer countries and for the developing world (Demirbas, 2001). Biomass is the third largest primary energy resource in the world, after coal and oil (Bapat*et al*., 1997). In all its forms, biomass currently provides about 1250 million tonnes of oil equivalent (m tone) of primary energy which is about 14% of the world's annual energy consumption (Werther*et al*., 2000). The average majority of biomass energy is produced from wood and wood wastes (64%), followed by solid waste (24%), agricultural waste (5%) and landfill gases (5%) (Demirbas, 2000).

At present, briquetting is commonly used in developing countries. The use of agricultural and forest wastes as well as industrial by-products for production of briquettes are increasing (Tabares*et al*., 2000). It is relevant to the use of the briquettes prepared with raw biomass and/or charcoal (Pastor *et al*., 2001). Some of the workers worked on the production of briquettes with out binder from wood sawdust (Cheremisinoff, 1980), cotton stalks (Abasaeed, 1992), straws of colza (Bartel, 1997). Briquetting of raw agricultural residues without binder is more commonly practicing in India (Tripathi*et al*.,, 1998). Few of the commonly used agricultural residues for briquetting in India include arhar stalk (*Cajanuscajan*), cotton stalk, mustard stalk, maize stalk, groundnut shells, rice husk, tamarind shells, coir pith, sun flower stalk, etc. (Tripathi*et al*., 1998). Both the energy consumption and the quality of the final product depend on technical–technological parameters of granulation or briquetting processes. Most essentially these parameters include the kind and moisture content of processed material, temperature of the process, working surface, length, diameter, and geometrical shape of the die holes (Laskowski*et al*., 1994).

The value of the proximate and ultimate analysis is that it identifies the fuel value of the raw biomass material, which provides an estimate of the ash handling requirement and describes the burning characteristics. Demirbas and Sahin (2004) stated that for briquette quality control, the physical parameters such as density, moisture content, and compressive strength were found to be the best indicators of additive quality and Several national standards (DIN 51731, 1996, O NORM M7135, 2000 and ASAE 269.4, 1996) describe the particle density of pellets and briquettes as a quality indicator of densified fuels. The factors that mainly influence the selection of raw materials are moisture and ash contents, flow characteristics and particle size. In view of the above facts an attempt has been made to assess the feasibility of agro-industrial wastes produced in the study area for production of solid bio-fuel by proximate, ultimate, SEM and FTIR analysis.

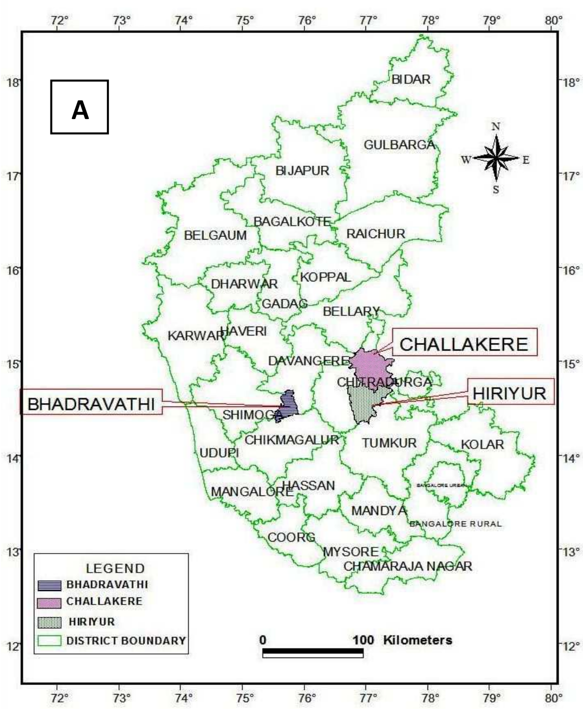

Plate 2: (A) Karnataka state map showing raw materials collected places and (B) Aerial views of Mysore Paper Mill and Sugar Factory sludge disposal site.

2.0 Materials and Methods:

Table 1 showing the raw materials used for the production of briquettes and their respective collected places (Plate 1(A)). There are two main agro based industries located in Bhadravathi town; Mysore Paper Mill and Sugar Factory, both having single effluent treatment plant. In the primary treatment unit an average of 3,907.2 tons per month press dug is producing (Plate 1 (B)). The agro-industrial wastes properties like moisture content was determined after drying a sample at 105ºC according to ASTM D2016-25. To obtain the ash content, a dried sample of 2g is burned at 800ºC during 5h according to ASTM D-5142. The volatile matter was determined according to ISO 562/1974. It was measured by introducing a dry sample of 1g into a crucible with a top at 950ºC for 5min. The fixed carbon (FC) was calculated by FC % = 100 % - ash % - volatile matter % (Tabares*et al.*, 2000). The Gross Calorific Value (GCV) was measured by a PARR 1261 bomb calorimeter in a dry basis using samples of 1g according to the standard method (ISO, 1976). In order to understand the chemical functional groups present in the agro-industrial wastes IR spectra were run taken from the Fourier Transform Infrared Spectroscopy (Perkin Elmer, FTIR1760). The FT-IR spectra were run on agricultural waste (1 mg, 1 wt %) co-adding 64 scans at a resolution of 2 cm^{-1}. These spectra were scaled to 1 mg sample. The morphological structure of the agricultural waste was determined by using scanning electron microscope (SEM, JEOL-JSM-6400, LF-Japan) at 25kv. The SEM analysis made to distinguish the agricultural waste based on their morphological structure and also it helped to predict their agglomeration properties in order to be briquetted (Blesa, *et al.*, 2003).The results obtained from the present study was evaluated using statistical software SPSS, var.12.

Table 1: Agro-wastes and respective collection places

Agro-Waste Samples	Place of Collection
Press Dug (PD)	Mysore Paper Mill (MPM), Bhadravathi
Saw Mill Dust (SMD)	Sri Veerabhadreshwara Saw Mill, Bhadravathi
Ground Nut Husk (GNS)	Oil extraction unit of Challakeri, Chitradurgha District
Jatropa Seed Cake (JSC)	Oil extraction unit of Hiriyuru, Chitradurgha District
Castor Seed Cake (CSC)	Oil extraction unit of Hiriyuru, Chitradurgha District
Tamarind Fruit Shell (TFS)	Challakeri, Chitradurgha District

3.0 Results and Discussion:

3.1 Characteristics of agricultural waste

Result of proximate and ultimate analysis of agricultural waste is presented in the Table 2.

Table 2: Characteristics of agricultural residue (mean ± SD)

Parameters	Moisture Content (%)	Bulk Density (kg/m^3)	Particle Density (kg/m^3)	Volatile Matter (%)	Ash Content (%)	Fixed Carbon (%)	Calorific ValueMJ/kg
Sawmill Dust	1.84 ± 0.23	14.74 ± 0.48	98.22 ± 3.93	78.86 ± 1.15	1.75 ± 0.09	18.59 ± 1.33	17.55 ± 0.03
Ground Nut Shell	1.67 ± 0.05	12.60 ± 0.21	104.81 ± 4.27	79.50 ± 1.95	1.67 ± 0.21	18.35 ± 1.21	19.07 ± 0.01
Press Dug	2.75 ± 0.10	31.43 ± 1.47	98.26 ± 1.44	68.58 ± 1.81	12.28 ± 1.41	19.50 ± 0.82	15.06 ± 0.01
Tamarind Fruit Shell	2.96 ± 0.14	33.37 ± 1.92	115.24 ± 3.75	76.12 ± 2.18	3.27 ± 0.10	20.53 ± 1.25	15.10 ± 0.01
Caster Seed Cake	2.22 ± 0.06	63.19 ± 4.72	305.30 ± 8.79	90.21 ± 2.09	0.84 ± 0.06	8.99 ± 0.15	20.09 ± 0.01
Jatropha Seed Cake	1.99 ± 0.17	42.32 ± 1.83	216.33 ± 4.16	88.91 ± 3.72	0.95 ± 0.04	10.53 ± 0.54	18.87 ± 0.01

A. Proximate analysis

3.2 Moisture content (%)

The lowest (mean ± SD) moisture content was recorded in ground nut shell i.e., 1.67 ± 0.05 % followed by sawmill dust (1.84 ± 0.23%), jatropha seed cake (1.99 ± 0.17%), caster seed cake (2.22 ± 0.06%), press dug (2.75 ± 0.10%) and tamarind fruit shell 2.96 ± 0.14% respectively was recorded. High percentage of moisture in biomass materials prevents their applications for thermo-chemical conversion processes including combustion similarly the water content has an influence on the net calorific value, the combustion efficiency and the temperature of combustion was noticed. Increasing biomass materials moisture content caused on decreasing the unit density of pellets considerably even at high applied pressures. The maximum pellet density of 1238.1 kg/m^3 was observed at the moisture of 5% in a prickly lettuce, while it decreased to 926.5 kg/m^3 in the moisture content of 20% (Affan, 2009).

3.3 Bulk density (kg/m^3)

The highest (mean ± SD) bulk density i.e., 63.19 ± 4.72 kg/m^3 was recorded in caster seed cake followed by jatropha seed cake (42.32 ± 1.83 kg/m^3), tamarind fruit shell (33.37 ± 1.92 kg/m^3), press dug (31.43 ± 1.47 kg/m^3), sawmill dust (14.74 ± 0.48 kg/m^3) and the lowest 12.60 ± 0.21 kg/m^3 was observed in ground nut shell. A major disadvantage of agricultural residues as a fuel is their low bulk density, which makes handling difficult, transport and storage expensive, and gives rise to poor combustion properties (Grover and Mishra, 1996). Briquettes have a certain bulk density resulting in convenient stove automation and dosing (Menind et al., 2012).

3.4 Particle density (kg/m^3)

The highest (mean ± SD) particle density was recorded in caster seed cake i.e., 305.30 ± 8.79 kg/m^3 followed by jatropha seed cake (216.33 ± 4.16 kg/m^3), tamarind fruit shell (115.24 ± 3.75 kg/m^3), ground nut shell (104.81 ± 4.27 kg/m^3), press dug (98.26 ± 1.44 kg/m^3) and lowest 98.22 ± 3.93 kg/m^3 was observed in sawmill dust. The particle density influences the bulk density and the combustion behaviour, as dense particles shows a longer burnout time (Ingwald and Gerold, 2004).

3.5 Volatile matter (%)

The highest (mean ± SD) volatile matter content was witnessed in caster seed cake i.e., 90.21 ± 2.09% followed by jatropha seed cake (88.91 ± 3.72%), ground nut shell (79.50 ± 1.95%), sawmill dust (78.86 ± 1.15%), tamarind fruit shell (76.12 ± 2.18%) and the lowest 68.58 ± 1.81% was found in press dug.According to Van and Koppejan (2002) the quantity of volatiles in biomass fuels is high and usually varies between 76 and 86 wt % (db.) in woody biomass. The higher proportion of volatiles results the major part of the biomass fuel being vaporised before homogeneous gas-phase combustion reactions take place. The remaining char undergoes heterogeneous combustion reactions. Char oxidation lasts considerably longer than the oxidation of combustible gases during the combustion process. The amount of volatile matter therefore strongly influences the thermal decomposition and combustion behaviour of solid fuels. Fuels with lower volatiles, or conversely a very high fixed carbon value, such as coal, need to be burnt on a grate as they take a long time to burn out if they are not pulverized to a very small size. A laboratory study of actual ash behaviour from switchgrass (*Panicumvirgatum*) showed that elements such as K, S, B, Na, and Cu were volatilized from the ash at high temperatures (Misra *et al*., 1993). Elements such as Ca, Mg, P, Mn, Al, Fe and Si were retained even to high temperatures (Steenari *et al*., 1999).

3.6 Ash content (%)

The lowest (mean ± SD) 0.84 ± 0.06% of ash content obtained from the caster seed cake followed by jatropha seed cake (0.95 ± 0.04%), ground nut shell (1.67 ± 0.21%), sawmill dust (1.75 ± 0.09%), tamarind fruit shell (3.27 ± 0.10%) and highest 12.28 ± 1.41% resulted from the press dug.One particular problem that is encountered during thermal processes of biomass is the deposition and agglomeration caused from minerals in ash melts. Baxter (1993) stated: "Ash behaviour of agro-waste during thermochemical conversion is one of the most important matters to be studied". The minerals present with the feedstock, when subjected to high temperature and certain conditions, can agglomerate and deposit inside the thermal device leading to slag formation, fouling and bed agglomeration. Inorganic constituents, such as organically bound cations, inorganic salts and minerals make up the ash present in or on the surface of biomass (Arvelakis and Koukios, 2002). Ashes are usually formed of CaO, K_2O, Na_2O, MgO, SiO_2, Fe_2O_3, P_2O_5, SO_3 and Cl (Reed *et al*., 1980). The ash content of agricultural waste affects its slagging behavior together with the operating temperature and mineral composition of ash.

3.7 Fixed carbon (%)

The lowest (mean ± SD) fixed carbon recorded in caster seed cake i.e.,8.99 ± 0.15% followed by jatropha seed cake (10.53 ± 0.54%), ground nut shell (18.35 ± 1.21%), sawmill dust (18.59 ± 1.33%), press dug (19.50 ± 0.82%) and highest 20.53 ± 1.25% recorded in tamarind fruit shell. The low fixed content making it tend to prolong cooking time by its low heat release (bake-oven effect) (Onchieku *et al.,*). It also reduced the calorific energy of the briquettes by causing what is called fuel-saving effect. The higher the fixed carbon content the better the charcoal produced because the corresponding calorific energy is usually high (FAO, 1995).

3.8 SEM images

The morphology structure of the agricultural waste was determined by using scanning electron microscope (JEOL-JSM-6400, LF-Japan) at 25kv (Plate 1). The morphological structure of the sawmill dust showed uniform short fibrous and coarser structure. Whereas, groundnut shell image showed the masses of loose spongy lignocellulosic structures. Further press dug image indicated long uniform fibrous lignocellulosic structure. Whereas castor and jatropha seed cakes images showed large and small dens granulated structures respectively. The tamarind fruit shell image illustrates large and dense structures. The morphology structure of the agricultural waste studies helps to predict their agglomeration properties in order to be briquetted. Blesa*et al*. (2003) reported that typical fibrous texture of sawdust could favor the coal–biomass agglomeration and, as a consequence, it would produce the increase of IRI and compression strength.

B. Ultimate analysis

3.9 Calorific value (MJ/kg)

Heat value or calorific value determines the energy content of a fuel. It is the property of biomass fuel that depends on its chemical composition and moisture content. The calorific value of caster seed cake resulted highest i.e., 20.09 ± 0.01 MJ/kg followed by ground nut shell 19.07 ± 0.01 MJ/kg, jatropha seed cake 18.87 ± 0.01 MJ/kg, sawmill dust 17.55 ± 0.03 MJ/kg, tamarind fruit shell 15.10 ± 0.01 and lowest observed in press dug i.e., 15.06 ± 0.01 MJ/kg (Table 2). The calorific value can be used to calculate the competitiveness of a processed fuel in a given market situation. There is a range of other factors, such as ease of handling, burning characteristics etc., which also influence the market value, but calorific value is probably the most important factor and should be recognized when selecting the raw material input. The most important fuel property is its calorific or heat value (Aina *et al.,* 2009).

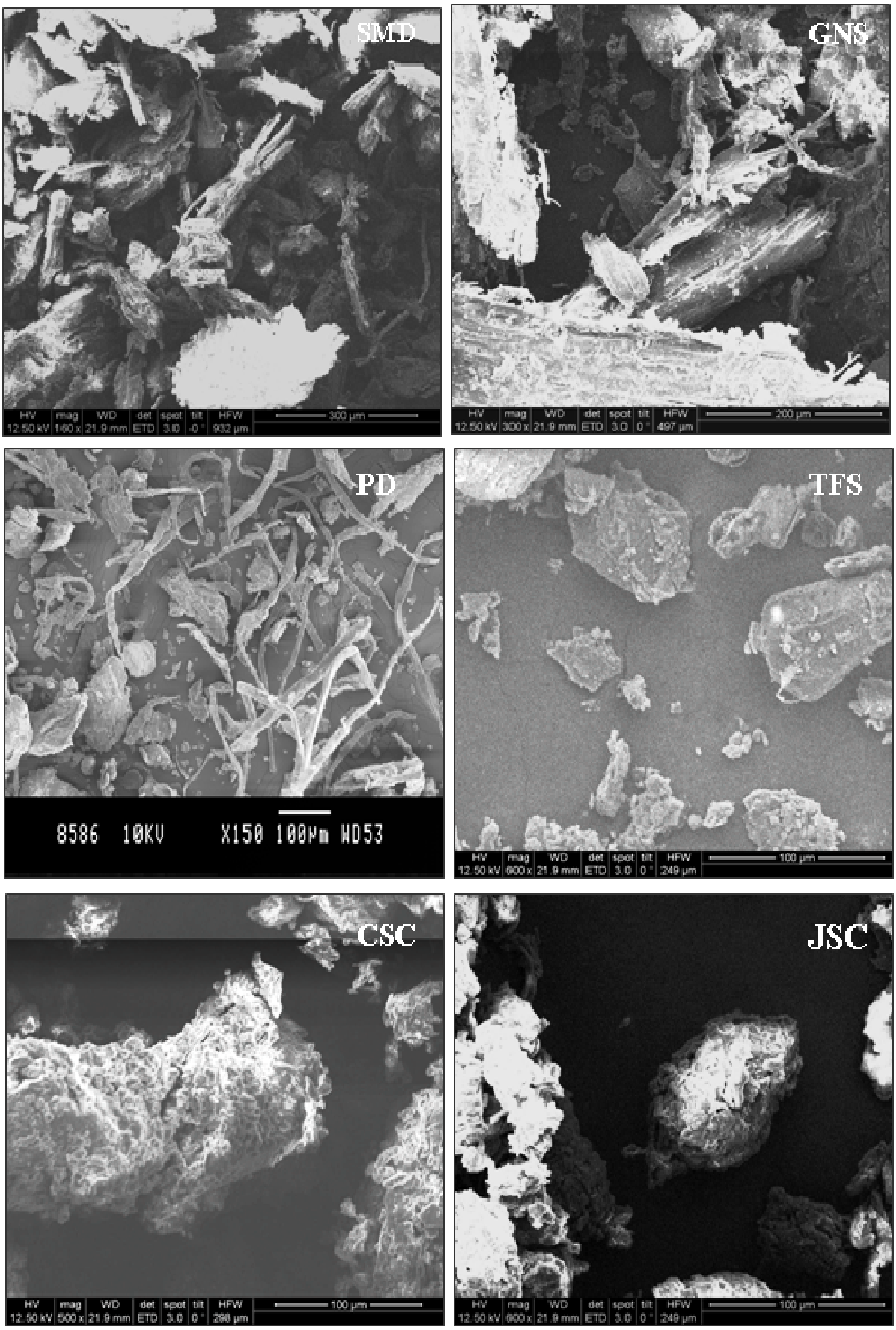

Plate 2: SEM images of agro-waste

3.10 FTIR spectra analysis

The presence of chemical groups influences the calorific value, binding properties and ash content of the agricultural waste (Akowuah *et al., 2012*). Fig. 1 shows theFT-IR spectra analysis of raw materials. The analysis detected alkyne C-H bend at around 670 cm^{-1}, Si-o stretch found around 670 cm^{-1}, sulfur compounds S=O stretch establish around 1162 cm^{-1}, aliphatic amines C-N stretch present around 1244 cm^{-1}, methylene C-H bend approximately 1458 cm^{-1} range, secondary amides N-H bend found near 1458 cm^{-1}, alkene C-C symmetric stretch detected around 1657 cm^{-1} range, methylne symmetric C-H stretch present around 2927 cm^{-1} range, methylne anti-symmetric C-H stretch found around 2928 cm^{-1}, amines N-H stretch established around 3419 cm^{-1} and urethanes amides stretch were detected around 1734 cm^{-1} range. These chemical groups were commonly found in all the samples of briquettes raw materials. But intensities of chemical groups were found to be varied from each other.

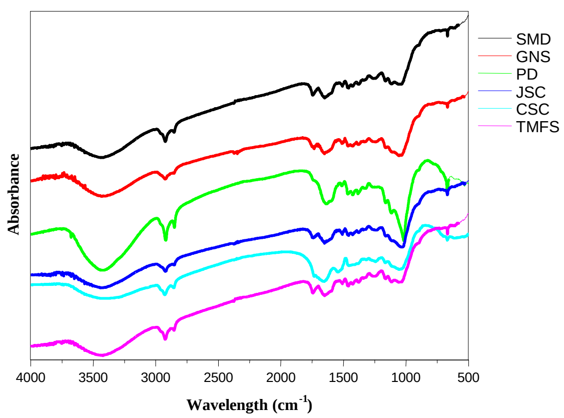

Fig. 1. FT-IR spectra of the briquettes raw materials

4.0 Conclusion:

Sawmill dust had good properties like lees moisture content, bulk density, particle density, ash content, fixed carbon, moderate calorific value and uniform short fibrous and coarser structure. It can be alone used for the production of briquettes and it will give good mechanical as well combustion properties to briquettes. Ground nut shell also had good properties like lees moisture content, particle density, ash content, fixed carbon, high calorific value but very less bulk density and it has loose spongy lignocellulosic structures. Press dug and tamarind fruit shells have high ash content and fixed carbon and very less calorific value and volatile matter but it has long uniform fibrous lignocellulosic structure i.e they give good mechanical property but fails in combustion properties. Caster Seed Cake and Jatropha Seed Cake have good combustion properties but they have high bulk density, particle density with large and dense structured particles hence they required high energy to compress and they produce poor mechanical strength briquettes. With this study suggests that the combination of raw materials used during production of bio-briquettes may give better mechanical strength as well as combustionproperties then the single raw material used.

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