Studies on the Fuel Characteristics of Empty Fruit and Seed of *Sterculia Foetida*

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Abstract: **Biomass characterization is the primary step to make use them as feedstock in energy conversion technologies. The empty fruits and seeds of *Sterculia foetida* tree drop down as waste. Hence, these samples were characterized for proximate content, elemental composition, heating value, thermal behavior and functional groups. Thermogravimetric analysis showed that the active pyrolysis of empty fruit and seed occurred with a mass loss of 59.821% and 51.315% respectively. The empty fruit decomposed in the oxidation atmosphere with a mass loss of 80.20%. Spectroscopic analysis exposed the presence of several organic compounds in the biomass samples. Empty fruit and seed were found to be excellent sources for thermal energy conversion.**

***Keywords: Sterculia foetida*, empty fruit, seed, TGA, pyrolysis, combustion, FTIR**

I. INTRODUCTION

The depletion of conventional energy resources and concerns of environmental pollution has been constantly demanding the researchers to look for renewable energy sources. Biomass is one of the largest sources of renewable and sustainable energy. Biomass is capable of providing a continuous supply of fuels and chemicals with zero CO_2 emission. In India, the biomass production is estimated to be in the range of 62–310 metric tons per year [1]. Major part of biomass is produced from farming activities and agro-industrial sector. Biomass materials such as bagasse, rice husk, soya husk, straw, cotton stalk, coconut shells, de-oiled cakes, coffee waste, jute waste, groundnut shells, saw dust etc. are used as solid fuels in pyrolysis, combustion and gasification processes for the production of fuels, chemicals and power [2]. Empty fruits [3] and non-edible seeds are also employed in these processes. The availability of oil makes the seeds more preferable for the production of bio-oil viz pyrolysis process. The chemical composition, heat content and pyrolysis characteristics of palm empty fruit bunch [4] and seeds such as mahua, karanja, niger and linseed [5] were characterized and pyrolysis properties were studied and reported.

The characterization of biomass is the first step to find the feasibility to use in thermochemical processes. In this context, this work was focused to characterize the empty fruit and seeds of *Sterculia foetida (S. foetida)* as solid fuel feedstock for thermochemical processes. *S.foetida* (Figure 1) is a soft wooded tree that belongs to the genus s*terculia (*family*: Malvaceae)*. It is found in deciduous forests and in the plains of India, Burma, Malaysia, Taiwan, Thailand, Phillipines, Hawaii, Kenya, Srilanka, Uganda, Oman, Tanzania, Indonesia and Northern Australia [6]. It is cultivated as an ornamental and shade tree. The tree yields fruits/seeds abundantly. Each fruit consists of 15-20 seeds attached to the inner margin. The fruits and seeds dry and fall down as waste. The empty fruits (~10cm x7cm) are heart shaped and fibrous. The kernel of the seeds yields 50–60% oil [6]. The oil contains fatty acids like sterculoyl acid, malvaloyl acid, palmitic acid, linoleic acid, oleic acid, stearic acid and archidic acid [7]. It is an excellent source for the production of biodiesel [7]. Devan et al 2009 reported reliable engine performance and low emissions while using biodiesel produced from *S.foetida* oil in a single cylinder diesel engine.

The empty fruit and seed of S.*foetida* may be prospective renewable solid fuels for gasification, combustion and pyrolysis processes. Hence, in this work, the proximate content, elemental composition, thermal behavior and functional groups of empty fruit and seed were analyzed through proximate, elemental, thermogravimetric (TGA) and Fourier transform infrared (FTIR) analyses.

Fig.1. Sterculia Foeitida of Empty fruit and seed

II. MATERIALS AND METHODS

The empty fruits and seeds of *S.foeitda* were collected in Puducherry, India. The samples were sun dried and ground into fine powders of around 1 mm. The proximate,elemental, thermogravimetric and Fourier transform infrared analyses were performed. The proximate analyses of the samples were carried out in a furnace by following standard test procedure. The elemental composition of the samples was measured in a PerkinElmer 2400 Series II CHNS analyzer. The higher heating value was calculated from the elemental composition using Dulong-Betherlot formula which considers the effect of fuel nitrogen [8].

The Dulong-Berthelot formula is given by,

$$\text{Heating value (MJ/kg)} = 0.3414C + 1.4445H - (N+O-1)/8 + 0.093S$$

TGA experiments were performed in a Perkin Elemer make TGA4000 analyzer. The empty fruit and seed samples of around 3 mg were placed in the crucibles and heated from ambient temperature to 700°C in the nitrogen gas atmosphere at a constant heating rate of 10°C/min to estimate the pyrolysis behavior. The combustion properties of empty fruit were found out by heating the sample from ambient temperature to 900°C in an oxygen environment at a constant heating rate of 10°C/min. The TG and derivative TG (DTG) profiles from the TGA were used to analyze the pyrolysis and combustion behaviors.

III. RESULTS AND DISCUSSION

3.1. Composition and higher heating value of empty fruit and seed

The results of proximate analysis, ultimate analysis and higher heating value are presented in Table 1. The moisture content is a significant parameter for the selection of suitable energy conversion method. The moisture content in the samples ranged between 8-12% indicating their suitability for thermal conversion technology. The empty fruit had the highest volatile matter and lowest ash contents. The proximate contents of the samples investigated in this work were similar to that reported for palm empty fruit bunch and karanja seed (Table 1). The elemental composition showed that the carbon, oxygen and hydrogen are the major elements in the empty fruit and seed. The analysis also revealed that the elemental compositions of *S.foetida* empty fruit and seed were

Comparable with that of the palm fruit bunch and karanja seed respectively. Both the empty fruit and seed possessed only trace amounts of nitrogen and sulfur, which is preferred as lower emissions of oxides of nitrogen and sulfur may be expected while burning these biomass materials. The heating value of *S.foetida* empty fruit is marginally higher compared to palm empty fruit bunch. The heating value of *S.foetida* seed is very similar to karanja seed.

Table 1

proximate and ultimate analysis of *S.foetida* empty fruit and seed

Samples	*S.foetida* empty fruit	Palm empty fruit bunch (Abdullah et al., 2008)	*S.foetida* seed	karanja seed (Niraj et al., 2012)
Proximate analysis				
moisture	8.120	7.95	6.2	15.2
volatile matter	61.822	83.86	67.9	73.8
ash	3.434	5.36	5.1	3.9
fixed carbon	26.624	10.78	20.8	7.1
Ultimate analysis				
C	42.41	51.00	50.51	52.79
H	8.70	5.70	6.50	6.26
N	0.58	0.36	2.63	3.88
S	0.02	0.03	0.3	0.06
O (by difference)	48.29	37.70	40.36	37.01
Higher heating value (MJ/kg)	21.06	19.32	19.16	22.41

3.2. Pyrolysis behavior of empty fruit and seed

TGA is widely employed to examine the pyrolysis and combustion behavior of biomass due to its reliable prediction. Figure 2 and Figure 3 shows the pyrolysis thermograms. It is seen that both biomass materials revealed three stages of decomposition. In stage I (~ 38-200°C), the slight mass loss occurred due to evaporation of moisture and some light volatile compounds. The empty fruit and seed suffered a moisture loss of 7.89 % and 12.06% respectively.

Biomass is made of protein, hemicelluose, cellulose and lignin. These constituents decompose at different temperature and at various rates. The literature shows that the decomposition of protein, hemicelluloses and cellulose take place in the temperature ranges of 200-400°C [9], 220-315° C and 315-400°C [10]. The thermal decomposition of lignin is reported to take place in a broad temperature region of 160-900°C [11]. In the present work, the active pyrolysis (stage II) of empty fruit and seed occurred between 200-600°C in a single phase mainly by the thermal decomposition of hemicelluloses and cellulose. Mass loss of empty fruit accounted for the release of 59.821% volatile compounds. The DTG profiles indicate the rate of thermal decomposition or reactivity of biomass. The DTG curve of empty fruit showed a single mass loss peak with a maximum mass loss rate of 4.035 %/min at 310°C. Chen et al., 2015 reported this kind of DTG profile for the pyrolysis of rapeseed straw. The active pyrolyisis of seed occurred in two phases with a total mass loss of 51.315%. The first peak indicated the decomposition of protein and hemicelluloses whereas second indicated the decomposition of protein and cellulose. The DTG profile showed peaks at 280°C and 315°C. The maximum rate of mass loss was 3.112 %/min and 3.281 %/min rate. Chen et al, 2015 reported that the seed biomass show multiple peaks in their DTG profile due to their high protein content. In stage III

(600-700°C), the empty fruit and seed suffered a mass loss of 2.938% and 4.165%, respectively due to the slow decomposition of char in the biomass.

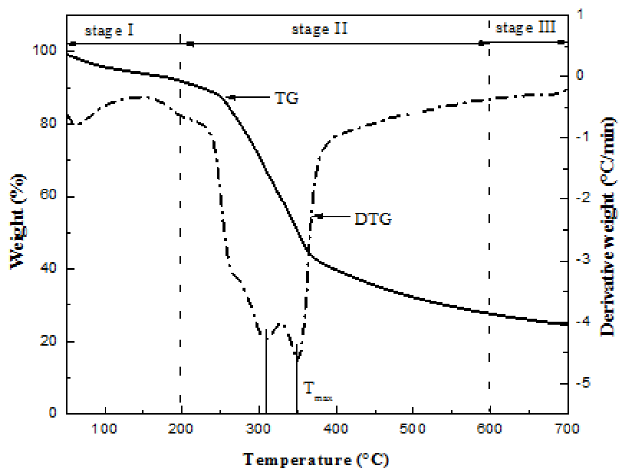

Fig.2.TG and DTG curves from the pyrolysis of S.foeitida seed in nitrogen atmosphere at a heating rate of 10^0C/min

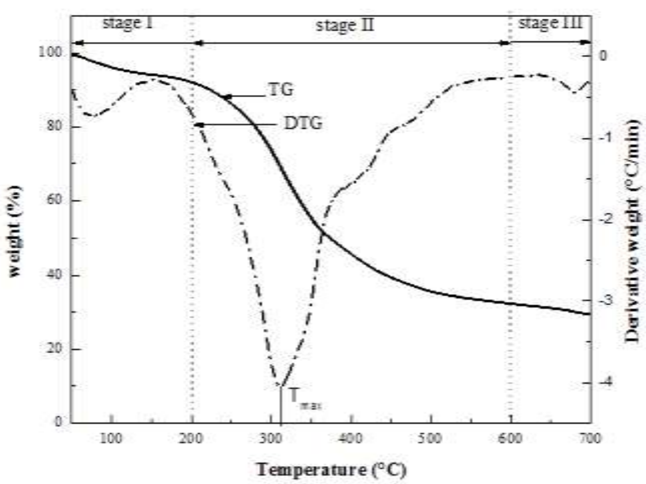

Fig.3.TG and DTG curves from the pyrolysis of S.foeitida empty fruit in nitrogen atmosphere at a heating rate of 10^0C/min

3.3. Combustion behavior of S.foetida empty fruit

TGA of biomass solid fuels in oxidative atmosphere is useful to assess their potential application for combustion process [12]. Figure 4 shows the TG and DTG combustion profiles of S.*foetida* empty fruit obtained at a heating rate of 10°C/min. Based on the changes in the slope of the TG curve, the combustion behavior of *S.foetida* empty fruit can be divided into three stages: stage I (38-200°C), stage II (200-500°C) and stage III (500-900°C). The mass loss in stage I that accounted for 10.95% was due to the evaporation of moisture in the empty fruit. The biomass sample started to release volatiles at around 200°C (stage II). The DTG curve exhibited two peaks at 299°C and 425°C with decomposition rate of 0.119%/min and 0.221%/min respectively. Literature suggests that the first peak was due to the decomposition of cellulose and hemicelluloses and partial decomposition of lignin [13]. The second peak was attributed to the decomposition of remaining lignin and the combustion of char. Major mass loss of 80.201% occurred in stage II within the temperature range of 200-500°C.

The comparison of mass losses during pyrolysis and combustion of empty fruit (at the same heating rate and temperature range) indicated that the mass loss was higher when it is burnt. The presence of oxygen appeared to enhance the decomposition of empty fruit and promoted the combustion of char residue [13]. The TGA experiments of empty fruit revealed that it is a potential solid fuel for combustion.

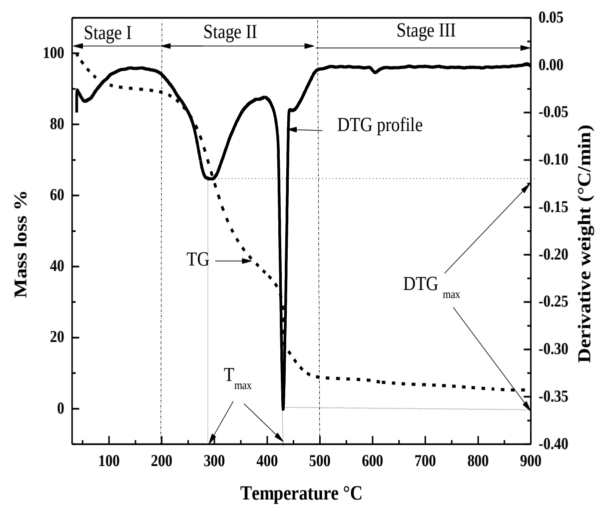

Fig.4.TG and DTG curves from the pyrolysis of S.foeitida of empty fruit in oxgen atmosphere at a heating rate of 10^0C/min

3.4. FTIR Analysis

The functional groups present in the empty fruit and seed were identified based on comparison of the Fig 5 transmitance spectra with those available in the literature [10]. The broad transmittance peaks at 3276.89 $cm^{-1}$and 3286.19 cm^{-1} is due to the O–H stretching. The sharp peak at 2855 cm^{-1} showed the existence of asymmetric C–H stretching vibration. The distinct peaks observed at 1709.94 cm^{-1} for the seed and increase in the transmittance at 1700 cm^{-1}(carbonyl stretch) proved the abundance of fatty acids in the seed. The transmission peaks that occurred in the range of 1500 cm^{-1} – 1700 cm^{-1} represented the carboxyl group in the analyzed samples. The sharp peak at 1000 cm^{-1} and weak peaks between 1000 cm^{-1} and 400 cm^{-1} indicated the availability of phenols and alcoholic groups in both empty fruit and seed.

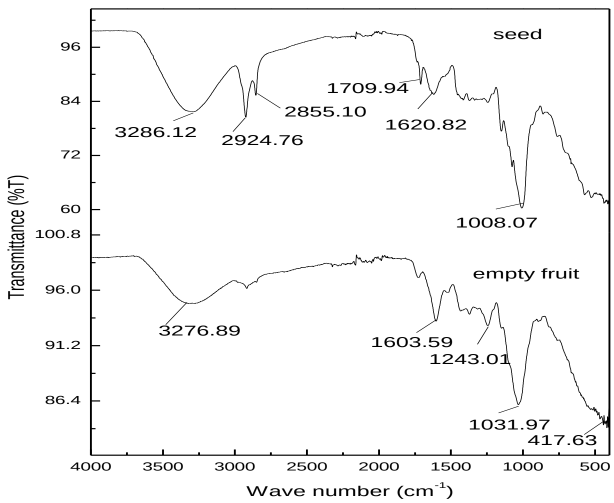

Fig.5.FTIR analysis of S.foeitida of empty fruit and seed at a heating rate of 10^0C/min

IV. CONCLUSION

The heating value of empty fruit and seed of *S.foetida* is higher. The nitrogen and sulphur contents are very less. This is a superior quality, since the combustion of these biomass wastes may result in lower emissions of oxides of nitrogen and sulphur. The results of TGA showed that the active pyrolysis of both empty fruit and seed occurred between 200-600°C. The active pyrolysis of empty fruit occurred in a single phase with a mass loss of 61.822%. The active pyrolysis of seed completed in two phases with a total volatile yield of 52.235%. The pyrolysis behavior indicated that the empty fruit and seed of *S.foetida* could be easily decomposed by pyrolysis reactions. The oxidative thermal degradation of empty fruit exhibited two major phases that accounted for 80% mass loss. This result expressed that the empty fruit is an excellent solid fuel for combustion reactions. The FTIR results showed the presence of carbonyl, phenols, alcohols and esters in the samples. The results suggested that the empty fruit and seed of *S.foetida* are potential sources of solid fuels for thermochemical energy conversion.

ACKNOWLEDGEMENT

The authors would like to offer their sincere thanks to NIT-Thiruchirapalli for the TGA, FTIR and elemental analysis of the feedstock.

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