

Physico-chemical evaluation of leaf litter biomass as feedstock for gasification

Author 1

Shaili A. Shah

*Research Scholar, Department of Chemical Engineering,
Sinhgad College of Engineering,
Vadgaon (BK), Pune 411041, Maharashtra, India.*

Author 2

Shailesh A. Ghodke

*Assistant Professor, Department of Chemical Engineering,
Sinhgad College of Engineering,
Vadgaon (BK), Pune 411041, Maharashtra, India*

Abstract

At present, the use of biomass gasification as an energy source has received a tremendous amount of interest from all over the world due to its advantage in providing continuous feedstock supply. Moreover, biomass fuels when compared to fossil fuels possess negligible sulphur and nitrogen concentrations thereby generate far less emissions into the air. Physico-chemical characteristics of leaf litter from largely grown tree species such as *Polyalthia Longifolia* and *Terminalia Catappa* were analyzed and studied for possible use in the gasifiers. The biomass samples were collected and examined for their physical and chemical characteristics using oxygen bomb calorimeter, thermogravimetric analyzer (TGA), CHNS(O) and ICP-AES. The biomass samples were subjected to two-step extraction process, that is alcohol and water extraction separately, and the raffinate from second step was subjected to compositional analysis for cellulose, hemicellulose and lignin content according to Van Soest fiber analysis. Among both the biomass samples studied, *P. Longifolia* shows low ash content (6.530%) and lignin content (14.89%). Significant amounts of Ca, K, and Na were found in both the biomass ash samples. The calorific value of the biomasses were in the range of 16.089-20.576 MJ/kg. *P. Longifolia* shows high cellulose and hemicellulose concentrations compared to *T. Catappa*. Delineation of all these properties combined together shows that *Polyalthia Longifolia* and *Terminalia Catappa* leaf litter biomass can act as probable feedstock for gasification.

Keywords: leaf litter, *Polyalthia Longifolia* (False Ashoka), *Terminalia Catappa* (Jungle Badam), characterization, gasification.

Introduction

The urban and the rural areas both are burdened by the wastes that are generated and this leads to the dumping it into landfills or by burning it off in open causing pollution. Thus, by this action we are not bringing any solution to the problem, instead we are translocating it. Rural areas due to its large availability of land, allows the biomass waste to degrade and increase the fertility of the soil. But this is not the case in urban areas. Forest residues, agricultural residues, industrial

residues, animal residues, municipal solid waste (MSW) and sewage are different sources of biomass [1]. Lignocellulosic biomass are plant or plant derived organic matter which are renewable. Each country is eco-rich with this type of biomass [2]. The quality of the lignocellulosic biomass varies according to the geographical and the local climatic conditions. Lignocellulosic biomass comprises mainly of cellulose, hemicellulose and lignin in the range of 30%-50%, 15%-35% and 10%-20% respectively. Several researchers in the past have worked on bamboo, sugarcane [3], wheat straw, barley straw, flax straw [4] and mango, poplar and ashoka leaves [5].

The current investigation focuses on the physical and chemical characterization of two different leaf litter biomasses such as *Polyalthia Longifolia* and *Terminalia Catappa* that are available in large number and evaluate the potential of these biomasses as feedstock for gasification.

Material and Methods

Collection of the biomass samples

The biomasses used in this study are the leaf litter from mature trees such as *Polyalthia Longifolia* and *Terminalia Catappa* collected from the soil surface during post monsoon (2016) from the campus of Indian Institute of Technology, Bombay. The botanical nomenclature of the two biomasses is represented in Table 1. The leaves were collected, cleaned and washed. They were first air dried and then oven dried and later crushed using grinder and sieved to obtain homogenous powder in the size range of 0.150 mm-0.106 mm (mesh no. 100 - mesh no. 150). The sieved biomass samples were stored at room temperature in air-tight bottles and were used as and when required for characterization studies.

Physical and chemical characterization

Calorific value

The calorific value of both the biomasses were determined using an oxygen bomb calorimeter, IKA 200, at IIT Bombay. The equipment is semiautomatic in operation and requires

only test sample weight. Approximately 0.5-1 g of biomass sample is taken in the crucible and a cotton thread is tied onto an ignition wire connected to the electrodes at both ends thus completing the circuit. This cotton thread is placed in contact with the sample in the crucible. The firing thread is pre-calibrated of known length. The crucible filled sample is placed in the bomb which is filled with oxygen at 30 bar and water input is 2000 cc between 18 °C - 25 °C. The calorimeter is then placed in an isothermal jacket and the output of the instrument obtained is Joule/g.

Table 1: Botanical nomenclature of biomass

Common Name	False Ashoka	Junglee Badam
Class	Magnoliopsida	Magnoliopsida
Family	Annonaceae	Combretaceae
Genus	Polyalthia	Terminalia
Scientific Name	Polyalthia Longifolia	Terminalia Catappa

Proximate analysis

Proximate analysis was done on Thermogravimetric Analyzer (TGA), Perkin Elmer, Pyris Diamond TG/DTA. The proximate analysis of the two kind of biomasses was done to know the moisture content, volatile matter, fixed carbon and ash content. A biomass sample (12-15 mg) was taken in a crucible and placed on the pan inside the TGA. The analysis was done from ambient temperature to 850 °C with a heating rate of 30 °C/min with a purge gas (nitrogen) flow rate of 80 ml/min and switching to air in the last to yield fixed carbon and ash content.

The TGA measurements yield data that are equivalent to a standardized proximate analysis. Figure 1 shows a typical thermodiagram of Polyalthia Longifolia and Terminalia Catappa biomasses subdivided into sections. The first part depicts the loss of moisture and volatiles under nitrogen atmosphere. Moisture content plays a vital role in the selection of a particular biomass for the purpose of gasification. The energy density of the biomass decreases with the absorption of moisture making it less feasible when applied to a massive scale [6]. Gasification experiments prefer feedstocks having moisture content below 15%. Moisture content determined in the first part represents only physically bound water whereas during pyrolysis, water released by chemical reaction is summarized among volatile matter [7]. The volatile matter in the lignocellulosic biomass is usually higher (>60%) and is due to the presence of cellulose and hemicellulose. Volatile matter also depends upon the pyrolysis process as well as the heating rate. The fixed carbon and the ash content are shown in the second part of the thermogram performed in air. Combustion of the fixed carbon results in the formation of ash. To check with the ash content from the TGA, 10 g of each biomass sample was taken in the crucible and placed in the muffle furnace at 575 ± 25 °C for 5 hours. The same experiment was repeated for 20 hours and the results obtained from experiments using muffle furnace

approximately matched with that obtained from the analysis using TGA.

Ultimate analysis

Ultimate analysis was done in Sophisticated Analytical Instrument Facility (SAIF), IIT Bombay. The analysis was done on CHNS(O) analyzer (Thermo Finnigan, Italy FLASH EA 1112 series). Oxygen % was calculated by subtracting C, H, N, S and ash content (obtained from TGA analysis) from 100. No Sulphur content was detected in both the biomass samples.

Thermogravimetric analysis (TGA) for devolatilization

Devolatilization characteristics of the biomass samples with temperature were analyzed using TGA, Perkin Elmer, Pyris Diamond TG/DTA. To prevent heat and mass transfer limitations 2 mg sample size was used [8] under nitrogen flow (80 ml/min). the sample were heated to 650 °C with a heating rate of 10 °C/min. The weight loss vs. temperature profile were recorded and analyzed.

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) of ash

The analysis of biomass ash (obtained from the muffle furnace) for the presence of different minerals was determined by ICP-AES (ARCOS from M/s. Spectro Germany) analyzed at SAIF,

IIT Bombay. ICP-AES is an emission spectrophotometric technique that uses the inductively coupled plasma to produce excited atoms and ions that emits electromagnetic radiations at wavelength characteristic of a particular element. The intensity of this emission indicates the concentration of the element with the ash sample. 0.1 g of powdered ash is taken in a Teflon digestion tube and then dissolved in acids, 5 ml nitric acid (about 69%), 5 ml hydrogen fluoride and 2 ml hydrogen peroxide (added dropwise). Then the mixture was digested for 2 hours and when the ash sample (excluding silicates) is completely digested, the sample is injected to ICP-AES to obtain the mineral concentration.

Determination of extractives and compositional analysis

The biomass sample (10 g) was subjected to two-stage extraction procedure using ethanol and water in Soxhlet extraction apparatus and each solvent extraction were carried out for 5-6 hours [9]. In the alcohol extraction, ethanol soluble compounds were carried out to separate polar compounds such as chlorophyll, waxes and other minor compounds. The raffinate biomass of the first step was extracted with distilled water to separate inorganic materials, non-structural carbohydrates [4] and nitrogenous material [9]. Raffinate biomass from second step was subjected to cellulose, hemicellulose and lignin estimation according to Van Soest fiber analysis [10-12].

Results and Discussion

Determination of calorific, proximate and ultimate values

The calorific values, proximate composition and ultimate composition of P. Longifolia and T. Catappa leaf litters are elicited in table 2. The calorific value of the biomass samples

was determined experimentally through oxygen bomb calorimeter as discussed above. The CV of P. Longifolia leaf litter biomass was found greater (20.576 MJ/kg) as compared

to T. Catappa leaf litter (16.089 MJ/kg). Similar results were obtained by N. Akhtar for Mango (18.37 MJ/kg), Poplar (18.50 MJ/kg) and Ashoka (19.32 MJ/kg) leaves. Calorific value of any feedstock is equivalent to its maximum value of energy produced or available and it will always be same irrespective of the conversion process used such as pyrolysis, combustion, gasification, fermentation or mechanical extraction [8]. The moisture content of P. Longifolia and T. Catappa were found to be below 15% proving it suitable for the gasification process. The weight percentage of ash of both the biomass samples were almost similar when estimated by TGA and muffle furnace and lies between 6.530% - 6.148% and 11.246% - 10.862% for P. Longifolia and T. Catappa leaf litters respectively. It was also observed that ash obtained from P. Longifolia was brownish in colour and that obtained from T. Catappa was greyish in colour when using muffle furnace. T. Catappa shows high percentage of ash compared to P. Longifolia accounting it less suitable for gasification. The weight percentage of fixed carbon of both the

* % of oxygen calculated by subtracting C, H, N, S and ash content (obtained from TGA analysis) from 100.

Longifolia and T. Catappa respectively. The volatile matter content in P. Longifolia was only 1.14 times higher than T. Catappa. High volatile matter and low ash content was observed with P. Longifolia were in good agreement with results reported by N. Akhtar et al.

The ultimate analysis reports carbon (C), hydrogen (H), nitrogen (N), Sulphur (S) composition and oxygen (O) composition is calculated very often by the difference in the solid fuel. The values determined from ultimate analysis were reported in table 2. CHNS(O) analyses are always reported on moisture free basis to avoid confusion otherwise indicated by moisture as additional hydrogen and oxygen. The analyses revealed that oxygen content of T. Catappa leaf litter is slightly higher than P. Longifolia leaf litter. Soumya et al reported that higher amounts of oxygen (51.61 wt %) is responsible for increase in volatile matter (82.4 wt %) in areca nut husks but it reduces the calorific value (17.83 wt %). Lower or no sulphur content in the biomass applies less SO_x emission which paves the use of these biomass as a potential feedstock for gasification process [3]. The maximum and minimum carbon percentage was observed in biomass P. Longifolia and T. Catappa respectively.

Biomass	Proximate Analysis (wt%)				Ash (muffle furnace)	Ultimate Analysis (wt%)					Calorific value (MJ/kg)
	Moisture	Volatiles	Fixed Carbon	Ash		C	H	N	S	O*	
P. Longifolia	8.274	68.742	16.451	6.530	6.148	49.815	5.778	1.577	-	36.3	20.576
T. Catappa	12.855	60.266	15.627	11.246	10.862	43.219	5.575	0.648	-	39.312	16.089

biomass were almost similar and lies between 16.451 % - 15.627 % for P.

Table 2: Proximate, ultimate and calorific value of biomass

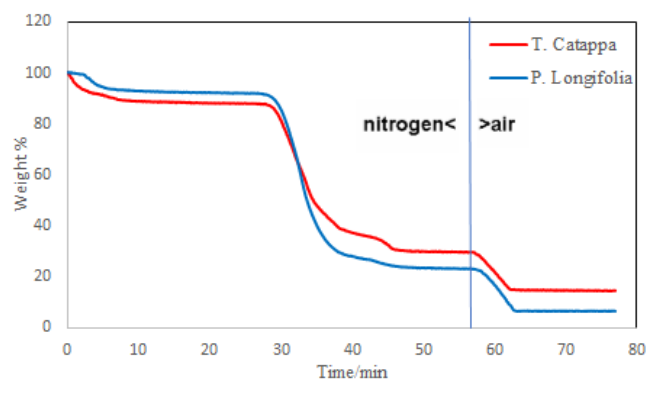


Figure 1: Thermodiagram of P. Longifolia and T. Catappa (proximate analysis)

Thermogravimetric analysis (TGA) for devolatilization

Thermogravimetry is a method used to determine temperature assisted decomposition profile of a material and kinetics of its thermal decomposition. Thermogravimetric analysis for devolatilization (figure 2) of both the biomass samples was evaluated at a constant heating rate of 10 °C/min. It was observed that the onset temperature of devolatilization was in the range of 190 °C-250 °C and is regarded as the former step due to primary devolatilization. Loss of major weight loss ends at 320 °C-360 °C and is regarded as the later step due to degradation of fibrous material from cellulosic and hemicellulosic contents. S. Naik et al reported that, quantitatively, the release of volatile matter in primary

devolatilization was more important than release volatile matter in secondary devolatilization, thus taking into account for more than 50% of the final volatile matter released at 500 °C. The weight loss profiles as depicted in figure 2 thus can be elaborated as: loss of water between 100 °C-130 °C and loss of volatiles between 130 °C-250 °C. 250 °C-380 °C depicted loss of hemicellulose followed by loss of cellulose between 380 °C-520 °C and beyond 520 °C depicts loss of lignin.

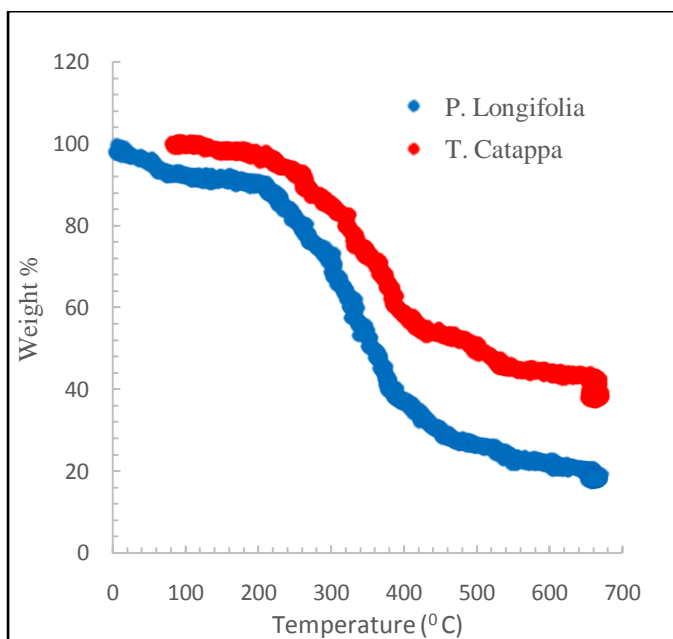


Figure 2: Thermogravimetric analysis of leaf litter biomass samples (for devolatilization)

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) of ash

Table 3 gives the elemental composition of biomass ash samples (in ppm). High K content was observed in both ash samples. R. Stahl reported that high K content lowers the ash sintering temperature at times below 700 °C and at the gasification temperature required for the conversion of the fuel, the ash becomes sticky thus raising the bar of risk associated with reactor slagging. Significant amounts of Ca, K and Na were detected in both biomass ash samples. The level of heavy metals like Al, Fe, Mg, Mn, Ni, Pb, Sr, and Zn was high in case of ash sample from P. Longifolia compared to T. Catappa. Biomass ash, a solid combustion residue is a complex inorganic-organic mixture with polycomponent, heterogenous and variable composition and contains intimately associated solid, liquid and gaseous phases [13].

Table 3: Elemental composition of biomass ash samples (in ppm)

Elements	Polyalthia Longifolia biomass	Terminalia Catappa biomass
Al	3865	250
B	1140	288.5
Ba	50	26.5
Ca	7305	9817

Co	10	11
Cr	95	49
Cu	305	197.5
Fe	14900	3281.5
K	64795	46008.5
Li	2.5	-
Mg	2805	1361.5
Mn	1205.5	874.75
Na	3782	18432.5
Ni	3035	32
Pb	26.5	13
Sr	379	228.5
Zn	340	277

Biomass extractives

The yield of biomass extractives viz; alcohol and water extracts for two different samples are listed in table 4. Leaf litter biomass of Terminalia Catappa shows minimum total extracts (26.8%) whereas Polyalthia Longifolia shows maximum total extracts (29.86%). T. Catappa shows least amount of alcohol extract (14.68%) may be due to least amount of waxy material present whereas P. Longifolia shows (18.09%). Cellulose and hemicellulose percentage of both the leaf litter biomass are almost same. More lignin content was observed for T. Catappa (20.04%) compared to P. Longifolia (14.89%). Comparable range of cellulose (44.46%-53.46%) and lignin (11.03%-22.97%) was reported by S. Sasmal et al in Areca nut husk, Bonbogori and Moj with slight varying percentage of hemicellulose (28.08%-6.37%). High lignin and/or high ash content in a biomass is ominous for gasification. In overall comparison, the hemicellulose and lignin percentage was much lower to that of the cellulose percentage and is because the plant biomasses are composed of 30-50% cellulose, 20-40% hemicellulose and 15-25% lignin [11].

Table 4: Determination of extractives (wt%)

Biomass	P. Longifolia	T. Catappa
Alcohol Extract	18.09	14.68
Water Extract	11.77	12.12
Cellulose	42.98	41.01
Hemicellulose	12.28	13.64
Lignin	14.89	20.04

Conclusion

Greater utilization of natural and renewable resources is very important for economically viable and environmentally sound society. Lignocellulosic biomasses are inexpensive and are readily available in abundance as a widely available feedstock for gasification. The present study confirms from the physico-chemical characterization the usage of leaf litter from the biomasses of Polyalthia Longifolia and Terminalia Catappa as a feedstock for gasification and can be used for cooking purpose in the community kitchens. For bio-energy production, an ideal biomass should have calorific value along with high cellulose and hemicellulose concentrations. On the

other hand, the biomass should possess low concentrations of lignin and ash. These lignocellulosic biomasses can compete favorably with the present day conventional substrates. The study of the above discussed biomass samples in the light for gasification ensures that these biomasses can be utilized for bio-fuel production and may meet the demand of the second-generation biofuel.

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