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Physico-chemical characteristics of leaf litter biomass to delineate the chemistries involved in biofuel production

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ABSTRACT

Increase in energy demand across the world has put immense pressure on utilization of widely available lignocellulosic agricultural waste biomass and forest residues. Physico-chemical characteristics of leaf litter from largely grown tree species such as *Mangifera indica*, *Populus deltoides* and *Polyalthia longifolia* were evaluated for possible use in biorefinery. Physical and chemical properties of these leaf litter biomasses were examined using bomb calorimetry, SEM, XRD, TGA, CHNSO analysis, FTIR and solid state ^{13}C CP/MAS NMR spectroscopy. Low ash content (3.70 wt%), high volatile matter (76.05 wt%) and cellulose (37.75 wt%) was observed from leaf litter biomass of *P. deltoides*. SEM of leaf litter biomass revealed compacted surface morphology of *M. indica*, however a fibrillar structure was observed in *P. deltoides* and *P. longifolia*. Maximum crystallinity index (*CrI*) was observed in leaf litter biomass of *M. indica* (23.13%) followed by *P. longifolia* (20.94%) and *P. deltoides* (20.93%). The calorific values of all biomasses were in the range of 18.37 to 19.32 MJ/kg. Delineation of these physico-chemical characteristics together *per se* shows that leaf litter biomass can also act as a potential feedstock for biofuel production.

1. Introduction

Considering world energy demand and its security, attention is being focused on inexpensive renewable lignocellulosic substrates for biofuel production. These energy resources are an alternatives to fossils fuel and their derivatives, and have become a high priority for chemical industries [1]. To solve the global warming problem and ensure sustainable development of the economy, it is necessary to increase the use of renewable biomass resources [2], as they lack the environmental risk and capital investment associated with fossil fuels. The available biomass of the world is 220 billion oven dry tones (ODT) per year or 4500 EJ (10^{18} J) [3]. India meets 70% of its energy requirement using fuel woods and in the process about 50 million tones of wood are removed from forests every year [4]. Substantial portion of cellulosic and hemicellulosic component of leafy biomass can be readily hydrolyzed into fermentable sugars by action of different hydrolytic enzymes, which is further biotransformed into ethanol [5]. Therefore, leaf litter biomass from tree plantation sites can be collected and used as a promising feedstock for biofuel production to mitigate energy crisis.

Lignocellulosic biomass refers to plant derived organic matter, composed of cellulose, hemicellulose, lignin, pectins, extractives, glycosylated proteins and several other inorganic materials. Cellulose is a linear condensation polymer consisting of D-anhydroglucopyranose joined by β-1, 4-glycosidic bonds with a degree of polymerization from 100 to 20,000 [6]. Hemicellulose, a complex carbohydrate, is comprised of pentoses (*e.g.* xylose and arabinose), hexoses (*e.g.* mannose, glucose and galactose) and sugar acids. The most abundant polymer after cellulose and hemicellulose is lignin, which consists of three different phenylpropane units (p-coumaryl, coniferyl and sinapyl alcohol) [7]. The cellulose, hemicellulose and lignin content of such biomasses fall in the range of 30–50%, 15–35% and 10–20%, respectively [8,9]. The accessibility of cellulose which is embedded in hemicelluloses-lignin matrix and highly crystalline nature of the cellulose are two main factors responsible for increasing the cost associated with processing of lignocellulosic biomass [10]. Determining relative quantities of cellulose, hemicellulose and lignin in lignocellulosic feedstock is often required in studies involving fractionation [11], fermentation [12], or other modification [13]. Besides biofuel, lignocellulosic biomass can be a source of other bio-based products such as levulinic acid, furfural and hydroxy methyl furfural [14].

Chemical and molecular characteristics of lignocellulosic feedstock vary with geo-climatic conditions and taxonomic rank too.

Abbreviations: CrI, crystallinity index; CP/MAS NMR, cross polarizing magic angle spinning nuclear magnetic resonance; FTIR, fourier transform infrared; SEM, scanning electron microscopy; TGA, thermal gravimetric analysis; XRD, X-ray diffraction.

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Table 1
Botanical nomenclature of biomass samples source.

Common name	Family	Genus	Scientific name
Mango	Anacardiaceae	*Mangifera*	*Mangifera indica*
Poplar	Salicaceae	*Populus*	*Populus deltoides*
Ashoka	Annonaceae	*Polyalthia*	*Polyalthia longifolia*

The primary obstacle impeding the widespread production of bioenergy from biomass lies in the availability of low-cost technology to overcome recalcitrant nature of lignin. To make cellulose more accessible for hydrolytic enzymes, lignin component must be separated [15], which primarily depends upon the degree of polymerization, crystallinity, structural composition and surface area [16]. Knowing accurately the physico-chemical composition of lignocellulosic biomass is gaining importance in assessing its potential for biomass to biofuel conversion [1,11,17].

The current investigation is based on evaluation of physico-chemical characteristics of different leaf litter biomasses from largely grown tree species such as *Mangifera indica*, *Populus deltoides* and *Polyalthia longifolia* to evaluate their potential as feedstock for bio-energy production.

2. Material and methods

2.1. Collection of biomass samples

Leaf litter biomass samples from largely grown trees such as *M. indica*, *P. deltoides* and *P. longifolia* were collected from soil surface in early spring (March 2014) from Thapar University campus, Patiala, Punjab (India), located at 30°19′48"N, 76°24′0"E and 310 m above the sea level. The detailed nomenclature of the source of biomasses is represented in Table 1. The air dried biomass samples were ground using mechanical blender and sieved to get homogeneous powder (diameter of particle < 0.5 mm) (Supplementary material, Plate 1). Sieved biomass samples were stored in air tight containers at room temperature for characterization studies. The general outline of the biomass characterization is presented in Fig. 1.

2.2. Physical characterization

2.2.1. Moisture content

Moisture content plays a key role in the selection of a suitable substrate for bioenergy application due to hydrophilic properties. Adsorption of moisture may lead to a decrease in the energy density of the biomass [18]. Comparative low moisture content feedstock (<15%) is preferred when using a thermal conversion process, while bio-conversion can utilize biomass with a high moisture content [19]. The moisture content of the biomass was determined using the procedure given in ASTM 3173-87 [20].

2.2.2. Ash content

Ash, the incombustible solid mineral matter present in the biomass, mainly contains oxides of silica (SiO), Aluminium (AlO), Iron (FeO), calcium (CaO) and Magnesium (MgO). The cations present in ash retards the enzymatic saccharification of biomass samples to glucose and other fermentable sugars [21]. Therefore it is prerequisite to analyze the biomass for ash content before using it as a feedstock for biofuel production. Determination of ash content in biomass samples were adopted as per the protocol described in ASTM D 3174-04 [22]. Oven dried biomass sample (1.0 g) was taken in oven dried moisture free crucibles and placed in muffle furnace maintained at 575 ± 10 °C for 4 h. Crucibles were removed from the furnace and placed in a dessicator and the process of heating and cooling was repeated until constant weight was obtained.

2.2.3. Volatile matter and fixed carbon

The volatile matter in the leaf litter biomass was determined by the procedure given in ASTM D 3175-07 [23]. A biomass sample (1.0 g) was taken in a covered crucible and placed in a muffle furnace regulated at 950 ± 10 °C for 7 min to obtain rapid heating. Then the crucible was removed from the furnace and placed in a desiccator. The loss of weight was interpreted as the volatile matter in the biomass. Fixed carbon was the resultant of the summation of percentage moisture, ash, and volatile matter subtracted from 100.

2.2.4. Calorific value

The calorific value of all biomass samples was determined in a static bomb calorimeter; BCM 211059, using the procedure described in NREL protocol [24]. Each biomass sample was mixed thoroughly in the sample bottle and was made into a pellet, taking care that the heavies and lights (fluff) were distributed well in the sample. Samples (1.0 g) in the form of pellet was measured out and put into pre-weighed crucibles. A cotton thread was attached to a platinum ignition wire and placed in contact with the pellet. Distilled water (1 ml) was poured into the bomb and then filled with oxygen to a consistent pressure between 20 and 30 atm (2.03 and 3.04 MPa). The calorimeter was placed in an isothermal jacket with an air gap separation of 10 mm between all surfaces. The electrical energy for ignition, discharged through a platinum wire of ~40 V, was calculated using the change in potential across a 1256 or 2900 mF capacitor. The bomb calorimeter was submerged in a calorimeter cane filled with distilled water. The jacket of the calorimeter was maintained at constant temperature by circulating water at 25° C.

2.2.5. Scanning electron microscopy (SEM)

The physical appearance of biomass samples were observed by SEM. The samples were coated to provide conductivity with gold using gold sputter at a voltage of 10–15 kV. Images were taken using SEM (Model: JEOL JSM-6510 LV, USA) at different magnifications.

2.2.6. X-ray diffraction (XRD) analysis

Crystallinity of the powdered biomass samples was analyzed at room temperature in the scanning angle of 5–50° at the scan speed of 5°/min using a PANalytical X'Pert PRO diffractometer (Netherlands) with Ni-filter, operated at 45 kV and 40 mA with λ (Cu Kα) = 1.5406 Å. The crystallinity index (*CrI*) of the biomass samples were determined as described by Segal et al. [25] as follows:

$$CrI = [(I_{002} - I_{am})/I_{002}] \times 100$$

Where I_{002} is the intensity for the crystalline portion of biomass (*i.e.* cellulose) at about 2θ of 21–23°, and I_{am} is the peak for the amorphous portion (*i.e.* cellulose, hemicellulose, and lignin) at about 2θ of 16–18° in most literatures [1,2,17,26].

2.2.7. Thermal gravimetric analysis (TGA)

To understand the devolatilization characteristics, TGA of biomass samples were performed using a Mettler Toledo instrument (Model: TGA/SDTA 851e). The devolatilizations of biomasses were studied from 20 to 700 °C with a heating rate of 10 °C/min with a purge gas (nitrogen) flow rate of 60 ml/min.

2.3. Chemical characterization of biomasses

2.3.1. CHNSO analysis

The basic elements of any biomass such as carbon (C), hydrogen (H), nitrogen (N), sulphur (S) and oxygen (O), were analyzed