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Physico-chemical characterization and thermal behaviour study of Lignocellulosic biomass obtained from a few wild grasses of Kamrup (Assam) and Thoubal (Manipur) for biofuel production

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Abstract-*We report here the physico-chemical characterization and thermal behaviour investigation of six species of wild grasses (Phragmites karka (Retz.), Thysanolaena agrostis Nees, Neyraudia reynaudiana, Coelorachis striata, Erianthus fultus and Sclerostachya fusca) collected from Assam and Manipur for their biomass content towards the alternative renewable biofuel production. This study investigates the physical analysis (proximate analysis, Thermogravimetric analysis (TGA), X-Ray diffraction (XRD) and Calorific value), chemical analysis (ultimate analysis and Fourier Transform Infra-Red (FTIR) and fibre analysis (cellulose, hemicellulose, lignin etc). The results confirmed that combustion conditions define the characteristics of each biomass sample having a different zone of degradation profile. Thermal degradation profile was seen at temperatures such as hemicellulose at 250-300 ^{0} C followed by cellulose at 300-350 ^{0} C and finally lignin at 350-500 ^{0} C. The crystallinity index was found maximum in Phragmites karka (33.82) and minimum in Coelorachis striata (13.54). The calorific value of the biomasses was calculated and the maximum was found in Erianthus fultus (16.20 MJ/Kg). FTIR analysis of these lignocellulosic grass biomass revealed that functional groups were present with a vast spectrum of wave number starting from 3400 to 873 cm^{-1}. The cellulose content derived from fibre analysis was found to be maximum in Erianthus fultus (39.2%). All these properties combined together shows that these lignocellulosic biomass can act as the potential candidate for bio-energy production.*

Keywords: *Lignocellulosic biomass. Crystalline index. Volatile matter. Thermogravimetric analysis. Cellulose. Biofuel.*

1. Introduction

The environment we live in has a pool of numerous energy resources. Since the last few decades, fossil fuels are rapidly depleting and there is a logical apprehension that at the current rate of utilisation, they will not last longer. That is why it is essential to look for alternative and sustainable energy resources. The alternative energy sources include biofuels, bioethanol, biodiesel, bio-oil, bio-butanol [1] etc. and their use will mitigate environmental risk as well.

Lignocellulosic biomass (LCB) are one of the most important renewable energy sources. From this biomass, energy such as liquid biofuel can be obtained through pretreatment and fermentation process. It is suggested that renewable biomass energy could be a great substitute for fossil fuels in near future.

It is essential to characterize a biomass before proceeding to any further processes. Biomass should fulfil certain characteristics to be used as feedstock for sustainable biofuel production. It should also satisfy all the criteria prevailing for fuel before being used as a source of bio-fuel. The major attributes of biomass include its composition such as hemicellulose, celluloses, lignin, volatile matters, ash content, fixed carbon, total solid, oxygen content, hydrogen content, nitrogen content, and sulphur content etc. These features act as the key factor for the production of biofuel from biomass.

When compared to traditional fossil fuels, LCB showed more reactivity and higher volatility than coal [2]. This could be achieved only when a biomass is well characterized. For example, the volatile content of same biomass may differ according to its climatic condition and nature of the soil in which it grows. Characterization of biomass based on chemical composition gives a better idea of determining the theoretical yield of biofuel. For example, the presence of high nitrogen and ash content in biomass reduces hydrocarbon yield during thermo-chemical conversion [3]. In addition to this, mathematical models can be created to further analyse the products more effectively and efficiently, hence, it is very important to characterize a biomass sample before biofuel production.

The current production of bioethanol mainly depends on the first generation of biomass fuels such as starch and sugars derived from food crops. Rising concerns of conflict between food versus fuels, which can lead to complications like famine and social unrest, the second generation of biofuel such as bioethanol from LCB is considered as an alternative to

the first generation as there is no competition with food crops. Moreover, LCB is easily available and less expensive than conventional agricultural feedstock.

It is worth mentioning here that biomass is a promising renewable energy resource with 220 billion oven-dry ton (odt) per year or 4500EJ (1018J) [4] and it is the world's largest and most sustainable energy resource. LCB is composed of organic and inorganic matter. It includes agricultural crop waste, forest residues, aquatic plants, energy crops, and grasses, etc. It mainly consists of cellulose, hemicelluloses and lignin. Structurally, cellulose is constituted by monomers of glucose link by (1-4) glycoside bonds. Hemicellulose is a branched carbohydrate composed of hexose and pentose sugar; whereas lignin is a complex polymer of aromatic alcohols.

The ethanol derived from LCB has great potential to replace the petrol fuel for transportation. The cellulose or hemicellulose component of biomass could be converted to respective sugars through the available technology. These sugars can be utilised further to produce ethanol by microbial fermentation. But, the main hurdle in the entire process is lignin contamination. It inhibits the enzymatic saccharification and reduced accessibility of cellulose fibre. Therefore, the characterization of LCB is important to determine the feasibility of biofuel production.

The North-Eastern region of India is an ecological hotspot having innumerable unexplored plant species. Among the 34 recognised global biodiversity hotspots, this region also represents an important part of the Indo-Burma (Myanmar) global biodiversity along with Himalayan Biodiversity Hotspot. Assam and Manipur are two distinct states belong to this region. Both the states provide parts and partial home ground of various native species of plants and animals.

In the present study, six grass species were characterized based on different physico-chemical parameters. The structural carbohydrate content was determined according to fibre plus analysis, which give neutral detergent fibre (NDF), Acid detergent fibre (ADF) and acid detergent lignin (ADL) [5]. The thermal degradation profile of biomass was obtained by Thermogravimetric analysis (TGA) study. The crystallinity index of raw material was described by X-Ray diffraction (XRD) analysis. The presence of different functional groups in the biomass sample was analysed by Fourier Transform Infra-Red (FTIR). The properties like proximate and ultimate analysis were also analysed.

2. Materials and methods

2.1. Sample collection and processing

LCB were collected from Kamrup (26.1814086 N and 91.7564929 E) district of Assam and Thoubal (24.6500° N and 93.9833° E) district of Manipur in North-East India. Six species of biomass belonging to Poaceae family were selected for the field study. The selected biomass are *Phragmitis karka (Retz.), Thysanolaena agrostis* Nees, *Erianthus fultus, Sclerostachya fusca* (Roxb.) A. Camus, *Neyraudia reynaudiana* (Kunth) Keng ex A.S.Hitchc. and *Coelorachis striata* A camus. Two species namely *Neyraudia reynaudiana* (Kunth) Keng ex A.S.Hitchc. and *Coelorachis striata* A camus were collected from Thoubal district of Manipur. Four species namely *Phragmitis karka (Retz.), Thysanolaena agrostis* Nees, *Erianthus fultus,* and *Sclerostachya fusca* (Roxb.) A. Camus were collected from Kamrup district of Assam. All the species were collected in full inflorescence stage. It was sun dried for 10-12h and powdered in a mixer grinder to achieve its size up to 1mm. The ground biomass powder was stored in plastic container. The plastic container was made air tight to protect from contamination and further degradation. The experimental data presented are the average of the three such readings. The general outline of the experimental procedure is presented in Fig.1.

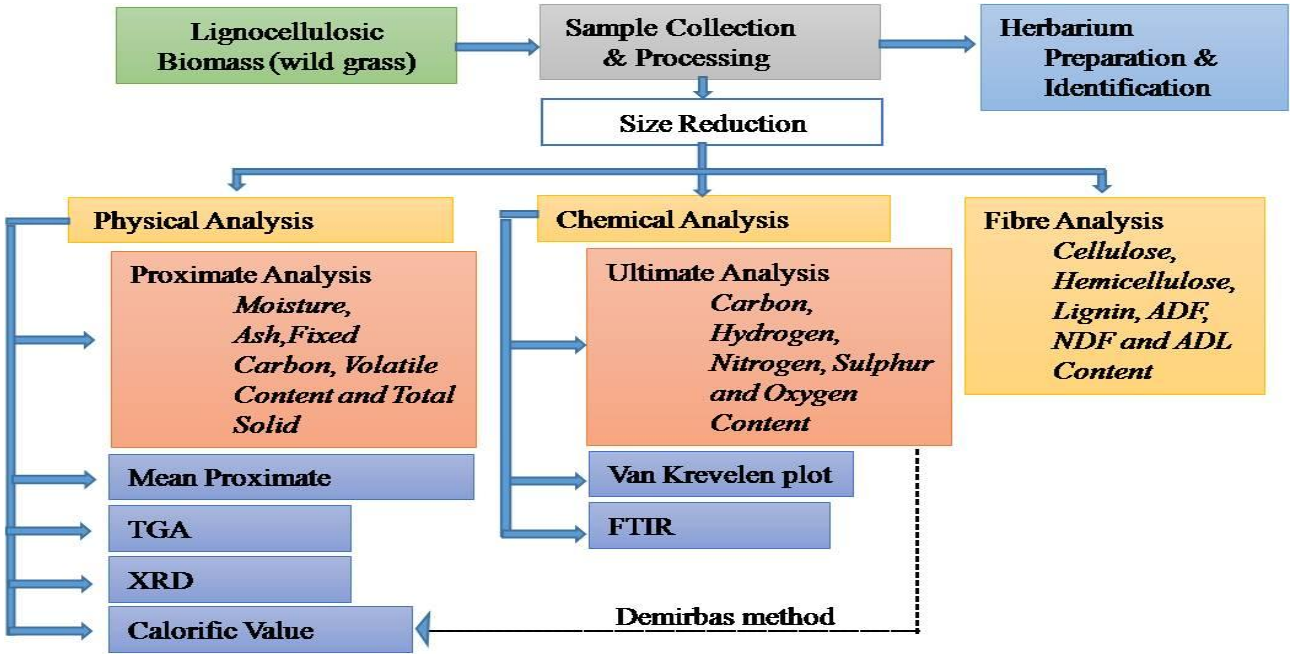

Fig.1. Scheme for characterization of lignocellulosic biomass.

2.2. Herbarium preparation and identification

For the herbarium specimen preparation, simple tools like scissor, knife, polythene, rubber, field data notebook, glue, mercury chloride, ethanol, sprayer and herbarium sheets were used. The collection of the sample was carried out in two different seasons, i.e. summer and winter. Collected plant biomass was washed under running tap water and pressed. It was treated with 0.03% mercury chloride and washed with 70 % ethanol. Two herbarium sheets for each sample were prepared by pasting the specimen with glue. The herbarium specimen was submitted to Post graduate department of Botany, Gauwahati University, Assam, India.

2.3. Physical properties of biomasses

The dried grinded biomass samples were subjected to physical characterization such as proximate analysis, moisture content, ash content, fix carbon content, volatile content, total solid, Thermogravimetric analysis (TGA), X-Ray diffraction (XRD) and calorific value.

2.3.1. Proximate analysis

The moisture content of the biomass was determined by convection oven dry procedure. 1g of biomass sample was taken into the tared weighing crucible and placed in an oven at 105 □ □ 2^0 C for 1h till dry to constant weight (□ 0.1% change in the amount of moisture present upon one hour of reheating) was achieved. The weight loss of the sample provides the percentage of moisture content [6].

The moisture content was calculated as follows:

$$\% \text{ Moisture} = \left[1 - \frac{(\text{weight dried sample plus dish} - \text{weight dish})}{(\text{weight sample as received})}\right] \times 100$$

Ash content was determined by using muffle furnace. 1g of oven-dried sample was heated at 575±10 ^{0} C for minimum 3hr and ash to constant weight. The remaining weight gives ash percentage [7]. The volatile matter in the biomass was determined by taking 1g of oven dried sample and placed in the muffle furnace at temperature 925±10 ^{0} C for 7 minutes. The difference in weight loss gives volatile content [8]. The fixed carbon content was calculated by using empirical formula as far reference [9]:

$$FC = 100 - (\% \text{ of moisture} + \% \text{ of volatiles} + \% \text{ of ash})$$

For the total solid, moisture percentage was subtracted from 100.

2.3.2. Mean proximate composition

The mean proximate composition of the selected LCB was derived on the basis of the proximate composition of the biomass by considering three factors such as ash, volatile matter and fixed carbon content [10]. The mean of volatile matter, fixed carbon content and ash content was taken and plotted the graph accordingly.

2.3.3. TGA analysis

The thermal degradation profile of the biomass samples was performed using STA7200, Thermal analysis system, Hitachi. A small dried powdered biomass sample of 5-10 mg was taken and the devolatilisation characteristics were studied from 40-900 ^{0} C at a heating rate of 10 ^{0} C/min with a flow rate of 40 ml/min of nitrogen gas.

2.3.4. XRD analysis

The XRD analysis was performed using Rigaku TT Rax diffractometer in conjunction with Cu-Ka radiation source and X-Ray generated at 18kW and 250 mA, scanning angle 2Ɵ range from 10 ^{0}- 40 ^{0} at a speed of 1^0 min^{-1}. The crystalline index (CrI) of the biomass was determined by the available methods [11].

$$CrI = 100\ X\ [(\ I_{002} - I_{amorphous}) / I_{002}]$$

Where I_{002} is the intensity of at 2Ɵ=20 for crystalline portion (cellulose) and $I_{amorphous}$ is the peak at 2Ɵ= 16.6 for amorphous portion (cellulose, hemicellulose and lignin).

2.3.5. Calorific value

The calorific values were determined using the derivative method given by [12].

$$HHV = \{ 33.5\ X\ \%\ C + 142.3\ X\ \%\ H - 15.4\ X\ \%\ O - 14.5\ X\ \%\ N \}\ X\ 10^{-2}$$

Where HHV represents the higher heating value, C,H,O,N represent the carbon, hydrogen, oxygen and nitrogen in percentage basis.

2.3.6. Van Krevelen Plot

The Van Krevelen Plot was drawn against the basis of the atomic ratio of Hydrogen (H)/ Carbon(C) to Oxygen (O)/ Carbon (C).

2.4. Chemical analysis of biomasses

2.4.1. Ultimate analysis

The ultimate analysis of the biomass samples was performed using CHNSO elemental analyser, FT-IR.

2.4.1.1. CHNSO

The common organic elements such as C,H,N,S and O were analysed using dry biomass sample with a CHNSO elemental analyser (Eurovector EA3000). The samples were calibrated using the 5 tin capsule packed with 5L- cystine test. The sample (0.1mg) was placed in the tin capsule, weigh and packed carefully. The prepared calibration and analysis samples were placed in the auto-sampler heated at 980 ^{0} C with a constant flow of helium stream enriched with high purity oxygen gas. The resulting signals proportional to the amount of eluted gasses are analysed by Callidus® software which automatically provides the sample elemental composition.

2.4.1.2. FTIR analysis

The functional groups analysis of the LCB were determined using Fourier Transform Infra-Red (FTIR) spectroscopy (Model FTS 3500 GX) attached with DRS. Dry biomass sample of 10 mg was mixed well with 200 mg of KBr and was compressed to form pellets. The spectra were collected at a scan rate of 40 with a step size of 4cm^{-1} within the range of 400 to 4000 cm^{-1} wave numbers.

2.5. Fibre analysis

Fibre analysis was done using fibra plus Automatic Fibre Estimation System, pelican. The biomass sample (0.5-1gm) of dried and powdered was subjected to fibra plus at 400 ^{0} C for 60 min. Neutral detergent fibre (NDF) was determined by dissolving 0.5-1gm of powdered biomass sample in neutral detergent solution of 6.9-7.1 pH value in a crucible. The mixer solution was heat to boil and reflux at 400 ^{0} C for 60 min. The crucible was washed with acetone and kept in an oven at 100 ^{0} C for 8h. The NDF percentage was calculated as follows [13]:

$$NDF\ \% = \frac{(Wt\ of\ crucible + NDF) - Wt\ of\ crucible}{Wt\ of\ sample} \quad x\ 100$$

Similarly, acid detergent fibre (ADF) was performed in acid detergent solution and weight loss was calculated as follows:

$$ADF\ \% = \frac{(Wt\ of\ crucible + ADF) - Wt\ of\ crucible}{Wt\ of\ sample} \quad x\ 100$$

For the acid detergent lignin (ADL) determination, ADF was prepared in a crucible and 72 % of H_2SO_4 was added. The mixture was filtered after 3h and washed with water twice. The crucible was kept in hot air oven at 100 ^{0} C for 8h. The weight loss was recorded and again this crucible was kept in the muffle furnace at 500 ^{0} C for 7 min. This weight was recorded. The percentage of cellulose, hemicellulose and lignin were calculated as follows:

$$Hemicellulose\ \% = NDF\ \% - ADF\ \%$$
$$Cellulose\ \% = (Y\text{-}L/W)\ X\ 100$$
$$Lignin\ \% = (L\text{-}A/W)\ X\ 100$$

Where, Y= weight of ADF+crucible, L= weight of crucible + lignin, A = weight of crucible + ash, W= weight of sample.

3. Results

3.1. Sample collection and processing

The six species of (two from Manipur and four from Assam) biomass sample were collected and presented in the form of herbarium specimen. The herbarium specimen was identified by the curator and it was well categorised according to the morphological characters. A systematic classification of collected grass biomass is given in table 1.

Table 1. Systematic classification of few Lignocellulosic biomass collected from North-East India.

Kingdom	Class	Order	Family	Genus	Species
Plantae	Liliopsida	Cyperales	Poaceae	Phragmites	P.karka
Plantae	Lilopsida	Poales	Poaceae	Thysanolaena	T.agrostis
Plantae	Lilopsida	Poales	Poaceae	Erianthus	E.fultus
Plantae	Liliopsida	Poales	Poaceae	Sclerostachya	S.fusca
Plantae	Liliopsida	Cyperales	Poaceae	Neyraudia	N.reynaudiana
Plantae	Liliopsida	Poales	Poaceae	Coelorachis	C.striata

3.2. Herbarium analysis

The herbarium sample was deposited to the Postgraduate Department of Botany, Gauwahati University, Assam and well maintained and one copy each of the specimen was retained at Indian Institute of Technology Guwahati for further documentation and references. The binomial nomenclature was given to each species and related kingdom; class, order, family, genus and species are presented in table 1.

3.3. Physical analysis

3.3.1. Proximate analysis

The data obtained from the proximate analysis (moisture content, ash content, volatile content, fix carbon content and total solid) in percentage basis is presented in table 2.

Table 2. Proximate analysis of LCB.

Analysis	Moisture (%)	Total solid (%)	Volatile matter (%)	Fix carbon[a] (%)	Ash (%)
Phragmites karka	8.8429	91.1571	84.3795	2.2611	4.5165
Thysanolaena agrostis	6.9665	93.0335	83.9020	0.8700	8.2611
Erianthus fultus	8.7387	91.2613	80.7212	2.9846	7.5555
Sclerostachya fusca	8.7295	91.2704	86.0826	0.6935	4.4944
Neyraudia reynaudiana	8.3832	91.6168	77.1168	11.7722	2.7278
Coelorachis striata	8.1351	91.8649	84.2356	1.5842	6.0451

[a] Fixed carbon content was calculated on the basis of *FC = 100 - (% of moisture + % of volatiles + % of ash)*

3.3.2. Mean proximate analysis

The plotted mean proximate composition (db) of lignocellulosic biomass is illustrated in Fig.2. It can be seen that the selected biomass have a relatively closer position of peat. As the biomass taken were grasses, the mean position was almost similar to one another.

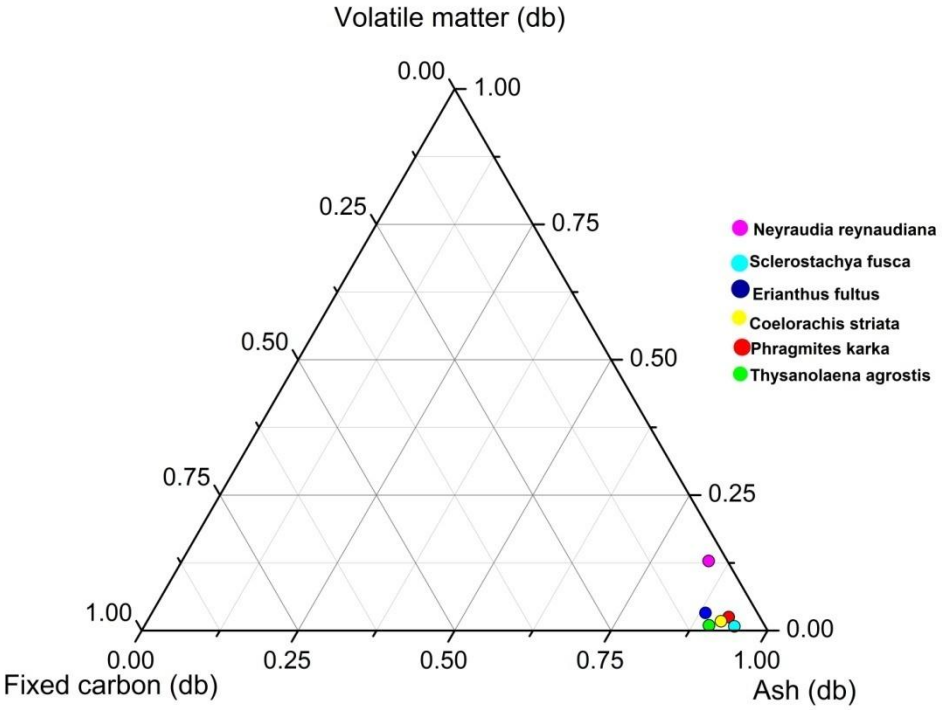

Fig.2. Mean proximate composition of lignocellulosic biomass

3.3.3. TGA analysis

The thermal degradation profile of the biomass is shown in Fig. 3. The weight losses in biomass sample due to rising in temperature was observed and found to be relevant to the composition of cellulose, hemicellulose and lignin [14]. From the TGA graph fig.3 (a), the degradation of biomasses took place in a different range of temperature. The degradation profile starts at 30-130 ^{0} C. Clear peak were also obtained in between 130-250 ^{0} C. The Derivative Thermogravimetric (DTG) of the biomass samples are shown in fig.3 (b).

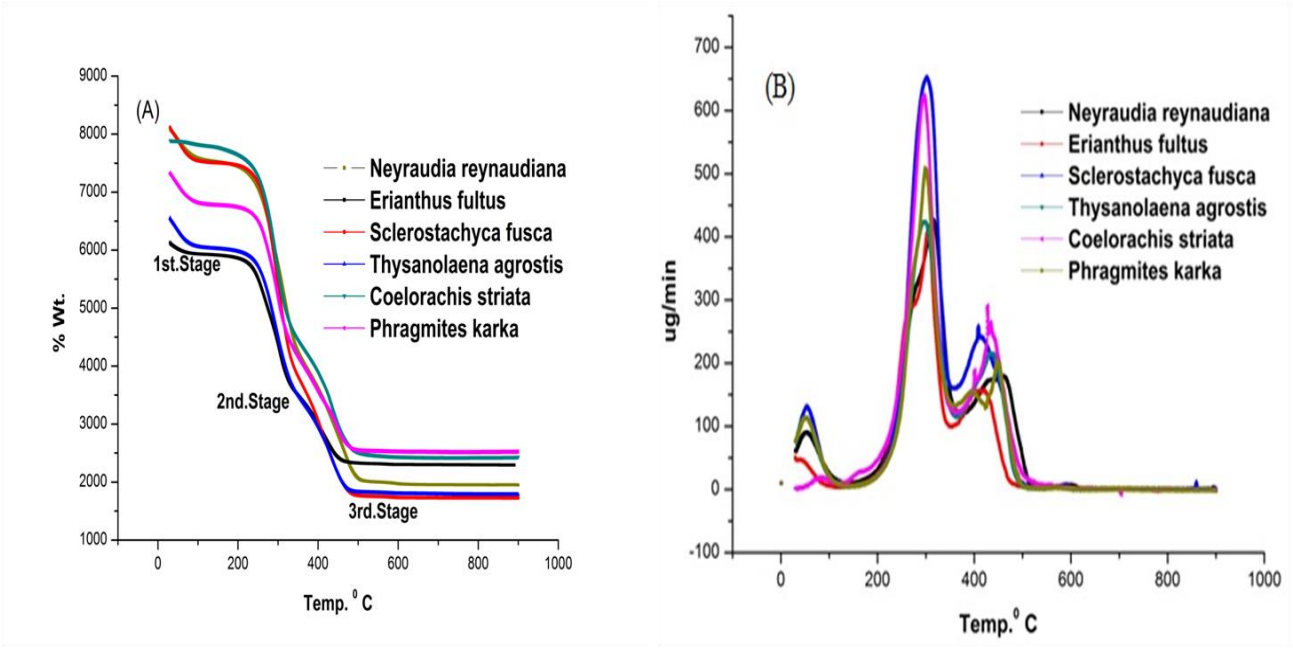

Fig.3 (a) TGA and (b) DTG thermograph of LCB

3.3.4. XRD analysis

The XRD analysis of biomass samples was presented in Fig.4. It was observed that certain peak at 0 0 2 plane at 2Θ = 22.1◦, 22.0◦, 22.1◦ and 21.9◦ are predominant. The $I_{amorphous}$ peak is seen in near 2Θ= 16.6. The crystalline index of the biomass sample is discussed in discussion section later.

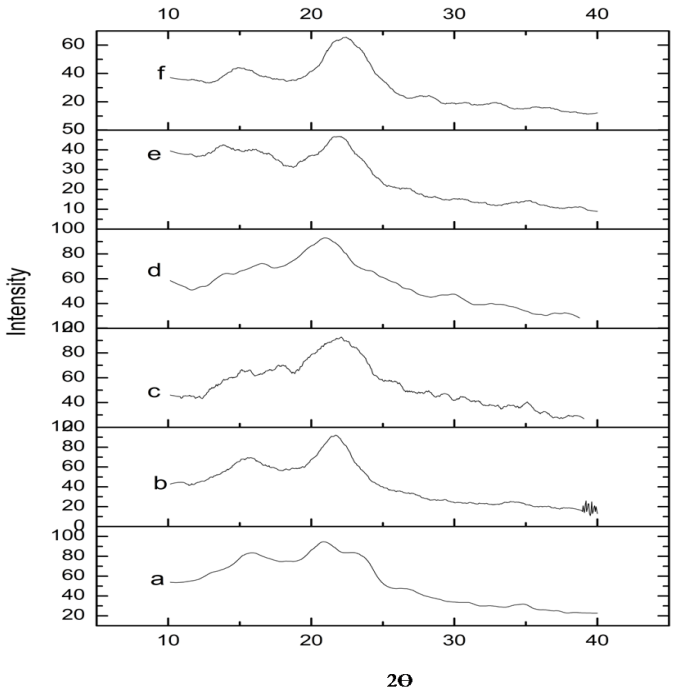

Fig.4. XRD spectra of LCB sample: a- *Coelorachis striata*, b- *Sclerostachyca fusca*, c- *Neyraudia reynaudiana*, d- *Erianthus fultus*, e- *Thysanolaena agrostis*, f- *Phragmites karka*.

3.3.5. Calorific value

The calorific value of the biomass samples was calculated as HHV. The data generated is given in fig. 5. It was observed that the calorific value (MJ/kg) range from 14.25 to 16.20.

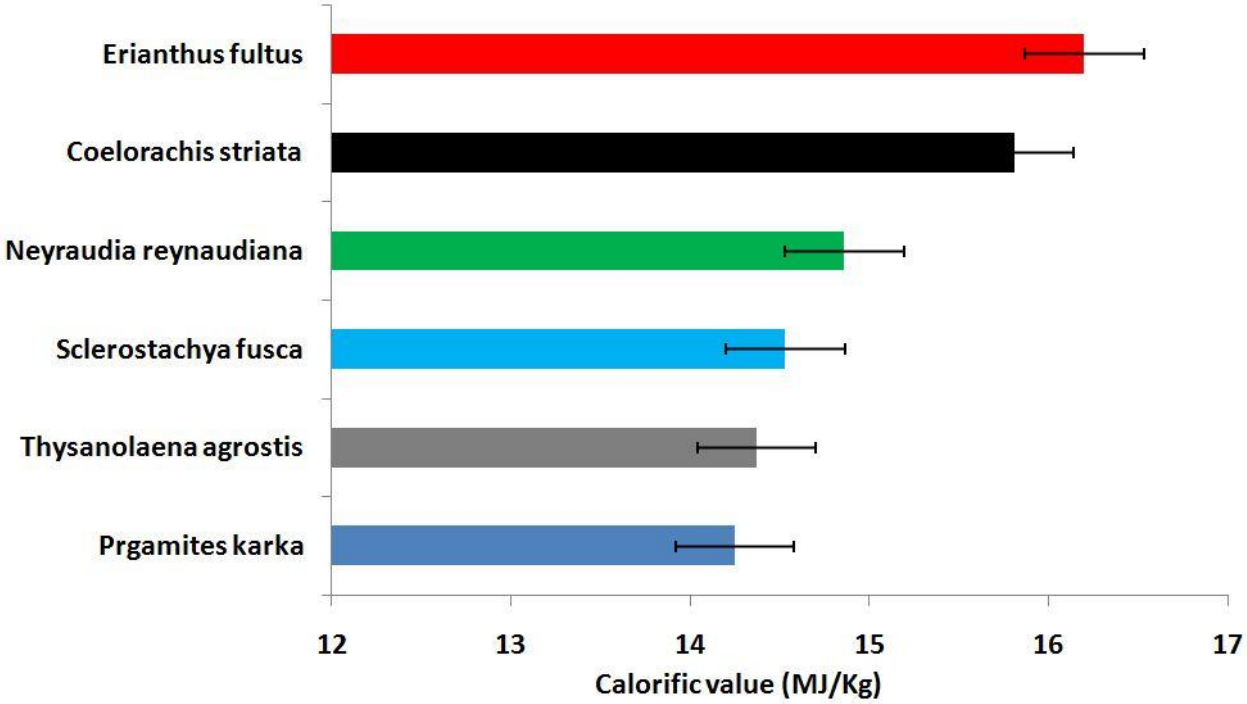

Fig. 5. Calorific value graph of LCB (values correspond to mean ± SD of measurement performed in triplicate).

3.3.6. Van Krevelen Plot

To understand more elaborately on fuel efficacy of biomass, the Van Krevelen plot was drawn (Fig.6). It can be seen that the biomass *Neyraudia reynaudiana* has high O/C value (1.2382) and H/C value (0.1305). The lowest H/C value was obtained in biomass *Erianthus fultus* (0.9892) and O/C (0.1193). In all biomass, the heating value was closed to each other.

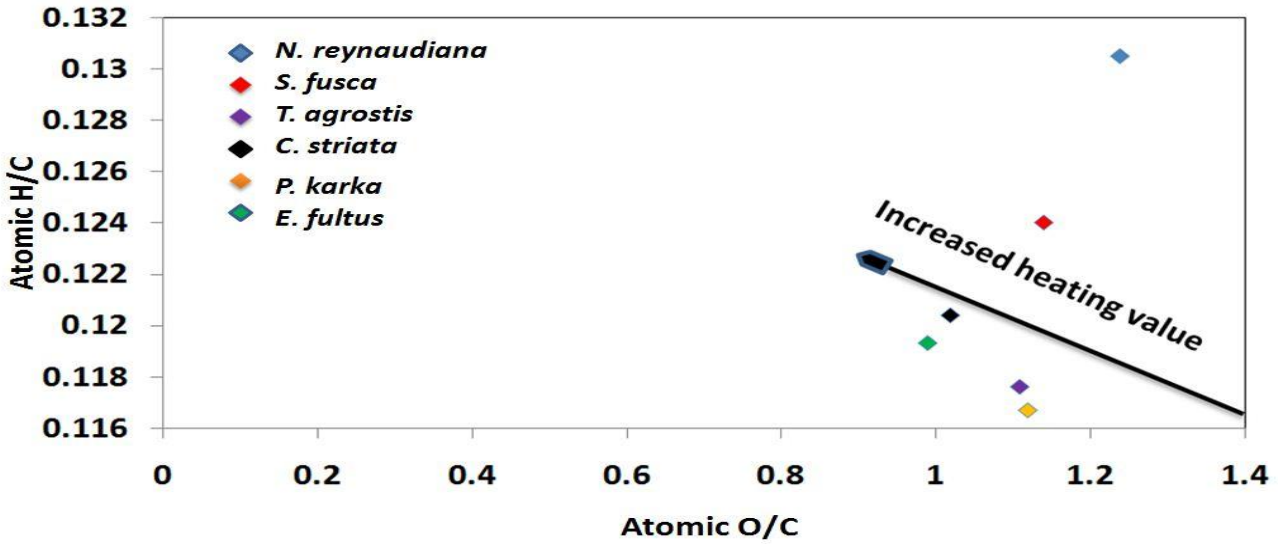

Fig.6. Van Krevelen plot of lignocellulosic biomass sample.

3.4. Chemical analysis

3.4.1. Ultimate analysis (CHNSO analysis)

The elemental composition of the biomass samples is given in table 3. It was observed that *Erianthus fultus* has highest carbon percentage (46.650 %) as compared to others. The minimum carbon percentage was seen in *Neyraudia reynaudiana* (41.264 %). O (wt.%) was measured by the difference of C, H and N from 100. The Oxygen percentage present can be ranked as *Neyraudia reynaudiana* (51.095 %) > *Sclerostachya fusca* (49.813 %) > *Phragmites karka* (49.292 %) > *Coelorachis striata* (46.850 %) > *Erianthus fultus* (46.150 %).

Table 3. Ultimate analysis of LCB.

Biomass	Carbon %	Hydrogen %	Nitrogen %	Oxygen [b] %
Phragmites karka	44.043	5.141	1.524	49.292
Thysanolaena agrostis	44.120	5.190	1.744	48.946
Erianthus fultus	46.650	5.568	1.632	46.150
Sclerostachya fusca	43.706	5.422	1.059	49.813
Neyraudia reynaudiana	41.264	5.389	1.252	51.095
Coelorachis striata	45.954	5.536	1.660	46.850

[b] % of oxygen calculated from the difference of C,H, and N.

3.4.1.1. FTIR analysis

The comparative absorption spectra obtained with wave number are presented in Fig.7. Interpretation of the spectra were given in discussion section referring to table 4 which provides the functional groups of the respective IR peaks of

biomass sample. Different spectral IR peaks were found from the biomass sample such as 3200-3400 cm^{-1} , 2862 cm^{-1}, 1710–1740 cm^{-1}, 1601 cm^{-1}, 1380 cm^{-1}, 1167.24 cm^{-1}, 1145 cm^{-1}, 895 cm^{-1}, 893 cm^{-1}, and 873 cm^{-1} etc.

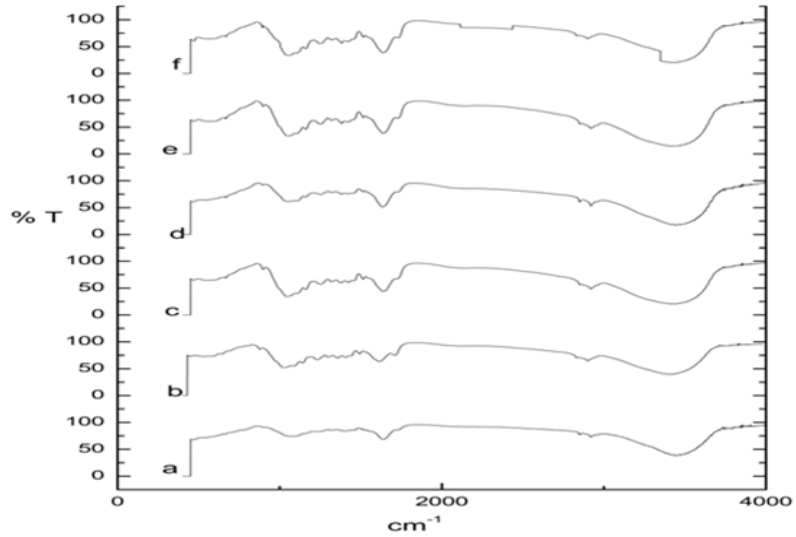

Fig.7. FT-IR spectra of LCB samples: a- *Neyraudia reynaudiana*, b- *Erianthus fultus*, c- *Sclerostachyca fusca*, d- *Thysanolaena agrostis* , e- *Coelorachis striata* , f- *Phragmites karka*.

3.5.Fibre analysis

From the Fig. 8, it is evident that *Erianthus fultus* (39.2%) has the highest cellulose content and lowest was visible in *Neyraudia reynaudiana* (29.26%). Accordingly, cellulose content of the plant can be ranked as in the following order *C.striata* (37.97 %)> *T.agrotis* (35.32%)> *P.karka* (33.86%)> *S.fusca* (30.23%).
Hemicellulose content was found to be highest in *P.karka* (32.26 %), whereas *T.agrostis* (18.35%) has lowest percentage value. The lignin percentage can be order in following according to their percentage values *S.fusca* (29.540%)> *T.agrotis* (17.201%)> *P.karka* (11.800%)> *N. Reynaudiana* (9.267%)> *C.striata* (8.192 %)> *E. Fultus* (5.870%).

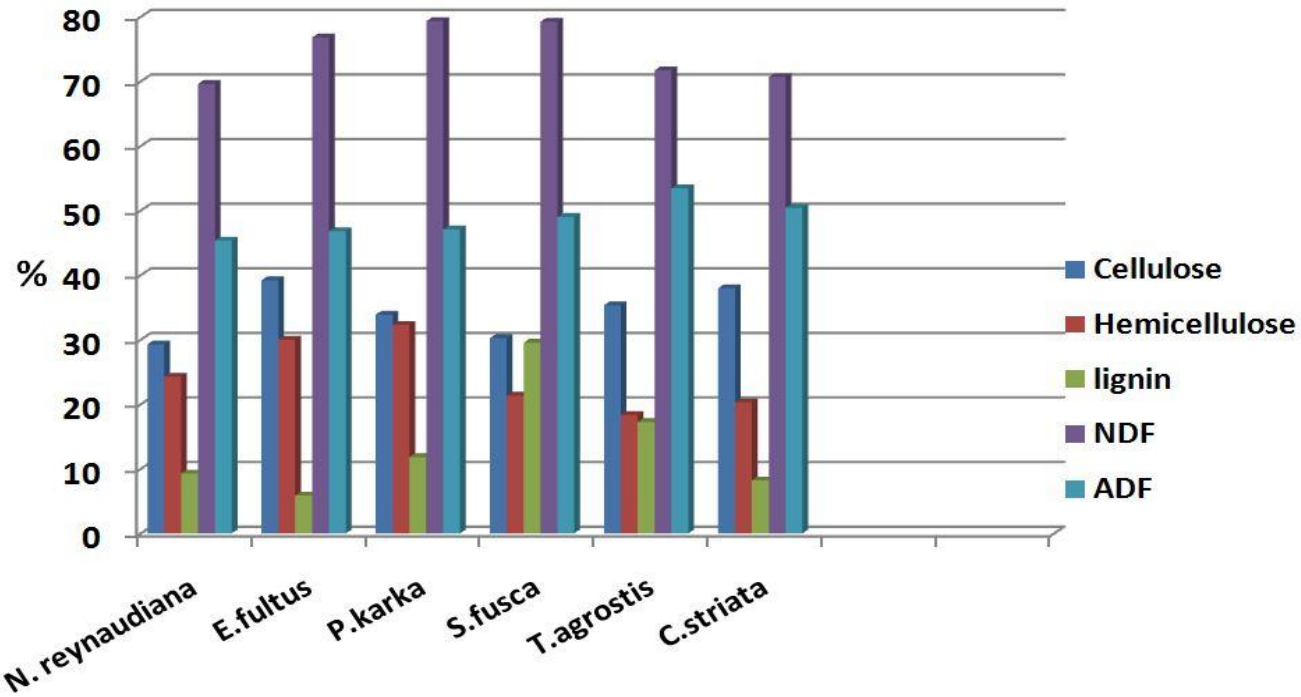

Fig.8. Carbohydrate composition of LCB

4. Discussion

In the backdrop of ever increasing population, the demand for fuel as well as cultivable land resources is galloping. The later is becoming scared due to the emerging competition between food verses fuel crops has become controversial. A favourable alternative is the need of the second generation of fuel crops which are the residue obtained from crops whose grains/fruits/food component are already harvested. The second generation of biofuel encompasses lignocellulosic biomass, agricultural wastes and plants residues, etc. There is continuous effort to explore new raw material for the production of biofuels that satisfy the standard criteria set for fuels and meet the demand for energy [15]. Our aim is to explore the ideal fuel crops that can be used in a sustainable manner. Our hypothesis is that the global demands for biofuel are best met at the local level to make the system of bioenergy sustainable. The exploration of indigenous raw materials for biofuel production is essential for maintaining the ecological balance and generation of socio-economic benefits. In our study, we have characterized the lignocellulosic biomass collected from Kamrup district of Assam and Thoubal district of Manipur.

Six species of biomass belonging to poaceae family were selected after a field study based on quadrate analysis of the species. Selection of species depended on the abundance and availability of the species in the locality. Since a proper identification of plant species prior to characterisation is necessary. The collection of grass sample was done in two seasons (summer and winter). As grasses have different flowering time throughout the year and due to ecological adaptability variations occurs in morphological characters.

For the taxonomical identification, herbarium specimen was prepared to protect from pest and fungi. Two herbarium sheets were made for each sample and deposited to Herbarium unit of Department of Botany, Gauwahati University, Assam, India. The biomass specimen was identified and well rank according to binomial nomenclature system. One specimen was maintained at Indian Institute of Technology (IIT)-Guwahati for further documentation and reference.

One of the most important goals for biomass characterization is to check its fuel properties by proximate and ultimate analysis. Usually, a proximate analysis is carried out based on the criteria of biomass such as moisture content, total solid, volatile matter, fix carbon and ash content. This analysis gives the idea of fuel energy present in the biomass in the form of physical and elemental composition. Proximate analysis is one of the key factors for fuel analysis.

The moisture content of the biomass is related to fuel efficiency. Moisture content on dry basis can be defined as the amount of water per unit mass of dry solids in the sample which is given by

$$MC_d = m_{h2o} / m_d$$

(where MC_d = moisture content on dry basis, m_{h2o} = mass of water (kg, lb), m_d = total mass of the dry solids in the sample (kg, lb).

Usually, two forms of moisture content in lignocellulosic biomass are considered, intrinsic (the moisture content of the material without the influence of weather effects) and extrinsic (the influence of prevailing weather conditions during harvesting of the overall biomass moisture content). In practical, intrinsic moisture content can be recorded. Low moisture content biomass is more efficient for thermal conversion to liquid fuels. However, high moisture content is more favourable for the production of ethanol by biochemical conversion [16]. The high moisture content of the biomass reduces fuel combustibility. The presence of moisture in the biomass usually decreases the heating value and has a negative effect on quality of biofuel. It was observed that almost all the biomass contain less than 10% of moisture. Relatively all the biomass contain 8-9 % of moisture except *Thysanolaena agrostis* which has lowest moisture content with 6.9665%. The highest moisture percentage was recorded in *Phragmites karka* with 8.8429%.

The ash content is the residual unburnt organic material present in the biomass and indicates about the calorific value of the sample. The ash content of biomass is involved in the pyrolysis and the gasification process. Ash acts as a catalyst in the process. It is reported that the ash content in the biomass is inversely proportional to the calorific value [10]. From our findings, highest and lowest ash content was found in *Thysanolaena agrostis* (8.2611 %) and *Neyraudia reynaudiana* (2.7278 %) respectively.

The fixed carbon content of *Phragmites karka, Thysanolaena agrostis, Erianthus fultus, Sclerostachya fusca, Neyraudia reynaudiana* and *Coelorachis striata* were 2.2611 %, 0.8700 %, 2.9846 %, 0.6935 %, 11.7722 % and 1.5842 % respectively. Fixed carbon and volatile matter are two factors that contribute to the heating value of any fuel. The fixed carbon act as heat generator during burning of biomass whereas, volatile matter is related to ignition of the fuel.

Volatile matter gives an idea about the gaseous fuels present in the biomass. Volatile matter includes hydrocarbons and various gases such as methane, hydrogen, carbon monoxide and carbon dioxide [17-18]. Higher the volatile matter lesser is the ignition of the fuel in biomass [17]. The volatile content was found to be maximum in *Sclerostachya fusca* (86.0826 %) and the minimum in *Neyraudia reynaudiana* (77.1168%) (table 2). *Phragmites karka* and *Coelorachis*

striata have similar volatile matter (84.3795 % and 84.2356 % respectively), whereas, *Thysanolaena agrostis* and *Erianthus fultus* have a volatile matter of 83.9020 % and 80.7212 %.

Total solid content is the total solid of the biomass after removing all the moisture from the sample. There is a relationship between the total solid content and moisture percentage of a biomass sample.
The total solid percentage was found to be highest in *Thysanolaena agrostis* (93.0335 %) and the lowest in *Phragmites karka* (91.1571 %).

The mean proximate composition of the lignocellulosic biomass was conducted in order to understand the closed relativity of the biomass sample based on the volatile matter, ash and fixed carbon [19]. (Fig.2). The biomass has closer peat position than coal [19]. The scattered plot was not seen due to the type of biomass taken (grass). This is the reason why the lignocellulosic biomass position confined closed to peat.

The purpose of TGA is to understand the devolatilisation characteristics of the biomass sample in a temperature gradient. The Lignocellulosic structure of biomass can be quantitatively identified from the thermo gravimetric analysis. The use of thermo gravimetric analysis (TGA) in lignocellulosic biomass for determining thermal degradation profile has been widely accepted. TGA is a powerful tool for characterizing the different woody biomass as well as herbaceous biomass and to determine the composition of cellulose, hemicellulose and lignin [20-21]. This technology is well accepted in studies of pyrolytic decomposition of woody plant biomass. The thermal degradation profile of such biomass occurs at different temperature, such as hemicellulose at 250-300 ^{0}C followed by cellulose at 300-350 ^{0}C and finally lignin at 350-500 ^{0}C or beyond [21-23].

During the thermal degradation profile, biomass went through three distinct stages fig.3 (a) TGA graph. In the first stage (temperature below 200^{0}C), moisture and more volatile compounds were removed at 150 ^{0} C. This is called drying period where the biomass liberated light volatiles and water molecules. The slight decay of sample weight can be observed as illustrated in fig. 3 (a), where the weight losses of all six tested materials were less than 10% at this early stage. The major devolatilisation of the sample occurred in the second stage at temperature 200-500^{0}C, where most of the thermochemical conversion, decomposition of biomass took place. At this temperature, remarkable slope of TG curves can be seen indicating significant lost of biomass weight. In this stage, a major liberation of volatile hydrocarbon, rapid thermal decomposition of hemicellulose, cellulose and some part of lignin took place. For stage 3, weight loss is not as significant as in stage 2. The remaining lignin and char material degrades slowly at 500 ^{0} C and above up to a final temperature at 900 ^{0} C. This shows that volatile matter plays a very important role in pyrolysis of biomass materials [24].
Derivative Thermogravimetric (DTG) gives about the zone of reaction in multi-reaction steps where biomass undergoes degradation over the entire temperature range. From the DTG profile figure 3 (b) of biomass indicated that evaporation of moisture and volatile compounds took place in the first peak below 130 ^{0} C. The peaks in between 130 to 250 ^{0} C denoted the removal of volatile matters. The degradation peaks for hemicelluloses were seen in temperature between 250-350 ^{0} C. The peaks in between 350-500 ^{0} C depict for cellulose degradation. Due to a higher thermal stability of lignin, it degrades at above 500 ^{0} C. This thermal stability of lignin is due to the presence of phenolic hydroxyl group in lignin structure. This made stiff, strong and hard to the biomass by encasing the polysaccharides of the cell wall [14, 25-26]. Others have reported that hemicellulose degrades at low temperature followed by cellulose and lignin [27-28].

There is a relationship between cellulose crystallinity and thermal degradation temperature. High cellulose crystallinity increases the thermal degradation activation energies and decreases the rate of depolymerisation and vice-versa. The cellulose, hemicelluloses and lignin content in the biomass are in mixed form. Therefore, it is very difficult to measure the cellulose crystallinity on the entire biomass. The biomass crystallinity usually depends on the wax content and fatty acid components. We knew that LCB contains moisture, cellulose, hemicelluloses, lignin, hydrocarbons, chlorophyll pigments, polar wax, sterol, phenols and other minor compounds. The cellulose crystalline structure is altered when a biomass are subjected to pretreatment technology. This is due to the breakdown of the inter-hydrogen bond present in the cellulose structure [29]. From our findings, the XRD crystallinity index showed an increasing order from biomass *Coelorachis striata* (13.54) to *Thysanolaena agrostis* (16.66), *Sclerostachya fusca* (25.53), *Erianthus fultus* (27.83), *Neyraudia reynaudiana* (30.10), and *Phragmites karka* (33.82). In all biomass samples, the intensity of the major peak decreased with increasing 2Θ. The decrease in the degree of crystallinity (XRD) is an indicator of a decrease in the degree of polymerization and increase in the surface area which in turn increase the hydrolysis of lignocellulosic materials depending upon the biomass sample used [30-32]. Whereas, an increase in the crystallinity index (XRD) may be due to decrease in the amorphous region in relation to the crystalline peak [21]. From Table 4, it can be observed that the crystallinity index of *Phragmites karka* was high whereas *Coelorachis striata* have lower CrI. *Erianthus fultus* and *Sclerostachya fusca* have very near CrI as compare to others.

Table 4. CrI biomass from XRD analysis

Biomass	I_{002}	$I_{amorphous}$	Crystallinity Index (CrI)
Phragmites karka	68	45	33.82
Thysanolaena agrostis	48	40	16.66
Erianthus fultus	97	70	27.83
Sclerostachya fusca	94	70	25.53
Neyraudia reynaudiana	93	65	30.10
Coelorachis striata	96	83	13.54

There are several approaches to predict the heating values of biomass [33, 24]. It can be done by using fixed carbon and volatile matter, or by using elemental composition of biomass. We have adopted the elemental composition of biomass for determining the heating values of biomass. The calorific values of the biomass were calculated according to the empirical formula given by [12]. based on elemental composition. Higher heating values of softwood and woody biomass have a high percentage as compared to lignocellulosic biomass. This is because the lignin percentage is very high in such biomass. This is the reason why our selected six biomass has less value of higher heating values as compared with woody biomass. The result from figure 5 showed that *Erianthus fultus* has a higher heating value of 16.20 MJ/ kg, while *Coelorachis striata*, *Neyraudia reynaudiana*, *Sclerostachya fusca*, *Thysanolaena agrostis* and *Phragmites karka* have 15.81, 14.86, 14.53, 14.37 and 14.25 MJ/ kg respectively**.**

Van Krevelen plot significantly elaborate about the correlation between heating values and atomic ratios of hydrogen, carbon and oxygen. It gives information about the differences in the elemental composition (C-H-O ratio) [34]. In the Fig. 6, the composition of typical lignocellulosic biomass fuels such as *Phragmites karka*, *Thysanolaena agrostis*, *Erianthus fultus*, *Sclerostachya fusca*, *Neyraudia reynaudiana* and *Coelorachis striata* is shown. The lower the atomic ratio, higher is the energy content. It is due to the fact that, the chemical bonding between C-C bond is stronger than the C-O bond. Hence, more energy is released. The selected biomass *Erianthus fultus* shows high energy content than other biomass (Fig.5 and 6).

Ultimate analysis generally gives an idea about the elemental composition of biomass samples such as Carbon (C), Hydrogen (H), Nitrogen (N), Sulphur (S) and Oxygen (O). This elemental component is very essential in order to determine the fuel efficacy. The ultimate analysis of biomass on the dry basis was presented in table 3. These elements form oxides during combustion of biomass at high temperature. The percentage of carbon present in the biomass is directly related to the heating value [35]. Likewise, carbon percentage and oxygen percentage has very closed relations in biomass. We can see in all biomass samples if the carbon percentage increase, the percentage of oxygen decreases and vice-versa (table 3). The data obtained from ultimate analysis shows that hydrogen and nitrogen percentage was very less in all biomass samples as compare to carbon and oxygen. This indicates that majority of the energy generated from biomass is carbon and oxygen based elemental component. The biomass sample *Erianthus fultus* has more carbon percentage than other biomass sample, hence produces more energy. This is the reason why the calculated HHV and Van Krevelen plot was high in *Erianthus fultus.*

FTIR was conducted to know the presence of different functional groups in biomass sample. The FTIR peak indicates the mixed presence of structural compound (cellulose, hemicellulose and lignin) of biomass on the basis of their functional groups. For further clarity with corresponding wave number and their respective spectral assignment the FTIR spectral is shown in table 5. The IR peaks in the range of 3200-3400 cm^{-1} indicate the presence of fibre due to axial deformation of OH group. The absorption peak at 2862 cm^{-1} gives about the CH_2 asymmetric stretching: mainly lipids with a little contribution from proteins, carbohydrates, and nucleic acids. The presence of a carbonyl group like ester (C=O) is observed in the range of 1710–1740 cm^{-1}, which gives an evidence of the hemicelluloses presence in the samples. The absorption peak at 1601 cm^{-1} indicates the stretching aromatic C=O which is lignin derivative. The presence of cell wall polysaccharide (C-H) due to bending of aliphatic CH_2 was observed at peak 1380 cm^{-1}. IR peak at 1167.24 cm^{-1} represent asymmetric deformation of C-O-C of the cellulose and hemicellulose portion (C-OH stretching vibrations). The presence of cellulose (β-1.4 glucan) was seen at peak 1145 cm^{-1}. Sugars like arabinan, galactan and B-D fructose were observed at lower peak value such as 895, 893, and 873 cm^{-1} [11, 20, 27].

Table 5. Determination of functional group of biomass by FTIR analysis.

Wave no. (cm-1)	Definition of the Spectral Assignments
3200–3400.	Presence of fibre in the sample which is attributed to the axial deformation of OH group.
2862	CH_2 asymmetric stretching: mainly lipids with a little contribution from proteins, carbohydrates, and nucleic acids
1710–1740	The presence of carbonyl group like ester (C=O) is observed in the range of which gives an evidence of hemicelluloses in the samples.
1733	Saturated ester C=O stretch: phospholipids, cholesterol esters, hemicellulose, and pectin
1601	C=O aromatic stretching: lignin
1452	C-H: cell wall polysaccharides
1420	O-H bending: cell wall polysaccharides, alcohols, and carboxylic acids
1380	C-H bending of aliphatic CH_2: cell wall polysaccharides
1320	N-acetylglucosamine: chitin and chitosan
1160	Symmetric bonding of aliphatic CH2, OH, or C-O stretch of various groups: cell wall polysaccharides
1167.24	The connection with the asymmetric deformation of C-O-C of the cellulose and hemicelluloses which is related to the presence of C-OH stretching vibrations.
1145	Cellulose (β-1.4 glucan)
1073	Rhamnogalactorunan. b-galactan
1064	C-O stretching: cell wall polysaccharides (glucomannan)
1035	OH and C-OH stretching: cell wall polysaccharides (arabinan)
895	Arabinan
893	Galactan
873	B-D-Fructose

Biomass fibre such as cellulose, hemicellulose and lignin are integral parts of the fuel properties. Their content differs according to a type of biomass. For example, the cellulose content of Switch grass was found to be 37 %, hemicellulose content was 29% and lignin content was 19% [36, 16, 37]. Corn stover is about 38% cellulose, hemicellulose 26% and 19 % lignin. Similarly, in wheat straw, it is about 38 % cellulose, 29% hemicellulose and 15% lignin. From our finding illustrated in figure 8, most of the biomass species have high cellulose content. *Erianthus fultus* (39.2%) has the highest cellulose content.

The hemicellulose percentages of the biomasses were less in overall comparison with the cellulose percentage. This is because the majority of the plant biomass contain high percentage of cellulose. One of the main hurdles in the conversion of biomass to ethanol is lignin percentage. As lignin act as the barrier in hydrolytic conversion of cellulose to ethanol, less lignin content in biomass sample is more preferable. We consider two methods for determining the lignocellulosic biomass composition of cellulosic feedstocks; detergent fibre analysis (DFA1) and dietary fibre analysis DFA2). DFA1 detects the neutral detergent fibre (NDF), acid detergent fibre (ADF) and acid detergent lignin (ADL) that correspond to the percentage present of cellulose, hemicelluloses and lignin. DFA2 directly detects the content of structural carbohydrates (principally glucan and xylan). We prefer DFA1 as it is convenient for estimation of cellulose, hemicellulose and lignin. NDF of *P.karka* (79.33%) and *S.fusca* (79.23%) were almost same and has closed NDF percentage. The lowest NDF % was visible in *N.reynaudiana* (69.6%). ADF percentage was highest in *T.agrostis* (53.44%) and the lowest was seen in *N.reynaudiana* (45.33%). *E.fultus* and *P.karka* have close vicinity of ADF with 46.80% and 47.06% from Fig.8.

5. Conclusion

There is a constant search of new raw material with zero waste for energy production from biomass. Maximum utilisation of the renewable resources is the key to improving economic growth and environmentally sound society. Various resources like agricultural waste, forest residues and grasses have been attempted to generate biofuel. As grasses are one of the most dominating species in North-East India, we thought of utilising it to produce biofuel after physico-chemical characterisation. These can be some of the best candidates for production of bioenergy. The short life span and wide availability throughout the hills terrain would make them more convenient for conversion to liquid fuel without disturbing the food crops. The LCB sample selected for this study such as *Phragmites karka*, *Thysanolaena agrostis*, *Erianthus fultus*, *Neyraudia reynaudiana*, *Coelorachis striat*a and *Sclerostachya fusca* are indigenous to North-East India. The cellulose content was found very high in *Erianthus fultus* (39.2%) which would be equally a good candidate as switch grass (37%). All the selected grasses have great potential to be utilised for gasification, bio-oil, bio-alcohol production and a good candidate for the production of second generation of biofuel to meet the energy demand.

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