CHAPTER 3

PHYSICAL AND CHEMICAL CHARACTERIZATION OF VARIOUS INDIAN AGRICULTURE RESIDUES FOR BIOFUELS PRODUCTION

Lignocellulosic biomass (LCB) is a multi-complex, and a highly heterogeneous material consisting of cellulose, hemicellulose, lignin, ash, extractives, protein etc. The chemical composition and structure of LCB vary widely depending on the source type and range of genotypic, phenotypic, and environmental growth factors. The relative abundance of this component in any particular biomass is the key factor in determining the feedstock suitability for biofuel production. Decades of research have been dedicated to understanding the complete physicochemical characterization of LCB for their biofuel potential and the responsible factors, which make lignocellulosic biomass cell wall to resist deconstruction. However, very few reports are available on complete characterization of LCB. In this chapter, we have described the complete physicochemical characterization of ten agricultural residues available in North Indian region to assess their biofuel potential. This study will be very useful to understand the physicochemical properties of biomass and help to select the appropriate biomass for commercial conversion into materials and fuels either by biological/ or thermochemical conversion processes.

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3.1 INTRODUCTION

India is a vast and agriculture dominant country, spanning very large area under agriculture and forestry. Agriculture sector contributes around 17% of India's GDP, and 70% of the population depends on it for energy. Around 686 MT of gross agricultural residues are produced annually, out of which 234 MT (34% of gross) is available as surplus. LCB is the widely available material across the globe, producing approximately 220 billion tonnes annually.[231] Table 3.1 shows the availability of different agricultural residues and their ethanol potential.

Table 3.1 Availability of agricultural residues and their ethanol potential

Biomass	Annual availability (Million metric tonnes/yr)	Theoretical ethanol potential* (Billion litres)
Cotton stalk	52.9	17.9
Maize cob	27	9.1
Mustard Stalk	8.7	2.9
Paddy straw	170	57.6
Sugar cane bagasse	12.1	4.1
Wheat straw	112	38
Total	382.7	129.6

*Calculated as per BRDB, 2008: 1 tonne dried biomass gives approximately 89.5 gallons of cellulosic ethanol[232]

A study conducted by the ministry of renewable energy estimated that the current availability of biomass in India is approximately 565 million tonnes (MT) per annum of which 189 MT can be used either to fully fulfil the transportation requirements of the country or generate a potential 18,000 MW of power. Amongst, India's crop residue biomass pool, sugar cane produces the highest amount of surplus residue followed by rice, wheat and cotton. The Northern part of India is particularly rich in agriculture and thus produces the majority of surplus agricultural residues, which can be used as a source of energy. Uttar Pradesh produces the highest amount of surplus residue in the country (40 MT) followed by Punjab, Maharashtra, Gujarat, Tamil Nadu, Haryana, Andhra Pradesh, Karnataka, Madhya Pradesh and Rajasthan. They all

together contribute 89% of India's surplus residue generation.[233] National, annual bioenergy potential from surplus lignocellulosic biomass is 4.15 EJ, which is equivalent to 17% of India's total energy demand.[233]

As discussed in Chapter 1, LCB is a complex matrix of several components as shown in Figure 3.1. LCB can be used for the production of energy and can replace fossils fuels with environmental, social and economic benefits.

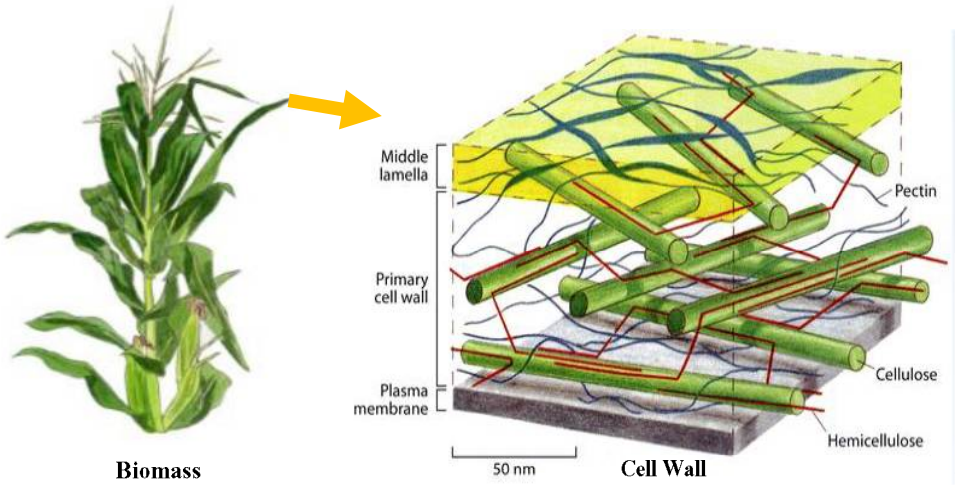


Figure 3.1 Lignocellulosic biomass and their component (Source:http://biogeonerd.blogspot.in/2014/)

There are mainly two technology platforms, which can convert the biomass into biofuels, i.e. thermochemical and biochemical.[234,235] Thermochemical route includes the gasification and pyrolysis.[236] Gasification converts the biomass to syngas as a source of energy and this process is carried out at a very high temperature in the presence of limited and controlled amount of air,[237] whereas, pyrolysis is carried out at a relatively lower temperature in the absence of air producing pyrolysis oil upgradable to liquid fuels.[238] The biochemical process is yet another option by which biomass can be converted to bioethanol. This technology comprises steps like pretreatment, which makes structural polysaccharides accessible for enzymatic hydrolysis producing fermentable sugars. Thus, pretreated biomass on downstream processing using enzymatic saccharification and fermentation can be converted to bioethanol. Both these processes have the potential to convert biomass to biofuels.

However, the effective utilisation of surplus biomass resources is often challenged and hindered by seasonal availability, extensive distribution over vast and distanced areas, and the embedded socio-cultural factors associated with its use. With that, the physical and chemical properties of any particular biomass differ significantly from one geographical condition to another, due to different soil conditions, environmental and climate variations. These variations have a profound impact on the biofuels production potential of LCB either via thermochemical or biochemical methods.[239] For instance, carbohydrate contents (cellulose and hemicellulose) of biomass vary from one region to another within the same species, in general, the higher carbohydrates content of biomass reflects its higher bioethanol potential. Similarly, the energy content, volatile matter, ash, moisture etc. directly influence the overall process economics of any thermochemical conversion process.[239]

Hence, complete assessment and understanding of the lignocellulosic biomass, their architect and physicochemical properties can help the technologist to design the process parameters either for the thermochemical or biochemical process.

3.2 AIM OF STUDY

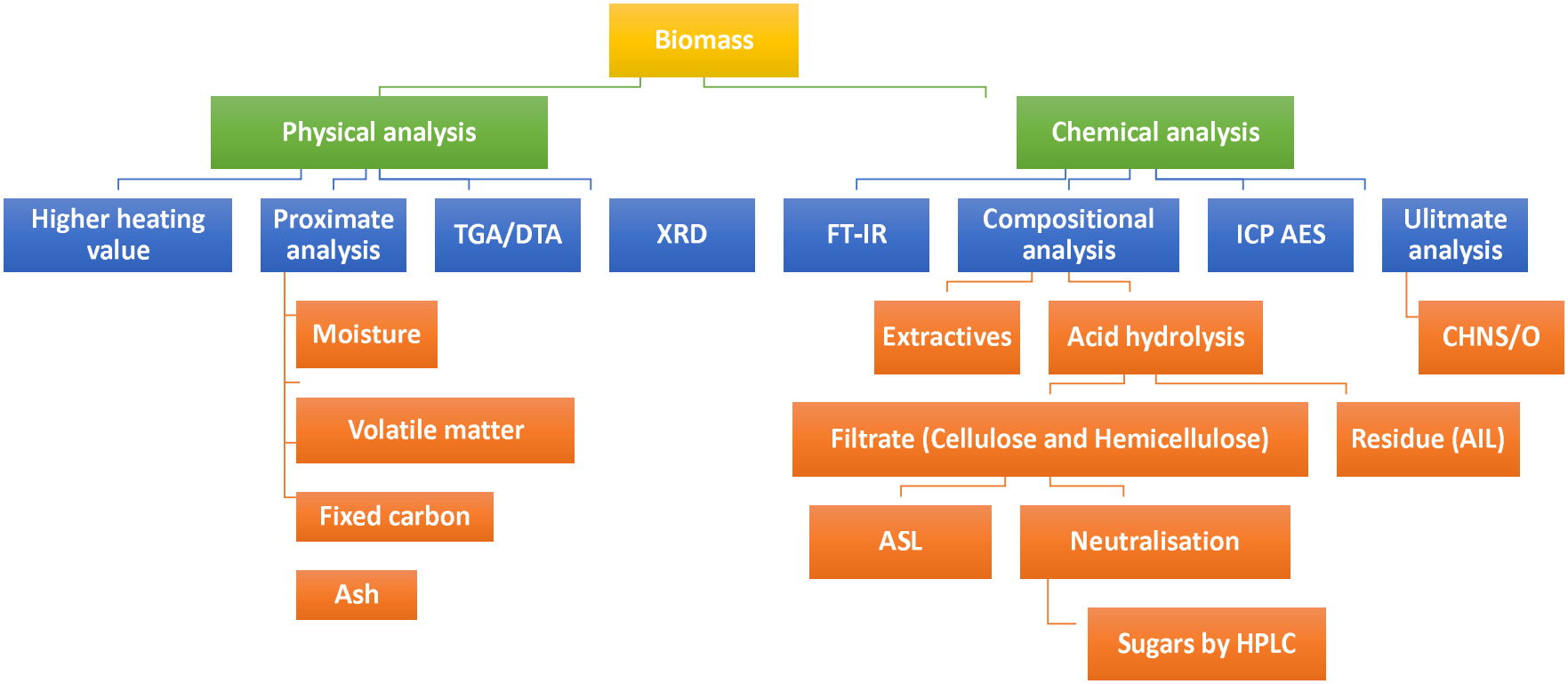
The current study aims for systematic and comprehensive assessment of physical and chemical properties of lignocellulosic agricultural residues available in North India (commonly found in Asia), i.e. rice straw (RS), rice husk (RH), cotton stalk (CS), wheat straw (WS), sugarcane bagasse (SCB), corn stover (CRS), sorghum stalk (SS), mustard stalk (MS), corn cob (CC) and jatropha pruning (JP). The selection of these biomasses is independent to impact of seed and cultivation study as we are using the waste residue of the crop and not the main product (food grains) of cultivation. Hence, variation in seed and cultivation method is not required in our studies.

In this study, we have applied a series of laboratory analytical procedures (LAPs) developed by the National Renewable Energy Laboratory (NREL), USA. Compositional analysis of all lignocellulosic residues in terms of extractives, structural polysaccharides, acid insoluble lignin (AIL), acid-soluble lignin (ASL), protein, ash and metal content has been undertaken.

Moreover, higher heating value, crystallinity index (CrI), CHNS/O analysis, thermogravimetric (TGA) and differential thermogravimetric analysis (DTA) are also studied. FT-IR analysis of all biomass samples was also carried out. The goal of these analyses is to characterise all constituents of biomass. These studies have enabled us to compare the structural features of this LCB for the first time. The data obtained will provide a better understanding of their potential as biofuels feedstocks for both the said platforms.

3.3 RESEARCH METHODOLOGY

The systematic methodology used for complete characterization of biomass is given in Figure 3.2, which is subdivided into two main sections, i.e. physical analysis and chemical analysis. The physical analysis includes the proximate, TGA, DTA, XRD, volatile, moisture, ash, fixed carbon and heating value estimation by using standard protocols. Similarly, chemical analysis deals with the analysis of chemical properties of biomass by using chemical digestion method, spectroscopic determination of functional groups, metal constituents and ultimate analysis for CHNS/O etc. This study will help to select the feedstock and to design the particular process parameters with their biofuel potential.



ASL= Acid Soluble Lignin; AIL= Acid Insoluble Lignin; FT-IR= Fourier transform infrared
XRD: X-Ray diffraction; TGA= Thermogravimetric Analysis; DTA= Differential Thermogravimetric Analysis

Figure 3.2 Schematics diag

3.3.1 MATERIALS AND METHODS

In order to meet the objective of this study to fully characterise different LCB for their potential for biofuels, DBT-IOC Centre for Advanced Bioenergy Research, IOCL (India) is fully equipped with all analytical facilities and has a proper human resource system for biomass collection, transportation and storage. The overall methodological approach to completely analyse the LCB has explained afterwards.

Chemicals: Sugar standards, i.e. xylose, glucose, cellobiose, galactose, arabinose, furfural, 5-hydroxymethylfurfural (HMF), microcrystalline cellulose were of analytical grade, procured from Sigma-Aldrich, India. Analytical grade acetic acid, sulfuric acid and calcium carbonate were obtained from Fisher Scientific, India. These chemicals were used without any further purification.

Biomass selection: Lignocellulosic biomass were selected based on their availability and abundance, which are suitable for the biorefinery. As we are focusing with an aim for waste utilisation for energy production, the biomass selected were independent of seed and cultivational method.

For this study, ten agricultural biomass samples, namely rice (*Oryza sativa*) straw (RS), rice husk (RH), cotton (*Gossypium arboreum*) stalk (CS), wheat (*Triticum aestivum*) straw (WS), sugarcane (*Saccharum officinarum*) bagasse (SCB), corn (*Zea mays*) stover (CRS), sorghum (*Sorghum bicolor*) stalk (SS), mustard (*Brassica campestris*) stalk (MS) and corn (*Zea mays*) cob (CC) were collected from Mathura District (27.28°N 77.41°E) in UP (North India) at the time of harvesting in the year 2011. Mathura has an average elevation of 174 meters with a tropical climate. Summer temperatures rise beyond 44 °C, and cold winters temperature dips down to 5 °C. The average rainfall is 595 mm, mostly during the monsoons from July to September. Jatropha (*Jatropha curcas*) prunings were collected from the campus of IOCL, Faridabad in the month of April 2012. All these residues were collected at the time of harvesting so these were fully matured and most of the moisture was removed by the natural process during ripening of the crops in the fields. The aim was to bring all the residues to the same level of maturity as these would be available in plenty for the production of biofuels. All samples were milled to ~2 mm size using a knife mill. All the biomass samples were air dried at ~30 °C to bring the

moisture content in the range of 8-10% (w/w) and then stored in plastic bags at 25 °C till further analysis.

3.3.1.1 Moisture content

Moisture in LCB plays a very important role in any conversion process. Higher moisture content in biomass samples will alter the properties of biomass and also speed up the rate of natural degradation. The moisture content of biomass samples was determined using a standard protocol developed by NREL (NREL/TP-510-42620)[240] using an infrared dryer from Sartorius MA-150C, Germany. The total solids are the solids present in the biomass after moisture correction. The percent total solids and ODW (oven dry weight) of any biomass can on a dry weight basis can be calculated as using given equations 3.1, 3.2 and 3.3:

$$\%\,Total\ Solids = \frac{Wt.of\ crucible + biomass\ sample - Wt.of\ crucible}{Wt.of\ sample\ as\ recieved} \qquad Eq.3.1$$

$$\%Mositure = 100 - \frac{(Wt.of\ crucible + biomass\ sample - Wt.of\ crucible)}{Wt.of\ sample\ as\ recieved} \times 100 \qquad Eq.3.2$$

$$\%\,ODWsample = \frac{Wt.of\ air\ dried\ samples \times \%Total\ solids}{100} \qquad Eq.3.3$$

Where Wt. is weight, O.D.W is oven dry weight of biomass.

3.3.1.2 Volatile matter

Volatile matter in the LCB samples was quantified using the protocol as given in ASTM D317, E872.[241] For this, ~1 g of biomass was placed in a muffle furnace at 950 °C for 7 min in a quartz crucible. The crucible was removed from the furnace and placed in a desiccator for cooling to room temperature and weighed. The weight loss was gravimetrically quantified as total volatile matter

present in lignocellulosic biomass.

The ash content is defined as the total mineral content and other inorganic matter present in biomass. Ash content was analysed using NREL (NREL/TP-510-42622) standard protocol.[242] For this, 1 g of biomass was burned in the air and then heated at 575±25 °C in muffle furnace for 4-6 h. Thereafter, the crucible was carefully removed from muffle furnace and placed in a desiccator to cool to room temperature. Ash content was calculated gravimetrically on ODW biomass using equation 3.4:

$$\%\,Ash = \frac{Wt.crucible + ash - Wt.crucible}{ODW} \times 100 \qquad Eq.3.4$$

3.3.1.3 Higher heating values

The calorific value of any fuel represents the energy content bound in it and can be determined experimentally using bomb calorimeter or can be calculated from ultimate and/or proximate analyses resulting from the Dulong equation.[243]

Higher heating values of biomass samples were quantified by following standard protocol[244] using Leco bomb calorimeter (Leco corporation, S.No. 603-300-500), St. Joseph MI, USA. For this, 1.0 g of a sample of each LCB was placed in a crucible and a fuse wire of ~10 cm length of the known heat of combustion per unit length was attached to the two terminals and adjusted to give firm contact with the LCB. Thereafter, oxygen was injected slowly at a pressure of 25 atm. The bomb was kept in the calorimeter and immersed in the water. After ignition, the temperature of the calorimeter rose quickly. The heat released in combustion was proportional to the calorific value of the LCB. Higher heating values of biomass samples were also calculated theoretically by using the following Eq. 3.5.[245]

$$Higher\ heating\ value\ (MJ/kg) = 0.42 * \left\{(8080 * C\%) + \left[34500 * \left(H\% - \left(\frac{O\%}{8}\right)\right)\right] + 2240 * S\right\} \qquad (Eq.3.5)$$

Where C is carbon; H is hydrogen; O is oxygen and S are sulphur.

3.3.1.4 Thermogravimetry and differential thermal analysis

Thermogravimetry (TG) and differential thermogravimetric analysis (DTA) of biomass provide information on thermal decomposition profile of respective components which can be used to follow the physicochemical changes that occur during pretreatment processes.[246] This technique is also helpful to determine the percentage of volatile matter and fixed carbon. There is a limited international trade in bioethanol feedstocks, partially due to variable characteristics of all lignocellulosic biomass.

DTA of biomass samples was carried out using (NETZSCH STA 449F1, Jupiter, USA) thermogravimetric analyser under a nitrogen atmosphere with a flow rate of 20 mL/min. For this, 5 mg of biomass was heated under a nitrogen atmosphere from 30-800 °C with a heating rate of 10 °C/min and weight loss was recorded vis-à-vis temperature.[247]

3.3.1.5 X-Ray diffraction

X-ray diffraction (XRD) of biomass helps to determine the crystallinity, which is attributed to the close packing of cellulose chains in the cell wall matrix. Lower crystallinity represents the distorted structure of cellulose chain (amorphous in nature), which is kinetically more favourable towards enzymatic saccharification than crystalline cellulose.[130] Higher crystallinity may be the result of a more packed cellulose structure in biomass hence results in higher chemical and thermal stability. XRD measurement of biomass samples was performed on Rigaku XRD Panalytical (Netherland), X-pert pro-diffractometer set at 40 kV, 30 Ma respectively. The XRD patterns with monochromatic Cu Kα radiation (λ=1.5406 Å) were recorded over the angular range of 2θ=30-50° with a scan step size of 0.003°. Approximately 100 mg of powdered biomass samples were pressed into disks at 200 kgf/cm^2 for 30 s. The background intensity without the sample was subtracted from the intensity obtained for respective samples. Crystallinity index (CrI) of biomass samples was calculated according to the empirical method as given in Eq. 3.6 proposed by Segal, et al. (1962).[248]

$$CrI(\%) = \left[\frac{I_{002} - I_{18.0}}{I_{002}}\right] * 100 \qquad (Eq. 3.6)$$

Where (I_{002}) is the highest peak intensity (002) at an angle of diffraction

$2\theta=22.4°$ and $I_{16.0}$ is the intensity diffraction for amorphous cellulose at $2\theta=16.3°$.

3.3.1.6 Proximate analysis

Elements such as CHNS/O were analysed in Vario EL III CHNS elemental analyser. Elements present in the ash were determined by inductively coupled plasma absorbance emission spectroscopy (ICP AES) using a standard method.[249] These elements were converted to their respective oxides. FT-IR spectra of biomass samples were recorded using Prestige-21, Model No. A21004802514, FT-IR instrument. All spectra were recorded in the absorbance mode from an accumulation of 128 scans at 4 cm^{-1} resolution in 4000–400 cm^{-1} range. Samples were analysed by grinding with KBr (1:100, w/w) and pressing into pellets in drift mode.

3.3.1.7 Compositional analysis for polysaccharides

Extractives analysis in biomass samples was carried out using Milli-Q water and 95% ethanol as solvent following a standard protocol LAP NREL/TP-510-42619[250] by using Buchi multiple Soxhlet extraction unit (Buchi Labortechnik, Model No. 1000133155), Switzerland. For this, 15g of lignocellulosic biomass was initially extracted with water followed by 95% ethanol. The extractives were then quantified gravimetrically by weighing the ethanol and water respectively. The extracted biomass was dried at room temperature to reduce to moisture <10% (w/w) and then sealed in plastic bags for further characterization.

Compositional analysis of biomass samples was performed by two-step acid hydrolysis method developed by NREL, USA (NREL/TP-510-42618). 300 mg of dried biomass in 3 mL of 72% (density 1.6338 g/mL) H_2SO_4 was incubated at 30°C while shaking at 300 rpm for 1 h. The content was diluted to 4% H_2SO_4 (density 1.025 g/L) by adding 84.00 ± 0.04 mL deionized water using an automatic burette and mixed solution was autoclaved at 121 °C for 1 h. The reaction was quenched by placing samples into an ice bath before neutralisation. The hydrolysate (20 mL) was neutralised using lime to pH 5.0, clarified through 0.22 µm filter and subjected to sugar analysis using HPLC (Waters, Switzerland) fitted with Bio-Rad Aminex HPX-87P column. Water was used as

mobile phase at 0.6 mLmin^{-1} with column temperature as 75 °C. Refractive index detector was used to detect sugars, degradation products (HMF, furfural and acetic acid) using Waters HPLC equipped with a Bio-Rad Aminex HPX-87H column and a UV detector using 0.005M H_2SO_4 as mobile phase (0.6 mL min^{-1}, column temperature 50 °C). Acid insoluble lignin (AIL) was calculated gravimetrically after ash correction as a dry weight percentage of the samples. Acid soluble lignin (ASL) was measured by UV-Vis Spectrophotometry (ε_{205}=110) calculated by Eq. 3.9. Total lignin was the sum of the AIL and ASL. Cellulose content was calculated from the glucose using anhydro-correction of 0.90 (132/150 for C6 sugars), whereas, hemicellulose was calculated from xylose and arabinose using 0.88 (162/180 for C5 sugars) using Eq. 3.10, 3.11 respectively. The crude protein content was estimated by the equation: % protein =% N *6.2 nitrogen factor (NF).[251]

$$\%\, ODW = \frac{\left(Wt._{Air\ dried\ sample}\right) * \%\, Total\ solids}{100} \qquad Eq.3.7$$

$$\%\, AIL = \frac{(Wt._{crucible+AIR} - Wt._{crucible}) - (Wt._{crucible+ash} - Wt._{crucible})}{ODW_{sample}} * 100 \qquad Eq.\ 3.8$$

$$\%ASL = \frac{UV_{abs} * Vol_{filtrate} * dilution}{\varepsilon * ODW_{sample} * pathlength} * 100 \qquad Eq.3.9$$

$$\%\, Cellulose = \frac{[glucose * 0.9 + HMF * 1.29]}{ODW_{sample}} * 100 \qquad Eq.3.10$$

$$\%\, Hemicellulose = \frac{(xylose+arabinose)*0.88+acetic\ Acid*0.78+furfural*1.32}{ODW_{sample}} * 100 \qquad Eq.3.11$$

3.3.1.8 FT-IR

Fourier transform spectroscopy (FTIR) is a widely-used tool for qualitative and quantitative determination of the chemical constituents of biomass and crystalline nature of biomass. The FT-IR spectrum of LCB was recorded by using Prestige-21, Model No. A21004802514, FT-IR instrument. All spectra were recorded in the absorbance mode from an accumulation of 128 scans at a 4 cm^{-1} resolution over 4000–400 cm^{-1} range. Samples were analysed

by grinding with KBr (1:100, w/w) and pressing into pellets in drift mode.

3.4. RESULTS AND DISCUSSION

3.4.1 THE PROXIMATE COMPOSITION, ULTIMATE COMPOSITION AND HIGHER HEATING VALUE

The proximate and ultimate composition and higher heating value of all biomass samples are shown in Table 3.2, which includes moisture content, volatile matter, fixed carbon and ash content, whereas ultimate analysis includes CHNS/O analysis. Fixed carbon indicates the extent of non-volatile organic matter present in the biomass and high heating value. CS contains highest fixed carbon (16.6%), which corresponds to the highest heating value (19.2 MJ/kg) whereas, CC has the lowest fixed carbon, i.e. 4.2% and hence, lower heating value (13.3 MJ/kg). High heating value (19.2 MJ/kg) for CS is attributed to the presence of high hydrogen (6.4%) and carbon (46.8%) whereas, the lower heating value of CC was attributed to the presence of low hydrogen (5.9%) and carbon (44.2%).

Volatile matter signifies the presence of volatile components in the biomass residue, which eliminates all organic moieties like cellulose, hemicellulose and most of the lignin as well as the moisture from the residue. Data summarised in Table 3.2 shows that CC has the highest volatile matter (80%) and lowest fixed carbon (4.2%), while WS has the lowest volatile matter (63%) and highest fixed carbon (15.9%). In general, biomass with high volatile matter produces high quantities of bio-oil and syngas, whereas fixed carbon increases the biochar production via thermochemical processes.[239] Non-volatiles contain char with a high content of heating value and ash-forming components like silica and a part of lignin. RH, RS and WS show lower volatile matter as these have much higher ash content (10.5 to 17.4%) whereas, CC, SCB and JP show higher volatility due to lower ash content as shown in Table 3.2.

Table 3.2: Proximate and ultimate analysis of various biomass[a]

Analysis	RS	RH	CS	WS	SCB	CRS	SS	MS	JP	CC
Proximate Analysis (% dry wt., w/w)										
Moisture	10.0±0.8	9.8±0.2	8.9±0.2	10.6±0.4	10±0.5	8.3±0.5	8.7±0.4	9.7±0.2	8.5±0.1	10.2±0.3
VM	65.0±1.8	64.0±2.1	71.0±1.2	63.0±0.2	76.0±1.0	73.0±0.4	66.0±0.7	70.0±1.5	71.0±1.4	80.0±1.2
Ash	13.7±0.7	17.4±1.1	3.5±0.3	10.5±0.2	4.4±0.2	11.1±0.3	8.8±0.5	7.9±0.8	5.1±0.2	5.7±0.4
Fixed Carbon[b]	11.3±0.7	8.8±1.1	16.6±0.4	15.9±0.3	9.6±0.3	7.9±0.7	16.5±0.8	12.3±0.7	15.4±0.2	4.2±0.3
Ultimate analysis (% dry wt., w/w)										
C	38.8 ± 1.1^{A}	39.8 ± 0.8^{A}	46.8 ± 1.0^{B}	41.7 ± 0.2^{C}	43.2 ± 0.8^{D}	45.7 ± 0.3^{B}	44.4 ± 0.2^{D}	43.8 ± 0.8^{D}	45.9 ± 0.1^{B}	44.2 ± 0.1^{D}
H	6.7 ± 0.3^{A}	5.7 ± 0.3^{B}	6.4 ± 0.2^{A}	5.0 ± 0.0^{C}	6.2 ± 0.1^{A}	6.3 ± 0.2^{A}	6.2 ± 0.5^{A}	5.9 ± 0.01^{A}	5.9 ± 0.2^{A}	5.9 ± 0.1^{A}
N	0.2 ± 0.0^{A}	0.5 ± 0.01^{A}	0.3 ± 0.01^{A}	0.4 ± 0.01^{A}	0.4 ± 0.01^{A}	0.4 ± 0.01^{A}	0.5 ± 0.01^{A}	0.3 ± 0.01^{A}	0.9 ± 0.1^{B}	0.4 ± 0.01^{A}
O[c]	38.8 ± 1.8^{A}	39.8 ± 0.8^{A}	46.8 ± 1.0^{B}	41.7 ± 0.8^{C}	43.2 ± 0.3^{D}	45.7 ± 0.01^{B}	44.4 ± 0.8^{D}	43.8 ± 0.8^{D}	45.9 ± 0.8^{B}	44.2 ± 0.2^{D}
S	0.2±0.01	0.2±0.01	0.2±0.01	0.3±0.01	0.8±0.01	0.5±0.01	0.9±0.00	0.3±0.0	0.04±0.0	0.08±0.0
C/H	5.8±0.01	6.9±0.03	7.4±0.01	7.1±0.04	6.9±0.01	7.3±0.1	7.1±0.2	7.4±0.05	7.8±0.1	7.6±0.1
Higher heating value (MJ/kg)										
Experimental	16.2±0.1	15.5±0.4	19.2±0.4	17.4±0.1	17.7±0.1	17.9±0.2	17.1±0.3	17.6±0.5	17.9±0.3	13.3±0.4
Calculated (Dulongs)	15.4±0.3	14.9±0.6	17.3±0.6	15.2±0.2	15.5±0.3	18.0±0.7	16.9±0.3	15.9±0.8	16.4±0.6	15.5±0.1
Std. Dev.	0.57±0.01	0.42±0.01	1.34±0.02	1.56±0.1	1.56±0.1	0.07±0.01	0.14±0.01	1.20±0.04	1.06±0.01	1.56±0.02

[a] All experiments were done in triplicate and the mean is reported here. Statistical significance has been determined for those components which are present in a higher amount. Values in the same row with different superscripts letters indicate significant difference at $P \leq 0.05$.

[b] % of fixed carbon calculated by the difference of moisture, ash & volatile matter.

[c] % of O calculated from the difference of CHNS and ash.

CHNS/O analysis of biomass is given in Table 3.2 and is used for calculation of higher heating value using Eq.1. (Materials and Methods). Carbon in all the samples is present in the range of 37.1-46.8%. Hydrogen lies in the range of 5.5-6.7% and oxygen, as calculated by the difference method, is in the range of 36.0-49.4%. Nitrogen and sulphur are found in the range of 0.2-1.2 and 0.04-0.9% respectively. The higher content of oxygen in CC was responsible for the higher volatile matter (80%) but it lowers the higher heating value (13.3 MJ/Kg).

In biomass, ash content may originate from the biomass itself, e.g. nutrient that the plant absorbs from the water or the soil during its growth (Na, K, Fe etc.) or during harvesting, e.g. soil collected along with biomass. Ash but also inorganic materials like P, mostly in the form of oxides. Estimation of the ash is essential before any biomass processing conversion process for biofuel production as it may significantly impact the conversion, especially in the biochemical process.[252] Moreover, these metals may deactivate the catalyst being used in the thermochemical process.[253] Ca, Mg and K are the most abundant metals found in most of the biomass residues. The difference in metal oxide concentration might be due to the variable physical demands for the mineral nutrition, osmatic pressure and cell maintenance during uptake from soil for plant growth.

The metal composition of ash is presented in Table 3.3. During ash determination, all the metals are converted to their oxides, even though remain in a different form in the agricultural residues. Table 3.2 shows that RS and RH have higher ash content, i.e. 13.7% and 17.4% respectively as compared to other biomass which may be due to the presence of high content of silica (Table 3.3). A similar observation was reported by Binod et al. (2010).[237]

In literature, it is mentioned that enzymatic hydrolysis of RS, RH, WS and other biomass were affected by metal cations (Mg^{2+}, K^{+}, Ca^{2+}, Al^{3+}, Mn^{2+}, Cu^{2+}, Fe^{3+} and Zn^{2+}) by affecting the cellulase enzyme activities.[253] β-glucosidase activity was reported to be promoted by Ca^{2+} and Mg^{2+}, while inhibited by K^{+}. Data in Table 3.3 shows the presence of significant amount of metals which need to be considered before processing the biomass for biofuels production.

The C/H ratio as given in Table 3.2 for each biomass is in the range of 5.8-7.8%. On C/H basis, it is observed that RS, WS, CS, JP and CRS have high energy content as they are rich in C/H ratio, whereas, CC has a low higher heating value (13.3 MJ/kg) due to low C/H ratio as given in Table 3.2. The Higher heating value of CS (19.2 MJ/kg) and JP (17.9 MJ/kg) shows their potential for the production of biofuels using thermochemical process due to the presence of high amount of carbon 46.8 and 45.9% with high C/H ratio respectively.

3.4.2 THERMAL PROPERTIES ANALYSIS

Thermogravimetric analysis (TGA) provides the loss in weight of biomass with an increase in temperature as shown in Figure 3.3. TGA is basically an indicator for the optimisation of process conditions for gasification and pyrolysis. Moreover, it is an indicator of the contents of moisture, cellulose, hemicellulose and lignin present in biomass. Thermal decomposition of biomass occurs in the order of hemicellulose (branched chain) followed by cellulose (highly crystalline), and lignin.[246] From the analysis of these superimposed DTA curve that TGA-DTA curves were almost similar (Figure 3.3 and Figure 3.4) and hence showing the similar components in a different amount.

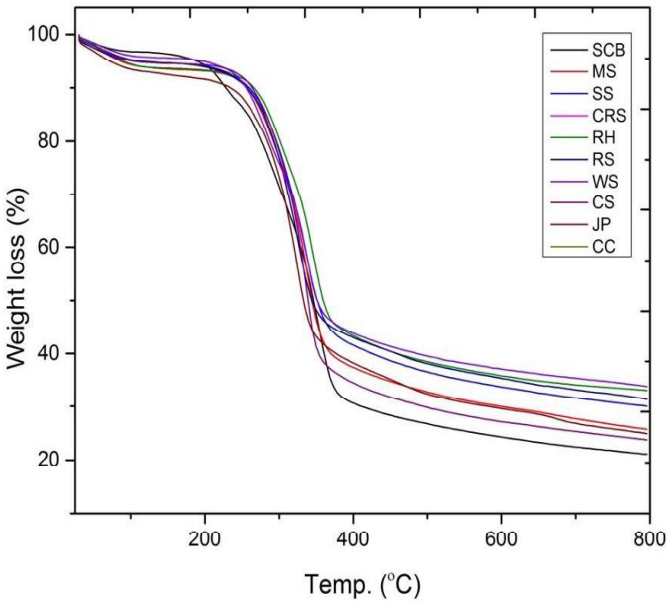


Figure 3.3 Thermogravimetric analysis of biomass samples

Table 3.3 Metal oxide content (% dry wt., w/w) in biomass

Metal Oxide (%w/w)	RS	RH	CS	WS	SCB	CRS	SS	MS	JP	CC
Al_2O_3	0.135	0.263	0.037	0.194	0.177	0.181	0.184	0.195	0.016	0.739
CaO	0.276^{A}	0.212^{A}	0.414^{B}	0.359^{B}	0.207^{A}	0.57^{C}	0.585^{C}	1.838^{D}	0.831^{D}	0.235^{A}
Fe_2O_3	0.099^{A}	0.075^{B}	0.017^{C}	0.094^{A}	0.081^{B}	0.16^{D}	0.099^{A}	0.123^{E}	0.011^{C}	0.261^{F}
K_2O	1.323^{A}	0.09^{B}	0.826^{C}	0.113^{B}	0.097^{B}	1.027^{D}	1.205^{D}	0.904^{C}	1.653^{E}	0.314^{F}
MgO	0.483^{A}	0.177^{B}	0.188^{B}	0.226^{B}	0.144^{B}	1.144^{B}	0.486^{A}	0.471^{A}	0.555^{A}	0.182^{B}
Na_2O	0.159^{A}	0.054^{B}	0.578^{C}	0.351^{D}	0.127^{A}	0.121^{A}	0.136^{A}	0.132^{A}	0.534^{C}	0.257^{D}
P_2O_5	0.123	0.183	0.079	0.075	0.103	0.739	0.448	0.110	0.283	0.153
TiO2	0.004	0.010	0.002	0.008	0.008	0.008	0.005	0.007	0.001	0.029
ZnO	0.002	0.005	0.000	0.001	0.001	0.003	0.004	0.001	0.001	0.003
Oxides[b]	2.604	1.069	2.141	1.421	0.945	3.953	3.152	3.781	3.885	2.173
SiO_2[c]	11.086	16.301	1.349	9.049	3.465	7.167	5.628	4.209	1.185	3.477

[a] All experiments were conducted in triplicate and the mean value is reported. [b] Sum of all oxides. [c] Silica content is calculated by the difference of ash and total oxide.

Statistical significance has been determined only for those metals which are present in a higher amount. Values in the same row with different superscripts letters indicate significant difference at $P \leq 0.05$.

Thermochemical decomposition of lignocellulosic biomass is a complex process, which involves a series of competitive and/or consecutive and parallel reaction and mainly occurs in four stages. The first stage corresponds to drying phase in which unbound moisture is lost from 30-150 °C across different biomass samples, corresponding to 4-12% weight loss as given in Table 3.4. Maximum degradation temperature (T_{max}) is observed from 52 to 70 °C. Second stage, contributes the depolymerization of hemicellulose from 150-350 °C with 43-54% due to the degradation, primarily a part of hemicellulose, cellulose, and bound water. T_{max} of hemicellulose in various samples is observed from 225.4 °C (SCB) to 287.9 °C (WS). The third stage is for cellulose degradation from 275-350 °C with 30-53% losses. T_{max} of cellulose in various samples is observed from 323.6 (RS) to 353.0 °C (SCB) (Table 3.4).

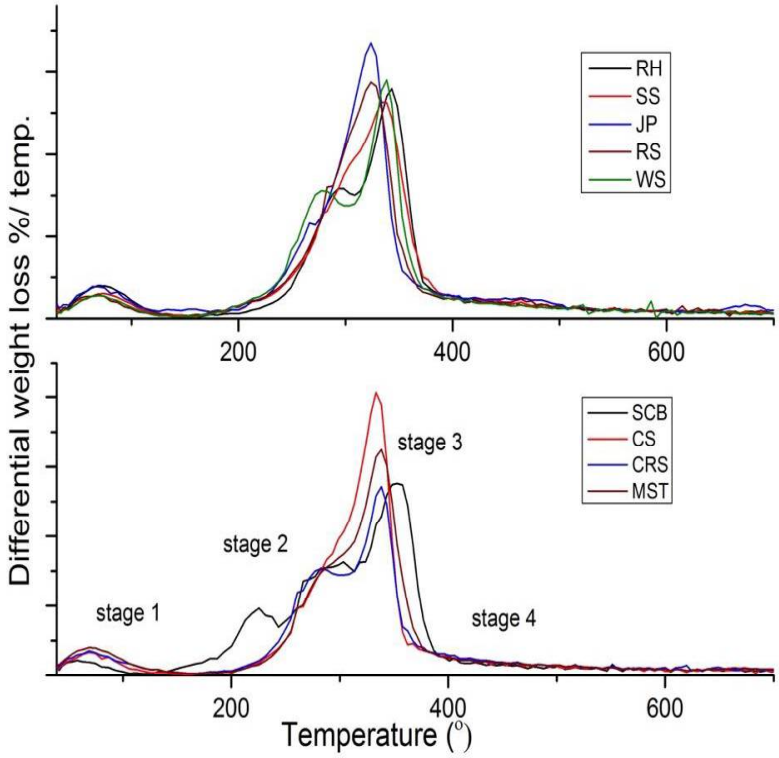


Figure 3.4 Differential thermogravimetric analysis of biomass samples

The fourth stage involves the degradation of lignin from 330-550 °C with 10-34% weight loss as given in Table 3.4. Lignin is a highly-branched,

aromatic, amorphous, water-insoluble heteropolymer, synthesized by three benzene propane units by free radical mechanism: coniferyl alcohol (guaiacyl propanol), coumary alcohol (p-hydroxyphenyl propanol) and sinapyl alcohol (syringyl propanol) having very high molecular weight and hence, has high thermal stability as compared to cellulose and hemicellulose. No prominent T_{max} is observed for lignin, which may be due to the nonspecific and a very large variation of structural features and a slower rate of decomposition.

Higher T_{max} shows higher thermal stability, which varies from one biomass to another depending upon the chemical constituents and their chemical structures.[254] Hence, the thermal stability of all the three components varied significantly. Among the three major components, the hemicellulose is easiest to decompose due to branched structural features with short side chains showing a broad range of T_{max} for different samples. A similar observation was reported by Wu et al. (2009).[255] In contrast, cellulose is associated with a semi-crystalline structure which makes it thermally more stable. The sharper T_{max} shows an abrupt weight loss of biomass observed for cellulose. That may be due to the highly specific and highly ordered structure of cellulose.

3.4.3 XRD ANALYSIS

CrI was measured by the ratio of the intensity of the main crystalline plane (002) at 22.4° and the amorphous at 16.3° of 2θ.[248] X-ray diffractogram obtained for biomass samples are given in Figure 3.5 and quantitative crystallinity was estimated by using Eq. 2. (Materials and Methods) Table 3.4 summarises the CrI for different biomass samples as calculated by peak intensity method. The peak at I_{002} indicates the presence of crystalline material in the biomass and the higher CrI is mainly due to the lower amount of amorphous material, i.e. hemicellulose and lignin.[256] It has been reported in the literature that highly crystal packing of cellulose fibrils in cell wall retards the activity of cellulases for enzymatic hydrolysis, hence lead to a lower sugar conversion and ethanol yield.[256] Highest and lowest CrI were found in RS (61.9%) and CC (43.0%) respectively. This shows that RS could be less effective towards enzymatic hydrolysis than other biomass, whereas CC could be more susceptible to enzymatic digestion.

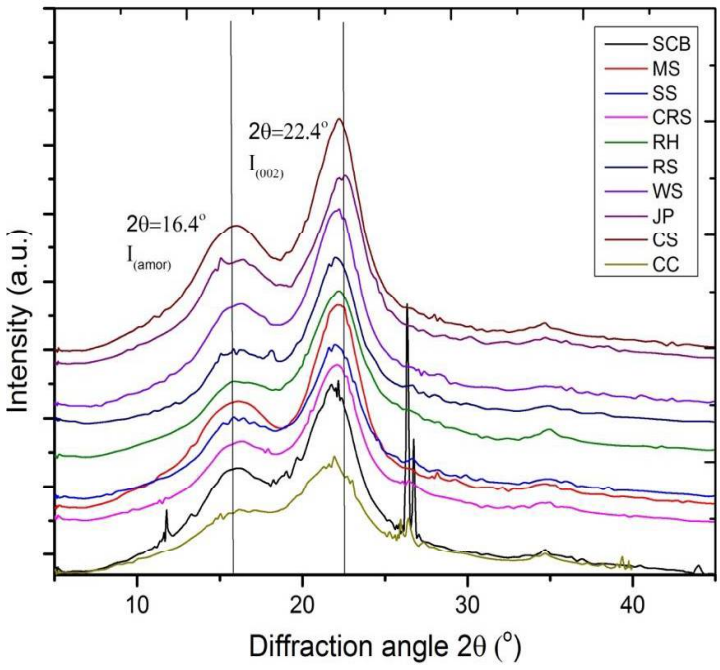


Figure 3.5 X-ray diffraction pattern of biomass samples

CrI and DTA (T_{max}) of cellulose are reported in the same order, i.e. increasing CrI leads to increase in T_{max}.[254] However, in the current study, the results obtained from Figure 3.4 and 3.5, as discussed above, show that the CrI and the T_{max} in some cases follow the reverse order. These results are contrary to cellulose and are unexplainable. However, crystallinity is dependent on the degree of polymerization, the content of cellulose, hydrogen bonding, and the ordered structure. The crystallinity discussed above only signifies the volume of ordered structure and hence, other factors also need a better understanding.

3.4.4 COMPOSITIONAL ANALYSIS

Compositional analysis of all biomass samples is summarised in Table 3.5, revealing that extractives, cellulose, hemicellulose, protein and lignin content vary significantly from one biomass to another. Analysis of water extractives indicates a complex mixture of soluble mineral, proteins, and non-structural carbohydrates, etc. whereas, ethanol extracts indicate the presence of proteins and fatty acids, etc. (characterization data is not reported here). Ethanol

extractives are in the range of 0.8-3.4% as given in Table 3.5. Cellulose is in the range of 28.3% (CRS) to 39.5% (MS), whereas, hemicelluloses, 13.9% (RH) to 29.0% (CC) (Table 3.5). CRS has the lowest cellulose (28.3%) content and maximum hemicellulose is found in CC (29.0%) followed by RS (19.9%) and CS (19.2%), as given in Table 3.5.

Lignin plays very important role in the biomass as a structural component which provides tensile strength and rigidity to biomass residues.[257] The AIL is present in the range of 11.9% (RS) to 26.4% (RH), whereas, ASL is 1.4-2.5%. Maximum ASL is in SCB (2.7%) and minimum in RH (1.4%) as given in Table 3.5. The protein content is in the range of 1.3 to 5.4% of dry biomass. All these components except moisture will be beneficial to produce more biofuels by thermochemical platform, whereas for biochemical, only structural carbohydrates are useful. An appropriate biomass for ethanol production should represent a higher amount of carbohydrates (cellulose and hemicellulose content) than lignin and ash content. The highest content of sugars present in CC (61.2%) and CS (58.6%) makes them a material of choice for bioethanol production.

CrI of RS (61.9%) was found to be higher than CC (43%) and this was due to the difference in their hemicellulose and lignin contents. Hemicellulose and lignin contents in RS are 19.9 and 13.2%, respectively, whereas in CC, 29.0 and 18.4% respectively (Tables 3.5).

Table 3.4 Crystallinity index and thermogravimetric analysis (weight loss%)[a]

Analysis	RS	RH	CS	WS	SCB	CRS	SS	MS	JP	CC
CrI (%)	61.9±1.1	58.8±1.7	56.0±1.0	58.0±1.2	52.6±1.2	56.0±0.2	55.0±1.1	59.6±1.1	57.8±1.1	43.0±1.3
$T_{max.}$ (Cellulose, °C)	323.6±1.0	343.3±3.4	333.5±2.2	338.8±4.2	353.0±1.2	338.4±1.2	333.5±1.9	338.4±1.2	323.6±1.2	332.3±1.7
$T_{max.}$ (Hemicellulose, °C)	282.6±1.8	287.9±1.9	282.2±3.2	287.9±4.2	225.4±3.0	277.5±2.2	277.4±1.2	287.6±1.1	266.2±1.3	287.3±1.5
TGA stages (°C)	Weight loss%									
Stage 1	6	7	6	5	4	6	6	7	8	9
Stage 2	46	43	54	47	42	53	44	49	50	51
Stage 3	38	37	46	35	34	33	53	31	32	38
Stage 4	21	20	10	13	34	25	16	14	12	29

[a]Ash content is included in Table 3.1 and all experiments were conducted in duplicate and the mean is reported.

Table 3.5 Chemical composition of various biomass[a]

(% dry wt., w/w)	RS	RH	CS	WS	SCB	CRS	SS	MS	JP	CC
Water extractives	13.3±0.2^{A}	6.2±0.3^{B}	6.2±0.2^{B}	10.9±0.1^{C}	17.4±0.4^{D}	17.6±0.2^{D}	17.4±0.4^{D}	8.9±0.2^{E}	10.1±0.1^{C}	12.6±0.2^{A}
Ethanol extractives	3.4±0.1^{A}	2.9±0.05^{A}	1.4±0.4^{C}	2.1±0.3^{D}	2.2±0.7^{D}	2.9±0.1^{A}	0.8±0.01^{C}	0.9±0.01^{C}	2.8±0.205^{A}	2.5±0.03^{A}
Cellulose	38.1±0.3^{A}	32.4±0.4^{B}	39.4±0.5^{A}	36.6±1.0^{A}	36.6±0.6^{A}	28.3±0.2^{C}	35.4±0.6^{A}	39.5±1.6^{A}	38.8±1.3^{A}	32.2±1.0^{A}
Hemicellulose	19.9±0.1^{A}	13.9±0.2^{B}	19.2±0.1^{A}	18.9±0.5^{A}	18.7±0.2^{A}	16.4±0.9^{C}	17.4±0.6^{C}	18.7±1.1^{A}	16.4±1.0^{C}	29.0±0.4^{D}
Lignin (AIL)	11.9±0.7^{A}	26.4±0.1^{B}	23.2±0.4^{C}	20.3±0.6^{D}	19.8±0.7^{D}	21.5±0.7^{E}	18.8±0.4^{F}	22.5±0.9^{C}	25.4±1.2^{G}	15.8±0.1^{H}
Lignin (ASL)	2.2±0.3^{A}	1.4±0.1^{B}	1.6±0.04^{B}	1.9±0.04^{A}	2.7±0.05^{C}	2.3±0.2^{A}	2.5±0.01^{A}	2.2±0.2^{A}	2.5±0.1^{A}	2.6±0.05^{A}
Protein content	1.3±0.7^{A}	3.3±0.2^{B}	2.0±0.03^{C}	2.5±0.04^{D}	2.7±0.04^{E}	2.6±0.6^{D}	3.2±0.2^{B}	2.1±0.2^{C}	5.4±0.2^{F}	2.6±0.04^{D}

[a]Ash content is part of the chemical composition and is included in Table 3.1 and all experiments were done in triplicate and the mean is reported. Values in the same row with different superscripts letters indicate significant difference at $P \leq 0.05$.

Interestingly, T_{max} of RS (323.6 °C) was found to be lower than CC (332.3 °C). In general, higher the CrI, higher is the T_{max}.[254] However, in the current study, the results obtained from Figure 3.4 and 3.5 show that the CrI and the T_{max} for some LCB do not follow this trend. This is due to the effect of degree of polymerization, cellulose and hemicellulose contents, hydrogen bonding and the ordered structure on crystallinity and thermal properties of biomass.[130]

3.4.5 FOURIER TRANSFORM INFRARED SPECTROSCOPY

The FT-IR spectrum shown in Figure 3.6 reveals that the peak at ~3388 cm^{-1} is originated due to stretching of O-H groups for intra-molecular hydrogen bonds between cellulose chains. Two bands at around 2920 and 2850 cm^{-1}, related to asymmetric and symmetric methylene stretching in the spectra of all of the LCB. The band at ~1629 cm^{-1} is due to water in the amorphous region and 1053, 1035 and ~1157 cm^{-1} is attributed to the characteristic of C-O-C stretching (I^{st} two) and C-O antisymmetric bridge stretching respectively. The bands around 1420-1430 cm^{-1} are associated with the amount of the crystalline cellulose and the intensity of this band is more pronounced in RS, MS and CS as compared to others due to high cellulose content (Table 3.5 and Figure 3.6). Band due to vibration of β-glycoside linkage in cellulose is detected as a sharp peak at ~896 cm^{-1} which represents the C_1-H deformation with a ring vibration contribution for amorphous nature. The bands at ~1246, ~1375 and ~1157 cm^{-1} are assigned to C-H stretching, CH_2 wagging and C-O stretching respectively in cellulose. Absorption bands at ~1629, ~1508 cm^{-1} are originated from lignin, which includes the aromatic skeleton vibrations involving both C-C stretchings. C=C of aromatic skeletal vibration in polymeric lignin appears around 1500-1700 cm^{-1} and C-H symmetric and asymmetric stretching bands appears in the region of ~2900 cm^{-1}.[258]

Stretching frequency at 1246 and 1732 cm^{-1} is attributed to C=O and C-O stretching bands of the acetyl ester units present in hemicelluloses. The intensity of 1732 cm^{-1} band is more pronounced in CC with reduced intensity at 1420-1430 cm^{-1} bands due to high hemicellulose content (29.0%) and low cellulose content (32.2%) resulting in its lower crystallinity (43%), which is

supported by XRD also. However, RS, RH, MS, and SS have high crystallinity (~ 58.5-61.9%) due to decreased intensity of 1246 and 1732 cm^{-1} bands and increased intensity of 1420-1430 cm^{-1} bands (Table 3.6 and Figure 3.6).

Table 3.6 Characteristic FT-IR bands of functional groups present in the LCM

Band position (cm^{-1})	Peak Assignments
3388	OH stretching
2918	C-H stretching of aliphatic structure of cellulose and hemicellulose
1732, 1726	C=O stretching vibration in acetyl groups of hemicellulose
1629	C=C stretching vibration in aromatic ring of lignin
1508	C=C stretching vibration in aromatic ring of lignin
1421	CH_2 scissoring at C6 in cellulose and C-H of crystalline cellulose
1462-1425	CH_2 cellulose and lignin
1375	Symmetric C-H bending and C-H deformation in cellulose and hemicellulose.
1325	C-H deformation (symmetric) of cellulose
1246	C-O stretching vibration in lignin, xylan and ester groups
1105	O-H association bands in cellulose and hemicellulose (crystalline cellulose)
1157	C-O-C vibration in cellulose and hemicellulose
1053	C=O at C-3 and C-C of cellulose
1035	C-O stretching vibration in cellulose and hemicelluloses
896	Glucose ring stretch C-H deformation and C-H of amorphous cellulose

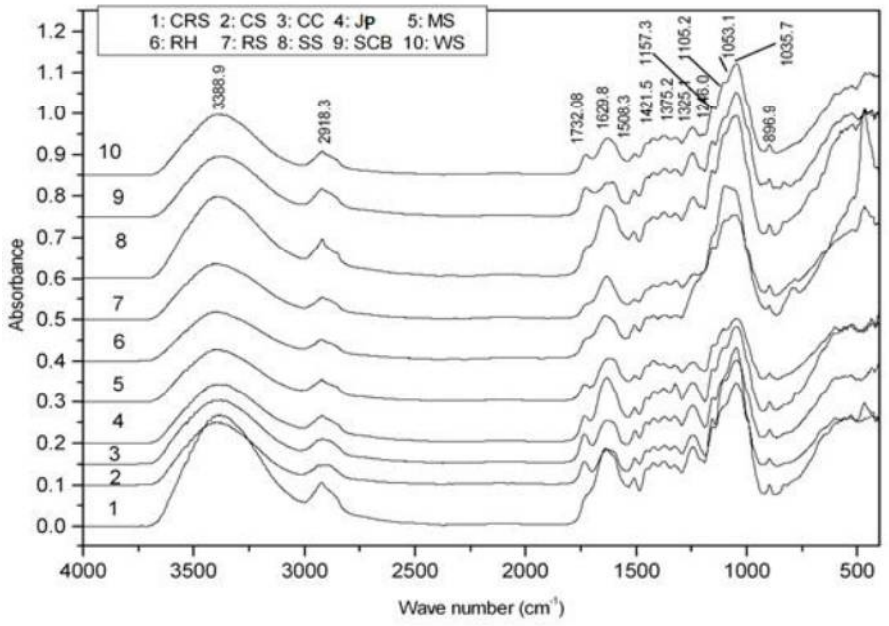


Figure 3.6 FT-IR Spectra of native biomass samples

3.5 CONCLUSION

The physicochemical characterization of all these biomass shows that CS, RS, and MS are the potential candidates for biofuel production by both for thermochemical and biochemical conversion platforms. This is due to their higher heating value, devolatilization, cellulose and hemicellulose content. Although many of these biomasses are found with a higher amount of inorganic salt yet, all of the biomass showed good potential for biofuels production. The highest content of polysaccharide present in CC and CS makes them a material of choice for bioethanol production. The higher heating value of CS and JP make them suitable for thermochemical conversion to biofuels. This is a systematic report of one of its kind on the physicochemical characterization of ten biomass residues available in North India. This study provides the baseline of the future work on biomass to biofuels conversion.