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LIGNOCELLULOSIC BIOMASS CHARACTERISTICS FOR BIOENERGY APPLICATION: AN OVERVIEW

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Abstract

Considering world energy demand and its security, much attention has been focused on identifying promising lignocellulosic substrates to generate a variety of downstream fuels and chemicals. In response, a recent key research area has centered on hydrolysis of cell wall polysaccharides by various physical, chemical and biological means. Due to their complex chemical and molecular structure, there is a substantial knowledge gap in understanding of biomass recalcitrance and its relationship with cell wall structure. It has delayed the response in meeting the target to achieve economically feasible large-scale conversion of lignocellulosic biomass to biofuel and market entrance. Biomass of wheat straw, rice straw, corn stover, sugarcane bagasse and switchgrass has been characterized to assess their potential for bioenergy application. The mechanism involved in digestibility of lignocellulosic biomass is complex since it is hindered by many physico-chemical, structural and compositional factors. This paper highlights recent advances in analytical methods employed for physico-chemical characterization of lignocellulosic biomass and its deconvolution to maximize the benefit of biomass as a material and energy feedstock.

Keywords: characterization, FTIR, lignocellulose, TGA, XRD

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1. Introduction

Lignocellulosic biomass as alternative and renewable energy resource for subsequent conversion to biofuel shows notable effect on economic dependency and technical advancement. Lignocellulosic biomass is most abundant organic material on earth, with an overall annual worldwide production of 1×10^{10} MT, a suitable source to provide alternative transportation fuels such as bioethanol or biodiesel (Hamelinck et al., 2005; Sanchez and Cardona, 2008; Sun and Cheng, 2002). In the future, potentials exist for inexpensive, ecofriendly, renewable and sustainable biofuel due to increasing energy demand (Chaturvedi and Verma, 2013; Zanoni et al., 2017). It has become imperative to search for alternative sources of energy which can replace conventional fossil fuels (Wan and Li, 2011). Recently, lignocellulosic biomasses have gained momentum for their conversion into high value products including biofuels (Adsul et al., 2011).

At present world ethanol market is dominated by United States and Brazil, accounting world ethanol production of 48% and 28%, respectively. World bioethanol production was 113 billion liters in 2013 and is expected to reach 168 billion liters by 2022 (OECD-FAO, 2013). Corn, starch and sugar substances need a preferred substitute as they have great food and feed value. In this context, there is an urge for suitable substrate which has definite potential for biofuel production. Lignocellulosic biomass comprises of cellulose, hemicelluloses, lignin, extractives and several 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

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20,000 (Zhang and Lynd, 2004). Hemicellulose, a complex carbohydrate, comprise of pentoses (e.g. xylose and arabinose), hexoses (e.g. mannose, glucose and galactose) and sugar acids (Hendriks and Zeeman, 2009). The dominant component of hemicellulose from hardwood and agricultural plants, like grasses and straw, is xylan, while this is glucomannan for softwood (Saha, 2003; Soudham, 2011). It establishes the connection of lignin with cellulose fibers making cellulose-hemicellulose-lignin network more rigid (Laureano-Perez et al., 2005). The most abundant polymer after cellulose and hemicelluloses is lignin, consists of three different phenylpropane units (p-coumaryl, coniferyl and sinapyl alcohol) (Hendriks and Zeeman, 2009).

Determining relative quantities of cellulose, hemicellulose and lignin in lignocellulosic feedstock is often required in studies involving fractionation (Gaspar et al., 2005; Shill et al., 2010; Zhang et al., 2007), fermentation (Qi et al., 2010; Shafiei et al., 2010;), or other modification (Chen et al., 2011a; Li et al., 2009; Sievers et al., 2009a).

Since last few years, various biomass such as rice straw, barley straw, timothy grass, flax straw, pine wood (Naik et al., 2010; Vasmara et al., 2017), areca nut husk, moj, bonbogori (Sasmal et al., 2012), broom, heath, carqueisa and gorse (Viana et al., 2012) have been characterized to assess the potential for bioenergy production. The mechanism involved in digestibility of lignocelluloses is still technically complex because the digestibility of cellulose is hindered by many physico-chemical, structural and compositional factors (Alvira et al., 2010). The cellulose microfibrils consist of both crystalline (around 2/3 of the total cellulose) and amorphous component and the crystallinity is given by the relative amounts of these two (Taherzadah and Karimi, 2008). It was believed that accessible amorphous portion of the cellulose was preferred over less accessible crystalline portion by the celluase enzyme. The concept was broadly established that depolymerization of lignocellulosic biomasses increase with decrease in the crystallinity (Chang and Holtzapple, 2000; Nanda et al., 2013). On the contrary, more crystalline lignocelluloses have been reported to show more digestibility (Akhtar et al., 2012; Kuila et al., 2011).

Globally, the biggest hurdle for the production of bioenergy is the lack of low-cost technologies to overcome the biomass recalcitrance, primarily due to presence of lignin (Palonen et al., 2004). To make cellulose more accessible for hydrolytic enzymes, lignin component must be separated (Selvi et al., 2009) which primarily depends upon degree of polymerization, degree of crystallinity, structural composition and availability of surface area (Qi et al., 2009). There is a need for selection of suitable lignocellulosic feedstock based on physico-chemical characteristics to assess biomass having potential for biofuel production. The general outline of biomass characterization is represented in Fig. 1.

A large number of studies focused on pretreatment techniques in context of lignocellulose hydrolysis have been reviewed (Alvira et al., 2010; Carvalheiro et al., 2008; Chaturvedi and Verma, 2013; Geddes et al., 2011; Hendriks and Zeeman, 2009; Taherzadeh and Karimi, 2008; Yang and Wyman, 2008;). Substantial knowledge gap exists in understanding the mechanism of biomass recalcitrance and its relationship to complex cell wall structure. In this review, the technical aspects of different physico-chemical techniques have been emphasized for selected biomass. Accordingly, improvements in recent analytical techniques will require a better understanding of mechanisms of biomass recalcitrance, hydrolysis and its relationship to cell wall structure. To the best of our knowledge, rare literature is available on recent technologies involved in characterization of biomass to liquid sustainable fuel.

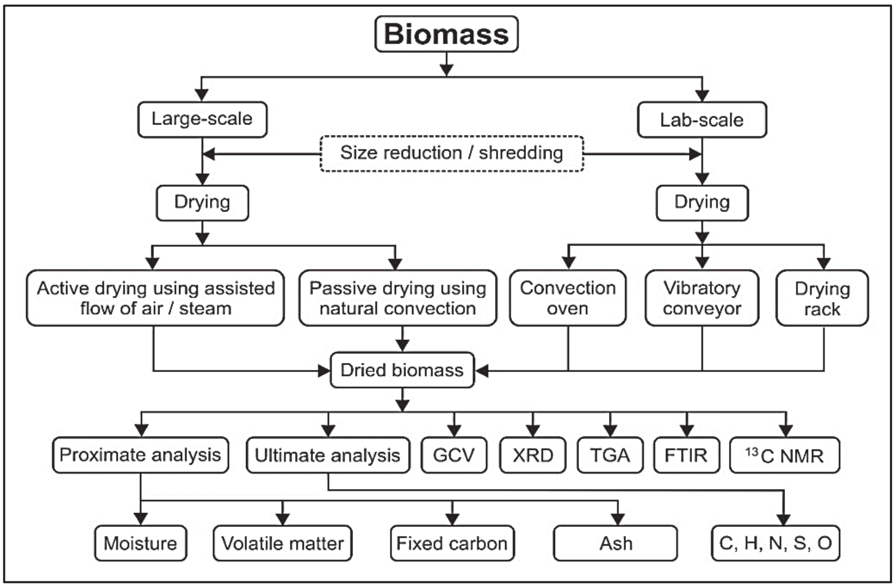

Fig. 1. Simplified schematic representation of physico-chemical characterization of biomass

2. Lignocellulosic biomass

Globally, rice straw, wheat straw, corn stover and sugarcane bagasse production amount reached to approximately 731, 354, 80-100 and 181 million tons (MT) per year, respectively (Binod et al., 2010; Kadam and McMillan, 2003; Sarkar et al., 2012). Amongst available lignocellulosic biomasses, rice straw and wheat straw are produced mainly by Asia, whereas America is the major producer of corn straw and bagasse (Sarkar et al., 2012). These feed stocks are most favorable for bioethanol production due to their availability throughout year (Sarkar et al., 2012). However, substrates such as rye husk, oat straw (Adapa et al., 2009), barley straw (Adapa et al., 2009; Garcia-Aparicio et al., 2011; Naik et al., 2010), rice straw, barley straw, timothy grass, flax straw, pine wood (Naik et al., 2010), biomasses of areca nut husk, moj, bonbogori (Sasmal et al., 2012), broom, heath, carqueisa and gorse (Viana et al., 2012) have been physico-chemically characterized. There is a need for selection of suitable lignocellulosic feedstock to maximize the benefit of biomass as a material and energy feedstock. The ability to conduct reliable material characterization at multiple length scales, targeting specific recalcitrance-related properties is essential (Foston and Ragauskas, 2012).

Knowing accurately the chemical composition of lignocellulosic biomass is getting more importance in this industrialized era for making the process of converting biomass to biofuel feasible. In this context, numerous wet chemical analytical methods are based on biomass fractionation followed by purification process that can be quantified using conventional analytical instruments. These analytical procedures are standardized by the American Society for Testing and Materials (ASTM) and the Technical Association of the Pulp and Paper Industry (TAPPI). Despite their accuracy and robustness, these methods cannot be applied in large-scale conversion process, as they are expensive and time consuming.

3. Parameters used to determine the viability of feedstock for biofuel production

Lignocellulosic biomass is considered as storehouse of renewable carbon and has enormous potentials for development of renewable energy system. There is a need for accurate and better understanding of biomass characteristics, mechanism of biomass recalcitrance and its relationship to cell wall structure to reveal the nature of feedstock. Conventional techniques and data of quantified parameters for proximate and elemental analysis, gross calorific value (GCV), cellulose, hemicellulose and lignin content have been employed to characterize the biomass since decade and discussed in this article. Further, recent advances in analytical methodology to characterize the chemical and molecular features of the biomass gained importance. Various physico-chemical characterization techniques have been developed during past decade to delineate properties of lignocellulosic biomass for biofuel generation (Alvira et al., 2010). In this context, characterization using Scanning electron microscopy (SEM), X-ray diffraction (XRD) analysis, Thermal gravimetric analysis (TGA), Fourier transforms infra-red (FT-IR) and Solid state ^{13}C cross polarizing magic angle spinning (CP/MAS) NMR spectroscopy continuously facilitating comprehensive research, have been reviewed thoroughly. Scanning electron micrographs of various lignocellulosic materials (0.5 mm) such as wheat straw (Fig. 2a), sugarcane bagasse (Fig. 2b), rice straw (Fig. 2c) and eucalyptus chips (Fig. 2d) are represented to compare the surface morphology of the biomass, with varying amount of cellulose, hemicelluloses and lignin (Table 4).

For better understanding and interpretation of the foreseeable results, we characterized dried wheat straw biomass (0.5 mm) using XRD, TGA, FT-IR and Solid state ^{13}C CP/MAS NMR spectroscopy (Fig. 3). Moreover, other characterization techniques based on near infrared spectroscopy (NIR), high-performance liquid chromatography (HPLC), multi-plate reactor, monoclonal antibody microarrays, mass spectrometry (MS) and pyrolysis molecular beam mass spectrometry (py-MBMS) have also been mentioned.

4. Proximate analysis

Proximate analysis is the most often employed practice for biomass characterization. It determines the weight percent of moisture, volatile matter (VM), fixed carbon (FC) and ash content of a biomass. Table 1 lists the moisture, ash, VM, FC and gross calorific value (GCV) of different biomass. Based on the values presented in Table 1, poplar wood can be considered as viable feedstock for biofuel production and the same has been exploited for ethanol production from southern Europe by Gonzlaez-Garcia et al. (2011). Characterization using proximate analysis is easy and time saving as it requires use of standard laboratory equipments, however ultimate analysis is utmost important for accurate results of major elements such as carbon (C), hydrogen (H), nitrogen (N), sulphur (S) and oxygen (O) present in biomass. Moisture content plays a key role in the selection of energy conversion process technology (Cuiping et al., 2004). High moisture (>40%) is generally observed in bagasse, sludge, wood bark etc., on the other hand low moisture (~6 to 16%) content has been reported in biomass of juliflora, cotton, chilly stalk, rice husk and straw (Patel and Ghami, 2012).

Comparative low moisture content feedstock (<15%) is preferred using thermal conversion process, while bio-conversion can utilize biomass with high moisture content (Nanda et al., 2013). In addition, biochemical conversion of lignocellulosic substrate is favored by high moisture content for submerged fermentation, whereas comparatively low moisture (40-50%) containing biomass is suitable for solid state fermentation.

Table 1. Proximate analysis (wt%) and gross calorific value (MJ/kg) of different biomass.

Biomass	*Moisture*	*Ash*	*Volatile matter*	*Fixed carbon*	*GCV*	*Reference*
Wheat straw	7	8	84	8	--	Bakisgan et al. (2009)
	6	1	78	14	20	Naik et al. (2010)
Rice straw	5	8	69	17	17	Deng et al., 2009)
Corn stover	--	8	75	--	18	Kumar et al. (2008)
Sugarcan bagaase	4	2	77	16	19	Patel and Ghami (2012)
	6	3	66	25	--	Capareda (2011)
Switchgrass	10	4	82	15	--	Capareda (2011)
	4	5	83	11	20	Greenhalf et al. (2012)
Poplar wood	9.6	3.7	75.54	11.15	--	Slopiecka et al. (2012)
Eucalyptus	8	1	75	16	--	Guerrero et al. (2005)

For biochemical conversion, herbaceous biomass with high moisture is more suited, but it reduces calorific value and creates maintenance problems. Chemical, thermo-chemical and bio-chemical breakdown of biomass produces solid residue, representing recalcitrant carbon, converted to ash when subjected to complete combustion. Ash, the incombustible solid mineral matter of the biomass, mainly contains oxides of silica (SiO), alumina (AlO), iron (FeO), calcium (CaO) and magnesium (MgO). The distribution of chemical in ash invites operational problems such as slagging, fouling, sintering and corrosion owed to high alkali concentration. Ash content varies from 1-10% in promising lignocellulosic substrate (Table 1) for biorefining industry. It was observed that ash and moisture have negative effects on GCV (Garcia-Aparicio et al., 2012). Ignition and combustion problems for use of biomass fuels are mainly due to high moisture and ash content (Demirbas, 2004). The cations present in ash content retards the enzymatic saccharification of biomass samples, hence washing is recommended in order to remove water soluble and sticky inorganic materials before hydrolysis (Bin and Hongzhang, 2010). In biomass fuel, chemical energy is stored mainly in the form of FC and VM. The ratio released as a gas (including moisture) by heating to 950°C for 7 min is VM whereas the non-volatile organic mass which may also contain oxygen with hydrogen, excluding the ash and moisture contents is FC (Parikh et al., 2007). The fixed carbon is used to relate the heating value of the product and co-products (Capareda, 2011). The extent of biomass ignition and gasification as energy source can be estimated with VM and FC content depending on biomass utilization (McKendry, 2002). FC and VM provides fuel properties which render comparison of fuel after biochemical production from lignocellulosic biomass. Both VM and FC have positive effects on the calorific value (Majumder et al., 2008). Highest VM and FC was revealed by poplar wood and rice straw, respectively (Table 1). Biomass with high VM and low ash content may be selected as promising substrate for biofuel production (Sanchez et al., 2012).

5. Ultimate analysis

Elemental analysis illustrates the biomass composition in respect of the most abundant five elements (C, H, N, S and O) and total mineral matter. Owing to high carbon and low nitrogen and sulphur content (Table 2), poplar wood is considered to be a plausible biomass for green fuel generation. Energy generation from poplar bioenergy system is favored in southern Europe by Gasol et al. (2009), based on energy balance and environmental perspective. It is particularly important in evaluating fuel feedstock in terms of its pollution potential, calculating higher heating value and also to determine theoretical air-fuel ratio. Table 2 compares the existing data on ultimate analysis of different lignocellulosic feedstock. Carbon is the most principal component of biomass fuels, accrued from atmospheric CO_2 during photosynthesis process and majorly contribute to total heating value of biomass. Lignin, hemicellulose and cellulose content of lignocellulosic biomass correspond to fuel carbon content. Nitrogen and sulphur, procured from soil generates oxides as gaseous emission (NOx, SOx) on combustion therefore does not contribute to total heating value of biomass. In contrast to conventional fuels, biofuels demonstrate relatively low proportion of C, compared with total proportion of O and H, deteriorating fuel energy value due to lower energy contained in C=O and C-H bonds, in comparison to C-C bonds (McKendry, 2002). As it can be seen in Table 2, most of the studied lignocellulosic biomass presents C and O values at about 40 - 60% and 32 - 55% respectively. Lower nitrogen and sulphur content in energy fuels is crucial for environment protection due to their gaseous emissions. Presence of sulphur also hampers the catalytic efficiency by forming metal sulphides. Rapid deactivation of catalyst in presence of small amounts of sulphur compounds has been reported by Sauciuc et al. (2011) during synthesis of synthetic diesel from biomass using Fischer-Tropsch's process. Since it was having low energy density with high oxygen and acid content (Czernik et al., 2004), a hydrotreatement process was performed at 100 - 200 bar (Zacher et al., 2014) for the production of low oxygen hydrocarbons.

Table 2. Ultimate analysis (wt%) of different biomass

Biomass	*C*	*H*	*N*	*S*	*O*	*Reference*
Wheat straw	42	6	0.1	0.06	52	Naik et al. (2010)
Rice straw	41	5	0.7	--	41	Murakami et al. (2012)
	40.24	5.44	3.4	0.17	37.22	Lou et al. (2010)
Corn stover	47	5	0.7	0.3	38	Kumar et al. (2008)
Sugarcane bagasse	47	6	0.0	0.0	35	Asthana (2009)
	56	7	0.7	0.03	36	Oasmaa and Peacocke (2001)
	49	6	0.4	0.06	44	Greenhalf et al. (2012)
Poplar wood	45.5	6.26	1.04	--	47.2	Slopiecka et al. (2012)
Eucalyptus char	48	6	0.3	--	45	Guerrero et al. (2005)

Hydrotreating of bio-oil is disadvantageous due to catalyst coking and reactor plugging during revaporization of the condensed bio-oil (Elliott et al., 2009). Oxygen removal from intact biomass using fast hydropyrolysis and vapor-phase catalytic hydrodeoxygenation process was reported to produce range of liquid fuels (Venkatakrishnan et al., 2015).High N and ash content reduce hydrocarbon yield, as composition of biomass affect the conversion process (Naik et al., 2010). In response, it can be advocated that lower nitrogen content (<0.3%) of native lignocellulosic biomass suits enzymatic saccharification for ethanol production.

6. Gross calorific value (GCV)

Heating value is the amount of heat produced by a complete combustion of fuel and it is measured as a unit of energy per unit mass or volume of substance (e.g., kcal/kg, kJ/kg, MJ/kg, J/mol and Btu/m^3). The heat of combustion of fuels is expressed by the higher heating value (HCV) or gross calorific value (GCV) and the lower heating values (LHV). The HHV is defined as the amount of heat released when fuel is combusted and the products have returned to a temperature of 25°C. Whereas, the LHV is the net calorific value, determined by subtracting the heat of vaporization of water generated during combustion of fuel from HHV (Mericboyu et al., 1998).

The HHV of lignocellulosic feedstocks is foremost aspect which signifies energy or amount of heat released when ignited in presence of excess air. Available energy from the biomass is reduced due to excess of moisture, referencing to calorific value of biomass (McKendry, 2002). Wheat straw and switchgrass showed calorific value of 20 and 19.6 MJ/kg, respectively which may be responsive for the production of biofuel (Table 1). Numbers of established correlations are reported in literature which provides approximate prediction of heating value based on proximate, ultimate and compositional analysis of lignocellulosic biomass (Table 3). Demirbas (2002) reported HHV of 18.60 kJ/g for holocellulose (cellulose and hemicelluloses), whereas it was in the range of 23.26 to 26.58 kJ/g for lignin due to higher state of oxidation. Gasoline and diesel has heating value of about 47 MJ/kg and 45 MJ/kg, respectively, used as fuel for running internal combustion engines (Capareda, 2011), whereas heating values of 15-25 MJ/kg was observed with different biomasses. High calorific value of wheat straw and pinewood makes the biomass more efficient for the production of bio-energy (Naik et al., 2010). Many efforts were undertaken to associate HHV with biomass composition; Dulong's equation is most common and first reported for coal and is valid only when oxygen content is less than 10%, so not suited for lignocellulose biomass (Izhar et al., 2012).

7. Cellulose, hemicelluloses and lignin in lignocellulosic biomass

Cellulose, hemicellulose and lignin content of different biomasses are cited in Table 4. Comparative more cellulose content was observed in sugarcane bagasse, switchgrass and eucalyptus chips, may be potent feedstock for biochemical refineries. Cellulosic fibrils are associated in the form of bundles called macrofibrils, attached to each other by hemicelluloses and covered by lignin making cellulose resistant to both biological and chemical treatment (Taherzadeh and Karimi, 2008). Unlike cellulosic, hemicellulosic component of the biomass contains a random, amorphous, and branched structure, which shows comparatively less resistance towards hydrolysis, and therefore hemicelluloses are prone to hydrolytic attacks by acids to their monomers (Betancur and Pereira, 2010; Wyman et al 2005). Lignin, a very complex and recalcitrant molecule linked in a three-dimensional structure which in turns reduces the efficiency of the hydrolysis. Enzymatic hydrolysis of recalcitrant biomass is favored for pretreated biomass (Sun and Cheng, 2002) or low lignin content biomass obtained from genetically engineered crops (Duan et al., 2013). More lignin content of soft wood in comparison to hardwood and agriculture residues render the hint to use soft wood for hydrolysis and fermentation for bioethanol production.

8. Scanning electron microscopy (SEM) and X-ray diffraction (XRD)

Scanning electron microscopy of the native biomass fractions exhibited different surface structure with intact morphology. Distinct surface structures were observed with micrographs (Fig. 2) of different biomass samples such as wheat straw, sugarcane bagasse, rice straw and eucalyptus chips, probably due to diverse nature of lignocellulosic biomass. More compact structure was seen with the micrographs of sugarcane bagasse (Fig. 2b) and eucalyptus chips (Fig. 2d), greater lignin content of these samples (Table 4) might be one of the reasons. However, comparatively less compact and fibrillar structure was observed with the biomass of wheat straw (Fig. 2a) and rice straw (Fig. 2c), respectively.

Rigid and compact structure is mainly due to encapsulation of cellulose fibres by lignin-hemicellulose matrix, hinders accessibility of cellulose to enzymes. Significant structural changes could be seen in treated biomass fractions as a result of depolymerization of lignocellulosic components. Scanning electron microscopy was found to be an important tool to see the altered surface morphology for many biomass samples such as pretreated *Tamarix ramosissima* (Xiao et al., 2011), sugarcane bagasse (Binod et al., 2012), sugarcane top (Sindhu et al., 2012) and rice straw (Singh et al., 2014).

Table 3. Recent and established correlations used for prediction of higher heating value (HHV) of different biomass

Correlation	***Based on***	***Biomass type***	***Reference***
HHV = 19.914 - 0.2324 Ash	Proximate analysis	*Dendrocalamus latiflorus*	Ko et al. (2013); Sheng and Azevedo (2005)
HHV = -3.0368 + 0.2218VM + 0.2601 FC	Proximate analysis	Mango, litchi and longan	Nagle et al. (2011); Sheng and Azevedo (2005)
HHV = 0.3536 FC + 0.1559 VM - 0.0078 Ash	Proximate analysis	Wheat straw, rice straw, corn stover, corn cob, *Eucalyptus grandis*, sugarcane bagasse	Misginna and Rajabu (2014); Moreno et al. (2012); Parikh et al. (2005)
HHV = 0.3543 FC + 0.1708 VM	Proximate analysis	*Quercus rotund folia, Pinus halepensis, Eucalyptus saligna*	Cordero et al. (2001)
HHV = 35,430 -183.5 VM - 354.3 Ash	Proximate analysis	*Quercus rotund folia, Pinus halepensis, Eucalyptus saligna*	Cordero et al. (2001)
HHV = - 10.8141 + 0.3133 (VM + FC)	Proximate analysis	Plum, apple, walnut, olive	Kricka et al. (2010)
HHV = 3.55 C^2 - 232 C – 2230 H + 51.2 C - H + 131 N + 20,600	Ultimate analysis	*Miscanthus*a, willow, sunflower, hemp waste	Bridgeman et al. (2010); Friedl et al. (2005); Toscano and Pedretti (2009)
HHV = 0.3491 C + 1.1783 H + 0.1005 S - 0.1034 O - 0.0151 N - 0.0211 Ash	Ultimate analysis	Wheat straw, rice straw, rape straw, maize, switchgrass	Channiwala and Parikh (2002); Chen et al. (2011b); Greenhalf et al. (2012); Wilaipon and Fung (2002)
HHV = 0.4373 C -1.6701	Ultimate analysis	Plum, apple, walnut, olive	Kricka et al. (2010); Saidur et al., (2011)
HHV = 8080 C + 34,460 H - 4,308 O +2250 S (Dulong's equation)	Ultimate analysis	Plum, apple, walnut, olive	Kricka et al. (2010)
HHV = 35,160C + 116,225 H – 11,090 O + 6,280 N + 10,465 S (Boie's equation)	Ultimate analysis	Plum, apple, walnut, olive	Kricka et al. (2010); Sami et al. (2001)
HHV = 0.335 C + 1.423 H - 0.154O-0.145 N (Modified Dulong's equation)	Ultimate analysis	Plum, apple, walnut, olive	Kricka et al. (2010)
HHV = - 1.3675 + 0.3137C + 0.7009 H + 0.0318 O	Ultimate analysis	Corn stover	Medic et al. (2012); Sheng and Azevedo (2005)
HHV = 0.0889 L + 16.8218	Lignin content	Olive husk, walnut, sunflower	Demirbas et al. (2002)
HHV = 0.0877 L + 16.495	Lignin content	Sugarcane bagasse	Chen et al. (2012)

Ash, Volatile Matter (VM), Fixed Carbon (FC), C, H, N, S, O and lignin content are expressed as wt% basis

Table 4. Cellulose, hemicellulose and lignin (wt.%) content of different biomass

Biomass	***Cellulose***	***Hemicellulose***	***Lignin***	***Reference***
Wheat straw	35	29	21	Naik et al. (2010)
	34	24	14	Adapa et al. (2009)
Rice straw	39	24	6	Chandra et al. (2012)
Corn stover	43	24	11	Zeng et al. (2011)
Sugarcane bagasse	35	24	22	Rezende et al. (2011)
	45	28	23	Sun and Cheng (2002)
Switchgrass	36	31	6	Greenhalf et al. (2012)
Poplar wood	44	32	21	Meng et al. (2012)
Eucalyptus chips	45	15	26	Emmel et al. (2003)

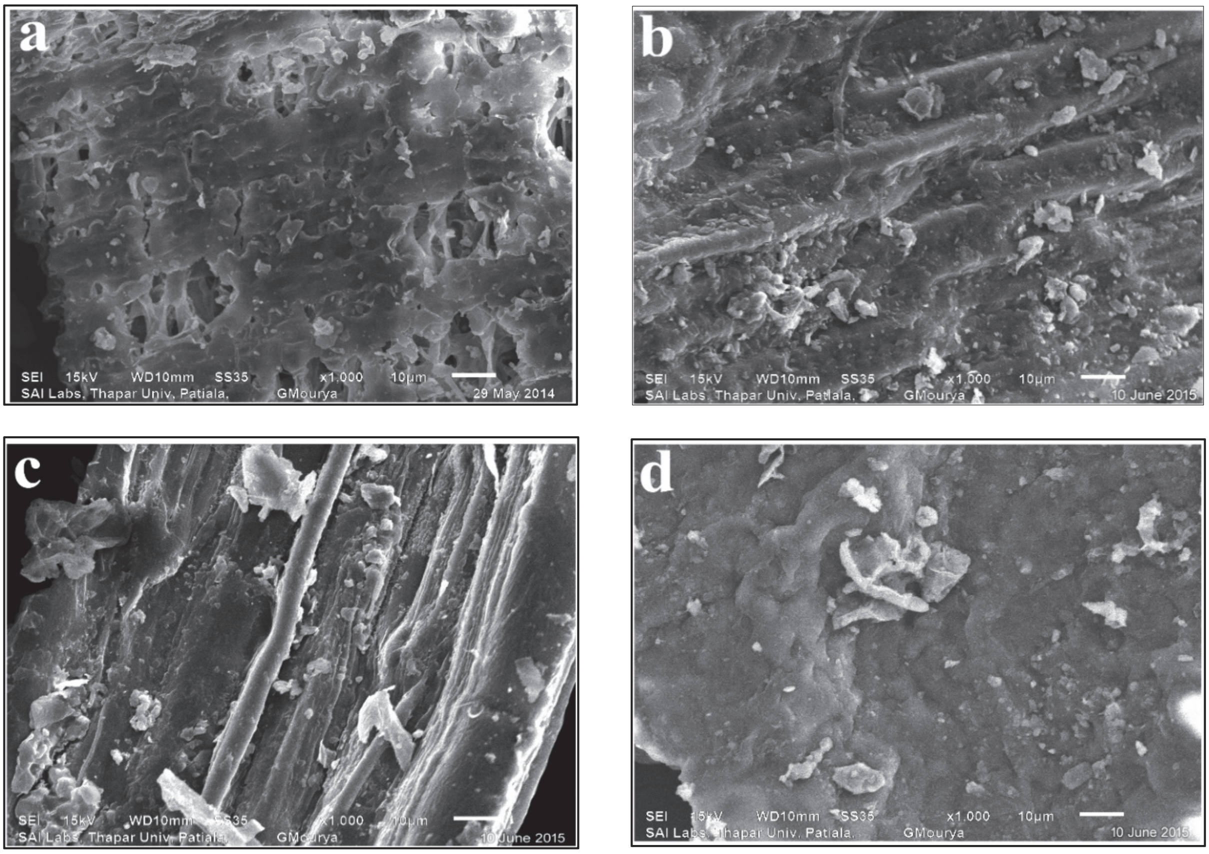

Fig 2. Scanning electron micrograph of different biomass sample (a) wheat straw, (b) sugarcane bagasse, (c) rice straw and d. eucalyptus chips (Magnification: 1,000X)

In addition to SEM, XRD, a central tool for polymer scientists to predict the structure of cellulose polymorphs (Harris and Debolt, 2008), known to reflect the degree of polymerization as well as structure (Andersson et al., 2004). Two-third of the cellulose is of crystalline nature, expressed as variable with pronounced effect on enzymatic digestibility but greater consideration needs to be given to the size, alignment and packing of cellulose fibrils within the cell wall matrix (Jung et al., 2008) as well as the co-organization with hemicelluloses and lignin (Pingali, 2010).

Physically evaluating the relative fraction and size of crystallites in cellulose can also be accomplished through infra-red spectroscopy along with XRD and electron diffraction or microscopic methodologies (Park et al., 2010). A common XRD method to determine cellulose crystallinity from randomly oriented fibers of cellulose considers the peak intensity at different angle of diffraction.

Crystallinity depends on relative amounts of crystalline and amorphous component of cellulosic microfibrils (Taherzadeh and Karimi, 2008). Determining true crystallinity of cellulose is ambiguous, as conventional X-ray methods measure the crystallinity of the entire material including the hemicellulose and lignin in addition to amorphous cellulose (Kim and Holtzapple, 2006; Zhu et al., 2008). The crystallinity index (*CrI*) of various biomass is calculated and determined as described by Segal et al. (1959) as Eq. (1):

$$CrI = [(I_{002} - I_{am}) / I_{002}] \times 100 \qquad (1)$$

where: I_{002} is the intensity for the crystalline portion of biomass (i.e., cellulose) and I_{am} is the peak for the amorphous portion (i.e., cellulose, hemicellulose, and lignin).

The peak near crystalline and amorphous regions at 2θ diffraction angle along with their *CrI* for different native biomass is detailed in Table 5. The peaks for crystalline and amorphous celluloses are generally observed at 2θ angle of 16 - 18° and 22 - 23°, respectively (Table 5, Fig. 3a) for different kind of biomass. The degree of crystallinity and changes in the crystal structure of cellulose are well established factors influencing enzymatic hydrolysis (Cetinkol et al., 2010). High crystallinity of biomass hinders enzymatic hydrolysis of lignocelluloses. Amorphous cellulose is readily accessed by cellulase as compared to crystalline microfibrils of cellulose (Taherzadah and Karimi, 2008) and it is widely accepted that decrease in crystallinity increases the digestibility of lignocelluloses (Chang and Holtzapple, 2000; Nanda et al., 2014). On the contrary, more crystalline lignocelluloses have been reported to show more digestibility (Xiao et al., 2010). Several factors such as enzyme inactivation, low reactivity of the substrate and non-specific adsorption of enzymes onto lignin, are related to higher crystallinity of the substrate and contribute to reduction in digestibility of cellulose at the lower enzymatic loading (Xiao et al., 2010).

However, due to the heterogeneous nature of celluloses, presence of hemicelluloses and lignin, it is not the only factor in effective enzymatic hydrolysis of biomass (Taherzadeh and Karimi, 2008). Among different native biomass reviewed, greater crystallinity (60%) has been reported for rice straw whereas wheat straw and corn stover showed 58% and 50% crystallinity, respectively (Table 5). Despite of greater crystallinity of rice straw, it is found to be promising candidate for production of second-generation biofuel (Binod et al., 2010) and biogas (He et al., 2008) production.

9. Thermal gravimetric analysis (TGA)

Different biomass shows different devolatilization behavior which may be used to know about the chemical constituent of biomass, mainly cellulose, hemicelluloses and lignin (Wang et al., 2008). The weight loss during devolatilization can be explained as follows: the weight loss at temperature less than 100°C was for loss of easily volatiles, 100 - 130°C for loss of water, 130 - 250°C for loss of volatile compounds, 250 - 350°C for loss of hemicellulose, 350 - 500°C for loss of cellulose, lignin and >500°C for lignin (Naik et al., 2010).

It is well established for instance that the pyrolytic decomposition of woody plant tissues in inert atmospheres occurs at mild temperatures for hemicelluloses (250-300°C) followed by cellulose (300 - 350°C) and finally lignin (300 - 500°C) (Song et al., 2004). Plateau formation of the TGA plot (Fig. 3b) in the temperature range of 250 - 500°C shows comparatively cellulose and hemicellulose rich biomass.

Table 5. Peak at crystalline and amorphous region and *CrI* of different biomass

Biomass	***Crystalline portion peak (I_{002})***	***Amorphous portion peak (I_{am})***	***CrI (%)***	***Reference***
Rice straw	--	18°	60	He et al. 2008
	22°	--	53	Nuruddin et al. (2011)
Wheat straw	22°	--	58	Nuruddin et al. (2011)
Sugarcane bagasse	22.5°	18.5°	48	Corrales et al. (2012)
Corn stover	22.6°	18.7°	33	Zeng et al. (2011)
	22.5°	16.2°	50	Kumar et al. (2009)
Switchgrass	22.5°	16.6°	26	Li et al. (2010)
Poplar solids	22.5°	16.2°	50	Kumar et al. (2009)
Eucalyptus chips	22.8°	18.5°	50	Cetinkol et al. (2010)

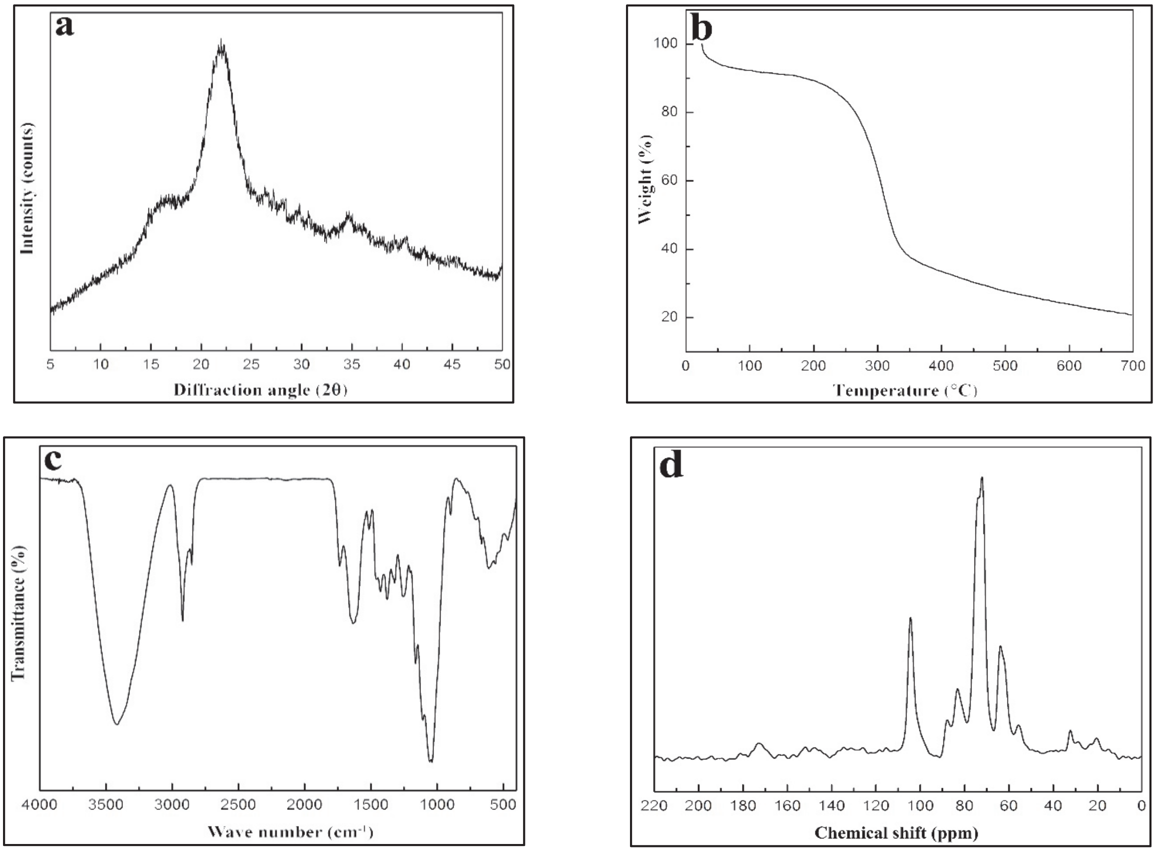

Fig 3. Physico-chemical characteristics of wheat straw: a. X-ray diffractograph, b. TGA pattern, c. FT-IR spectrum and d. Solid state ^{13}C CP/MAS NMR spectrum

A sharp decline beyond temperature of 500°C generally shows more cellulose and hemicelluloses, whereas slow rate of devolatilization beyond that temperature may primarily be due to high mannose or lignin content (Naik et al., 2010). The difference in the thermal stability of the cellulose, hemicellulose and lignin attribute to their different chemical structure (Wang et al., 2008). Table 6 shows devolatilization pattern in terms of approximate percent weight loss for different biomass considered. Devolatilization above 350°C is ascribed for lignin loss, more weight loss beyond this temperature showed greater lignin content. The hemicellulose decomposition usually appears as a pronounced "shoulder" instead of a well-defined peak as more cellulose and lignin devolatilization was observed for biomass obtained from eucalyptus wood whereas hemicellulose devolatilization was maximum for wheat straw and corn stover (Table 6).

Moreover, the combination of TGA and differential thermogravimetric (DTG) analysis allows obtaining the compositional analysis of lignocellulosic biomass. A more precise "wood industry method" was developed for quantitative analysis of cellulose, hemicellulose and lignin was employed using TGA (Carrier et al., 2011) and compared with other methods such as "food industry method" (Thiebaud, 1995) and methods used for softwood, hardwood (INERIS, 2006) and grasses (Lee et al., 2007). Cellulose and hemicellulose content of poplar wood and fern have been successfully estimated using technique based on TGA and deconvolution of DTG curves (Carrier et al., 2011). DTG curves have been analyzed by means of an algorithm for quantitative estimation of cellulose, hemicellulose and lignin in rice husk, sawdust, pellets, and rumex (Saldarriaga et al., 2012). Jiang et al. (2010) revealed systematic investigation of the pyrolysis kinetics of various types of lignin (alkali lignin, hydrolytic lignin, organosolv lignin and Klason lignin) using dynamic thermal gravimetric technique.

10. Fourier transform infra-red (FT-IR) spectroscopy

Studying the biomass materials for compositional analysis using FT-IR has attracted much attention during last decades. Quantification of data, accurate attribution of chemical functional groups and cell wall components is challenging without proper models (Foston and Ragauskas, 2012). It has been broadly used for investigating plant cell wall developmental and compositional variations among feedstcoks (Kacurakova et al., 2000). The FT-IR spectrum is a complex chemical fingerprint (Fig. 3c) delineating to adsorption bands due to the bond vibration frequencies of the chemical functional groups comprising the cell wall (Foston and Ragauskas, 2012). Different peak pairs are attributed for crystallinity and amorphous characters of cellulose molecules, among them two pairs (1430 cm^{-1} for crystalline and 893 cm^{-1} for amorphous) are suggested (Sasmal et al., 2012).

Prominent peaks in the region of 2960 - 2850 cm^{-1} for -CH asymmetric and symmetric stretching of cellulose and 1730 - 1750 cm^{-1} for -CO stretching of hemicellulose render a clue for the presence of more cellulose and hemicellulose. FT-IR technique was employed to estimate carbohydrate content in hardwood and softwood pulps by Bjarnestad and Dahlman (2002). Quantitative analysis of lignocellulosic components on untreated and steam exploded barley, canola, oat and wheat straw was also reported by Adapa et al. (2011) using FTIR. The technique can be used in biomass research including analysis of native biomass, biomass decomposition and reaction kinetics (Kalisz et al., 2008). The FT-IR spectra are targeted mainly for assignment of functional group for cellulose, hemicellulose and lignin of different biomass and are represented in Table 7. Lignocellulose biomass is most likely consisted of alkene, esters, aromatics, ketone and alcohol, with different oxygen-containing functional groups.

The wave number 1400 to 900 cm^{-1} is designated to vibrations of variety of bonds such as C-H, C-O, C-N and P-O (Wang et al., 2009). Absorption for wave number in between 1450 - 1000 cm^{-1} corresponds to chlorogenic acids (a family of esters formed between quinic acid) and one to four residues of caffeic, p-coumaric and ferulic acids (Briandet et al., 1996), contributing to majority of observed bands. Glycosidic skeletal vibrations in starch are ascertained in the wavenumber range of 950 - 700 cm^{-1} (Kizil et al., 2002; Reis et al., 2013).

Table 6. Devolatilization pattern of different biomass

Biomass	***Approximate weight loss (%)***			***Reference***
	250-350℃	***350-500℃***	***500-700℃***	
Wheat straw	25	15	0	Naik et al. (2010)
	69	7	0	Gao et al. (2012)
Rice straw	30	20	3	Chen et al. (2003)
Corn stover	54	10	1	Yang et al. (2011)
Sugarcane bagasse	26	27	3	Munir et al. (2009)
Switchgrass	38	28	3	Lee et al. (2009)
Poplar chips	41	31	1	Kim et al. (2012)
Eucalyptus wood	26	32	7	Silva et al. (2012)
	37	7	9	Hafsi et al. (2007)

Table 7. Assignments of peaks obtained from FT-IR spectroscopy analysis of different biomass

Peak range (cm^{-1})	*Assignment*	*WS[a]*	*RS[b]*	*CS[c]*	*SB[d]*	*SG[e]*	*PS[f]*	*EW[g]*	*Reference*
3600-3000	OH stretching in cellulose and lignin	3354	3320	3420	3386	3340	3500	3337	Pang et al. (2012); Schwanninger et al. (2004); Xu et al. (2013)
2960-2850	CH stretching (related to rupture of methyl/methylene group of cellulose)	--	2916	2920	2920	2920	2909	2891	Cetinkol et al. (2010); Pang et al. (2012)
	C-H deformation within the methoxyl groups of lignin	--	2859	--	2852	--	--	--	Hsu et al. (2010)
1750-1630	Deformation vibration of H-O-H in absorbed water	--	1648	--	--	1655	--	1649	He at el. (2008); Xiao et al. (2011)
	C=O stretching of hemicelluloses	1734	1733	1730	1735	1735	1744	1735	Hu et al. (2012)
1600-1510	Aromatic C=C stretching from aromatic ring of lignin	1508	--	1510	--	1515	--	1505	Xiao et al. (2011)
	aromatic skeletal vibrations and C=O stretch	--	1600	--	--	--	1593	1593	Hu et al. (2012)
1470-1420	Aromatic skeletal vibration combined with C-H in plane deformation in lignin	--	1422	--	1427	1427	1425	1424	Xiao et al. (2011)
	Aromatic C-H deformation in lignin	--	--	--	1462	1464	1455	1460	Xiao et al. (2011)
1400-1310	C-H deformation in cellulose and hemicelluloses	--	1364	--	1376	1376	--	1372	Cetinkol et al. (2010
	CH_2 wagging in cellulose	--	1313	--	--	1321	1327	1328	Colom et al. (2003); Hu et al. (2012)
1300-1260	Guaiacyl ring and C-O stretch in lignin and xylan	--	--	--	--	1260	--	--	Hu et al. (2012)
1250-930	O-H association band in cellulose and hemicellulose	--	--	1100	1110	1108	--	1109	Cetinkol et al. (2010)
	O-H Bending in cellulose and hemicellulose	--	--	--	--	1206	--	--	Sills et al. (2012)
	Syringyl ring breathing and C-O stretch in lignin and xylan	--	--	--	--	--	1238	1235	Cetinkol et al. (2010)
	C-O-C connection bridge in hemicelluloses and cellulose, aromatic C-H deformation of the syringyl and guaiacyl units in lignin	--	--	1160	1165	--	1155	1157	Li et al. (2012)
	Alkyl ester of the acetyl group in hemicelluloses.	1248	1245	1240	1250	--	--	--	Hsu et al. (2010)
	C-O stretching in cellulose and hemicellulose	1055	--	1060	1050	--	1051	1056	Hsu et al. (2010)
	C-O-C vibration at β- glucosidic linkages in cellulose and hemicelluloses	--	1160	--	--	1165	--	--	Cetinkol et al. (2010); Xiao et al. (2011)
930-800	C-O-C stretching at β- glucosidic linkages in cellulose and hemicelluloses	--	896	900	897	900	900	897	Xiao et al. (2011)

WS: Wheat straw; RS: Rice straw; CS: Corn stover; SB: Sugarcane bagasse; SG: Switchgrass; PS: Poplar stem; EW: Eucalyptus wood. Data taken from [a]Zhang et al., 2008; [b]Li et al., 2012; [c]Pang et al., 2012; [d] Corrales et al., 2012; [e] Hu et al.,2012; [f] Jung et al., 2010; [g]Cetinkol et al., 2010

The quantification of the components in gas phase and the moieties in liquid phase was based on transformation of functional groups in liquid phase and the corresponding gaseous products using FT-IR has been successfully achieved (Grilc et al., 2014a).

11. Solid state ^{13}C cross polarization (CP) magic angle spinning (MAS) NMR spectroscopy

Solid state ^{13}C CP/MAS NMR spectroscopy has gained importance as tool to investigate the structural features of lignocelluloses. Different chemical shifts (Fig. 3d) are related to crystalline and amorphous cellulose in chemically equivalent nuclei environment due to magnetic non-equivalences in solid-state NMR (Foston and Ragauskas, 2012). The technique has been extensively applied to reveal the structural features of biomass derived from wood-derived materials (Liitia et al., 2003; Sievers et al., 2009b; Wikberg and Maunu, 2004; Xiao et al., 2011), seeds (Bardet et al., 2001; Bootten et al., 2003), grasses (Sathitsuksanoh et al., 2011; Yen et al., 2009), rice straw (Sun et al., 2002; Singh et al., 2014), wheat straw (Sun et al., 2004), sugarcane bagasse (Rezende et al., 2011), corn stover (Shi et al., 2011), *Poplar* sp. (Kohn et al., 2011) and *Eucalyptus* sp. (Yu et al., 2012).

Chemical shifts obtained from solid state ^{13}C CP/MAS NMR studies of various biomasses were reviewed and presented in Table 8. Peaks assigned in the region of 50 to 120 ppm are being assigned mostly to cellulosic carbons in addition to the signal contributions from hemicellulose and lignin. Signals from lignin are concentrated between 100 to 200 ppm. An aliphatic region for lignin lies from 0-95 ppm whereas, an aromatic region falls in between 100 and 160 ppm (Gao et al., 2012). Chemical shift deflection for the C4 and C6 carbon in the anhydroglucose unit rely upon the cellulosic source, variations in cellulose crystallinity and crystal lattice structure (Foston and Ragauskas, 2012).

12. Other characterization techniques

The high throughput (HTP) chemical analysis of biomass has included FT-IR, near infrared spectroscopy (NIR), nuclear magnetic resonance (NMR), mass spectrometry (MS) and monoclonal antibody microarrays, which have binding specificities for cell wall components (Alonso-Simon et al., 2010; Grilc et al., 2015; Lerouxel et al., 2002; Moller et al., 2007; Mittal et al., 2009; Robinson et al., 2009; Ropartz et al., 2011). Sharma et al. (2009) studied characterization of biomass extractives using high-performance liquid chromatography (HPLC) in combination with ultraviolet (UV) absorbance and tandem mass spectrometry (MS/MS). In addition, chromatographic extraction technique (Grilc et al., 2014) on an HTP based platform may reduce pretreatment severity and enzyme loading. However, these techniques produce complex data sets that are challenging to interpret on large sample sets. Scientists at National Renewable Energy Laboratory (NREL) reported the use of a multi-plate reactor for analysis of biomass recalcitrance (Decker et al., 2009; Selig et al., 2010). An NREL's system has also been used to analyze chemical composition of agricultural fibers for thousands of samples using pyrolysis molecular beam mass spectrometry (py-MBMS) (Sykes et al., 2008).

Accuracy in determining chemical composition and molecular structure of lignocellulosic biomass are getting more importance for making the process of converting biomass to biofuel feasible. Despite their accuracy and reproducibility, these methods are expensive, labor intensive and time consuming. Prime concern exists for better understanding biomass composition, mechanism of biomass recalcitrance and its relationship to cell wall structure. At present, large-scale commercialization and utilization of lignocellulose base biofuel is under critical evaluation. A promising sign for their mass utilization is that they have been tested in modified engines, turbines and boilers successively with considerably lower emissions (Czernik and Bridgwate, 2004). The study of physico-chemical characteristics of biomass in the light of biofuel production ensures its utilization for gasification, bio-oil and bio-alcohol production and may meet the demand of the second-generation biofuel.

Table 8. Signal assignments for chemical shifts obtained from solid state ^{13}C CP/MAS NMR spectroscopy of different biomass

Chemical group	***WS***[a]	***RS***[b]	***CS***[c]	***SB***[d]	***SG***[e]	***PW***[f]	***ES***[g]
Carboxyl group of hemicelluloses	171.1	170.7	--	173.6	175-168	173	--
Carboxyl group in lignin	--	--	--	163-180	168-164	--	165-180
C3 and C5 aromatic carbons of syringyl lignin (e)	153	--	--	153.5	155-151	153	--
C3 and C5 aromatic carbons of syringyl lignin (ne) and C1 and C4 aromatic carbon of guiacyl in lignin	--	--	--	148	--	--	147
C1 and C4 aromatic carbons of syringyl lignin (ne)	--	--	--	136.9	--	--	--
C1 and C4 aromatic carbons of syringyl lignin (e)	--	--	--	134.5	--	135	--
C2 of aromatic carbon of guiacyl lignin	--	--	--	126.6	113-110	--	--
C2 and C6 aromatic carbons of syringyl lignin (ne) and C5 and C6 aromatic carbon of guiacyl lignin	116	--	--	110-115	110-102.5	--	--
C1 of cellulose	106.2	--	105	105.5	108-103	105	105
Shoulder of C1 carbon of hemicelluloses	--	--	--	101.8	101.6	--	
C4 of crystalline cellulose	90.0	90.1	89	87.9	89.7	89	89
C4 of amorphous cellulose and hemicelluloses, $OC_{\beta}H_2$ carbon of lignin	85.1	84.7	84	83.5	88.1	84	84
C2, C3, C5 of cellulose and hemicelluloses	75.6	75.3	75	74.4	--	75	75
C2, C3, C5 of cellulose, $OC_{\alpha}H_2$ carbon of lignin	--		72	72.5	--	73	72
C6 of crystalline cellulose	65.2	65.4	64	64.8	--	66	65
C6 of non-crystalline cellulose, C6 carbon of hemicellulose, $OC_{\gamma}H_2$ carbon of lignin	--	--	--	62.5	61-57	62	--
Aryl methoxyl group in lignin	58.4	58	58	56.2	57-54	56	57
CH_3 in acetyl group in lignin	21.4	21.5	--	21.5	21-19	22	21

WS: Wheat straw; RS: Rice straw; CS: Corn stover; SB: Sugarcane bagasse; SG: Switchgrass; PW: Poplar wood; ES: Eucalyptus wood chips. Assignments obtained from [a]*Sun et al., 2004;* [b]*Sun et al., 2002;* [c]*Shi et al., 2011;* [d]*Rezende et al., 2011;* [g]*Yu et al., 2012;* [f]*Kohn et al., 2011;* [e]*Yan et al., 2010*

Moving forward, a useful strategy to identify the mechanisms of and overcome biomass recalcitrance must include the choice of improved methodologies to characterize the chemical and molecular features.

Extensive application of FT-IR can be done in supplementation with compositional analysis, XRD, TGA for analysis of biomass to compare differences between sample characteristics owing to diverse nature of biomass. However, it would be difficult to quantify the data or even correctly attribute the functionality to the proper chemical moiety or component within the cell wall without proper models (Foston and Ragauskas, 2012). Further, solid state NMR spectroscopy might be an alternate tool for accurate analysis of molecular features of plant cell wall characteristics. Two-dimensional ^{1}H-^{13}C NMR experiments, which are not quantitative but resolve a variety of overlapping spectral features, are even more useful, providing information about a wide array of chemical moieties (Samuel et al., 2010). Though these methods can facilitate considerable advancement, fundamental features of lignocellulosic biomass could simply be made if more comprehensive research studies were conducted.

13. Conclusions

Lignocellulosic biomass, including agricultural and forestry residues is a highly complex heterogeneous material, the composition of which varies tremendously on its habitat, source, range of tolerance for adverse environmental niche conditions, seasonal variation and availability of nutrients. Although, correlating effect of multiple characteristics may lead to conflicting or even erroneous conclusions towards combined and integrated effect of an array of compositional analysis, crystallinity, recalcitrance and degree of polymerization.

Though some characteristics are more influential than others, the relationship between biomass characteristics, recalcitrance and hydrolysis is clearly multi-variant and non-linear, thus virtually impossible to appreciate fully in the absence of a comprehensive characterization.

Advanced characterization strategy may identify the integrated effect of cell wall characteristics for renewable fuel production. Identification and selection of feedstock from a wide range of sources require specific expertise to deal with the ultra-structure, organization of biomass and the interactions between of biomass with enzymes. For optimal utilization of feedstock for biofuel generation, improved methodologies to characterize at chemical and molecular level may facilitate substantial progress, advances and market entrance.

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