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An aggregated understanding of physicochemical properties and surface functionalities of wheat straw node and internode

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ABSTRACT

The variation of physicochemical characteristics across wheat straw node and internode with their surface functionalities was investigated. Node yielded slightly higher klason lignin, extractives and ash content than internode, which could be related to their morphology; specifically the higher ash and extractives content in the node are explained by thicker epidermis tissue. These properties make nodes defects in composite and bio-energy production, while internodes could be more favourable for aerobic digestion for biogas production. Surface chemical distribution examinations revealed, higher intensities of the hydrophobic aliphatic fraction of waxes on the outer surface, whereas the hydrophilic tendency of inner surface was reflected by the broad and more intense band in the 3200–3600 cm^{-1} region, due to —OH stretching vibration of hydroxyl groups. This could translate into better interface when water-based resins are used for wheat straw composites. An environmentally friendly pre-treatment was employed to further investigate the effects on the physicochemical properties. The results showed: i) the reduction of waxes from the outer surface, ii) significantly lower ($P < 0.05$) extractives, along with iii) significant dissolution of Si (weight%) on the outer surface of both node and internode. These results could be beneficiary for composite production or for pulp and paper manufacturers.

1. Introduction

Wheat straw is an agricultural by-product which is annually produced in abundance around the world. The world's wheat production in 2014 was 716 million tonnes (Bhattarai et al., 2015). Assuming a residue/crop ratio of 1.3 (Talebnia et al., 2010), around 931 million tonnes of total wheat residue is annually produced. If 60% is used for ground cover to prevent soil erosion, 559 million tonnes of wheat straw is available as waste (Bhattarai et al., 2015). Agricultural crop residues have the potential of being a valuable renewable resource for bio-refinery feedstocks. Extensive studies in the past 10 years have been carried out to extend the uses of wheat straw and increase its additional value (Alemdar and Sain, 2008; Ghaffar et al., 2015; Ghaffar and Fan, 2015a, 2015b, 2014, 2013; Halvarsson et al., 2009; Hansen et al., 2013; Kaparaju et al., 2009; López-Abelairas et al., 2013; Motte et al., 2014; Petrik et al., 2013). The bridging between the research-based adaptation of efficient pre-treatments on the extraction, separation and fractionation of waste crops components, has the unique potential to yield innovative added value green chemicals and bio-products. Straw biomass utilisation requires the detailed understanding of material sciences. Direct extraction of specifically engineered or naturally occurring chemicals from the complex molecular components of different parts of straw biomass is also a possibility which requires the detailed investigation of anatomical parts. It must be recognised that not all parts of the crop residue are equally valuable. For an efficient utilisation of straw biomass, in different applications, the undesirable parts must be removed (Harper and Lynch, 1981; Hess et al., 2003). For instance biofuel and chemical processors only require the high yielding cellulose and hemicellulose biomass parts delivered. A strategy for identifying and subsequently reducing the number of undesirable residue parts for feedstock is, therefore, vital. The heterogeneous nature of straw, where their chemical composition varies with species, location, storage time, harvest, stage of maturity, environmental conditions and anatomical parts, i.e. node and internode, makes their comprehensive characterisation essential prior to bioconversion process (Ghaffar and Fan, 2015a, 2015b). It is almost impossible to control the compositional variability of straw biomass, but it is feasible to monitor the variability and accordingly select the processing technologies for the specific bio-refinery. Hence, this paper thoroughly investigates internode and node, with inner and outer surface profiles, and monitors the changes in 1) surface chemistry, 2) elemental composition, 3) extractives yield, 4) klason lignin and 5) the ash content,

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to deliver an aggregate understanding of material science leading to valorisation of wheat straw for bio-refinery pathways.

2. Material and experimental methods

2.1. Sample preparation

Wheat straw (*Triticum aestivum* L.) harvested in summer was obtained from Dixon Brothers Porters Farm, United Kingdom (East of England). Wheat straw bales were prepared and dried directly on site. Bales were collected and homogenised carefully. They were stored in an ambient room temperature atmosphere to confirm air-dryness. The wheat straw is composed (on a mass basis) of 57 ± 10% internodes, 18 ± 3% leaves, 10 ± 2% nodes, 9 ± 4% chaffs and 6 ± 2% rachis (Motte et al., 2014). The whole stem of wheat straw was selected, cleaned and grouped for characterisation. The pith of a wheat straw is mostly hollow except for the intermediate growth sections, known as nodes. In between the nodes are the internode sections. In order to investigate the surface profiles, the node and internode were carefully cut in half longitudinally so that the outer and inner surface could be exposed to testing. Samples were oven dried (100° C for 24 h) prior to testing.

2.2. Analysis of various profiles of node and internode

All samples for chemical compositional analysis were prepared according to NREL/TP-510-42620 (Hames et al., 2008). Surface functionalities and elemental composition of straw profiles were also investigated. Five replicates were taken for the wet chemistry (i.e. klason lignin and extractives content), ten replicates for surface chemistry (i.e. surface functional groups and elemental composition) and ash content. Table 1 summarises the methodologies and drives for each analytical technique used. The results from each parameter analysed are interpreted to establish the correlation between various characteristics which will contribute to the understanding of wheat straw as a whole and precisely node and internode of various surface profiles.

All the procedures (i.e. extraction, klason lignin), were made separately for each sample (node and internode, treated and untreated) and for each extraction medium (hot-water and ethanol).

2.3. Pre-treatment

Apart from the untreated samples, a group of node and internode samples were also pre-treated to further elucidate the difference of node and internode. The pre-treatment was carried out as follows: the straws were firstly introduced to the pressure cooker with water at an initial temperature of 100° C. The cooker was then sealed to maintain a pressure of about 0.1 MPa. The internal temperature was monitored for the duration of the pre-treatment (30 min) and meanwhile increased to a maximum of 106 ± 1° C with advancing of time and pressure. The solid to liquid ratio of 1:20 (by weight) was used for this pre-treatment. Wheat straws were then removed from the hot water and placed in a mesh basket positioned above hot water inside the pressure cooker, and such, steam at 100° C passes through the wheat straw for another 30 min in order to complete hot water and steam pre-treatment (H + S).

3. Results and discussion

3.1. Surface chemical distribution of node and internode

The surface chemical distributions of wheat straw node and internode, inner and outer surfaces are shown in Fig. 1. The most relevant bands have been summarised in Table 2 where the characteristics of surface profiles are qualitatively compared in node and internode. It is observed that the intensity of 2850 and 2920 cm^{-1} is much higher in node (Fig. 1), which may be attributed to the higher intensity of waxes on the surface. On the other hand, comparing inner to outer surface, it is recognised (Fig. 1a and b) that the hydrophilic tendency of inner surface of both node and internode is reflected by the broad and more intense band in the 3200–3600 cm^{-1} region, which may be due to the —OH groups present in their main components. Interestingly, some bands were present in node but absent in internode and vice versa, i.e. 2955, 720 and 790 cm^{-1} in node and 985 cm^{-1} in internode, this observation is interpreted later in the paper in correlation with wet chemistry analysis.

FTIR technique is also used for quantitative investigations. The cellulose assigned bands at 897 cm^{-1} (asymmetric out-of-phase ring stretch in the C1—O—C4 glycosidic linkage), 1372 cm^{-1} (C—H bending), 1429 cm^{-1} (C—H wagging), and 2900 cm^{-1} (C—H stretching) are used for quantitative indices evaluation of the overall crystallinity of cellulose (Nelson and O'Connor, 1964). The lower order index (LOI) and total crystallinity index (TCI) are calculated based on FTIR spectra (Akerholm et al., 2004). Higher values of TCI (H1372/H2900) and LOI (H1429/H897) indicate higher crystallinity of cellulose in the material (Cao and Aita, 2013; Ninomiya et al., 2012). H1429/H897 increased by 15% (0.74 for UN to 0.85 for H + S) in internode and by 11% (0.9 for UN to 1.0 for H + S) in node. Then again H1372/H2900 also increased by 24% (1.1 for UN to 1.4 for H + S) in internode and by 9% (1.1 for UN to 1.2 for H + S) in node. The alteration in the crystalline structure of cellulose varies in different regions, while improvement in the crystallinity of cellulose in H + S straw could provide a great stability to the cellulose chain (Xiao et al., 2014) and therefore increase the mechanical performance of straws as observed in our previous study (Ghaffar and Fan, 2015a), where the tensile strength of the H + S treated straws increased significantly ($P < 0.05$) by 35% in internode and 62% in node.

The cellulose crystallinity index for node and internode was estimated with the LOI as proposed in the literature (Monlau et al., 2012; Motte et al., 2014) according to the equation (Eq. (1)).

$$\text{Crystallinityindexofcellulose} = \frac{\text{LOI}}{1 + \text{LOI}} \quad (1)$$

Motte et al. (2014), using the same Eq. (1) for crystallinity index calculation of cellulose, found values of 49± 1% for the internodes and 52±4 for the nodes. In this study for untreated samples the crystallinity index (% of cellulose) is calculated to be 43% for the internodes and 47% for the nodes.

The degradability of cellulose is correlated to its crystallinity. This analysis suggests that around 47% of the cellulose of nodes is crystalline and hence less degradable by anaerobic digestion processes. Internodes are however, only 43% of crystalline cellulose, showing more amorphous cellulose content that could be favourable for anaerobic digestion. These trends would suggest improved feedstock qualities for the intended bio-refinery pathway, thus a potential for upgrading the raw material by fractionating out the less desirable properties of the feedstock. In aerobic digestion, biodegradation is inhibited by the straw biomass recalcitrance (i.e. highly complex structures). Hence there are various pre-treatments of straw biomass for increasing the cellulose accessibility, solubilising the hemicellulose and deconstructing