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Nitrogen fertilization affects silicon concentration, cell wall composition and biofuel potential of wheat straw

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ABSTRACT

Nitrogen is an essential input factor required for plant growth and biomass production. However, very limited information is available on how nitrogen fertilization affects the quality of crop residues to be used as lignocellulosic feedstock. In the present study, straw of winter wheat plants grown at six different levels of nitrogen supply ranging from 48 to 288 kg nitrogen ha^{-1} was analyzed for major cell wall components and mineral elements. Enzymatic digestion of the straw was carried out to evaluate the saccharification efficiency. The nitrogen concentration in the straw dry matter increased linearly from 0.32% to 0.71% over the range of nitrogen treatments. Cellulose and hemicellulose were not affected by the nitrogen supply while lignin peaked at medium rates of nitrogen application. The nitrogen treatments had a distinct influence on the silicon concentration, which decreased from 2.5% to 1.5% of the straw dry matter when the nitrogen supply increased from 48 to 192 kg ha^{-1}. No further decline in Si occurred at higher rates of nitrogen application. The most abundant metals in the straw were potassium and calcium and their concentrations almost doubled over the range of nitrogen supplies. The enzymatic saccharification efficiency was negatively correlated with the rate of nitrogen supply. We conclude that the level of nitrogen supply to wheat plants alters the composition of cell wall components in the straw and that this may result in reduced saccharification efficiency.

1. Introduction

1.1. Background

Bioenergy is becoming increasingly important to ensure future energy security as a consequence of the increase in energy consumption, the depletion of fossil fuels, and the need to reduce carbon emissions to the atmosphere [1,2]. Agricultural residues such as cereal straw constitute a lignocellulosic biomass feedstock which can be utilized for bioenergy production [2,3]. This utilization requires either biochemical degradation of the biomass feedstock to obtain energy products such as biofuels and biogas or

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thermochemical degradation to obtain heat and electricity [4]. During biochemical degradation, lignocellulosic biomass feedstock is given a chemical and physical pretreatment in order to break the lignocellulosic complex to enable further enzymatic saccharification [5]. Monomeric sugars are released from cellulose and hemicellulose by cellulases in enzymatic saccharification, and are further fermented into liquid biofuels and other organic chemicals [5]. Due to the complex structure of lignocellulosic material, it has been a challenge to establish low cost processes for hydrolysis of lignocellulosic feedstock to monomeric sugars [4,5].

Lignin is considered a major inhibitor of the enzymatic degradation of lignocellulosic feedstock [5]. In plant cell walls, lignin binds covalently to hemicellulose and covers cellulose microfibrils, which increases the rigidity of the cell wall and the plant tissue. Lignin thereby reduces the accessibility of cellulases to cellulose and inhibits hydrolysis during saccharification [5]. For thermochemical degradation, higher lignin concentration is desirable because it increases the energy values of biomass feedstock [6].

Silicon (Si) accumulates in plant cell walls and increases their physical strength [7]. Si is the second most abundant element in soil after oxygen, yet Si concentrations in plants vary with plant species. Rice (*Oryza Sativa*) is an example of a species that accumulates Si at high levels up to 10% of dry matter in the shoots [7,8]. Wheat is also considered a Si accumulator with typical wheat straw Si concentrations of 1–4% on dry matter basis [4,6,9]. Studies focusing on utilization of plants as animal feed have reported that higher concentration of Si in forage reduces enzymatic digestibility in ruminants probably by limiting the access of enzyme to the substrates or by inhibiting activity of hydrolyzing enzymes [10,11]. However, it is not well known how Si in plant biomass feedstock affects the saccharification reaction during biofuel production. For thermochemical degradation, a negative effect of Si has been shown [6,9]. Si reacts with alkali and alkaline earth metals such as potassium (K), calcium (Ca) and magnesium (Mg) at high temperatures. This may cause severe ash deposition and corrosion, which can damage the reaction chamber and force the plant to operate at lower temperatures, thereby reducing its efficiency [12,13]. In addition, gases and aerosols formed from the released ash-forming elements may pose significant environmental and health concerns [14]. Therefore, the combination of high concentrations of Si, alkali and alkaline earth metals in biomass feedstock decreases the quality in terms of thermochemical processing.

Nitrogen is an essential plant macronutrient, which normally constitutes 1–5% of plant dry matter. Increasing demand for biomass for bioenergy purposes would therefore also imply additional N fertilizer inputs [15]. While it is known that high N concentration in biomass may have negative impacts in terms of increasing NO_x emissions during thermochemical processing [16], there is, to the best of our knowledge, no information available on how N supply affects the saccharification efficiency of cereal straw. On this background, the objective of the present work was to study how the level of nitrogen supplied to a wheat crop affected major cell wall components, mineral elements and enzymatic digestibility of the straw.

1.2. Objectives

The main objective of the present work was to study the effect of N supply on the enzymatic saccharification efficiency of winter wheat straw (*Triticum aestivum* L. cv. Hereward). Changes in straw composition with respect to mineral elements (Si, N, K, Ca, Mg and C) and organic cell wall components (cellulose, hemicellulose and lignin) in response to increasing N supply were also analyzed in order to elucidate the influence of these parameters on the saccharification efficiency.

2. Materials and methods

2.1. Plant material

Winter wheat (*T. aestivum* L. cv. Hereward) was grown in field plots fertilized with ammonium nitrate (48, 96, 144, 192, 240 and 288 kg N ha^{-1}) at the Broadbalk experiment at Rothamsted Research, Harpenden, UK in 2008. Ammonium nitrate was applied in mid-April as a single application. All field plots were also supplied with K (90 kg ha^{-1} as potassium sulfate), Mg (30 kg ha^{-1} as magnesium sulfate) and phosphorous (35 kg ha^{-1} as triple superphosphate). At full maturity, wheat straw was harvested from three psudo-replicates per plots for each treatment. The plants remained air dried and were milled to <1 mm pieces on a cyclone mill (President, Holbæk, Denmark).

2.2. Inorganic elements in straw

Straw tissue was digested using a microwave oven (Multiwave 3000, software version 1.24, Anton Paar GmbH, Graz, Austria) following the method of [17]. The samples were diluted to 50 ml with ultrapure water (Milli-Q Element, Millipore, Billerica, MA), centrifuged at 3220× *g* for 10 min and 0.2 ml of the supernatant was diluted with 9.8 ml of 7% (v/v) ultrapure nitric acid (SCP SCIENCE, Baie D'Urfé, QC). The concentration of Si in the digests was analyzed by inductively coupled plasma-optical emission spectroscopy (ICP-OES) (Optima 5300 DV, PerkinElmer, Waltham, MA). Reference material (spinach leaf, NCS ZC73013, China National Analysis Center for Iron and Steel, Beijing, China) was included in the analysis.

The concentrations of K, Mg and Ca were measured by inductively coupled plasma-mass spectrometry (Agilent 7500ce, Agilent Technologies, Manchester, U.K.). For these analyses, 250 mg of milled wheat straw was weighed into 70 ml HD polyethylene vials (Capitol Vial, Fulton Ville, NY). Digestion was carried out on a graphite-heating block (Mod Block, CPI International, Amsterdam, Holland) following the modified EPA method 3050B described by Ref. [18]. Reference material (Apple leaf, standard reference material 1515; National Institute of Standards and Technology, Gaithersburg, MD) was also digested and included in the analysis.

Nitrogen and carbon in the straw material was analyzed based on the Dumas dry-combustion method in an ANCA-SL Elemental Analyser coupled to a 20–20 Tracermass Mass Spectrometer (SerCon Ltd., Crewe, UK).