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Monitoring switchgrass composition to optimize harvesting periods for bioenergy and value-added products

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ABSTRACT

Switchgrass (*Panicum virgatum*) is a perennial grass that has emerged as an ideal candidate for production of biofuel and value-added co-products. One of the primary requirements for the successful manufacturing of these switchgrass-derived bioproducts is to produce a consistent feedstock with reliable and adequate amounts of the substrate constituent needed. For example, the biofuels industry requires a fast-growing energy crop with higher cellulose content and lower inhibitors found in secondary constituents. Other industries would profit from higher lignin content for products such as carbon fibers, or higher water and ethanol-soluble extracts containing compounds of interest. Two switchgrass field plots in eastern Tennessee were monitored over a period of six months, including before and after traditional harvesting times for the biorefinery. Characterization of the biomass and its constituents, such as water and ethanol extracts, cellulose, hemicelluloses, lignin, and ash, was performed to examine chemical changes in switchgrass that occurred prior to, during, and after traditional harvesting times used in a biorefinery setting. Total carbohydrate (65.6–66.7 wt%) and lignin (21.7–23.2 wt%) content was found to peak in January. Extractives content was at a maximum in early harvests at 15.9–16.6 wt% and decreased to 5.5–5.8 wt% in February. An inverse relationship exists between the extractives and lignin content ($R^2 = 0.94$). Nonstructural soluble sugars peaked in early October with 5.1 wt% of the switchgrass composition. Remobilization efficiencies of K, Mg, P, and Fe increased with time, indicating conservation of soil nutrients if harvests were completed in late winter.
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1. Introduction

Switchgrass (*Panicum virgatum*) is widely considered a potential feedstock for bioprocessing of liquid fuels such as ethanol. In addition, cellulosic biomass may be a source for valuable co-products. Determination of dedicated perennial crops as a potential renewable energy feedstock with supplementary value-added applications is dependent upon two main conditions: the quality of the feedstock in terms of the chemical composition, and compositional changes of the material in the field over the harvesting season and during storage. Overall consideration of these conditions will help to determine the ideal feedstock characteristics, as well as optimization of the harvesting process to improve the complete utilization of the feedstock for multiple co-products in the bioenergy and bioprocessing industries.

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Switchgrass is a common perennial species that is native to most of the eastern United States and does not require annual reseeding. It is typically harvested in early November through December and is considered a late harvest until mid-February. Like all plant materials, it is comprised of the same basic constituents: carbohydrates (cellulose and hemicellulose), lignin, extractives, and ash. Cellulose is a highly linear polymer of approximately 10–15,000 β-(1,4)-linked glucose units that gives strength and rigidity to plant cell walls. Hemicellulose is a biopolymer of mostly five-carbon sugars such as xylose, mannose, and arabinose with an amorphous structure. Lignin is a high energy content complex aromatic polymer consisting of phenylpropane units that further acts as a structural and protective element in the cell wall around the carbohydrate constituents.

Nonstructural components include material soluble in either water or ethanol. These extracts are composed of a multitude of compounds, including waxes, oils, fats, resins, nonstructural sugars, chlorophyll, organic acids, alditols, inorganics, and polyphenolics [1]. In addition to serving as a feedstock for cellulosic fuel production, switchgrass could be a source of valuable chemicals in that many of these compounds can be extracted from the plant with hot water, allowing for collection and utilization prior to pretreatment processing for fuel production, thus increasing profitability with these additional product streams [2]. The collection of nonstructural or free sugars should be included in feasibility studies as part of the biorefinery processing of the biomass as these carbohydrates have been reported to be the principal water-soluble component in switchgrass extractives [3]. However, the impact of these nonstructural sugars should be extended to feedstock storage studies to determine what percentage of these free sugars is lost if stored outside or in conditions prone to mold growth. These sugars, in particular glucose, should be considered as fermentable and usable if present in significant fractions within the water-soluble extracts. However, in various pretreatment processes there is a potential for degradation of glucose and fructose to 5-hydroxylethylfurfural, a known fermentation inhibitor [4]. Some other specific compounds of interest within switchgrass extractives include plant secondary metabolites called flavonoids, known for their antioxidant activity [2]. Rutin (quercetin-3-O-rutinoside) and quercetrin (quercetin-3-O-rhamnoside) which share the alycon, quercetin, have been shown to be present in switchgrass extractives and display beneficial health effects, including cardioprotection, and act as an antimicrobial agent [2,5]. The quantity of phenolic compounds in plant leaves has been reported to increase in response to biotic and abiotic stressors [6,7]. Therefore, switchgrass extractives could be used in the development of co-products utilizing their protective biological and anti-microbial properties. Specific antimicrobial compounds include *p*-coumaric and ferulic acids, associated with resistance to plant pathogens [6,8]. While the effects of extractives on the fermentation process is not completely understood, phenolics have been implicated in the literature and through our own research as inhibitors of fermentation of cell wall polysaccharides [4].

Ash consists of inorganic elements and silica [9]. In order to maintain and maximize switchgrass yield each year, nutrients that are removed with each harvest must be replaced. Therefore, if the levels of phosphorus (P) and potassium (K) and other nutrients contained in switchgrass plants as it is harvested are known, better field practices can be established for nutrient management to ensure maximum yield. Consideration of the nutrient efficiencies is essential since the cost of biofuel production is also increased as certain inorganics, such as K, can inhibit biomass pretreatment and fermentation [10]. Previous work involves calculation of switchgrass yields and nutrient removal during traditional harvest periods, or determination of best management practices by investigating optimal harvest frequency, and remobilization of nitrogen and phosphorus translocation within the plant with age and various fertilization rates [11,12].

The relative concentrations of all these components vary depending on plant age, tissue type, genetics, and environment. For instance, the extractives content in Alamo switchgrass has been shown to range from 5 to 25 wt% for samples from various environments and of different ages [3]. If a commercial-scale biorefinery is to be considered extractives could play a significant role in the optimization of the processing, and production of high-value co-products from this fraction could be added to the ethanol conversion process of switchgrass by optimizing the harvesting time of the plant to produce the desired composition. Therefore, the objectives of this study were to examine temporal changes in switchgrass composition as part of the species' natural variability and to determine how long biomass can be left in the field while still maintaining quality. Classification techniques such as Fourier Transform Infrared (FTIR) in conjunction with multivariate statistics, such as principal component analysis (PCA), were utilized to help identify these changes between sampling periods.

2. Materials and methods

2.1. Sample collection and preparation

The switchgrass fields utilized in this study are part of the University of Tennessee Biofuels Initiative (UTBI). Since 2008, the UTBI has worked with local farmers to plant over 2064 ha (5100 acres) of lowland switchgrass for conversion to energy in eastern Tennessee. Switchgrass material was harvested from Fall 2009 to Winter 2010 from two plots located on a producer's field in Loudon County, Tennessee. The two plots (henceforth known as upper and lower plots) were located approximately 100 m from each other but differed in landscape position and soil type. One plot comprised a severely eroded Waynesboro clay loam (fine, kaolintic, thermic Typic Paleudult), a well-drained soil formed in old alluvium which occurred on a high terrace with 5–12% slope. The lower elevation plot consisted of a Leadvale silt loam (fine-silty, siliceous, semiactive thermic Typic Fragiudult), a moderately well-drained soil containing a fragipan and occurred on an alluvial terrace with 2–5% slope. The field in which the plots were located was 6.9 ha (17 acres) of Alamo switchgrass. This field was planted to switchgrass in 2007 and was concluding its third growing season, reaching mature yields, at the time of sampling. Starting in September 2009, whole plant switchgrass samples consisting of the above ground stems and leaves were harvested every two weeks, including the early part of the traditional harvest window for the region, mid-November. After this time, the switchgrass

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