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[illegible] (*Pa c ga .*) [illegible] 40% ([illegible] 4.4 [illegible] $^{-1}$) [illegible] ([illegible] 350 [illegible] 0 [illegible] $^{-1}$) [illegible] 10% [illegible] 0% [illegible]

A NUMBER OF PLANT SPECIES have been considered as dedicated energy crops (Lewandowski et al., 2003b; Walsh et al., 2003; Angelini et al., 2005), representing both annual and perennial herbaceous crops and short-rotation trees. Perennial grasses have several advantages over annual crops such as lower establishment costs, reduced soil erosion, increased water quality, and enhanced wildlife habitat (McLaughlin et al., 2002; Roth et al., 2005).

Switchgrass has been evaluated as a biofuel crop in the Midwest (Vogel et al., 2002; Casler and Boe, 2003), the Southern (Sanderson et al., 1999; Muir et al., 2001; Cassida et al., 2005) and Northern Great Plains of the USA (Berdahl et al., 2005; Lee and Boe, 2005), southeastern Canada (Madakadze et al., 1999), and Europe (Elbersen et al., 2001). The latitude-of-origin has a large impact on switchgrass yield potential and ability to survive in extreme environments (Casler et al., 2004); lowland ecotypes from the southern latitudes have higher yield potential than upland ecotypes from the north, but are not as cold tolerant.

Seasonal time of harvest affects switchgrass yield (Madakadze et al., 1999; Sanderson et al., 1999; Vogel et al., 2002; Casler and Boe, 2003). In the south-central USA, a single harvest in mid-September maximized biomass yields (Sanderson et al., 1999), in the Midwest maximum yield was found in mid-August (Vogel et al., 2002). However, Casler and Boe (2003) found that a mid-August harvest in north-central USA reduced stand density over time and recommended harvesting later in the season when regrowth would be minimized or not occur.

Conversion systems have different requirements for biofuel feedstock quality; the composition of the biomass affects its quality as a biofuel. Several biomass conversion technologies have been under investigation to generate energy from biomass: ethanol production from biorefineries, direct combustion, and thermo-

The experiments were conducted over a range of landscape scales from small plot- to field-scale. The plot-scale study was conducted in Rock Springs, PA, between fall 2002 and spring 2005. The soil at Rock Springs was a Hagerstown silt loam (fine, mixed, mesic Typic Hapludalfs). Three switchgrass cultivars, Cave-In-Rock, Shawnee, and Trailblazer, were planted in a completely randomized design with six replicate plots (plot size, 0.014 ha). Plots were established in 1999. Each plot was split in half and harvest time was randomly assigned. Switchgrass cultivars were whole plots and harvest times were subplots. A 1-m swath of switchgrass was harvested at 10-cm height from the center of each plot using a sickle-bar mower. Nitrogen was applied in the spring annually at the rate of 112 kg N ha^{-1}.

The field-scale sites were at Rock Springs (central PA in Centre County) and Ligonier, PA (western PA in Westmorland County). Weather data were collected from nearby meteorological sites (Table 1). The soil at Ligonier was a Gilpin-Upshur complex (Gilpin- Fine-loamy, mixed, active, mesic Typic Hapludults; Upshur- Fine, mixed, superactive, mesic Typic Hapludalfs). At Rock Springs five switchgrasss cultivars (Pathfinder, Trailblazer, NJ-50, Cave-In-Rock, and Shawnee) were planted in seven blocks (block size, 0.12–1.22 ha) with Pathfinder and Cave-In-Rock in two blocks; the experiment was conducted between fall 2001 and spring 2004. The switchgrass cultivars Pathfinder and NJ-50 were established in 1979, Trailblazer in 1986, Cave-In-Rock in 1995 and 1996, and Shawnee in 2000. The grasses were either not harvested or harvested only once per year, and either no fertilizer input or 56 kg ha^{-1} annually. Visual observations of the plots indicated good stands of all plots. In Ligonier, two conservation land fields were planted with ‘Shelter’ switchgrass in 1999 at Monona Farms and harvested from fall 2002 to spring 2004 (plot size, 0.2–0.89 ha). Nitrogen was applied in the spring annually at 56 kg ha^{-1} at Rock Springs, but no N was applied to the conservation lands at Ligonier. The experimental design at each location was a randomized complete block design with blocks split in half and harvest time randomly assigned.

During the 3 yr of the field-scale experiment, the actual harvest time ranged from 15 October to dfdHovem(October)-337(29)-284(

sucrose) were extracted with 80% vol vol^{-1} ethanol and analyzed by high-pressure liquid chromatography (HPLC). The alcohol-insoluble residues were extracted with cold water to remove fructans that were quantified using the ketose assay of Boratynski (1984). Starch in the water-insoluble residue was enzymatically hydrolyzed to glucose, which was measured by HPLC. The remaining crude, alcohol-insoluble cell wall residue was subjected to a two-stage sulfuric acid hydrolysis using the Uppsala Total Dietary Fiber Method (Theander et al., 1995). An aliquot from the first stage of the acid hydrolysis was analyzed for uronic acids using glucuronic acid as the reference standard (Ahmed and Labavitch, 1977). Neutral sugars from the two-stage acid hydrolysis were analyzed by gas chromatography (GC) as alditol-acetate derivatives. The acid-insoluble residue provided the Klason lignin concentration estimate after correction for ash. The cellulose values were reported as cell wall glucose and hemicellulose as the sum of xylan, arabinose, mannose and uronic acid from the cell wall.

The potential ethanol yield was calculated from the sum of six-C carbo(an0Tcl)-360(glu707TD1a02(usin4;334ijrd)-33[(sucrose)35(,)-230(glucose)35(-)]TJT*8(fruuco;id)-40st(Bogure)-395(rolaccharovi:re)-8

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Cell-wall carbohydrates increased over winter. Glucose was the dominant monosaccharide residue in the cell wall polysaccharide fraction in switchgrass from both harvest seasons, with xylose being the second most abundant polysaccharide component (Table 6). The ratio of glucose to xylose was less than 1.5 to 1. Concentrations of both glucose and xylose increased in the spring. Arabinose was the third most abundant monosaccharide residue in the samples. Seasonal harvest time had no consistent effect on minor monosaccharide composition of the cell wall material of switchgrass. Cell wall cellulose, hemicellulose, and Klason lignin all increased over winter in spring harvested switchgrass (Table 7). Klason lignin increased over winter from 10 to 33% while cellulose and hemicellulose increased from 5 to 14%. The five-C carbohydrates were more affected by harvest time than six-C carbohydrates, and the resulting predicted ethanol yield tended to increase in spring-

and Mg (elements typically not associated with organic matter) were typically less than 50% of the fall concentration, while the concentration of Ca, S, and N (elements typically associated with organic matter) were greater than 75% of the concentration in fall-harvested biomass. The reduced concentration of alkali metals in the switchgrass biomass improve biofuel quality because these can increase the formation of fusible ash, causing slagging and fouling of boilers used in direct combustion (Miles et al., 1996). All switchgrass was below the critical elemental limits (10, <3, and 2 g kg^{-1} DM for N, S, and Cl, respectively) described by Lewandowski and Kicherer (1997) and were similar to values reported from *Miscanthus* (Lewandowski et al., 2003a; Lewandowski and Heinz, 2003) and switchgrass (Cassida et al., 2005) harvested during similar seasons. Time of harvest affects the ability to achieve the desired moisture concentration of switchgrass for stable storage and burning efficiency. The moisture concentration was about 350 for fall harvest and 70 g kg^{-1} for spring harvest averaged for 3 yr. To store well, the switchgrass moisture concentration should be less than 230 g kg^{-1} (Lewandowski and Kicherer, 1997) or even less (standard recommendations for hay storage are 150–180 g kg^{-1}). Increased moisture leads to an increase in danger of self-ignition during storage, reduced burning efficiency at the power plant, and microbial degradation of soluble and storage carbohydrates.

Carbohydrate concentrations in switchgrass changed with the delay of harvest from fall until spring. Ethanol yields are higher from glucose than most other sugars and it can be fermented by industrial yeast strains (Dien et al., 2003). Although switchgrass harvested in the spring had higher concentrations of cell wall glucose and nonglucose sugars, lignin concentrations also increased. Noncell wall carbohydrate concentrations declined over winter. A negative relationship between Klason lignin concentration and efficiency of glucose recovery after dilute-acid pretreatment and enzymatic saccharification has been observed (Dien et al., 2006), similar to the negative impact of lignification on digestibility of forages by ruminants (Jung and Deetz, 1993). Glucose recovery could be increased with higher pretreatment temperature, but this would increase conversion costs. The noncell wall carbohydrates accounted for 0.5 to 9.6% of the potentially fermentable carbohydrates in these biomass crops. Unlike cell wall polysaccharides, these noncell wall carbohydrates are directly fermentable without harsh pretreatment; however, they are particularly susceptible to microbial degradation. The starch was probably from the mature switchgrass seeds in the fall and the decrease when harvest was delayed until spring because seeds dropped off over the winter. The higher cell wall values in the spring were due to leaching of soluble components such as sugars, protein, and organic acids, over winter.

Fermentative gas production by a mixed ruminal inoculum provides a measure of forage quality for ruminants, and a more general measure of the fermentability of biomass by microbes producing their own hydrolytic enzymes (e.g., in consolidated bioprocessing [Lynd et al., 2002]). This analytical technique has also been shown to provide a reasonable prediction of ethanol production in an enzyme/yeast (simultaneous sac-

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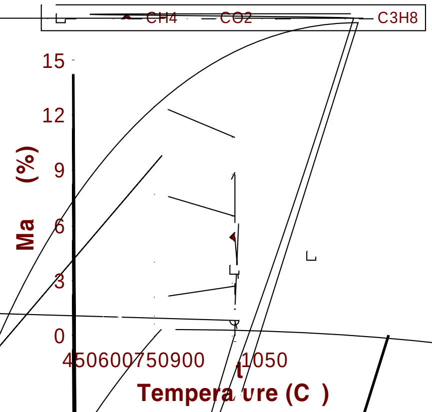

charification and fermentation system [Weimer et al., 2005]). In vitro gas production from switchgrass samples in this study decreased almost 25% with the delay in harvest over winter. The decrease in fermentability when switchgrass harvest was delayed until spring is consistent with reports in maize (*Z a a s* L.) silage, that digestibility decreases with multiple frosting events of the maize crop, although the mechanism causing the decrease is not known (St. Pierre et al., 1983; St. Pierre

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