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Biomass Yield and Biofuel Quality of Switchgrass Harvested in Fall or Spring

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ABSTRACT

Seasonal time of switchgrass (*Panicum virgatum* L.) harvest affects yield and biofuel quality and balancing these two components may vary depending on conversion system. A field study compared fall and spring harvest measuring biomass yield, element concentration, carbohydrate characterization, and total synthetic gas production as indicators of biofuel quality for direct combustion, ethanol production, and gasification systems for generation of energy. Switchgrass yields decreased almost 40% (from about 7–4.4 Mg ha^{-1}) in winters with above average snowfall when harvest was delayed over winter until spring. The moisture concentration also decreased (from about 350–70 g kg^{-1}) only reaching low enough levels for safe storage by spring. About 10% of the yield reduction during winter resulted from decreases in tiller mass; however, almost 90% of the yield reduction was due to an increase in biomass left behind by the baler. Mineral element concentrations generally decreased with the delay in harvest until spring. Energy yield from gasification did not decrease on a unit biomass basis, whereas ethanol production was variable depending on the assessment method. When expressed on a unit area basis, energy yield decreased. Biofuel conversion systems may determine harvest timing. For direct combustion, the reduced mineral concentrations in spring-harvested biomass are desirable. For ethanol fermentation and gasification systems, however, lignocellulose yield may be more important. On conservations lands, the wildlife cover provided by switchgrass over the winter may increase the desirability of spring harvest along with the higher biofuel quality.

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 thermochemical conversion by gasification/pyrolysis (Boateng et al., 2006). The water concentration of biomass affects its safety in storage, the cost of transportation, and its combustion efficiency (Lewandowski and Kicherer, 1997). In direct combustion systems, the mineral concentration can cause corrosion, slagging, and fouling of boilers and increased emissions (Lewandowski and Kicherer, 1997). The composition of C compounds in the biomass can also affect conversion and yield of ethanol from biomass (Weimer et al., 2005; Dien et al., 2006). The energy density affects the energy production from gasification (Boateng et al., 2006), as it does in other energy-production systems.

Seasonal time of harvest not only affects switchgrass yield, but also biofuel quality. The ash concentration of switchgrass decreases as it matures during the growing season (Sanderson and Wolf, 1995), leading to increased biofuel quality and potentially lower N requirements with a fall vs. summer harvest (Vogel et al., 2002). When harvest is further delayed until spring, the mineral concentration of reed canarygrass (*Phalaris arundinacea* L.) (Burvall, 1997) and *Miscanthus* sp. (Lewandowski et al., 2003a) have decreased further, although yields decreased. Our objective was to examine how the seasonal time of harvest, comparing fall and spring harvest, affected switchgrass biomass yield and biofuel quality for energy production from fermentation, gasification, or direct combustion systems.

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Abbreviations: DM, dry matter; GC, gas chromatography; HPLC, high-pressure liquid chromatography; MS, mass spectrometer.

MATERIALS AND METHODS

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 15 November in the fall and 6 April to 4 May in the spring (see Table 2 for actual dates). Before harvest at Rock Springs, 100 tillers were collected from each plot and separated into stems (plus leaf sheaths), leaf blades, and panicles to identify and quantify change in biomass with plant part. Switchgrass was harvested with standard farm equipment (John Deere 926 MoCo Discbine with 2.97-m cut and a John Deere model 457 Silage Special Round Baler set at 1.22-m wide by 1.52-m diam.). All plots were harvested at a 10-cm stubble height. Samples of residue remaining after machine harvest were taken from five 1-m^2 quadrates along a transect across each field from fall 2002 to spring 2004 at Rock Springs. Residue included any switchgrass that was not cut to a 10-cm stubble height because it had lodged or that was cut but not picked up during baling. After cutting the switchgrass, samples were collected from the windrows and dried at 55°C to determine moisture concentration at harvest. Switchgrass was baled after samples were collected, individual bale weights determined, and yield calculated by dividing the moisture corrected bale weight by the area harvested. After drying, samples collected for moisture determination were ground in a hammer mill and then ground to pass a 1-mm screen of a Wiley mill (Thomas Scientific, Swedesboro, NJ). Total N was determined with a Leco FP-528 (Horneck and Miller, 1998) and total S with a Leco SC-432 (Kowalenko and Van Laerhoven, 1998) (LECO Corp., St. Joseph, MI). The five other elements were quantified by inductively coupled plasma emission spectroscopy (Isaac and Johnson, 1998) after extraction by dry ashing (P, K, Ca, Mg) (Miller, 1998) or water (Cl).

Carbohydrate analyses were conducted on Cave-In-Rock switchgrass in the plot-scale study on samples harvested from fall 2002 to spring 2004. Carbohydrates and lignin were determined using a sequential procedure described by Dien et al. (2006). Briefly, soluble carbohydrates (glucose, fructose, and

Table 1. Monthly average of the mean daily temperature and total precipitation at the two sites from 2001 to 2005 compared with the 30-yr average (1961–1990).

	Rock Springs, PA					Ligonier, PA		
Month	2001	2002	2003	2004	30-yr mean	2002	2003	30-yr mean
				Air temperature, °C				
Jan.	−3.4	0.4	−6.6	−6.7	−4.3	2.6	−5.2	−1.3
Feb.	−0.1	1.2	−5.4	−4.4	−2.9	1.8	−2.7	−0.6
March	0.2	3.0	2.3	4.3	2.5	5.3	5.0	4.0
Apr.	9.2	9.4	8.7	9.5	8.7	12.3	11.1	10.0
May	13.9	12.6	13.5	17.8	14.8	14.7	14.9	15.6
June	18.9	19.5	18.0	18.2	19.5	21.5	18.7	20.2
July	19.0	21.8	20.6	19.4	21.8	24.2	21.5	22.5
Aug.	21.2	21.5	21.6	19.4	20.9	23.4	21.9	21.3
Sept.	14.6	17.6	16.1	17.4	16.8	19.2	17.0	18.1
Oct.	10.4	8.7	9.4	10.2	10.6	10.4	9.6	11.9
Nov.	6.9	3.5	7.1	6.4	5.0	4.7	7.9	7.7
Dec.	1.8	−1.6	−0.8	−0.5	−1.3	−0.5	0.0	0.6
				Precipitation, cm				
Jan.	0.0	3.8	4.7	6.5	6.1	4.6	7.2	9.2
Feb.	0.6	3.4	6.3	4.7	6.6	4.0	4.9	8.6
Mar.	2.9	9.9	6.1	5.8	7.9	11.6	5.9	10.4
Apr.	6.5	2.8	6.2	11.6	7.4	12.4	5.5	10.4
May	4.3	15.1	12.0	10.3	9.2	13.4	16.0	10.8
June	15.8	12.5	11.8	8.3	10.2	12.0	14.5	11.2
July	6.8	3.4	14.3	23.9	9.2	3.3	11.5	12.2
Aug.	9.8	5.2	23.6	15.7	8.1	6.6	17.8	10.2
Sept.	9.0	9.2	17.7	27.2	8.2	9.5	11.3	8.6
Oct.	4.1	12.6	8.0	4.9	7.2	9.6	9.3	7.6
Nov.	6.7	8.4	11.0	7.5	8.4	6.6	8.8	8.3
Dec.	4.1	6.9	9.2	5.8	6.6	6.3	9.0	8.6

Table 2. Harvest dates of switchgrass at two locations from 2001 to 2005.

Harvest season	Year	Harvest date: Plot-scale, Rock Springs, PA	Field-scale, Rock Springs, PA	Field-scale conservation lands, Ligonier, PA
Fall	2001		31 Oct.	
	2002	15 Oct.	8 Nov.	15 Nov.
	2003	30 Oct.	3 Nov.	4 Nov.
	2004	9 Nov.		
Spring	2002		18 Apr.	
	2003	15 Apr.	16 Apr.	14 Apr.
	2004	8 Apr.	7 Apr.	4 May
	2005	6 Apr.		

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 carbohydrates (soluble carbohydrates: sucrose, glucose, fructose; storage polysaccharide: starch; and cell-wall carbohydrates: mannose, galactose, and glucose) and five-C cell wall carbohydrate xylose (USDOE, 2006). The potential ethanol yield from the fall- and spring-harvested switchgrass, without prior chemical treatment, was predicted by using in vitro gas production as a surrogate measure of the fermentability of cellulosic biomass to ethanol (Weimer et al., 2005). In vitro gas production analyses were conducted on Cave-In-Rock switchgrass from the plot-scale study on samples harvested from fall 2002 to spring 2005.

Gas analyses were conducted on Cave-In-Rock switchgrass samples in plot-scale study harvested from fall 2002 to spring 2004. The gas components of gasification (CO, CO_2, CH_4, C_2H_6, and C_3H_8) were quantified using flash pyrolysis at 600, 750, and 900°C with a pyroprobe (Pyroprobe 2000, CDS Analytical)-GC-mass spectrometer (MS) (6890N gas chromatograph and HP 5973 MS, Agilent Technologies) (Boateng et al., 2006). Char yield (elemental C plus ash) was determined gravimetrically. All other gases evolved during pyrolysis that were not quantified were combined together as tar; this included condensable and noncondensable gases with molecular weight greater than C_4 and H. Hence, tar was determined as the difference between the initial biomass and the sum of the measured gas and char.

Data were analyzed using the ANOVA procedure for a split-plot design in SAS (SAS Institute, 1999) with switchgrass cultivar as the main plot and harvest time as the subplot in the plot-scale experiment, and as a randomized complete block design for field-scale experiments. Harvest season, switchgrass cultivar, and harvest year were considered to be fixed effects while replication was treated as random. Since only Cave-In-Rock switchgrass was used in the carbohydrate, in vitro ruminal gas production, and gasification analysis, samples were analyzed as a completely randomized design. Where the season × year interaction was significant, results were not averaged over years. Least square means were separated by Tukey's HSD ($P \leq 0.05$).

RESULTS

Switchgrass yield decreased at all landscape-scales when harvest was delayed until spring (Table 3). At the plot-scale, the yields of all three switchgrass cultivars decreased from fall to spring (20–24%). At the field-scale in Rock Springs, yield significantly decreased all years (32–43%) except the first. At the field-scale in Ligonier, the trend for yield reductions in the spring harvest was also present. The lower yields at the Ligoiner site in 2002 may be due to water stress (Table 1). To identify the source of yield reduction, tiller weights and residue after harvest were collected. Over winter, tiller weight decreased about 7%. The leaf and panicle weights decreased over winter and stem weight increased (Fig. 1). About 21% of the switchgrass biomass in the field was not picked up by harvest equipment in the fall and was left behind as residue; in the spring the amount of residue left behind increased to 45% (Table 4). Including residue, total spring biomass was 11% lower than fall, similar to the amount of reduction in tiller weight over winter. Switchgrass water concentration decreased from 352 ± 85 in the fall to 72 ± 27 g kg^{-1} in the spring.

The element concentration decreased over winter (Table 5). The change in element concentration from fall to spring was similar over landscape-scale. Potassium and Cl decreased the most of any elements over winter (38–83%). Magnesium and P decreased 41 to 67% from fall to spring harvest, and Ca, S, and N decreased the least (5–28%). The general decrease in elements over winter accounted for the 30% reduction in ash concentration.

While ash decreased over winter, Klason lignin and cell wall carbohydrate concentrations were higher (Table 6 and 7). The composition of total carbohydrates in terms of soluble, storage, and cell wall fractions differed in fall and spring samples (Table 6). Soluble carbohydrates decreased over winter. Sucrose was the predominant form

Table 3. Switchgrass yield harvested in fall and spring at two locations.

Location	Fall	Spring
	Mg ha^{-1}	
	Plot-scale, Rock Springs PA	
Cave-In-Rock	8.57a†	6.72b
Shawnee	8.45a	6.74b
Trailblazer	6.72b	5.09c
	Field-scale, Rock Springs PA	
2001–2002	6.69a	6.83a
2002–2003	6.95a	4.72b
2003–2004	7.02a	4.03b
	Field-scale conservation lands, Ligonier PA	
2002–2003	2.87ab	2.08b
2003–2004	5.07a	2.61ab

† Least square means within columns and landscape scale were separated by Tukey's HSD ($P \leq 0.05$).

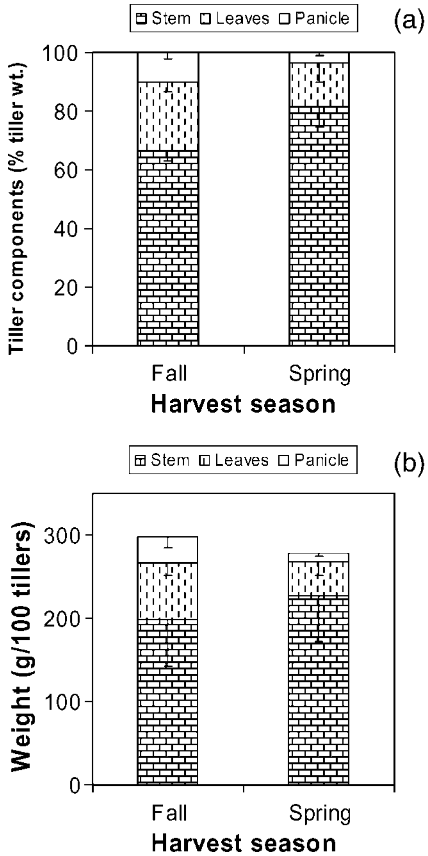

Fig. 1. Stem, leaf, and panicle weights of fall 2002 to spring 2004 harvested switchgrass from field-scale blocks at Rock Springs expressed as: (a) % of total tiller weight and (b) component weight of tiller. Vertical bars denote ± SD.

of soluble carbohydrate and it decreased in spring samples as did glucose and fructose. Storage carbohydrates also decreased over winter. The storage form of carbohydrate in switchgrass is starch, although small amounts of fructans were also detected, possibly from contaminating cool-season grasses present in the plots. The total amount of noncell wall carbohydrates present as soluble and storage carbohydrates ranged from 6.9 ± 2.6 g kg^{-1} DM for the spring harvested switchgrass to 47.3 ± 28.1 g kg^{-1} DM for the fall samples.

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-harvested switchgrass. In vitro ruminal gas production, a measure of forage quality and of direct fermentability of biomass without pretreatment, decreased about 20 to 25% over winter (Table 8).

Table 4. Average switchgrass machine harvested yield, residue, and total biomass at two seasonal harvest times from fall 2002 to spring 2004 at Rock Springs, PA, field-scale experiment (means of 2 yr ± SD).

Harvest season	Yield	Residue	Total biomass
	Mg ha^{-1}		
Fall	6.98 ± 1.08	1.91 ± 0.61	8.92 ± 1.54
Spring	4.38 ± 0.89	3.59 ± 0.93	7.97 ± 1.28

The seasonal time of switchgrass harvest did not affect gas production from pyrolysis. Pyrolysis is heating in the absence of O_2. Products from pyrolysis are the synthetic gases, char, and tar. Total gases (synthetic gas) (CO, CO_2, CH_4, C_2H_6, and C_3H_8) were about 15 to 25% of the total mass from pyrolysis (Fig. 2). Unfortunately we lacked the necessary instrumentation to measure the H component of the synthetic gas produced. Char, which is ash plus elemental C, was about 5 to 8% of the total mass from pyrolysis. The remainder was tar, about 69 to 77% of the total mass from pyrolysis. Tars are high-molecular weight hydrocarbons that at higher temperatures can undergo further pyrolysis to yield lightweight hydrocarbons (tar cracking). Carbon dioxide decreased with temperature whereas other gases increased (Fig. 3). Methane increased at about twice the rate with the increase in temperature as CO, C_2H_6, or C_3H_8.

DISCUSSION

Biomass Yield

Switchgrass yield decreased when harvest was delayed from fall to spring. When standard farm machinery was used for harvest, there was a larger amount of residue remaining in the field after harvest in the spring. In the fall, switchgrass stems are still slightly green and leaves still pliable, whereas in the spring, the whole plant is very dry and brittle, and seeds have dropped off over the winter. There can also be greater lodging after heavy snows in the winter, contributing to the difficulty of removing biomass from the field. The effect of delaying harvest from fall to spring varied depending on snowfall. During the winter of 2001-2002, there was little snowfall, about 56 cm, and switchgrass yields were similar between fall 2001 (6.69 ± 1.45 Mg ha^{-1}) and spring 2002 (6.83 ± 1.78 Mg ha^{-1}). However, snowfalls were almost three times higher in the following two winters, from fall 2002 to spring 2004, about 153 cm each year, and yields decreased an average of almost 40%. The long-term snowfall average at Rock Springs is about 117 cm.

The decrease in biomass yield between fall and spring at Rock Springs occurred from two sources, biomass that was not picked up by the baler, either because it was not cut due to lodging or cut but not picked up by the baler, and a decrease in standing tiller weight. Tiller weight decreased less than 10% during the winter, with weight

Table 5. Change in elemental concentration between fall and spring harvested switchgrass averaged over years.

Harvest season	Ash	N	P	K	Ca	Mg	S	Cl
	g kg^{-1}							
				Plot-scale, Rock Springs, PA				
Fall	34.15a†	6.21a	0.89a	3.33a	4.36a	1.73a	0.68a	0.99a
Spring	24.71b	5.40b	0.52b	0.59b	3.49b	0.71b	0.59b	0.27b
Residual (%)‡	72.36	86.90	58.62	17.60	80.10	41.00	85.77	27.37
				Field-scale, Rock Springs, PA				
Fall	34.61a	4.29a	0.89a	3.36a	3.58a	1.22a	0.64a	0.60a
Spring	22.62b	4.05a	0.43b	0.69b	2.77b	0.60b	0.46b	0.15b
Residual (%)	65.35	94.36	47.93	20.66	77.35	49.35	71.90	25.44
				Field-scale conservation lands, Ligonier, PA				
Fall	33.85a	3.28a	0.80a	3.45a	5.05a	0.98a	0.50a	0.73a
Spring	23.95b	2.92a	0.40a	0.60b	3.75b	0.33b	0.48a	0.45a
Residual (%)	70.75	89.02	50.00	17.39	74.26	33.33	95.00	62.07

† Least square means within columns and landscape scale were separated by Tukey's HSD ($P \leq 0.05$).
‡ Percentage of fall element content remaining in spring.

reductions due to loss of leaves and panicles. In the fall, about 21% of the biomass yield was left in the field as residue not picked up by the baler. More than twice as much residue was not picked up by the baler in the spring. The largest source of biomass loss at spring harvest resulted from biomass not picked up by the baler, almost 90% when expressed on an adjusted yield basis. When these two sources of biomass loss were added back onto the spring yield, fall and spring yields were within 5% of each other.

In the midwestern USA, maximum switchgrass yields occurred in mid-August at the full panicle emergence to postanthesis developmental stages (Vogel et al., 2002); yields decreased 10 to 20% with harvests after a killing frost in October. However, Casler and Boe (2003) found that a mid-August harvest in the north-central USA reduced stand density over time compared with a fall harvest, similar to recent observations made in Pennsylvania (data not shown). The magnitude of yield decline when harvest is delayed until spring will be greater in high snow fall years. Although switchgrass yields are reduced in the spring, the water concentration of fall harvested switchgrass was too high for stable storage. A mid-August harvest in Pennsylvania would be able to meet the water concentration requirements for stable storage with field drying, however, twice the amount of N would be removed with harvest and other minerals are also higher. The long-term stand densities may decrease as has been observed in the north-central USA (Casler and Boe, 2003) and lead to reduced yields in Pennsylvania. Spring harvest also provides over-winter wildlife cover during the winter, and since it occurs in April, before primary nesting and brood rearing in Pennsylvania, impact on spring nesting is minimized.

Biofuel Quality

Although switchgrass yield decreased when harvest was delayed from fall to spring, biofuel quality varied from increasing to decreasing depending on the assessment parameter and target energy generation system. Generally, bioenergy crop production seeks to maximize the concentration of lignocellulose in the feedstock, minimize N and mineral concentrations, and limit water concentration (Lewandowski and Kicherer, 1997). The efficiency and end products of the various conversion processes depend on the chemical composition of biomass. Biomass contains higher concentrations of inorganic elements compared with fossil fuels, resulting in decreased energy density for combustion (Agblevor et al., 1992; Nordin, 1994). The concentration of elements usually decreases in forages as they mature (Sanderson and Wolf, 1995; Jorgensen, 1997; Madakadze et al., 1999); delaying the harvest until late winter–early spring further decreases elements and moisture concentration in reed canarygrass (Burvall, 1997) and *Miscanthus sp.* at harvest (Lewandowski and Kicherer, 1997; Lewandowski et al., 2003a). Similar results were found in this study; both the element and moisture concentration decreased in spring- compared to fall-harvested switchgrass biomass. In the spring-harvested switchgrass, all elements did not decrease equally. The concentration of Cl, K, P,

Table 6. Soluble, storage, and cell wall carbohydrate composition of Cave-In-Rock switchgrass harvested in fall 2002 to spring 2004 from plot-scale fields.

		Soluble carbohydrates			Storage polysaccharides		Cell wall carbohydrates					
Year	Season	Glc†	Fru	Suc	Starch	Fructan	Glc	Xyl	Ara	Gal	Man	UA
		g kg^{-1} DM										
2002	fall	9.6a***	7.4a	38.2a	14.6a	3.9a	286c	215b	30.7b	9.9b	5.6b	13.8a
2003	spring	0.0c	1.8c	2.1c	5.0b	0.3c	327b	244a	33.2a	11.2a	7.4a	13.9a
2003	fall	3.0b	4.0b	8.9b	3.8b	1.2b	325b	228b	30.2b	9.8b	6.1b	14.0a
2004	spring	0.0c	1.4c	2.1c	0.8c	0.2c	348a	243a	29.0b	9.1b	7.0a	12.8b

† Ara , Arabinose; fructan; Fru, fructose; Gal, galactose; Glc, glucose; Man, mannose; starch; Suc, sucrose; UA, uronic acids; Xyl, Xylose.
*** The season × year interaction was significant at the $P \leq 0.01$. Least square means within columns were separated by Tukey's HSD ($P \leq 0.05$).

Table 7. Lignin, cellulose, and hemicellulose concentrations, and the sum of 5- and 6-C carbohydrates that can be converted to ethanol with the resulting predicted ethanol yield of Cave-In-Rock switchgrass harvested in fall 2002 to spring 2004 from plot-scale fields.

Year	Season	Klason lignin	Cellulose†	Hemicellulose	Carbohydrates 6C	Carbohydrates 5C	Ethanol
		g kg^{-1} DM					L Mg^{-1}
2002	fall	130b*	286c	265c	371a	215c	426b
2003	spring	173a	327b	299a	355b	244a	436ab
2003	fall	165a	325b	278bc	361ab	228b	428b
2004	spring	182a	348a	292ab	368ab	243a	445a

* The season × year interaction was significant at the $P \leq 0.05$, except ethanol that was not significant. Least square means within columns were separated by Tukey's HSD ($P \leq 0.05$).
† Cellulose (as cell wall glucose) and hemicellulose (based on the sum of cell wall xylose + arabinose + mannose + uronic acids).

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-

Table 8. Net normalized gas accumulation (L gas kg^{-1} DM added) from Cave-In-Rock switchgrass harvested in fall 2002 to spring 2005 from plot-scale fields over 24- and 96-h *in vitro* incubation with mixed ruminal microorganisms.

Harvest season	24 h	96 h
	L kg^{-1} DM	
Fall	74.17a*	152.70a
Spring	54.31b	120.98b

* The season × year interaction was not significant at the $P \leq 0.05$. Least square means within columns were separated by Tukey's HSD ($P \leq 0.05$).

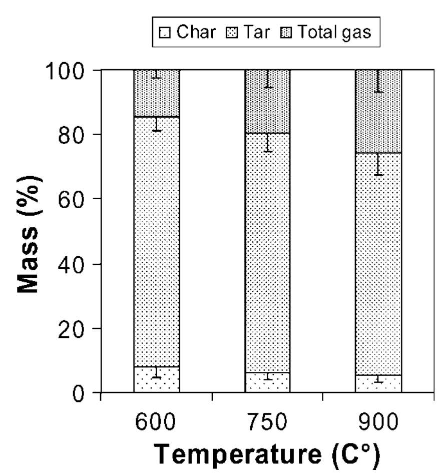

Fig. 2. The components of pyrolysis are total gas, tar, and char. As the temperature of pyrolysis increases, tar and char are broken down to smaller C chemicals and gas. There were no differences in component yields between seasonal time of harvest, so data presented are means of Cave-In-Rock switchgrass samples harvested in fall 2002 to spring 2004 from plot-scale fields. Vertical bars denote ± SD.

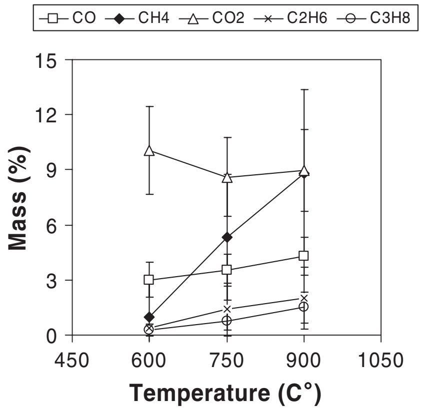

Fig. 3. The measured gas components of pyrolysis are CO, CH_4, CO_2, C_2H_6, and C_3H_8. As the temperature of pyrolysis increases, tar and char are broken down to smaller C chemicals and gas. There were no differences in component yields between seasonal time of harvest, so data presented are means of Cave-In-Rock switchgrass samples harvested in fall 2002 to spring 2004 from plot-scale fields. Vertical bars denote ± SD.

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 (*Zea mays* 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 et al., 1987). Presumably this decreased fermentability results either from lower concentrations of sugars and readily fermentable storage carbohydrates, or from losses of more degradable cell wall polysaccharide fractions. In contrast to the in vitro ruminal gas yields, ethanol yields predicted based on carbohydrate composition and concentration increased slightly when switchgrass harvest was delayed until spring. These predicted ethanol yields assumed that there was no negative impact of lignin on conversion, and that switchgrass contained no inhibitors of yeast fermentation. Fall-harvested biomass may also be less expensive to convert to ethanol due to its higher concentration of some nutrients that would otherwise have to be added to the fermentation medium to support microbial growth. This benefit would be counterbalanced by the increased costs of transporting the fall-harvested materials at lower dry matter concentration.

Yields from gasification were not affected by delaying switchgrass harvest from fall until spring. The synthetic gas yield was temperature dependent: CH_4, C_2H_6, and C_3H_8 are produced at higher temperatures than CO and CO_2. The mass of char tended to be higher in fall-harvested switchgrass. This result is consistent with higher ash concentration measured in fall-harvested switchgrass. Char mass decreased with temperature due to its pyrolysis at elevated temperatures thereby decreasing the elemental C while ash remains constant. These values are similar to a previous study of switchgrass (Boateng et al., 2006), but total gas was a higher percentage of mass, and char a lower percentage in this study. Co-locating gasification systems with ethanol plants may yield operational and economic synergies. Although yield per unit weight remained the same when harvest was delayed until spring, with the reduction in biomass yield, gasification yields per unit area would decrease with spring harvest.

CONCLUSIONS

Switchgrass yield generally decreased when harvest was delayed from fall to spring. However, assessing the impact of the delayed harvest on biofuel quality depended on the target method of energy generation. Delaying harvest reduced ash and water concentration thereby increasing the energy content of the biomass for all conversion systems. The high water concentration of the fall harvest would increase transport costs and may preclude stable storage of switchgrass. The reduced concentration of selected minerals in a spring harvest would also reduce the potential for formation of fusible ash, which cause slagging and fouling of boilers used for direct combustion. The impact of potential for conversion of biomass to ethanol is largely dependent on the means by which bioconversion to ethanol would be conducted (a conventional enzyme/yeast process vs. a direct bacterial fermentation). There was no impact of harvest delay on the energy yield from gasification. When total yield was expressed on a unit area basis, energy yields decreased for all conversion systems with a spring harvest. The disadvantage of yield reductions with spring harvest may be eliminated if more efficient harvest systems could be developed to reduce the quantity of residue remaining in the field. The highest biofuel quality appears to be obtained when switchgrass harvest is delayed over winter until spring. On conservations lands, the wildlife cover provided by switchgrass (Murray and Best, 2003; Roth et al., 2005) over the winter may increase the desirability of spring harvest along with the higher biofuel quality. Spring harvest would occur in April, before primary nesting and brood rearing in Pennsylvania thereby providing wildlife cover over winter while minimizing impact on spring nesting. The seasonal time of switchgrass harvest may depend on individual farm operations, including distance to conversion facility, other crops on the farm, or even wildlife habitat value.

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