2009

# Switchgrass for Bioethanol and Other Value-Added Applications: A Review

Deepak R. Keshwani
*University of Nebraska - Lincoln*, dkeshwani2@unl.edu

Jay J. Cheng
*North Carolina State University*

Published in *Bioresource Technology* **100** (2009), pp. 1515–1523; doi: 10.1016/j.biortech.2008.09.035


Paper No. BAE-2008-05 of the Journal Series of the Department of Biological and Agricultural Engineering, North Carolina State University, Raleigh, NC 27695-7625, USA

Submitted January 2, 2008; revised September 11, 2008; accepted September 11, 2008; published online October 30, 2008.

# Switchgrass for Bioethanol and Other Value-Added Applications: A Review

Deepak R. Keshwani † and Jay J. Cheng

Department of Biological and Agricultural Engineering, North Carolina State University, Raleigh, NC 27695-7625, USA
† *Present address* — Department of Biological Systems Engineering, University of Nebraska–Lincoln, Lincoln, NE 68588

*Corresponding author* — J. J. Cheng, tel 919 515-6733, fax 919 515-7760, email jay_cheng@ncsu.edu

**Abstract**

Switchgrass is a promising feedstock for value-added applications due to its high productivity, potentially low requirements for agricultural inputs and positive environmental impacts. The objective of this paper is to review published research on the conversion of switchgrass into bioethanol and other value-added products. Environmental benefits associated with switchgrass include the potential for carbon sequestration, nutrient recovery from runoff, soil remediation and provision of habitats for grassland birds. Pretreatment of switchgrass is required to improve the yields of fermentable sugars. Based on the type of pretreatment, glucose yields range from 70% to 90%, and xylose yields range from 70% to 100% after hydrolysis. Following pretreatment and hydrolysis, ethanol yields range from 72% to 92% of the theoretical maximum. Other value-added uses of switchgrass include gasification, bio-oil production, newsprint production, and fiber reinforcement in thermoplastic composites. Future prospects for research include increased biomass yields, optimization of feedstock composition for bioenergy applications, and efficient pentose fermentation to improve ethanol yields.

**Keywords:** switchgrass, bioenergy, ethanol, lignocelluloses, pretreatment

## 1. Introduction

Switchgrass (*Panicum virgatum* L.) is a perennial warm-season $C_4$ grass native to North America. It occurs naturally from 55°N latitude to central Mexico (Lewandowski *et al.*, 2003). Tolerance to heat, cold, and drought have enabled adapted ecotypes of switchgrass to inhabit regions throughout North America (Casler *et al.*, 2007). Historically, switchgrass was one of the dominant grasses in the North American tall-grass prairie and was adapted to other regions by European settlers (Hitchcock, 1971). Perennial grasses like switchgrass have been widely used for forage purposes in their native state prior to being established as a crop. Since the 1940s, switchgrass has been used for conservation and warm-season pasture purposes in the Great Plains and Midwest states (Vogel, 2004). There are two general ecotypes of switchgrass: lowland ecotypes that are vigorous, tall, thick-stemmed, and adapted to wetter conditions, and upland ecotypes that are shorter, thinner-stemmed, and adapted to drier conditions (Gunter *et al.*, 1996). Switchgrass was identified by the U.S. Department of Energy as a model herbaceous energy crop (McLaughlin, 1993). Switchgrass shows promise due to its high productivity, suitability for marginal land quality, low water and nutritional requirements, environmental benefits, and flexibility for multipurpose uses (McLaughlin *et al.*, 1999). Switchgrass can be easily integrated into existing farming operations because conventional equipment for seeding, crop management, and harvesting can be used (Lewandowski *et al.*, 2003; Vogel *et al.*, 2002).

Research on the feedstock potential of switchgrass has been effectively summarized in previous studies such as those presented by Sanderson *et al.* (2006) and Parrish and Fike (2005). Traditionally switchgrass has been bred primarily to improve its nutritional value for use as a forage crop. Consequently, breeding strategies typically emphasized high leaf to stem ratio and high nutrient content. However, later studies emphasized the importance of high cellulose content for bioethanol production and low ash content for combustion systems (McLaughlin *et al.*, 1999).

With newer varieties of switchgrass, yields in excess of 20 Mg $ha^{-1}$ have been reported for test plots. For example, Sanderson *et al.* (1996) reported 26 Mg $ha^{-1}$ in field trials in Texas, and Thomason *et al.* (2004) reported 36.7 Mg $ha^{-1}$ from field work in Oklahoma. Although these high yields are site-specific for test plots and do not reflect realistic expectations, Parrish and Fike (2005) state that with well-adapted cultivars from breeding and biotechnology research, annual yields of over 15 Mg $ha^{-1}$ are feasible for lands that receive annual rainfall of at least 70 cm with nitrogen applications of 50 kg N $ha^{-1}$ $year^{-1}$. Schmer *et al.* (2008) reported on-farm yields ranging from 5.2 to 11.1 Mg $ha^{-1}$ for field trials in the mid-continental U.S., which are more realistic expectations for long-term yields. Dunn *et al.* (1993) identified the benefits associated with the perennial nature of switchgrass—such as less intensive agricultural management practices, reduced energy and agrochemical consumption and positive effects on soil and wildlife quality.

While the conversion of lignocellulosic materials has been previously summarized, a review of the significant amount of research specific to the conversion of switchgrass has not been presented to date. The objective of this paper is to review published research on the conversion of switchgrass into bioethanol and other value-added products in addition to discussing research on potential environmental benefits associated with switchgrass.

## 2. Environmental benefits

When the U.S. Department of Energy chose switchgrass to be a major focus of research for bioenergy production, among the reasons cited was the expected positive environmental impact as evidenced by results from the conservation reserve program (CRP). The U.S. Congress established this program in 1985 to remediate the negative effects of decades of row-crop production. The program designated 90% of impacted land areas to perennial grasses like switchgrass. Since soil tillage is only required in the establishment year, there is a reduced risk of soil erosion (Ma *et al.*, 2000a). Hohenstein and Wright (1994) estimated a 95% reduction in soil erosion rates and a 90% reduction in pesticide use for herbaceous energy crops such as switchgrass relative to annual row crops like corn and soybean. While, the initial establishment of harvestable stands of switchgrass requires the use of high quality seed and herbicides for weed control, subsequent stand maintenance requires only limited and periodic herbicide applications (Sarath *et al.*, 2008).

Bransby *et al.* (1998) stated that switchgrass could reduce $CO_2$ emissions and improve soil quality by carbon sequestration. In addition to the large amount of above-ground biomass, switchgrass has an extensive and deep root system that is beneficial for increasing soil carbon storage in addition to being at least 50% more effective in water use compared to cool-season grasses (Stout *et al.*, 1988). The root system can account for up to 80% of the total biomass (Liebig *et al.*, 2005). Garten and Wullschleger (2000) presented a model that predicted a 12% increase in soil organic carbon inventory over a 10-year period following switchgrass establishment with experimental data indicating that the majority of increase is observed in the first 10 cm of the soil. Gebhart *et al.* (1994) reported that perennial grasses like switchgrass can store 1.1 Mg of carbon per hectare annually in the upper 1 m of the soil on CRP lands. Bransby *et al.* (1998) stated that these studies on CRP lands are probably not representative of switchgrass grown for energy production since the emphasis would shift from conservation to maximizing yields. However, McLaughlin *et al.* (2002) indicated that switchgrass grown on bioenergy research plots could add 1.7 Mg of carbon per hectare annually, which is higher than CRP estimate reported by Gebhart *et al.* (1994). Sanderson (2008) reported a 33% increase in soil carbon in the 0–5-cm layer and a slight decrease in the 5–15-cm and 15–30 cm layers seven years after planting. A systematic study of carbon dynamics following the establishment of switchgrass showed that over a two year period, the top 15 cm of sandy loam soil exhibited a 122% increase in carbon mineralization, a 168% increase in microbial biomass carbon, and a 116% increase in net carbon turnover (Ma *et al.*, 2000b).

Wu *et al.* (2006) estimated that the net amount of $CO_2$ sequestered would be around 48.5 kg per dry metric ton of switchgrass. Frank *et al.* (2004) examined Sunburst and Dacotah switchgrass cultivars and noted that the net system carbon gain doubled over a three-year period. Combined with the zero net carbon exchange as a result of burning bioethanol from switchgrass, addition of soil carbon results in the overall reduction of atmospheric release of $CO_2$ (Lynd *et al.*, 1991). However, such gains as a result of carbon sequestration are not guaranteed. Bransby *et al.* (1998) noted that switchgrass will provide net gains in C sequestration when grown on soil with a history of annual row crops and not when it replaces grazed pasture. McLaughlin *et al.* (2002) also predicted smaller gains in soil carbon sequestration following conversion of pastures to switchgrass and noted that significant gains can be achieved for highly degraded soils in warm climates.

The use of switchgrass to improve surface water quality has also been examined. Lee *et al.* (1998) compared switchgrass filter strips to cool-season grass filter strips and reported that switchgrass was more effective in removing phosphorous and nitrogen from runoff. Sanderson *et al.* (2001) treated a switchgrass filter strip with dairy manure and noted similar results for phosphorous and nitrogen reduction. They also noted a 40–44% reduction in chemical oxygen demand as a result of the filter strip. Mersie *et al.* (1999) utilized switchgrass filter strips to reduce the amount of dissolved herbicides (atrazine and metachlor) by 52% and 59%, respectively. These reductions were attributed to slower runoff velocities and increase in soil retention. Mersie *et al.* (2006) reported significant levels of sorption of atrazine and metachlor to switchgrass residues that accumulate over time on filter strips.

Entry and Watrud (1998) tested the ability of Alamo switchgrass to remediate soil contaminated by cesium-137 and strontium-90. These elements are radionuclides released during nuclear testing, nuclear reactor accidents, and weapons production. The authors reported a 36% removal of cesium and a 44% removal of strontium over a five month period.

Switchgrass also has positive impacts on wildlife by providing a suitable habitat for grassland birds that are rapidly declining in numbers (Murray *et al.*, 2003). Switchgrass is typically harvested in late summer or the fall. By this time, the breeding season for most grassland birds is over and there is minimal disturbance to nesting birds (Roth *et al.*, 2005). Murray and Best (2003) proposed a balance between harvested and non-harvested switchgrass fields to preserve species richness of grassland birds. While most studies suggest that switchgrass on CRP lands offers the best habitat for grassland bird species, the scenario is short-term, as these lands are typically in the program for a 10-year period. Switchgrass grown on lands for biofuel harvesting could offer a longer-term habitat given that they will be tied into the life of an energy production facility (Roth *et al.*, 2005).

## 3. Bioethanol production

With the steady increase in energy consumption and current dependence on crude oil to meet energy demands, there is considerable and immediate interest in developing alternative energy sources. Campbell and Laherrere (1998) predicted a steady decline in crude oil production in the coming decades and stated that the world is already in a peak-oil situation. More optimistic estimations predict a peak-oil situation within the next two decades (Wood *et al.*, 2003). Bioethanol is a promising alternative to reduce dependence on crude oil. Currently, the U.S. produces most of its bioethanol from corn grain. This may not be a viable long-term option as increasing demand for corn-based ethanol will have significant arable land requirements (Sun and Cheng, 2002). Increased use of corn for ethanol production will result in higher corn prices and will negatively impact the food and feed industries and could result in reduced exports of animal products (Elobeid *et al.*, 2007). In lieu of these issues, lignocellulosic feedstocks have been considered for ethanol production. These materials include agricultural residues, cellulosic waste such as newsprint and office paper, and herbaceous and woody crops. In particular, herbaceous energy crops such as switchgrass are viewed as a potential long-term ethanol feedstock to replace corn.

Morrow *et al.* (2006) state that a mature bioenergy crop production system would yield 330–380 l of ethanol per Mg of dry switchgrass. These estimates are consistent with those from the National Renewable Energy Laboratory's theoretical ethanol yield calculator ( http://www.nrel.gov/biomass/energy_analysis.html ) that assumes conversion of both hexoses and pentoses. Using a biomass yield of 15 Mg $ha^{-1}$ (Parrish and Fike, 2005), the corresponding theoretical ethanol production potential from highly adapted switchgrass varieties is between 5000 and 6000 l $ha^{-1}$. With more realistic biomass yields reported by Schmer *et al.* (2008), theoretical ethanol yields are likely to be between 2000 and 4000 l $ha^{-1}$. In comparison, theoretical ethanol yields from corn starch is approximately 4000 l $ha^{-1}$, based on data from Gulati *et al.* (1996) and 2000 l $ha^{-1}$ from corn stover, based on data from Perlack and Turhollow (2003). However, Perlack and Turhullow noted that the actual yields from corn stover would be much lower (~700–800 l $ha^{-1}$) since a large portion of the stovers must be left in the fields for maintenance of soil quality.

The major components of lignocelluloses are cellulose, hemicellulose, and lignin, which are closely associated in a complex crystalline structure. Table 1 shows the amount of cellulose, hemicelluloses, and lignin in different switchgrass varieties in the National Renewable Energy Laboratory's biomass feedstock properties and composition database available online ( http://www.nrel.gov/biomass/energy_analysis.html ). Figure 1 describes the general process for converting the carbohydrates in switchgrass into ethanol. Unlike corn, where starch carbohydrates are easily depolymerized into fermentable sugars, carbohydrate fractions in lignocelluloses (cellulose and hemicellulose) are not readily available for hydrolysis. The efficiency of enzymatic hydrolysis is reduced due to limited accessibility of the enzymes to cellulose (McMillan, 1994). Hence, as shown in Figure 1, pretreatment is required to improve accessibility of enzymes to cellulose and hemicellulose fractions. Following pretreatment, cellulose and hemicellulose fractions can be hydrolyzed into fermentable sugars, while lignin can be recovered and used as a fuel to meet some of the energy requirements in a bioethanol production system (Wyman, 1994). After hydrolysis, the resulting sugars are fermented into ethanol, which is then distilled for fuel purposes. Currently, there are technological and economic limitations to ethanol production from lignocelluloses in each step in the conversion process shown in Figure 1. Cost effective pretreatment processes, cheaper hydrolytic enzymes, and fermentation of pentose sugars have been identified in this regard (Gray *et al.*, 2006; Wyman, 2003).

### 3.1. Pretreatment processes

The purpose of pretreatment processes is to reduce crystallinity of cellulose, increase porosity of the biomass, and achieve the desired fractionation (Sun and Cheng, 2002). Effective pretreatments must improve enzymatic hydrolysis, minimize carbohydrate losses, and prevent formation of by-products that might inhibit subsequent hydrolysis and fermentation steps. Physical, physico-chemical, chemical, and biological processes have been studied extensively for the pretreatment of lignocellulosic materials, and detailed descriptions of these processes have been previously described by Mosier *et al.* (2005), Sun and Cheng (2002), and Weil *et al.* (1994). This section briefly describes the major types of pretreatment and reviews research related to switchgrass in each case.

**Table 1.** Composition (% dry basis) of different switchgrass varieties from NREL's biomass feedstock composition and properties database

| Switchgrass variety | Cellulose | Hemicellulose | Lignin |
|---|---|---|---|
| Alamo – whole plant | 33.48 | 26.10 | 17.35 |
| Alamo – leaves | 28.24 | 23.67 | 15.46 |
| Alamo – stems | 36.04 | 27.34 | 17.26 |
| Blackwell – whole plant | 33.65 | 26.29 | 17.77 |
| Cave-in-Rock – whole plant | 32.85 | 26.32 | 18.36 |
| Cave-in-Rock – whole plant (high yield) | 32.11 | 26.96 | 17.47 |
| Cave-in-Rock – leaves | 29.71 | 24.40 | 15.97 |
| Cave-in-Rock – stems | 35.86 | 26.83 | 17.62 |
| Kanlow – leaves | 31.66 | 25.04 | 17.29 |
| Kanlow – stems | 37.01 | 26.31 | 18.11 |
| Trailblazer | 32.06 | 26.24 | 18.14 |

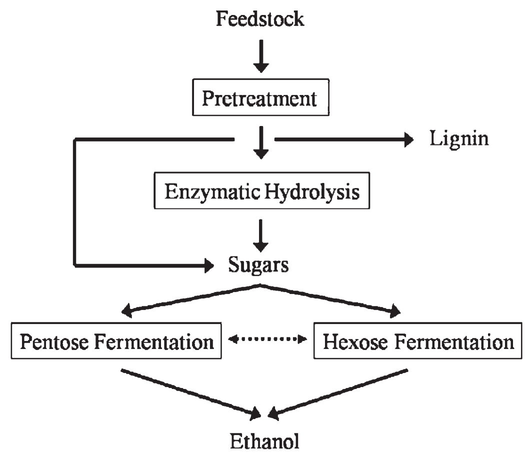


**Figure 1.** General process for conversion of lignocelluloses into ethanol.

#### 3.1.1. Physical pretreatment

Physical pretreatment of lignocelluloses typically involves size comminution by grinding, milling, or chipping. The goal is to reduce the crystallinity of the cellulose fibers in the biomass. Size reduction of lignocelluloses is also necessary to eliminate mass and heat transfer limitations during the hydrolysis reactions (Schell and Harwood, 1994). The size of the resulting materials is typically 10–30 mm after chipping and 0.2–2 mm after milling or grinding (Sun and Cheng, 2002).

Bridgeman *et al.* (2007) studied the effects of size reduction of switchgrass achieved via ball milling. The study reported that for particle sizes smaller than 90 μm, cellulose content was 13.4% lower than for larger sized particles. The losses in lignin and hemicellulose were appreciably less (3.43% and 4.74%, respectively). These results indicate that extensive size reduction is undesirable as it causes significant carbohydrate losses which ultimately results in less reducing sugars and reduced ethanol yield.

Mani *et al.* (2004) examined the energy requirements for size reduction of switchgrass using a hammer mill. At 8% moisture content, energy requirements increased linearly as particle size reduced and at 12% moisture content, the energy requirements tended to level off for particle sizes less than 2 mm. The study noted that energy requirements for size reduction of switchgrass were higher than that of corn stover, barley straw, and wheat straw at the same moisture content. Additionally, it was reported that higher moisture content biomass required greater energy inputs for size reduction. Yu *et al.* (2006) reported that size reduction of switchgrass based on shear stress is more efficient than size reduction based on tensile stress and noted that shear stress of switchgrass was less affected by moisture content than tensile stress. Igathinathane *et al.* (2008) reported a significant increase in cutting energy requirements for switchgrass with high moisture (51%) in comparison to low moisture (9%) using a shear based knife grid for size reduction using a linear grid of knifes. Table 2 presents estimates of energy consumption from studies on the size reduction of switchgrass.

#### 3.1.2. Physico-chemical pretreatment

The three types of physico-chemical pretreatments discussed in literature are steam explosion, ammonia fiber explosion (AFEX), and $CO_2$ explosion. In steam explosion, size reduced biomass is subjected to high-pressure saturated steam for a short time before a sudden drop in pressure causes an explosive decompression of the biomass (McMillan, 1994). Typical conditions are 160–260 °C and 0.69–4.83 MPa (Sun and Cheng, 2002). The process causes transformation of lignin and degradation of hemicelluloses, which improves the enzymatic hydrolysis of cellulose. Steam explosion is known to be a cost effective pretreatment for hardwoods and agricultural residues. However, the process produces inhibitory by-products that may impact downstream processes (Mackie *et al.*, 1985). AFEX and $CO_2$ explosion are similar to steam explosion. The biomass is exposed to liquid ammonia or $CO_2$ at high temperature and pressure for a short period of time, followed by a sudden drop in pressure. Unlike steam explosion, AFEX does not solubilize hemicelluloses (Vlasenko *et al.*, 1997) but does require recovery of the ammonia for cost and environmental reasons (Sun and Cheng, 2002). $CO_2$ explosion is not as effective as AFEX or steam explosion (Dale and Moreira, 1982).

To date, AFEX is the only physico-chemical pretreatment that has been applied for the pretreatment of switchgrass to improve enzymatic hydrolysis. Dale *et al.* (1996) reported a 5–8-fold improvement in reducing sugar yields over untreated samples after a 48-h enzymatic hydrolysis of AFEX pretreated switchgrass. These results were similar to a more comprehensive study presented by Alizadeh *et al.* (2005) that optimized AFEX pretreatment of switchgrass by examining the impact of ammonia loading, moisture content, and reactor temperature on the efficiency of enzymatic hydrolysis. The authors reported optimum pretreatment conditions of 100 °C reactor temperature, ammonia loading of 1 g $g^{-1}$ of biomass and a residence time of 5 min. These conditions yielded a 6-fold improvement in hydrolysis efficiency.

### *3.1.3. Chemical pretreatment*

Chemical pretreatment of lignocelluloses includes the use of ozone, acids, alkali, organic solvents, and peroxides. Ozonolysis is carried out at room temperature and is effective at lignin removal without the formation of toxic by-products (Vidal and Molinier, 1988). However, the large ozone requirement makes the process expensive (Sun and Cheng, 2002). Dilute acid pretreatment with sulfuric acid has been studied extensively and is efficient at removal of hemicelluloses but fails to effectively remove lignin. While dilute acid pretreatments are known to improve enzymatic hydrolysis, their cost is relatively high compared to physico-chemical pretreatments. Dilute alkali pretreatments using sodium hydroxide targets intermolecular bonds between lignin and hemicelluloses and improves the porosity of the biomass (Tarkow and Feist, 1969). Other studies on dilute alkali pretreatments have examined the use of ammonia water and hydrated lime. Ladisch *et al.* (1978) showed that pretreatment of lignocelluloses with cadoxen, a cellulose solvent, resulted in 90% conversion of cellulose into glucose. The use of organic solvents such as methanol, ethanol, acetone, and ethylene glycol, along with inorganic and organic acids as catalysts, has also been studied (Wood and Saddler, 1988; Chum *et al.*, 1988; Thring *et al.*, 1990).

Dilute acid pretreatment of switchgrass for bioethanol production was first examined by Wyman *et al.* (1992). The pretreatment was conducted at 140 °C for 1 h using sulfuric acid at low concentrations (up to 0.5% v/v). Enzymatic hydrolysis of the resulting biomass yielded up to 70% conversion of cellulose into glucose over a five-day period. Since the removal of hemicellulose during dilute acid pretreatment correlates with enhanced reactivity of cellulose to enzymes (Torget *et al.*, 1990), several studies have used percentage of xylose recovery as a means of optimizing dilute acid pretreatments. Wu and Lee (1997) used a two-stage dilute sulfuric acid pretreatment with an acid concentration of 0.0785% (w/w) to successfully remove 100% of hemicellulose from switchgrass. Esteghlalian *et al.* (1997) determined that up to 90% of xylose was recovered as a result of pretreatment at 180 °C with an acid concentration of 1.2% (w/w). It was also noted that temperature was a more significant parameter than acid concentration. Fenske *et al.* (1998) reported a 96% xylose recovery in a similar study. Chung *et al.* (2005) reported optimal conditions of 1.2% (w/w) at 180 °C for sulfuric acid pretreatment of switchgrass and determined that 90% of cellulose in the pretreated biomass was converted into reducing sugars during a 72 h enzymatic hydrolysis. Dien *et al.* (2006) reported yields greater than 80% for both glucan and non-glucan sugars for dilute sulfuric pretreatment of switchgrass with an optimal acid concentration of 1.2% (w/v). Although pretreatment temperature was not optimized, the study indicates higher conversion rates at 150 °C in comparison to 120 °C.

Dilute acid pretreatment of switchgrass does not significantly impact lignin removal. Wu and Lee (1997) noted that high lignin content could lead to increased enzyme consumption due to irreversible adsorption of cellulase enzymes to lignin. Hence, they proposed combining dilute acid pretreatment with an ammonia percolation step to remove lignin. Their results indicate that with this additional step, 20% more lignin can be removed to significantly increase enzymatic digestibility of the pretreated biomass. Kong *et al.* (1992) noted that alkalis remove acetate groups from hemicellulose, which result in reduced steric hindrance to enzyme molecules in addition to saponification of ester groups that cross-link lignin and hemicelluloses.

Kim and Lee (1996) reported up to 99% delignification using a combined ammonia–hydrogen peroxide percolation pretreatment at 170 °C. They reported reagent loadings of 0.28 g loading of hydrogen peroxide $g^{-1}$ biomass, and 10% (w/w) of ammonia. Their results indicated that the enzymatic digestibility of the resulting pretreated biomass was higher than that of pure alpha cellulose. This could be a sign of significant reduction in crystallinity and increase in porosity of cellulose in the pretreated biomass. Kurakake *et al.* (2001) used ammonia water (25–28%) for the pretreatment of switchgrass (2 ml/g biomass) for 20 min at 120 °C and noted a 3–5-fold improvement in reducing sugar production over untreated switchgrass after a 24-h enzymatic hydrolysis. Isci *et al.* (2008) pretreated switchgrass in 30% aqueous ammonium hydroxide with liquid–solid ratios of 5 and 10 ml/g and residence times of 5 and 10 days. The study reported a 40–50% reduction in lignin content and 50% reduction in hemicelluloses content as a result of pretreatment.

Lime (calcium hydroxide) pretreatment of switchgrass was investigated by Chang *et al.* (1997). With a lime loading of 0.1 g $g^{-1}$ of dry switchgrass, a pretreatment time of 2 h at 100 °C, the study showed that a 72-h enzymatic hydrolysis of pretreated biomass yielded five times higher reducing sugars than untreated switch-

**Table 2.** Energy requirements of size reduction of switchgrass from published studies

| Reference | Energy consumption (kWh/t) | Moisture content (%) | Size reduction |
|---|---|---|---|
| Samson *et al.* (2000) | 44.9 | Not reported | 5.6 mm pellets |
| Jannasch *et al.* (2001) | 55.9 | 10–12 | 2.8 mm screen size |
| Mani *et al.* (2004) | 27.6 | 8 | 3.2 mm screen size |
| Mani *et al.* (2004) | 23.8 | 12 | 3.2 mm screen size |
| Igathinathane *et al.* (2008) | 2.4–3.2 | 9 | 25.4 mm knife grid spacing |
| Igathinathane *et al.* (2008) | 2.7–5.4 | 54 | 25.4 mm knife grid spacing |

grass. A follow-up study reported that simultaneous saccharification and fermentation of lime-pretreated switchgrass gave an ethanol yield of 72% of the theoretical value (Chang *et al.*, 2001).

A combined microwave–alkali pretreatment of switchgrass by Keshwani *et al.* (2007) looked at microwave irradiation of switchgrass immersed in dilute sodium hydroxide (NaOH) solution. The resulting pretreated biomass yielded 5–7 times higher reducing sugars than untreated switchgrass after a 72-h enzymatic hydrolysis. Optimal conditions of 10 min irradiation at 250 W with dilute NaOH were identified. Hu and Wen (2008) reported that microwave based pretreatment of switchgrass with NaOH caused significant disruption of recalcitrant structures and reported optimum conditions of 190 °C, 50 g/L solid content, and 30 min treatment time with 1% NaOH. Alkali pretreatment of switchgrass with NaOH using radio frequency (RF) dielectric heating was studied by Hu *et al.* (2008). The study reported optimal conditions of 0.20– 0.25 g NaOH/g biomass, heating temperature of 90 °C, and solid content of 20%, and noted a significant improvement in pretreatment of switchgrass with high solids content using RF heating over conventional heating.

#### 3.1.4. Biological pretreatment

Biological pretreatment involves the use of microorganisms that selectively degrade lignin and hemicellulose. Several studies have shown that white-rot fungi are the most effective microorganisms for pretreatment of lignocelluloses such as wood chips (Ander and Eriksson, 1977), wheat straw (Hatakka, 1983), and Bermuda grass (Akin *et al.*, 1995), and softwood *Pinus densiflora* (Lee *et al.*, 2007). Biological pretreatments are less energy intensive compared to chemical and physico-chemical processes and require mild reaction conditions. However, the process is very slow, making it unattractive for commercial use. To date, biological pretreatment of switchgrass has not been reported in literature.

### 3.2. Enzymatic hydrolysis

As shown in Figure 1, following the pretreatment of lignocelluloses, enzymatic hydrolysis is carried out to break down cellulose and hemicelluloses into fermentable sugars such as glucose and xylose. Strong acids such as sulfuric acid and halogen acids are capable of hydrolyzing a wide variety of lignocelluloses into simple fermentable sugars (Wyman, 1994). However, high acid concentrations and extreme conditions make this approach environmentally and economically unsound (Wright and Dagincourt, 1984). Enzymatic hydrolysis is an environmentally friendly alternative that involves using carbohydrate degrading enzymes (cellulases and hemicellulases) to hydrolyze lignocelluloses into fermentable sugars.

#### 3.2.1. Enzymatic hydrolysis of cellulose

Enzymatic hydrolysis of cellulose is typically carried out by cellulases. Unlike conventional hydrolysis using concentrated acid or alkaline reagents, enzymatic hydrolysis requires mild conditions (pH of 4.5 and temperature of approximately 50 °C). Although cellulases are also produced by several bacterial species such as *Clostridium*, *Cellulomonas,* and *Bacillus* (Bisaria, 1998), fungal cellulases have the best potential for commercial scale use (Duff and Murray, 1996). Cellulases are a complex system of three enzymes that act synergistically to hydrolyze cellulose. The three enzyme components are: 1,4-β-D-glucan glucanohydrolase (EC 3.2.1.3), 1,4-β-D-glucan cellobiohydrolyase (EC 3.2.1.91) and β-glucosidase (EC 3.2.1.21) (Ladisch *et al.*, 1983; Wright *et al.*, 1988). These enzymes are commonly referred to as endoglucanase, exoglucanase, and cellobiase, respectively.

Endoglucanase randomly cleaves cellulose chains to form glucose, cellobiose, and cellotriose. Exoglucanase attacks the non-reducing end of cellulose to release cellobiose units. Cellobiase cleaves cellobiose units into fermentable glucose units. Most fungal cellulases are deficient in β-glucosidase activity, which must be supplemented since cellobiose accumulation results in cellulase inhibition (Ryu and Mandels, 1980). A cellulase dosage of 10 FPU (filter paper units) per gram of biomass is often used in studies as it enables high glucose yields in 48–72 h (Gregg and Saddler, 1996). However, a range of dosage and hydrolysis conditions have been reported depending on composition of the substrates and pretreatment used. Table 3 summarizes information on reported cellulase activities and hydrolysis conditions from studies specific to switchgrass.

#### 3.2.2. Enzymatic hydrolysis of hemicelluloses

Complete hydrolysis of xylan involves three main enzymes: endo-β-1-4-xylanase which primarily targets the internal β-1-4 bonds between xylose units, exoxylanase that releases xylobiose units and β-xylosidase that releases xylose from xylobiose and short chain xylooligosachharides (Saha and Bothast, 1999). While these enzymes are primarily involved in depolymerization, there are also several ancillary enzymes that are responsible for cleaving side-groups. These include α-L-arabinofuranosidase, α-glucuronidase, acetylxylan esterase, ferulic acid esterase, and *p*-coumaric acid esterase (Saha and Bothast, 1999).

*Penicillium capsulatum* and *Talaromyces emersonii* have been identified as microorganisms that have complete enzyme systems that degrade xylan (Filho *et al.*, 1991). Other microorganisms that have been reported as sources for hemicellulose-degrading enzymes are *Aureobasidium pullulans* (Christov *et al.*, 1997) and several *Fusarium* species (Saha, 2001, 2002). As in cellulase systems, xylan-degrading systems also exhibit synergism (Bachmann and McCarthy, 1991). While the number of enzymes required for xylan hydrolysis is much greater than for cellulose hydrolysis, accessibility to the substrate is easier since xylan does not form tight crystalline structures (Gilbert and Hazlewood, 1993). To date, no comprehensive effort has been reported to optimize hydrolysis of switchgrass using hemicellulose-degrading enzymes.

### 3.3. Fermentation

The supernatant from enzymatic hydrolysis of lignocelluloses can contain both hexoses and pentoses (if both cellulose and hemicellulose are hydrolyzed). Depending on the lignocellulose source, the hydrosylate typically consists of glucose, xylose, arabinose, galactose, mannose, fucose, and rhamnose (Saha, 2003). Glucose and xylose are the dominant sugars in the mixture. *Saccharomyces cerevisiae* and *Zymomonas mobilis* are capable of efficiently fermenting glucose into ethanol, but are unable to ferment xylose. Other yeasts such as *Pachysolen tannophilus, Pichia stipitis,* and *Candida shehate* are known to ferment xylose into ethanol (Wang *et al.*, 1980; Schneider *et al.*, 1981). Dupreez (1994) and Hahn-Hagerdal *et al.* (1994) noted the difficulties associated with commercial use of xylose fermenting yeasts. These include low ethanol tolerance, difficulty in optimization of fermentation parameters and slow rate of fermentation. An alternative approach is to convert xylose into an isomer called xylulose using xylose isomerase (Chiang *et al.*, 1981; Gong *et al.*, 1981; Jeffries, 1981). Xylulose can then be fermented by traditional yeasts. However, Saha (2003) stated that this approach is not cost effective and indicates that focus should be on development of genetically engineered microorganisms capable of fermenting hexoses and pentoses into ethanol. *S. cerevisiae* is of particular interest in this regard, and recent reviews detail the efforts to improve pentose fermentation using this microorganism (Chu and Lee, 2007; Hahn-Hagerdal *et al.*, 2007).

In addition to separate hydrolysis and fermentation (SHF), other approaches include direct microbial conversion (DMC) and simul-

**Table 3.** Cellulase activities and hydrolysis conditions from various studies on switchgrass

| Reference | Pretreatment | Enzyme activity[a] | Conditions | Result/yield |
|---|---|---|---|---|
| Alizadeh *et al.* (2005) | AFEX | cellulase: 15 FPU $g^{-1}$ glucan, cellobiase: 40 IU $g^{-1}$ glucan | 50 °C, 75 RPM, 168 h | 93% glucan conversion, 70% xylan conversion |
| Wyman *et al.* (1992) | dilute acid | cellulase: 26 IU $g^{-1}$ biomass, cellobiase: 208 IU $g^{-1}$ biomass | 45 °C, 150 RPM, 192 h | 70% cellulose conversion |
| Chung *et al.* (2005) | dilute acid | cellulase: 60 FPU $g^{-1}$ cellulose | 50 °C, 68 RPM, 192 h | 91.4% cellulose conversion |
| Chang *et al.* (1997) | lime | cellulase: 5 FPU $g^{-1}$ biomass, cellobiase: 28.4 CBU $g^{-1}$ biomass | 50 °C, 100 RPM, 72 h | 85% conversion of biomass into reducing sugars |

[a] FPU, filter paper unit; IU, international enzyme activity unit; CBU, cellobiase unit

taneous saccharification and fermentation (SSF). DMC involves the use of microorganisms that simultaneously produce cellulase to hydrolyze cellulose and ferment the resulting sugars into ethanol. *Clostridium thermocellum* and *Clostridium thermosaccharoliticum* have been used in DMC studies (Wyman, 1994). Significant by-product formation and low ethanol tolerance are limitations to this approach. In SSF, enzymatic hydrolysis and fermentation take place in the same vessel. The rationale for this approach is that since cellulase activity is inhibited by glucose, rapid fermentation into ethanol would increase the rate and efficiency of the overall process.

Wyman *et al.* (1992) reported significantly higher ethanol yields from dilute acid pretreated switchgrass using SSF over SHF. The study also noted ethanol yields from switchgrass were less than those from corn cobs and corn stover with SSF. Using a co-culture of *Brettanomyces clausenii* and *S. cerevisiae,* 87% (of theoretical maximum) conversion into ethanol using SSF was reported. Chung *et al.* (2005) reported comparable ethanol yields for SSF and SHF of dilute acid pretreated switchgrass (90.3% and 91.4%, respectively). Other studies have reported lower ethanol yields: 40% for SHF of AFEX pretreated switchgrass (Alizadeh *et al.*, 2005) and 72% for SSF of lime-pretreated switchgrass (Chang *et al.*, 2001). Reshamwala *et al.* (1995) used recombinant *Klebsiella oxytoca* to ferment both glucose and xylose in the enzymatic hydrolsylate of AFEX pretreated switchgrass. Their results indicate that xylose fermentation was slower and less complete than glucose fermentation and greatly reduced at higher sugar concentrations. Fenske *et al.* (1998) used *P. stipitis* to ferment pentoses in the pretreatment liquor obtained from xylose-optimized dilute acid pretreatment of switchgrass and reported an 83% ethanol yield.

## 4. Thermal conversion

Combustion of biomass like switchgrass is problematic because of the presence of alkali metals that react to form sulfates, chlorides, silicate, and hydroxides that contribute to slag formation and fouling of combustion systems (Dayton *et al.*, 1995). Leaching of switchgrass with water was proposed by Dayton *et al.* (1999) to remove alkali metals and chlorine prior to combustion. The study reported that leached biomass produced less alkali metal vapors and resulted in reduced char formation during combustion. Biomass cofiring with coal is a promising environmentally-friendly technology that has been shown to be economical with switchgrass replacing up to 20% of coal requirements (Tillman, 2000). Boylan *et al.* (2000) described plans for pilot scale testing of cofiring of switchgrass with coal. Preliminary experiments indicated a reduction in sulfur and nitrous oxide emissions for a mixture of 10% switchgrass–90% coal. Blevins and Cauley (2005) investigated the particulate matter formation during the combustion of coal and cofiring of coal-switchgrass mixtures and noted that fine particulate matter number densities were two orders of magnitude higher for mixtures. However, the particle mass concentrations remained unchanged. Brown *et al.* (2000) studied the synergistic effects during the co-gasification of coal-switchgrass and noted an almost 8-fold increase in the rate of coal char gasification.

Pyrolysis of Cave-in-Rock switchgrass to produce bio-oil was conducted by Boateng *et al.* (2007) using a fluidized bed system. The study reported bio-oil yields greater than 60% by mass with energy conversion efficiencies ranging from 52% to 81%. A previous study on pyrolysis of Cave-in-Rock switchgrass noted an interaction effect between pyrolysis temperature and plant maturity on profile of pyrolysis products (Boateng *et al.*, 2006). Zhang *et al.* (2004) used switchgrass for thermochemical production of hydrogen. The process involved thermal gasification in a fluidized bed gasifier followed by steam reforming of tars in the producer gas. The high ratio of carbon monoxide to hydrogen was reduced by reacting carbon monoxide in the producer gas with steam. The study reported an increase in hydrogen concentration from 8.6% to 26.7% (by volume) in the producer gas.

## 5. Pulping and paper making

Although wood is the most common raw material for pulping applications, environmental issues such as forest preservation and reduction of $CO_2$ emissions have resulted in an interest in non-wood sources. Perennial grasses like switchgrass have low lignin content and can be harvested without annual reestablishment, making them an attractive raw material for pulping. Fox *et al.* (1999) conducted a regional economic evaluation for eastern Ontario and western Quebec and concluded that switchgrass was an attractive crop for farmers and the local pulp industry. Ververis *et al.* (2004) assessed pulping suitability of several plant materials and concluded that switchgrass could be used for producing paper for writing and printing or mixed with conventional woody sources for making paper with a wider range of applications.

Madakadze *et al.* (1999) assessed pulping characteristics of different grasses and reported the highest pulp yield (51%) and pulp brightness (36%) for switchgrass. Although the study noted that fiber uniformity was an issue, the resulting paper had good printability. Law *et al.* (2001) reported pulp yields of 50–55% from soda-sulfite pulping of switchgrass and concluded that while brightness was low, the resulting pulp had excellent mechanical properties and could be used as a reinforcement component in newsprint production. In a later study, Law *et al.* (2002) reported pulp yields of 60–80%, but observed good mechanical strength only for switchgrass pulps in the yield range of 55–60%. Ruzinsky and Kokta (2000) also reported acceptable pulp quality using steam explosion pulping of switchgrass.

Kraft pulp from switchgrass has short fibers with a high proportion of fines (Madakadze *et al.*, 1999). Reddy and Yang (2007) used alkaline pretreatment to extract cellulose fibers from leaves and stems of switchgrass and noted tensile properties of fibers were similar to those of linen and cotton. Van den Oever *et al.* (2003) recognized that these fibers could be used as a reinforcing and filling agent for thermoplastic composites because of good fiber quality and sustainable production at low cost. They noted that the addition of 30% (by weight) switchgrass pulp to polypropylene resulted in an increase of the flexural modulus by a factor of approximately 2.5 compared to pure polypropylene. This increase was only slightly lower than for jute and flax which are commonly used reinforcement fibers (Note: flexural modulus is an indicator of the ability of a material to resist deformation under load). The study concluded that optimization of the pulping process could further improve properties of the composite.

## 6. Conclusions and future prospects

Switchgrass is a promising feedstock for bioethanol production, thermal energy conversion and pulping applications. The positive environmental benefits associated with switchgrass include enhancement of wildlife diversity, improvement of soil and water quality, reduced pesticide use, and carbon sequestration. Most current research has focused on bioconversion into ethanol with an emphasis on pretreatment methods. While the technology for corn-to-ethanol is well established, the conversion of lignocellulosic feedstock to ethanol has challenges—such as cost of pretreatment methods, cost of hydrolytic enzymes, and inefficient fermentation of pentoses. The economics of bioethanol production from switchgrass can also be improved by developing value-added by-products. For example, Bals *et al.* (2007) present a scheme for extraction of proteins while simultaneously producing fermentable sugars from AFEX pretreated switchgrass. There is a lack of research on utilization of hemicellulose, which accounts for about 20–25% of switchgrass. With the development of genetically engineered microorganisms capable of efficient pentose fermentation, ethanol production from hemicelluloses in switchgrass needs to be optimized. Sarath *et al.* (2008) highlight opportunities in the area of genetics and agronomy to improve the biofuel characteristics of switchgrass. Along with increasing biomass yields, research on plant breeding should focus on modifying the composition of switchgrass to minimize recalcitrance to bioconversion. For example, a feedstock with lower levels of lignin can potentially reduce the severity and cost of the pretreatment required. However, the potential negative consequences on crop yields and fitness—as noted by Casler *et al.* (2002) and Pedersen *et al.* (2005) due to such modifications in biomass composition—need to be assessed against any potential benefits. While improvements in genetics, agronomy, and the conversion process will undoubtedly help in the development of a feasible biofuel production system from switchgrass, environmental and social stresses associated with dedicating large geographic areas for feedstock production needs to be addressed.

## References


Akin, D. E., Rigsby, L. L., Sethuraman, A., Morrison, W. H., Gamble, G. R., Eriksson, K. E. L., 1995. Alterations in structure, chemistry, and biodegradability of grass lignocellulose treated with the white-rot fungi *Ceriporiopsis subvermispora* and *Cyathus stercoreus.* Appl. Environ. Microbiol. 61 (4), 1591–1598.

Alizadeh, H., Teymouri, F., Gilbert, T. I., Dale, B. E., 2005. Pretreatment of switchgrass by ammonia fiber explosion (AFEX). Appl. Biochem. Biotechnol. 121, 1133– 1141.

Ander, P., Eriksson, K. E., 1977. Selective degradation of wood components by white-rot fungi. Physiol. Plantarum 41 (4), 239–248.

Bachmann, S. L., McCarthy, A. J., 1991. Purification and cooperative activity of enzymes constituting the xylan-degrading system of *Thermomonospora fusca.* Appl. Environ. Microbiol. 57 (8), 2121–2130.

Bals, B., Teachworth, L., Dale, B., Balan, V., 2007. Extraction of proteins from switchgrass using aqueous ammonia within an integrated biorefinery. Appl. Biochem. Biotechnol. 143 (2), 187–198.

Bisaria, V. S., 1998. Bioprocessing of agro-residues to value added products. *In:* Martin, A. M. (Ed.), Bioconversion of Waste Materials to Industrial Products, second ed. Chapman and Hall, UK.

Blevins, L. G., Cauley, T. H., 2005. Fine particulate formation during switchgrass. J. Eng. Gas Turbines Power-Trans. ASME 127 (3), 457–463.

Boateng, A. A., Daugaard, D. E., Goldberg, N. M., Hicks, K. B., 2007. Bench-scale fluidized-bed pyrolysis of switchgrass for bio-oil production. Ind. Eng. Chem. Res. 46 (7), 1891–1897.

Boateng, A. A., Hicks, K. B., Vogel, K. P., 2006. Pyrolysis of switchgrass (*Panicum virgatum*) harvested at several stages of maturity. J. Anal. Appl. Pyrolysis 75 (2), 55–64.

Boylan, D., Bush, V., Bransby, D. I., 2000. Switchgrass cofiring: pilot scale and field evaluation. Biomass Bioenergy 19 (6), 411–417.

Bransby, D. I., McLaughlin, S. B., Parrish, D. J., 1998. A review of carbon and nitrogen balances in switchgrass grown for energy. Biomass Bioenergy 14 (4), 379–384.

Bridgeman, T. G., Darvell, L. I., Jones, J. M., Williams, P. T., Fahmi, R., Bridgwater, A. V., Barraclough, T., Shield, I., Yates, N., Thain, S. C., Donnison, I. S., 2007. Influence of particle size on the analytical and chemical properties of two energy crops. Fuel 86 (1–2), 60–72.

Brown, R. C., Liu, Q., Norton, G., 2000. Catalytic effects observed during the cogasification of coal and switchgrass. Biomass Bioenergy 18 (6), 499–506.

Campbell, C. J., Laherrere, J. H., 1998. Preventing the next oil crunch—The end of cheap oil. Sci. Am. 278 (3), 77–83.

Casler, M. D., Buxton, D. R., Vogel, K. P., 2002. Genetic modification of lignin concentration affects fitness of perennial herbaceous plants. Theor. Appl. Genet. 104 (1), 127–131.

Casler, M. D., Vogel, K. P., Taliaferro, C. M., Ehlke, N. J., Berdahl, J. D., Brummer, E. C., Kallenbach, R. L., West, C. P., Mitchell, R. B., 2007. Latitudinal and longitudinal adaptation of switchgrass populations. Crop Sci. 47 (6), 2249–2260.

Chang, V. S., Burr, B., Holtzapple, M. T., 1997. Lime pretreatment of switchgrass. Appl. Biochem. Biotechnol. 63 (5), 3–19.

Chang, V. S., Kaar, W. E., Burr, B., Holtzapple, M. T., 2001. Simultaneous saccharification and fermentation of lime-treated biomass. Biotechnol. Lett. 23 (16), 1327–1333.

Chiang, L. C., Hsiao, H. Y., Ueng, P. P., Chen, L. F., Tsao, G. T., 1981. Ethanol-production from xylose by enzymic isomerization and yeast fermentation. Biotechnol. Bioeng. Suppl. 11, 263–274.

Christov, L. P., Myburgh, J., vanTonder, A., Prior, B. A., 1997. Hydrolysis of extracted and fibre-bound xylan with *Aureobasidium pullulans* enzymes. J. Biotechnol. 55 (1), 21–29.

Chu, B. C. H., Lee, H., 2007. Genetic improvement of *Saccharomyces cerevisiae* for xylose fermentation. Biotechnol. Adv. 25 (5), 425–441.

Chum, H. L., Johnson, D. K., Black, S., Baker, J., Grohmann, K., Sarkanen, K. V., Wallace, K., Schroeder, H. A., 1988. Organosolv pretreatment for enzymatic-hydrolysis of poplars: 1. Enzyme hydrolysis of cellulosic residues. Biotechnol. Bioeng. 31 (7), 643–649.

Chung, Y. C., Bakalinsky, A., Penner, M. H., 2005. Enzymatic saccharification and fermentation of xylose-optimized dilute acid-treated lignocellulosics. Appl. Biochem. Biotechnol. 121, 947–961.

Dale, B. E., Leong, C. K., Pham, T. K., Esquivel, V. M., Rios, I., Latimer, V. M., 1996. Hydrolysis of lignocellulosics at low enzyme levels: application of the AFEX process. Bioresour. Technol. 56 (1), 111–116.

Dale, B. E., Moreira, M. J., 1982. A freeze-explosion technique for increasing cellulose hydrolysis. Biotechnol. Bioeng. Suppl. 12, 31–43.

Dayton, D. C., French, R. J., Milne, T. A., 1995. Direct observation of alkali vapor release during biomass combustion and gasification. 1. Application of molecular-beam mass-spectrometry to switchgrass combustion. Energy Fuels 9 (5), 855–865.

Dayton, D. C., Jenkins, B. M., Turn, S. Q., Bakker, R. R., Williams, R. B., Belle-Oudry, D., Hill, L. M., 1999. Release of inorganic constituents from leached biomass during thermal conversion. Energy Fuels 13 (4), 860–870.

Dien, B. S., Jung, H. J. G., Vogel, K. P., Casler, M. D., Lamb, J. F. S., Iten, L., Mitchell, R. B., Sarath, G., 2006. Chemical composition and response to dilute-acid pretreatment and enzymatic saccharification of alfalfa, reed canarygrass, and switchgrass. Biomass Bioenergy 30 (10), 880–891.

Duff, S. J. B., Murray, W. D., 1996. Bioconversion of forest products industry waste cellulosics to fuel ethanol: a review. Bioresour. Technol. 55 (1), 1–33.

Dunn, C. P., Stearns, F., Guntenspergen, G. R., Sharpe, D. M., 1993. Ecological benefits of the conservation reserve program. Conserv. Biol. 7 (1), 132–139.

Dupreez, J. C., 1994. Process parameters and environmental-factors affecting D-xylose fermentation by yeasts. Enzyme Microb. Technol. 16 (11), 944–956.

Elobeid, A., Tokgoz, S., Hart, C., 2007. The ethanol outlook for Brazil and the United States and implications for livestock. Int. Sugar J. 109 (1299), 174–177.

Entry, J. A., Watrud, L. S., 1998. Potential remediation of Cs-137 and Sr-90 contaminated soil by accumulation in alamo switchgrass. Water Air Soil Pollut. 104 (3–4), 339–352.

Esteghlalian, A., Hashimoto, A. G., Fenske, J. J., Penner, M. H., 1997. Modeling and optimization of the dilute-sulfuric-acid pretreatment of corn stower, poplar and switchgrass. Bioresour. Technol. 59 (2–3), 129–136.

Fenske, J. J., Hashimoto, A., Penner, M. H., 1998. Relative fermentability of lignocellulosic dilute-acid prehydrolysates—application of a *Pichia stipitis*-based toxicity assay. Appl. Biochem. Biotechnol. 73 (2–3), 145–157.

Filho, E. X. F., Tuohy, M. G., Puls, J., Coughlan, M. P., 1991. The xylan-degrading enzyme-systems of *Penicillium capsulatum* and *Talaromyces emersonii*. Biochem. Soc. Trans. 19 (1), S25.

Fox, G., Girouard, P., Syaukat, Y., 1999. An economic analysis of the financial viability of switchgrass as a raw material for pulp production in eastern Ontario. Biomass Bioenergy 16 (1), 1–12.

Frank, A. B., Berdahl, J. D., Hanson, J. D., Liebig, M. A., Johnson, H. A., 2004. Biomass and carbon partitioning in switchgrass. Crop Sci. 44 (4), 1391–1396.

Garten, C. T., Wullschleger, S. D., 2000. Soil carbon dynamics beneath switchgrass as indicated by stable isotope analysis. J. Environ. Qual. 29 (2), 645–653.

Gebhart, D. L., Johnson, H. B., Mayeux, H. S., Polley, H. W., 1994. The CRP increases soil organic-carbon. J. Soil Water Conserv. 49 (5), 488–492.

Gilbert, H. J., Hazlewood, G. P., 1993. Bacterial cellulases and xylanases. J. Gen. Microbiol. 139, 187–194.

Gong, C. S., Chen, L. F., Flickinger, M. C., Chiang, L. C., Tsao, G. T., 1981. Production of ethanol from D-xylose by using D-xylose isomerase and yeasts. Appl. Environ. Microbiol. 41 (2), 430–436.

Gray, K. A., Zhao, L. S., Emptage, M., 2006. Bioethanol. Curr. Opin. Chem. Biol. 10 (2), 141–146.

Gregg, D. J., Saddler, J. N., 1996. Factors affecting cellulose hydrolysis and the potential of enzyme recycle to enhance the efficiency of an integrated wood to ethanol process. Biotechnol. Bioeng. 51 (4), 375–383.

Gulati, M., Kohlmann, K., Ladisch, M. R., Hespell, R., Bothast, R. J., 1996. Assessment of ethanol production options for corn products. Bioresour. Technol. 58 (3), 253– 264.

Gunter, L. E., Tuskan, G. A., Wullschleger, S. D., 1996. Diversity among populations of switchgrass based on RAPD markers. Crop Sci. 36 (4), 1017–1022.

Hahn-Hagerdal, B., Jeppsson, H., Skoog, K., Prior, B. A., 1994. Biochemistry and physiology of xylose fermentation by yeasts. Enzyme Microb. Technol. 16 (11), 933–943.

Hahn-Hagerdal, B., Karhumaa, K., Jeppsson, M., Gorwa-Grauslund, M. F., 2007. Metabolic engineering for pentose utilization in *Saccharomyces cerevisiae*. Biofuels 108, 147–177.

Hatakka, A. I., 1983. Pretreatment of wheat straw by white-rot fungi for enzymic saccharification of cellulose. Eur. J. Appl. Microb. Biotechnol. 18 (6), 350–357.

Hitchcock, A. S., 1971. Manual of the Grasses of the United States, second ed. Dover Publications, New York (rev. by Agnes Chase).

Hohenstein, W. G., Wright, L. L., 1994. Biomass energy-production in the United States—An overview. Biomass Bioenergy 6 (3), 161–173.

Hu, Z. H., Wang, Y. F., Wen, Z. Y., 2008. Alkali (NaOH) pretreatment of switchgrass by radio frequency-based dielectric heating. Appl. Biochem. Biotechnol. 148 (1–3), 71–81.

Hu, Z. H., Wen, Z. Y., 2008. Enhancing enzymatic digestibility of switchgrass by microwave-assisted alkali pretreatment. Biochem. Eng. J. 38 (3), 369–378.

Igathinathane, C., Womac, A. R., Sokhansanj, S., Narayan, S., 2008. Knife grid size reduction to pre-process packed beds of high- and low-moisture switchgrass. Bioresour. Technol. 99 (7), 2254–2264.

Isci, A., Himmelsbach, J. N., Pometto, A. L., Raman, D. R., Anex, R. P., 2008. Aqueous ammonia soaking of switchgrass followed by simultaneous saccharification and fermentation. Appl. Biochem. Biotechnol. 144 (1), 69–77.

Jannasch, R., Quan, Y., Samson, R., 2001. A Process and Energy Analysis of Pelletizing Switchgrass; http://www.reap-canada.com/library.htm

Jeffries, T. W., 1981. Fermentation of xylulose to ethanol using xylose isomerase and yeasts. Biotechnol. Bioeng. Suppl. 11, 315–324.

Keshwani, D. R., Cheng, J. J., Burns, J. C., Li, L., Chiang, V., 2007. Microwave Pretreatment of Switchgrass to Enhance Enzymatic Hydrolysis. 2007 ASABE Annual Meeting Paper No. 077127.

Kim, S. B., Lee, Y. Y., 1996. Fractionation of herbaceous biomass by ammonia–hydrogen peroxide percolation treatment. Appl. Biochem. Biotechnol. 57 (8), 147–156.

Kong, F. R., Engler, C. R., Soltes, E. J., 1992. Effects of cell-wall acetate, xylan backbone, and lignin on enzymatic-hydrolysis of aspen wood. Appl. Biochem. Biotechnol. 34 (5), 23–35.

Kurakake, M., Kisaka, W., Ouchi, K., Komaki, T., 2001. Pretreatment with ammonia water for enzymatic hydrolysis of corn husk, bagasse, and switchgrass. Appl. Biochem. Biotechnol. 90 (3), 251–259.

Ladisch, M. R., Ladisch, C. M., Tsao, G. T., 1978. Cellulose to sugars—New path gives quantitative yield. Science 201 (4357), 743–745.

Ladisch, M. R., Lin, K. W., Voloch, M., Tsao, G. T., 1983. Process considerations in the enzymatic-hydrolysis of biomass. Enzyme Microb. Technol. 5 (2), 82–102.

Law, K. N., Kokta, B. V., Mao, C. B., 2001. Fibre morphology and soda-sulphite pulping of switchgrass. Bioresour. Technol. 77 (1), 1–7.

Law, K. N., Kokta, B. V., Szczesiul, B., Ruzinsky, F., 2002. High-yield pulping of switchgrass. Tappi J. 1 (6), 21–24.

Lee, J. W., Gwak, K. S., Park, J. Y., Park, M. J., Choi, D. H., Kwon, M., Choi, I. G., 2007. Biological pretreatment of softwood *Pinus densiflora* by three white rot fungi. J. Microbiol. 45 (6), 485–491.

Lee, K. H., Isenhart, T. M., Schultz, R. C., Mickelson, S. K., 1998. Nutrient and sediment removal by switchgrass and cool-season grass filter strips in central Iowa, USA. Agrofor. Syst. 44 (2–3), 121–132.

Lewandowski, I., Scurlock, J. M. O., Lindvall, E., Christou, M., 2003. The development and current status of perennial rhizomatous grasses as energy crops in the US and Europe. Biomass Bioenergy 25 (4), 335–361.

Liebig, M. A., Johnson, H. A., Hanson, J. D., Frank, A. B., 2005. Soil carbon under switchgrass stands and cultivated cropland. Biomass Bioenergy 28 (4), 347– 354.

Lynd, L. R., Cushman, J. H., Nichols, R. J., Wyman, C. E., 1991. Fuel ethanol from cellulosic biomass. Science 251 (4999), 1318–1323.

Ma, Z., Wood, C. W., Bransby, D. I., 2000a. Soil management impacts on soil carbon sequestration by switchgrass. Biomass Bioenergy 18 (6), 469–477.

Ma, Z., Wood, C. W., Bransby, D. I., 2000b. Carbon dynamics subsequent to establishment of switchgrass. Biomass Bioenergy 18 (2), 93–104.

Mackie, K. L., Brownell, H. H., West, K. L., Saddler, J. N., 1985. Effect of sulfur-dioxide and sulfuric-acid on steam explosion of aspenwood. J. Wood Chem. Technol. 5 (3), 405–425.

Madakadze, I. C., Radiotis, T., Li, J., Goel, K., Smith, D. L., 1999. Kraft pulping characteristics and pulp properties of warm season grasses. Bioresour. Technol. 69 (1), 75–85.

Mani, S., Tabil, L. G., Sokhansanj, S., 2004. Grinding performance and physical properties of wheat and barley straws, corn stower and switchgrass. Biomass Bioenergy 27 (4), 339–352.

McLaughlin, S. B., 1993. New switchgrass biofuels research program for the southeast. *In:* Proceedings 1992 Annual Automative Technology Development, pp. 111–115.

McLaughlin, S. B., Bouton, J., Bransby, D., Conger, B. V., Ocumpaugh, W. R., Parrish, D. J., Taliaferro, C., Vogel, K. P., Wullschleger, S. D., 1999. Developing switchgrass as a bioenergy crop. *In:* Janick, J. (Ed.), Perspectives on New Crops and New Uses. ASHS Press, Alexandria, VA, pp. 282–299.

McLaughlin, S. B., Ugarte, D. G. D. L., Garten, C. T., Lynd, L. R., Sanderson, M. A., Tolbert, V. R., Wolf, D. D., 2002. High-value renewable energy from prairie grasses. Environ. Sci. Technol. 36 (10), 2122–2129.

McMillan, J. D., 1994. Pretreatment of lignocellulosic biomass. *In:* Himmel, M. E., Baker, J. O., Overend, R. P. (Eds.), Enzymatic Conversion of Biomass for Fuels Production. American Chemical Society, Washington, DC, pp. 292–324.

Mersie, W., Seybold, C. A., McNamee, C., Huang, J., 1999. Effectiveness of switchgrass filter strips in removing dissolved atrazine and metolachlor from runoff. J. Environ. Qual. 28 (3), 816–821.

Mersie, W., Seybold, C. A., Wu, J., McNamee, C., 2006. Atrazine and metolachlor sorption to switchgrass residues. Commun. Soil Sci. Plant Anal. 37 (3–4), 465– 472.

Morrow, W. R., Griffin, W. M., Matthews, H. S., 2006. Modeling switchgrass derived cellulosic ethanol distribution in the United States. Environ. Sci. Technol. 40 (9), 2877–2886.

Mosier, N., Wyman, C., Dale, B., Elander, R., Lee, Y. Y., Holtzapple, M., Ladisch, M., 2005. Features of promising technologies for pretreatment of lignocellulosic biomass. Bioresour. Technol. 96 (6), 673–686.

Murray, L. D., Best, L. B., 2003. Short-term bird response to harvesting switchgrass for biomass in Iowa. J. Wildl. Manage. 67 (3), 611–621.

Murray, L. D., Best, L. B., Jacobsen, T. J., Braster, M. L., 2003. Potential effects on grassland birds of converting marginal cropland to switchgrass biomass production. Biomass Bioenergy 25 (2), 167–175.

NREL Biomass Feedstock Composition and Properties Database, 2004; http://www.nrel.gov/biomass/energy_analysis.html

NREL Theoretical Yield Calculator, 2006. http://www.nrel.gov/biomass/energy_analysis.html

Parrish, D. J., Fike, J. H., 2005. The biology and agronomy of switchgrass for biofuels. Crit. Rev. Plant Sci. 24 (5–6), 423–459.

Pedersen, J. F., Vogel, K. P., Funnell, D. L., 2005. Impact of reduced lignin on plant fitness. Crop Sci. 45 (3), 812–819.

Perlack, R. D., Turhollow, A. F., 2003. Feedstock cost analysis of corn stover residues for further processing. Energy 28 (14), 1395–1403.

Reddy, N., Yang, Y. Q., 2007. Natural cellulose fibers from switchgrass with tensile properties similar to cotton and linen. Biotechnol. Bioeng. 97 (5), 1021–1027.

Reshamwala, S., Shawky, B. T., Dale, B. E., 1995. Ethanol-production from enzymatic hydrolysates of AFEX-treated coastal bermudagrass and switchgrass. Appl. Biochem. Biotechnol. 51 (2), 43–55.

Roth, A. M., Sample, D. W., Ribic, C. A., Paine, L., Undersander, D. J., Bartelt, G. A., 2005. Grassland bird response to harvesting switchgrass as a biomass energy crop. Biomass Bioenergy 28 (5), 490–498.

Ruzinsky, F., Kokta, B. V., 2000. High-yield pulping of switchgrass using the Na(2)So(3)–$NaHCO_3$ system. Cellulose Chem. Technol. 34 (3–4), 299–315.

Ryu, D. D. Y., Mandels, M., 1980. Cellulases—Biosynthesis and applications. Enzyme Microb. Technol. 2 (2), 91–102.

Saha, B. C., Bothast, R. J., 1999. Enzymology of xylan degradation. *In:* Imam, S. H., Greene, R. V., Zaidi, B. R. (Eds.), Biopolymers: Utilizing Nature's Advanced Materials. American Chemical Society, Washington, DC, pp. 167–194.

Saha, B. C., 2001. Xylanase from a newly isolated *Fusarium verticillioides* capable of utilizing corn fiber xylan. Appl. Microbiol. Biotechnol. 56 (5–6), 762–766.

Saha, B. C., 2002. Production, purification and properties of xylanase from a newly isolated *Fusarium proliferatum.* Process Biochem. 37 (11), 1279–1284.

Saha, B. C., 2003. Hemicellulose bioconversion. J. Ind. Microbiol. Biotechnol. 30 (5), 279–291.

Samson, P., Duxbury, P., Drisdelle, M., Lapointe, C., 2000. Assessment of Pelletized Biofuels; http://www.reap-canada.com/library.htm

Sanderson, M. A., 2008. Upland switchgrass yield, nutritive value, and soil carbon changes under grazing and clipping. Agron. J. 100 (3), 510–516.

Sanderson, M. A., Adler, P. R., Boateng, A. A., Casler, M. D., Sarath, G., 2006. Switchgrass as a biofuels feedstock in the USA. Can. J. Plant Sci. 86 (5), 1315–1325.

Sanderson, M. A., Jones, R. M., McFarland, M. J., Stroup, J., Reed, R. L., Muir, J. P., 2001. Nutrient movement and removal in a switchgrass biomass-filter strip system treated with dairy manure. J. Environ. Qual. 30 (1), 210–216.

Sanderson, M. A., Reed, R. L., McLaughlin, S. B., Wullschleger, S. D., Conger, B. V., Parrish, D. J., Wolf, D. D., Taliaferro, C., Hopkins, A. A., Ocumpaugh, W. R., Hussey, M. A., Read, J. C., Tischler, C. R., 1996. Switchgrass as a sustainable bioenergy crop. Bioresour. Technol. 56 (1), 83–93.

Sarath, G., Mitchell, R. B., Sattler, S. E., Funnell, D., Pedersen, J. F., Graybosch, R. A., Vogel, K. P., 2008. Opportunities and roadblocks in utilizing forages and small grains for liquid fuels. J. Ind. Microbiol. Biotechnol. 35 (5), 343–354.

Schell, D. J., Harwood, C., 1994. Milling of lignocellulosic biomass—Results of pilot-scale testing. Appl. Biochem. Biotechnol. 45 (6), 159–168.

Schmer, M. R., Vogel, K. P., Mitchell, R. B., Perrin, R. K., 2008. Net energy of cellulosic ethanol from switchgrass. Proc. Natl. Acad. Sci. USA 105 (2), 464–469.

Schneider, H., Wang, P. Y., Chan, Y. K., Maleszka, R., 1981. Conversion of D-xylose into ethanol by the yeast *Pachysolen tannophilus.* Biotechnol. Lett. 3 (2), 89–92.

Stout, W. L., Jung, G. A., Shaffer, J. A., 1988. Effects of soil and nitrogen on water-use efficiency of tall fescue and switchgrass under humid conditions. Soil Sci. Soc. Am. J. 52 (2), 429–434.

Sun, Y., Cheng, J. J., 2002. Hydrolysis of lignocellulosic materials for ethanol production: A review. Bioresour. Technol. 83 (1), 1–11.

Tarkow, H., Feist, W. C., 1969. A mechanism for improving the digestibility of lignocellulosic materials with dilute alkali and liquid $NH_3$. *In:* Advance Chemistry Series 95. American Chemical Society, Washington, DC, pp. 197–218.

Thomason, W. E., Raun, W. R., Johnson, G. V., Taliaferro, C. M., Freeman, K. W., Wynn, K. J., Mullen, R. W., 2004. Switchgrass response to harvest frequency and time and rate of applied nitrogen. J. Plant Nutr. 27 (7), 1199–1226.

Thring, R. W., Chornet, E., Overend, R. P., 1990. Recovery of a solvolytic lignin—Effects of spent liquor acid volume ratio, acid concentration and temperature. Biomass 23 (4), 289–305.

Tillman, D. A., 2000. Biomass cofiring: the technology, the experience, the combustion consequences. Biomass Bioenergy 19 (6), 365–384.

Torget, R., Werdene, P., Himmel, M., Grohmann, K., 1990. Dilute acid pretreatment of short rotation woody and herbaceous crops. Appl. Biochem. Biotechnol. 24 (5), 115–126.

Van den Oever, M. J. A., Elbersen, H. W., Keijsers, E. R. P., Gosselink, R. J. A., De Klerk- Engels, B., 2003. Switchgrass (*Panicum virgatum* L.) as a reinforcing fibre in polypropylene composites. J. Mater. Sci. 38 (18), 3697–3707.

Ververis, C., Georghiou, K., Christodoulakis, N., Santas, P., Santas, R., 2004. Fiber dimensions, lignin and cellulose content of various plant materials and their suitability for paper production. Ind. Crops Products 19 (3), 245–254.

Vidal, P. F., Molinier, J., 1988. Ozonolysis of lignin—Improvement of *in vitro* digestibility of poplar sawdust. Biomass 16 (1), 1–17.

Vlasenko, E. Y., Ding, H., Labavitch, J. M., Shoemaker, S. P., 1997. Enzymatic hydrolysis of pretreated rice straw. Bioresour. Technol. 59 (2–3), 109–119.

Vogel, K. P., 2004. Switchgrass. *In:* Moser, L. E., Sollenberger, L. E., Burson, B. L. (Eds.), Warm-season ($C_4$) Grasses. American Society of Agronomy, Crop Science Society of America, and Soil Science Society of America, Madison, WI, pp. 561–588.

Vogel, K. P., Brejda, J. J., Walters, D. T., Buxton, D. R., 2002. Switchgrass biomass production in the midwest USA: Harvest and nitrogen management. Agron. J. 94 (3), 413–420.

Wang, P. Y., Shopsis, C., Schneider, H., 1980. Fermentation of a pentose by yeasts. Biochem. Biophys. Res. Commun. 94 (1), 248–254.

Weil, J., Westgate, P., Kohlmann, K., Ladisch, M. R., 1994. Cellulose pretreatments of lignocellulosic substrates. Enzyme Microb. Technol. 16 (11), 1002–1004.

Wood, J. H., Long, G., Morehouse, D., 2003. World conventional oil supply expected to peak in 21st century. Offshore 63 (4).

Wood, T. M., Saddler, J. N., 1988. Increasing the availability of cellulose in biomass materials. Methods Enzymol. 160, 3–11.

Wright, J. D., Dagincourt, C. G., 1984. Evaluation of sulfuric-acid hydrolysis processes for alcohol fuel production. Biotechnol. Bioeng. Suppl. 14, 105–123.

Wright, J. D., Wyman, C. E., Grohmann, K., 1988. Simultaneous saccharification and fermentation of lignocellulose—Process evaluation. Appl. Biochem. Biotechnol. 18, 75–90.

Wu, M., Wu, Y., Wang, M., 2006. Energy and emission benefits of alternative transportation liquid fuels derived from switchgrass: A fuel life cycle assessment. Biotechnol. Prog. 22 (4), 1012–1024.

Wu, Z. W., Lee, Y. Y., 1997. Ammonia recycled percolation as a complementary pretreatment to the dilute-acid process. Appl. Biochem. Biotechnol. 63 (5), 21–34.

Wyman, C. E., 1994. Ethanol from lignocellulosic biomass—Technology, economics, and opportunities. Bioresour. Technol. 50 (1), 3–16.

Wyman, C. E., 2003. Potential synergies and challenges in refining cellulosic biomass to fuels, chemicals, and power. Biotechnol. Prog. 19 (2), 254–262.

Wyman, C. E., Spindler, D. D., Grohmann, K., 1992. Simultaneous saccharification and fermentation of several lignocellulosic feedstocks to fuel ethanol. Biomass Bioenergy 3 (5), 301–307.

Yu, M., Womac, A. R., Igathinathane, C., Ayers, P. D., Buschermohle, M. J., 2006. Switchgrass ultimate stresses at typical biomass conditions available for processing. Biomass Bioenergy 30 (3), 214–219.

Zhang, R. Q., Brown, R. C., Suby, A., 2004. Thermochemical generation of hydrogen from switchgrass. Energy Fuels 18 (1), 251–256.