EVALUATING PHYSICAL, CHEMICAL, AND ENERGETIC PROPERTIES OF PERENNIAL GRASSES AS BIOFUELS

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ABSTRACT

The suitability of energy crops for either energy conversion into fuels or energy release through combustion can be measured by several indices that reflect energy content, density, and ease of recovery. These properties ultimately determine both the suitability and diversity of potential end uses of feedstocks and their potential value as agroindustrial resources. Our analyses indicate that switchgrass should be a versatile bioenergy feedstock. Energy content of switchgrass is comparable to that of wood with significantly lower initial moisture content. Early analyses of ethanol recovery from enzymatic hydrolysis by the National Renewable Laboratory (NREL), indicate that switchgrass is very suitable substrate and produces high ethanol yield using current simultaneous saccharification and fermentation (SSF) technology. Contrary to earlier reports, more extensive analysis of ash and alkali content of switchgrass indicates that it typically has a relatively low alkali content and should have low slagging potential in coal-fired combustion systems. As an agrofiber source for pulping, switchgrass has a relatively high cellulose content, low ash content, and good fiber length to width ratios. It appears to be a promising substitute for hardwoods in the production of high quality paper. Harvesting and handling strategies can improve switchgrass suitability for industrial endpoints.

Keywords: switchgrass, energy, fuel quality, feedstock

INTRODUCTION

As biomass energy technologies continue to develop, a broad array of potential end uses and endproducts can be envisioned from lignocellulosic feedstocks. The chemical and physical properties of the dedicated energy crops that will ultimately supply a significant fraction of these feedstocks will be important to many of these processes. This is true not only from the perspective of chemical or energetic yield of the conversion process, but also from the standpoint of the economics of both agronomic and industrial sectors.

Feedstocks that are suitab herbaceous energy crop, *Panicum virgatum*, energy feedstocks le for a wide variety of end uses, for example, will provide additional economic insurance

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to the grower that a suitable market and price can be found. The industrial consumer, on the other hand, may experience increased price competition for a more versatile feedstock, but perhaps realize a broader spectrum of suppliers.

This paper focuses on the energy-related attributes of an herbaceous energy crop species, switchgrass (<u>Panicum virgatum</u>). This species has been selected as a model herbaceous crop for the Oak Ridge National Laboratory's Biofuels Feedstock Development Program (BFDP) (McLaughlin, 1992). Results from selected studies over approximately 8 years are presented to evaluate fuel properties which will influence the range of viable applications of switchgrass as a biofuel. This includes summary chemical and physical data on fuel quality as well as information on how managing, handling and storing the crop influence fuel quality. The latter factors may be of interest to economists in calculating tradeoffs between fuel quality and costs of management operations.

SUMMARY OF SWITCHGRASS FUEL QUALITY CHARACTERISTICS

In Table 1, data on several relevant aspects of switchgrass fuel quality are summarized. These include the energy content of dried material, moisture content at harvest, the energy density as typically handled and transported after harvest, and the energy recovery. We define the energy recovery here as the net energy return after subtracting energy loss involved in vaporizing fuel moisture. Also included in Table 1 are data specifically related to the use of switchgrass as a combustion fuel, including ash content, ash fusion temperature, and sulfur content, as an index of potential atmospheric pollution. Contrasts with alternate fuels such as corn, poplar, and coal are provided where appropriate. Data indicate that the energy content of switchgrass is nearly the same as that of wood per unit of dry weight, but 33% less than that of coal. On the other hand, switchgrass has a much lower total ash content and much lower sulfur emissions than coal. On a volumetric basis wood and switchgrass are also very comparable, but energy content of switchgrass bales at harvest is higher by about 45% than that of poplar chips. In terms of recoverable energy from harvested biomass, switchgrass with its lower moisture content has a slightly higher level of recoverable energy than wood, because less drying is required.

CHEMICAL CRITERIA AND INDUSTRIAL ENDPOINTS

Currently, the primary industrial endpoints for energy crops are, ethanol production for use as transportation fuels; direct combustion or gasification to produce heat or electricity; or thermochemical conversion to produce a wide variety of chemicals that can be synthesized into secondary products, including chemical feedstocks for industry as well as transportation fuels. The chemical criteria and limitations for each of these processes are quite different and will be summarized only briefly here.

Table 1. Chemical and physical properties of switchgrass as a biofuel relative to selected alternate fuels.

Fuel property	Switchgrass Value	Units	Alternate fuel	
			Value	Fuel type
Energy content (dry)	17.4	MBtu·Mg ⁻¹	18.6 26.0	Wood Coal
Moisture content (harvest)	15	%	45	Poplar
Energy density (harvest)	14.8	MBtu·Mg ⁻¹	10.2	Poplar
Net energy recovery	17.0	MBtu·Mg-1	16.4	Poplar
Storage density (6' x 5') round bale (4' x 5') round bale Chopped	133 105 108	Kg·m ⁻³ (dry weight)	150	Poplar chips
Holocellulose	54-67	%	49–66	Poplar
Ethanol recovery	280	L·kg-1	205	Poplar
Combustion ash	4.5–5.8	%	1.6	Poplar
Ash fusion temperature	1016	°C	1350 1287	Poplar Coal
Sulfur content	0.12	%	0.03 1.8	Wood Coal

Notes: Energy content of switchgrass was determined from 6 samples from Iowa. Bale density and chopped density of switchgrass are from Alabama (D. Bransby, Auburn). Poplar chip density is from studies of White et al. (1984). Poplar energy moisture content, combustion ash and ash fusion temperatures are from NREL, as are ash fusion temperatures and sulfur contents of all fuels. Energy density is the energy per unit of wet harvest weight. Net energy recovery considers energy lost in drying fuel prior to combustion. Holocellulose content of switchgrass is from 7 varieties in AL (Sladden et al. 1971) and from 7 hybrid poplar vareties in PA (Bowersox et al. 1979). Ethanol yields are averages of SSF recovery on 3 analyses per species using a standard recovery procedure for all feedstocks. Ethanol yields can likely be improved somewhat by tailoring reaction mixtures to each specific feedstock, thus those should be considered preliminary measures of potential recovery.

Ethanol Production - Since ethanol production from lignocellulosic feedstocks involves initial breakdown of cell walls to sugars that can be enzymatically converted, the content of cellulose and other structural polysaccharides of the cell walls is the primary determining factor in ethanol yield. For herbaceous energy crops (Sladden and Bransby, 1989), the total cell wall fraction, about 80% of the plant dry weight, includes primarily cellulose (30-50% of dry weight) and other cell wall polysaccharides, referred to as hemicellulose (10-40% of d.wt.). The third principal constituent is a high energy cellular "cement" lignin . Lignin (5-20% d.wt.) cannot be converted to sugars by conventional hydrolysis/enzymatic systems. However, lignin is an energy rich coproduct with an energy content of 26.1 Gj*Mg¹, a value similar to that of coal (Johnson et al., 1991). This compares to a typical energy content of 18.3 Gj* Mg¹ for the whole switchgrass plant. In the NREL SSF process (Wyman,1993) lignin is an important coproduct used to produce all of the heat required in the production process. Holocellulose content of switchgrass and hybrid poplar are very similar (Table 1) and current SSF technology works well on herbaceous energy crops like corn stover and switchgrass. Switchgrass ethanol yields

(280 L*Mg⁻¹) were among the highest found among six species examined in preliminary trials (Art Wiselogel, personal communication).

<u>Combustion</u> - Three primary fuel attributes determine the suitability of energy crops for combustion or gasification: the total energy content, the moisture content, and the chemistry of ash produced upon combustion. Total energy content determines the maximum amount of heat that can be recovered and the potential electricity that can be generated from combustion. For switchgrass, energy content on a dry weight basis averages approximately 18.4 Gj compared to 19.6 Gj for poplar.

Moisture content at harvest influences the cost of transportation and handling, as well as the recoverable energy level, since moisture vaporization requires energy during the combustion process. Switchgrass is typically baled at moisture contents of 13-15%, while poplar typically contains 45-50% moisture at harvest. This water influences the usable energy that can be derived from a unit of harvested biomass, reducing the switchgrass and poplar energy yields to 18.0 and 17.3 Gj, respectively (Table 1).

Ash content and chemistry is important in the combustion process because it can contribute to slagging of internal boiler surfaces leading to formation of deposits that reduce boiler efficiency and increase maintenance costs (Miles et al., 1993). The critical ash characteristic which promotes slagging is the alkali content and the presence of silicates. These constituents lower the ash melting point to the range of normal furnace operations and can cause plating out of liquid ash on internal surfaces.

In previous analyses the high ash content and more specifically high alkali content of switchgrass ash has led other authors to regard switchgrass as unsuitable for combustion in conventional boilers (Miles et al., 1993, 1995). However, subsequent analyses indicate that those original samples were likely contaminated during handling. Much of the early evaluation of switchgrass for combustion came from a single sample, collected from baled switchgrass from a field in Iowa. The prior storage history of this sample was not known, and sample handling included hammer milling in the field, blowing into a truck, and transport to an uncovered parking lot in Colorado for storage. These conditions are conducive to contamination from surface-deposited dirt and likely explain the high mineral content of samples from this collection. To illustrate this point, we show in Figure 1 the ash content and analyses of a slagging index (lb of water soluble alkali in ash per MM Btu of fuel energy) of the initial analysis that has been widely cited as indicative of the poor quality of switchgrass as a combustion fuel. The slagging index of the original sample (1.4) was in fact quite high and well above the value (0.80) considered as excessive for combustion purposes. This sample is in marked contrast to results of the 5 more recent analyses (Figure 1). With a slagging index of about 4 times that of the remaining 5 samples (0.37 lb*MBtu-1) and an ash level approximately double that of subsequent samples, the original sample does not appear to be typical of switchgrass. The average ash content determined from over 36 analyses of switchgrass across a wide

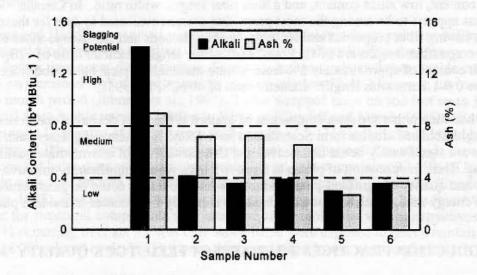


Figure 1. More Recent Analyses of Switchgrass Combustion Characteristics (Samples 2-6) Indicate Relatively Low Slagging Potential

variety of locations, varieties and treatments within the BFDP was 4.5% (range 2.8%-7.6%), close to that of samples 2-6 in Figure 1. Thus the conclusion that switchgrass is unsuitable for combustion in conventional boilers is not supported by more recent and more extensive data.

Thermochemical Conversion - Because thermochemical processes break down the chemical bonds of biofuels they are less influenced by fuel quality issues. Lignin, which cannot be converted directly into ethanol in the SSF process, is converted with all other constituents during thermochemical conversion into carbon monoxide and hydrogen, used in synthetic pathways to produce a wide variety of useful end products. However, if pyrolysis oils are produced for use as fuel in turbine generated electrical power, some reduction of ash levels of switchgrass may be required since alkali metal can combine with sulfur to produce corrosive sulfates (Abglevor et al., 1995). The low sulfur content of switchgrass (Table 1) may reduce this possibility in practice, however.

FIBER AND ENERGY COPRODUCTS FROM GRASSES

One opportunity to improve market opportunities for using grasses may be to fractionate the plants and use some of the various grass components for higher value markets than energy - the biorefinery concept. An area receiving significant research attention in both North America and Northern Europe is the use of grass fiber as a substitute for hardwood fiber in pulp and paper manufacture. Typically the fiber used to make fine quality paper consists of 80% hardwood and 20% softwood. Pulp companies in the Scandinavian countries and Canada are examining the potential of grass fiber as a substitute for part of the hardwood component used in the production of paper.

Some of the desirable composition traits for grasses to be used in pulping are a high cellulose content, low silica content, and a high fiber length: width ratio. In Canada, switchgrass appears to be among the most promising grasses evaluated to date for these attributes, having fiber properties similar to those of hardwoods and superior to those of straw. Average fiber lengths are of 1.35 mm, with a fiber length: diameter ratio of 120, and an ash content of approximately 3% from mature material. Typical hardwood fiber lengths are 0.9-1.8mm with length: diameter ratio of 40 (CSPP, 1995).

Research has shown that the stem component of grasses is the most desirable component for pulping. Published studies form Scandinavia have found that stems of grasses such as tall fescue are significantly better than leaves and that sheaths are of intermediate quality for pulping. Thus fractionation of plants to remove leaves would significantly improve the yields and quality of agrofiber pulp produced, while the leaves could be transformed into other energy uses, much as wood and bark are currently fractionated in modern pulp mills.

PRODUCTION PRACTICES THAT AFFECT FEEDSTOCK QUALITY

There are three principal opportunities for modifying the biofuel properties for lignocellulosic crops such as switchgrass: genetic selection, harvest management, and storage conditions.

Genetics - To date the BFDP has evaluated genetic variability in feedstock chemical attributes, but has not attempted to optimize for any specific trait. We have reasoned that trait selection is premature and may not be cost effective relative to selecting for optimum yield in this still-developing technology. For example, in Alabama, holocellulose content varied by only 12% and lignin by less than 4% (% of mean contents at late harvest) between two varieties, Cave-in-Rock and Alamo, that differed in yield by over 200%. Likewise in the midwest, Hopkins et al. (1995) found that 28 switchgrass cultivars had a within-site coefficient of variation for yield of 45% and for digestibility of 4-14%, depending on harvest date and location.

Management - Considerable emphasis has been placed in the BFDP on optimizing harvest schedules to maximize yields of switchgrass. In general, in the deeper south a two-cut system with cuts in July and October, has provided somewhat higher yields under the longer southern growing season, whereas a single cut system may be more advantageous further north. While mid-western studies show that switchgrass digestibility for cattle decreases with the later harvests (Hopkins et al., 1995), studies in Alabama suggest total cellulose content averaged slightly lower (12%) for second harvests of southern varieties (Sladden et al., 1989) than did mid-summer harvests. More recent studies have now included a very late season cut, delayed to after frost to permit restranslocation of nutrients belowground and a more flexible harvest schedule (Parrish et al., 1996). While yields may be reduced by approximately 20% by post-frost harvest, this can result in improved yields the following year and improved quality of the late harvest biomass due to reduced mineral content. Parrish et al., (1996) for example, found that late harvest K levels were reduced to 73% of those from earlier harvests. Both retranslocation and leaching from senescent foliage undoubtedly contributed to these low nutrient levels. Thus delayed harvest may significantly improve switchgrass as a combustion fuel. In addition the increases in stem: leaf biomass ratios improve lateharvested feedstock for fiber recovery. Spring harvest of over-wintered reed canary grass

is currently the proposed production system for fiber in northern regions (Paavilainen and Torgilsson, 1994).

Storage and Handling - Annual supply of herbaceous feedstocks to industry will require storage of biodegradable supplies. Both quantitative and qualitative changes in switchgrass may occur during storage. Studies in Indiana indicated that outside storage of bales on a crushed rock substrate, results in relatively low (2-4%) losses of dry mass over a 8.5 month period (Johnson et al., 1991). Twine wrapped bales on sod lost up to 15% of original mass in this interval. Studies in Virginia (Cundiff and Marsh, 1995) indicated the losses over 12 months of storage were in the range of 5-11% regardless of initial bale moisture (13% or 22%) or wrapping (net or twine). Weathering of an outside core of unprotected bales does occur, visible discoloring an area comprising 22-29% of bale dry weight after four months. No further changes occurred through 12 months (Cundiff and Marsh, 1995). Biochemical changes associated with weathering have been found to be minor for structural components with losses of lower molecular weight extractives of up to 11% occurring over six months only when bales were exposed to heavy rainfall during storage (Wiselogel et al., 1995). Under drier conditions losses were negligible.

Experience within the BFDP indicates that sample collection and handling during and after harvest is important to reducing contamination. In one instance, the use of a Carter flail harvester which sucks samples from the ground and blows them into the collecting container, resulted in quite variable sample ash levels (2.1% to 11.1%) from the same location (Sladden et al., 1991). Subsequent analyses at this Alabama site have documented an increase in ash (from initial plant levels of 2.9% to baled levels of 4.0%) during conventional baling operations (D.Bransby, personal communication). Thus substantial contamination of samples may result from deposited dirt where harvesting systems occur in, or generate, a dusty environment. Similarly, bales allowed to sit at field side near dust generating agricultural operations may be significantly contaminated by wind-blown dust and rendered less suitable for end points requiring a cleaner fuel. In summary, future market value and diversity for switchgrass will likely be influenced by fuel quality and it will be important to recognize and promote management practices designed to optimize not only quantitative but qualitative aspects of feedstock supply.

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