The Feasibility of Using Cattails from Constructed Wetlands to Produce Bioethanol

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Abstract This project investigates the feasibility of harvesting the cattails in the constructed wetlands of the North Carolina A&T Farm to be converted into ethanol. Using the cattails to produce renewable energy will add value to the land as well as reduce emissions of greenhouse gases by replacing petroleum products. Pretreatment of the dried cattails with dilute NaOH was followed by solid-liquid separation and enzymatic hydrolysis and fermentation of the solids. Two trials gave an average conversion efficiency of 43.4% for the pretreated solids alone which, in conjunction with the crop yield for the cattails, would give up to 4,012 L ethanol/ha, a favorable comparison with corn stover's 1,665 L/ha at a 60% conversion rate. Given the high potential – 9,680 L/ha at 60% conversion efficiency for solid and liquid streams – and the social and environmental benefits gained by adding value to the waste management system and reducing carbon emissions otherwise made by gasoline, it is recommended that further studies be made using cattails as a feedstock for bioethanol.

Introduction

Renewable transportation fuels are being developed to lower emissions of greenhouse gases and to enhance energy security. Biodiesel and starch-based ethanol predominate, but the technology required for conversion of cellulose to ethanol is improving; some pilot plants are currently in operation, and the first full-scale plants are due to come on line in 2007 and 2008. Cellulosic ethanol has a better environmental profile than starch-based ethanol, with a 90% reduction in carbon emissions over gasoline as compared to a 29% reduction using starch-based ethanol (Wang, 2005), and it has the advantages of not requiring fertile agricultural land and of adding value to marginal farmland. Another benefit of cellulosic ethanol is the

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supply distribution afforded since it can be converted from a variety of cellulosic materials according to growing conditions and availability around the country.

One possible source of cellulosic feedstock is the cattails used for phytoremediation in constructed wetlands. Whereas harvesting plants from natural wetlands is a sensitive issue because of possible environmental harm, harvesting the above-water portion of cattails once a year from a constructed wetland is a sustainable practice which will not interfere with their role in cleaning the wastewater. There is no energy input required to grow them, as they receive their water and nutrients from the wastewater. Using the cattails as a feedstock for bioethanol is one way to add value to the land with little environmental impact.

This project examines the feasibility of using the cattails from constructed wetlands to produce bioethanol. The focus is on pretreatment, followed by enzymatic hydrolysis and fermentation of the solid fraction. Environmental impact, in terms of emissions reductions, is calculated, and economic factors are considered. The preliminary results are presented.

Methods

The basic steps to be followed in producing ethanol from cellulosic plant material include harvesting, cleaning and shredding the feedstock, pretreatment, enzymatic hydrolysis, fermentation, distillation and drying. This paper focuses on pretreatment of the feedstock with sodium hydroxide followed by enzymatic hydrolysis and yeast fermentation.

Feedstock Characteristics. Cattails were cut and chopped with pruning shears, dried at 70°C for 5 days, and ground in a Wiley mill to 2 mm mesh size. The energy content for cattails was determined using a Parr bomb calorimeter. Dried samples were sent to Dairy One Forage Lab (Ithaca, NY) to be analyzed for cellulose, hemicellulose, and lignin content by ANKOM 200 Fiber Analyzer.

Pretreatment of the feedstock. Alkaline pretreatment was carried out in order to render the cellulose more accessible to the cellulase for enzymatic hydrolysis. About 500 g of the dried, ground cattails were stirred into 5 L of a 1.0 N NaOH solution and left at room temperature overnight. The mixture was then centrifuged for 20 min, after which, the liquid was poured off, the solids rinsed with water and re-suspended in the water two times with centrifuging and decanting of the supernatant after each rinse. Moisture content of the pretreated mix was determined by drying a sample at 60°C until weight was constant. Another sample was sent to Dairy One Labs for cellulose, hemicellulose and lignin analysis.

Culturing the yeast for fermentation. *Saccharomyces cerevisiae* (ATCC 24858) and *Yamadazyma stipitis* (ATCC 58784) were used to ferment the sugars. *Y. stipitis* breaks xylose down producing ethanol, and *S. cerevisiae* produces ethanol from glucose. Aseptic technique was used to rehydrate the freeze-dried yeasts. They were incubated at 30°C (*S. cerevisiae)* and 25°C (*Y.* stipitis) and stepped up until 1.0 L was obtained.

Enzymatic hydrolysis and fermentation. Enzymatic hydrolysis was carried out in two batches in a BioFLo 110 Fermentor/BioReactor (New Brunswick Scientific, Edison, NJ) at 50°C, 4.8 pH and 200 rpm agitation. Pretreated cattails were mixed with deionized water to a concentration of 50 g/L. Cellulase enzymes (Spezyme CP, Genencor International, Rochester, NY) were added at 82 GCU/g dry matter. The pH was monitored and adjusted with buffer solutions of 5% NaOH and 5% HCl. Samples were taken throughout the process for later analysis by high pressure liquid chromatography (HPLC) using a 717 Plus Autosampler (Waters, Milford, MA). Hydrolysis proceeded for 24 h before yeasts were added. At 24 h, the temperature was reduced to 37°C and the yeasts, *S. cerevisiae and Y. stipitis,* were added. A condenser was attached to the fermentation vessels to allow cooling water to condense the evaporating ethanol back into the vessel. Fermentation proceeded at 37°C, 250 rpm agitation, and pH of 4.8, and the process was allowed to run for five days.

Results and Discussion

Feedstock Characteristics. Two years of data from the A&T Farm indicate that the average yield of cattails from the constructed wetlands is 16.1 mton/ha with a maximum of 42.7 mton/ha (Dr. G.B. Reddy, personal communication, October 2006). The harvested plants had average moisture content (w.b.) of 78.6%. The energy content at 5.4% moisture content (w.b.) was found to be 17.4 MJ/kg. Cellulose, hemicellulose and lignin content for the dry material were determined as 28.7%, 23.4%, and 10.1%, respectively. Because a large part of the energy in the process is used to dry the feedstock, further studies should look at the possibility of using it without drying.

Pretreatment. Supernatant from the pretreated material was analyzed by HPLC to determine the concentration of xylose, glucose and arabinose in the liquid portion of the hydrolyzate. The only sugar detected was xylose at 0.156% which was decided to be too little to pursue further. However, later it was questioned exactly how much 0.156% might have been as the supernatant had been diluted with the rinse water. It may be possible to use suction filtration or a reverse osmosis membrane to separate the liquids and solids and get higher yields from the solid stream. Future plans are to track and ferment the liquid fraction separately.

After pretreatment, cellulose content had increased from 28.7% to 46.2% total dry solids. Calculating the cellulose content based on the mass of pretreated dry solids shows that 28.7% of the cellulose was actually lost during pretreatment. Likewise, hemicellulose and lignin were reduced in the solids, with lignin diminishing by 51.4%, and hemicellulose by 67.5%. Evaporation of the supernatant showed that there were suspended solids, presumably the lost cellulose. Hemicellulose is alkaline soluble, and most was expected to be dissolved by the NaOH, while lignin has alkaline-soluble fractions (Reith et al., 2002; Walthers et al., 2001).

Enzymatic Hydrolysis and Fermentation. Enzymes began to convert the biomass to sugars within 2 min of being added (Fig. 1). The initial glucose

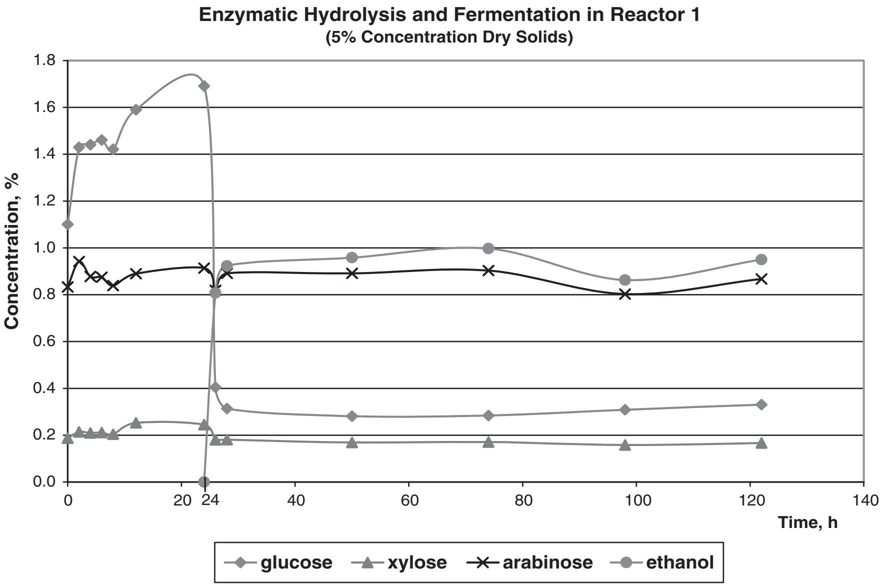

Fig. 1 Enzymatic hydrolysis and fermentation in reactor 1

concentration measured 1.100% and 1.041% respectively, in reactor 1 and reactor 2. Just before addition of the yeast, at 24 h, the glucose concentration had reached 1.691% and 1.615%. Xylose showed an increase in concentration from 0.187% and 0.158% to 0.245% and 0.229% in reactors 1 and 2 respectively. The xylose in two reactors and the glucose in one had actually started to decline in concentration before the yeast was added. Possibly they were further degrading into compounds that were not being measured.

Arabinose concentration during enzymatic hydrolysis and fermentation was steady at about 0.8%. The enzymes and yeast had no effect on it. The arabinose must have been released during pretreatment. With addition of arabinose-fermenting yeasts, the ethanol yield could be increased.

Results of the HPLC showed ethanol yield in this study was 0.997% and 0.951% in the two reactors, which yields an average efficiency of 43.4%. This is equal to 94 L ethanol/mton cattail. Badger (2002) reports a reasonable efficiency of 57% using acid hydrolysis to give 227 L ethanol/mton dry corn stover. Using enzymatic hydrolysis was expected to give a higher yield. One reason for the low yield could be that the enzymes used in this study, Spezyme CP, are tailor-made for corn stover. Supplemental enzymes might improve yields. Better fermenting organisms have been developed and a way of obtaining them for future studies is being studied. The two yeasts used have different optimum temperatures. It is supposed that the ethanol produced came from the glucose because of the higher than optimum temperature for *Y. stipitis*.

Tying the alcohol yield in with the yield of cattails from the wetlands gives an average of 1,521 L ethanol/ha cattails, and a maximum of 4,018 L ethanol/ha cattails. Based on current DOE estimates of 60% conversion efficiency (334 L/mton), and using the sustainable harvest amounts of corn stover for current tillage practices, we have an ethanol yield from corn stover of 804 L/ha, and for no-till farming, 1,665 L/ha (Perlack et al., 2005). Assuming that further trials with cattails will approach 60% efficiency, the yield of ethanol per acre of cattails could reach as much as 3,917 L/ha.

Environmental Analysis

The preliminary study did not address the environmental impact of harvesting cattails. There will be no need for machinery, except for the once yearly sustainable harvest in late summer, so the detrimental environmental impact should be less than for feedstocks requiring fertilization and irrigation. In addition, the cattails are being used for phytoremediation of wastewater, a benefit to the environment in itself.

The major benefit to the environment, if cattails were to be used as a feedstock for bioethanol, is the reduction in greenhouse gas emissions. Using a life cycle analysis, pure bioethanol emits 90% less carbon dioxide than an equivalent energy amount of gasoline (Wang, 2005). Pure ethanol has two thirds the energy of gasoline liter per liter, and one liter of gasoline, over its life, emits 2.32 kg carbon dioxide. To determine the reductions in emissions achieved by using bioethanol, the following formula can be used,

$$0.67 \times 2.32 \times 0.90 \times \mathrm{EtOH} = \mathrm{E_S} \tag{1}$$

where EtOH is the amount of bioethanol in L/ha, and E_S is the emissions (kg/ha) saved by using the bioethanol. By using this formula, it can be seen that using the bioethanol from corn stover with current tillage practices will save 1,115 kg CO_2/ha. Cattails at average yield will save 2,128 kg CO_2/ha and cattails at maximum production will save 5,621 kg CO_2/ha. Once 60% conversion efficiency for cattails to ethanol is achieved, the savings will rise to 5.2–13.4 mtons of carbon dioxide per hectare.

Economic Analysis

A complete economic analysis needs to be carried out including the cost of harvesting. Because of the wet nature of the cattail environment, special machinery must be designed to cut the plants without sinking into the soft soil. In the case where the wetlands are constructed with ethanol production in mind, the dimensions can be designed to accommodate existing long-armed machinery such as those used to cut grass on highway banks. Sizing, storing, and processing costs are assumed to be approximately equal to those of corn stover.

Based on corn stover costs, a plant must have about 453–907 mtons/day to stay in operation (Fraser, 2006). Converting this weight of corn stover to a volume of ethanol gives a required 151,000–302,000 L/day. Assuming the plant operates 330 days a year, the amount of land required per crop per year can be determined from the following formula,

$$(302,800 \times 330)/(\mathrm{EtOH}) = \mathrm{A} \tag{2}$$

where EtOH is the amount of bioethanol in L/ha, and A is the area of land required in hectares. Using this formula gives a land requirement of about 60,000–124,000 ha/yr for corn stover and 25,000–66,000 ha/yr of cattails at the preliminary 43% conversion rate.

Although cattails are abundant in North Carolina, particularly in the eastern part of the state, there are not very many constructed wetlands. However, some mid-size municipalities across the country have found them to be cost effective as part of their wastewater treatment (Gelt, 1997). In addition, cattails have been used to clean some industrial wastewater streams. An integrated system which uses mixed feedstock including the cattails from constructed wetlands in the community should be investigated as a promising scenario.

Conclusion

Although the initial trials using cattails to make bioethanol achieved only 43.4% conversion efficiency, it is believed that further trials will obtain better results by using more advanced conversion organisms, and by combining the liquid and solid fractions. The low conversion rate is more than made up for by the high productivity of the wetlands, and by the reduction in emissions in the life cycle analysis of the fuel produced. With advances in technology, it is not unlikely that ethanol plants will soon be able to use a variety of feedstocks. Cattails from constructed wetlands could be a valuable part of an integrated system with their role as cleaning agents and clean fuel feedstock.

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