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Cellulosic Materials Recovered from Steam Classified Municipal Solid Wastes as Feedstocks for Conversion to Fuels and Chemicals

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ABSTRACT

A process has been developed for the treatment of municipal solid waste to separate and recover the cellulosic biomass from the nonbiomass components. The process, known as steam classification, transforms the pulp and paper materials, food wastes, and soft yard wastes into a fairly uniform product that appears to be highly suitable as a feedstock for conversion to fuel, fertilizer, and/or fermentable sugars. The physical and chemical properties of this cellulosic feedstock have been determined. The material has also been tested as a feedstock for composting and for cellulytic enzyme hydrolysis to yield glucose.

Index Entries: Municipal solids waste; biomass production; resource recovery; cellulosic feedstock; biomass conversion.

INTRODUCTION

It was estimated that the United States generated over 195 million tons of municipal solid waste (MSW) in 1990 (*1*). Cellulosic biomass, either as pulp and paper products, food wastes, and yard wastes, typically comprises about 50% of MSW by weight and an even higher percentage by volume. Thus, MSW is potentially an abundant source of cellulosic biomass that could be utilized to produce fuels and chemicals. MSW

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already has an infrastructure for collection and transport to disposal facilities that could also be utilized in conjunction with MSW processing facilities.

Separation and recovery of the cellulosic biomass from the commingled waste stream can be expensive and is often only partially successful. Source segregation recycling programs require separate collection and transport to materials recovery facilities, which essentially duplicates the process for commingled MSW. Such programs typically only recover selected materials, leaving most of the waste stream for disposal. Some facilities have been built to process MSW into a combustion fuel, known as refuse-derived fuel (RDF). Such facilities typically shred the commingled MSW and then attempt separation of noncombustibles and "wet" biomass. About the only material recovered for recycling is ferrous metal. The RDF usually has a fairly high ash content and has substantial amounts of plastics. The RDF is suitable for combustion, but as a feedstock for conversion to fuels and chemicals, the contaminating nonbiomass materials make the material undesirable.

Steam classification of commingled MSW has been found to provide a means of treatment that facilitates separation of the biomass and nonbiomass components. Most of the biomass is transformed under heat and pressure into a fairly uniform material that can be separated from most of the metals, plastics, textiles, and glass by vibratory or trommel screening over a 1.3-cm screen. The wet <1.3 cm material is usually contaminated with about 20% plastics and broken glass. Some of these contaminants can be removed from the wet material by processing with a stoner. However, destoning is much more effective after drying. The <1.3 cm fraction that has been processed with a stoner before drying is the cellulosic biomass feedstock used in this investigation (2).

METHODS

Biomass Feedstock Preparation

A total of 407.7 kg of MSW, collected from dumpsters at an apartment complex, was conveyed into the 10-m^3 prototype steam classification process unit. The unit was sealed, and saturated steam was injected into the unit with continuous agitation. After the internal pressure and temperature reached about 380 kPa and 150°C, respectively, the pressure and temperature were maintained with continuous agitation for 30 min. The unit was then depressurized to atmospheric pressure. The unit was operated and the MSW was processed as previously described in more detail (3). After vibratory screening and destoning, 256.4 kg of wet biomass feedstock was recovered in the <1.3 cm fraction. Several samples of this feedstock were placed in plastic bags and stored at −20°C. These frozen samples were used for the subsequent experiments.

Chemical Analyses

The moisture was determined by weight difference after drying to a constant weight at 105°C. The ash content was determined by weight difference after ignition to a constant weight at 800°C. Samples to be analyzed for environmental pollutants were preserved and analyzed by standard EPA approved methods (*4–6*). All other analyses were performed using appropriate standard methods and equipment, and the results in Tables 2–5 are reported on a dry wt basis. Glucose analyses were performed with a YSI glucose analyzer.

Composting Procedure

A sufficient quantity of liquid plant fertilier was added to a known weight of feedstock to produce a desired final C/N ratio. A known weight of nitrogen-supplemented feedstock was placed in plastic jars, covered with cheesecloth, and incubated in an incubator at 40°C. Humidity was partially maintained by placing a dish of water in the incubator. The material was removed from the jars weekly and manually mixed to aerate the material completely. The material was analyzed for moisture, and water was added, if necessary, to maintain a moisture content of 55–60% by weight.

Cellulytic Enzyme Hydrolysis

The cellulytic enzyme was "Cellulase Tr Concentrate" obtained from Solvay Enzymes, Inc., Elkhart, IN, which is a food-grade cellulase complex obtained by a controlled fermentation of *Trichoderma reesei.* The enzyme complex consists of endo- and exo-glucanases and liberates significant quantities of glucose from native cellulose. The feedstock was suspended in 0.2*M* sodium citrate buffer, pH 4.8 to provide a slurry of known wt% total dry solids. A higher buffer concentration was used because the pH tended to drift during the 24-hr incubation period at 0.05*M*. The hydrolysis was initiated by the addition of a known weight of dry powdered enzyme. The mixture was gently stirred to dissolve the enzyme with minimal foaming. The mixture was then incubated for 24–48 h with gentle shaking at 45°C.

RESULTS

The moisture and ash content of the feedstock as received and on a dry wt basis are shown in Table 1. The moisture content of the material is 58.7% by wt. At this and higher moisture, the bulk density of the biomass and the contaminating finely broken glass are similar, thus reducing the efficiency of the separation by destoning. The ash content of the feedstock is therefore also greater in high-moisture samples.

Table 1
Moisture and Ash Content of Biomass

Component	As received	Dry wt
Moisture	58.7%	—
Combustibles	29.3%	71%
Ash	12.0%	29%

Table 2
Analysis for Heavy Metals

Metal	Conc., mg/kg
Arsenic	<0.05
Barium	<0.01
Cadmium	<0.01
Chromium	<0.01
Lead	<0.05
Silver	<0.01
Mercury	<0.005
Selenium	<0.005

The feedstock was analyzed for the presence of toxic heavy metals. The results on a dry wt basis are shown in Table 2. None of the EPA-designated heavy metals were found to be in concentrations above the detection limits of the method and instrumentation.

Other analytical tests related to potential environmental hazards were also included. The results of these analyses are shown on a dry wt basis in Table 3. The feedstock was found to contain fairly high concentrations of organic substances, but these organics were apparently not of the environmentally hazardous type.

The ultimate analysis of the organic constituents on a dry wt basis is shown in Table 4. This indicates that the feedstock consists of mostly carbohydrate-type organics. The nitrogen content is relatively low, and for composting, supplemental nitrogen would be required.

Mineral analysis was also performed on the feedstock for macro- and micronutrients for plants for composting purposes. These results are shown on a dry wt basis in Table 5. The relatively high concentration of silica is an indication of the contaminating glass, as indicated also by the high ash content of the sample. The relatively high concentration of iron, also indicative of the high ash content, probably comes mostly from rust that forms on the mild steel surfaces of the prototype process unit and separation equipment. The high aluminum contant probably comes from the aluminum components of the MSW. The calcium and alkali metals probably come from the food and yard wastes in the MSW.

Table 3
Other Analytical Test Results

Test	Conc., mg/kg
BOD	1956
COD	4,248
Oil and grese	44
Ammonia N	246
Kjeldahl N	3605
Chloride	1.0
Sulfate	0.3
Nitrate	0.05
Nitrite	<0.01
Cyanide	<0.01
Volatile organics	<0.005
Total phenols	<0.0001

Table 4
Ultimate Analysis

Element	Conc., wt%
Carbon	37.7
Hydrogen	4.7
Oxygen	28.4
Nitrogen	1.0

The compost test trials on the feedstock were conducted over a 3-mo period. The best results in terms of weight and volume reduction were obtained with a sample supplemented with liquid nitrogen fertilizer to a final C/N ratio of 12.5/1. Figure 1 shows the weight loss with time over the incubation period. The data show that the most dramatic changes occur during the last half of the test period. The results indicate about a 70% weight loss on composting. About a 50% reduction in volume of the feedstock was also observed.

For the cellulytic enzyme hydrolysis tests, the first variable to be investigated was the quantity of enzyme necessary to achieve hydrolysis in a reasonable time frame. Figure 2 shows the results of enzyme dilution on glucose production at two different concentrations of total dry biomass feedstock with 24 h of incubation. Other studies indicated that longer incubation periods did not substantially alter glucose concentration. Each data point is the average of three replicates. The data indicate that glucose yield increases with enzyme concentration at both 1 and 2% solids (dry wt) up to 0.01 wt fraction of enzyme. Although not shown, higher enzyme concentrations of 0.02 and 0.04 wt fraction actually produced lower

Table 5
Mineral Analysis

Mineral	Conc.
Phosphorus	0.1 wt%
Sulfur	0.2 wt%
Potassium	0.4 wt%
Calcium	2.1 wt%
Magnesium	0.2 wt%
Iron	4.4 wt%
Silica	5.8 wt%
Aluminum	1.2 wt%
Sodium	0.8 wt%
Titanium	0.2 wt%
Chlorine	0.2 wt%
Manganese	512 mg/kg
Zinc	178 mg/kg
Copper	36 mg/kg
Nickel	22 mg/kg
Cobalt	12 mg/kg
Molybdenum	18 mg/kg
Vanadium	18 mg/kg
Antimony	1 mg/kg
Beryllium	6 mg/kg
Selenium	< 0.005 mg/kg

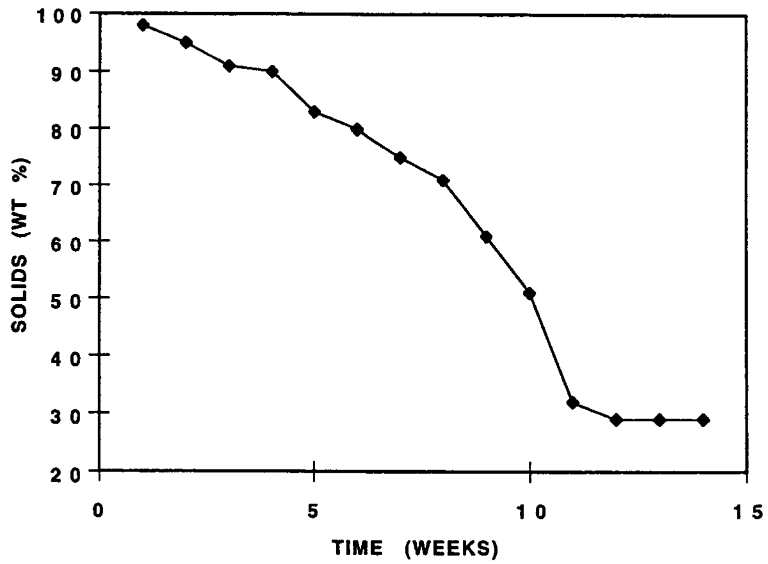

Fig. 1. Weight loss of biomass feedstock with time.

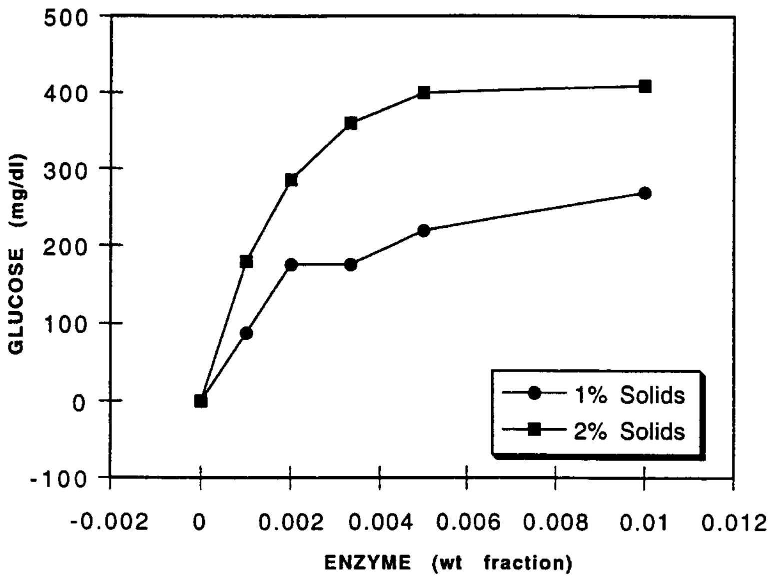

Fig. 2. Effect of enzyme concentration on cellulose hydrolysis at two different concentrations of biomass feedstock.

glucose yields. Correcting for the ash content of 29% by wt (dry), the efficiency of conversion of biomass feedstock to glucose was 38 and 28.2% for the 1 and 2% solids, respectively. Interestingly, higher biomass solids concentrations do not alter the optimum enzyme concentration results. For the subsequent experiments, 0.01 wt fraction (1% by wt) of enzyme was used.

Although substrate concentration had little effect on the optimum concentration of enzyme for hydrolysis, substrate concentration does affect the rate and total yield of glucose produced. Figure 3 shows the effect of biomass feedstock concentration on glucose yield in 24 h. Each data point is the average of three replicates. A double reciprocal plot of the data in Fig. 3 is shown in Fig. 4. The V_{max} obtained from this latter plot is 1000 mg/dL/24 h or 1% by weight glucose. The K_m obtained from the data in Fig. 4 is 3.5% by weight dry biomass, which would equate to 2.5% dry solids after correcting for the ash content. The concentration of substrate for most enzymes that produces V_{max} is usually several times the K_m value. The results shown here indicate that higher concentrations of substrate should produce higher rates of glucose production, but product inhibition by glucose interferes with such results.

As indicated above, glucose inhibits the cellulytic enzyme reaction. Figure 5 shows the effects of glucose concentration on glucose production using 1% by weight dry biomass and 24 h reaction time. The data clearly show that added glucose higher than 1% by weight exhibits an

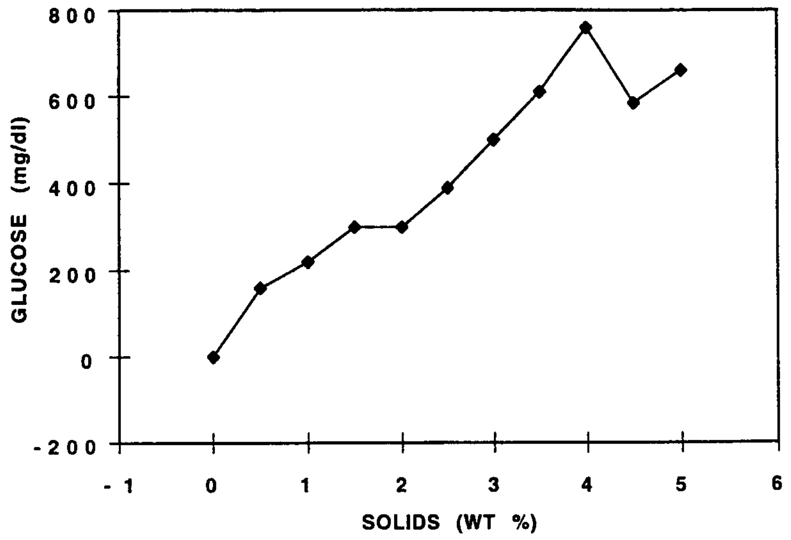

Fig. 3. Effect of substrate concentration on glucose production using biomass feedstock.

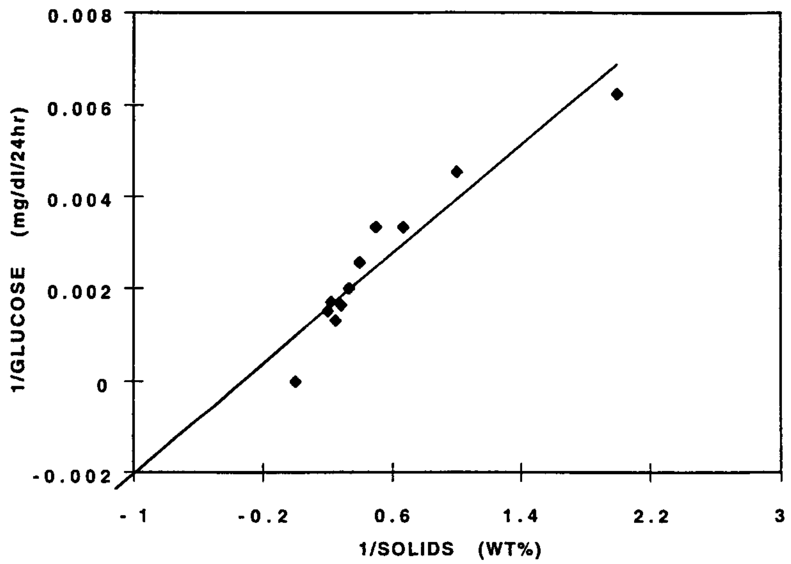

Fig. 4. Double reciprocal plot of enzyme activity vs substrate concentration.

inhibitory effect on glucose production. Total glucose concentration includes both added and produced, such that 1.5% by weight glucose is the effective concentration where the inhibition begins. Data points are the average of three replicates.

Since the pH optimum for the cellulytic enzyme activity stated in the vendor literature (*5*) was obtained using a 1-h filter paper assay, there was a possibility that the pH optimum for the enzyme with the biomass

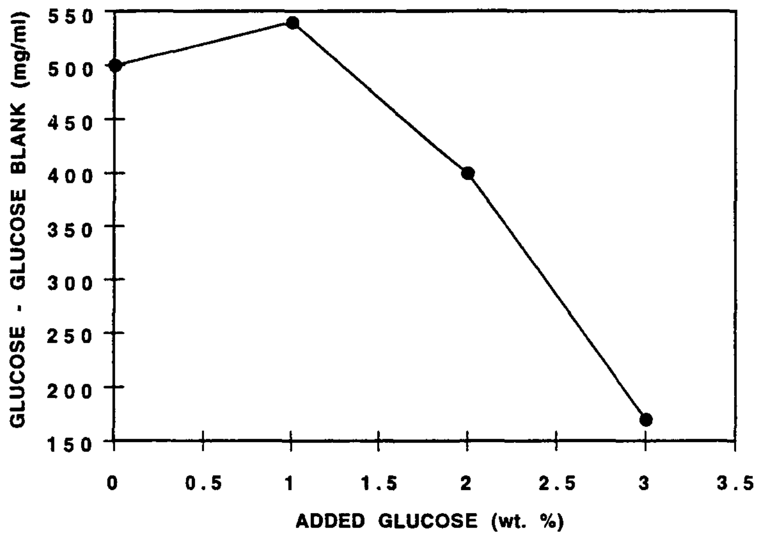

Fig. 5. Inhibitory effects of glucose on cellulose hydrolysis of biomass feedstock.

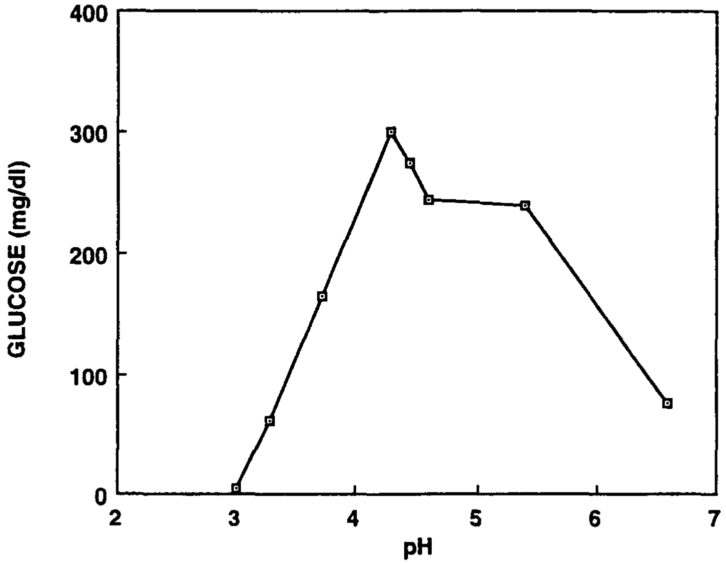

Fig. 6. Effect of pH on cellulase activity with biomass feedstock.

feedstock could be different. The relationship of glucose production in 24 h at 1% by weight dry solids and pH was determined. The results are shown in Fig. 6, which were in agreement with the pH optimum of about 4.0–5.0. Each data point is the average of three tests.

The enzyme product literature (5) specified an optimum temperature range of 40–50°C and extended enzyme stability at 45°C using a 1-h filter paper assay. Figure 7 shows the results of tests at different temperatures

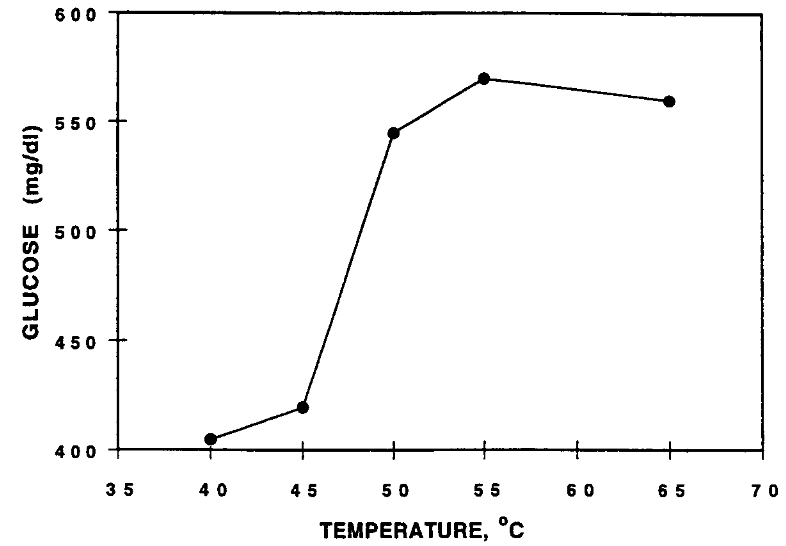

Fig. 7. Effect of temperature on cellulase activity with biomass feedstock.

using the biomass feedstock as substrate. These results differ significantly from the vendor literature. Figure 7 indicates that the optimum temperature range for feedstock hydrolysis in 24 h is 50–65°C, with maximum activity at 55°C. The glucose yield was 40% higher at 55°C than at 45°C. No studies were conducted on extended enzyme stability at the higher temperature, but the activity remained relatively stable up to 24 h.

DISCUSSION

Owing to the fact that the prototype steam classification unit is located outside, the ambient temperature plays a role in the results obtained by affecting the amount of steam condensed during processing. The sample of material for this study was produced during cold weather, and as a result, the moisture content was higher than desired at 58.7% by weight. The best results are obtained when the moisture content is <50% by weight. When the moisture content is high, the bulk density of the biomass prevents effective separation of the contaminating finely broken glass during destoning.

The biomass feedstock was chemically analyzed for potentially toxic or hazardous substances, and none were found. The material is about 70% combustible, although this particular sample has a relatively high ash content. The main inorganic substituents were silica and iron (the silica probably owing to the contaminating glass, and the iron owing to rust from the process equipment). The feedstock is readily compostable with about a 70% reduction in weight and 50% reduction in volume. For optimal composting results, the C/N ratio was adjusted by the addition of nitrogen supplement to 12.5/1. The feedstock also is partially hydrolyzed by cellulytic enzymes, with 30–50% of the solids converted to glucose in 24 h. Relatively high enzyme concentrations (1% by wt) produce the highest glucose yields. Optimum results were obtained at about 3.5% (2.5%, corrected for ash content) biomass feedstock concentration, and glucose production is inhibited at glucose concentrations above 1.5% by weight. The pH optimum was 4.0–5.0. The temperature optimum for the commercially available enzyme used in these studies with the biomass feedstock as substrate was 55°C.

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