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USE OF ANIMAL MANURE AS FEEDSTOCK FOR BIO-PRODUCTS

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ABSTRACT

Animal manure is an under utilized biomass resource that potentially can be used for producing biochemicals and biofuel. The duel purpose of this project was to characterize dairy manure as a sugar platform feedstock for biochemical and biofuel production and to describe the efficiency of acid hydrolysis processes for producing sugars from manure fiber. First, dairy manure was analyzed for dry matter distribution in different sized particles and chemical composition. Second, dilute acid hydrolysis was tested for converting manure fibers to sugars. The results indicated that (1) more than 75% of the dry matter in dairy manure consisted of particles greater than 0.125 mm, (2) protein content is significant in the dairy manure, 3) a little over 50% of the dry matter in the dairy manure was fiber, 4) the hemicellulose component in the fiber was readily converted to sugar through acid hydrolysis, and 5) the yield of glucose from cellulose in the hydrolysis process was low.

KEYWORDS. Waste characterization, Biomass, Acid hydrolysis

INTRODUCTION

The U.S. animal industry, driven by competition and environmental regulations, is undergoing a change that is featured by rapid reduction in the number of animal operations and an increase in herd size on the remaining farms. The large amount of manure generated from these concentrated animal operations has created environmental concern. Presently, the majority of manure is disposed of by direct application to croplands. However, land application alone is no longer an adequate solution for many large animal operations due to the large amount of manure produced compared with the available land base. Excess manure on farms can create potential environmental risks including surface and ground water contaminations (Sutton et al., 1986) and air pollution (Dewes et al., 1990 and Paul et al., 1993). As a result, there has been increased pressure from government agencies and the general public for the animal industry to tighten its manure management practices. The increasing requirement for pollution control from animal operations challenges the scientific community and the industry to develop new waste management strategies. The consensus among the producers, the governmental agencies, and the scientific community is that new technology or a new application of existing technology is the key to the solution of the problems.

Animal manures are a potentially large source of feedstock for producing renewable biobased chemicals and fuels. It has been estimated that a total of about 160 million dry tons of animal manure are produced annually in the United States (Council for Agricultural Science and Technology, 1995). Of this total, approximately 55 million tons (dry basis) are collected for subsequent disposal. Nearly three-fourths of the collected material is from dairy and feedlot cattle, with the remainder being primarily from swine and poultry operations. The collected manure amount represents a large potential source of biomass for producing biobased chemicals, material, and energy. Unfortunately, compared with other areas, progress in new technology development for animal waste management has been limited. Innovative, environmentally friendly processes for converting manure to renewable, biobased chemicals and materials are urgently needed. Such processes could potentially change manure from a disposal problem to an important biomass resource for chemical production.

The major resource components of manure are carbon, protein, or nutrients. The utilization of carbon involves breakdown of fiber components (cellulose, hemicellulose, lignin) into simple sugars. Once produced, sugars can be converted to other chemicals via chemical or biological processes. The fiber to sugar conversion process is typically accomplished through hydrolysis (Sun and Cheng, 2002). The objectives of this paper are to present the results of manure composition characterization and hydrolysis studies. The information will be useful for further investigations into manure as a biomass for chemical or fuel production.

MATERIALS AND METHODS

Manure Source

The dairy manure used for the experiments was obtained from the Dairy Center of Washington State University (WSU) located near Pullman, Washington. Manure produced at the WSU Dairy Center was managed by a typical flush system. The flushed manure was then separated into a solid and a liquid fraction by a stationary inclined screen separator. The liquid stream was transferred to a two-chamber settling pit. The effluent from the settling pit flowed into an anaerobic lagoon. The fresh, clean "as excreted" dairy manure (feces) samples were taken from the barn floor for the majority of the study except the solids samples taken from the stationary screen separator for amino acid determination.

Analytical methods

Analysis of total solids (TS), total volatile solids (TVS), total phosphorus, K, Ca, Mg, and Na were carried out using standard methods (APHA, 1998). Nitrogen and crude protein were determined using the AOAC method (Association of Official Analytical Chemists, 1990). Total carbon and sulfur were measured using the LECO CNS-2000. Amino acids were analyzed using HPLC. The neutral detergent fiber (NDF), acid detergent fiber (ADF), and acid detergent lignin (ADL) of the manure were analyzed using the reflux apparatus (Goering et al., 1970). NDF is usually used to estimate the total lignocellulosic materials (including cellulose, hemicellulose, and lignin), while ADF is used to estimate the content of lignin and cellulose. Hemicellulose content can be determined by the difference between them (%NDF-%ADF).

The size distribution of particles in the manure was determined by sieving the manure with a set of American Standard sieves. Manure samples were added at the top of six sieves of decreasing mesh size (2.4, 1.68, 1.19, 0.84, 0.42, and 0.125 mm, respectively). The manure sample was washed through the continuous shaking sieves. The filtrate, composed of effluent and washed water, was collected in a tray at the bottom of the sieving set.

The content of each mono-sugar in the hydrolyzed solution was determined using an ion chromatograph (IC) from Dionex. Hydrolyzed solutions were adjusted to a pH value of 5.0 to 6.0 using sodium hydroxide. Diluted hydrolyzed solutions (400x) were filtered with a 0.45 µm filter. Sugars were separated on CarboPac PA 10 Guard (4x50 mm) and Analytical (4x250 mm) Columns at room temperature (approximately 25°C). Sugars were detected using an ED 40 electrochemical detector. An AS 40 sampler was used for continuous running and Dionex PeakNet 5.1 chromatography software was used for data analysis.

Hydrolysis of the samples

The fresh dairy manure (feces) sample used for acid and combination hydrolysis was taken "as excreted". Five kilograms of manure were mixed with 5 kg of water. This mixture was blended for 1 minute on the liquefy setting for size reduction. This manure mixture was used for hydrolysis.

Moderate acid concentrations of up to 5% sulfuric acid were adopted to hydrolyze the fiber in manure under low-temperature (less than 130°C). These moderate conditions helped ensure that the quality of the resulting hydrolyzed mono-sugars was high. Five acid concentrations (from 1% to 5%) and four treatment durations (from 30 minutes to 4 hours) were studied at three different temperatures (100°C, 120°C, and 130°C). Each sample was 50 grams (16 grams of manure mixed with 34 grams of acid solution). After hydrolysis, the sample was centrifuged at 10,000 rpm for 10 minutes to separate liquid from solid. Samples were analyzed for sugar concentrations.

The objective of acid hydrolysis was to obtain as much mono-sugars such as arabinose, xylose, galactose, and glucose as possible from the manure. Three acid hydrolysis procedures were conducted to fulfill this objective, including one-stage acid hydrolysis, two-stage acid hydrolysis, and two-stage acid hydrolysis with alkaline extraction (Figure 1).

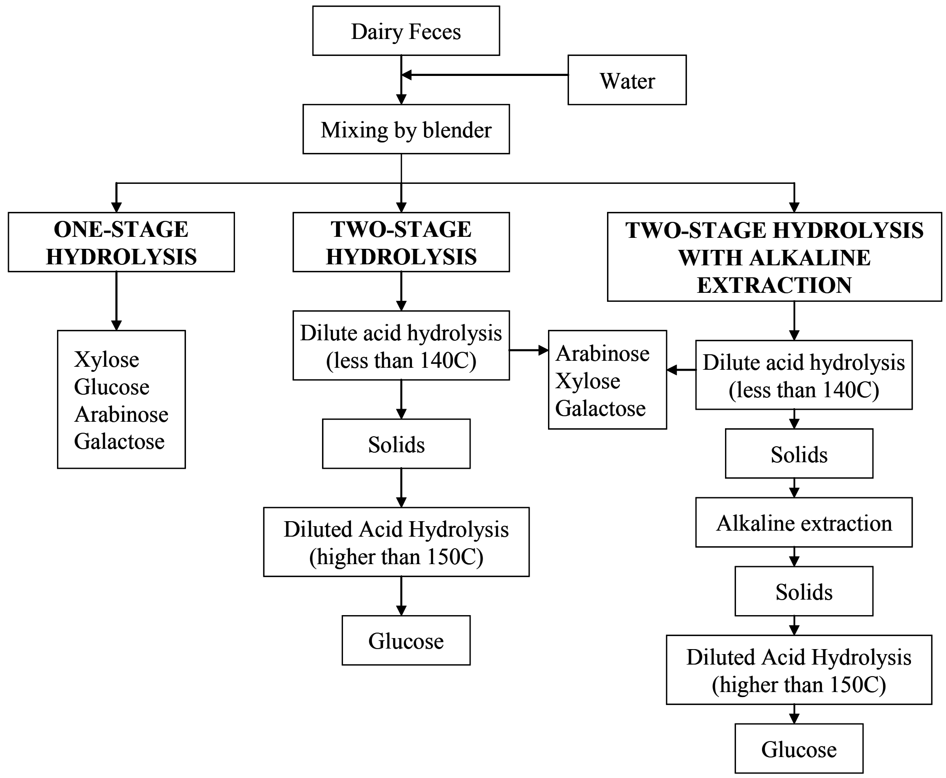

Figure 1. Procedure of acid hydrolysis of dairy manure

RESULTS AND DISCUSSIONS

<u>Basic nutrients</u>

Typical parameters used for animal waste characterization include two physical properties (total solids (TS) and moisture content (MC)) and three chemical constituents (nitrogen (N), phosphorus (P), and potassium (K)). The results of the manure characterization and related chemical compositions are shown in Table 1.

Table 1. Basic nutrient information for dairy manure characterization

Parameters	Content in dairy "as excreted" manure (%)	Elements	Content in dry manure (%)
Water	86.61	Nitrogen	2.90
Total solids	13.39	*Phosphorus*	0.48

Total volatile solids	11.21	*Potassium*	2.86
Total fixed solids	2.18	*Calcium*	2.22
		Magnesium	0.46
		Sodium	0.21
		Carbon	45.37

<u>Fiber content</u>

The information presented in Table 1 can satisfy the requirement of land application of dairy manure. However, it is not sufficient for the study of utilization of animal manures as feedstock for value-added chemical production. More detailed information on manure composition such as cellulose, hemicellulose, lignin, protein, and even amino acid content are desirable for biorefinery applications.

The contents of cellulose, hemicellulose, and lignin in manure as determined by analysis of neutral detergent fiber (NDF), acid detergent fiber (ADF), and acid detergent lignin (ADL) are given in Table 2. It is apparent that the fiber was the largest component in dairy manure, accounting for 52% of dry matter. Fiber provides the substantial resources of cellulose and hemicellulose, which can be degraded to mono-sugars and then used as feedstocks to produce value-added products.

Table 2. Fiber content in dairy manure

Parameters	Content in Dairy manure (% dry base)
Neutral detergent fiber (NDF)	52.51
Acid detergent fiber (ADF)	40.35
Acid detergent lignin (ADL)	12.96
Cellulose (=ADF-ADL),	27.39
Hemicellulose (=NDF-ADF)	12.17

<u>Protein and amino acid content</u>

In addition to fiber, protein is also an important composition of dairy manure. Crude protein content in the manure was 18.11% (dry base) while the total nitrogen in manure was measured at 2.90% (dry base). The detailed amino acid composition of manure solids (from the stationary screen separator) is shown in Table 3. The information can be used to explore the possibility of developing protein-based products from manure.

<u>Size distribution of dairy manure</u>

The results of distribution of the total solids in each particles size class are presented in Table 4. It is clear that the dairy manure was mainly composed of particles larger than 1.680mm. This fraction accounted for 52.43% of total solids. Fine particles that passed the 0.125mm sieve contributed 23.37% of the manure total solids.

The data indicate that solid/liquid separation can be an effective manure treatment method for producing carbon and nutrient-rich organic solids for multiple uses. The majority of carbon and nutrients, especially most carbohydrates and proteins within manure are associated with solids particles. Therefore, solid/liquid separation should be the first step for using manure as a feedstock.

Table 3. Amino acid composition of manure solids

Amino Acid	Concentration (% Dry base)	Amino Acid	Concentration (% Dry base)
Taurine	0.06	Hydroxyproline	0.04
Aspartic Acid	0.23	*Threonine*	0.11
Serine	0.10	*Glutamic Acid*	0.38
Proline	0.12	*Lanthionine*	0.00
Glycine	0.13	*Alanine*	0.17
Cysteine	0.07	*Valine*	0.15
Methionine	0.05	*Isoleucine*	0.21
Leucine	0.21	*Tyrosine*	0.05
Phenylalanine	0.13	*Hydroxylysine*	0.00
Histidine	0.05	*Ornithine*	0.00
Lysine	0.12	*Arginine*	0.14
Tryptophan	<0.04	*Total*	2.43

Table 4. Total solids of different portions of dairy manure after solid/liquid separation

Portion	>2.362mm	>1.680mm	>1.190mm	>0.840mm	>0.420mm	>0.125mm	Filtrate	Total
TS/g	25.51	4.15	3.90	3.14	2.99	3.66	13.22	56.57
%DM	45.10	7.33	6.89	5.55	5.29	6.47	23.37	100

Acid Hydrolysis

The optimal conditions for one-stage acid hydrolysis were temperature of 120oC, acid concentration of 3%, and reaction time of 1-hour. The highest yield for one-stage acid hydrolysis at the optimal conditions was 14% of the dry manure. The amount of each individual sugar produced is shown in Figure 2. The yield of total mono-sugars such as arabinose, galactose, and xylose from hemicellulose was 12%, which means that manure hemicellulose was almost completely broken down. However, the glucose yield of 1.67% was still low compared with the 27% of cellulose content of the dry manure. Although increasing temperature will be beneficial to increasing glucose yield, higher temperature will cause dehydration reactions to rapidly degrade the produced mono-sugars. Therefore, a multi-step acid hydrolysis is preferred to obtain and retain these mono-sugars.

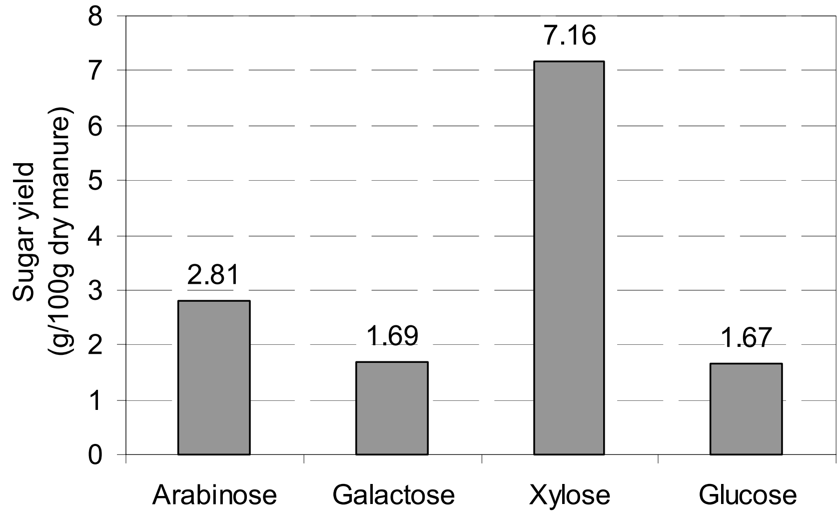

Figure 2. Individual sugar yields at the optimal condition of one-stage hydrolysis

Figure 3 illustrates glucose yield comparisons between different acid hydrolysis procedures, including one-stage hydrolysis and two-stage hydrolysis with or without alkaline extraction. The purpose of the alkaline extraction was to eliminate the effect of lignin on cellulose hydrolysis. The optimal conditions for the two-stage hydrolysis were temperature of 170oC, reaction time of 10 minutes, and acid concentration of 3%. The highest glucose yield under these conditions was 7.78% for the two-stage hydrolysis treatment without alkaline extraction and 6.70% for the hydrolysis with alkaline extraction. The reason for alkaline extraction's lower value might be that although alkaline treatment extracted lignin from the manure fiber and allowed for much easier contact between cellulose and the hydrolysis solution, the alkaline might also have oxidized the cellulose to oxycellulose, which is very difficult to be degraded by acid or other chemicals. As a result, the two-stage acid hydrolysis without alkaline treatment was the best option among these three hydrolysis procedures tested in terms of the amount of mono-sugars produced.

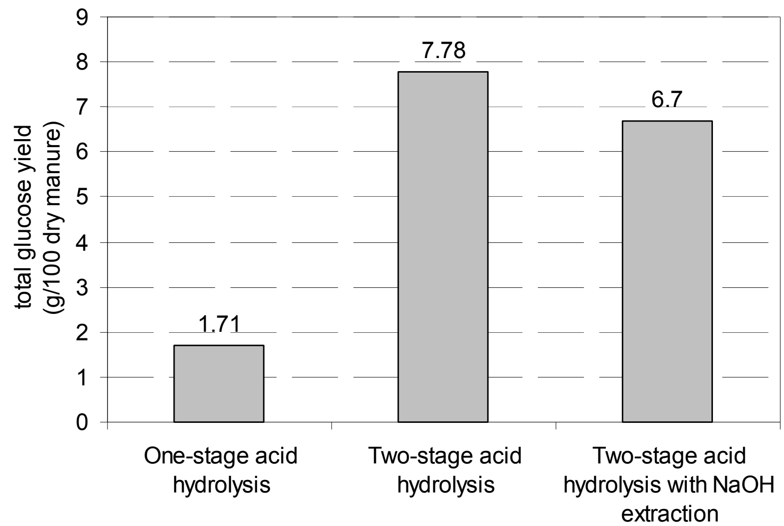

Figure 3. Comparison of total glucose yields of different hydrolysis

Compared with other lignocellulosic material such as softwood and yellow poplar sawdust (Nguyen, 1998 and Kim et al., 2001), the glucose yield of 30% from dairy manure is still lower (Figure 4). The characterization results of this study showed that the dairy manure contains close to 20% protein. The high protein content might have caused a browning reaction between protein and reducing sugars at the higher temperature used for cellulose hydrolysis. Furthermore, the cellulose content in dairy manure (27%) is lower than that in wood and other lignocellulosic material, which usually ranges above 50% (Sun and Cheng, 2002). These points suggest that the utilization of manure to produce mono-sugars is more challenging due to the complexity of the material.

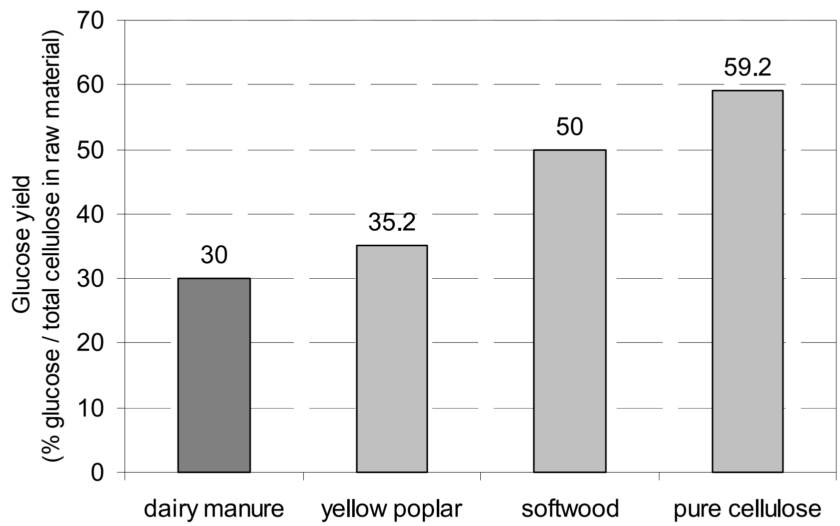

Figure 4. Comparison of glucose yields with other raw materials

CONCLUSION

The following can be concluded from this study: (1) more than 75% of the dry matter in dairy manure consisted of particles greater than 0.125 mm, (2) protein is a significant component of the dairy manure (18% of the dry mass) that may affect manure hydrolysis, 3) a little over 50% of the dry matter in the dairy manure was fiber, 4) the hemicellulose component in the fiber was readily converted to sugar through acid hydrolysis, and 5) the yield of glucose from cellulose in the hydrolysis processes was low. Further research is necessary to improve glucose yield.

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