0273-2289/05/121–124/999–1016/$30.00

Studies into Using Manure in a Biorefinery Concept

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Abstract

Animal manure is an underutilized biomass resource containing a large amount of organic carbon that is often wasted with the existing manure disposal practices. A research project funded by the US Department of Energy explored the feasibility of using manure via the sugar platform in a biorefinery, converting the carbon from fiber to biochemicals. The results showed that (1) fiber was the major component of manure dry material making up approx 50%, 40%, and 36% of the dry dairy, swine, and poultry manure material, respectively; within dairy manure, more than 56% of the dry matter was in particles larger than 1.680 mm; (2) in addition to being a carbon source, manure could provide a variety of nutrient for fungi *T. reesei* and *A. phoenicis* to produce cellulase; (3) the hemicellulose component in the manure fiber could be readily converted to sugar through acid hydrolysis; while concentrated acid decrystallization treatment was most effective in manure cellulose hydrolysis; (4) purification and separation was necessary for further chemical conversion of the manure hydrolysate to polyols through hydrogenation; and (5) the manure utilization strategy studied in this work is currently not profitable.

Index Entries: Biorefinery; manure.

Introduction

Animal manures are a potentially large source of organic carbon that is currently under utilized. An estimated 160 million dry tons of animal manure are produced annually in the United States (*1*), of which approx 55 million tons (dry basis) is collected and in need of proper disposal or treatment. Nearly three-fourths of the collected material is from dairy and feedlot cattle, with the remainder being primarily from swine and poultry

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operations. Presently, the predominant manure man/agement practice is lagoon storage followed by direct application to croplands. This practice is no longer an adequate solution for many large animal operations because excessive nutrient loading and relatively limited amount of available land creates environmental risks including surface and ground water contaminations *(2)* and air pollution (*3*,*4*). In addition, the majority of the carbon in the manure is wasted in the uncollectible form of either methane or carbon dioxide. Increasingly comprehensive requirements for pollution control from animal operations challenge the scientific community and the industry to develop new waste management strategies. Clearly, it is desirable to develop an innovative, environmentally friendly process to convert manure to renewable, more valuable biobased chemicals and materials.

As the major resource component of manure is fiber, converting fiber to biochemicals via a sugar platform provides an approach for this new level of manure utilization. This process involves hydrolysis of fiber components (cellulose and hemicellulose) into simple sugars, which can be converted to fuel ethanol or other chemicals via chemical or biological processes. However, using manure carbon as biorefinery feedstock for producing chemical bioproducts and biofuels is more technically challenging than the use of most other biomass feedstocks because manure is more heterogeneous and has been pre-processed through the animal digestive tract.

The objective of this study was to explore the possibility of using manure for value-added chemicals within a biorefinery framework. The basic concept is to produce sugar from manure, then to convert the sugars into sugar alcohols through a hydrogenation process. Sugar alcohol such as sorbitol is valued as dietetic sugar and an intermediate for manufacture of certain organic chemicals. This article summarizes findings related to this manure refinery concept, including characterization of manure, use of manure for cellulase production, hydrolysis of manure fibers, hydrogenation of manure hydrolysate, and process economics.

Materials and Methods

Manure Sources

Manure was taken from dairy, beef, swine, and poultry operations. These operations included Washington State University's Dairy, Beef, and Swine Research Centers and commercial farms. The samples were collected "fresh" as excreted and frozen at −10°C for later use.

Use of Manure for Cellulase Production

Two mutants of the celluloytic fungi *Trichoderma reesei*, RUT-C30 and QM 9414, were tested for cellulase production on dairy manure. The two mutants were maintained (at 4°C) on potato dextrose agar slants and malt extract agar slants, respectively. The spores from one slant were

suspended in 2 mL of medium (10^6–10^7 spores/mL) and were transferred into a 250-mL Erlenmeyer flask containing 50 mL of medium. The subculture medium was Mandel salt solution *(5)* supplemented with 2 mL/L Tween-80, 1 g/L peptone, and 10 g/L glucose. Fungal cells were subcultured in an orbital shaker (175 rpm) at 30°C for one or two generations with the mycelium being used for inoculum.

For cellulase production experiments, the medium composition was 6.7 g/L manure (dry basis) with 2 g/L KH_2PO_4, 2 mL/L Tween-80, and 2.0 mg/L $CoCl_2$. Both the untreated manure (as collected) and homogenized manure [mixing raw manure with water (2:1, w/w) and blending with an Osterizer® blender] were used. The manure was dispensed into 250-mL flasks containing 50 mL of medium. The medium pH was adjusted to 5.5 before being autoclaved at 121°C for 15 min. Each mutant of *T. reesei* (at 10% inoculum ratio, v/v) was inoculated into flasks. The flasks were incubated in an orbital shaker (175 rpm) at 27°C.

Manure Hydrolysis

Manure fiber (cellulose and hemicellulose) was hydrolyzed by sulfuric acid to convert the fiber into sugars. Figure 1 summarizes the procedures employed in the acid hydrolysis. As shown in the figure, freshly collected dairy manure was mixed with water (2:1 w/w) and homogenized by an Osterizer® blender. The homogenized samples were separated into solid and liquid portions by passing through an American Standard sieve (with 1.680 mm opening). The solid portion was acid-hydrolyzed by five different methods, i.e., one-stage hydrolysis with decrystallization; one-stage hydrolysis; two-stage hydrolysis; two-stage hydrolysis with alkaline extraction; and two-stage hydrolysis with decrystallization. For all the procedures, 10% (dry basis) of solid loading was used. Decrystallization was performed in a 200 mL glass mortar with continuous pestle-stirring at room temperature (approx 25°C). Any procedure involving temperatures of 100°C or higher was performed in a 300-mL Parr bomb reactor (Parr Instrument Company, IL).

Hydrogenation of Manure Hydrolysate

A hydrogenation process was employed to convert manure-derived sugars into sugar alcohol products. The hydrolysate from acid hydrolysis of dairy manure (by a two-step hydrolysis with a decrystallization procedure) was used as the feedstock solution. The hydrolysate contained around 30 g/L of total monosacchrides (determined by HPLC) including 21 g/L glucose, 6.4 g/L xylose, 2.3 g/L arabinose, and 0.4 g/L galactose.

The protein/peptide residues of the hydrolysate was determined by the Lowry method (*6*). Two purification strategies, adsorption and ion exclusion (IE), were applied prior to hydrogenation to remove the protein/peptide residues of the hydrolysate. In the adsorption methods,

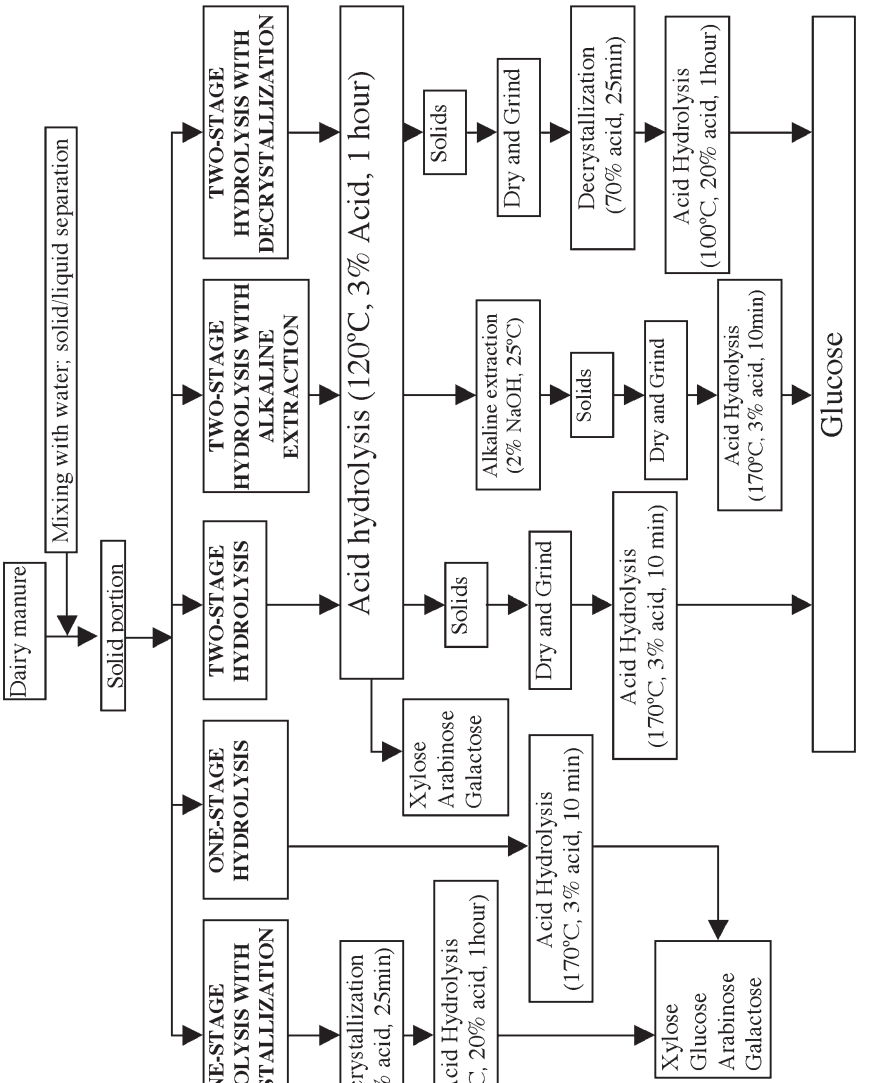

Fig. 1. Different procedures for acid hydrolysis of dairy manure.

the hydrolysate was first neutralized by NaOH, and then the resin Duolite XAD 76 was used to adsorb the peptides in the solution. In the IE methods, the resins Dowex 99H and Amberlite 120 were used. The solution passing the resin and the elution fraction (eluted by water) were each tested in the hydrogenation experiments.

Hydrogenation was performed in a 300-mL Parr bomb reactor. The feedstock solution and catalyst particles (3 wt% ruthenium metal on rutile titania) were stirred in the reactor, which was maintained at constant temperature (typically 100°C) and hydrogen overpressure (8.3 MPa). Multiple liquid samples were removed over the 6-h test period, and the products in the samples were analyzed by high-pressure liquid chromatography (HPLC). The HPLC instrument was equipped with a conventional carbohydrate column (Bio-Rad Aminex HPX- 87H, 300 × 7.8 mm) and a refractive index detector. Using this single-column method provided the necessary data on the relevant sugars and polyols; however, it did not always resolve the galactose from the xylose, nor the xylitol from the arabinitol. The column was maintained at 65°C with a 5-m*M* sulfuric acid as mobile phase (isocratic). The flow rate of the mobile phase was 0.6 mL/min. Column calibration was maintained by continual analysis of standard compounds. Detailed description of the experimental system and the analysis procedure can be found elsewhere *(7)*.

Manure Characterization and Chemical Analysis

Manure samples were characterized for their basic composition. Total solids (TS), total volatile solids (TVS), total phosphorus, K, Ca, Mg, Na, and other elements were analyzed using standard methods (*8*). Nitrogen and crude protein were determined using the AOAC method (*9*). Total carbon and sulfur were measured using an automatic combustion system (CNS-2000, LECO Cooperation, MI). The content of cellulose, hemicel-lulose, and lignin can be determined by the analysis of neutral detergent fiber (NDF), acid detergent fiber (ADF), and acid detergent lignin (ADL) values (*10*). Here, NDF is used to estimate the total amount of cellulose, hemicellulose, and lignin, while ADF is used to estimate the amount of lignin and cellulose, while lignin can be directly estimated from ADL value (*10*).

The size distribution of manure particles was tested by sequentially passing the manure (55.45 g dry weight in total) through a set of American Standard sieves (1.68, 1.19, 0.84, 0.42, and 0.125 mm openings), with continuous washing and sieve-shaking. The filtrate, composed of effluent and washed water, was collected in a tray at the bottom of the sieving set. The total solid of each portion were determined (*8*).

The activity of cellulase produced by the fungi culture was presented as filter paper unit (FPU) and determined according to standard IUPAC procedures (*11*). One unit of FPU was defined as the amount of enzymes that release 1 μmol of glucose equivalents from Whatman No. 1 filter paper in 1 min.

The monosaccharides produced in the acid hydrolysate were analyzed by a Dionex ion chromatograph (IC) equipped with an ED 40 electrochemical detector and a CarbonPac^{TM} PA 10 a guard (4 × 50 mm) and an analytical (4 × 250 mm) column (Dionex). Before IC analysis, the hydrolysate was adjusted to a pH value of 5.0–6.0, diluted to an appropriate concentration range, and filtered through a 0.45 μm filter. The details of IC opera-tion and elution procedure are the same as previously reported (*12*).

Economical Analysis

A techno-economic assessment of converting waste manures to valuable products was developed using laboratory results obtained above and standard chemical engineering plant design concept. Three flows were developed for the conversion process: (1) BASELINE: the proteins contained in the manure are extracted from the solid portion and the remaining fiber is converted to polyols via the two-stage acid hydrolysis as shown in Fig. 1; (2) SIMPLE: manure solids/fiber are hydrolyzed directly without protein extraction; and (3) DECRYSTAL: manure solids are decrystallized with concentrated sulfuric acid followed by dilute acid hydrolysis as shown in Fig. 1.

A large Excel spreadsheet was used for modeling these processes. The model began with a design basis and flowsheets, calculated specific stream data, summarized the baseline unit operations equipment list, calculated the baseline equipment costs, calculated the total capital investment, summarized the annual operating cost, and conducted a sensitivity analysis. The sensitivity analysis was performed to determine the effect of herd size, manure cost, and product values on the rate of return. The details for flowsheet cost estimation and model development are presented elsewhere (*13*).

Results and Discussion

Characterization of Animal Manure

Although the compositions of cattle, swine, and poultry manure were quite different, fiber and crude protein are always of most concern because they are the major components of animal manure that can be converted into value-added products. The fiber (including hemicellulose, cellulose, and lignin) and protein contents of different types of manure are presented in Table 1. The results show that the protein content of poultry manures was the highest among the manure types analyzed, ranging from 28% to 50% of the dry matter. Swine manures had about 22–25% of dry matter as protein, whereas protein contributed to no more than 20% of dry matter in cattle manures. In contrast, the fiber (include hemicellulose, cellulose, and lignin) content in cattle manures was the highest, accounting for more than 50% of the dry matter. Total fiber in swine and poultry manures was less than 40% of dry matter. Because of the high content of fiber and relatively low

Table 1
Fiber and Protein Contents (as % DM) in Cattle, Swine and Poultry Manure

		Crude protein	Total fiber	Hemicellulose	Cellulose	Lignin
Cattle manure	Dairy	18.1	52.6	12.2	27.4	13.0
	Beef	12.1	51.5	17.4	21.9	12.2
	Feedlot	17.0	41.7	21.4	14.2	6.1
Swine manure	Nursery	25.1	39.2	21.9	13.2	4.1
	Grower	22.7	40.8	20.5	13.9	6.4
	Finisher	22.0	39.1	20.4	13.3	5.4
Poultry manure	Chick starter	39.8	31.7	18.3	8.5	4.9
	Pullet grower	48.4	36.4	21.5	7.7	7.2
	17–40 wk	31.6	34.5	20.2	12.0	2.3
	Post-molt	28.0	31.2	16.4	10.7	4.1

concentration of protein, cattle manure is most suitable for monosaccharides production, and more detailed characterization of this type of manure is presented in the follows.

The element distributions of different types of cattle manure are presented in Table 2. For dairy manure, carbon was the most abundant, followed by nitrogen, potassium, and calcium. Other elements contained in the manure such as phosphorus, magnesium, sodium, sulfur, and trace elements comprised less than 1% of dry weight. It was also found that the element distributions for beef and feedlot manure were similar with that of dairy manure (Table 2). The contents of macro- and microelements in manure play important roles for both biological and chemical conversion of manure into value-added chemicals. For biological processes, the elements such as nitrogen, phosphorus, magnesium, calcium, and some trace elements are essential for the metabolism of microorganisms; for chemical processes, however, some elements may negatively influence of conversion yield of final products. For example, high nitrogen content will cause the Millard side reaction during the acid hydrolysis of manure fiber.

It is of interest from a raw-material-handling perspective to determine the average size of the fibers and the size distribution of manure solid particles. As presented in Table 3, the majority of the manure solid in dairy manure were in particles larger than 1.68 mm. This fraction accounted for 56.36% of total solids, while the particles larger than 0.125 mm contributing more than 75% of the total solids in the manure. These results have significant practical implications. First, the majority of the carbon can be separated relatively easily using a screen with a size of 1.68 mm. Second, such a size separation should also help to reduce the influence of protein because most fiber particles tend to have larger size than protein-enriched materials.

Table 2
Elements Content of Different Types of Cattle Manure

Elements	Manure type		
	Dairy manure (% of dry matter)	Beef manure (relative % of dairy)	Feedlot manu (relative % of dairy)
Carbon	45.37	96.6	96.0
Nitrogen	3.03	64.0	89.8
Phosphorus	0.48	87.5	168.7
Potassium	2.86	50.3	32.2
Calcium	1.20	88.3	57.5
Magnesium	0.55	54.5	61.8
Sodium	0.47	53.2	25.5
Copper	0.0030	4.8	60
Zinc	0.0320	13.1	27.2
Iron	0.0300	196.7	183.3
Sulfur	0.31	80.6	67.7
Aluminum	0.0140	121.4	150
Cadmium	BDL	N/A	N/A
Cobalt	0.000089	134.8	179.8
Chromium	0.00021	100	47.6
Manganese	0.0510	117.6	23.5
Molybdenum	0.00026	92.3	0.78
Nickel	0.00097	103.1	N/A
Lead	BDL	N/A	N/A
Vanadium	0.00047	119.1	N/A

BDL, below determination limit; N/A, not available.

Table 3
Distribution of Solid Particles in Total Dairy Manure Solid (TS) After Solid/Liquid Separation by Passing the Manure Through American Standard Sieves with Different Openings (1.68 mm, 1.19 mm, 0.84 mm, 0.42 mm, 0.125 mm)

Portion	Solid particles (g)	Solid particles (% of TS)
>1.68 mm	31.25	56.363
1.68 mm–1.19 mm	2.49	4.49
1.19 mm–0.84 mm	2.62	4.73
0.84 mm–0.42 mm	3.16	5.70
0.42 mm–0.125mm	2.71	4.88
<0.125 mm (Filtrate)	13.22	23.84

Production of Cellulase from Manure Substrate

Manure has cellulosic components that induce the production of cellulase when used as a carbon source for fungi growth. Of all the celluloytic fungi, *T. reesei* has been the most extensively studied, with the mutants *T. reesei* RUT-C30 and *T. reesei* QM 9414 identified as possessing improved

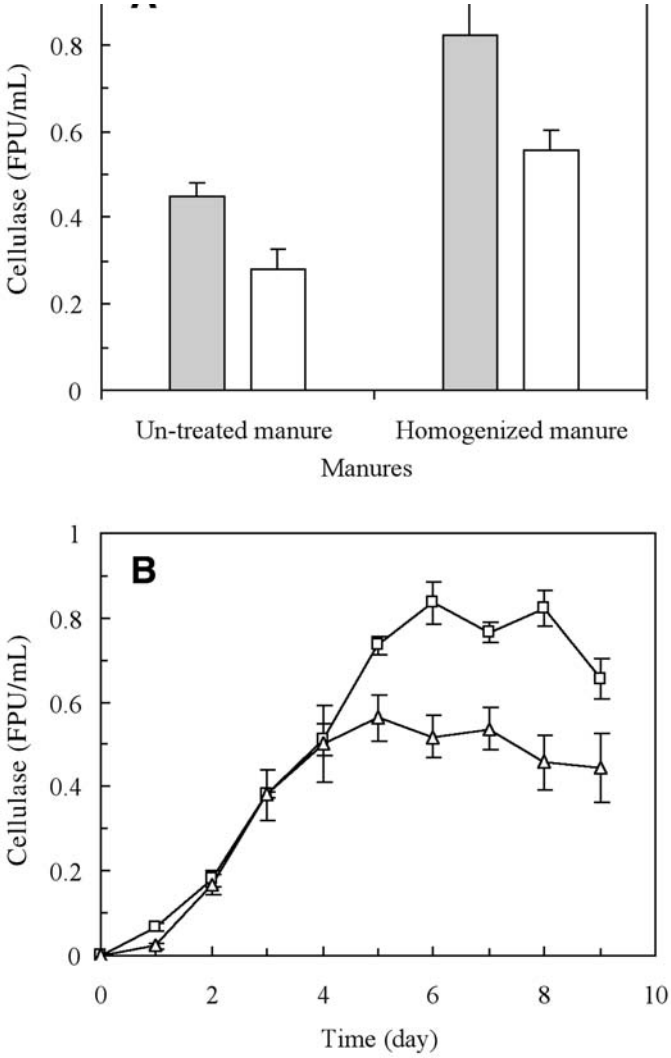

Fig. 2. Cellulase production by *T. reesei* RUT-C30 and *T. reesei* QM-9414 using dairy manures as a substrate. **(A)** cellulase production after 6 d of cultivation in medium containing untreated manure and homogenized manure (solid bars: *T. reesei* RUT-C30; open bars: *T. reesei* QM -9414). **(B)** Time course of cellulase production from homogenized manure (squares: *T. reesei* RUT-C30; triangles: *T. reesei* QM- 9414). Data are means of three fermentation replicates and error bars show standard deviation.

filter paper activity (*14*). It should be noted that the cellulase produced can be used on-site for enzymatic hydrolysis of the manure fiber or can be used for other applications with different levels of purification depending on specific requirements.

The production potential of cellulase from dairy manure was investigated by growing the fungi *T. reesei* on medium containing raw untreated manure (as collected) or homogenized manure. As shown in Fig. 2A, the

untreated manure resulted in a lower cellulase activity than the homogenized manure. This was probably caused by the different fiber sizes presented in manure. It was found that the average length of fiber size was about 10 mm in untreated manure and less than 2 mm for homogenized manure. Indeed, longer fiber reduces the specific surface area of cellulose-accessible fungi cells, which could decrease cellulase production. Based on this result, homogenized manure was further used as substrate for fungal cultures, and the time courses of cellulase production are shown in Fig. 2B. The patterns of cellulase production were similar for the two mutants, while the mutant *T. reesei* RUT-C30 produced higher cellulase activity than *T. reesei* QM-9414. The fungi *T. reesei* RUT-C30 and homogenized manure were thus the preferred combination of fungi species and substrate for cellulase production.

The cellulase titer produced by *T. reesei* RUT-C30 on 6.7 g/L manure (dry basis) resulted in a cellulase yield of 460 FPU/g cellulose. Although the cellulase yield based on added cellulose reflects the efficiency of the fungal culture, the total cellulase titer was considered more important in this work as the substrate (manure cellulose) is a nonvalue material.

These results suggested a potential approach for low-cost production of cellulase by using dairy manure. The highest cellulase production titer reached in further optimization experiments was 1.72 FPU/mL, which is higher than the cellulase activity obtained from other lignocellulosic residues such as wood, straw, wastepaper, and bagasse *(15)*. However, this cellulase level (1.72 FPU/mL) is still lower than those obtained by using pure cellulose or sugars *(15)*. The reason is probably due to the crystal structure of cellulose in manure fiber, which limits the ability of fungal cells to efficiently utilize cellulose. Therefore, pretreatment of manure fiber (for example, by acid hydrolysis) might provide an alternative for fungi cells to utilize manure cellulose more efficiently. To date, there have been no reports about using pretreated manure solids as a substrate for cellulase production. Further investigations on using this type of substrate should be performed.

Manure Hydrolysis

Impact of Nitrogen/Protein Content

Dairy manure has a nitrogen content of approx 3%, which is considerably higher than 1% of other fibrous materials such as wheat straw *(16)*. The nitrogen is in the form of indigestible forage proteins, proteins from the metabolism of rumen bacteria, and inorganic nitrogen such as urine and ammonia *(17)*. During the hydrolysis, ammonia and amino acids from hydrolyzed protein can react with sugars by Millard reaction under the high-temperature acidic conditions *(18,19)*, and ultimately can influence the final sugar yield. To reduce the negative influence of nitrogen on manure fiber hydrolysis, a washing and solid/liquid separation method was employed before applying various acid-treatment procedures.

Table 4
Fiber Composition and Nitrogen Content of Raw Dairy Manure Solid and Solid Particles Separated by an American Standard Sieve (1.68 mm Openings)

Parameters	Raw manure solid	Solid after separation
Dry matter (%)	15.50	13.26
NDF (% of DM)	48.27	67.11
ADF (% of DM)	35.80	52.23
ADL (% of DM)	13.91	16.56
Cellulose (% of DM)	21.89	35.67
Hemicellulose (% of DM)	12.47	14.88
Lignin (% of DM)	13.91	16.56
N (% of DM)	3.64	2.40
Crude protein (% of DM)	22.75	15

The fiber content of the raw manure and solid particles after liquid/solid separation was compared in Table 4. It was found that the relative proportions of cellulose, hemicellulose, and lignin increased in solid portion, while the nitrogen and corresponding crude protein content decreased. Further acid hydrolysis of the two types of solid particles shows that the yield of total reducing sugar from the solid portion after separation was higher than that from raw manure (*13*). Meanwhile, the color of hydrolysate, a direct indication of Maillard byproducts content, was significantly different. The formation of Maillard compounds from raw manure was five times more than that from manure solids after sieving treatment (*20*). Based on these results, manure solid after separated by 1.68 mm screen was used in the following acid-hydrolysis experiments.

Comparison of Different Acid-Hydrolysis Procedures

The sugar yields from the five acid-hydrolysis procedures are summarized in Fig. 3. For hydrolysis of manure hemicellulose, the first stage of the two-stage procedures had an approx 104% of sugar yield, indicating that hemicellulose was completely converted to sugars, whereas one-stage hydrolysis procedures had rather low hemicellulose-derived sugar yields. In terms of cellulose conversion, two-stage hydrolysis with decrystallization converted almost 90% cellulose into sugars, while the cellulose-sugar yield of all the other procedures was less than 35%. The monomer sugars in the hydrolysate of two-stage with decrystallization were 21 g/L glucose, 6.4 g/L xylose, 2.3 g/L arabinose, and 0.4 g/L galactose.

Because hemicellulose is easier to be hydrolyzed than cellulose, two-stage hydrolysis has been studied for separate hydrolysis of hemicellulose and cellulose fraction in wood materials (*21*). It involved dilute-acid (at lower temperature) hydrolysis of hemicellulose at lower temperature,

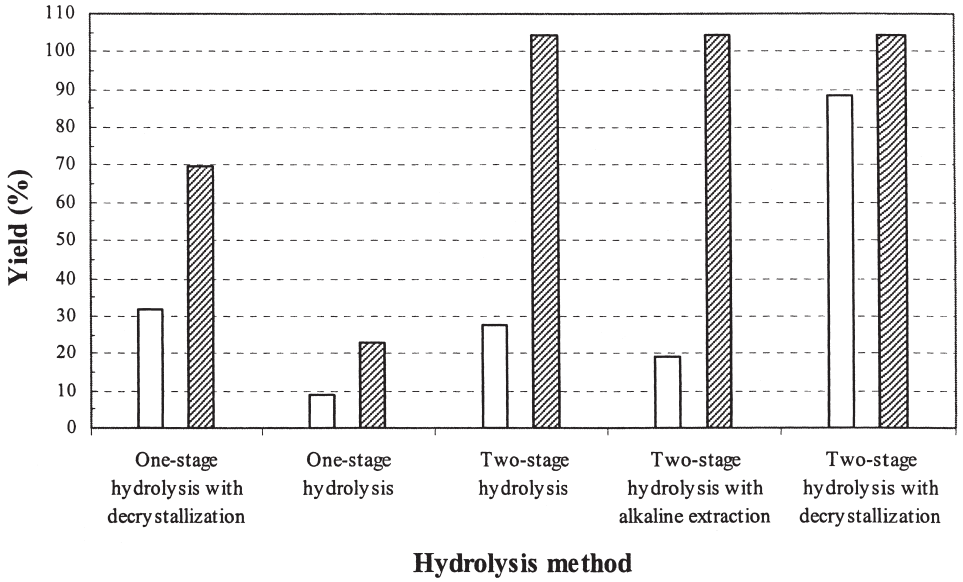

Fig. 3. Comparison of cellulose-derived sugar yield (open bars) and hemicellulose-derived sugar yield (dashed bars) with different acid hydrolysis procedures (Fig. 1). The sugar yield is calculated by total amount of sugars over the corresponding cellulose/hemicellulose amount.

follow by dilute/concentrated acid hydrolysis of cellulose (at high temperature up to 240°C) (*22*). In this work, the lower hemicellulose sugars yield in the one-stage hydrolysis might be due to the formation of sugar degradation products such as HMF, while two-stage hydrolysis avoids the degradation of sugars produced in the first step because these sugars can be effectively removed before applying more severe conditions for hydrolyzing cellulose.

The above results also suggest that the crystal structure of manure cellulose is the most difficult part to be attacked and the critical factor influencing glucose yield during acid hydrolysis. This was further verified by a microscopic observation of the structure of manure fiber before and after the decrystallization treatment (Fig. 4). Figure 4A presents the structure of manure fiber after hydrolyzed by 3% sulfuric acid at 120°C for 1 h, but before decrystllization. It was found that the striations on the fiber surface are thin, the main crystal structure was not destroyed. Decrystallization (70% sulfuric acid, 25 min, room temperature) of this material showed that the fiber turned into amorphous powders (Fig. 4B), which resulted in a high sugar yield because the crystal structure was destroyed (Fig. 3). The results suggested that dilute acid treatment could hydrolyze most of hemicellulose, while the back-bone structure of manure fiber is apparently composed of cellulose, which can only be degraded after decrystallization by concentrated acid.

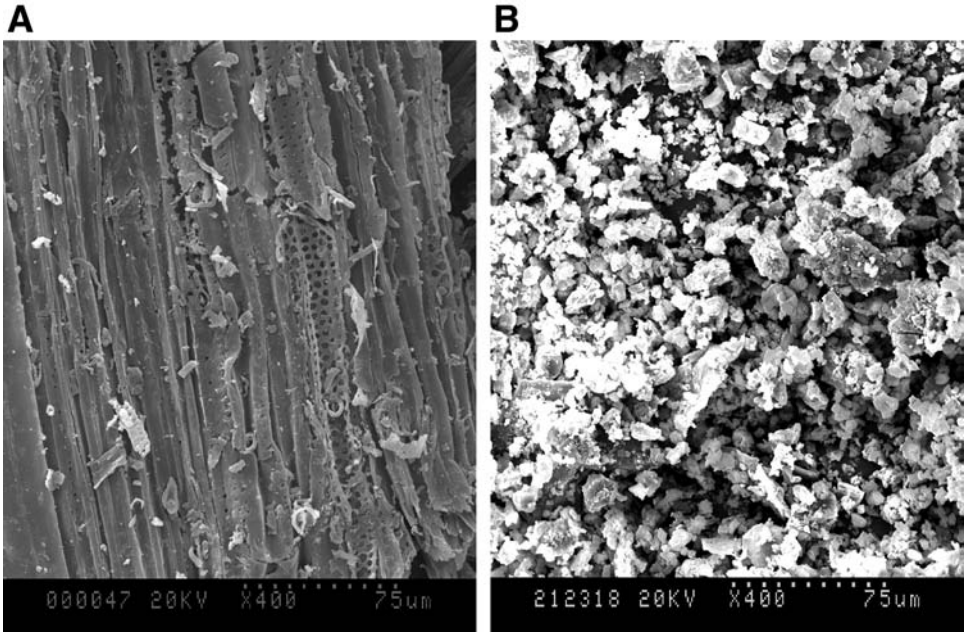

Fig. 4. Scanning electron microscope of manure fiber before and after decrystallization treatment of acid hydrolysis (400 ↔). **(A)** Solid particles (treated by 3% sulfuric acid at 120°C for 1 hour) before decrystallization; **(B)** solid particles after decrystallization.

Acid hydrolysis, particularly with sulfuric acid, is widely used to treat lignocellulosic materials to obtain sugars (*21*,*23*). This type of application commonly utilizes either concentrated acid hydrolysis at a low temperature or dilute acid hydrolysis at a high temperature (*24*). In general, concentrated-acid hydrolysis is much more effective than dilute-acid hydrolysis (*25, 26*), but causes severe environmental concerns. Another method converting lignocellulosics into sugars is enzymatic hydrolysis. Our previous study has obtained an approx 40% glucose yield from cellulose (*12*). Although the yield of enzymatic hydrolysis was not as high as acid hydrolysis with decrystallization, enzymatic hydrolysis is still a promising method for producing sugars from lignocellulosic materials, because it is performed at moderate conditions and is environmentally friendly.

Hydrogenation of Two-Stage Hydrolysates with Decrystallization

The results of hydrogenation of the raw hydrolysate and following cleanup steps are presented in Table 5 for experiments at 100°C and 1200 psig with hydrogen overpressure for a total of 6 h. The monosaccharides (glucose, galactose, xylose, and arabinose) were lumped together in the table as total product, polyols (sorbitol, dulcitol, xylitol, and arabinitol). However, as 91% of monosaccharides in the two-stage hydrolysate are

Table 5
Hydrogenation of Monosccharides With and Without Cleanup[a,b]

Feed stream	Monosaccharides (g/L)	Protein/ peptide (g/L)	Monosaccharides conversion (%)	Polyol yield (%)	Glucose conversion (%)	Glucose conversion (3 h) (%)
hydrolysate	30	9.7	62.1	75.1	31.8	17.4
adsorption	22	8.5	88.4	140	74.2	57.3
IE 1 passing	21	7.9	84.0	99.5	65.5	40.0
IE1 elution	6.4	2.4	91.2	105	80.8	70.4
IE 2 passing	34	11	85.0	91.2	79.4	60.9
IE 2 elution	7.4	2.4	93.8	95.7	90.1	86.6

[a]Unless specified, the yield and conversion are obtained at 6 h. Polyol yield is a percentage based on the monosaccharides in the feedstock.
[b]IE 1 = ion exclusion with Dowex 99H; IE 2 = ion exclusion with Amberlite 120.

Table 6
Economical Analysis of Three Processes of Converting Dairy Manure into Value-Added Products[a]

Flows/processes	BASELINE	SIMPLE	DECRYSTAL
Products	Proteins and polyols	Polyols	Polyols
Capital cost	$8.85 M	$4.50 M	$8.2 M
Annual operating cost	$2.66 M	$2.0 M	$2.9 M
Value of product(s)	$1.13 M	$0.79 M	$1.2 M
Annual return on investment	−17%	−26%	−21%

[a]The analysis is based on a 2000-cow dairy farm.

glucose and xylose (see *Manure Hydrolysis* section), the major polyols produced were sorbitol and xylitol. Thus the xylitol yield is approximately the difference between monosaccharides conversion and glucose conversion (Table 5), while the sorbitol yield can be estimated by subtracting xylitol yield from polyols yield (Table 5).

It should be noted that the yield of polyols is based on the amount of monosaccharides in the feedstock and is greater than 100% in some cases, apparently because additional monomer sugars were generated from residual oligomers in the hydrolysate and then hydrogenated to polyols. The adsorption-treated hydrolysate exhibited greatly improved hydrogenation, although the hydrogenation was still significantly inhibited compared to reagent glucose and xylose (*7*). The IE process produced a similarly improved product for catalytic hydrogenation. The Amberlite resin gave somewhat better results with less loss of sugar onto the adsorption column. There was little difference between the passing hydrolysate and the elute fraction, except that the elute was more dilute and as a result was hydrogenated more quickly. The results suggest that acid hydrolysis within manure's complex composition resulted in inhibition of the hydrogenation process and therefore requires sugar purification prior to the conversion of the sugars to the sugar alcohols.

Economic Analysis

The economical analysis of the three flows developed for converting dairy manure into value-added products are summarized in Table 6. In all three processes, the total capital investments ranged from $4.5 M to $8.85 M. Annual operating costs varied only slightly, from $2.0 M to $2.9 M, with costs primarily from labor and plant overheads. The value of the products varied and depended on the conversion and separations efficiencies. Such a value does not include the purification cost. It is clear that for a 2000 cow dairy farm, the proposed concept of converting manure into value-added products is currently not economical.

The sensitivity analysis showed that farm size significantly influenced annual return on investment (ROI). Taking the DECRYSTAL process

as an example, increasing the herd size to 3000 animals raised the ROI from −21% to −13%. Breakeven occurs at just over 5000 animals. Varying the cost of manure by ± $10/ton changed the ROI only a few percent either way. Product value had a marginal effect on profitability. Each 10% increase in product value produces around 1% improvement in ROI (*13*).

The unprofitability of the proposed manure utilization processes may be due to (1) poor conversion of manure solids to glucose, (2) complicated separation processes, and (3) high labor costs relative to products produced. If manure conversion is to be profitable using the proposed approach, large collections of manure must be available for processing at low cost. Otherwise, specific high-value products must be identified or an artificially high negative cost (tipping fee) must be placed on the manure, or both.

Conclusions

The results presented in this work showed that fiber accounted for more than 50% (dry basis) of cattle manures, while poultry manures contained the highest protein content (more than 33%, dry basis). Among the different types of manure, dairy manure is the most suitable for fiber utilization because of its high fiber and low protein content. The majority (> 50%) of the dairy manure solids are particles (assumed to be fiber) larger than 1.68 mm. Acid hydrolysis with decrystallization proved an effective procedure for converting manure fiber into sugars. Once sugars are produced, they can be converted into more valuable sugar alcohols by hydrogenation reaction. In addition to sugar production, dairy manure was a suitable substrate for cellulase production by the fungi *T. reesei*, which may provide a low-cost approach for cellulase production. Although the concept of a manure biorefinery for value-added products provides a potential alternative to traditional animal manure management practices, the process developed in this work is currently still not economical. We believe that the feasibility will improve if farm size (animal number) increases and manure liability increases.

Acknowledgment

This work was funded by the U.S. Department of Energy (Grant #DE-FC36-01GO11048).

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