Application of the MixAlco Process to In-Situ Conversion of Dairy Manure and Chipped Yard Waste For Production of Fuels and Chemicals

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Extended Abstact

The MixAlco process converts biomass into organic chemicals and alcohols via lime pretreatment; non-sterile, acidogenic digestion; product concentration; thermal conversion and hydrogenation. Because they have low capital costs and relatively simple operation, it is proposed that the pretreatment and fermentation steps of the process may be suitable to be carried out on location at confined animal feeding operations or municipal landfills. This project investigates converting dairy manure and chipped yard waste into carboxylic acids using a counter-current fermentation system and a solid state percolation system, respectively.

The counter-current pretreatment and digestion system converting dairy manure was constructed on a dairy farm in Central Texas and operated for several months to determine the effectiveness of on-site conversion. The system consisted of five plastic barrels that served as both pretreatment and fermentation reactors. The setup was configured with a series of pumps to transport liquids from barrel to barrel enabling the counter-current fermentation system. Sample product concentration results are presented.

The application of a percolation system for in-situ solid state conversion of particulate biomass is being investigated using chipped yard waste as a model substrate. This study presents the equipment design for a percolation column capable of performing oxidative lime pretreatment and acidogenic fermentation. Initial performance results for the apparatus are presented.

1 Introduction

Since the industrial revolution, America has relied heavily on fossil fuels to sustain its economic growth and prosperity. In 2004, petroleum accounted for over 40% of America's total energy demands in 2004 and more than 99% of the fuel used in cars and trucks (EIA Annual Energy Outlook 2004). Since the United States oil production peak in 1970, the United States has steadily increased its dependency on foreign oil. In 2003, approximately 62% of the 20 million barrels of oil consumed by the United States each day was imported from abroad. By 2020, the Department of Energy projects that international countries will be supplying up to 2/3 of the United States oil demands (EIA Annual Energy Outlook 2004). Although the United States has been diversifying its oil import sources for a long time, the fact remains that current sources have limited productive and export capacities and cannot satisfy the United States growing oil needs in the long term (Salameh 2003).

America's heavy reliance on fossil fuels has caused significant damage to air quality, degraded environments and has jeopardized our nation's energy and economic security (Li 2004, U.S. Department of Energy 2004). In our current situation, the United States has little control over oil supply disruptions and oil price fluctuations. In order to decrease the United States dependency on foreign oil, alternative forms of energy need to be developed. The most likely resource that can be used to meet our transportation energy requirements is biomass. Biomass energy generates far less air emissions than fossil fuels (especially net CO_2 emissions), reduces the amount of waste sent to landfills and decreases our reliance on foreign oil (Demirbas 2001).

In 2003, biomass was the leading American source of renewable energy for the fourth year in a row, providing 2.9 Quadrillion Btu of energy in the United States (DOE 2004). Biomass includes plant matter such as trees, grasses, agricultural crops or other biological material. It can be used as a solid fuel, or converted into liquid or gaseous forms, for the production of electric power, heat, chemicals, or fuels.

Worldwide, the majority of biomass energy is produced from wood (64%), followed by MSW (24%), agricultural waste (5%) and landfill gases (5%). The United Nations Conference on Environment and Development (1996) stated that biomass could potentially supply about half of the world's present energy demands by the year 2050 (Demirbas 2001). The Department of Energy believes that the United States could produce enough biomass fuel by 2010 to supply up to 10 percent of our transportation fuels, and as much as 50 percent by 2030 (NREL 2002). Converting biomass into biofuels can be environmentally friendly by reducing toxic air emissions, greenhouse gas buildup, and dependence on imported oil, while supporting agriculture and rural economies (DOE 2004).

A potential biomass substrate that can be used to fuel our nation's energy requirements while reducing an environmental complication is dairy manure. Dairy manure offers two noteworthy advantages over conventional biomass substrates. First, it is often relatively concentrated in its geographic availability. Because confined animal feeding operations (CAFOs) import cattle feed from distant sources, much of the transportation cost of using biomass has been paid for by the dairy business. CAFOs in Erath County, central Texas, produce as much as 1.8 million tons of dairy animal waste each year, with each 1000 cow dairy farm producing 20,580 lbs of dry manure and about 142,800 lbs of wet manure daily (Sweeten 1991, Brazos River Authority, 1993). This excess amount of animal manure in Erath County is capable of providing an estimated 25 million gallons of fuel each year.

The second factor is that the environmental consequences associated with dairy manure have caused significant impairments to ground and surface water worldwide. Indeed, it is the aforementioned concentration of biomass into a small region that renders CAFO operations an environmental liability. In Central Texas, the excess manure has adversely affected 190 miles of the North Bosque Watershed and 25 flood prevention structures throughout Central Texas (US Department of Agriculture Soil Conservation Service 1992). The elevated nutrients released from dairy farms contribute to excessive algae growth in rivers that can deplete a water body of needed oxygen, potentially causing fish kills and creating taste and odor problems in drinking water (TCEQ 2003). The limiting nutrient from agricultural products that is known to contribute to accelerated eutrophication of waterways is phosphorus (Sims et al., 1998; Toor et al., 2003).

Traditionally, anaerobic digestion has been one of the most widely used processes for treating organic wastes, such as dairy manure, for biogas production as an alternative energy source. Anaerobic digestion is a biodegradation process that uses a community of bacteria to form a stable, self-regulating fermentation that converts a large portion of organic solids into biogas (Sterling et al. 2001, Dugba and Zhang 1999). The biogas contains a mixture of methane and carbon dioxide that can be used as an energy source if captured properly. In addition, anaerobic digestion of manure has the capability of reducing odors, mineralizing nutrients, inactivating weed seeds and lowering pathogen levels (Wilkie et al. 2004).

The applicability of anaerobic digestion systems for the treatment of cattle wastes have been studied for many years. Much research has been applied to anaerobic digestion of dairy manure operated at different temperatures ranging from psychrophilic (< 25 C), mesophilic (25-40 C) and thermophilic (>45 C) to evaluate biogas production (El-Mashad et al. 2005). While methane is a clean and valuable fuel, it is not well suited to powering transportation and thus does little to ease domestic reliance on liquid petroleum.

A long standing and widely researched method for converting biomass into liquid fuels has been to convert biomass fiber into ethanol. Various methods have been proposed to accomplish this conversion in an economic fashion, and most employ a series of four processing steps: first a thermochemical pretreatment, second the production of cellulolytic enzymes, third a hydrolysis, and fourth a fermentation. Because a pure fermentation product (ethanol) is desired, the biologically mediated process steps must be carried out in a sterile environment. This need to handle a large quantity of dilute process medium (ethanol concentrations of 5% are common) under sterile conditions leads to high construction and operating costs. The use of genetically modified organisms also increases the need for a high level of quality control over a large volume process. Because of these limitations, conversion of manure to ethanol through fermentation is unlikely to succees.

A promising waste recycling technology that can convert agricultural wastes such as dairy manure into liquid mixed alcohol fuels (and chemical feedstocks) is the MixAlco process developed by Dr. Mark Holtzapple at Texas A&M University. The process uses alkaline pretreatment at low to moderate temperatures and fermentation in a non-sterile, acidogenic digester. The acid products produced during fermentation are concentrated to carboxylate salts which can be dried, thermally converted to ketones and hydrogenated to alcohols (Holtzapple et al. 1999). The MixAlco process may be economical as an effective waste treatment process because its use of a non-sterile culture greatly reduced the costs associated with hydrolysis and fermentation. In addition, because the pretreatment conditions are mild and long retention times in the fermentor do not increase risk of contamination, Mixalco conversion offers possibilities of unit operation configuration not possible with more conventional ethanol conversion. For example, pretreatment and fermentation can be carried out in the same reaction vessel, since there is no need to design for extreme operating conditions or sterility. This reduces the need to transport solids through the process, which is particularly problematic when sterile operating conditions need to be maintained. Another example is solid state conversion. Part of this study seeks to demonstrate the ability to convert solid particulate biomass to liquid products through a percolation process. Using percolation to contact liquid and solids in a none sterile system eliminates the need for reactor vessels and mixing systems, enabling very inexpensive operating and construction costs.

This project seeks to demonstrate the application of Mixalco conversion to address two waste handling problems in Central Texas.

1) Dairy manure wastes, already described above. The general process configuration for this conversion is illustrated in figure 1. Because lime pretreatment and mixed acid digestions are relatively simple to operate and monitor, these conversions could potentially be carried out on site at the CAFO generating the waste. Coupled with a concentrating step, this would greatly reduce the need to transport bulky biomass feedstock to a central facility. Once concentrated on site, the salt brine product could be transported, possibly by a dedicated pipeline, to a central processing facility where the product conversions and separations could be carried out on a larger, regional scale.

In acidogenic digestion, higher product concentrations and conversion rates are achievable by employing a continuous countercurrent fermentation process in which solids and liquids pass in opposite directions (Figure 2). Fresh biomass is added to the fermentator containing the highest carboyxlic concentration, while fresh water is added to the fermentator with the most highly digested biomass.

2) Yard wastes: the City of Waco landfill accepts 6,000 tons of yard wastes per year. Recycling yard waste as compost or mulch has saturated local markets. Already chipped, collected and stored at the landfill, the yard waste represents a clean biomass feedstock. As in the case of the dairy process, conversion of landfill yard waste could bepartially carried out on site, reducing transport costs, and then the concentrated brine product shipped to a larger, central facility. A synergy achieved in locating the first conversion steps at a landfill may allow use of poor quality landfill gas as fuel in the evaporation stage of the process. Currently, there is no local market for the landfill gas produced, trapped (and flared) at the Waco city landfill. Solid-state MixAlco processing could be performed at the landfill site by piling solid biomass on top of a lined drainage field and creating a continuous percolation regime for both pretreatment and fermentation operations. This concept is illustrated in figure 3.

Figure 1. General conception of Mixalco conversion of CAFO-derived dairy maure. Initial conversion of the manure to a concentrated brine would be carried on site, with further processing and product separation carried out at a central facility.

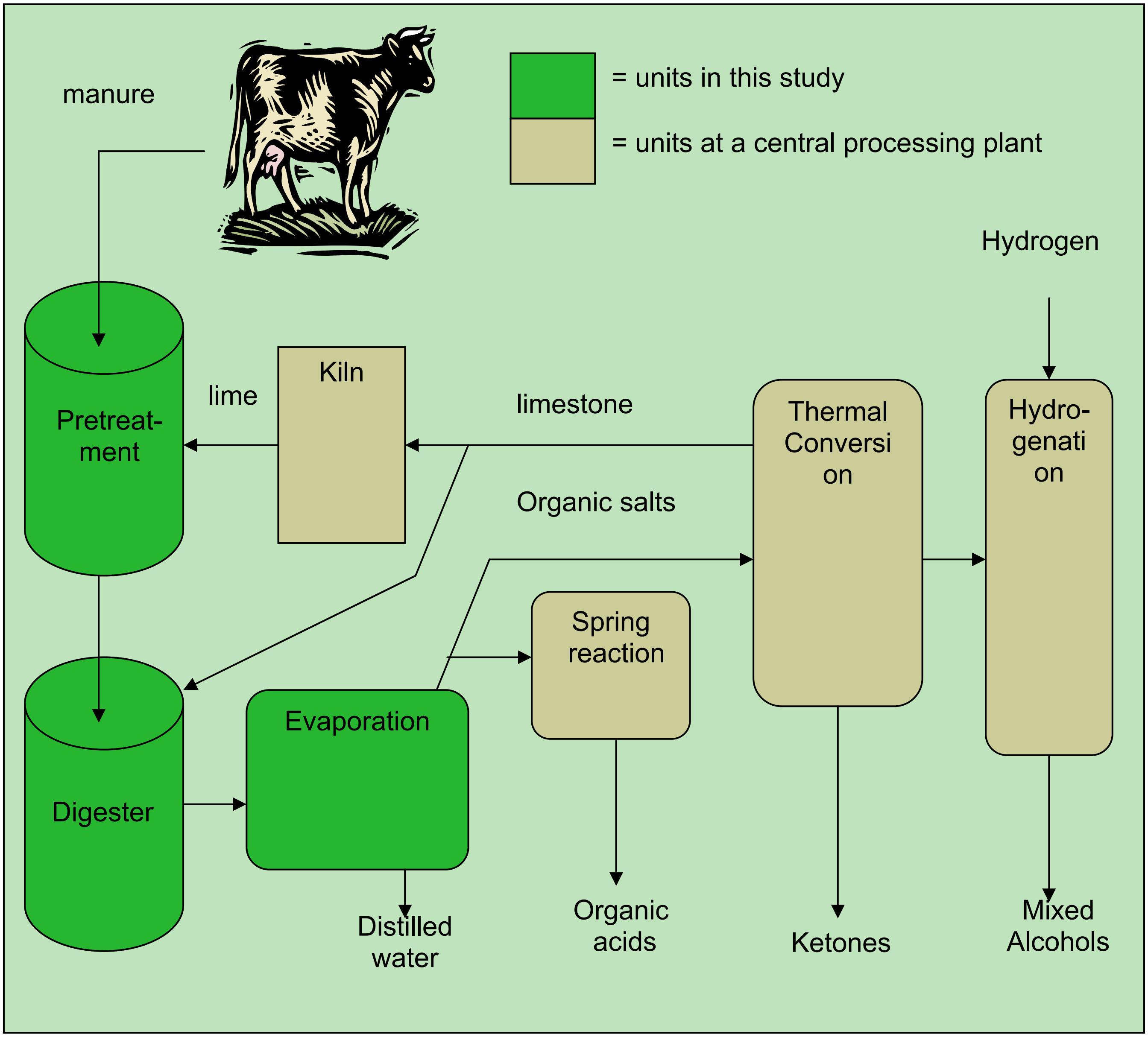
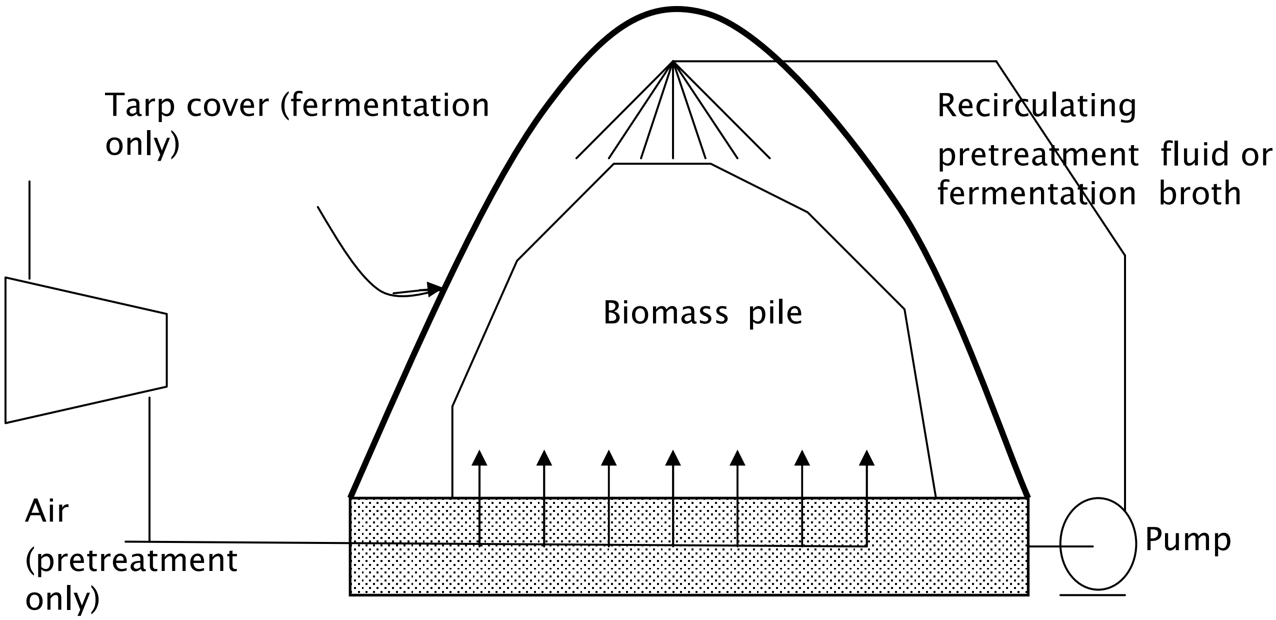


Figure 3. Conceptual representation of solid state, percolation conversion of biomass. Recirculation of liquid trhough the pile of biomass is applied to both pretreatment and digestion. During pretreatment, air is blown in from the bottom of the pile. During digestion, the air is turned off and anaerobic conditions (and odor control) are maintained by covering the pile with an impermeable tarp.



Materials and Methods

Substrates

Dairy manure was collected from a holding lagoon located on Mr. Ed Jackson's farm in Waco, Texas and placed into a 55-galloon drum that contained 45-gallons of well-water. A Zoeller N267 septic sewage pump was submersed in the drum to circulate the manure with the well-water to obtain a dry weight concentration of 10%. The manure was transferred to individual digesters by connecting a 1" PVC pipe to the sewage pump and then attaching flexible tubing from the PVC pipe to an inlet on the digester.

To obtain a 10% dry weight concentration, 5 samples were extracted from the substrate and dried in an oven at 60° C for 48 hours to determine the amount of solid weight present.

Chipped yard waste was acquired from the City of Waco Landfill. Derivation of the yardwaste was likely a mixture of southern hardwoods. Particle size ranged from very small to 1cm as smallest dimension.

Start-Up and counter-current operation at the dairy farm operation

Located on site at a dairy farm, five 55-gallon plastic drums were configured into a reactor system that contained 1 pre-treatment and 3 fermentation vessels, with one drum in reserve. The digesters were fitted with 1" PVC piping and a septic sewage pump so that the supernatant liquids could be pumped to the allocated digester to develop the continuous countercurrent fermentation process. Figure 4 shows a schematic representation of the filling, pretreatment, fermentation, and emptying sequence that was performed to develop the counter-current configuration. Through the entire sequence, only the supernatant liquid was pumped from one vessel to the next, settled solids were allowed to remain in the same barrel for the duration of the pretreatment and fermentation steps.

Temperature control at the dairy farm operation

A temperature controlled water circulation system was designed to regulate the temperature during the two stages The temperature controlled water circulation system was designed with a domestic 44 gallon hot water heater fitted with ¾ inch PVC piping (Figure 5). The temperature was set to obtain a uniform temperature of 40˚C inside the digesters. The hot water from the heater circulated the barrels through ½ inch tubing wrapped along the exterior of the barrels. The barrels were then wrapped with a hot water heater blanket to retain additional heat. Control valves were placed before and after each barrel to regulate water flow through the tubing. The water then entered an elevated 55-gallon plastic drum reserve where it was re-circulated into the hot water heater using a Grundfos UP15-42SU water circulation pump. The pump was located approximately 3 feet below the top of the elevated reserve barrel and sustained a flow rate of 13.5 gallons per minute. A check valve was installed between the hot water heater and the circulation pump in case of power failure to the circulation pump.

Lime Pre-Treatment at the dairy farm operation

Lime pre-treatment was used to enhance digestibility of the manure. Before lime pre-treatment, the percentages of solids were identified by drying the manure. To determine the dry weight, five samples were extracted from the digester and dried in an oven at 60 ˚C for 48 hours. The amount of calcium hydroxide (bought at a local feed store) added to the manure was set to either ten or five percent lime by weight of solid manure present (Holtzapple et al., 1999). The manure was vigorously mixed in the lime solution at 40°C for 128 hours using a Neptune (Manufacturer # B-1.0) ¼ horsepower open drum mixer. The mixers were elevated on a saw horse that was located approximately one foot above the barrel and connected to a repeat cycle timer by Omron (Manufacturer # H3CR-F8-300AC100240). The timer was set to be ON for 2 minutes and then remain dormant for 5 minutes to ensure sufficient mixing of the manure slurry. In some experiments, ambient air was purged into the pretreatment reactor to aid oxidation of the fiber content.

pH and temperature measurement at the dairy farm operation

To monitor the pH and temperature, an Omega OM-CP-PH101 pH and temperature logger was connected to an 18" ¼ diameter RTD probe (Manufacturer # PR-10-2-100-1/4-6-E) and a standard general purpose pH probe (Manufacturer # PHE-4201). The RTD probe was placed 12 inches into the barrel so that the wires would not be exposed to any water vapor. The pH probes were submersed in the slurry and calibrated with a pH buffer solution of 7 every three weeks to ensure accuracy.

Fermentation at the dairy farm operation

After pretreatment, approximately 1 L of sulfuric acid (H2SO4) that was diluted to 30% solution by volume of distilled water was added to the effluent to lower the pH to 7.5. A 100 mL solution containing 6.97 mL of bromoform to 1 L of ethanol was then added to the digester to inhibit methanogens. Finally, the digester culture was enhanced with a small amount of organic marine sediment (approximately 5% of dry weight volume) obtained from a salt marsh near Corpus Christi, TX. The contents were then allowed to settle and the submersible sewage pump transferred the liquid from one digester to the next. Figure 4 shows the pattern used to transfer the liquids from the solids. In order to transfer the liquids, the submersible sewage pump was elevated and connected to 1" PVC piping using adjustable tubing. The PVC piping (Figure 5) was fitted with ball valves to aid in distributing the liquids to the reserve barrel. The freshly pretreated liquid was always moved to the digester with the next to oldest solid. Also, during the countercurrent fermentation process, the pH was monitored hourly and adjusted when necessary with calcium carbonate, to maintain a pH of 6.5 to 7.

Percolation column design:
A percolation column apparatus has been assembled to simulate solid state conversion in a pile of biomass. The apparatus consists of a cylindrical column 6ft in length and 1ft in diameter, made of clear, cast plexiglass. It is supported on a bed of gravel and sand inside a 100 gallon rectangular bath and is stabilized with a super structure built of PVC pipe. System plumbing is also constructed of PVC pipe. Percolate from the column is collected in the bath and is recirculated through a heating coil and back up the column. A separate temperature-controlled circulating bath heats the column with both an external coil and the percolate recirculation. A compressor and air sparging system are also installed for oxidative pretreatment operation. The whole system is mounted on a mobile platform. Figure 6 illustrates the main components of the system.

Analytical Methods

Liquids from each fermentator were collected and analyzed for carboxylic acids. The acid concentrations were determined using a Shimadzu 2010 gas chromatograph with a capillary column (Restek Rtx-1). The liquid samples were combined with a 1.162 g/L of internal standard (4-methyl-n-valeric acid) and acidified with 3M phosphoric acid before injection into the gas chromatograph. A volatile acid standard mix from Matreya, Inc. was used as an acid standard before analyzing the acid concentrations.

Methane Inhibitor

Bromoform ($CHBr_3$) was added to the acidogenic fermentations in order to inhibit the formation of methane. Additions were made at the beginning of a fermentation, and at intermediate points during the experiment. The bromoform consisted of 20 g of the inhibitor (Sigma # XYZ) per every L of ethanol. The solution was stored in a tinted bottle, and after each use, the cap was replaced due to light and air sensitivity

Experimental Design:

The 4-stage pretreatment and anaerobic fermentation system was operated for several months. The system had three digesters operating for a three week residence time to employ the countercurrent fermentation system. The remaining two digesters were used as pretreatment containers and holding barrels to aid in implementing the countercurrent fermentation system.

Once the countercurrent fermentation system was established in all three of the digesters, the system removed the oldest solids and liquids from each digester as a finished product.

RESULTS

Dairy Farm operation

The pretreatment and digestion experiment was carried out over five months on site at the dairy farm. Logged values of pH and temperature showed relatively stable conditions for pH but somewhat variable temperature control, which was apparently affected by the ambient temperature. Measured acid concentration in the reactors was seen to produce a reproducible saw tooth pattern, as the digesters cycled through their three week residence time. (see figure 7)

Concentration of acids approached 10g/L, which appears to represent a relatively low conversion to product, given that the initial volatile solids were typically on the order of at least 50 g/L. The initial manure fed to the system was on the order of 10og/L dry weight, but the mineral content of the manure was quite high, sometimes as measuring as much as 50%. Smaller scale laboratory experiments were carried out in parallel with the on-site experiments and conversion results were found to be similar in both the field and laboratory settings.

Percolation system.

Construction of the percolation system is complete. Testing of the temperature control and hydraulic performance have demonstrated that the system can attain 60ºC and liquid flows of up to 6 gallons per minute.

In preliminary operation of the percolation column, dissolved solids accumulated over time in the liquid percolate. Both lime pretreatment and biological conversion cause the bed to collapse over time, confirming that conversion is taking place, despite the relatively large particle sizes employed in the system.

Conclusions

It appears that conversion of dairy manure by acidogenic digestion is relatively easy to implement and operate, with relatively low costs for equipment and energy input. Yields of organic acids from digestion of cattle manure is relatively low, though many aspects of the process have not yet been optimized. Important variables to consider include carbon to nitrogen ratio, which is low in dairy manure (i.e the system would benefit from increased fiber loads) and reaction time, since the accumulation rate for the acids was apparently still increasing at the end of the three week residence time.

Conversion of chipped yard wastes appears feasible, though quantified productivity data are not yet available.

Figure 4: Filling, moving and emptying sequence that allowed for countercurrent conversion without moving solids from one vessel to another. Each row of vessels illustrates one time step in the process. Solids remain in their original vessel through the entire cycle, being sequntially contacted with increasingly “new” liquid product streams.

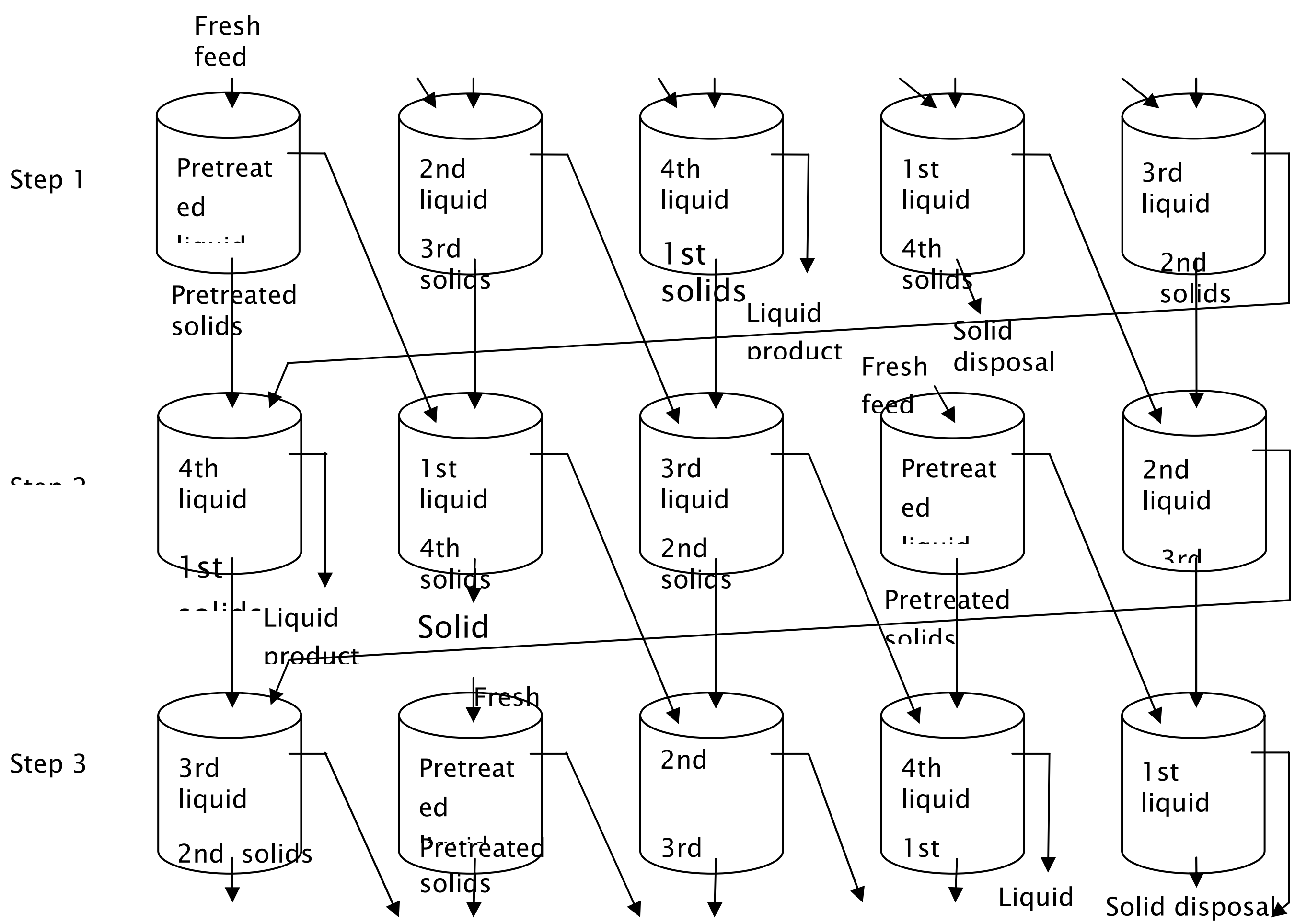


Figure 6: Percolation column apparatus for the simulation of solid state percolation conversion of a pile of biomass.

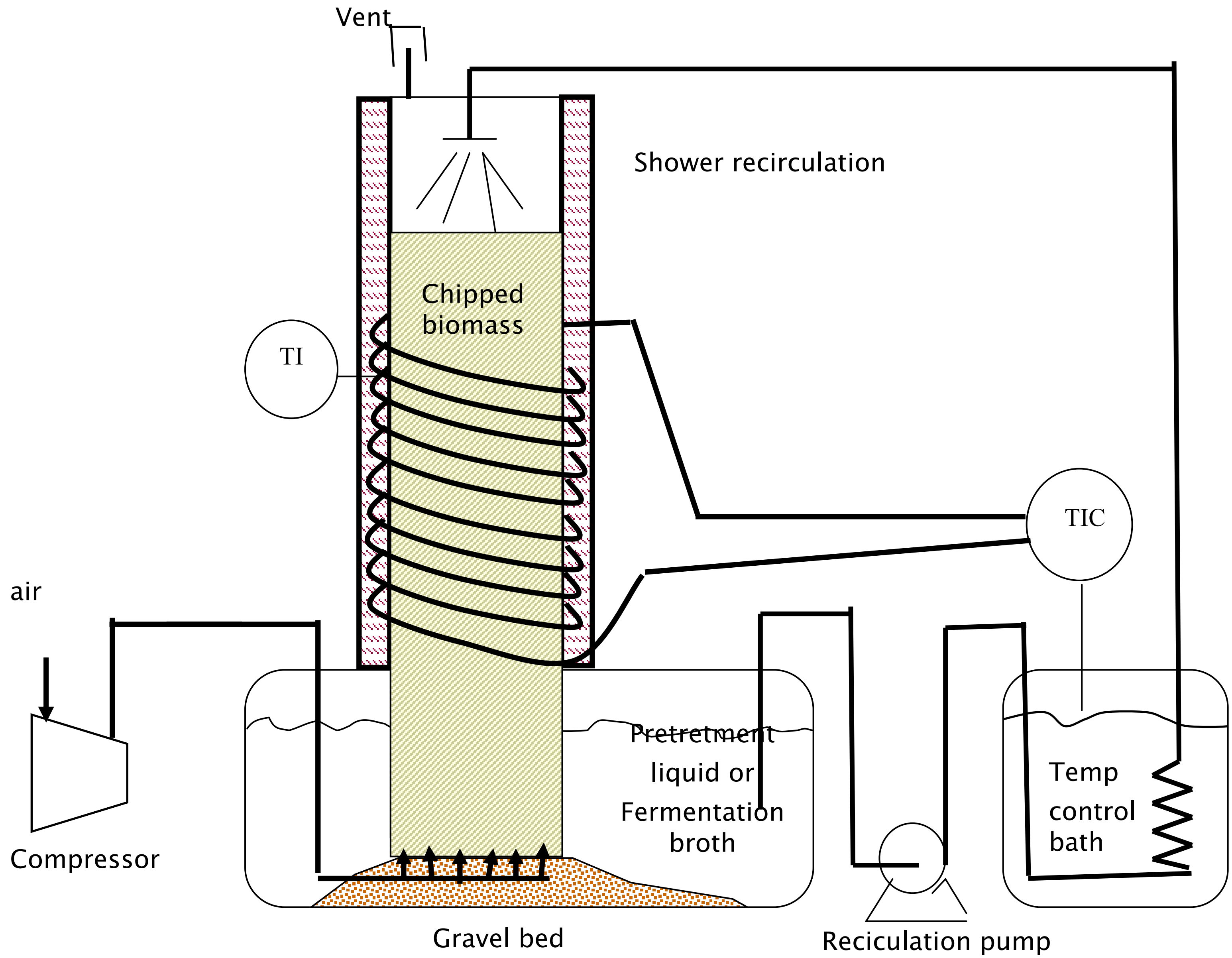


Figure 2: Countercurrent Fermentation. By passing liquids and solids through the conversion process in opposite directions, product inhibition is minimized.

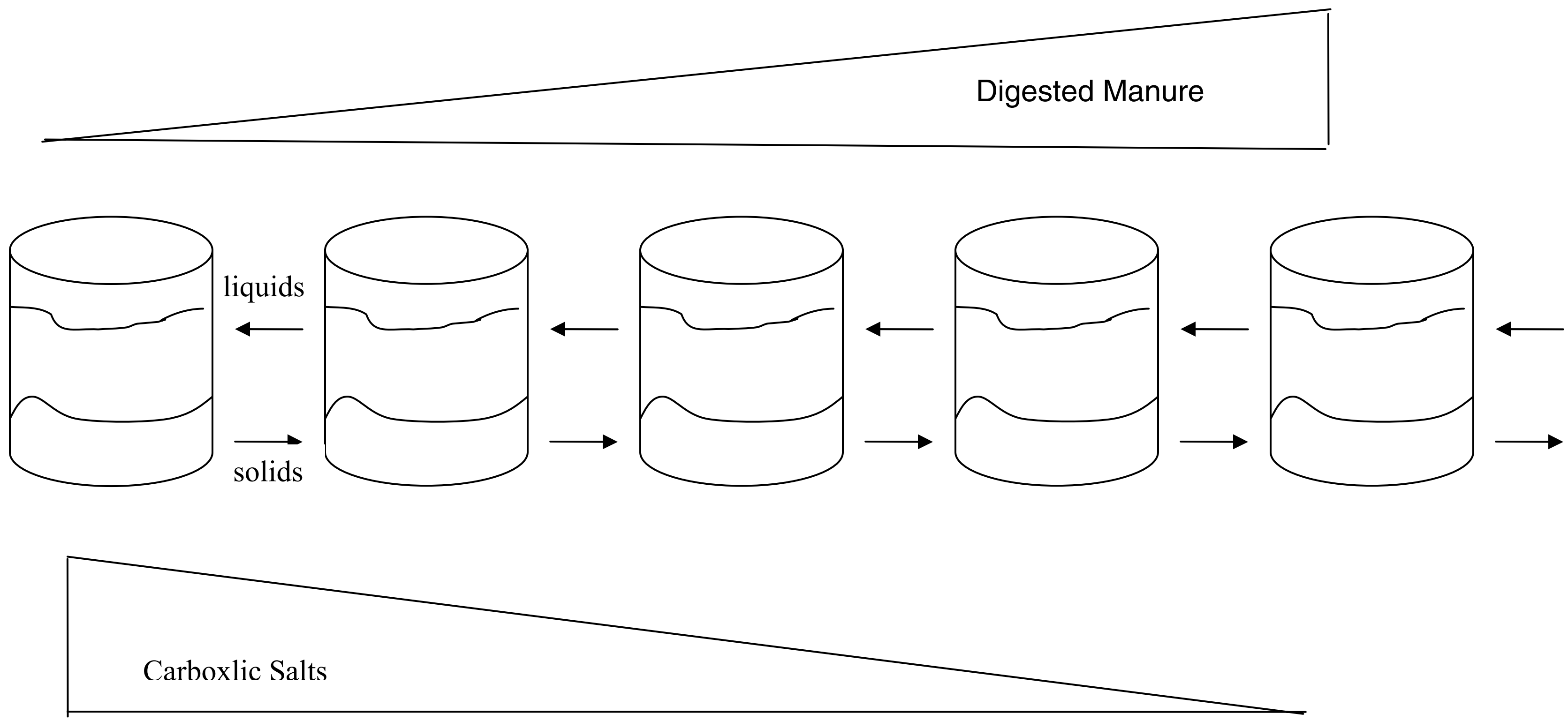


Figure 5: Schematic layout of pretreatment and digester apparatus installed on site at a dairy farm. Each barrel was equipped with a mixer, pH and temperature indicator-loggers, a sewage pump to pump liquid out of the reactor, valved inlet and outlet pipes and a temperature control coil with insulation. Reactors were able to run continuously for weeks at a time.

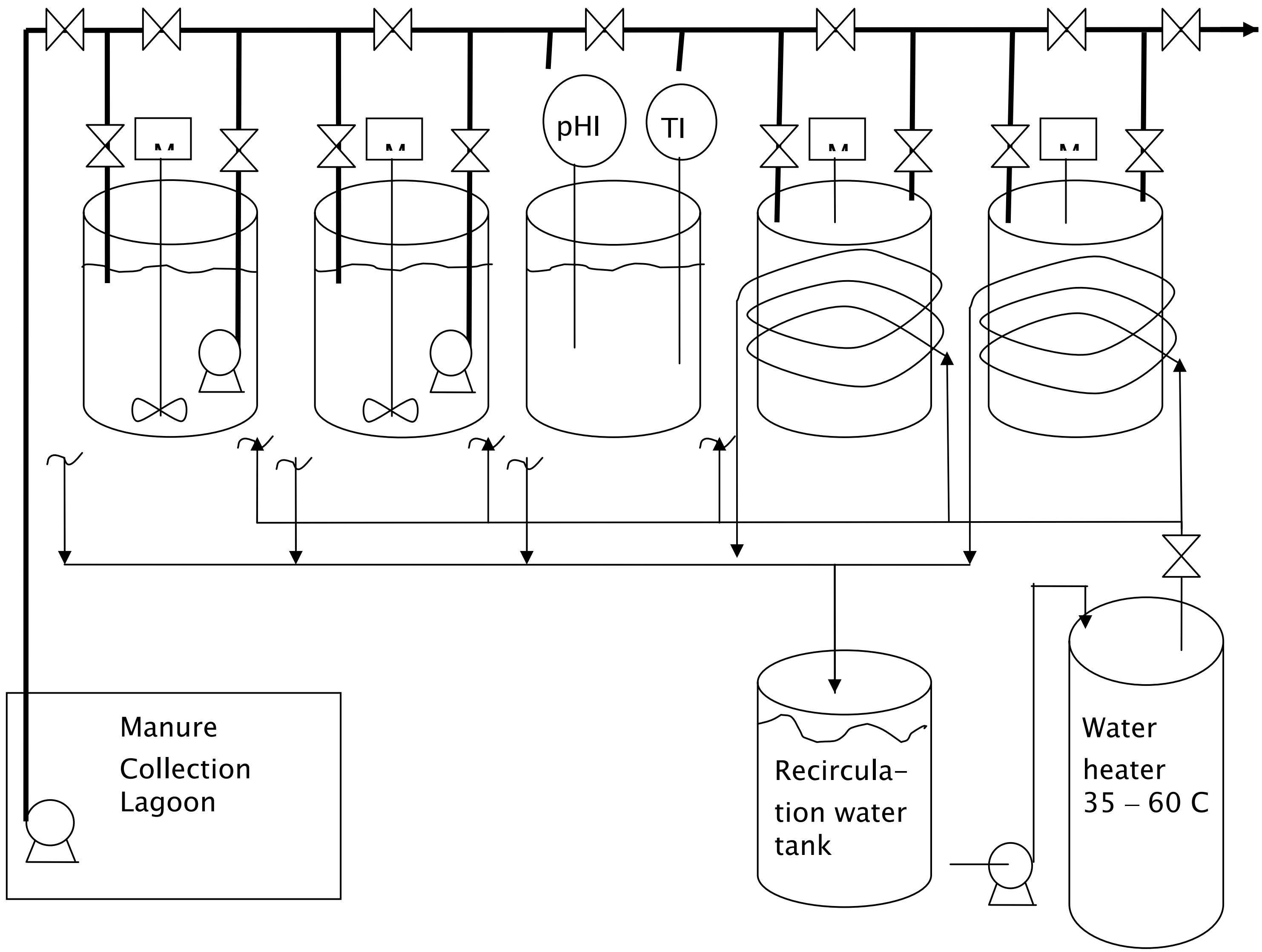


Figure 7 Total Acid concentration vs time. Lime pretreated cattle manure, 40ºC, three week residence time. Relatively reproducible results suggest that increased product concentration could be achieved with a longer residence time.