Fair Oaks Dairy Farms

Cellulosic Ethanol Technology Review - Summary

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Background

At Fair Oaks Dairy, dried manure solids ("DMS") are currently used as a low value compost. United Power was engaged to evaluate the feasibility of processing these DMS into ethanol utilizing commercially available cellulosic biofuels conversion platforms. The deliverables of this project were:

- An evaluation of the DMS to determine their suitability as a feedstock for conversion.
- An overview and survey of appropriate technologies that may be available for conversion of DMS into ethanol or other energy products.
- An evaluation of technologies and vendors of appropriate technology.
- A nominated list, if any, of technologies and vendors.
- A recommendation of technologies and vendors for final consideration.
- Financial and operating analysis for any proposed technology
- Recommendation forward, including descriptions of alternative pathways for energy utilization from DMS, if appropriate.

Executive Summary

The Fair Oaks Dairy group is transitioning their traditional "manure to methane" mesophilic anaerobic digester platform to an integrated bio-refinery centered upon thermophilic digestion. Presently, the Digested Manure Solids (DMS) are used as a low value soil amendment (compost). United Power evaluated the feasibility of processing DMS into higher value ethanol utilizing commercially available cellulosic biofuels conversion platforms. DMS was analyzed and over 100 potential technology providers were reviewed and evaluated.

DMS contains enough carbon to be suitable as a biomass feedstock for conversion into ethanol by gasification technology, or as part of a conversion process that would include combined heat and power. In the first process, 100% of the feedstock is converted into ethanol. In the second process, the feedstock is combusted to provide heat to generate electrical power supporting other processes.

Of the 100 technology vendors evaluated, a short list of nine technology providers was developed. From this, two vendors were selected as finalists (one was an enzymatic platform and one was a gasification platform). Their selection was based upon the technical feasibility of their systems, engineering expertise, experience in commercial or pilot scale operations, the ability or willingness to integrate the system into the Fair Oaks Biorefinery, the know-how or experience in producing bio-ethanol, and a clear path to commercial development.

Methodology

Digested Manure Solids

Manure slurry from nearly 30,000 dairy cows is currently delivered to dairy manure processing facilities via tractor-pulled vacuum tanks. Following sand removal, the slurry enters anaerobic digesters where the volatile solids are converted into raw biogas. In the future, a portion of the biogas will be refined into "pipeline quality" gas to be used as heavy-duty vehicle fuel, with the balance available for Combined Heat and Power (CHP) units. Partially digested manure solids will be separated from the liquid fraction and be partially dehydrated through a dryer run on waste heat from the gas refinery and CHP units. This will produce 108 dry tons per day of residual fiber.

DMS – Windy Ridge Dairy

DMS – Fair Oaks Dairy

Prior to drying, the composition of the DMS is as follows:

Parameter	Measure
Tons per Day	384
Total Solids	28%
Volatile Solids	19.7%
Fine Sand	5.2%
Nitrogen as Ammonia	0.7%
Organic Nitrogen	0.8%
CO2	1.6%
P	0.9%
K	0.2%
S	0.1%
Other	5.9%

From the table above, the DMS appear to be suitable as feedstock for ethanol production (adequate total and volatile solids, with minimal sand/ash), providing it is economically feasible to convert this feedstock using currently available methods. This would produce 108 dry tons per day with ash content near 5%. To asses the opportunities for conversion, test quantities of DMS were shipped to cellulosic ethanol technology vendors to analyze for specific suitability for conversion.

DMS are fibers comprised mostly of lignin [$C_9H_{10}O_2$ $(OCH_3)_n$], cellulose [$(C_6H_{10}O_5)_n$], and hemi-cellulose {[$(C_6H_{10}O_5)_n$]-[$(C_5H_{10}O_5)_n$]-[$(C_6H_{10}O_7)_n$]}, and devoid of simple sugars. Lignin, the majority component, is unusual in that even though it is a naturally-occurring polymer, it lacks a primary structure. That is, its "backbone" does not repeat in a regular manner, but is more or less random. This creates difficulties in "unraveling" or "de-crystalizing" the lignin molecule in order to allow exposure to subsequent treatments to release the contained carbon for incorporation into convenient fuels such as ethanol.

Even with the lignin structural issue described in the preceding paragraph, DMS compounds can be converted into ethanol (CH_3-CH_2-OH) through the following technologies.

Pathway #1 - Acid Hydrolysis and Fermentation Platforms

Acid hydrolysis (disassembling or "cutting" cellulose chains using acid) is well understood and has been commercially practiced since the 1st century[1]. However, the process to remove lignin from biomass and intermediately break long chain cellulose fibers via dilute acid was not industrialized until the late 1800s. In the mid 1940s, the US Forest Service developed and operated two plants based on the original German Scholler process[2] Conversion rates reached 50 gallons ethanol per dry ton of wood, but operations were never profitable.

Recent improvements in acid separation and recovery, increased mechanical efficiencies, utilization of concentrated acid rather than dilute formulations (which avoids the development of fermentation inhibitors), and the development of more economic pretreatments of lignin and cellulose have allowed a resurgence of acid hydrolysis. Under an acid hydrolysis platform, in most instances plant material is ground into a small particle size before treatment. DMS appears to be already of adequate size to require no subsequent reduction for most technologies. However, some vendors claim a substantial increase in conversion rates (carbon in feedstock to carbon in ethanol) using specific pre-treatments. The DMS must be dried to a degree that when combined with acid, the resulting acid-DMS solution is at the proper concentration for the chemical reaction (de-crystallization and hydrolysis) to take place. During the de-crystallization stage, lignin is separated from the cellulose/hemi-cellulose. Lignin cannot further be used as a feedstock for ethanol in this process unless it undergoes additional pre-treatment(s). Instead, it is usually dried and incinerated (such as in a fluidized bed boiler) and heat is recovered.

After incubation, the resulting mixture is a hexose – pentose – acid solution. The sugars are separated from the acid, neutralized, and fermented. Acid is recovered from the liquid remaining after sugar separation. Fermentation of hexose and pentose occurs simultaneously by separate organisms or in some systems by organisms that are able to co-ferment both hexose and pentose. As in typical fermentation platforms, the result is beer and carbon dioxide. The beer is centrifuged and filtered to remove yeasts and solids. The clear beer is distilled to capture the "wet" (95%) ethanol, which is followed by molecular sieve dehydration to produce 99%, or "anhydrous ethanol".

[1] Pliny the Elder, The Natural History (Pliny), Book XIII, Chapter 26, The paste used in preparation of paper.

[2] Katzen, R. and Schell, d.J., "Lignocellulosic feedstock Biorefinery: History and Plant Development for Biomass Hydrolysis", pp 129-138 in Biorefineries - Industrial processes and Products, Volume 1, Kamm, B., Gruber, P.R., and Kamm, M., eds. Wiley-VCH, Weinheim, 2006.

Regarding complete conversion of carbon in DMS to carbon in ethanol, the limiting factors in acid hydrolysis are the inability of the system to convert lignin, and the loss of carbon through production of carbon dioxide.

The Pros and Cons of an acid hydrolysis process are as follows:

PROS	CONS
Well understood technology	High consumption of acid, even with recovery system
Relatively high yield of ethanol	May be problems with off-taking calcium sulfate
Production of other chemicals is possible (furfural, etc.)	Does not work on lignin fraction

Pathway #2 - Enzymatic Conversion and Fermentation Platforms
The conversion of complex sugars in the form of mostly cellulose and hemi-cellulose into simple sugars in the stomachs of ruminants is an example of enzymatic conversion of biomass. An example of conversion of more recalcitrant biomass such as lignin is found in the digestive tracts of termites. In these naturally-occurring processes, dozens of enzymes are produced directly by the organism, or by bacteria living in the host organism.

To commercialize this general process, companies directly employ fungi or bacteria to produce the desired enzymes, or develop bacteria to manufacture and excrete the enzymes. Depending on the system employed, bacteria and fungi can be added directly to a cellulosic solution, or enzymes can be recovered from the organisms and the purified enzyme added to the solution. According to one supplier, over a hundred enzymes are needed to completely convert a biomass such as wood entirely to simple sugars. It has historically been very expensive to produce all of these enzymes. Therefore, only enzymes (or combinations of relatively few enzymes) that can cost effectively hydrolyze the majority of the feedstock are produced.

As is the case with acid hydrolysis, in an enzymatic conversion platform the DMS must be pre-treated to de-crystallize the lignin / cellulose / hemi-cellulose compounds using steam explosion, micro mechanical degradation, or a chemical treatment such as a sulfite (e.g. SPORL)[3]. This pre-treatment is not only essential, but has a direct impact on the efficiency and quality of downstream processes, and can account for up to 20% of the total costs of conversion. The resulting de-crystallized mixture is then subjected to enzymes which break down the cellulose and hemi-cellulose into simple hexose and pentose sugars. This ultimately is similar to the biological systems in the stomachs of ruminants organisms, while the remaining solid fraction containing mostly cellulose is simultaneously enzymatically reduced to hexose and fermented with a second proprietary organism, termed simultaneous saccharification and fermentation
lignin as a feedstock (similar to acid hydrolysis).

[3] Bin Yang and Charles E. Wyman. Pretreatment: the key to unlocking low-cost cellulosic ethanol. Biofuels, Bioproducts and Biorefining. Volume 2, Issue 1, pages 26–40, January/February 2008.

The Pros and Cons of an enzymatic hydrolysis process are as follows:

PROS	CONS
Enzymes are highly specific for their substrate	Until perhaps recently, enzymes have been very costly
Enzymes are not consumed in the reactions and are recoverable and reusable	May be too highly feedstock specific
Technology used with wood and wood bi-products is well-known.	Enzymes to degrade lignin may not be readily available.

Platform #3 - Gasification and Pyrolysis Platforms
Gasification and Pyrolysis have been available for many years. Gasification is the thermal conversion of biomass in a reduced oxygen environment into combustible gas (syngas). Pyrolysis is the thermal conversion of biomass in the absence of oxygen into syngas, oil, and char. Depending on its resulting BTU value, syngas can serve as a substitute for natural gas to, for example, fire boilers for heat or to generate electricity. Gasification results in syngas, which can be further converted into ethanol, the object of our study.

In a gasification system, DMS would be heated to over 2,000 F in a pressurized, low oxygen environment. Under these conditions, the feedstock does not "burn", but instead gasifies into molecular hydrogen, carbon monoxide, and carbon dioxide. By manipulating these parameters (temperature, pressure, and oxygen), the quality and composition of the syngas can be controlled. The reactor is heated by using some of the produced syngas to fire the reactor (i.e. parasitic load), or by using a electricity driven plasma arc as the heat source. Once cooled and filtered, the syngas is further converted to ethanol by using specific bacteria (e.g. *Clostridium ljungdahlii*) that digests syngas and emit ethanol (bio-catalyst) or by using a metal catalyst that directly converts the syngas into ethanol (Fischer Tropsch method). In the case of the bio-catalyst, ethanol is removed from the digester using a selective membrane technology or standard distillation, as with the Fischer Tropsch method. In both instances, ethanol must still be dehydrated with industry standard molecular sieves.

Over 150 companies are producing gasification and pyrolysis equipment and technologies. Because of design differences, some are more appropriate for use with wet feedstocks (greater than 50% moisture) while others are designed for drier feedstocks (less than 50% moisture). As composition of syngas varies according to the parameters of a gasifier, the selection of gasification equipment, from a technological aspect, should be based upon the quality and quantity of syngas that would be produced from DMS and be most suited for the production of ethanol.

The Pros and Cons of gasification platforms are noted below:

PROS	CONS
Gasification well-understood	High capital costs
Can use any carbonaceous feedstock	High economy of scale
High ethanol to feedstock yields	Not suitable for high moisture feedstocks
Low operating/conversion costs	No operating commercial scale feedstock to ethanol facility

Summary and Conclusions

DMS contains enough carbon to be suitable as a biomass feedstock for conversion into ethanol by gasification technology, or as part of a conversion process that would include combined heat and power. In both processes, DMS is augmented by corn stover to reach economies of scale. With gasification, 100% of the feedstock is converted into ethanol. Using an enzymatic process, the available sugars from the corn stover are converted to ethanol, while the lignin from the DMS and stover is combusted to generate electrical power.

There are four cellulosic conversion platforms currently available, which are gasification to syngas followed by conversion to ethanol using a metal or bio catalyst, exo-enzymatic conversion (with or without pretreatment) of feedstock to simple sugars followed by fermentation of C5 and C6 sugars to ethanol, and biological digestion of biomass with co-saccharification to ethanol. Metal catalytic systems are elegant, but remain economically prohibitive. With a consistent feedstock, particularly one with higher moisture content, both enzymatic platforms (exo-enzymatic or co-saccharification) appear technically practical and feasible. There are no acid hydrolytic systems available for use, or that are compatible, with the Fair Oaks Biorefinery.

Following a survey of available technologies, an enzymatic platform and a gasification platform were selected as finalists. This selection was based upon the technical feasibility of their systems, engineering expertise, experience in commercial or pilot scale operations, the ability or willingness to integrate the system into the Fair Oaks Biorefinery, their know-how or experience in producing ethanol (as opposed to jet fuel, diesel fuel, or bio-char), commitment and available resources (time, management, manpower, economic), and economic viability.

Following an integration scoping review of the two finalist systems with the Fair Oaks BioRefinery, United Power recommended the enzymatic hydrolysis technology for a more detailed engineering design process, financial evaluation, and ultimate path forward to project development as additional grant funding, tax incentives and other funding opportunities become available.