Final Technical Report

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LIST OF ACRONYMS

ADM	Archer Daniels Midland
BTU	British Thermal Unit
MBTU	Thousand BTU
CFD	Computational Fluid Dynamics
DDGS	Dried Distillers Grains with Solubles
DPT	Differential Pressure Transmitter
EtOH	Ethanol
gpy	Gallons per year
HAZOP	Hazard and Operability Analysis
MSE	Membrane Solvent Extraction
NREL	National Renewable Energy Laboratory
P&ID	Process & Instrumentation Diagram
USDA	United States Department of Agricultural

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Executive Summary

Ethanol is the leading biofuel in the U.S. with 13 billion gallons produced in 2013. Ethanol represents approximately 10 percent of the nation's gasoline supply today and can be found in more than 96 percent of all gasoline sold.[1]

Distillation is the industry standard for separating water from ethanol and is an energy intensive process, accounting for a significant portion of the total energy usage in an ethanol plant. Existing distillation systems also require high volumes of cooling water, resulting in about four gallons of water used for every gallon of ethanol produced.[2]

3M and Archer Daniels Midland (ADM) collaborated with the U.S. Department of Energy (DOE) to develop and demonstrate a novel membrane solvent extraction (MSE) process that can substantially reduce energy and water consumption in ethanol production, and accelerate the fermentation process. A cross-flow membrane module was developed, using porous membrane manufactured by 3M. A pilot process was developed that integrates fermentation, MSE and vacuum distillation. Extended experiments of 48-72 hours each were conducted to develop the process, verify its performance and begin establishing commercial viability.

In these experiments, 91-94% ethanol was produced from fermentation broth having 6-12% ethanol. Distillation re-boiler duties, condenser duties, and temperature profiles from the experiments compare favorably to Aspen models developed for the system. These models show process energy of 9,700 BTU/gal, compared to 13,000 BTU/gal for a similar capacity conventional distillation process (25 – 30% savings). This translates to 44 million BTU/hr savings for a 100 MM gallon/year ethanol plant. In process experiments leading to this program, it was demonstrated that fermentation could be accelerated by a factor of 2 to 3X, by continuously removing ethanol from the fermentors.

An Aspen model for the combined process was developed by NREL, and incorporated into the USDA dry mill ethanol plant model. The USDA model includes an economic spread sheet which provides process detail for a generic dry mill ethanol plant. Integration of the MSE process into this allows us to model the impact of experimental changes on a future plant process, and enable us to model the processes of ethanol producer customers.

The MSE pilot process can be applied to recovery of bio-butanol and to the cellulosic ethanol process: 1) concentration of the dilute final product and 2) removal of pre-treatment-induced inhibitors, enabling C5 fermentation. Lab experiments were conducted to demonstrate efficacy of these two processes, and pilot trials will follow.

In summary, this project demonstrated that the MSE process could increase industrial efficiency by reducing the energy requirements of separating ethanol and water. Reduction in cooling water requirements that MSE provides will allow decreases in water usage, thereby improving the environmental impact of the industry. In addition, fermentation acceleration can provide a benefit to manufacturing productivity. A commercialization plan is being developed.

[1] Renewable Fuels Association (RFA) 2014 Pocket Guide to Ethanol www.ethanolrfa.org
[2] Economic Model of an Ethanol Production Facility, Iowa State University, University Extension, http://www.extension.iastate.edu/agdm/energy/html/d1-10.html

1. Introduction

1.1. Project Objectives

3M has developed a membrane solvent-extraction (MSE) technology that shows promise to substantially decrease the energy and water consumption in the production of bioethanol. The intent of this project was to develop this technology to an advanced prototype pilot stage, conduct process experiments to verify performance, and establish its economic viability as a future production process. DOE funding enabled refinement of the membrane, development of membrane modules, selection of extraction solvents, and development of Aspen and economic models. It further enabled the design and construction of an integrated, fully automated fermentation, MSE and distillation process with Archer Daniels Midland (ADM), and the process experiments which are on-going.

Overall project objectives were:

Objective 1 – Develop a cross-flow membrane module, housing unit, and a process to produce modules. Develop a pilot plant scale membrane solvent extraction process incorporating nine of these modules and housing units.

Objective 2 – Develop a continuous ethanol recovery process integrating three stage fermentation, membrane extraction, and two stage vacuum distillation. For this process, design a control program, select instruments, and construct the control system to operate at ADM.

Objective 3 – Conduct experiments on process components and modify to meet project targets.

Objective 4 – Conduct full pilot process experiments in straight through and acceleration mode.

Objective 5 – Develop an Aspen model for the process, compare experimental results with model parameters, and calculate energy and water savings compared to conventional ethanol distillation.

1.2. Background

Ethanol is produced from corn by first converting the starch in the corn to sugar by an enzyme process, and then fermenting the sugar to ethanol. In the dry mill ethanol process, corn is milled and soaked in slightly acidic hot water, and then treated with alpha amylase and gluco-amylase enzymes to convert starch to glucose. Batch or continuous yeast fermentation convert the glucose to ethanol, at a final concentration of 10-14 wt.%. The ethanol is then distilled (Figure 1-1) directly from this broth in two stages: the "beer column" concentrates it to about 42% and the "rectifier" takes it to 91%. A gas phase molecular sieve process de-waters the 91% ethanol to 100% for fuel use. The energy to drive the first stage (beer column) is the largest energy draw in the plant. Overall, the process of making ethanol (from field to fuel) is net energy positive by 38% or more.

Some producers use a 'wet-mill' process. In this process, components of the corn such as corn oil, starch, cell wall materials etc are separated out first, and then the starch (and sugar) is used separately to produce ethanol by fermentation. Typically a series or cascade process (similar to Figure 3-13) is used where the fermentation progresses down through several stages, with the ethanol concentration increasing until it reaches 10-14% in the last stage.

Membrane solvent extraction (MSE) can be applied to recovery of ethanol from either process. Dry mill will require a solids separation step prior to MSE, but broth from the wet-mill process can be processed directly.

1.2.1. Energy Savings

In a 100 MM gallon/year ethanol plant (which is becoming typical size), about 133 MM BTU/hr are consumed in the distillation process (ASPEN simulations verified by ADM). The goal of this project is to reduce this energy usage by more than 25% to about 84 MM BTU/hr, or less, by integrating the MSE process into ethanol recovery, essentially eliminating the first stage of distillation, as shown in Figure 1-2.

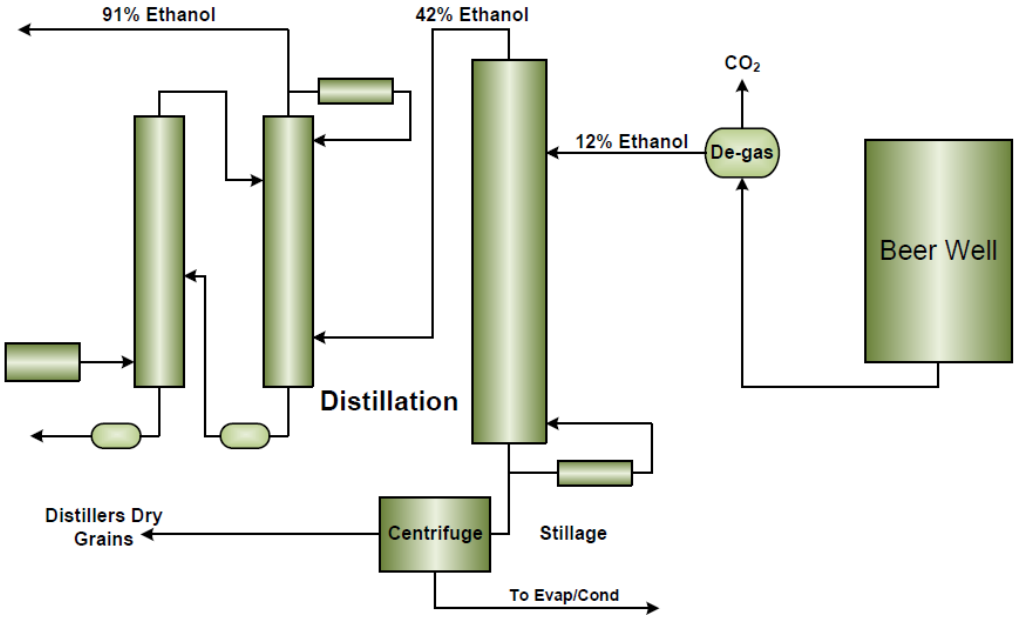


Figure 1-1: Conventional dry mill ethanol process.

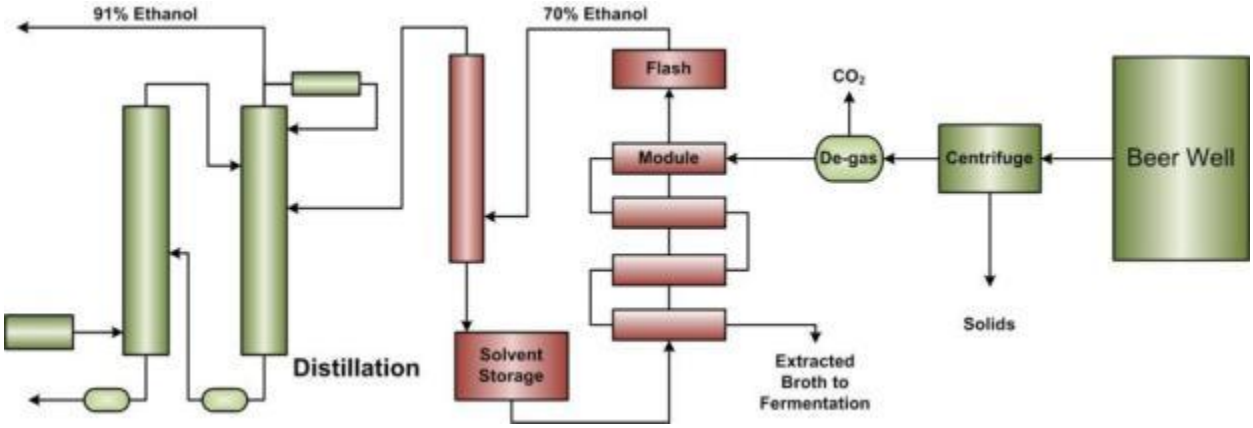


Figure 1-2: Modified dry mill ethanol process with MSE.

1.2.2. Water Savings

The current ethanol production process requires about 4 gallons of water for every gallon of ethanol produced. Much of the water usage comes from evaporation losses in cooling towers, which provide the cooling for distillation. This water evaporation loss can be so large, that it can threaten the aquifer from which the plant draws its water. It is not uncommon for permits to be denied because of this threat. The MSE process can reduce this water loss substantially, by reducing the cooling water requirement on the distillation.

1.2.3. Fermentation Acceleration

Ethanol is a feed-back inhibitor of the yeast that forms it. By removing ethanol from the fermentor as it is formed, it is possible to accelerate fermentation by maintaining the concentration at a level where the yeast is active (typically 7.8% or below). In trials leading up to this program, it was demonstrated (on wet-mill cascade fermentation) that the MSE process can accelerate fermentation by a factor of 2 to 3 by removing ethanol continuously from the fermentors. Acceleration should also occur in both continuous and batch dry mill fermentation, although we have not demonstrated this yet.

2. Membrane Extraction Module Development

In the MSE process, one side of a porous film is in contact with the ethanol-containing fermentation broth, and the opposite side with a high boiling extraction solvent. The two liquids, which are immiscible with one another, form an interface in the pores of the membrane, and ethanol transfers from the broth to the solvent phase by liquid/liquid extraction, under a concentration gradient driving force (Figure 2-1). The porous polypropylene membrane that 3M manufactures for this application, has an average pore size of 0.1 to 0.4 microns, and is usually 1 to 3 mm thick.

Extraction solvents which have high ethanol solubility, but minimal water solubility were selected for use (2,6-dimethyl-4-heptanol). Separation takes place in the liquid/liquid extraction, as ethanol is selected, and water is essentially rejected. The membrane is a flow-by membrane, meaning the two phases are flowed past opposite surfaces and extraction occurs across a liquid/liquid interface.

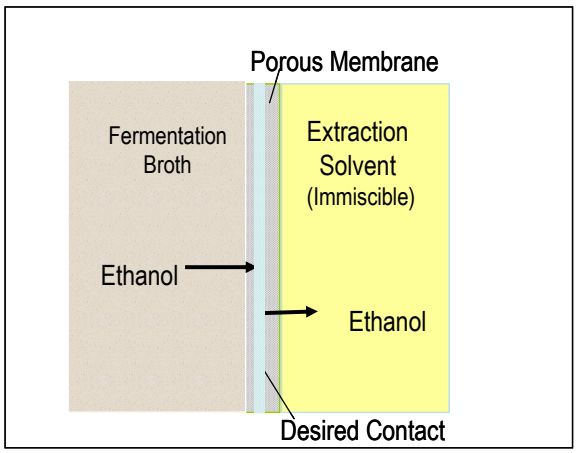


Figure 2-1: MSE Process.

The membrane serves two purposes: it provides a large contact surface area between phases and it prevents emulsion formation. The two phases come into intimate contact with one another within the pores of the membrane, and ethanol transfer takes place, but the broth stays on its side and the solvent on its side (the solvent will remain clear). Solvent cross-over can be minimized and controlled.

Direct addition of the solvent to the broth results in formation of an intractable emulsion. Solvent entrainment losses kill the economics (and the yeast). The membrane eliminates this problem. As an example of the process, equilibrium extraction of a broth stream containing 9% ethanol with 2,6-dimethy-l-4-heptanol, will form a solvent ternary with a composition of 4.5% ethanol / 1.7% water / 93.8% solvent. When this mixture is flashed, 70% ethanol and 30% water comes off. The high boiling solvent stays behind. Single layer experiments with hydrophobic membranes have determined that:

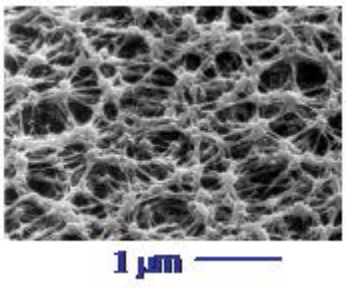


Figure 2-2: TIPS membrane.

1. Transfer rate increases with temperature.
2. Transfer rate increases with solvent flow rate.
3. Transfer rate has minor response to broth flow rate.
4. Transfer rate is pressure neutral – i.e. pressure does not increase or decrease the rate.
5. Higher pressure on the aqueous side will pin the liquid/liquid interface in the membrane.
6. Uniform pore size is important: larger pores will cause flooding of phases into one another.

2.1. Cross flow module

To implement membrane extraction at an industrial scale, cartridge-loading cross-flow modules(Figure 2-3) are being developed. Membrane is bonded to a corrugated or rail film spacer layer. The spacer layer serves as a fluid flow channel. These membrane/spacer layer laminates are then stacked and fused together to form a module "brick". The flow channels of each layer are oriented perpendicular to those in the layers above and below. Broth flows through the module in one direction, solvent flows through in the other direction (perpendicular to the broth flow). Contact between phases occurs only within the pores of the membrane.

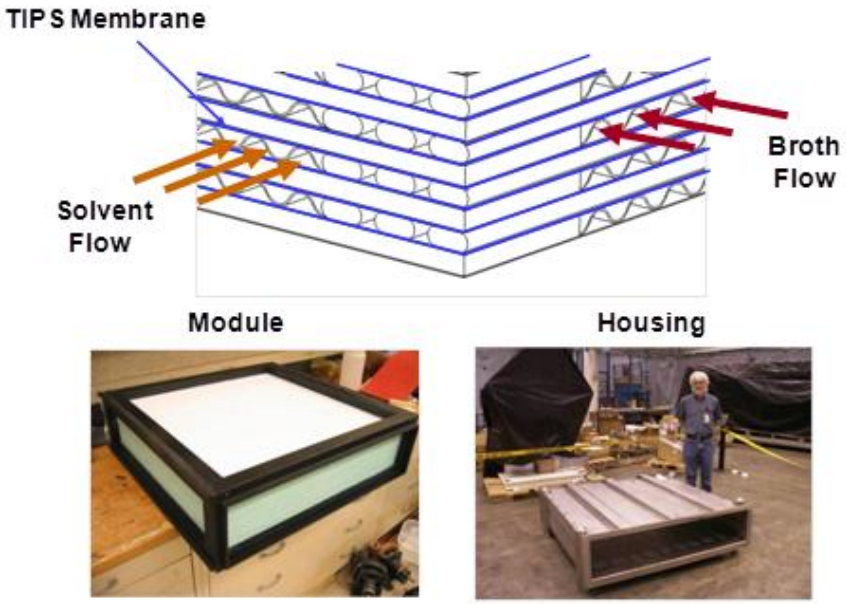


Figure 2-3: MSE membrane module and housing.

Modules slide into the housing units like a drawer, and fit lock and key with the housing unit. Ends of the module are pressed into gaskets in the doors of the housing unit, forming fluid tight perimeter seals that isolate the phases from one another, when the doors are bolted in place. Broth would flow for example into the housing unit in the picture through ports in the bottom, travel from left to right in the photograph, exit through the bottom on the opposite side. Solvent would flow from front to back.

2.2. MSE Process Concept

In the conventional ethanol process, finished fermentation broth is sent directly to distillation for ethanol recovery. The MSE process adds a membrane module, pumping broth past one side and returning it to the fermentor, with part or all of the ethanol removed as illustrated in Figure 2-4. Solvent is sent past the opposite side, forming a ternary, which is flashed, using vacuum distillation, to recover the 70+ % ethanol. The stripped solvent, which acts as a carrier, is returned to extract more ethanol.

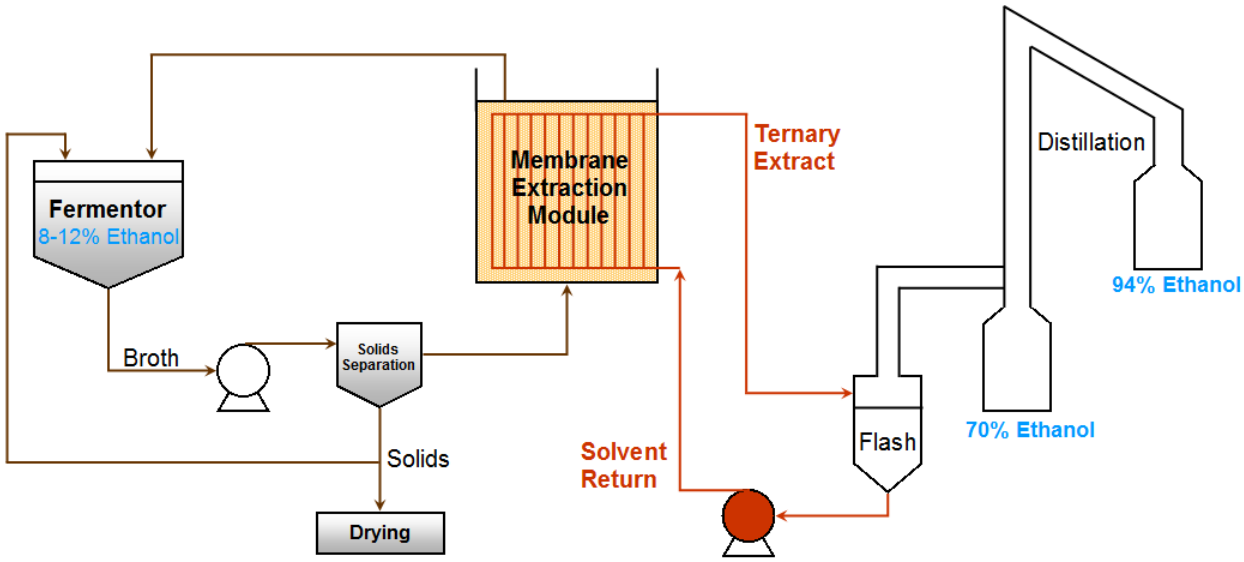


Figure 2-4: MSE process concept.

3. Pilot Process Development

3.1. Overview

For this project, a process was developed which integrates fermentation, membrane solvent extraction and distillation (Figure 3-1). Fermentation broth containing the ethanol is pumped through nine membrane modules in series. Extraction solvent is pumped through the modules essentially counter-current to the broth. The ethanol transfers to the solvent in the modules, forming a ternary (approximately 4% ethanol, 2% water, and 94% solvent). The ternary is sent to a two stage vacuum distillation process, where ethanol/water is stripped from the solvent in the first stage (coming over as 72-84% ethanol), and further concentrated in a second stage, coming off as 91% ethanol / 9% water. The cleaned up (stripped) solvent is returned to extraction as "Fresh Solvent".

Energy required to flash the ethanol/water from this ternary is significantly less than that required to separate the same amount of ethanol from a 10% ethanol / water mixture. Most of the separation takes place in the partitioning process in the MSE modules at room temperature. Pump energy required is only about 1-3% of the total process energy.

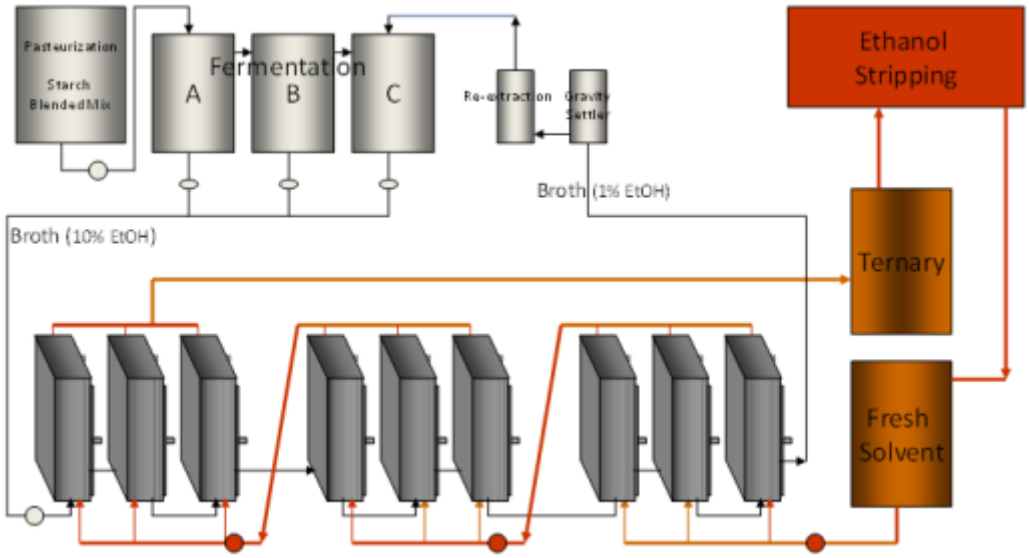


Figure 3-1: EWA facility MSE prototype process concept.

3.2. EWA Facility

The prototype pilot plant process was constructed at ADM Development Products, referred to as the EWA facility, an 18,746 ft^2 multi-purpose production/pilot facility located 1.5 miles from the ADM James R. Randall Research Center in Decatur, Illinois. The EWA facility has its own laboratory that provides analytical support to R&D and production. About 12,000 cubic feet of space was made available to this project. The site was selected for cost efficiency and all necessary infra-structure (e.g. cooling tower, electric power, etc.) was in place at the start of the project.

The process as installed in EWA is shown in the 3D concept drawing (Figure 3-2). Final design, construction, and commissioning were completed on all three portions in 2012. Design capacity is 10.5 kg ethanol/hour or about 30,000 gallons/year.

3.3. Fermentation Process Design

The fermentation process is shown to the left in Figure 3-2. The Process & Instrumentation Diagram (P&ID) for this was developed by ADM and is shown in Figure 3-3. Fermentation is carried out in 270 gallon stainless steel vessels that have impeller agitation. These vessels were piped so that fermentation can be conducted either in a continuous cascade or a batch process mode. Whole broth from the fermentors is collected in a 300 gallon beer well and then passed through a disc centrifuge. The centrifuge separates the broth into a thin broth fraction which goes to membrane extraction where ethanol is removed, and a solid fraction which is processed separately.

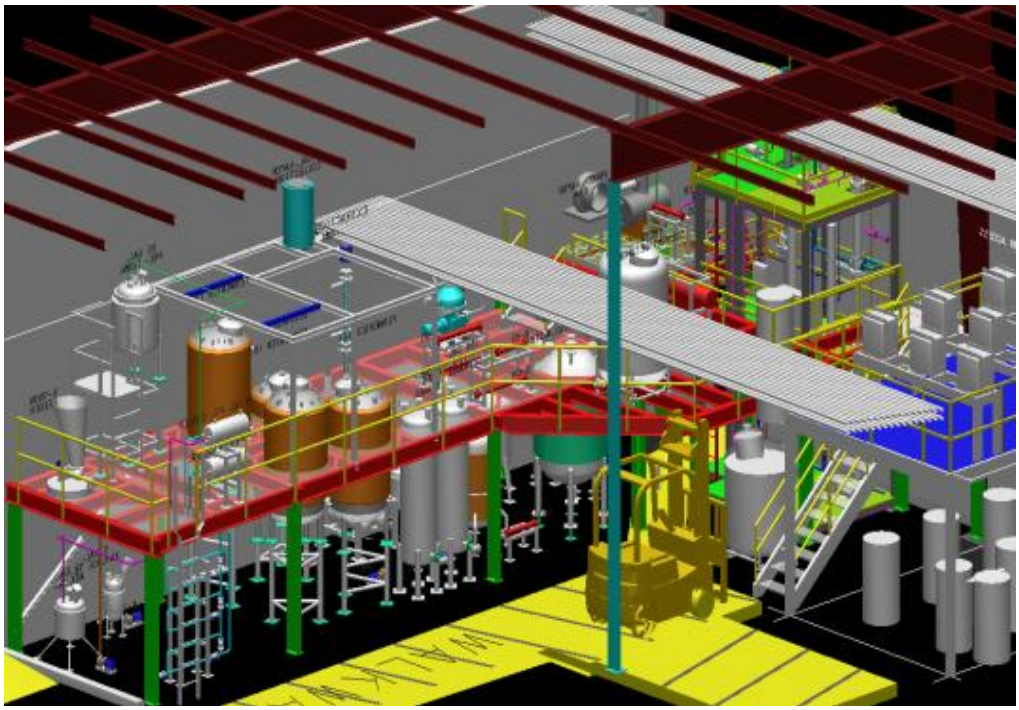


Figure 3-2: MSE prototype process design for installation at the ADM-EWA facility. The fermentation process skid is on the left, the distillation skid is in the center and the membrane skid is on the right (blue).

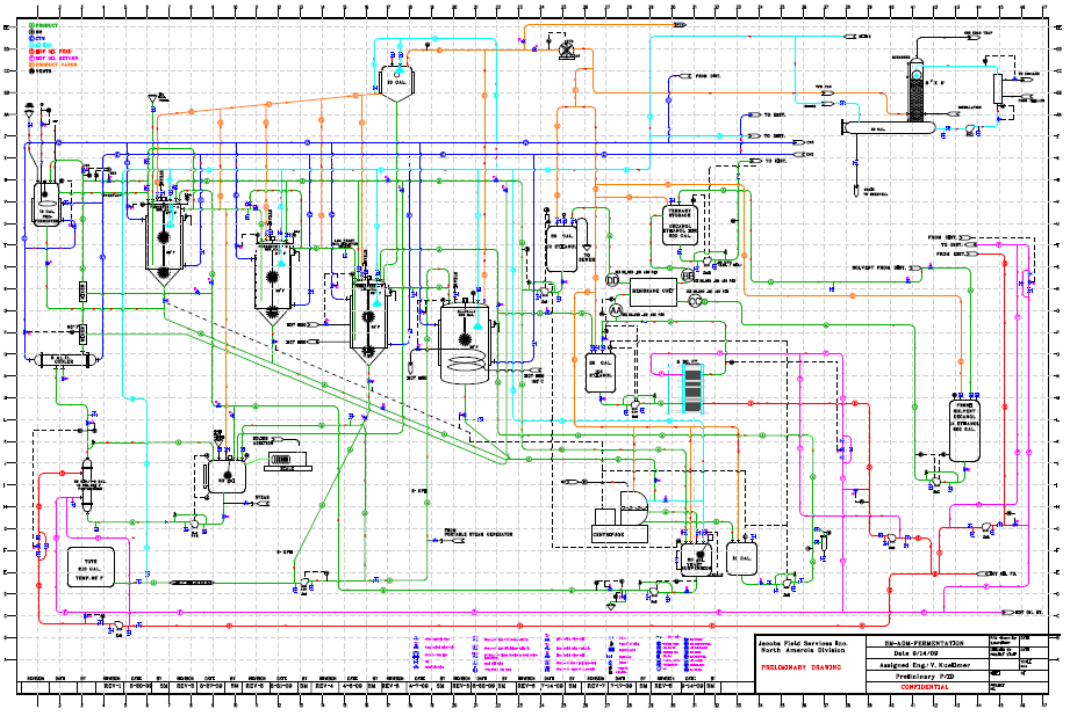


Figure 3-3: Fermentation Process P&ID

Figure 3-4: Fermentation process skid.

3.4. MSE Process Design

The membrane extraction skid utilizes nine inter-connected 20 x 20 x 10 inch membrane modules and housing units to recover ethanol from the fermentation broth. The P&ID of the MSE process is shown in Figure 3-5. Figure 3-6 is a P&ID for a single module housing unit. Modules are mounted vertically as shown in Figure 3-7. In normal operation, broth (brown line, Figure 3-6) enters the housing through valve FV01, passes through the module, exits through the base of the module, over the loop, and out valve FV12, returning to the broth header.

The solvent (red line) comes from an overhead solvent header, enters the top of the module through valve FV08 and exits through valve FV-07, going to a collection header at the bottom. The system was designed so that an individual module/housing unit could be taken out of service and isolated, with the other eight units continuing to operate. To isolate a module:

a. Broth valves FV01 and FV12 are closed and bypass valve FV10 is opened;
b. Solvent valves FV-08 and FV-07 are closed.

All five valves are pneumatically actuated and can be switched automatically. Pilot valves, which respond to a 4-20 mA signal from the controller, regulate compressed air flow to them. Once a module is isolated, it can be drained by opening hand valves and then clean-in-place (CIP) solution can be circulated through both broth and solvent sides of the module.

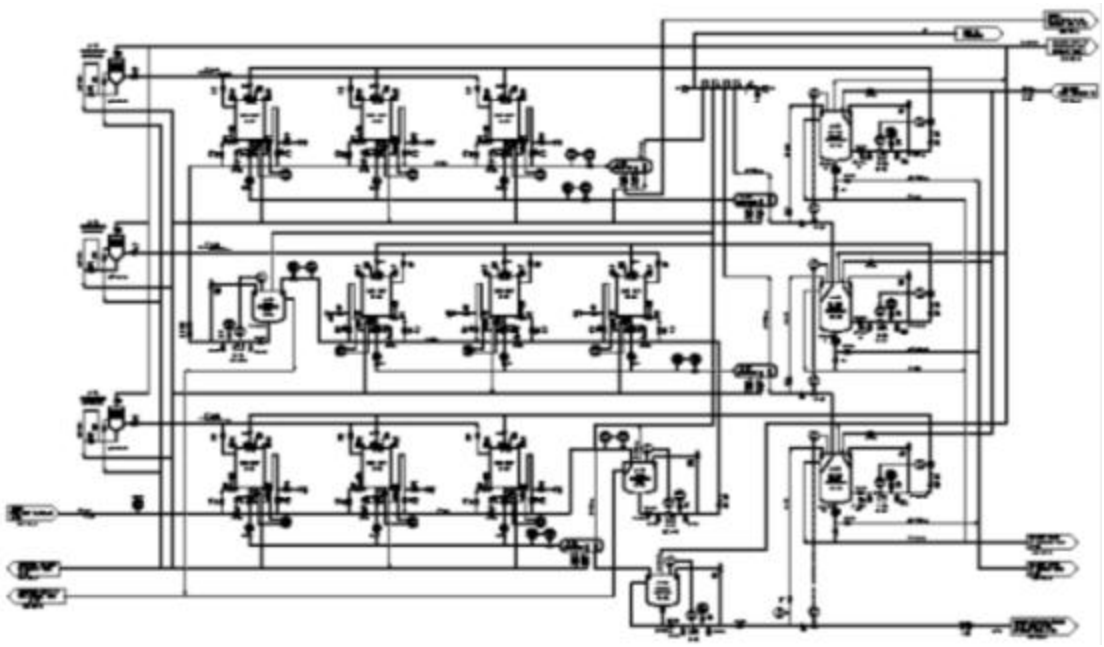


Figure 3-5: MSE Process and Instrumentation Diagram

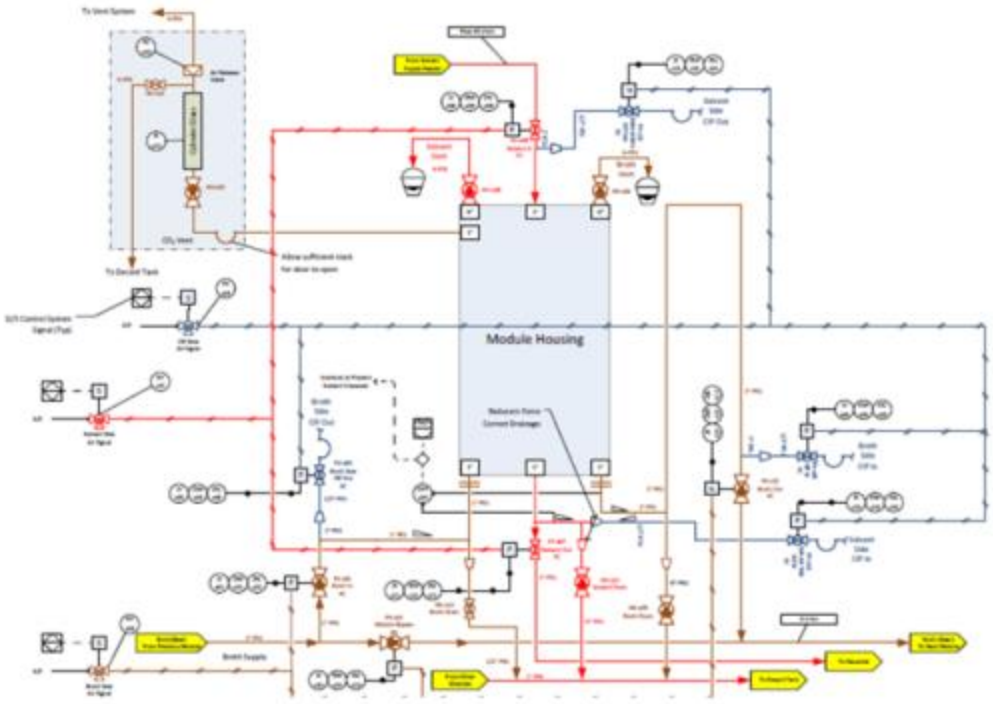


Figure 3-6: P&ID for a single module housing unit.

Modules and housing units are configured to fit lock and key with one another as shown in Figure 3-7, forming four fluid manifolds between the faces of the module and the walls of the housing unit (an inlet and an outlet for each phase). The units are mounted vertically (long axis up) in three tiers of three units each (Figure 3-9). The ethanol-rich broth serum enters the housing unit through a 1 inch port in the base and is directed into an entrance manifold in one of the doors of the housing unit. The broth then passes horizontally through the membrane module to an exit manifold in the other door and from there exits through a port in the bottom of the housing unit. Solvent enters from the top of the housing unit, passes down through the module, and exits from a port in the bottom. Solvent and thin broth serum make liquid/liquid contact within the pores of the membrane, bringing about ethanol transfer from the broth to the solvent phase.

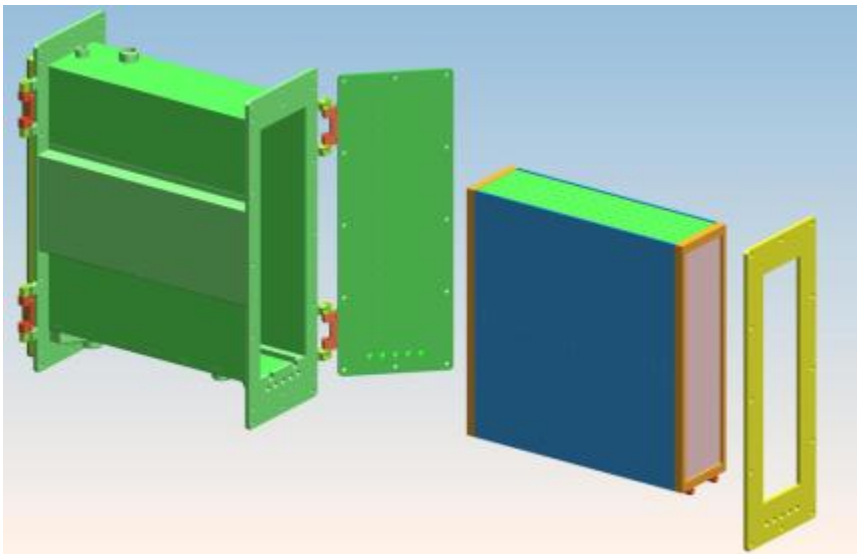


Figure 3-7: Module and housing – exploded view.

Ethanol partitions from the broth serum (ethanol concentration: 6-14%) into 2,6-dimethyl-4-heptanol in the membrane extraction process, forming the solvent ternary. In the module array, solvent and broth pass counter-current to one another. Broth is pumped through all nine modules in series, starting with one tier and progressing through the other two. A back pressure valve, mounted in the line coming from each tier of three modules, maintains a pressure set point within the modules of that tier. After passing through the back pressure valve, broth goes to a 10 gallon intermediate tank which is open to the atmosphere. Broth is pumped from this tank into the next tier in the sequence. In this way, internal pressure of a tier can be controlled independently from the other tiers.

At the end of membrane solvent extraction, broth is passed counter-currently to a re-extraction solvent, Dodecane in a vertical liquid / liquid extraction column (Scheibel or Karr column) to remove any entrained solvent, and then stored as fermentor makeup. The goal of this re-extraction is to maintain solvent entrainment below 400 ppm in the thin broth returned to fermentor makeup. Measurements were made in the lab that show a minimum inhibitory concentration for Saccharomyces Cerevisiae of 400 ppm 2,6-dimethyl-4-heptanol. With re-extraction, it has been possible to maintain the fermentor return at or below this level.

Fresh solvent (from distillation) is pumped to a 120 gallon solvent intermediate tank (tank A-03 in the P&ID) in the MSE unit (typically 5-10 liters/minute). Solvent is circulated from this intermediate tank to the first tier of modules. After passing through the modules, solvent is passed through a gravity separator (to settle off any crossed-over broth) and then through a back pressure valve (to maintain a baseline solvent pressure in the modules). The solvent is split at this point: most (e.g. 80 liters/min) is recycled to the solvent intermediate tank for that tier. A smaller portion (e.g. 10 liters/min) is advanced to the second (middle) tier re-circulation tank (A-04). Solvent advance rate is controlled ultimately by the fresh solvent feed rate but responds to the level in the re-circulation tank from which it came (A-03 in this case). A back pressure valve in the line going to the next tier is coupled to a level transmitter in the tank, and keeps the level in that tank at a set point.

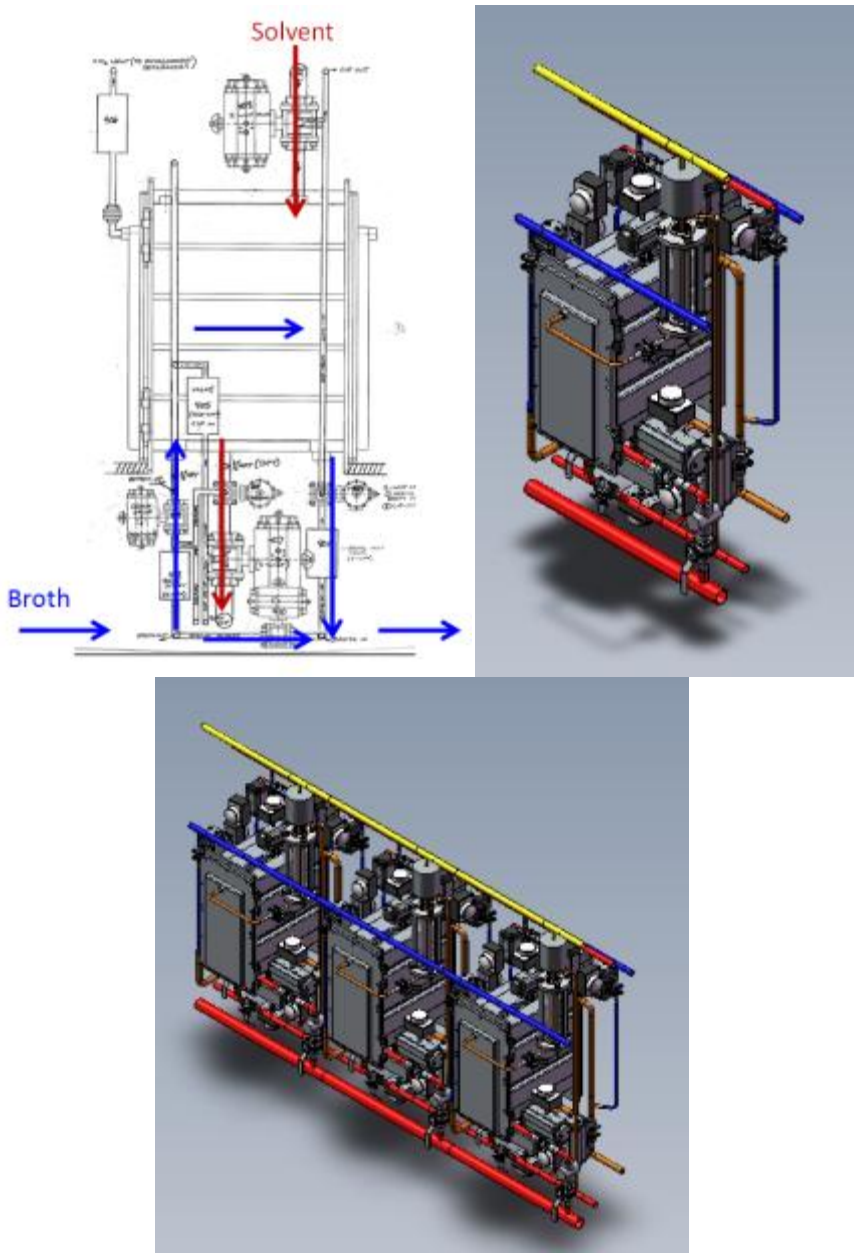


Figure 3-8: Housing unit piping flow.

Each housing unit can be taken out of service automatically, while the remaining 8 units continue operation. To do this, housing units are piped as illustrated in Figure 3-8. In order to isolate, four pneumatically actuated valves close (solvent inlet and outlet, broth inlet and outlet), and a pneumatically actuated broth by-pass valve opens. Once it is isolated in this manner, the housing unit can be drained by opening manual valves and cleaned in place. To clean in place, 0.1N NaOH is circulated to both sides of the module (solvent and broth), and then water is circulated to both sides (with drain valves closed). CIP removes a thin bio-film that can form on the membrane surface over a period of months and potentially occlude the pores. It does not appear that the flow channels of the module get plugged (with wet-mill broth), but if that were to occur, the sodium hydroxide would remove this material as well. If desired, the module can be replaced at this time, by opening the doors and removing.

Housing units are mounted in a single plane, with access to each side (Figure 3-9). Vent lines in the doors of the modules allow the escape of CO_2. Fluid lines from the vents go to a high point valve that releases gas, while maintaining the internal pressure of the fluid.

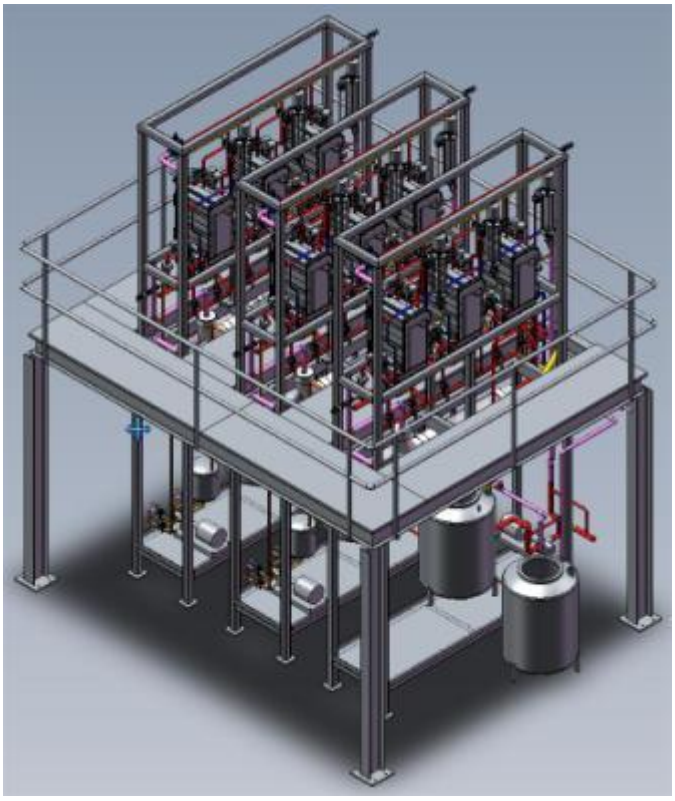


Figure 3-9: 3-D model of A-D membrane extraction skid.

Slightly higher pressure is maintained on the broth phase, compared to the solvent phase, within each module, to prevent solvent from crossing over. Each housing unit has a differential pressure transmitter coupled to ports in the broth and solvent lines at the exit to the housing unit. The control system can be programmed to trigger an alarm if the differential pressure approaches zero, and can automatically isolate the module if necessary. Anderson-Dahlen (Minneapolis) was the contractor responsible for construction of the module skid.

The cartridge-loading concept was adopted because it is a convenient way for maintenance to perform module change-out. The module fits into a stainless steel sleeve (which is perforated top and bottom to distribute solvent flow). During loading, module and sleeve slide into the housing unit together, and are centered. Doors and gaskets are then bolted on. Unloading consists of isolating the housing unit, draining both phases to a decant tank, circulating water and then removing the module.

Modeling indicates that solvent flow velocity through the module (vertical direction) is uniform in cross section. Likewise, broth flow is uniform (horizontal flow) because the overflow tube at the outlet eliminates path-of –least-resistance flow through the module. Broth and solvent streams can be heated, first by heat exchanging inlet / outlet and then heat exchanging with hot water.

3.5. Distillation Process Design

Stripping and recovery of ethanol from the solvent ternary is done by two stage vacuum distillation (P&ID Figure 3-10 and 3-D model Figure 3-11). There are two 6 inch diameter (15 ft.) packed columns. In the first column ("Solvent Column"), ternary from membrane extraction is fed mid column, cascading down through the packing material. Ethanol/water is stripped, rising as a vapor in the column. Ethanol vapor is enriched as it rises in the column, coming out at 72-84% ethanol (16-28% water). Stripped solvent becomes the bottom product of the solvent column. Bottoms product is then re-circulated to a re-boiler unit (tube and shell heat exchanger with hot oil as the heating fluid) and returned to the solvent column. A portion of this solvent bottoms product is drawn out from the system, and returned to the MSE process as fresh solvent, after cooling by heat exchange with incoming ternary, and a subsequent water cooling.

Only enough product ethanol is condensed in the partial condenser at the top of this column to provide reflux back to the solvent column (necessary for distillation). The majority is passed in a vapor state to a second distillation stage, the rectifier "Ethanol Column". In this stage, ethanol is further concentrated, coming out the top of this column at 91%. Solvent residual in this overhead product is minimal. Bottoms product in this ethanol column (rectifier) is essentially water, which is returned to the fermentation process. The condenser for this second stage is total, with almost all vapor being condensed, and either collected as product or returned to the column as reflux. A final condenser, the sub-cooling condenser, uses chilled water coolant to wring the last bit of ethanol out of the vapor, before it goes to the liquid ring vacuum pump.

Distillation operates with modest vacuums (approximately 5.5 psia in the solvent column, 4.5 psia in the ethanol column). Re-boiler duties for the two columns are measured from heat input to re-boilers B-07 and B-10, condenser cooling loads from heat transfer in partial condenser B-09, total condenser B-12 and sub-cooling condenser B-14. Cooling water supply to these condensers is from ADM's cooling tower. Fusel oils accumulating in the ethanol column can periodically be purged by a side draw and recovered through a separate line going to the sub-cool condenser. The process is designed for a feed rate of 10,500 g/hr ethanol at a composition of 3.9 wt.% ethanol, 1.7% water, 94.4% 2,6-dimethyl-4-heptanol.

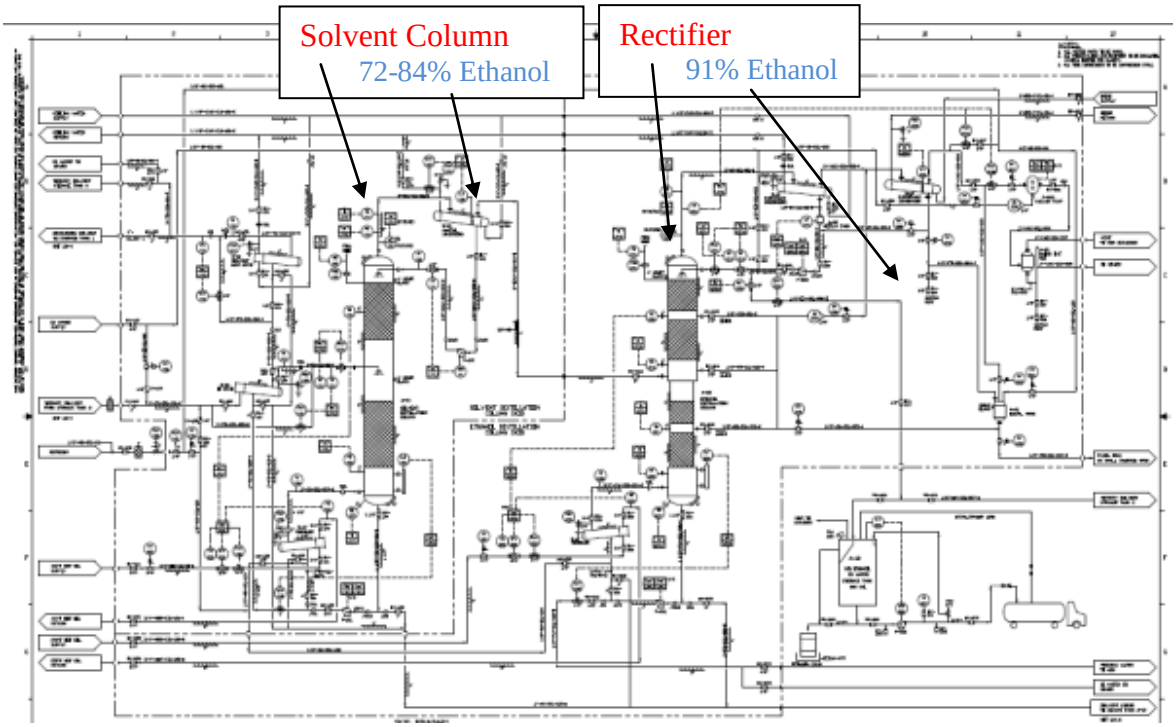


Figure 3-10: EPIC distillation P&ID.

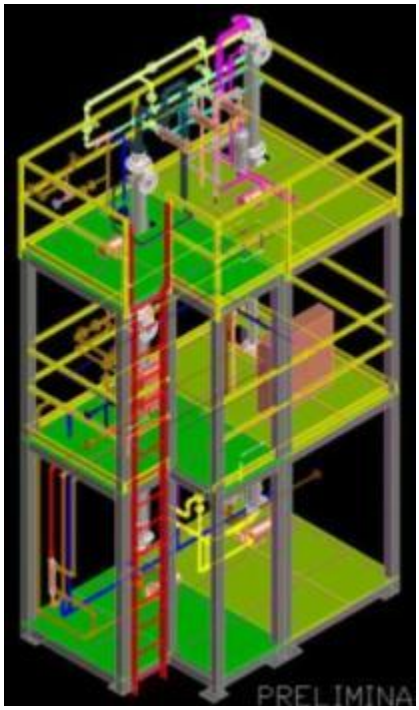


Figure 3-11: 3-D model of the distillation skid.

3.6. Process Instrumentation and Control

Because of process complexity and vulnerability of fermentation to process upsets, modern ethanol plants typically employ sophisticated instrumentation and control to maintain tight specifications during continuous 24/7 operation. It is common for the entire operation to be run from a control room with two or three operators. In design of this process, a decision was made to employ a similar level of sophistication in instrumentation and control, as this will be expected at the next level. The system design is the same as will go into a full scale plant of the future. The only difference will be size of tanks, pumps etc. Much of this instrumentation and control package can be, and likely will be, put into actual use on the full scale process to follow.

Process information derived from these experiments will be acceptable to the bio-fuel industry, as it will have answered relevant process questions their experts will have about such a new approach, using equipment and control procedures familiar to them. Solutions for most process specific problems likely to occur in continuous operation have been identified and mitigated. One of the tasks in the trials is to develop specifications for full scale plant operation - experience and data from the fully instrumented process will enable us to do this.

In January 2011, ADM Operations assigned an experienced instrumentation and controls engineer to develop the control architecture for the process. Each of the three sections (Fermentation, Membrane Extraction, and Distillation) has a dedicated programmable logic controller (PLC). Individual PLC's are linked to a central (ADM "D-3") control system. The system concept is shown in Figure 3-12. Details of the system were developed and documented. The entire process is monitored and controlled from a central graphic control panel/touch screen HMI. The control room (not Class 1 rated) is located immediately behind the Fermentation section. Individual HMI's at the membrane extraction and distillation skids themselves enable input during situations, such as startups, where it is necessary to see the process and make rapid changes in response.

Process narratives were completed for all three sections. To develop these narratives, the process and instrumentation diagrams are systematically reviewed for detailed operation at anticipated normal operation, interrupted operation, start-up etc, as seen from the perspective of an operator. From this written description of the desired operation of the system, the valve and instrument types, locations, etc. are specified. A plan of communication between transmitters (sensors) and motor controllers, valve actuators etc., is selected to provide the necessary response. Particular attention is paid to system response to upsets such as a pump failure, total and partial electrical failure, dead-heading of pumps etc. This all was input to a formal Hazard and Operability Analysis (HAZOP) review.

Since the process was installed in a flammability Class 1 area, all wiring had to be intrinsically safe. For scale-up, distillation may require intrinsically safe or explosion proof, but membrane solvent extraction and fermentation will not. The extraction solvent, 2,6-dimethyl-4-heptanol is classified as combustible (it burns like candle wax).

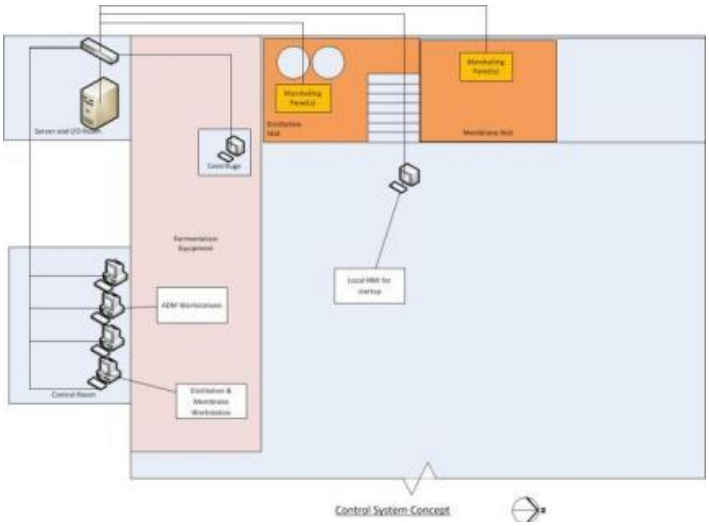


Figure 3-12: Programmable logic controller system concept.

3.7. Construction / Installation

3.7.1. Fermentation Construction and Installation at EWA: January – August 2012

Figure 3-13: Top of skid view of fermentation process.
Fermentor C (left) and Beerwell tank (right) in the foreground.
Fermentor B (left) and Fermentor A (right) in the background.

3.7.2. MSE Skid Assembly and Installation (2012)

Figure 3-14: MSE skid assembly at Anderson-Dahlen.

Figure 3-15: MSE skid installed at ADM EWA.

3.7.3. Distillation Skid Assembly and Installation (2012)

Figure 3-16: Distillation skid assembly at EPIC Systems (2012).

Figure 3-17: Distillation skid installation at EWA (2012).

3.8. Experimental Plan

An experimental plan (Figure 3-18) was drawn up to structure process experiments around 72 hour continuous operation (essentially one week experiments accounting for startup and shut down). For baseline experiments (Figure 3-19), thin broth after extraction with MSE would be discarded; yeast solids would also be discarded. For acceleration mode (Figure 3-20), the extracted broth would be returned to the fermentation process.

A sampling plan (Figure 3-21 and Table 3-1) was drawn up that includes High Performance Liquid Chromatography (HPLC) measurement of fermentation parameters such as concentrations of glucose, fructose, maltose, ethanol, acetic acid, glycerol, lactic acid. Also included are gas chromatograph (GC) measurements of ethanol / water concentrations in solvent ternaries in the MSE and distillation processes.

Data logging was established to continuously record key process parameters such as temperatures, flow rates and pressures. Analytical and data logging information during MSE extraction were recorded in a Master Data Table. This table includes calculations of distillation re-boiler and condenser duties.

Full process startup can take as much as 24 hours to complete, and changes to the system can take 24 hours or more to work their way through. Re-boiler and condenser duties can be calculated from 24 hour steady state intervals, but to get realistic fermentation acceleration information (which requires a material balance comparison of fermentors operating in the acceleration mode versus baseline mode), a longer interval is needed.

Figure 3-18: Full Process Experimental Plan (Wet-Mill Cascade)

B Stage Extraction / Yeast Recycle

Fermentation/MSE/Distillation – Full Process
Comparative experiments with 31% solids – blended mix + malto dextrin (CR-15)
1. Blended mix + CR-15 / extract thin broth / discard yeast (pre-extraction baseline)
2. Blended mix + CR-15 / extract thin broth / recycle yeast to Fermentor B
3. Blended mix + CR-15 / extract thin broth / recycle yeast to Fermentor B / extracted broth to Ferm B
4. Blended mix + CR-15 / extract thin broth / discard yeast / no broth return (post-extraction baseline)

Comparative experiments: increase solids to 36% (increase malto-dextrin)
1. Blended mix + CR-15 / extract thin broth / discard yeast (pre-extraction baseline)
2. Blended mix + CR-15 / extract thin broth / recycle yeast to Fermentor B
3. Blended mix + CR-15 / extract thin broth / recycle yeast to Fermentor B / extracted broth to Ferm B
4. Blended mix + CR-15 / extract thin broth / discard yeast / no broth return (post-extraction baseline)

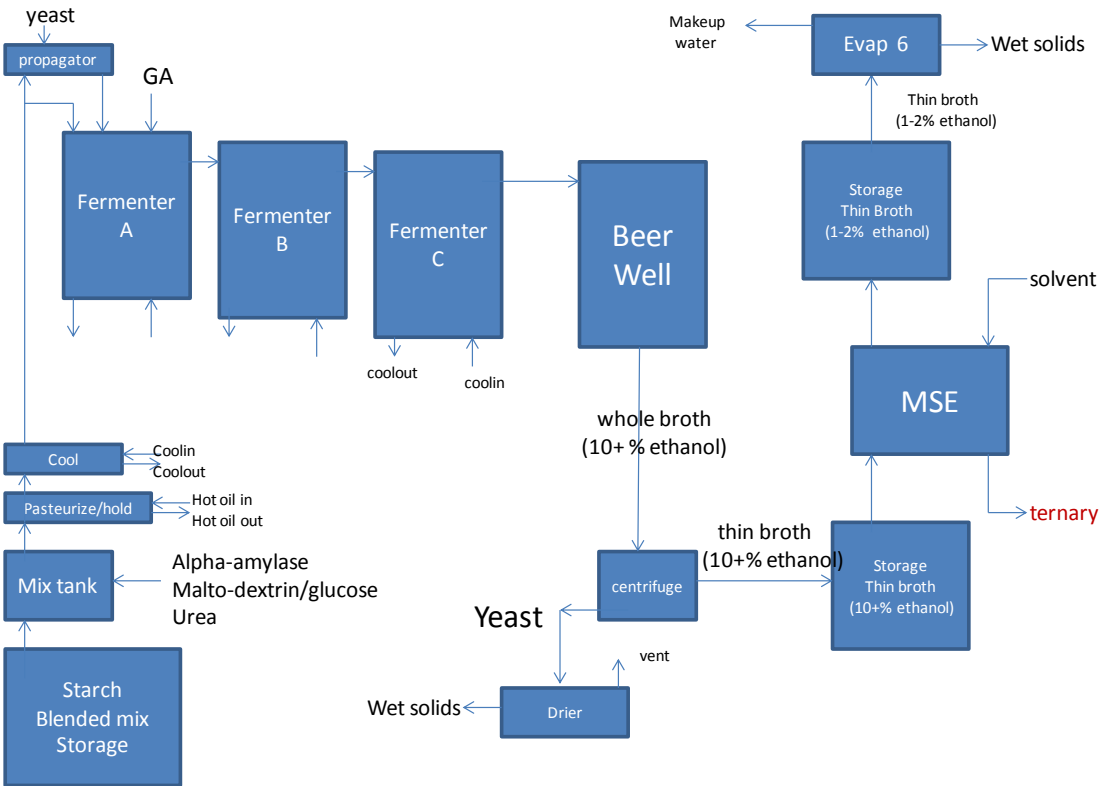


Figure 3-19: Wet-Mill Cascade Baseline (Straight Through) – flow diagram

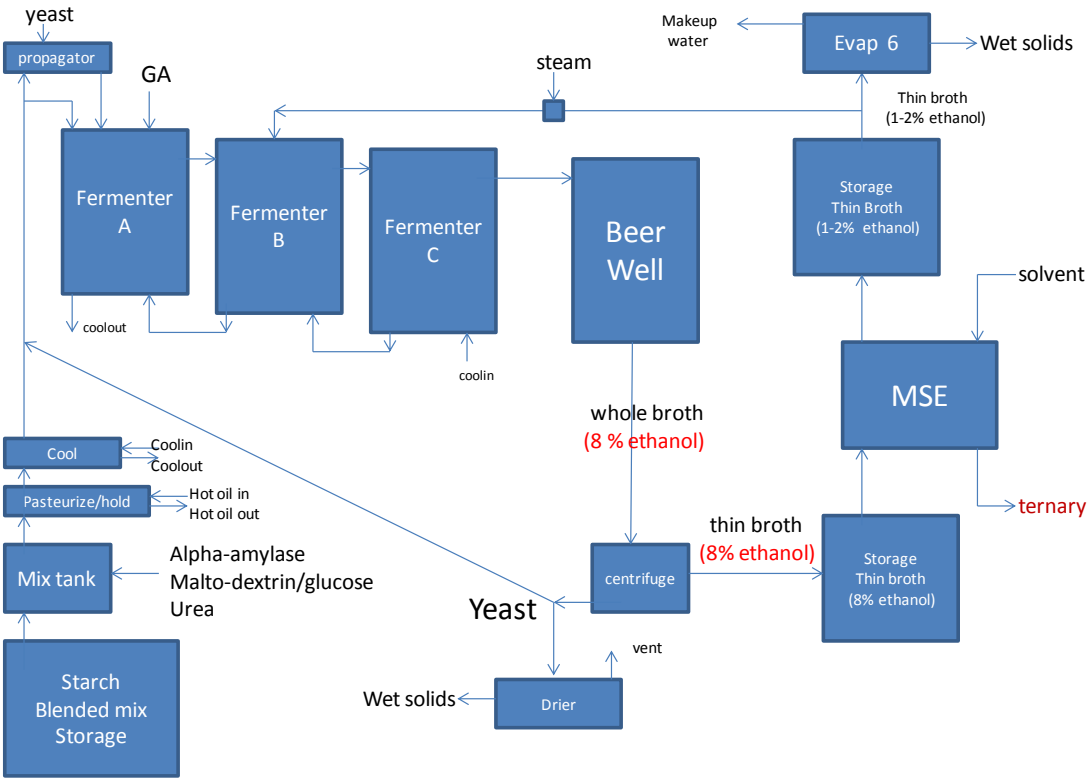


Figure 3-20: Wet-Mill Cascade (Acceleration Mode) – flow diagram

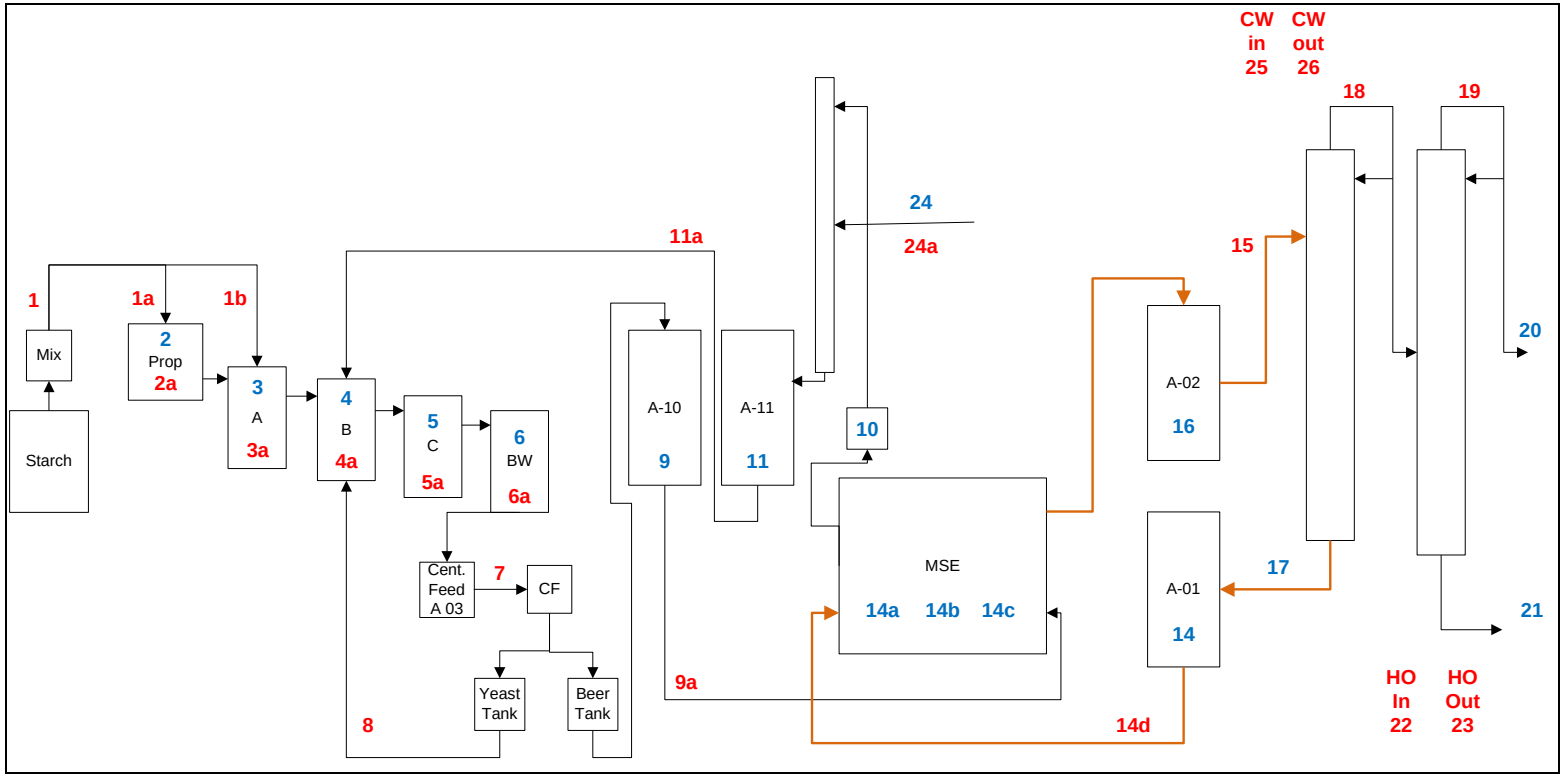


Figure 3-21: Experimental Sampling Plan

Table 3-1: Experimental Sampling Plan

Analytical Data			Computer Data Log	
2	Broth Composition of Pre-ferm	HPLC	1	Flow Rate of Broth to Fermentors (pump 4)
3	Broth Composition of Ferm A	HPLC	1a	Flow Rate of Broth to Pre-ferm (flow meter)
4	Broth Composition of Ferm B	HPLC	1b	Flow Rate of Broth to Ferm A (flow meter)
5	Broth Composition of Ferm C	HPLC		
6	Broth Composition of Beerwell	HPLC	2a	Temperature of Pre-ferm
			3a	Temperature of Ferm A
9	Composition of Clarified Broth in A10	HPLC	4a	Temperature of Ferm B
10	Composition of Broth out of MSE	HPLC	5a	Temperature of Ferm C
11	Composition of Broth after Karr Extraction in A11	HPLC	6a	Temperature of Beerwell
14	Composition of "fresh" solvent in A-01	GC	7	Flow from Beer Well to Centrifuge (pump 20)
14a	Composition of ternary tank A-03	GC	8	Rate of yeast recycle. (no way to monitor)
14b	Composition of ternary tank A-04	GC		
14c	Composition of ternary tank A-05	GC	9a	Flow Rate of clarified broth to MSE (pump 10)
				No Flow rate measurements of Broth out of MSE
16	Composition of Solvent/EtOH out of MSE	GC	11a	Flow Rate of Broth Recycle to Ferm B (pump 11 and flow meter)
17	Composition of Solvent column Bottoms	GC		
20	Composition of Final Product	HPLC	14 d	Flow rate of Solvent from A-01 to MSE (pump 01)
21	Composition of Process Water off Rectifier Bottoms	HPLC	15	Flow Rate to distillation from MSE through A-02 (pump 02)
24	Composition of Dodecane Input.	GC		
			18	Reflux Rate (pump 162)
			19	Reflux Rate (pump 262)
			22	Hot Oil Input Flow Rate and Temperature
			23	Hot Oil Output Flow Rate and Temperature
			24	Flow rate of Dodcecane in. (pump 15)
			25	CW Supply Flow Rate and Temperature
			26	CW Return Flow Rate and Temperature

4. Summary of EWA Experiments

4.1. Process Commissioning: September - December 2012

Once installation was complete, instrument checkout and calibration was conducted. Proper communication between transmitters and the various motor controllers, valve actuators etc. was established.

The system controller used for the process is a NovaTech D/3 System. D3 is used throughout ADM as a production control process. The EWA process is a sub-set and therefore, can be developed and adapted for a full scale version of this process. Human-machine interface (HMI) computers were installed in the control room, and next to the process itself. The EWA process is controlled from seven touch screen control panels shown in Figure 4-1 to Figure 4-7

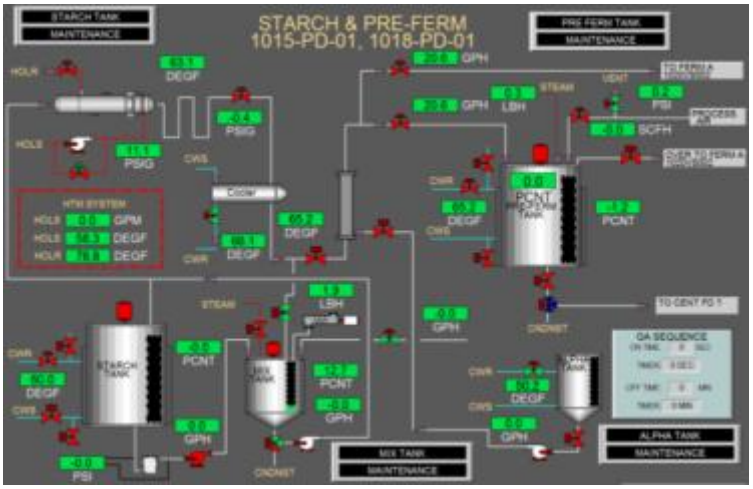


Figure 4-1: Example of Starch Feed Screen in the D3 System

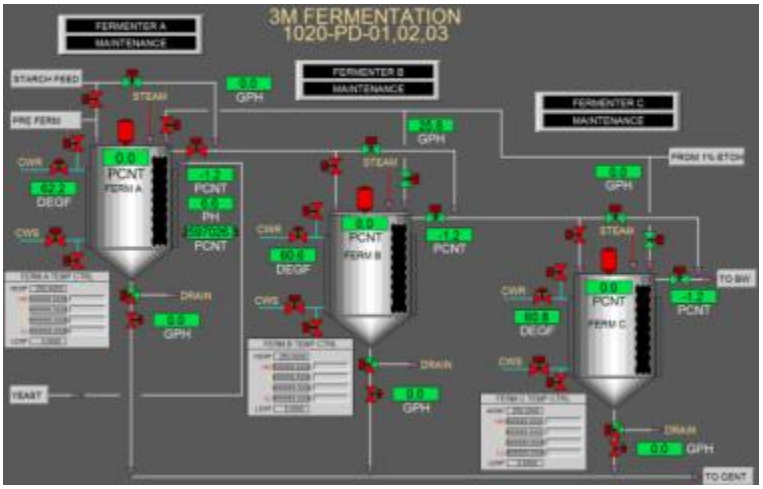


Figure 4-2: Example of Fermentation Screen in the D3 System

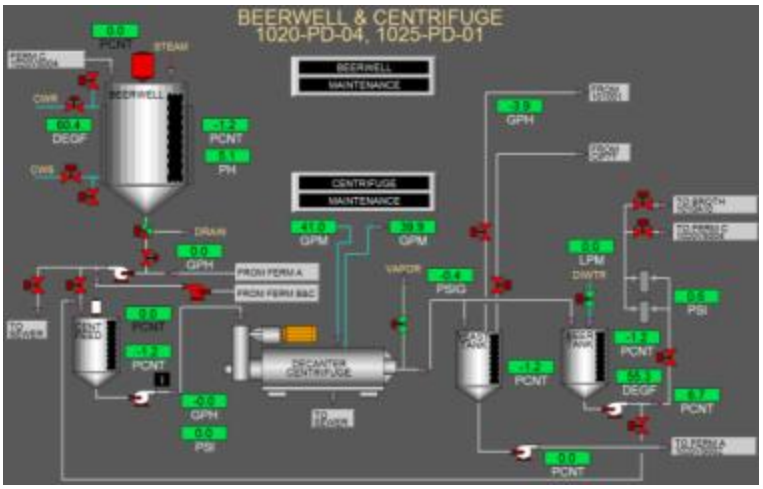


Figure 4-3: Example of Beerwell and Centrifuge Screen in the D3 System

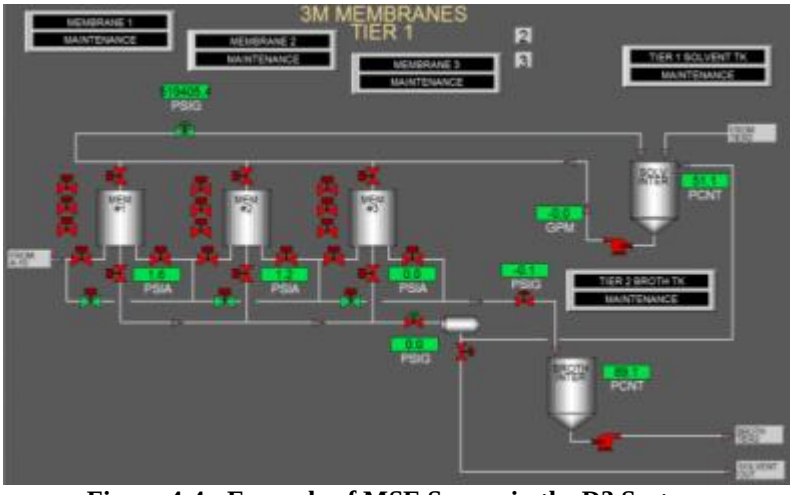


Figure 4-4: Example of MSE Screen in the D3 System

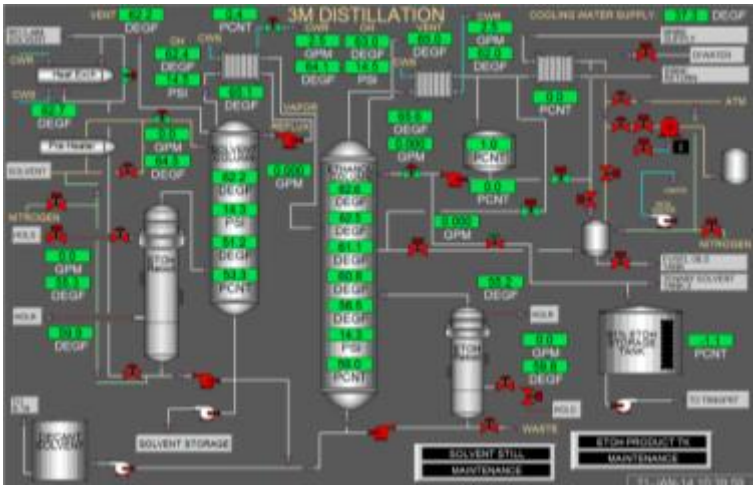


Figure 4-5: Example of Distillation Screen in the D3 System

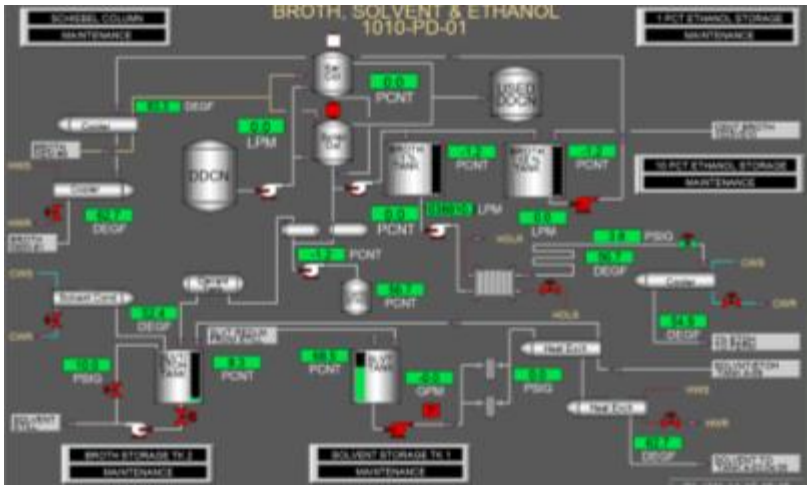


Figure 4-6: Example of Broth Solvent Loop Screen in the D3 System

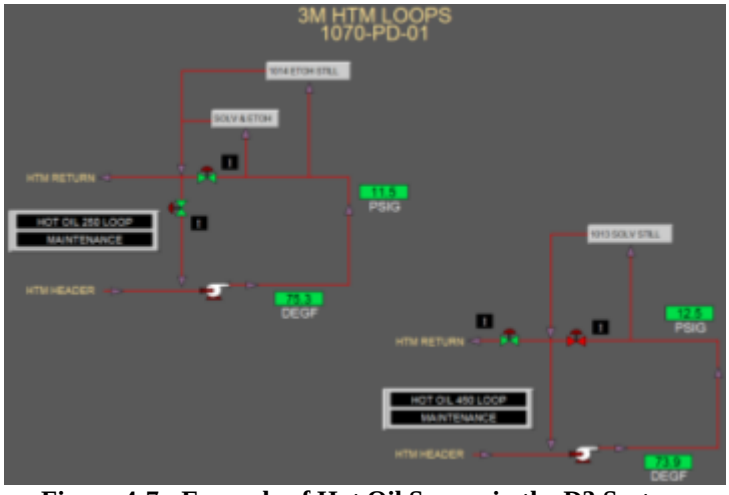


Figure 4-7: Example of Hot Oil Screen in the D3 System

4.1.1. Membrane solvent extraction (MSE)

For MSE, the following commissioning experiments were performed:

1. Control function tests were completed on all instruments, valves and pumps.
2. Ranges were specified for proportional (Baumann) valves.
3. Ranges were specified for intermediate tank level transmitters.
4. Logic in the selection of fail-safe positions was worked out during hazard review meetings in the design phase.
5. Fail safe positions were assigned for valves.
6. Control gain and sampling interval on proportional valves were tuned to get stable, oscillation damping response to changes.

MSE takes about 3 hours to start up and line out; once completed, the system is stable, and will effectively run itself. Correction of one design anomaly in the way MSE is controlled is recommended for future work: action of the solvent advance valves is coupled to the solvent pressures within the modules and these valves can be over-ridden by large hand valves in series with them. Valve re-location and a configuration change need to be considered.

4.1.2. Distillation

For distillation, the following commissioning experiments were performed:

1. Control function tests were performed on all instruments, valves and pumps.
2. Ranges were specified for proportional (Baumann) valves.
3. Ranges were specified for bottoms product level transmitters
4. Fail safe positions were assigned for valves.

4.2. Process Development Experiments

The first step, begun in November 2012, was to learn how to operate individual sections and develop operating procedures. It was March 2013 when the first full process experiments were performed, integrating the three sections. More problems were encountered than anticipated, particularly with distillation. This was caused in part by the deposition of sugar and vegetable oil from the solvent and its subsequent charring from hot oil heating.

4.2.1. Fermentation

Blended starch mixture from the ADM East Plant was supplied daily in 250 gallon totes. Initially this was fed to the process at a rate of 9 gal/hr; later the rate was increased to 16 gal/hr. Feed rates were chosen to produce approximately 10.5 kg ethanol/hr. HPLC measurements of fermentor parameters (concentrations of maltose, glucose, fructose, ethanol, acetic acid, lactic acid and glycerol) were made every 12 hours, and fermentor temperatures and broth flows were recorded continuously by data log. This information was transferred to a Master Data Table for the intervals in which the full process was run. Fermentor logs, MSE analytical data, Data Log and the Master Data Tables are not included in this report for reasons of brevity, but are available on request.

During shake-down trials in September 2012, the tube and shell feed pasteurizer plugged with sugar char (from hot oil heating). A decision was made at that time to instead hold the starch mixture at 180^{o}F between receiving from the plant, and introduction to the fermentors. For high solids experiments, solids were blended in the heated storage tanks. This became standard practice.

Fermentation was seeded in January 2013, to provide stock for MSE / distillation trials, and was operated more or less continuously until November 1st. There were three upsets that required clean out / CIP and re-start, but other than that, operation was continuous. Feed was slowed to 9 gallons/hour on weekends. Ethanol in the finished broth was consistently in the 8 - 12 wt % range. Most MSE extractions used broth with this ethanol content. Sugar levels varied. Broth was separated by disc centrifuge into a serum fraction which was extracted by MSE, and a yeast solids fraction which was re-cycled to fermentation during some experiments, to augment the yeast.

4.2.2. Membrane Solvent Extraction (MSE Process)

Startup was conducted first on a single tier of modules, using water and solvent. Modules were filled in sequence with water on the "broth" side and air on the solvent side. All pressurized properly, and held a 2 to 3 psia pressure differential. Once solvent was introduced in parallel mode, it was found that a nearly uniform 1 psia differential could be obtained in all three modules, by adjusting "broth" back pressure to about 2 psia, and maintaining a slight back pressure (0.5 to 1.0 psia) on the solvent.

Experiments were repeated with ethanol / water mixtures, and then with fermentation broth. Fermentation broth was the most difficult of the three to control. Its ion content is higher than ethanol /water and appears to have a little more mutual solubility with the solvent. Cross-over of average wet-mill broth to the solvent was found to be about 1-2 liters/hr for a tier of three modules. This is OK, and actually was found, based on transfer rate, to be one of the indicators that modules were operating properly, i.e. pores are open. Broth is collected in a decant tank, and can be discarded, or returned to the process through the Scheibel column.

Rupture tests were performed on these three modules. Broth back pressure was ramped up until differential pressures were about 6 psia, and then this pressure was held for several hours. None of the three ruptured. Differential pressures were increased to 8 psia and there was no rupture. However, at 10 psia, one module did rupture after about one hour. Pressure, however, may have spiked during that time at a pressure above 10. On the basis of these experiments, pressure relief valves with 6 psia release were installed on the module doors. 5 psia was specified as a safe operating differential. In the ten months of experiments following this, differential pressures were kept at or below 5 psia, and no module ever ruptured under those conditions.

High point gas ejector valves were installed above each housing unit, anticipating CO2 release from the broth (which was prominent in whole broth experiments in 2008, causing severe pressure swings in the modules). There was no sign of CO2 release in the housing units in these experiments, probably because the centrifuge had de-gassed the broth serum. These valves, which release gas but hold fluid pressure, did aid in keeping the housing units filled with broth, and were effective skimmers of crossed-over solvent. If whole broth is processed, there will be CO2 release, and so they need to be a part of any MSE design.

The MSE process design performed as expected, and within design parameters. Consensus of the ADM operators is that the MSE process is, with the exception of the solvent advance, a stable, forgiving process which controls well, and performed quite satisfactorily. Once current issues with transfer rate and module sealing are resolved, the overall design can serve as a model for a production unit.

Eighty modules were produced at 3M to support the EWA process development experiments. One lot of TIPS membrane from a production run in the 3M Decatur Alabama plant was used throughout, to keep that part constant (the material was polypropylene; membrane pore size varied from 0.3 to 0.4 micron - film thickness was 3 mil). Modules, however, were assembled under a variety of conditions as part of the module development portion of the DOE program. Thus it is possible to correlate assembly conditions with module performance in these experiments.

Mounting modules vertically eliminated the problem of displacing air from the solvent side during startup, and likely reduced the possibility of vapor lock in flow channels. Feeding solvent from the top down cleanly displaced crossed – over aqueous phase out the bottom. Operating with about a 1 psia back pressure on the solvent phase insured that solvent level stayed at the top of the housing unit. This level was checked periodically by opening a hand valve at the top and bleeding air (insuring that all membrane surface gets used). Vertical mounting should be used in future design.

Seal integrity between module and housing unit was sound for most new modules. Integrity was probed by applying differential pressure of about 2-3 psi (initially with broth on one side / air on the solvent side, but after introduction of solvent, with both phases present). Good units hold pressure indefinitely. As modules were continually immersed in solvent over several months in the housing units, seal integrity deteriorated in some cases. Examination indicated two likely causes: 1. Seal internal separation or displacement of the seal from the flat between module and door, 2. module expansion and layer de-lamination in the perimeter seal areas (where the module is under compression). The original two part seal was replaced with a single piece molded seal made of a 3M Dyneon Fluoroelastomer. This design will be used in the future. Seals will be secured in a gasket well in the door. Modifications will be made to the module to address expansion and de-lamination.

4.2.2.1. Broth Series Circulation

Control of broth flow was flawless. The design and procedures used in these experiments should be considered in any future design. Standard Operating Procedures were written with the two ADM operators, and will be part of an internal report. Controlling three modules independently as a tier was the correct decision. Pneumatic valves and the pilot valve system were used for two reasons: 1) This combination is safe for operation in the flammability Class 1 area where the experiment was located, 2) control is operator-friendly, linking opening and closing of the two or three valves to a single control function. These valves and this control scheme were virtually 100% reliable throughout the experiments.

Once startup pressure oscillations had damped out, pressures within a tier became stable. This was in part due to proper tuning of the control, but also because the long fluid path through three modules provided "cushion". Set point adjustment of the tier broth back pressure was an effective method to control the differential pressures within individual modules, to ensure that they did not approach a zero point. Both the solvent and broth (tier) back pressures were sufficiently stable that differential pressures really did not drift that much in parallel solvent mode. There was ample warning before drifting into dangerous territory - only periodic tuning was required.

Rates for the broth pumps supplying Tiers 2 and 3 effectively controlled from levels in the intermediate tanks. The only problem is that there is no way to bypass if a feed pump were to seize.

Broth circulation was left on for months at a time, continuously going through the nine modules. This circulation was to minimize bio-film formation on the membrane surface.

Consideration should be given to increasing the number of modules within a control string, to economize on controls. Differential pressure monitoring should be continued for now, until additional experience has been gained.

4.2.2.2. Solvent Circulation within a Tier

Parallel solvent flow produced stable differential pressures in all three modules of a tier, provided a small back pressure was applied to the solvent exiting the tier. The back pressure valves controlling this are a bit remote from the solvent collection header (exiting solvent must go through the gravity separator before encountering the valve). This can create anxious moments during startup, but during normal operation, control is fine. Solvent level in modules was checked about once a day, and if necessary, adjusted by bleeding air.

Solvent was circulated to the three modules at 75% of the circulation pump maximum in all experiments (90 liter/min to the tier, 30 liters/min each module). These flow conditions were selected from previous experiments with similar size cross-flow modules.

4.2.2.3. Solvent Advance

The solvent advance system described earlier, worked well in parallel flow. Intermediate tank levels remained stable provided that large, abrupt changes were not made to the solvent feed rate. Experience led to making small changes (20% or less) each time, to allow solvent surge to work its way through (to avoid upset of differential pressures).

There is one configuration flaw that should be corrected before this solvent advance system is taken forward (and it should be). The hand valve in the recirculation line (which creates back pressure to drive the solvent through the automatic advance valve), over-rides the action of the auto valve, and effectively becomes the control. Small adjustments to this hand valve create exaggerated effects, making control difficult, particularly in series mode.

The second problem is that the action of the automatic advance valve currently is coupled to solvent pressure within the modules. As this valve opens and closes, it can create a large oscillation in module solvent pressure. There were times, particularly in series solvent flow, that pressure differential in the modules went negative (solvent pressure went above the broth pressure). This will cause rapid cross-over of solvent to broth, and the situation can quickly get out of hand. This will be examined by ADM control engineers and a plan drawn up to address.

4.2.2.4. Gravity Separator

The gravity separator system to draw off crossed-over broth from the solvent, works fine, and it should be part of any new design. Some cross-over of broth to the solvent is a normal part of the process. However, solvent only crosses over to broth if there is a process upset – it winds up in the high point vent valves of the modules, or in the tops of the module doors. It can be returned to Decant Tank A-18 by opening a hand valve. These events were rare, except in series operation. When they do happen, they

need to be dealt with quickly. The indication of trouble is deterioration in differential pressure. The fix is to remove the solvent from the top of the housing unit, and allow broth level to re-establish.

4.2.2.5. Line Filters

A 400 micron 3M (CUNO) bag filter was installed in the broth feed to MSE, and a cartridge filter was installed in the solvent line. Both are there primarily to remove particulate debris, such as machining slag. Whole wet-mill broth will pass readily through the bag filter.

4.2.2.6. Module Life

Robustness of the modules was very good. Modules appear to be capable of standing up to months of continuous broth circulation, multiple 50 to 72 hour intervals of solvent extraction, repeated clean in place procedures with 0.1% NaOH at room temperature, and multiple low pressure upsets (up to 6 psia pressure difference between phases). Three of the modules are in their seventh month of more or less continuous service, with continuous immersion in broth and solvent.

Modules have withstood an internal pressure differential (broth to solvent) of up to 10 psia, without rupturing. In one occurrence due to a power outage over the weekend, pressure spiked (with unknown peak pressure) and apparently ruptured two modules, as the back pressure valves failed to open (air loss) at a time that the positive displacement broth feed pumps turned on. Pressure relief valves with a 6 psia release were installed on the broth sides of the modules that should have prevented this, but did not. An inter-lock between broth back pressure valves and the broth feed pumps will be programmed to automatically shut down the feed pump if broth pressure exceeds 6 psia.

4.2.2.7. Transfer Rate

Transfer rate was less than expected, particularly in later experiments. This is likely due to one of several causes: first, the room temperature clean in place (CIP) procedure to remove bio-film was inadequate. It was determined that higher temperatures and longer circulation intervals, as well as inclusion of a surfactant with the hydroxide would improve the performance. Second, the membrane pores may have been occluded by residual sugar from the broth. Finally, hot air bonding used in part of the module making process may have collapsed the pores in the membrane, particularly in modules run during later experiments. Potential membrane damage in fabrication is being investigated.

4.2.2.8. CIP

The Clean in Place (CIP) system, which is independent of the solvent and broth valving, provided rigorous circulation of CIP solution (0.1 N NaOH) to a single module, a tier of 3 modules, or if desired, all nine modules. CIP solution circulates through broth and solvent sides of the modules. Pressure differential in modules went as high as 3.5 psia during filling, but then settled down to 2 psi or less during circulation. Thus, there was no risk of damage. However, efficacy of the room temperature CIP process needs to be verified.

There was no apparent damage to the modules from 4 to 5 CIP cycles at room temperature. However, problems were encountered in an experiment in which CIP was run at 135^{o}F. All nine modules were destroyed as a result of module expansion and de-lamination, and seal separation. Module expansion like that encountered in this experiment can be compensated for in the initial manufacturing process, however, some re-design of the module may be required. The original two part housing seals were replaced with a single piece molded seal made with a 3M Dyneon fluoropolymer. This seal design should be carried forward.

The CIP system was easy to operate, but, as stated, gave mixed performance in restoring transfer rate, when operated at room temperature for one hour. For a commercial process, CIP will be performed routinely on a preventive maintenance schedule. The system is designed so that any number of modules can be taken out of service, while the others remain in operation (modules do not have to be removed).

Currently it is expected that this would be done every month or so, but additional experiments will be performed to define the interval.

4.2.3. Distillation

4.2.3.1. Design

Overall design of the two stage vacuum distillation process is correct. This skid is producing 91+ % ethanol final product, when solvent ternary mixtures containing 2-4% ethanol/ 1-2% water are fed to the solvent column. There was initial concern that the sweep design (i.e., a single vacuum drawing through both the rectifier and solvent columns) would not work. The experiments indicate that this design does function. Therefore, there is no reason to change to individual pressure controls on the solvent column and rectifier.

4.2.3.2. Initial Distillation Experiments

Distillation was started up with ternary mixtures made by spiking the solvent with ethanol and water in Storage Tank A-02. Ternary was fed to the mid-point of the evacuated (and inerted) solvent column and the distillation bottoms product was returned through a level control valve to Tank A-02. Product (91% ethanol) was re-cycled to Tank A-02 so a constant composition could be maintained in the ternary.

Hot oil flow to the solvent column re-boiler initially was controlled automatically off the upper column temperature. This procedure led to a solvent blow-over to the rectifier due to the column heating too rapidly, thus causing a vapor bubble in the packing. Therefore, after that incident, the hot oil flow was manually controlled and the column was heated at a slower pace. The mid-column was monitored through a sight glass, in order to not over fill the column with solvent.

To generate sufficient pressure to drive the bottoms product solvent out of the column (back to storage A02), an orifice plate was installed in the re-boiler recirculation loop at the entrance to the column. The re-circulation pump generated enough pressure between its discharge side and the orifice plate to drive the solvent out of the solvent column and over to storage Tank A-02. This scheme worked well initially. Consistent solvent levels in the solvent column were maintained, but in a number of the experiments complications arose when two things occurred: First, char from sugar and vegetable oil deposition accumulated on the orifice plate and began plugging its opening; secondly, seals on the re-circulation pump failed, so that insufficient pressure was developed to drive the solvent over.

Level control in the rectifier was maintained by a similar orifice plate mechanism. This worked better in the rectifier since the bottoms product stream did not contain the char encountered in the solvent column. However, its control also eventually proved to be erratic, likely due to pressure reductions on the discharge side of the re-circulation pump from similar failures of the water cooled seals.

4.2.3.3. Heat Delivery to Solvent Column

Throughout the experiments, inadequate heat delivery to the solvent column was a problem. This problem manifested during initial trials with spiked ethanol/water mixtures. While supplying feed to the column, pot temperature could not reach a temperature of >200^{o}F, that was necessary to strip ethanol/water at the specified levels of 10.5 kg/hr. The problem was determined to be in part due to inadequate sizing of the column re-boiler and inadequate sizing of the solvent / solvent heat exchanger. The problem was made considerably worse by deposition of sugar and vegetable oil on the surfaces of these two heat exchangers, and subsequent baking on by exposure to 400+ F hot oil. Sugar and vegetable oil dissolve (to about 0.1 %) in the extraction solvent as a result of contact with fermentor broth. This deposited layer can build up to 1/16” to 3/8”, impeding and eventually shutting down heat transfer. Heat delivery to the column, which already was below specification, deteriorated to unusable levels within 24-48 hours of operation in a number of the experiments.

This insufficient heating caused incomplete stripping of the ethanol from the ternary. Ethanol levels in the ternary typically would not go below 1% in the solvent bottoms (need about 0.3%).

Therefore, ethanol yield in the product was lower than planned. These problems were contributing factors to the decreased MSE transfer rates. Performance of the overhead reflux and product flows was also affected by the insufficient heat (as well as design issues in the distillation overhead).

The original (2 ft^2) tube and shell heat exchanger was replaced with a 5 ft^2 tube and shell. This improved heating performance initially. However, its performance deteriorated as well, with exposure to 400+ F hot oil. The ¼" to 3/8" tubes in these units became restricted, and in some cases totally plugged. After each run, char in the heat exchangers was rodded and then the heat exchangers were cleaned in place (CIP) by circulating NaOH solution through the solvent side. This improved heating at the start of the next experiment, but eventually heat delivery would again deteriorate.

Char buildup at the orifice plate caused a restriction in the solvent re-circulation, further exacerbating the problem. To alleviate this problem, parallel in-line filter baskets in the solvent re-circulation line were installed in order to capture char. In some of the experiments, these filters were cleaned out as often as every hour to maintain flow. After each cleanout, the pot temperature would rise for a period of time, as circulation to the re-boiler improved. A gate valve was installed in the solvent recirculation line to act as a variable diameter orifice plate. This functioned for awhile before it too plugged with char. The hot oil system was eventually modified to deliver lower temperatures to the column resulting in a reduction of temperature from 450°F to 260-280°F. This extended the time before heat transfer deteriorated, but performance eventually deteriorated to unusable levels. Reducing the temperature of the heating medium is one improvement that should be implemented in future designs. Steam heating is a likely candidate.

4.2.3.4. Decant Unit

In later experiments, a decant unit was installed to remove sugar from the solvent returning from distillation. Solvent is passed through a layer of water to strip some of the sugar. The solvent became noticeably cleaner once the decant system was used. These decant experiments were conducted in conjunction with solvent stripping using an ADM evaporator unit (ADM R4). Before coupling in the decanter, this evaporator quickly fouled with sugar char. The re-circulation line underneath the pot began filling with char, eventually plugging completely. Once the decanter was installed, the solvent cleaned up, and within a few days, showed no further build-up of char. The combined evaporator / MSE system then operated cleanly (with continuous extraction of broth (in some cases with sugar levels as high as 20%) for about two months without char buildup problems. The decant system proved invaluable as an addition to the system design, and should be carried forward in future designs.

4.2.3.5. Distillation Column Overhead

In virtually all experiments, there was erratic flow in the reflux and product streams of the rectifier, and in the reflux to the solvent column. This made measurement of reflux flow and reflux ratio nearly impossible. This likely can be attributed to a combination of inadequate flow (ethanol delivery) and vapor lock created by a combination of vacuum imbalances and low diameter piping. In addition the configuration of the flow control valves and transmitters was not optimal. In order to overcome these issues the overhead piping and instrument configuration was rebuilt. The majority of these changes were made in May 2013, and used in subsequent experiments. The changes did improve performance.

4.2.4. Full Process Experiments

Fermentation, MSE and Distillation were integrated in extended run experiments of 48-72 hours duration. Nine of these were in baseline mode (extracting broth from the beer well and discarding post-MSE broth) and two were in acceleration mode (returning MSE-extracted broth to the fermentors (with Karr column counter-current re-extraction with Dodecane to remove any entrained solvent)). Process conditions were deliberately varied during these experiments, to probe the performance envelope.

Blended starch mixture from the ADM East Plant was fed to fermentation at 9 to 16 gallons / hour. During acceleration experiments, solids were augmented by addition of sugar. All experiments

were conducted in cascade mode, with finished broth typically in the 6-12 wt% ethanol range. The combined process of MSE extraction and distillation consistently produced 91-94% ethanol from this. For a brief period, ethanol in the broth was at 4%; after MSE extraction of this and distillation, overhead was 86% ethanol.

4.2.5. Full Process Baseline Mode

Broth feed rate to MSE was adjusted to basically match fermentation, i.e. maintaining a constant level in broth storage Tank A-10. "Fresh" solvent feed rates to MSE were varied over a range of 0.5 to 1.5 gal/min, to probe conditions that might give the best ethanol transfer. While ethanol and water concentrations in the solvent ternary coming out of the MSE process varied widely, final ethanol product from distillation was consistently 91-94%. This probably reflects that the relative partition of ethanol and water into the 2,6-dimethy/-4-heptanol was fairly consistent, and also that the distillation process is effective. A comparable flash process would have produced 60 to 70% ethanol. Ethanol production capacities varied, and were below expectations, for reasons given above.

4.2.6. Temperature Profiles

Distillation temperature profiles were extracted from data log over what were considered representative (stable) intervals. These were recorded in the Master Data Table, and averaged over these intervals. In Table 4-1, these temperature profiles are compared to those predicted by Aspen modeling. An attempt was made to compare these at approximately the same positions in the columns. Intervals over which these temperatures were averaged are given to the right.

Experimental temperature profiles were reasonably close to Aspen temperature profiles. The real deviations from Aspen were solvent column pot and feed temperatures. Aspen calls for 264.7^{o}F pot temperature, which was only reached once for a brief period of time at the beginning of the experimental runs. Notably, this only occurred when feed to the column was shut off. With this exception, the columns were operated close to the temperature profiles of the model.

Operator experience led to running the rectifier with an overhead temperature of 120-125^{o}F to get 91% ethanol (at 4.5 psi). Running the solvent column overhead at about 136^{o}F to prevent solvent carry-over was determined by trial and error. Both these procedures became standard operating conditions after April 2013. The rectifier operated consistently as might be expected from experience with rectifiers in conventional ethanol distillation, the only difference being that the feed to this column is much richer (72-84% ethanol) than would be entering the rectifier in a conventional process (42-50%). It is this factor that enables this new process to operate with lower reflux ratios, and consequently get lower condenser duties than conventional distillation.

Table 4-1: Distillation Temperature Profile

Solvent Column							
	TT-117 (Overhead)	**TIC 107** (Top)	**TT 101** (Bottom)	**TIC 110** (Feed)	**PT 118** (Top)	**PT 105** (Mid)	**Interval**
Aspen	***136***	***136***	***265***	***237***	***4.5***	***5.5***	
April 17-19	137	137	165	126	4.7	5	18 Apr 0100 to 19 Apr 0700
April 23-26	136	142	160	122	4.7	5.2	24 Apr 0000 to 26 Apr 0700
May 7-9	127	132	143	117	4.6	5.1	7M1400-8M600/8M1700-9M100
June 18-21	125	130	125	154	4.3	4.9	20 June 1400 to 20 June 2200
June 26-28	126	126	144	139	4.5	5.1	26 June 2000 to 28 June 0800
July 1-3	129	136	127	141	3.6	4.1	2 July 0000 to 3 July 1300
July 9-12	135	140	128	144	3.4	3.9	10 July 1900 to 12 July 0400
July 16-19	135	142	126	145	4	4.6	16 July 2100 to 19 July 0500

Rectifier							
	TT-217 (Overhead)	**TIC 200** (Top)	**TT 210**	**TT 212**	**TT 211**	**TT 207** (Bottom)	
Aspen	***124***	***124***	***131***	***137***	***147***	***166***	
April 17-19	127	129	140	162	164	166	18 Apr 0100 to 19 Apr 0700
April 23-26	124	130	137	148	152	155	24 Apr 0000 to 26 Apr 0700
May 7-9	129	126	133	142	147	153	7M1400-8M0600/8M1700-9M0100
June 18-21		139	148	159	161	163	20 June 1400 to 20 June 2200
June 26-28	124	135	143	153	155	152	26 June 2000 to 28 June 0800
July 1-3	122	125	132	144	146	145	2 July 0000 to 3 July 1300
July 9-12	121	129	137	152	154	157	10 July 1900 to 12 July 0400
July 16-19		128	139	156	159	162	16 July 2100 to 19 July 0500

4.2.6.1. Distillation Re-boiler Duties

Re-boiler duties for the two columns were estimated from hot oil flows and temperatures. These are compared to Aspen of 25,180 BTU per hour for the solvent column re-boiler duty and 8,090 BTU per hour for the rectifier column re-boiler duty. The duties were calculated using the following equations and assumptions.

Assumption: Hot Oil Heat Capacity = 0.65 BTU/lb ^{o}F (XCELTHERM® 600)

$$Q = M_{HO} \times 0.65(T_{in} - T_{out})$$

Where Q is the reboiler duty (BTU/hr), M_{HO} = Hot Oil Flow (lb/hr), T_{in} = Temperature in (^{o}F) and T_{out} = Temperature out (^{o}F). These values are shown in Table 4-2 over the same intervals chosen in Table 4-1 for the temperature profiles. Re-boiler duties are slightly lower than predicted by Aspen, because ethanol yields are low. Much of the heat is consumed maintaining inventories of solvent and water vapor at the ethanol flash points in the columns. In an attempt to estimate re-boiler energy for the full 10.5 kg ethanol/hr, a compensation calculation for the flash energy of the missing ethanol was done.

Table 4-2: Distillation Re-Boiler Duties

Solvent Column			
	Re-boiler Duty (BTU/hr)	**Ethanol In Broth Feed**	**Ethanol Out Product**
Aspen	***25,180***	***%***	***%***
April 17-19	20,344	9.4	88.5
April 23-26	21,037	11.1	88.6
May 7-9	14,151	9.6	91.4
June 18-21	26,558	9.5	81.3
June 26-28	27,391	6.5	89.5
July 1-3	30,403	9.6	86.3
July 9-12	27,274	6.4	81.2
July 16-19	24,952	13.3	90.1

Rectifier	
	Re-boiler Duty (BTU/hr)
Aspen	***8,090***
April 17-19	8150
April 23-26	7676
May 7-9	7192
June 18-21	9008
June 26-28	8844
July 1-3	7386
July 9-12	7450
July 16-19	6291

4.2.6.2. Distillation Condenser Duties

Condenser duties were estimated from Cooling Tower Water (CTW) flows and temperatures where the heat capacity of water is 1.0 BTU/lb ^{o}F with a density of 8.32 lb/gal. Condenser duties for the two columns were estimated from Cooling Tower Water (CTW) flows and temperatures. These are compared to Aspen of 4,727 BTU per hour for the solvent column condenser duty and 11,570 BTU per hour for the rectifier column condenser duty. The duties were calculated using the following equations and assumptions.

Assumption: Water Heat Capacity = 1.0 BTU/lb ^{o}F

$$Q = M_{CTW} \times 1.0(T_{in} - T_{out})$$

Where Q is the condenser duty (BTU/hr), M_{CTW} = CTW Flow (lb/hr), T_{in} = Temperature in (^{o}F) and T_{out} = Temperature out (^{o}F). These values are shown in Table 4-3 over the same intervals chosen in Table 4-1 for the temperature profiles. Rectifier condenser duties for eight of the nine experiments were in the 7,000 to 13,000 BTU/hr range (compared to Aspen at 11,570 BTU/hr). The July 16-19 values are an anomaly. The solvent column condenser duties and the Aspen-derived values are not comparable to one another.

Table 4-3: Distillation Condenser Duties

Solvent Column			
	Condenser Duty (BTU/hr)	**Ethanol In Broth Feed**	**Ethanol Out Product**
Aspen	4,727	%	%
April 17-19		9.4	88.5
April 23-26		11.1	88.6
May 7-9		9.6	91.4
June 18-21		9.5	81.3
June 26-28		6.5	89.5
July 1-3		9.6	86.3
July 9-12		6.4	81.2
July 16-19		13.3	90.1

Rectifier	
	Condenser Duty (BTU/hr)
Aspen	11,570
April 17-19	12,058
April 23-26	12,406
May 7-9	7,861
June 18-21	8,616
June 26-28	7,475
July 1-3	8,871
July 9-12	8,813
July 16-19	33,103

4.2.7. Acceleration Mode

Preliminary acceleration experiments were conducted to establish operational and control procedures and to check if yeast viability would be adversely affected by return of the extracted broth. It is intended to follow these preliminary trials with complete extended interval trials. In previous acceleration experiments, broth was extracted from the final stage of Fermentation (Figure 3-20 – Fermentor C in this case) and returned to stage B to accelerate fermentation in that and subsequent stages. This effectively maintained the ethanol content at a plateau level of 8% in the B stage, resulting in a 2 to 3-fold acceleration in that stage.

One of the important factors in this is the performance of the Karr column in removing entrained solvent. Previous trials demonstrated that yeast was not adversely affected at solvent levels of 400 ppm or less in the returning broth. This was the first time an attempt was made to use a Karr column to "polish" the returning extracted broth prior to re-introducing to the fermentors. A great deal of learning was involved, but it appears this is an effective method for removing entrained solvent. A second issue is dealing with the increased sugar content of the broth coming from these earlier stages of fermentation, from the standpoint of its adverse effect on MSE transfer rate and distillation solvent column performance.

Five pilot-scale experiments were designed and implemented to achieve the primary objective while simulating wet-mill ethanol production conditions. These experiments were as follows and each experiment is described in further detail in the following paragraphs.

- Fermentation Media Composition, average % ds (dry solids)
- Post-Fermentation Centrifugal Mass Recycle
- Fermentation Media Composition, high % ds
- Fermentation Broth Extraction (Fermentation Tank B)
- Fermentation Broth Extraction (Fermentation Tank A)
- Returning Filtered Supernatant Water Phase to Fermentation Tank A.

Fermentation Media Composition, average % ds
Approximately 510 gallons of average % ds, corn wet-mill production media was pumped into a 1052 gallons (total working volume) continuous fermentation system at 9 gallons/ hour. The pre-fermentation tank was inoculated using a commercial *Saccharomyces cervesiae* strain. When fermentation broth surpassed 1052 gallons, overflow (beer well) was centrifuged and centrate ethanol was separated from water, sugar, organic acids etc. using membrane technology and distillation.

Post Fermentation Centrifugal Mass Recycle
510 gallons of average % ds, corn wet-mill production media was pumped into a 1052 gallons (total working volume) continuous fermentation system at 16 gallons/ hour. The pre-fermentation tank was inoculated using a commercial *Saccharomyces cervesiae* strain. When fermentation broth surpassed 1052 gallons, the beer well was centrifuged and centrate ethanol was separated from water, sugar, organic acids etc. using membrane technology and distillation. Solid-phase mass (cake) was pumped into fermentation tank A, in an effort to increase viable yeast cell quantity.

Fermentation Media Composition, high % ds
510 gallons of high % ds, corn wet-mill production media was pumped into a 1052 gallons (total working volume) continuous fermentation system at 16 gallons/ hour. For the purpose of this experiment, 26% ds production media was supplemented with a high glucose dilution to achieve high % ds. The pre-fermentation tank was inoculated using a commercial *Saccharomyces cervesiae* strain. When fermentation broth surpassed 1052 gallons, the beer well was centrifuged and centrate ethanol was separated from water, sugar, organic acids etc. using membrane technology and distillation. Solid-phase mass (cake) was pumped into fermentation tank A.

Fermentation Broth Extraction (Fermentation Tank B)
510 gallons of high % ds, corn wet-mill production media was pumped into a 1052 gallons (total working volume) continuous fermentation system at 16 gallons/ hour. The pre-fermentation tank was inoculated using a commercial *Saccharomyces cervesiae* strain. Broth was simultaneously extracted from fermentation tank B at 0.8-1.5 L/min and centrifuged with beer well. Centrate ethanol was separated from water, sugar, organic acids etc. using membrane technology and distillation. Solid-phase mass (cake) was pumped into fermentation tank A.

Fermentation Broth Extraction, Returning Filtered Supernatant Water Phase (Fermentation Tank B)
510 gallons of high % ds, corn wet-mill production media was pumped into a 1052 gallons (total working volume) continuous fermentation system at 16 gallons/ hour. The pre-fermentation tank was inoculated using a commercial *Saccharomyces cervesiae* strain. Broth was simultaneously extracted from fermentation tank A at 0.8-1.3 L/min and centrifuged with beer well. Centrate ethanol was separated from water, sugar, organic acids etc. using membrane technology and distillation. Solid-phase mass (cake) was pumped into fermentation tank A. Membrane filtered water phase was pumped to fermentation tank B, increasing total flow rate to 21 gal/hr (approx.).

5. Modeling

Four Aspen models were developed. All show that the overall energy of this process is 20 to 30% less than a conventional ethanol process. All show a reduction in condenser duties compared to conventional. Since evaporative cooling tower water is used to cool these condensers, this translates into a substantial water savings.

5.1. Two Stage Vacuum Distillation / Conventional Distillation Comparison

The operative model to which experimental re-boiler and condenser duties are compared is the two stage vacuum distillation process of Figure 5-1. This process is compared to a conventional distillation process with a beer column and rectifier, and simultaneous recovery of Fusel Oils. The conventional model assumes a feed of 10.1 wt% ethanol, with heat exchange between the broth feed and beer column bottoms product. Product rate in both cases is 10.5 kg/hour of 91% ethanol.

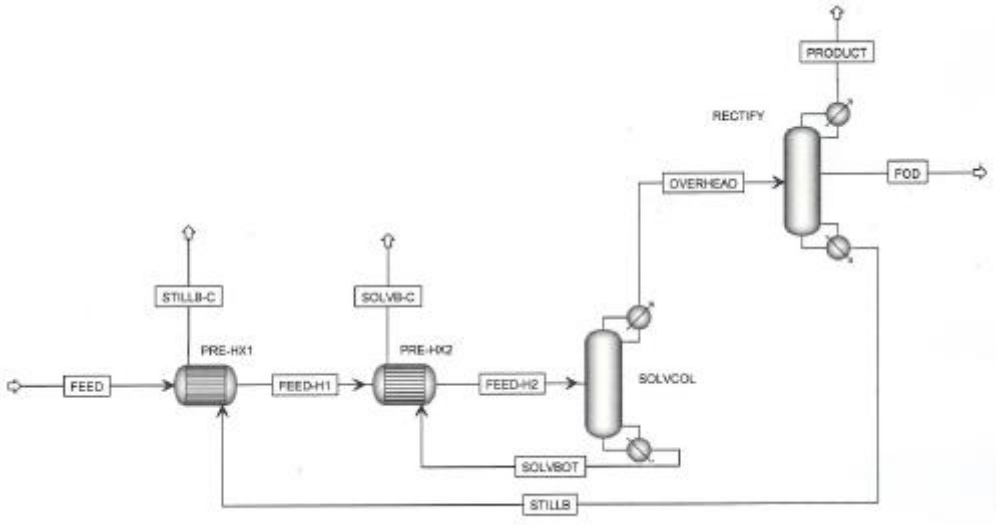


Figure 5-1: Two stage vacuum distillation process (solvent column / rectifier)

Feed to the solvent column is a ternary: 4.5% ethanol / 2.1% water / 93.4% 2,6-dimethyl-4-heptanol. Ethanol concentration in the rectifier bottoms product was set to < 500 ppm, and to 0.3% in the solvent column bottoms. Reflux ratio for the rectifier was set to 1.0.

Table 5-1: Duties for this EWA scale distillation process

	BTU/hr
Solvent Column Re-boiler duty	25,180
Rectifier Re-boiler duty	8,090
Solvent Column Condenser duty	- 4,727
Rectifier Re-boiler Duty	- 11,570

In Table 4-2 and Table 4-3, these Aspen values are compared to re-boiler and condenser duties calculated from experiments, using hot oil and cooling tower water flows and temperatures. MSE pump energies were calculated from Aspen, using typical experimental flows and pressure drops:

- Parallel solvent flow: 250 BTU/hr (includes solvent re-circulation and solvent and broth feed)
- Series solvent flow: 25 BTU/hr (includes solvent re-circulation and solvent and broth feed)

These MSE pump energies are added to the distillation re-boiler energies to get a total energy for the process. Energy savings for MSE / distillation compared to the conventional process is 3299 BTU/gal ethanol, or 25%. A similar comparison was made with a feed of 8.5% ethanol / 1.2% water / 90.3% 2,6-dimethyl-4-heptanol. Savings for this is 3883 BTU/gal ethanol (or 30%).

5.2. Tolliver Model (100 MM Gallon/year plant)

The Tolliver model, which was developed during early design stages of EWA, calculates energy and water savings for the two stage distillation process, compared to a conventional process. The capacity basis for Tolliver's model is 100 MM gallons ethanol /year. The ternary feed composition used in the model (3.9% ethanol / 2% water / 94.1 % Decyl Alcohol) is based on earlier experiments extracting live broth having 8% ethanol content.

The two processes that Tolliver compares are shown in Figure 5-3 (Ethanol Base Case - Conventional Distillation) and Figure 5-4 (Solvent ternary with 3.9% Ethanol). Total process energy and cooling duties are summarized in Figure 5-2, for several assumed conditions. The energy and water savings represented by conditions 2030 b-d in the model are considered to be a successful outcome. An example that is realistic is Case 2030d, with an energy savings of 44.1 MM BTU/hr and a cooling savings of 45.4 MM BTU/hr.

Tolliver assumes heat integration of the molecular sieve vaporizer with the solvent column bottoms product. This integration should be considered in a plant scale design.

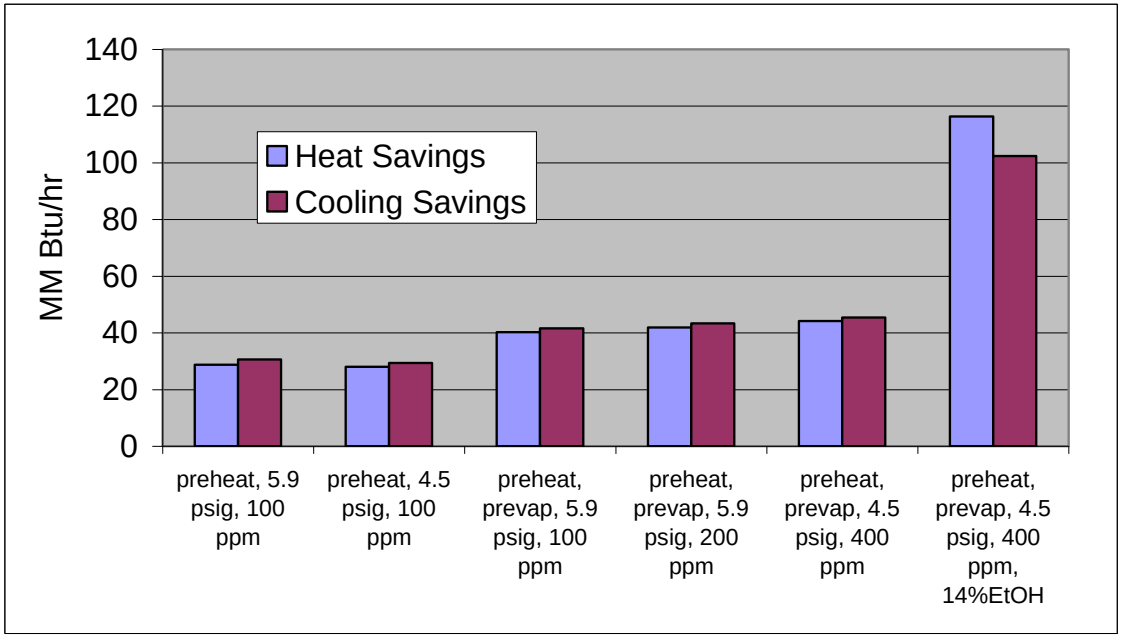
Higher concentrations of ethanol in the ternary were modeled as shown in Figure 5-5 (Solvent ternary with 14% Ethanol) to determine the benefit of running richer. 14% ethanol is theoretical; intermediate concentrations, however are achievable.

Table 5-2: Energy savings for two conditions

Feed to solvent column	Energy savings
3.9% ethanol / 2 % water / 94.1 % solvent:	44 MM BTU/hr
14% ethanol / 2% water / 84 % solvent :	100 MM BTU/hr

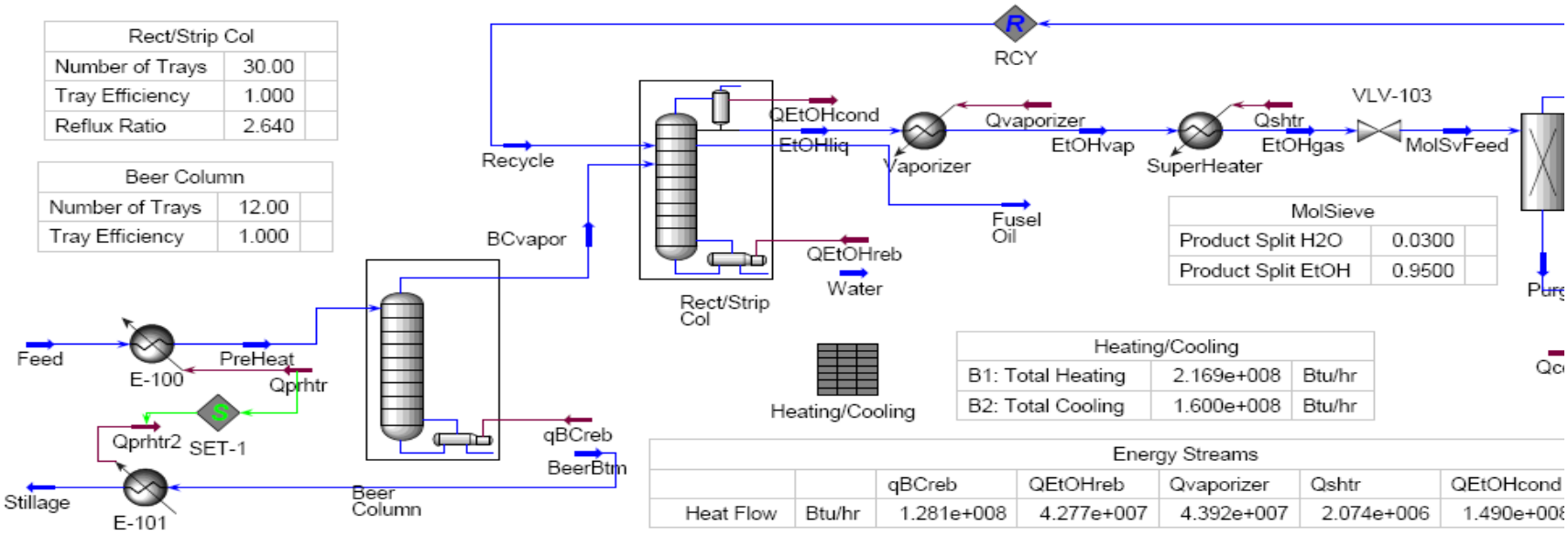
The concept of saving energy by using solvent extraction to recover ethanol from broth is not in dispute. It is a thermodynamic fact. The issue is that if solvent is added directly to the fermentor, it forms an intractable emulsion, and entrainment losses will kill the economics. Membrane extraction provides a process to make contact between the two phases, without forming this emulsion.

Figure 5-2: Aspen Hysis Modeling Summary: Energy and Cooling Savings Comparison



Case Name	Description	Total Heat MM Btu/hr	Heat Savings MM Btu/hr	Total Cool MM Btu/hr	Cool Savings MM Btu/hr	Electrical MM Btu/hr
Base Case 1230	typical EtOH	216.9		160.0		
3M Case 2030	preheat, 5.9 psig, 100 ppm	188.2	28.7	129.4	30.6	
3M Case 2030a	preheat, 4.5 psig, 100 ppm	188.9	28.0	130.6	29.4	1.1
3M Case 2030b	preheat, prevap, 5.9 psig, 100 ppm	176.7	40.2	118.4	41.6	1.2
3M Case 2030c	preheat, prevap, 5.9 psig, 200 ppm	175.0	41.9	116.7	43.3	1.2
3M Case 2030d	preheat, prevap, 4.5 psig, 400 ppm	172.8	44.1	114.6	45.4	1.2
3M Case 2030d14	preheat, prevap, 4.5 psig, 400 ppm, 14%EtOH	100.6	116.3	57.6	102.4	0.7

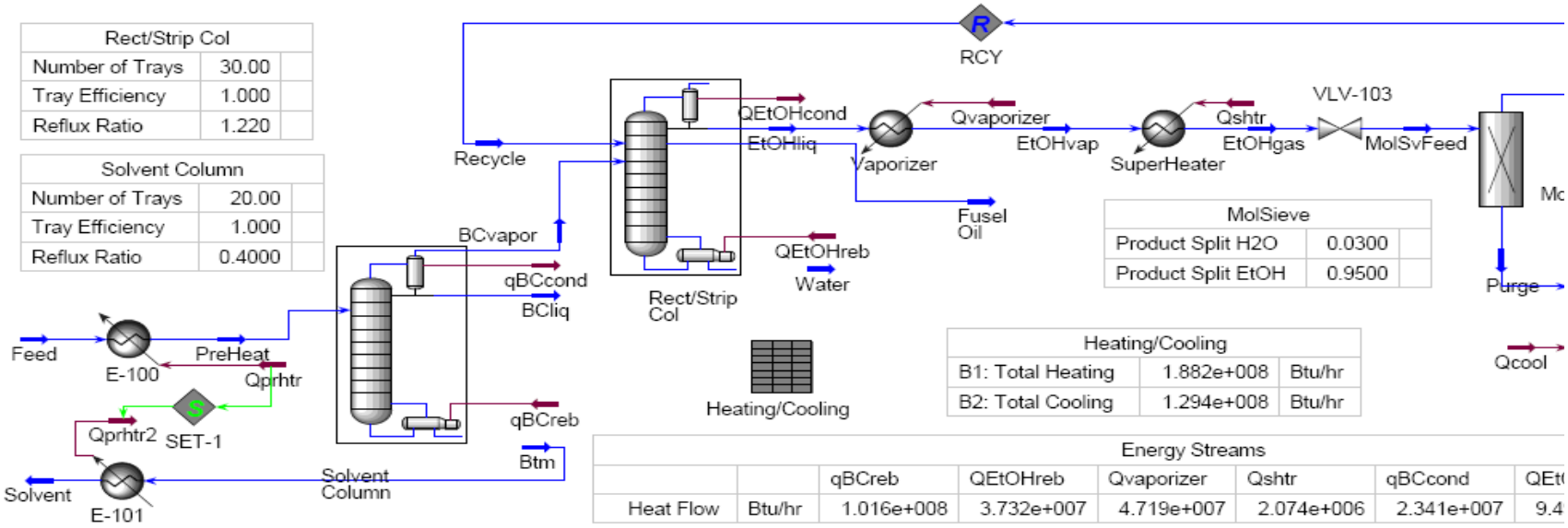
Figure 5-3: Aspen Hysis Model – Ethanol Base Case (Conventional Distillation)



Energy Streams						
		qBCreb	QEtOHreb	Qvaporizer	Qshtr	QEtOHcond
Heat Flow	Btu/hr	1.281e+008	4.277e+007	4.392e+007	2.074e+006	1.490e+008

Compositions										
		Feed	PreHeat	BeerBtm	Stillage	Water	BCvapor	EtOHliq	Recycle	MolSvFeed
Master Comp Mass Frac (Ethanol)		0.100000	0.100000	0.000100	0.000100	0.000100	0.517465	0.911941	0.349978	0.911941
Master Comp Mass Frac (H2O)		0.829553	0.829553	0.913138	0.913138	0.998496	0.480266	0.087216	0.650022	0.087216
Master Comp Mass Flow (Ethanol)	lb/hr	84000.00	84000.00	67.55	67.55	7.71	83932.45	88295.56	4414.78	88295.56
Master Comp Mass Flow (H2O)	lb/hr	696824.50	696824.50	618925.75	618925.75	77035.93	77898.75	8444.40	8199.66	8444.40
Mass Flow	lb/hr	840000.00	840000.00	677800.88	677800.88	77151.95	162199.12	96821.56	12614.44	96821.56
Temperature	F	131.0	192.5	224.1	149.1	217.6	202.5	163.8	122.0	300.0
Pressure	psia	20.00	20.00	18.60	18.60	16.50	16.60	15.00	62.00	62.00

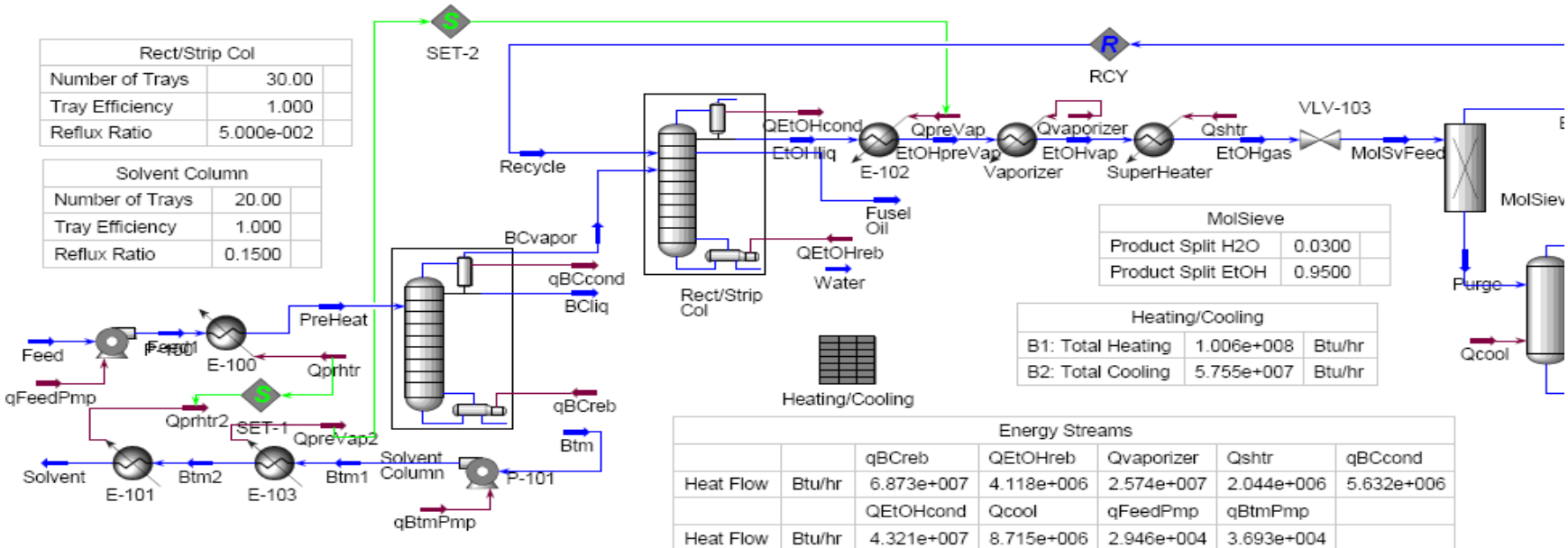
Figure 5-4: Aspen Model – Solvent Ternary with 3.9% Ethanol



Energy Streams							
		qBCreb	QEtOHreb	Qvaporizer	Qshtr	qBCcond	QEt
Heat Flow	Btu/hr	1.016e+008	3.732e+007	4.719e+007	2.074e+006	2.341e+007	9.4

Compositions										
		Feed	PreHeat	Btm	Solvent	Water	BCvapor	EtOHliq	Recycle	MolSvFeed
Master Comp Mass Frac (Ethanol)		0.039000	0.039000	0.000100	0.000100	0.000100	0.766825	0.911134	0.347775	0.911134
Master Comp Mass Frac (H2O)		0.017000	0.017000	0.005513	0.005513	0.998974	0.231930	0.088271	0.652225	0.088271
Master Comp Mass Flow (Ethanol)	lb/hr	84000.00	84000.00	204.46	204.46	2.50	83795.54	88188.32	4409.37	88188.32
Master Comp Mass Flow (H2O)	lb/hr	36615.40	36615.40	11271.01	11271.01	24939.57	25344.39	8543.72	8269.42	8543.72
Mass Flow	lb/hr	2153846.90	2153846.90	2044570.90	2044570.90	24965.19	109276.00	96789.66	12678.79	96789.66
Temperature	F	131.0	273.6	300.3	149.1	179.1	150.4	124.4	122.0	300.0
Pressure	psia	20.00	20.00	8.500	8.500	7.400	7.500	5.900	62.00	62.00

Figure 5-5: Aspen Model – Solvent Ternary with 14% Ethanol



Rect/Strip Col		
Number of Trays	30.00	
Tray Efficiency	1.000	
Reflux Ratio	5.000e-002	

Solvent Column		
Number of Trays	20.00	
Tray Efficiency	1.000	
Reflux Ratio	0.1500	

MolSieve		
Product Split H2O	0.0300	
Product Split EtOH	0.9500	

Heating/Cooling		
B1: Total Heating	1.006e+008	Btu/hr
B2: Total Cooling	5.755e+007	Btu/hr

Energy Streams						
		qBCreb	QEtOHreb	Qvaporizer	Qshtr	qBCcond
Heat Flow	Btu/hr	6.873e+007	4.118e+006	2.574e+007	2.044e+006	5.632e+006
		QEtOHcond	Qcool	qFeedPmp	qBtmPmp	
Heat Flow	Btu/hr	4.321e+007	8.715e+006	2.946e+004	3.693e+004	

Compositions													
		Feed	PreHeat	Btm	Btm1	Btm2	Solvent	Water	BCvapor	EtOHliq	EtOHpreVap	Recycle	MolSvFeed
Mass Frac (EtOH)		0.139913	0.139913	0.000401	0.000401	0.000401	0.000401	0.000100	0.935898	0.933421	0.933421	0.420887	0.93342
Mass Frac (H2O)		0.017989	0.017989	0.009970	0.009970	0.009970	0.009970	0.999899	0.063737	0.066237	0.066237	0.579113	0.06623
Mass Flow (EtOH)	lb/hr	84600.00	84600.00	206.23	206.23	206.23	206.23	0.55	84393.77	88820.79	88820.79	4441.01	88820.7
Mass Flow (H2O)	lb/hr	10877.00	10877.00	5129.59	5129.59	5129.59	5129.59	5518.87	5747.41	6302.85	6302.85	6110.55	6302.8
Mass Flow	lb/hr	604660.50	604660.50	514486.43	514486.43	514486.43	514486.43	5519.43	90174.07	95156.20	95156.20	10551.56	95156.2
Temperature	C	55.00	85.00	138.2	138.2	102.1	65.00	76.67	58.93	45.49	121.2	50.00	148.9
Pressure	psia	14.70	20.00	7.500	21.70	19.70	14.70	6.000	6.500	4.500	65.00	62.00	62.0

5.3. 3M EWA Model (Distillation and MSE)

An Aspen model was developed which combines the Tolliver distillation process with a nine-module version of the membrane solvent extraction (MSE). This 3M model confirmed the distillation energy and water savings of Tolliver. Additionally, this model enables us to track ethanol and metabolite concentrations within MSE, and in distillation. This is important, as it is not possible to operate a completely closed system. Metabolites, such as the organic acids, fusel oils etc, must be removed from the process or they will eventually poison fermentation. Part of the discharge of non-volatile metabolites can be achieved by discarding a fraction of the extracted broth. A second "venting" option (which could be complementary to the first) is to remove them from the solvent.

For this reason, a water extraction process was added to this model. Solvent bottoms product from the first distillation stage is contacted with water as a counter-current liquid / liquid extraction process. This removes metabolites by partition to the water phase.

A simple version of this water extraction process has been incorporated into the EWA process, in the form of the Solvent Decanter. Intent here was to remove sugar and vegetable oil, but it also can remove metabolites. Future experiments should include the quantifying of metabolite removal in this process.

5.4. Decatur EWA Process Model / USDA Full Plant Model (NREL)

An initial AspenPlus model of the EWA membrane extraction and distillation process was originally developed by 3M to plan experiments, with the intention to refine the model as experiments progressed, replacing assumptions with real operational data. The ultimate goal is to use the model for techno-economic analysis. NREL expanded the original Aspen Plus model to include the fermentation portion of the Decatur pilot plant facility. This section provides a high-level description of the NREL effort to model the entire pilot plant at Decatur, IL.

The process starts with 30 wt% starch feed, modeled as dextrose, received at 180^{o}F. The feed is held temporarily in a feed tank from which it is fed to a mixing tank. In the current version of the model, nothing is added to the feed in the mixing tank. The mixing tank is merely a placeholder for adding additional feed or nutrients if desired. Although nothing is added to the feed, the mixing tank does serve additional purposes as a surge tank and allowing the feed to cool to a temperature approaching the desired pre-fermentor and fermentor temperatures. Following the mixing tank, the feed passes through a heat exchanger where it is further cooled with cooling water, to 90^{o}F, close to the pre-fermentor and fermentor temperatures of 88^{o}F. A screenshot fermentation section of the Decatur EWA Aspen model is presented in Figure 5-6.

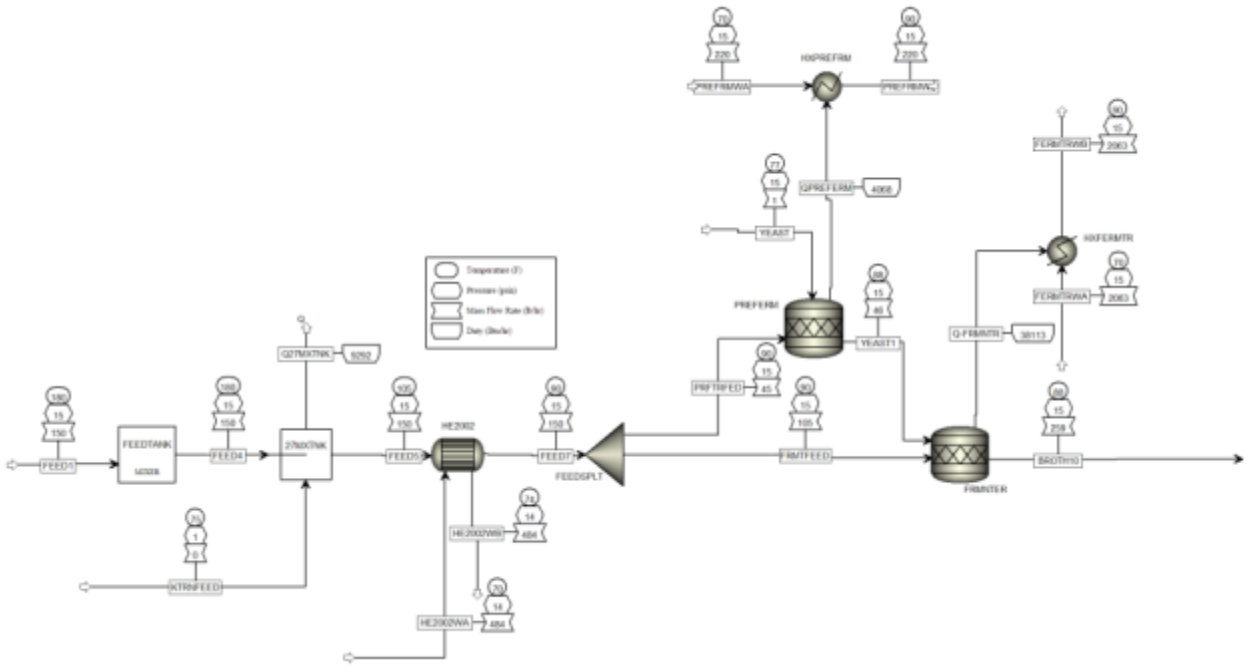


Figure 5-6: Screen shot of fermentation section of the Decatur EWA Aspen model.

After cooling, about 70 wt% of the feed is sent to the fermentor, while 30% is diverted to the pre-fermentor to grow yeast. As fresh feed enters the pre-fermentor, overflow from the pre-fermentor enters to the fermentor, joining the feed sent directly from the mixing tank to the fermentor. In the fermentor, dextrose is converted to ethanol, carbon dioxide, and non-fermentable dissolved solids (NFDS) according to the following reaction:

$$\text{Dextrose} \rightarrow 1.9\ \text{EtOH} + 1.9\ \text{CO2} + 0.06\ \text{NFDS}$$

The conversion of dextrose can be adjusted manually in the fermentation unit operation. Additionally, the pre-fermentor and beer well are modeled as reactors, as some conversion occurs in these unit operations as well. The overall conversion of dextrose is modeled at 92%. Cooling water is used to keep the pre-fermentor, fermentor and beer well unit operations at 88°F. The fermentation step is modeled as a single vessel, although more can be added to simulate a cascading fermentation arrangement. The current configuration of the model does not have the ability to predict dextrose conversion based on variables such as ethanol concentration in the fermentation tank.

Following the fermentation tank the broth proceeds to the beer well, as presented in Figure 5-7. Carbon dioxide and product vapors evolve out the top of the beer well to the scrubber, where product vapors are condensed and returned to the beer well. The return stream from the scrubber to the beer well is not currently connected due to performance issues with the scrubber unit in the AspenPlus model. The broth leaving the beer well goes directly to a centrifuge, where 98% of solids are removed, and 85% of liquids leave with the broth stream. This is a very optimistic performance assumption, but the solids must be removed via some sort of centrifuge and filter sequence. Therefore while the performance of the centrifuge is optimistic, the overall performance of the solids removal strategy in the separation step will most likely have to perform as modeled here to protect the downstream MSE membranes. A recycle stream from the centrifuge recovers yeast by returning it to the fermentation vessel from a yeast suspension tank.

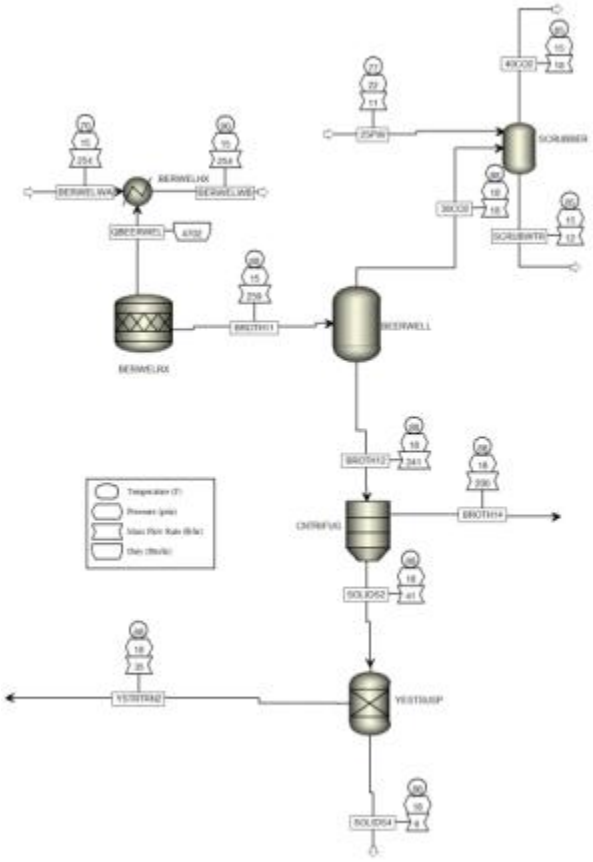


Figure 5-7: Screen shot of the beer well and centrifuge section of the Decatur EWA Aspen model

The broth stream from the beer well goes directly to the MSE section, where it passes through a 3X3 array of nine MSE modules for extraction using 2,6-dimethyl-4-heptanol. The overall ethanol removal in the MSE section is 77%, although the performance of each module can be easily changed in the model. Some water is also extracted from the broth, resulting in a solvent-water-ethanol ternary mixture on the solvent side of the membranes. Also, the model passes a slight amount of solvent to the broth side of the membrane to simulate solvent crossover. After having removed most ethanol from the broth, the broth stream passes through a Scheibel column, where the solvent passed through the membrane can be scrubbed with dodecane from the broth. The solvent-free, scrubbed broth is recycled to the fermentor.

Following the MSE section, the solvent-water-ethanol ternary mixture goes through the solvent extraction distillation column, where solvent is separated from ethanol. Water leaves out the top and bottom of the solvent column, but is less than 1% of the bottoms. The overhead from the solvent column is sent directly to the rectifier, where ethanol is purified to 93.5%. A mol sieve package is not currently included in the AspenPlus model, but would be a customary final dehydration step following the rectifier. Where possible, experimental data collected from the pilot plant has been included in the AspenPlus model, and the model will be continuously updated by 3M and ADM as experimental work continues.

5.4.1. USDA Corn Dry-Grind Ethanol AspenPlus Modeling Effort

The United States Department of Agricultural (USDA) has developed a techno-economic model of a corn dry-grind ethanol production process [Kwiatkowski et al. 2005[1]]. The model is not intended to replicate a specific existing fuel ethanol plant, but rather to model the processing steps and unit operations typical of most corn-based ethanol facilities. For this study the USDA corn dry-grind model has been modified to assess the impact of replacing the beer column with the membrane solvent extraction (MSE)

technology. For this report, the USDA corn dry-grind ethanol model as published [Kwiatkowski et al. 2005[3]] is referred to as the baseline model, and as illustrated in Figure 5-8, separates ethanol from water using a beer column followed by a rectifier.

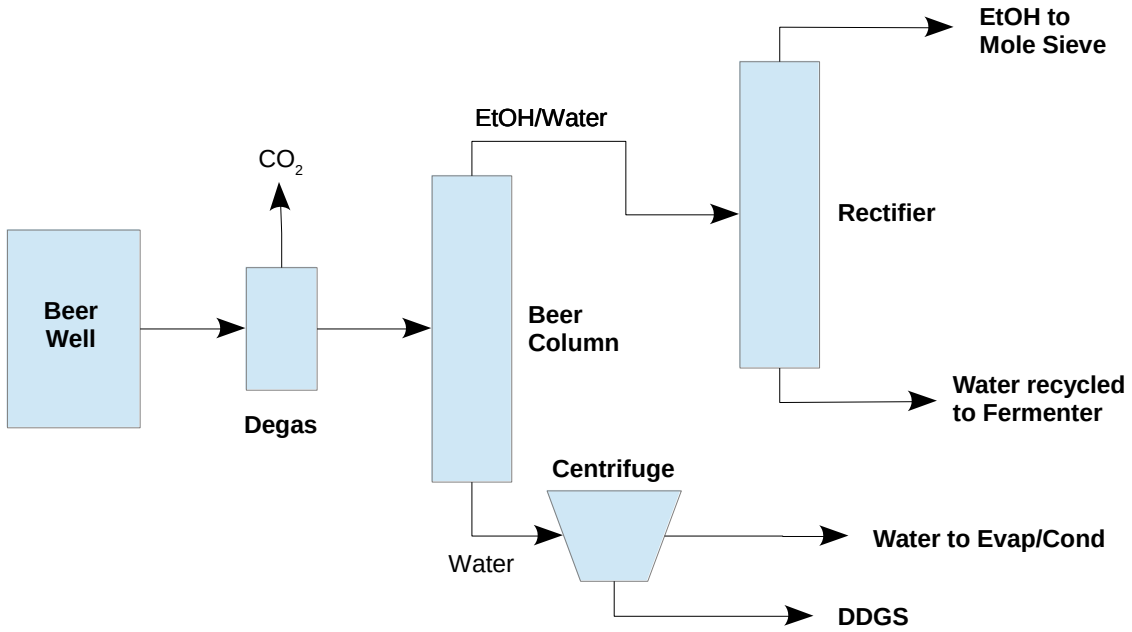


Figure 5-8: Block flow diagram of the separation steps in the baseline model.

The modified model uses MSE technology in place of the beer column. The MSE membrane modules cannot accept the solids present in the dry-grind process beer, therefore the centrifuge was moved to immediately after the beer well, as illustrated in Figure 5-9. In the modified model presented here, the MSE array in Figure 5-9 represents a 3x3 array of membrane separation modules and a solvent extraction distillation column, along with all the associated pumps, heat exchangers, and holding tanks. In both models the rectifier is followed by a molecular sieve package to dehydrate.

[3] Kwiatkowski (2005). J. Kwiatkowski, A. J. McAloon, F. Taylor, and D.B. Johnston. "Modeling the process and costs of fuel ethanol production by the corn dry-grind process". Industrial Crops and Products 23 (2006) 288–296. http://naldc.nal.usda.gov/download/4338/PDF

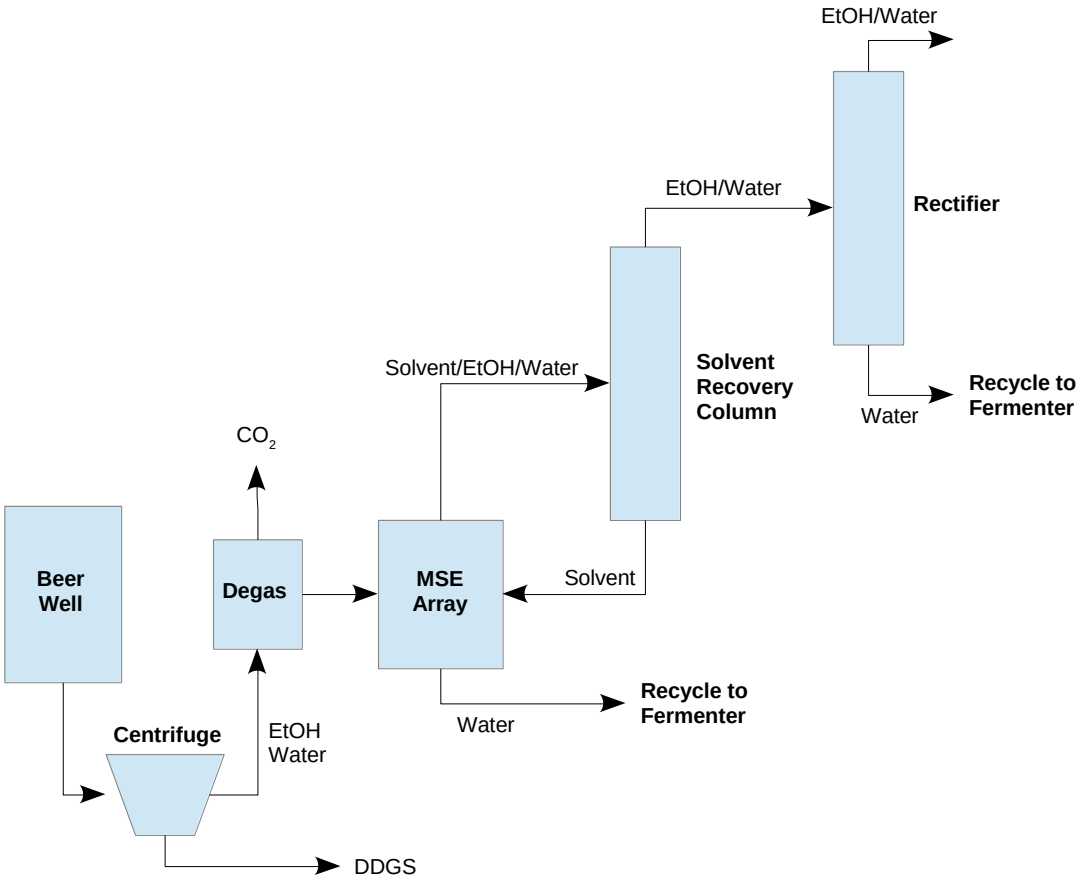


Figure 5-9: Block flow diagram of the separation steps in the modified model.

5.4.2. Energy Balance

As expected, the MSE technology reduces the amount of heating and cooling required to separate ethanol from water versus conventional methods represented by the baseline model. Table 5-3 presents a summary of the heat and cooling demands of the separation steps of the process. The most significant reduction is attributed to eliminating the beer column, which is the most energy-intensive unit operation in the process. The beer column is replaced with the MSE array, and a solvent extraction column necessary to separate ethanol and water from the ethanol/water/solvent ternary mixture. The solvent extraction column does require heat for a preheater and reboiler, although the total heat demand of the solvent extraction system is about 20% less than the conventional distillation process. Additionally, an MSE and solvent extraction column produce a more concentrated ethanol-water mixture than the beer column. As a result, rectifier reboiler, which is common to both models, requires less energy in the modified model than the baseline model to achieve the same overhead purity.

Cooling demands are reduced in the modified model as well, although by a less significant factor than heat demand. As with the heat demand for the rectifier reboiler, the cooling demand for the rectifier condenser in the modified model is less than the in the baseline model. The modified model does introduce a new cooling demand, the solvent extraction column condenser, although the total cooling demand is reduced. The beer column in the baseline model does not have a condenser. Interestingly, cooling water use is not significantly affected, as the primary demand for cooling in both models is the rectifier condenser, which is used to supply heat to a multiple-effect evaporator. MSE separation technology can potentially reduce cooling water demand in cases when cooling water is used in the rectifier condenser, or when the beer column has a condenser.

Heating and cooling demands for the remaining separation steps, such as degassing and the mole sieve package, were comparable between the models and were insignificant compared to the differences presented in Table 5-3. For completeness, it is worth noting that the distillation columns in the baseline model are operated slightly above atmospheric pressure (18-20 psia), whereas the columns in the modified model are operated at vacuum pressure (5.5-8.5 psia), which aids in separation.

Table 5-3: Energy balance summary of the separation steps in the modified model.

	Baseline Model	**Modified Model**
	Duty, MMBTU	Duty, MMBTU
Heat Demand		
Beer Column Reboiler	40.5	
Solvent Extraction Column Reboiler		8.9
Solvent Extraction Column Preheater		23.0
Rectifier Reboiler	9.2	7.0
Total Heat Demand	**49.7**	**38.9**
Cooling Demand		
Solvent Extraction Column Condenser		-3.8
Rectifier Condenser	-28.0	-20.9
Total Cooling Demand	**-28.0**	**-24.7**

5.4.3. Fermentation Acceleration

In both models the fermentation step is represented by a single vessel, and conversion in fermentation is set manually, therefore fermentation acceleration could not be verified using the existing models. The effect of a cascading fermentation arrangement can be confirmed more credibly with experimental and pilot plant results.

5.4.3.1. Lower Ethanol Product Yield

The MSE array cannot tolerate high solids typically present in dry-grind fermentation broth, therefore, the centrifuge must be moved from after the beer column to before the MSE array. This has significant effects on the final ethanol product yield. In the modified model, the centrifuge achieves 92% removal of solids from the fermentation broth (the rest is removed in a filter), although 15% of the liquid in the broth stream leaves the centrifuge with the solids. In the baseline model this is acceptable as ethanol has already been removed in the beer column, but in the modified model the liquid fraction entering the centrifuge contains about 10% ethanol. If 15% of the liquid component in the broth leaves the centrifuge with the solids, then so does 15% of the ethanol produced in the fermentor. This 15% ethanol is lost as the solids are dried to produce DDGS coproduct.

Reducing ethanol losses at the centrifuge step will be critically important to maintaining high ethanol product yield. A potential solution may be following the centrifuge with a pressure filter as described in the lignin separation section of Humbird et al. 2011[4]. Also, the ethanol vapors evolved in the DDGS drying step can be recovered in a scrubber, although most of the recovered liquid will be water, therefore a condensing step must be justified with a careful cost analysis.

[4] [1]Humbird (2011). D. Humbird, R. Davis, L. Tao, C. Kinchin, D. Hsu, A. Aden, P. Schoen, J. Lukas, B. Olthof, M. Worley, D. Sexton, and D. Dudgeon. "Process Design and Economics for Biochemical.

5.4.3.2. Opportunities for Improvement and possible future work

The modified model introduces new heating and cooling requirements, while eliminating others. This creates a potential efficiency improvement by modifying the heat exchange network manually or through a pinch analysis. Manually increasing conversion will not prove the advantage of a cascading fermentation process, but it can provide insights to downstream effects of such a change.

5.5. Technoeconomic Analysis

The Decatur EWA Process Model integrated with the USDA Full Plant Model by NREL is completed, but is being revised and tested with pilot data from the experiments. This model will provide much of the same information currently available in the 2007 version of the USDA dry-grind techno-economic model (Kwiatkowski et al). The USDA Aspen model communicates with the economic spreadsheet by generating "sensitivity parameters" which are transferred to the spreadsheet by click-and-drag. The spreadsheet then provides process and economic details for specific unit operations in a generic ethanol plant. Among other things, the spreadsheet provides a summary of variable operating costs as illustrated in the conventional ethanol process example in Table 5-4.

Table 5-4: USDA Dry-Grind Techno-Economic Summary [Kwiatkowski et al.]
(40 MM Gallon/year conventional ethanol process)

Variable Operating Costs	2006 Cost ($/lb or $/kWh)	$/yr (2006)	$/Gallon Ethanol (2006)
Raw Material			
Corn Feedstock	$0.06250	$50,591,441	$1.265
Caustic	$0.05500	$221,995	$0.006
Alpha-Amylase	$1.03000	$579,943	$0.014
Gluco-Amylase	$1.03000	$837,655	$0.021
Gasoline	$0.32787	$1,723,102	$0.043
Sulfuric Acid	$0.05000	$80,288	$0.002
Lime	$0.04000	$38,379	$0.001
Makeup Water	$0.00002	$29,222	$0.001
Urea	$0.10000	$160,575	$0.004
Yeast	$0.85000	$167,586	$0.004
Subtotal		$54,430,186	$1.361
Utilities			
Steam - 150 PSI		Generated On Site	
CT Water - 85 F		Generated On Site	
Cool Water 60 F	$0.00003	$308,027	$0.008
Electricity	$0.05000	$1,832,888	$0.046
Natural Gas	$7.50000	$9,785,777	$0.245
Subtotal		$11,926,692	$0.298
By-Product Credits			
DDGS	$0.04717	$12,603,000	$0.315
Carbon Dioxide	$0.00000	$0	$0.000
Subtotal		$12,603,000	$0.315
Total Variable Operating Costs		$53,753,878	$1.344

The USDA techno-economic analysis shows that natural gas accounts for 24.5 cents/gallon of the total variable operating costs for natural gas at $7.50 per thousand cubic feet which is approximately the same at per thousand BTU (MBTU).

There are several points of reference for gas markets in the US, but the most commonly quoted is the Henry hub, which is a distribution hub on the natural gas pipeline system in Louisiana. The market price for natural gas was historically around $7.50/MBTU and peaked near $14 near the start of this DOE project (FOA) in 2008. A previous peak of $18/MBTU occurred in 2003. During the course of this project, the market price of natural gas has declined substantially due to the US hydraulic fracturing (fracking) boom. Before shale gas came on stream, the price of natural gas was closely linked to the price of oil, as both energy sources were tapped from the same fields. A good example of this link between

increased oil and gas prices is the market peak seen in 2008, when rising production costs caused oil prices to shift beyond the $100/bbl, which in turn hiked gas prices.

Now, a plentiful supply of natural gas has entered the market from shale formations, which use the hydraulic fracturing technique to extract the gas, meaning new areas can be tapped and the two commodities are no longer linked and it is difficult to predict the future price of natural gas.

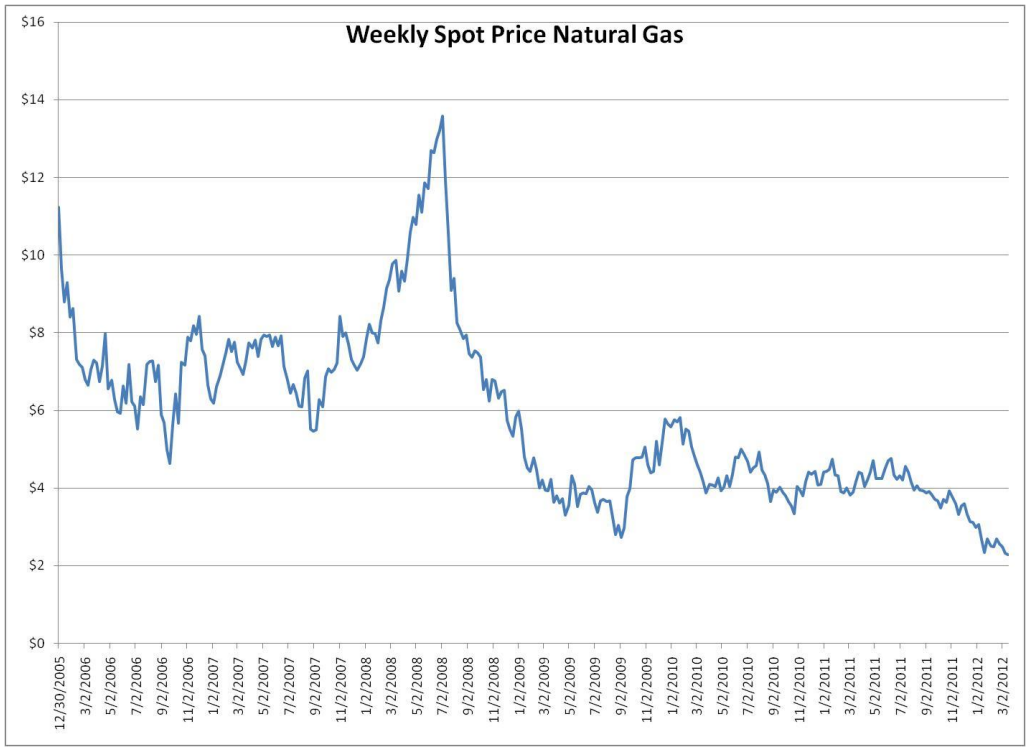


Figure 5-10: : Weekly Natural Gas pricing through 2012 (source: EIA)

Natural gas reached lows of near $2-3/MBTU during the 2012-2013 timeframe. At this price, techno-economic modeling by ADM and 3M indicated the payback time for MSE capital installation was too long to be economically attractive. However, over the past year, pricing has rebounded into the $4 range with short-term spikes to $8 during the cold winter with supply chain shortages. Many utility plants have been converting from coal to natural gas, and also many large scale petrochemical processes (e.g. polyolefin feedstock) have been shifting from crude oil to natural gas. Therefore, demand for natural gas will increase in the future which could drive up prices further.

Based on the preliminary techno-economic model (and 2013 capital expenditure estimates), a 25% reduction in utility costs over this conventional process is marginally financially attractive at a natural gas price of $4 MBTU, but is attractive at $8 / MBTU.

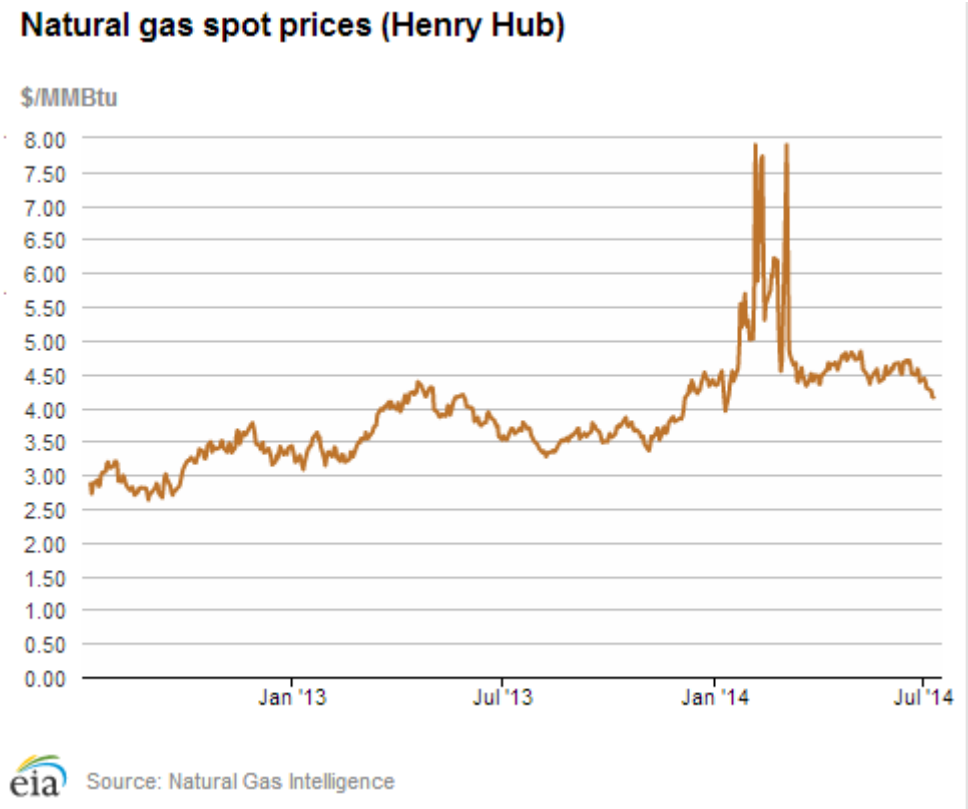


Figure 5-11: Recent Natural Gas prices (source: EIA)

6. Conclusions versus Project Objectives

6.1. Objective 1

- *Develop cross-flow membrane module and housing unit; develop process to produce modules and develop a membrane solvent extraction process, incorporating nine modules and housing units.*

Module and housing design was completed by 3M. Eighty of the new 20" x 20" x 10" modules were produced to support these experiments. Anderson-Dahlen constructed nine housing units from this 3M design, and incorporated these into a three tier skid configuration with control instrumentation.

6.2. Objective 2

- *Develop ethanol recovery process by integrating fermentation, membrane solvent extraction and two stage vacuum distillation.*

ADM, 3M and vendors, Anderson-Dahlen and Epic Systems, designed and constructed a fully integrated process, which this year was demonstrated to continuously produce wet-mill fermentation broth with a final titer of 6-12 wt % ethanol and to continuously recover this ethanol by membrane solvent extraction, and distil to 91-94% ethanol.

Fermentation is capable of cascade or batch processing and is adaptable to a variety of ethanol and other fermentation processes. It is ready for scale-up, as is.

Membrane Solvent Extraction: MSE process was demonstrated to continuously extract ethanol and metabolites from fermentation broth, without forming an emulsion. The process is stable, robust and operates with full automatic control. With some modification to the module and the solvent advance configuration, it is ready for design of a scaled-up version (using essentially the same design).

Vacuum Distillation: the two stage vacuum distillation design concept is correct, and the experiments have proven that the process will produce 91-94% ethanol from solvent ternaries with compositions up to 4% ethanol / 2% water / 94% 2,6-dimethyl-4-heptanol (and with lower ethanol content). Process parameters come close to a match with Aspen models. The system will most likely perform to the productivity specification of 10.5 kg ethanol / hour after proper modifications to address low heat delivery to the solvent column, and correct erratic reflux and product flow in the overheads. It currently is not ready for scale-up.

System controller for the EWA process is a subset of ADM's D3 system. An experienced instrumentation and control engineer from ADM Operations developed the control architecture. It was commissioned and tested extensively during process trials, and found to be reliable and user-friendly. The EWA system is transferable (with scale related modifications) to production.

Process and instrumentation diagrams were developed cooperatively with engineers from ADM Operations and 3M Division Engineering. These were reviewed and modified as part of the hazard review (HAZOP) process and sight environmental review. MSE process final engineering was done cooperatively between Anderson-Dahlen, and 3M. This included module housing design and fabrication, construction and piping of module tiers and selection and installation of control instruments. Installation in ADM EWA was completed July 2012.

The distillation process was conceived by Terry Tolliver, Washington University, under contract with EPIC Systems, St Louis. Design was completed by engineers from EPIC, 3M and ADM, with installation in June 2012. Fermentation process design was completed by ADM, and constructed on site by local contractors between June 2011 and July 2012. Commissioning of the combined process was completed in November 2012.

6.3. Objective 3

- *Conduct experiments on process components; modify to meet project targets.*

MSE: Twenty-seven process trials were conducted on the nine module array, using finished wet-mill broth serum (after disc centrifuge to remove solids), to learn control methods, and assess performance. Standard operating procedures were developed. Most experiments were conducted in solvent parallel mode.

Operational performance was excellent. Startup took about 3 hours, but once completed, and the process was lined out, flows, differential pressures and level controls were stable, and the automatic control

system was such that the combined process operated essentially hands off. Only occasional monitoring was required in most experiments. Two deficiencies were found that need correction:

1. Ethanol transfer rates were lower than specification, likely caused by occlusion of membrane pores through bio-film formation, sugar deposition or pore size reduction in the module making process.

2. At times, there was excessive solvent and broth cross-over, possibly caused by two part seal separation and displacement, and /or by solvent induced module expansion / de-lamination. The former was corrected by developing a single piece molded seal.

In best cases, ternary from MSE reached target levels of 3.9% ethanol / 2% water / 94.1% 2,6-dimethyl-4-heptanol. Entering solvent composition varied due to inadequate stripping in distillation. This contributed to the low transfer rate.

Modules are physically rugged. Membrane rupture pressure (differential pressure) was found to exceed 10 psia. Differential pressure during operation was 4-5 psia; no module ever ruptured under these conditions. Three modules are currently in the 7th month of operation, with continuous broth circulation and continuous exposure to extraction solvent.

Distillation: Eighteen experiments were conducted, both with total internal recycle, using spiked ethanol / water mixtures, and later using solvent ternary from MSE. From these trials, standard operating procedures were written. It was found that temperature profiles and re-boiler and condenser duties approximately match Aspen. There was inadequate heat delivery to the solvent column, resulting in lower than expected ethanol production and incomplete stripping of the ternary. This was found to be due to a combination of design problems and sugar / vegetable oil deposition and charring in the hot oil heated re-boiler.

Reflux and product flows in the column overheads were erratic and difficult to measure. Modifications were made to the instrument and valve configuration of the rectifier. This improved performance, but additional modifications are required.

A solvent decanter was installed in the distillation return, that effectively reduced dissolved sugar content in the solvent (solvent is passed through a water layer). This noticeably cleaned up the solvent, and reduced sugar deposition and formation of char in distillation experiments with the ADM R-4 unit.

6.4. Objective 4

- *Conduct full process experiments in baseline and acceleration mode.*

Nine full process experiments (52 to 72 hours each) were conducted, extracting from the fermentor beer well, and discarding extracted broth. Starting with broth having 5.5% to 12% ethanol content, the combined extraction and distillation process produced 91-94 % ethanol. Yields varied from 30 to 60% of the 10.5 kg ethanol/ hour spec.

In one case, broth with ethanol content of 4% was extracted, producing 86% ethanol in the final product. This has significance for the cellulosic ethanol process, which currently appears to be limited to 5.5% final ethanol titer, something that is not economic to distil. Controlling rectifier overhead temperature to 120-125^{o}F (4.5 psia) guarantees production of 91% ethanol. For the solvent column, it was found that maintaining an overhead temperature of 136^{o}F avoids solvent carry-over to the rectifier.

Initial acceleration mode experiments were conducted, in which broth was drawn from A and B stages of fermentation, processed through MSE, Karr column (remove entrained solvent) and returned to fermentation. This was primarily a demonstration that the process sequence can be employed in future experiments. Temperature profiles, re-boiler and condenser duties approximately match Aspen model values.

6.5. Objective 5

- *Develop Aspen model for this process; compare experimental and model process parameters; calculate energy and water savings compared to conventional ethanol.*

Four models were developed independently for the two stage distillation process by Tolliver, 3M, ADM and NREL. All four show energy savings of 20 to 30% compared to conventional ethanol processes of the same capacity. An ADM developed rigorous model shows an energy savings of 3299 BTU/gal ethanol (25%) compared to conventional distillation (ternary feed: 4.5% ethanol / 2.1% water / 93.4 % 2,6-dimethyl-4-heptanol).

NREL added a fermentation component to the 3M Aspen model, and integrated this into the USDA Dry Mill Plant model. The combined model provides operational implications of substituting EWA for the beer column. Sensitivity parameters from the Aspen model can be transferred into an economic spread sheet that generates relevant process and economic information for a complete plant process. This provides a basis for working with ethanol producers to understand economic implications for specific plants.

6.6. Other Accomplishments

Presentations: "Energy Reduction & Advanced Water Removal via Membrane Solvent Extraction Technology." Presented at the AiChE Regional Meeting, Chicago, IL, January 31, 2013.

Patents: Filings from 3M on membrane module design improvements (details upon request).

7. Recommendations

1. Modifications should be made to sections of the EWA process to address problems identified in trials:

   Distillation:

   Heat delivery to the solvent column should be improved by modification of the solvent re-boiler system. Overhead of both columns should be modified to eliminate erratic reflux and product flows.

   MSE:

   Some modifications should be made to the module configuration and process for making it, as part of an effort to increase ethanol transfer rate. The solvent advance system should be re-configured to eliminate auto-valve over-ride and pressure coupling to the module housing.

   Fermentation:

   The original feed pasteurization system should be made to work.

2. Design experiments should be conducted on process sections to demonstrate performance after these changes. These would take 3 to 6 months to complete, and would include:

   Distillation:

   Running on internal re-cycle, to check match to performance targets.

   MSE:

   Parallel vs. series flow – comparison of ethanol transfer rate
   CIP with higher temperatures, longer times and inclusion of surfactant
   Extraction of whole broth
   Higher temperature extraction

   Fermentation:

   Elimination of plugging in starch feed pasteurizer

3. Once section experiments are complete, the original full process wet-mill baseline and fermentation experiments should be conducted. These include baseline and acceleration modes, and will take 3 to 6 months.

4. Brief trials should be conducted on batch dry mill. These should focus on the solids separation step, and a demonstration of membrane extraction of the serum fraction, to compare composition and performance with the wet-mill process (there will be an oil component and potentially higher ethanol titer). Experiments should take 1 to 2 months.

5. A full plant economic analysis will be conducted using the combined USDA Dry Mill Plant / EWA model. This tool will be used for customer visits. This should be completed during the experiments above. It will involve an experienced 3M marketer.

6. A plan will be drafted to manufacture membrane modules of full scale. This can be internal or at a third party vendor. Plan should be completed during the experiments above.

7. The existing EWA process can be further utilized to conduct research on Butanol as a bio-fuel, and in the production of ethanol from cellulosic feed stocks. The latter would involve accelerating the C5 fermentation process by removing inhibitors such as acetic acid from the pre-treatment hydrolysate, and concentrating the 5.5% ethanol product.

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* Dedicated to the memory of our late colleague and contributor to the MSE project, Volker Kuellmer, who was instrumental in designing the EWA pilot plant scale up process.