COMPACT MEMBRANE SYSTEMS, INC. CMS

# Final Scientific/Technical Report

**Covering Period:** **June 30, 2006 thru March 31, 2013**

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**Project Title:** **Development of Applied Membrane Technology for Processing Ethanol from Biomass**

**Project Period:** **June 30, 2006 thru March 31, 2013**

**Recipient Organization:** **Compact Membrane Systems, Inc.**

**Project Director/**
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## Executive Summary

The technical objectives of this program were to demonstrate, with Compact Membrane Systems, Inc. (CMS) membrane technology, a water-ethanol system that would have significantly improved water transmission rate and would be economically attractive for a low cost azeotrope-breaking process. The overall objective was to indicate that a CMS membrane in line with existing distillation equipment can dramatically reduce the overall cost of dewatering ethanol for fuel-grade ethanol (FGE). The objectives of this program fell into three areas. The first objective was to demonstrate the feasibility that the CMS membranes have a unique capability for rapid transport of water or water vapor and significant water vapor-ethanol separation. The second objective was that the purity of ethanol and the inherent process is consistent with the needs and uses in the fuel grade ethanol industry. Thirdly, that this can be done in a manner that is significantly superior to existing processes.

The cornerstone of this program was the development of composite membrane systems based on the copolymers of PDD-TFE. The nonporous, glassy CMS perfluoro membrane coating consists of perfluoro-2,2-dimethyl-1,1,3-dioxole (PDD) copolymerized with tetrafluoro-ethylene (TFE). CMS-3 and CMS-7 are PDD-TFE copolymers with different copolymer ratios; CMS-3 has 64% PDD and CMS-7 has 83% PDD. These copolymers are commercial and, based on our collaborative effort with E.I. DuPont, we had access to both commercial materials and developmental materials as they become synthesized. Figure 1 shows the CMS membrane module without housing.

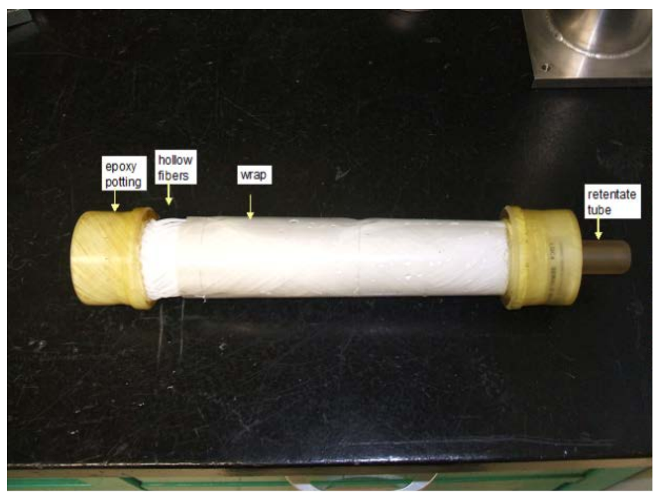

**Figure 1. CMS Membrane Module (Without housing)**

Therefore to develop membranes the focus was not on the PDD-TFE since we have that well in hand, but on the appropriate porous support and system design. The porous support work fell into two broad areas, the flat sheet composite design and hollow fiber composite design. In both cases we evaluated fabrication of membrane modules and hollow fiber designs as modules in contrast to technology that was available in a plate and frame mode. Spiral wound flat sheet modules or hollow fiber modules were preferred designs since they were expected to lead to overall lower cost systems with no sacrifice in overall performance compared to flat sheet design. Throughout this work we focused on composite structures using a thin nonporous layer of PDD-TFE on appropriate microporous support.

Key components in the overall choice of materials and design was the need to operate at high temperatures and associated high pressures, as well as operating with harsh chemicals (e.g., ethanol) and design to minimize pressure drop within the system in order to maintain driving force for enhanced separation.

In the dewatering of ethanol and related biofuel, size and space does not matter so the production of thicker walled fibers which may take up more space is an added positive consideration. These thicker wall fibers were easier to process and were therefore actually less expensive. Throughout this work the structure of choice is a composite membrane. The CMS PDD-TFE polymers will be on the top surface and underneath will be an appropriate microporous support.

The tasks below describe the membrane development associated with optimizing the porous support and actual membrane. Work during the first phase was done at the laboratory stage. At the end of the first year we planned to have small laboratory devices. Plans for year two was to take the basic data from the first year and build larger scale prototype systems for pilot evaluation, at an appropriate site. The third and fourth years would be focused on demonstrating the capability to manufacture in an appropriate large scale environment in building an appropriate transportable system for a split stream and a full operating stream associated with a small ethanol plant.

Therefore this program's focus and target were to develop the appropriate porous support/substrate in either a flat sheet or hollow fiber configuration. Our initial targets in Tasks 1 and 3 with the flat sheet and hollow fiber materials were to focus on using commercially available membrane materials from suppliers. These materials inherently were designed for filtration and not necessarily for our intended use in a composite structure. Filtration materials that are optimized for filtration may not work as an appropriate porous support/substrate. Therefore our expectations for the overall program were to evaluate these unoptimized filtration materials in the first year and to work both in-house and with appropriate partners in years 2-4 to optimize these porous supports in an effective overall composite structure.

This program has produced excellent module level results in terms of water permeability and water-ethanol selectivity. Figure 2 shows that the permeability increases from about 1700 to 2000 barrer as the ethanol gets drier in the range of 14 to 0.4% water in the feed. In the same range, the ethanol permeability is approximately constant and about 100 barrer. Therefore, the water/ethanol selectivity (ratio of water to ethanol

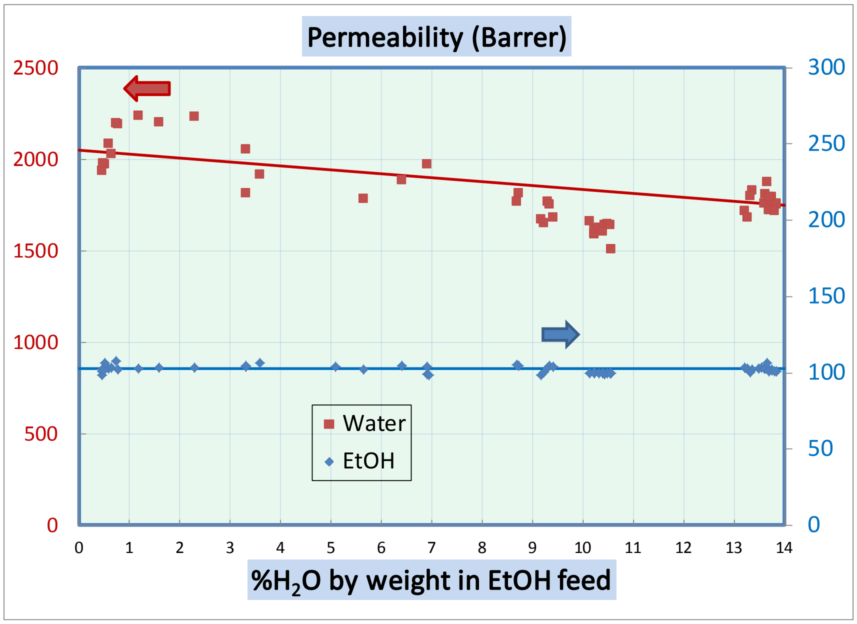


*Figure 2. CMS hollow fiber membrane module*

permeabilities) increases from about 17 to about 20 as the water content in ethanol decreases from 14 to 0.4% water. This demonstrates that the CMS membrane system dries ethanol efficiently from 14% water to 0.4% water ($\le$0.5% water is required for fuel grade ethanol). The system drying efficiency increases by about 18% as the ethanol water content decreases from 14 to 0.4%.

## COMPARISON OF THE ACCOMPLISHMENTS WITH GOALS/OBJECTIVES

There were nine key objectives in this program corresponding to the individual tasks, and all tasks were completed in a timely manner.

Task 1.0: Develop HT-HP Potting System: ***Completed***

Task 2.0: Develop Robust Epoxy Bonding: ***Completed***

Task 3.0: Flat Sheet Optimization: ***Completed***

Task 4.0: Development and optimization of hollow fiber membranes: ***Completed***

Task 5.0: Optimize module performance: ***Completed***

Task 6.0: Demonstrate CMS membranes can operate in excess of 30 days: ***Completed***

Task 7.0: Determine optimal module geometry: ***Completed***

Task 8.0: Demonstrate ability to produce 99.5% FGE: ***Completed***

Task 9.0: Project Management and Reporting: ***Completed***

## Accomplishments and Results

a. Samples of two epoxies identified in Task 1 were tested in ethanol at 120$^oC$ for 1 year. The new epoxy showed superior performance in three critical categories: Bonding, Resistance to ethanol at 120$^oC$, and Durability. Specifically, the new epoxy leaked ethanol at much lower rate (by 10x) than the old epoxy. In addition, the new epoxy was intact after the 1-year test, while the old epoxy started cracking after 3 months.
b. Hollow-fiber (HF) modules built with the optimum epoxy were developed. A long term test of this module with ethanol at high temperature shows that the epoxy forms a strong bond with the membrane so that it sustains stable module performance.
c. For these modules, the water permeance declines during the first four days and then stabilizes for the remaining 21 days of the test when a stable selectivity of 8 is maintained.
d. CMS has optimized and scaled up two processes for making flat sheet membrane: Spray Coating and Microgravure coating. Developmental quantities of flat sheet membrane have been manufactured: 1200 ft$^2$ by spray coating, and 500 ft2 by microgravure coating.
e. The primary hollow fiber support of interest for ethanol dehydration is PEEK (poly(ether ether ketone)) because of its higher chemical and thermal stability.
f. About 25000 linear feet of CMS3 coated hollow fiber membrane were produced, suitable for making larger modules (5 to 10 ft$^2$) for testing.

g. Membrane modules with at least 5 $ft^2$ were made. These modules were made with the chemically/thermally resistant materials.
h. The modules met single gas performance specifications; therefore the module scale-up was successful.
i. Each module was tested with a particular feed technique to determine its effect on ethanol/water permeation performance. One of the feed techniques resulted in optimum mass transfer and enabled the attainment of the water/ethanol selectivity goal of at least 15.
j. The module performance obtained with the feed through the middle port yields the optimum performance since it approximates the performance measured in small flat sheet samples.
k. We continued the long-term testing for an additional 50 days which adds up to 100 days of testing. The module continued performing at very high water permeability with no permanent performance decline.
l. The cause of the apparent water permeability decline observed after day 44 noted in the previous report, can be explained by variability in process conditions. Specifically, changes in the ethanol feed concentration and the feed flowrate affect the water permeability. In addition, some variability can be attributed to experimental error in the measurements.
m. The additional data show that there is no permanent permeability declining trend. After day 50, the water permeability was restored to the high values observed in the first 50 days. Therefore, this extended test has demonstrated stable module performance in the dehydration of ethanol for 100 days. This exceeds our initial goal of demonstrating module stability for at least 30 days.
n. Flat sheet coated with CMS3 membrane was fabricated for building a spiral wound module. The flat sheet was sent to our subcontractor Sepro, Inc. to build the spiral wound module.
o. We started building a CMS3 hollow fiber module in-house. This will serve as a control for comparing with the spiral wound module. The spiral wound module has a radically different geometry than the hollow fiber module. By measuring the performance of both modules we will be able to determine if one is better than the other.
p. We measured the performances of a spiral-wound membrane module (flat sheet) and a hollow fiber module. We found that the normalized performances of both modules are essentially the same despite the very different geometries.
q. However, significantly more membrane area can be packed in a hollow fiber module than in a spiral wound module of the same volume. Thus, the productivity per unit volume of the hollow fiber module is significantly larger than in the spiral-wound module.
r. Therefore, the hollow fiber geometry is preferred for ethanol dehydration over the spiral wound geometry. This geometry will be pursued as we attempt to commercialize membrane systems for the dehydration of ethanol.
s. :We measured the performance of a hollow fiber membrane module system with feed concentrations in the range of 0.5 to 14% water. The data show that the system efficiently removes water from ethanol in the whole range studied. The data also shows that the drying efficiency increases somewhat as the ethanol

gets drier. The tests demonstrate that the CMS membrane system can dry ethanol to produce fuel grade ethanol (FGE), i.e., containing no more than 0.5% water by weight.

t. The permeability of the FGE modules in Task 8 seems to increase from about 1700 to 2000 barrer as the ethanol gets drier in the range of 14 to 0.4% water in the feed. In the same range, the ethanol permeability is approximately constant and about 100 barrer.
u. Therefore, the water/ethanol selectivity (ratio of water to ethanol permeabilities) increases from about 17 to about 20 as the water content in ethanol decreases from 14 to 0.4% water. This demonstrates that the CMS membrane system dries ethanol efficiently from 14% water to 0.4% water ($\leq$0.5% water is required for fuel grade ethanol).
v. The system drying efficiency increases by about 18% as the ethanol water content decreases from 14 to 0.4%.
w. All reports were completed as required.

## SUMMARIZE PROJECT ACTIVITIES

In the first phase of funding we evaluated a number of components/materials for our overall composite structure. Most specifically, porous supports for our CMS non-porous membrane were evaluated. We combined the results of this evaluation with our engineering and economic model to project that the CMS system, if appropriately scaled up, would be significantly more attractive than existing commercial polyvinyl alcohol membranes and molecular sieves for drying of ethanol. While initial high temperature tests provided attractive results, testing in excess of 5-6 days lead to loss in performance of our overall system when operating on ethanol at temperature.

In this second phase of the program we focused on demonstrating the feasibility, not of individual fibers or sheets, but on small modules containing 2-10 sq. ft. Major uncertainties that will be addressed were included in the statement of work.

This phase represented a research program which builds on phase one feasibility. The second phase of the research program focused on building small research modules (e.g., 2-10 sq. ft) and demonstrating an ability to address all of these issues. As part of this building of research modules we planned to benchmark our performance against other drying devices in the industry. While the second phase focus will be on resolving issues related to hollow fiber systems, a small carry over from the first phase will include modest effort at evaluating low cost and high quality flat sheet materials.

3M informed CMS that they were discontinuing manufacture of the solvent being employed in our membrane formation process. Thus a major new addition to the outlined task was necessary to identify a new processing solvent. Five new solvents received preliminary screening and final selection had yet to be completed. It was recognized that many of the original tasks involved in screening and coating supports of flat sheet and hollow fiber for product application needed to be repeated with the newly selected solvent. DuPont, the supplier of the two CMS membrane polymers investigated in this project, also advised CMS that they were reformulating their manufacturing process for environmental reasons and would be substituting new polymers in the coming year. CMS received a 20 gram sample of one of the polymers for bench comparisons against the current product, nevertheless, more work was required to ensure the new materials could be processed into membranes. Thus some of the advanced tasks outlined for the first phase needed to be addressed in the second phase.

### Task 1.0: Develop HT-HP Potting System

*Objective: Obtain a potting system that can operate with ethanol-water up to 130 C and 60 psig either in the vapor phase or the liquid phase:*

The potting in a membrane module prevents the hot and pressurized ethanol feed from bypassing the hollow fiber membrane and leaking into the permeate side (see Figure 3). Therefore, the potting material must be resistant to ethanol at high temperature and pressure. Working closely with two epoxy suppliers we have identified two epoxy materials suitable for ethanol/water application at high temperature and high pressure.

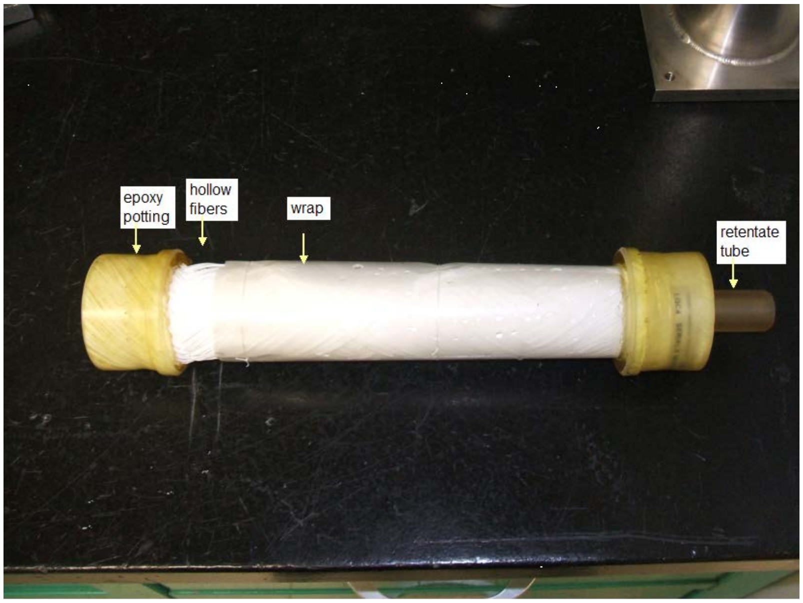


*Figure 3. Hollow fiber membrane module*

### Task 2.0: Develop Robust Epoxy Bonding

*Objective: Obtain a potting system that can effectively bond to the non-porous CMS perfluoromembrane system for operation up to 130°C and pressures up to 60 psig.*

*Plan*

- *Build test samples and run test.*
- *Measure long term bonding performance for 3 months.*

*metric: sample leak rate*

***Accomplishment :*** Samples of both epoxies identified in Task 1 were tested in ethanol at 120°C for 1 year. The new epoxy showed superior performance in three critical categories:

- Bonding
- Resistance to ethanol at 120°C
- Durability

Specifically, the new epoxy leaked ethanol at much lower rate (by 10x) than the old epoxy. In addition, the new epoxy was intact after the 1-year test, while the old epoxy started cracking after 3 months. Therefore, the new epoxy will be used for fabricating permeation modules.

***Experimental Details:*** The procedure for evaluating an epoxy consisted of measuring the leakage rate of a ¼" OD by 5" long tube filled with ethanol that was potted with epoxy in one end and capped with a compression fitting at the other end. The test was done in duplicates with each epoxy. The samples were filled with about 1.5 cc of ethanol and capped. They were maintained at 120°C for 1 year. The leakage rate was determined by measuring the weight loss of each sample. As Table 1 shows, the new epoxy had about 10x lower leakage rate than the old epoxy.

***Table 1. Leakage rate in epoxy samples exposed to ethanol at 120°C for 1 year***

| Epoxy Sample | Average ethanol leak rate (mg/day) |
|---|---|
| new | 0.078 |
| new | 0.089 |
| old | 0.716 |
| old | 0.952 |

Figure 4 shows pictures of the epoxy samples after the 1 year test, The new epoxy samples were intact after 1 year exposure to ethanol (Fig. 4a). In contrast both old epoxy samples developed visible cracks after about three months. The cracks in the old epoxy became gradually larger (Fig 4b).

***Figure 4a. New epoxy samples after exposure to ethanol at 120°C for 1 year***

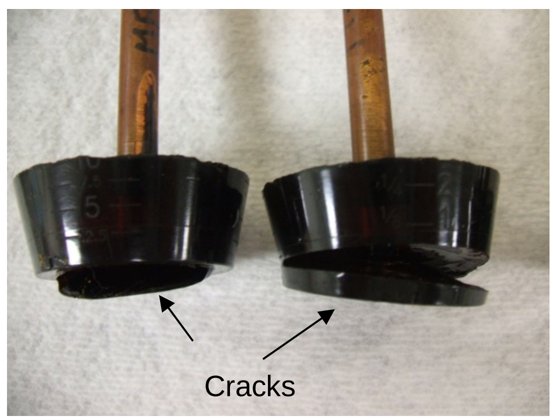


***Figure 4b. Old epoxy samples after exposure to ethanol at 120°C for 1 year***

***Accomplishment:*** A module was built with the optimum epoxy developed. A long term test of this module with ethanol at high temperature shows that the epoxy forms a strong bond with the membrane so that it sustains stable module performance.

***Experimental Details***: A module, identified as MM06, was built with 48 PEEK 1-foot long hollow fibers coated with CMS3 membrane. The module ends were potted with the new epoxy that was shown to be resistant to ethanol at 120°C. The membrane effective area was about 200 cm$^2$. This module was tested for a period of 25 days for about 8-hrs. per day with daily startups and shutdowns. The feed to the membrane was a vapor consisting of 90% ethanol by weight at 120°C and 55 Psia. The feed was put through the shell side of the module. The permeate was collected from each fiber lumen, which was maintained under vacuum of about 2 Psia. This 25-day test with daily start-ups and shutdowns is more severe than a 25-day continuous test with only one startup and one shutdown. This is because daily cyclings subject the module components, specially the epoxy, to the thermal and mechanical stresses of heating and cooling cycles and compression and decompression cycles. In addition, during every shutdown the vapor remaining in the module condenses and wets the membrane and support. Therefore, the membrane is dried during every start-up. Microporous membrane supports are known to be adversely affected by drying because of shrinkage. This is particularly deleterious when the wetting liquid has a high surface tension such as in water.

The water and ethanol permeances, measured every day, are shown in 5. The water-ethanol selectivity, which is the ratio of the water permeance to the ethanol permeance, is shown in 6. Notice that the water permeance declines during the first four days and then stabilizes for the remaining 21 days of the test when a stable selectivity of 8 is maintained (Figure 6). Examination of the module after the test revealed that the epoxy was intact and the fibers-epoxy bond was excellent. Therefore, this demonstrates that the new epoxy is resistant to ethanol at high temperature and that it develops and maintains a strong bonding with the membrane fibers so that stable performance of the module is obtained.

It must be noted that the selectivity of 8 obtained in this test is relatively low. Short term tests with flat sheets show that the inherent selectivity of the CMS3 membrane is at least 16. The low selectivity value obtained for module MM06 is attributed to the fact that the hollow fiber membrane and the module design have not been optimized

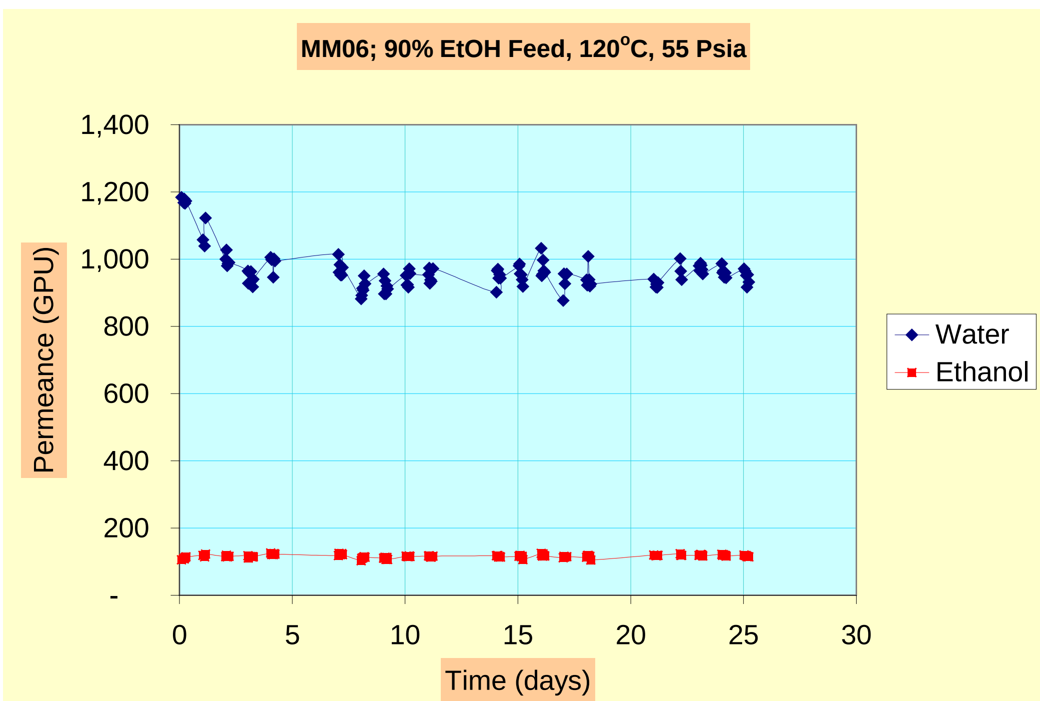


*Figure 5. Permeance in module MM06 during long term test*

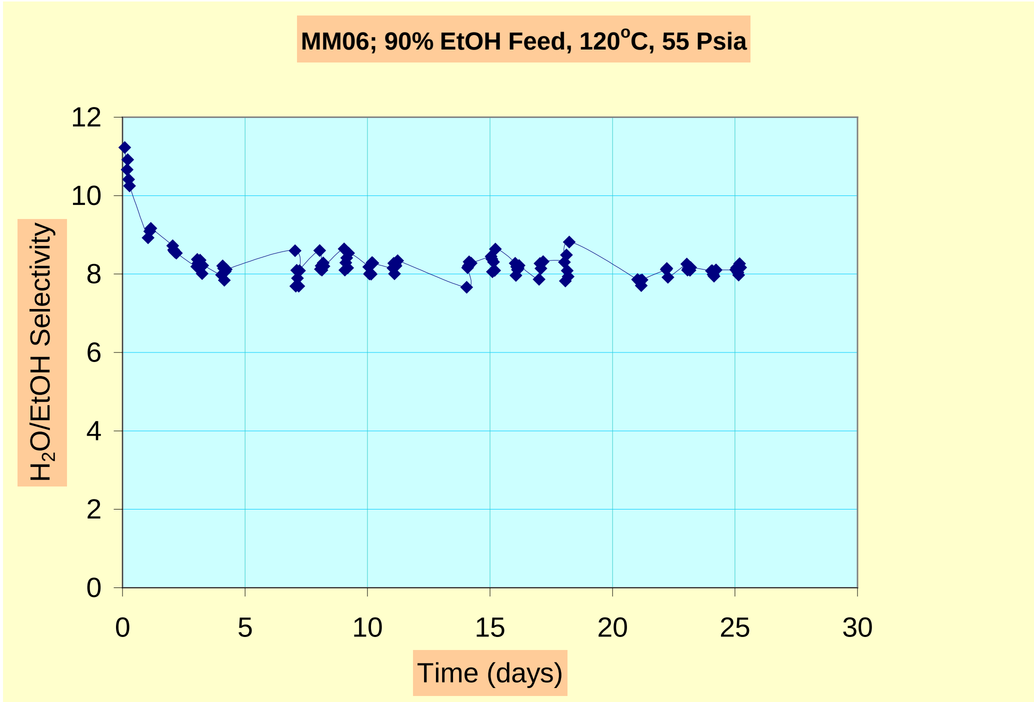


***Figure 6. Selectivity in module MM06 during long term test***

**Task 3.0: Flat Sheet Optimization**

*Objective: To optimize membrane performance by (1) measuring the inherent selectivity and flux properties of CMS-12, -5, and -3 flat-sheet membranes, supported by a PAN substrate, (2) identifying the best candidate membrane from this group, and thereby, (3) defining the performance targets to be used in the follow-on module design and gas permeation studies of later tasks.*

The successful completion of this focused scouting task has the advantage that it permits the membrane's intrinsic performance to be specified separately from the module design and evaluation stages. If needed, an iterative approach can be taken in later tasks because the core membrane properties will have been established in this task.

Specifically, the goals of this task are (a) to identify the CMS membrane type with the best combination of selectivity and flux properties, and to specify whether or not post-fabrication processing steps, *e.g.*, those for a tailored heat treatment scheme, can be used to fine-tune and to optimize membrane behavior; and (b) to optimize the coating process for flat sheets in a manner that the results can be extended to candidate hollow-fiber substrates for membrane modules.

Scale up and optimize flat sheet production by spray coating. Scale up and optimize microgravure coating process for making flat sheet membrane. Produce developmental quantities of optimum CMS membrane for manufacturing spiral wound modules. Optimum flat sheet membrane must have minimum gas selectivities shown in Table 2 below.

***Accomplishments***: CMS has optimized and scaled up two processes for making flat sheet membrane: Spray Coating and Microgravure coating. Developmental quantities of flat sheet membrane have been manufactured: 1200 $ft^2$ by spray coating, and 500 ft2 by microgravure coating. These membranes meet specifications and are sufficient to to make many spiral wound modules in support of this program. CMS has an arrangement with Sepro to manufacture spiral wound modules with membrane supplied by CMS. Therefore, Task 3 has been completed.

**Table 2. Minimum acceptable gas selectivities of flat sheet or hollow fiber membranes**

| Polymer | O2/N2 selectivity | He/N2 selectivity | CO2/N2 selectivity |
|---|---|---|---|
| CMS-3 | 2.5 | 10 | 5.5 |
| CMS-5 | 2.6 | 15 | 5.5 |
| CMS-7 | 1.8 | 4.0 | 4.0 |

***Experimental Details***:

***Spray Coating***: A semiautomated facility process was developed and optimized for producing flat sheet membrane by spray coating. Using this facility (shown in Figure 7), we produced 1200 $ft^2$ of good flat sheet membrane. This latest coating campaign gave a yield of about 90%, meaning that 90% of the total membrane area gives excellent permeation properties. Table 3 shows the gas permeation properties of CMS membranes made by spray coating on PAN porous support, which meet the criterion shown in Table 2. Spray coating tends to give relatively thicker membranes than microgravure coating (discussed below). This is because at least two coating passes are required in spray coating to produce membranes with minimum defects. The resulting thicker coating obtained in spray coating insures that the membrane selectivities meet the specifications of Table 2. The downside of thicker membranes is that they give lower $N_2$ permeance. This can be appreciated when comparing the $N_2$ permeances results of spray coating (Table 3) versus those obtained in microgravure coating (Table 4).

**Figure 7. CMS facility for flat sheet spray coating**

| Table 3. Gas permeation properties of flat sheet membranes made by spray coating on PAN support | | | | | |
|---|---|---|---|---|---|
| Polymer | Membrane Thickness (micron) | N2 permeance (GPU) | O2/N2 selectivity | He/N2 selectivity | CO2/N2 selectivity |
| CMS-3 | 1.5 | 90 | 2.8 | 14.3 | 7.2 |
| CMS-5 | 2.0 | 32 | 2.9 | 23.8 | 7.1 |
| CMS-7 | 2.7 | 363 | 2.1 | 5.7 | 5.2 |

***Microgravure Coating***: In collaboration with AKC, CMS has developed and optimized a process for producing flat sheet membrane by microgravure coating. This facility (shown in Figure 8) was used to produce about 500 ft2 of CMS3, CMS5 and CMS7 flat sheet membranes. These membranes gave acceptable values of gas selectivities (see Table 4 and compare with Table 2) but not as high as those obtained with spray coating (Table 3). This is because the membranes in Table 4 were made with a single coating, which produces significantly thinner membranes than in spray coating, which required two coating passes. Microgravure coating has the advantage over spray coating that it produces membranes with higher $N_2$ permeances (compare Table 3 vs. Table 4).

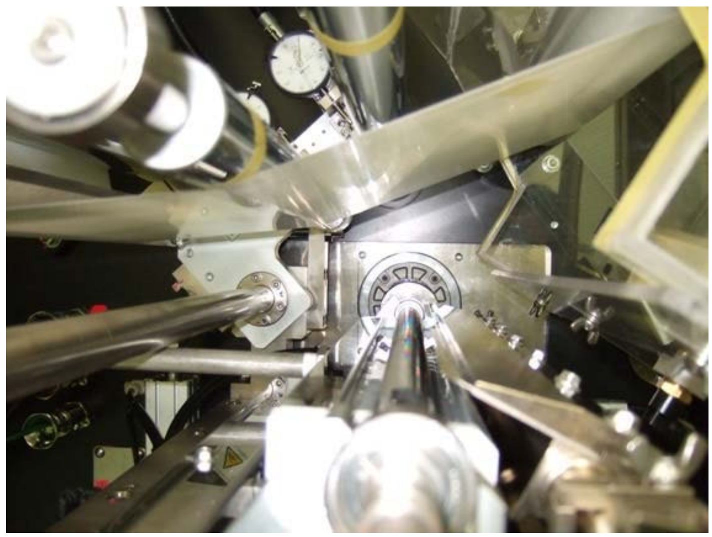

**Figure 8. AKC facility for flat sheet microgravure coating on PAN support**

| Table 4. Gas permeation properties of flat sheet membranes made by microgravure coating | | | | | |
|---|---|---|---|---|---|
| Polymer | Membrane Thickness (micron) | N2 permeance (GPU) | O2/N2 selectivity | He/N2 selectivity | CO2/N2 selectivity |
| CMS-3 | 1.0 | 133.5 | 2.6 | 11.0 | 6.7 |
| CMS-5 | 0.8 | 76.6 | 2.8 | 17.0 | 6.7 |
| CMS-7 | 0.5 | 1786.7 | 1.9 | 4.3 | 4.5 |

**Task 4.0: Development and optimization of hollow fiber membranes**

*Objective: To optimize membrane performance by developing coating techniques and optimizing the coating characteristics for enhanced performance.*

At the end of task 3, one will have the necessary information on the best CMS membrane and the membrane characteristics (e.g. transport properties, thickness of the selective layer) for the dehydration of ethanol. In the current task, findings from Task 3 will be applied to develop hollow fiber membranes with optimized performance.

The primary hollow fiber support of interest for ethanol dehydration is PEEK (poly(ether ether ketone)) because of its higher chemical and thermal stability. Applying the findings from Task 3 to develop hollow fiber membranes involves i) developing a scalable coating technique and necessary equipment to coat the outside/inside surface of PEEK hollow fibers with the appropriate CMS membrane, ii) optimizing the coating characteristics for the enhanced performance. In order to optimize the coating characteristics, ethanol dehydration will be studied in membrane modules made out of these hollow fibers. All of these subtasks will be carried out on a mini-module level before they are scaled up to a small modules containing 2 to 10 sq. ft. At the end of this task, we will have a supply of PEEK hollow fibers coated with appropriate CMS membrane and a membrane device made out of these hollow fibers for ethanol dehydration.

***Accomplishments***: About 25000 linear feet of CMS3 coated hollow fiber membrane were produced.

***Experimental Details***: In collaboration with Porogen, Inc. we have manufactured 25000 linear feet of CMS3 membrane coated on PEEK hollow fiber porous support. PEEK (polyetheretherketone) is chemically resistant to ethanol. The nominal CMS3 membrane coating thickness is about 1 micron. The fiber inside diameter (ID) is about 0.01" and the fiber OD is about 0.017".

Fourteen hollow fiber modules were made with membrane areas ranging from 10 to 280 $cm^2$. Each module was made with a nominal fiber length of 12", and the number of fibers was varied to achieve a given membrane area. The modules were potted using the ethanol and thermally resistant epoxy previously demonstrated. The module is

**Figure 9. Hollow fiber membrane minimodule made for qualifying batch of membrane made for ethanol dehydration.**

encased in a metal housing, which has ports for connecting the feed, retentate and permeate. Figure 9 shows a picture of a minimodule made with 70 fibers and with a membrane area of 280 $cm^2$. The gas permeation performance specifications for a hollow fiber module are listed in Table 5. Each module was tested with single gases ($N_2$, $O_2$, He, and $CO_2$) and the results are shown in Table 6. All 14 modules met or exceeded the N2 permeance and gas selectivitiy specifications (See Tables 5 and 6). Based on this high rate of success with this set of modules we conclude that the available 25000 $ft^2$ of membrane is suitable for making larger modules (5 to 10 $ft^2$) for testing in subsequent tasks.

***Table 5. Minimum acceptable gas permeation properties for hollow fiber modules***

| Polymer | $N_2$ Permeance (GPU) | $O_2/N_2$ selectivity | $He/N_2$ selectivity | $CO_2/N_2$ selectivity |
|---|---|---|---|---|
| CMS-3 | 90 | 2.5 | 10 | 5.5 |

***Table 6. Gas permeation performance of hollow fiber modules***

| Module | Membrane area ($cm^2$) | Average $N_2$ GPU | Selectivity $O_2/N_2$ | Selectivity $He/N_2$ | Selectivity $CO_2/N_2$ |
|---|---|---|---|---|---|
| 1 | 11 | 128 | 2.5 | 11 | 6.0 |
| 2 | 14 | 94 | 2.6 | 11 | 6.5 |
| 3 | 14 | 159 | 2.6 | 11 | 6.4 |
| 4 | 15 | 137 | 2.6 | 11 | 6.3 |
| 5 | 18 | 92 | 2.6 | 11 | 6.4 |
| 6 | 54 | 163 | 2.6 | 11 | 5.6 |
| 7 | 54 | 125 | 2.5 | 11 | 5.7 |
| 8 | 56 | 138 | 2.6 | 11 | 5.7 |
| 9 | 193 | 120 | 2.5 | 10 | 5.6 |
| 10 | 193 | 105 | 2.6 | 11 | 5.8 |
| 11 | 193 | 105 | 2.6 | 11 | 5.7 |
| 12 | 193 | 105 | 2.6 | 11 | 6.3 |
| 13 | 281 | 110 | 2.6 | 12 | 6.0 |
| 14 | 281 | 106 | 2.6 | 11 | 6.2 |

Earlier we discussed the performance of a hollow-fiber module that did not meet water/ethanol selectivity objective of at least 15. We stated then and still believe that this is due to suboptimum module design and inadequate mixing of the feed in the module. This is being addressed in Task 5, but we need to extend the duration of this task to achieve the goal selectivity.

**Task 5.0: Optimize module performance**

*Objective: Develop optimum cartridge housing design and feed configuration to maximize module flux/selectivity.*

*Plan:*

- *Design cartridge housing that minimizes pressure drops, facilitates heat tracing and insulating, and allows easy cartridge change-over.*
- *Build housing.*
- *Evaluate module performance with shell side feed vs. lumen side feed.*

*Metric: module flux/selectivity*

***Planned Activities***: Scale up membrane modules from 280 $cm^2$ to at least 5 $ft^2$. Build at least two modules with membrane area of at least 5 $ft^2$. Study the effect of the feed technique on the module performance.

***Accomplishments***: Two membrane modules with at least 5 $ft^2$ were made. These modules were made with the chemically/thermally resistant materials that were demonstrated and discussed in previous reports. The modules met single gas performance specifications; therefore the module scale-up was successful. Each module was tested with a particular feed technique to determine its effect on ethanol/water permeation performance. One of the feed techniques resulted in optimum mass transfer and enabled the attainment of the water/ethanol selectvity goal of at least 15. Therefore, Task 5 has been completed.

***Experimental Details***:

**a)** ***Module scale-up***: Two modules were manufactured with CMS3 coated hollow fibers supported on chemically resistant polyetheretherketone (PEEK). The modules were potted with the chemically/thermally resistant epoxy. To check the quality of the modules they were tested with single gases $O_2$ and $N_2$. The module areas and the results of the gas tests are shown in Table 7. Both modules met the minimum $O_2/N_2$ selectivity of 2.5. The $N_2$ permeance of both modules is within 7% of the permeance minimum spec of 90 that was set for minimodules with less than 300 $cm^2$ of membrane area. This is acceptable since the scaling-up factor is 20x for module A and 30x for module B. Therefore, the module scale-up was successful.

***Table 7. Gas permeation performance of scaled-up hollow fiber modules***

| Module | membrane area ($ft^2$) | Permeance $N_2$ GPU | Selectivity $O_2/N_2$ |
|---|---|---|---|
| A | 6.6 | 86 | 2.7 |
| B | 9.5 | 84 | 2.6 |
| Spec* | $\geq$5 | $\geq$90 | $\geq$2.5 |

*Spec set for minimodules with 300 $cm^2$ or less membrane area.

**b)** ***Module feed techniques***: Figure 10 shows a schematic of a membrane module. It consists of a hollow fiber cartridge inside a shell. Figure 11 and 12 show the two ways in which the feed can be made to flow around the outside surface of the hollow fibers. In Figure 11 the feed enters the shell through the end port and exists through the shell middle port. In Figure 12 the feed enters the shell middle port and exits through the shell end port.

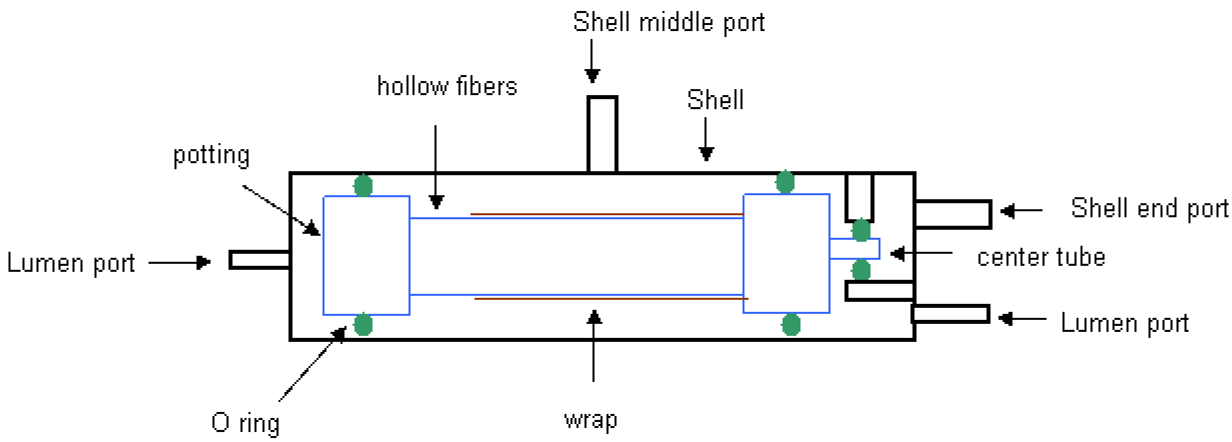


*Figure 10. Module schematic.*

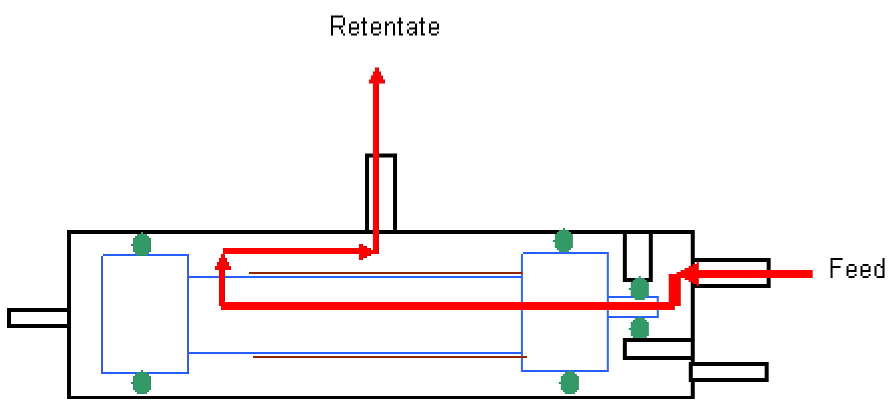


*Figure 11. Shell side feed through the end port.*

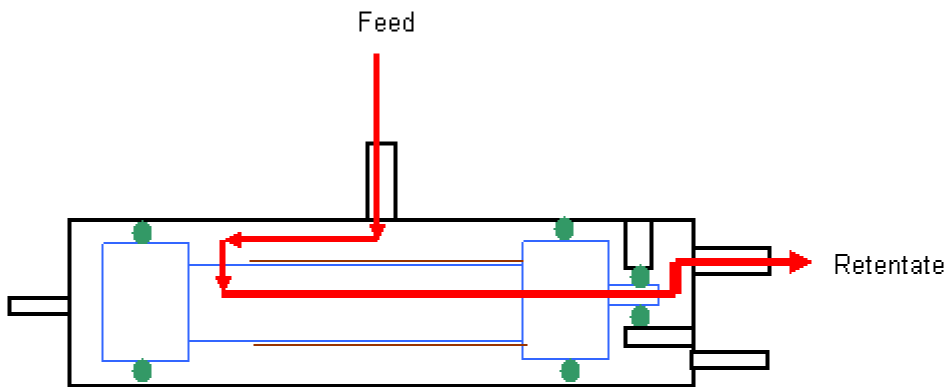


*Figure 12. Shell side feed through the shell middle port.*

c) ***Effect of module feed technique on ethanol/water permeation***: Modules A and B were tested with a mixture of ethanol/water to determine the effect of the feed technique on the module performance. The tests were run with a vapor feed of 45% ethanol at 120$^{o}$C and 30 Psia. As seen in Table 8, the effect on performance of the feed technique is significant. Changing the feed technique by feeding the middle port instead of the end port increased the water permeance by 44% and increased the selectivity from 12 to 17, which is above the goal of 15 for a scaled-up module. The difference can be explained by poor contacting and bypass occurring when we feed through the end port (see Figure 11 and Figure 12). This is because in the end-port feed mode the feed flows radially from the cartridge center tube towards the plastic wrap and expands the wrap. This creates a channel between the wrap and the fiber bundle for the feed to substantially bypass the membrane area. Observation of the cartridge tested with the feed through the end port (Figure 11) reveals that the plastic wrap is permanently deformed and its optimum performance is not restored even when the feed is put through the middle port (Figure 12). Therefore, a module should never be fed through the end port. The module performance obtained with the feed through the middle port yields the optimum performance since it approximates the performance measured in small flat sheet samples. In conclusion, feeding the cartridge through the middle port and removing the retentate through the end port is the optimum way to feed the module, as shown in Figure 12.

***Table 8. Effect of feed technique on module performance.***

| Module | Feed technique | Water Permeance (GPU) | Water/Ethanol Selectivity |
|---|---|---|---|
| A | Middle port (See Fig. 12) | 1090 | 12 |
| B | End port (See Fig. 11) | 1570 | 17 |

**Task 6.0: Demonstrate the CMS membranes can operate in excess of 30 days**

***Planned Activities***: Determine the effect on gas permeation properties of exposing a membrane module to ethanol at high temperature and pressure around the clock for at least 30 days.

***Accomplishments***: Three membrane modules made with pretreated hollow-fibers were exposed to ethanol at high temperature and pressure for 100 days. Despite this drastic exposure, the three modules retained most of their initial gas permeation performance. Depending on the membrane pretreatment method, the maximum gas permeance loss ranged from 3 to 20%. Similarly, the maximum selectivity loss ranged from 0 to 10%. In the case when the fibers were not pretreated, the permeance loss was 13% and the selectivity loss was 6%. This is a moderate loss considering the exposure to such harsh conditions.

***Experimental Details***:

***Modules manufacture***: Two membrane modules (A, B and C) were manufactured with CMS3 coated hollow fibers supported on chemically resistant polyetheretherketone (PEEK). The modules were potted with the chemically and thermally resistant epoxy that was discussed in a previous report. The three modules were made in the same way except that the hollow-fiber membrane was pretreated in a different manner to determine its effect on each module long term performance. The fiber pretreatment for each module is described in Table 9.

***Table 9. Hollow fiber pretreatment before making modules***

| Module | Fibers pretreatment |
|---|---|
| A | Control ( no soak or slack) |
| B | Soaked in EtOH/H2O overnight then dried at 70C |
| C | 4% slack added to fiber length (no soak) |

***Liquid ethanol exposure test***: About half of the space in the shell side of each module was filled with 90% ethanol/10% water and all the ports were plugged. Then the modules were placed in an oven at 100$^oC$ for 31 days. At this temperature the pressure inside the module was about 33 Psia. After 31 days, the modules were removed from the oven, cooled, drained and dried.

***Effect of the ethanol exposure on permeation properties***: The permeation properties of each module were measured with $N_2$, $O_2$, He and $CO_2$ before and after the ethanol exposure. The results are shown in Table 10 and 11. Table 10 shows the permeation properties before and after exposure. Table 11 shows the % change in permeation properties. Tables 10 and 11 show that:

- In module A, in which the fibers were not pretreated, the maximum permeance loss was 13% and the maximum selectivity loss was 6%.
- In module B, in which the fibers were presoaked, the maximum permeance loss was 3% and the maximum selectivity loss was 10%.
- In module B, in which the fibers were given about 0.4% slack in the length, the maximum permeance loss was 20% and there was no selectivity loss. In fact, the average gas selectivity increased by about 4%.

***Table 10. Gas permeation performance of modules exposed to 90% ethanol at 100$^oC$***

| Module | $N_2$ GPU | $O_2$ GPU | He GPU | $CO_2$ GPU | $O_2/N_2$ | $He/N_2$ | $CO_2/N_2$ |
|---|---|---|---|---|---|---|---|
| A before exposure | 159 | 412 | 1767 | 1009 | 2.6 | 11.1 | 6.4 |
| A after exposure | 147 | 386 | 1540 | 906 | 2.6 | 10.5 | 6.2 |
| B before exposure | 128 | 326 | 1409 | 766 | 2.5 | 11.0 | 6.0 |
| B after exposure | 138 | 326 | 1361 | 758 | 2.4 | 9.9 | 5.5 |
| C before exposure | 137 | 352 | 1538 | 860 | 2.6 | 11.2 | 6.3 |
| C after exposure | 110 | 294 | 1269 | 728 | 2.7 | 11.5 | 6.6 |

**Table 11. % change in module gas permeation performance due to exposure to 90% ethanol at 100°C**

| | % Change | | | | | | |
|---|---|---|---|---|---|---|---|
| Module | $N_2$ GPU | $O_2$ GPU | He GPU | $CO_2$ GPU | $O_2/N_2$ | $He/N_2$ | $CO_2/N_2$ |
| A | -7 | -6 | -13 | -10 | 1 | -6 | -3 |
| B | 8 | 0 | -3 | -1 | -7 | -10 | -8 |
| C | -20 | -16 | -17 | -15 | 4 | 3 | 6 |

***Long-Term Testing Experimental Details***:

***Module***: The long-term test module was fabricated in-house and identified as LGC6-02JA072122. The module was made using CMS3 membrane, which was coated on the chemically and thermally resistant PEEK hollow fiber support. The CMS3 layer thickness is about 1.5 micron. The module was potted using a chemically and thermally resistant epoxy, which was previously demonstrated and discussed in a preceding report. The active membrane area of the module is 7.5 $ft^2$.

***Long Term Test Description***: The test was run in a system that is depicted schematically in Figure 13. The feed to the module consisted of an ethanol-water mixture that was obtained from one bioethanol plants built by ICM[1]. The test originally was run for 36 days. Each day the test was started up and run for about 8 hours and then shut down. The start-up consisted of heating up the evaporator and module to the desired operating temperature. When operating temperature was achieved, the ethanol feed was pumped to the evaporator to produce a vapor that was fed continuously to the module. The permeate side of the module was maintained under a partial vacuum. The process was allowed to run at steady state for several hours. The shutdown involved stopping the ethanol feed, shutting down the heater, and then allowing the module to cool down over a period of several hours. This operation was repeated each day for 36 days. During the steady state operation samples of the feed, and permeate were obtained for measuring the ethanol concentration. In

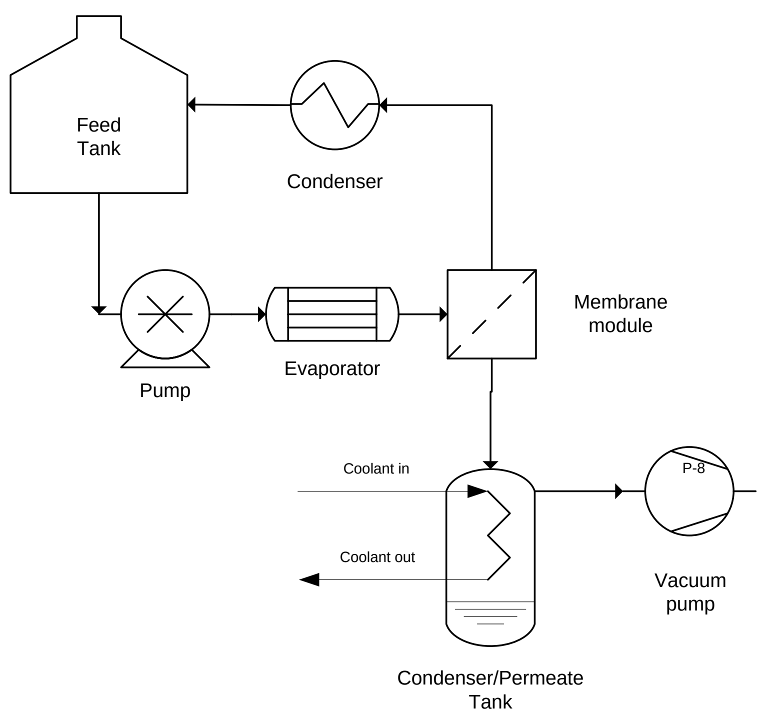


***Figure 13. Schematic of the Ethanol membrane dehydration***

[1] ICM Inc. is an industry leader for the design, construction, and support of ethanol plants.

addition, the feed, retentate and permeate flowrates were measured. Also temperatures and pressures of the feed, retentate and permeate were computer recorded. The test process conditions are summarized in Table 11.

***Table 12. Ranges of test parameters in the ethanol dehydration long-term test***

| | |
|---|---|
| Module ID | LGC6-02JA072122 |
| Feed mixture | Ethanol-water |
| Feed EtOH concentration (weight %) | 86 to 95 |
| Retentate EtOH concentration (weight %) | 89 to 96 |
| Permeate EtOH concentration (weight %) | 51 to 76 |
| Feed temperature ($^oC$) | 100 to 114 |
| Retentate temperature ($^oC$) | 105 to 111 |
| Permeate temperature ($^oC$) | 91 to 101 |
| Feed pressure (Psia) | 24 to 31 |
| Retentate pressure (Psia) | 22 to 29 |
| Permeate pressure (Psia) | 5 to 7 |
| Closed end permeate pressure (Psia) | 6 to 8 |
| Feed flowrate (Kg/h) | 5 to 13 |
| Permeate flowrate (Kg/h) | 0.4 to 0.54 |
| Stage cut (%) | 3.6 to 9.4 |

The long term test started during the previous quarter was continued during this period to complete a 50-day test. This test involved the dehydration of an authentic sample of ethanol derived from biomass with a full size membrane module. Up to day 43 the membrane showed stable performance and the observed variability in that period can be explained by changes in process parameters and experimental error. After day 43 there appeared to be an unexpected decline that needs further investigation for determining the root cause.

***Experimental Details***:

***Module***: A module was fabricated in-house and identified as LGC6-02JA072122. The module was made using CMS3 membrane, which was coated on the chemically and thermally resistant PEEK hollow fiber support. The CMS3 layer thickness is about 1.5 micron. The module was potted using a chemically and thermally resistant epoxy, which was previously demonstrated and discussed in a preceding report. The active membrane area of the module is 7.5 $ft^2$.

***Discussion of long term test results***: The process parameters were used for calculating the module daily permeation properties. The module permeation properties consist of the water permeability and the water/ethanol selectivity. These properties are displayed in Figure 14. The performance results are summarized in Table 13. After day 33 there appears to be a step increase in the water permeability (see Figure 14). This step increase correlates with a step increase in feed flowrate after day 33 (see Figure 15). This can be explained by the better mixing of the feed at higher flowrate. With better mixing the contacting of the feed with the membrane area is enhanced and, thus the permeability increases. The permeability of water increases in higher proportion than that of ethanol because better mixing favors the minor component, which is water, thus increasing the selectivity.

Figure 14 shows that there is up and down performance variability. Analysis of the data indicates that there is not a good correlation between the performance variability and any of the process parameters other than the feed flowrate. Thus, part of the variation in permeability is due to changes in the feed flowrate. The unexplained variability appears random and is probably due to experimental errors in the measurements. This suggests that on average the membrane performance is quite stable at least up to day 43. However, there appears to be a decline in water permeability that started after day 43 and continued through day 50. This decline cannot be plausibly explained by variations in the process parameters. This needs to be investigated further to determine if that decline is real and persists or if it is due to random variability.

***Table 13. Summary of module performance in the ethanol dehydration long-term test***

| | |
|---|---|
| $H_2O$ permeability range (Barrer) | 1700 to 2100 |
| Average $H_2O$ permeability (Barrer) | 1900 |
| $H_2O$/EtOH selectivity range | 17 to 20 |
| Average $H_2O$/EtOH selectivity | 18 |

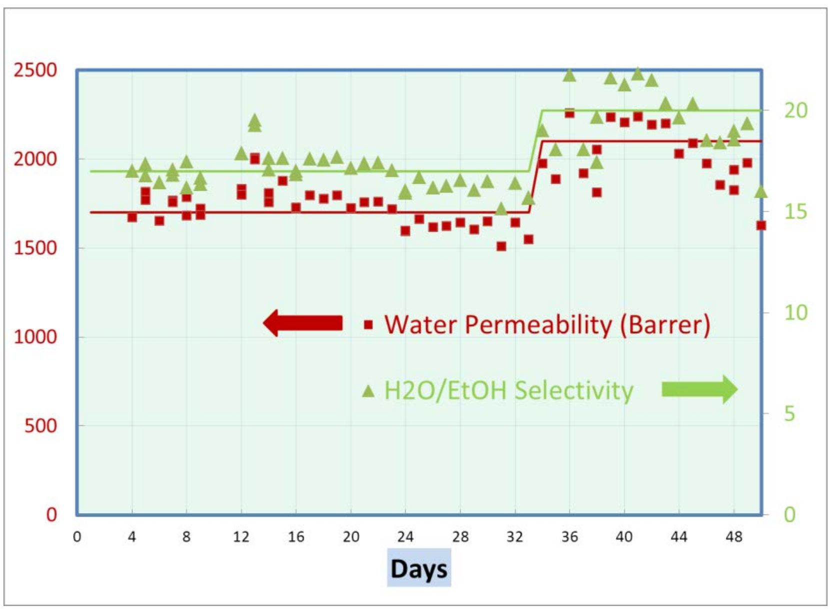


***Figure 14. Effect of time on membrane module performance during the dehydration of ethanol***

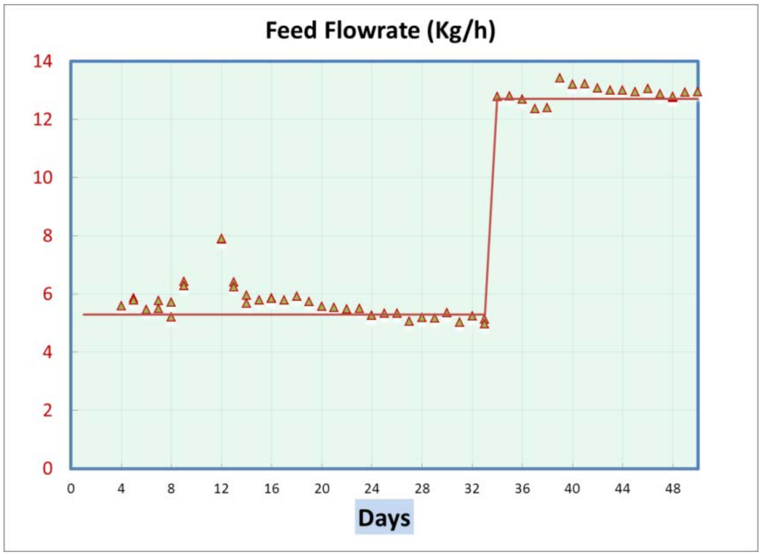


*Figure 15. Feed flowrate versus time in the dehydration of ethanol long term test*

***Explanation of Variance***: Testing in Task 6 was extended in order to further investigate membrane stability and performance variability. The additional data appears to indicate some unexpected performance decline in the last few days of the test. This Task needs to be extended for determining root causes and whether or not the decline is irreversible

***Discussion of 100-day long term test results***: The water permeability and the ethanol permeability were calculated using the measured process parameters. The water permeability is displayed in Figure 16. The water permeability shows significant variability with time. Throughout the 100-day test the process parameters were varied within the ranges shown in Table 12. Most of the variability can be explained by variability in two process parameters: feed composition and feed flowrate. This is illustrated in Figures 17, 18, and 19 and is explained below. The remaining unexplained variability is likely due to experimental error in the measurements..

**Does module performance decline with time?**: Water permeability decline was observed between days 44 and 50 and was discussed in the previous report but not explained. This decline was reversed after day 52 as shown in Figure 16. As shown below, this decline is not due to deterioration in the module performance but to sensitivity to changes in process parameters. The data shown in Table 14 indicate that, at a given set of operating conditions (high or low feed %alcohol) the water permeability did not change significantly with time.

*Table 14. Effect of time on water permeability at constant % alcohol feed and feed flowrate*

| Day | *Feed alcohol (% weight)* | *water permeability (barrer)* |
|---|---|---|
| 4 | 92.0 | 1670 |
| 59 | 92.5 | 1660 |
| 87 | 67.5 | 2720 |
| 100 | 68.2 | 2737 |

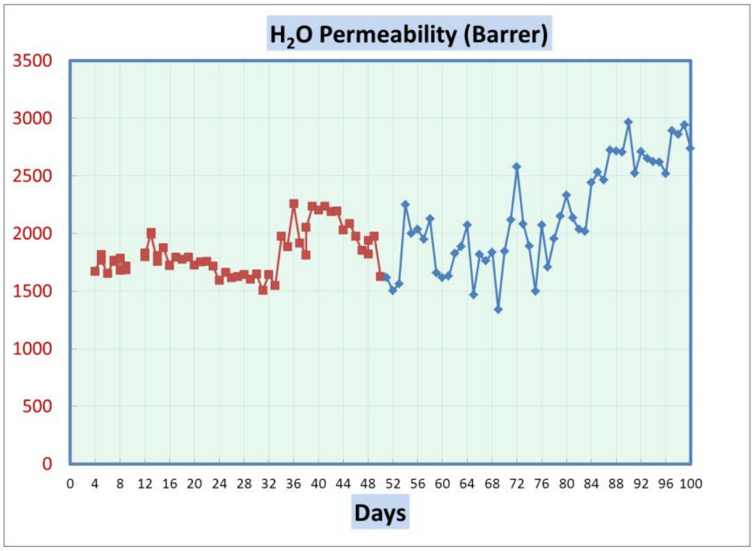


***Figure 16. Effect of time on the membrane module water permeability during the dehydration of ethanol***

**<u>Effect of feed composition:</u>** The same permeability data from Figure 16 was plotted as a function of % ethanol in the feed. Figure 17 shows that the feed composition has a strong effect on the water permeability. Most of the changes in water permeability with time seen in Figure 16 coincide with changes in the feed composition. For instance, the high water permeability seen in days 84 to 100 coincided with those tests being run at alcohol feed concentration between 66 to 68%. The low water permeability seen in days 1 to 32 (see Fig. 16) occurred at alcohol feed concentration in the range of 94 to 99+%.

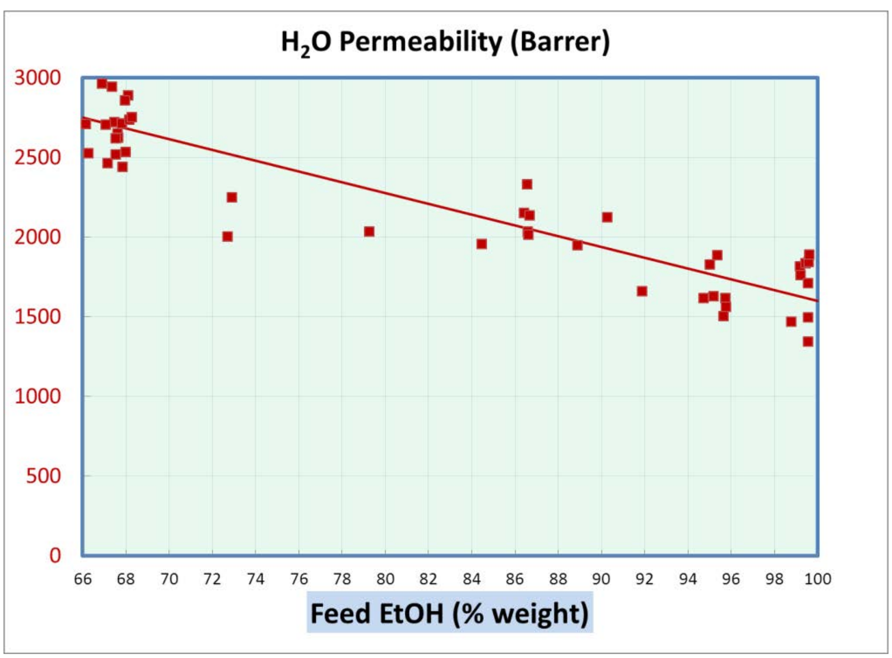


***Figure 17. Effect of the feed composition on the water permeability***

**Effect of feed Feed Flowrate:** A significant portion of the variability seen in figure 17 at a given feed composition is explained by variations in the feed flowrate. This is illustrated in Figure 18, which shows that an increase in water permeability coincides with an increase in the feed flowrate after day 33. This cause-effect relationship is plausible because increasing feed flowrate enhances the feed-membrane contacting, which improves the mass transfer efficiency.

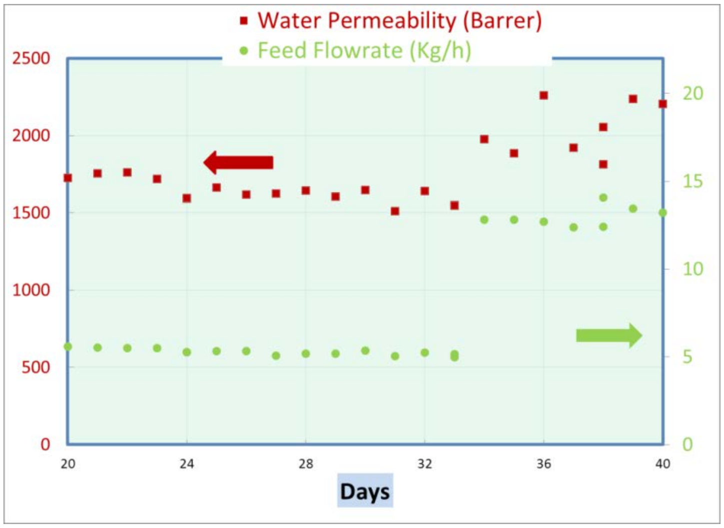


*Figure 18. Correlation between the feed flowrate and the water permeability*

**Effect of temperature:** At constant feed flowrate, and feed composition varying the feed temperature does not appear to affect the water permeability significantly. This is shown in Figure 19. Therefore, variations in temperature during the 100-day test do not explain the variations seen in the water permeability seen in Figure 16.

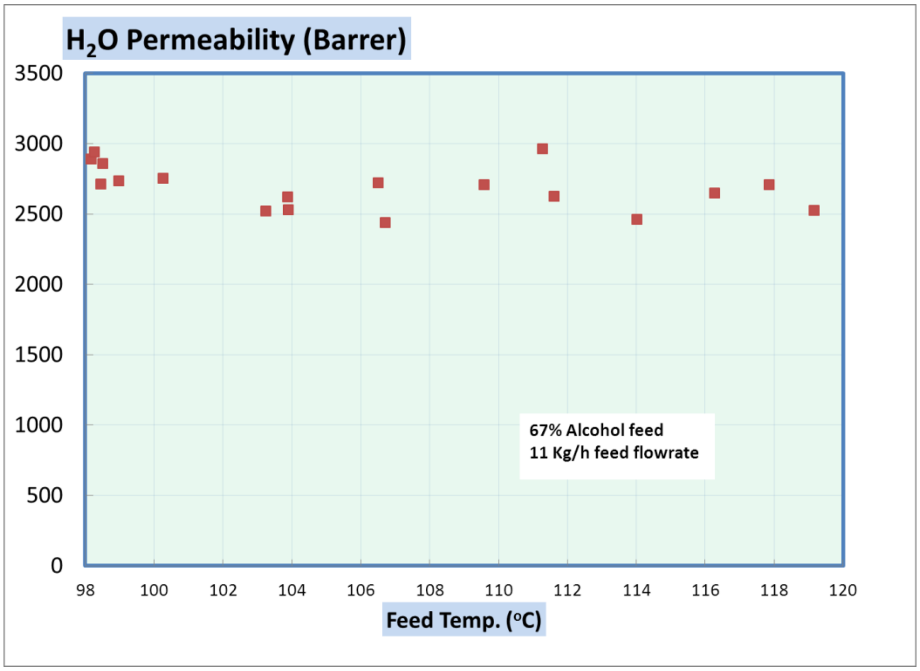


*Figure 19. Effect of feed temperature on the water permeability*

***Accomplishments***: We continued the long-term test for an additional 50 days which adds up to 100 days of testing. The module continued performing at very high water permeability with no permanent performance decline. The cause of the apparent water permeability decline observed after day 44 noted in the previous report, can be explained by variability in process conditions. Specifically, changes in the ethanol feed concentration and the feed flowrate affect the water permeability. In addition, some variability can be attributed to experimental error in the measurements. The additional data show that there is no permanent permeability declining trend. After day 50, the water permeability was restored to the high values observed in the first 50 days. Therefore, this extended test has demonstrated stable module performance in the dehydration of ethanol for 100 days. This exceeds our initial goal of demonstrating module stability for at least 30 days.

### Task 7.0: Determine optimal module geometry.

Residence time distributions (RTD) have evidenced non-uniformities in the hollow fiber module geometries of some current modules. The RTDs typically show premature breakthrough or short circuiting of fluid elements as well as low flow regions on the shell side. Variations in curvature of hollow fiber winding patterns between inside and outside of wound cartridges also contribute to variations in lumen flow rates. The combination of these factors leads to separation inefficiencies that must be addressed to achieve high performing membrane devices. In addition, the difference in wound verses parallel flow modules should be evaluated.

***Planned Activities***: Build a spiral wound membrane module and a hollow fiber membrane module. Measure the performance of both modules and compare them for determining the optimum module configuration (geometry).

***Accomplishments***: Flat sheet coated with CMS3 membrane was fabricated for building a spiral wound module. The flat sheet was sent to our subcontractor Sepro, Inc. to build the spiral wound module. This module is expected in time for completing Task 7 on schedule. Meanwhile, we started building a CMS3 hollow fiber module in-house. This will serve as a control for comparing with the spiral wound module. The spiral wound module has a radically different geometry than the hollow fiber module. By measuring the performance of both modules we will be able to determine if one is better than the other.

We measured the performances of a spiral-wound membrane module (flat sheet) and a hollow fiber module. We found that the normalized performances of both modules are essentially the same despite the very different geometries. However, significantly more membrane area can be packed in a hollow fiber module than in a spiral wound module of the same volume. Thus, the productivity per unit volume of the hollow fiber module is significantly larger than in the spiral-wound module. Therefore, the hollow fiber geometry is preferred for ethanol dehydration over the spiral wound geometry. This geometry will be pursued as we attempt to commercialize membrane systems for the dehydration of ethanol.

**The spiral wound module:** The spiral wound module is made of flat sheet membrane. A leaf is made of two membrane sheets glued together back-to-back with a permeate spacer in-between them. One end of the leaf is attached to a perforated tube and the leaf is rolled in spiral fashion around the tube. The permeate is collected in the center tube. Figure 20 shows a picture of the spiral wound module that was built for this program.

*Figure 20. CMS spiral-wound membrane module*

**The hollow fiber module:** The hollow fiber module is made of many capillary size hollow fibers. The fibers are wound around a center tube and potted at the ends with epoxy. Figure 21 shows a picture of a hollow fiber module. The feed contacts the outside surface of the hollow fibers. The permeate is collected in the lumen of the fibers.

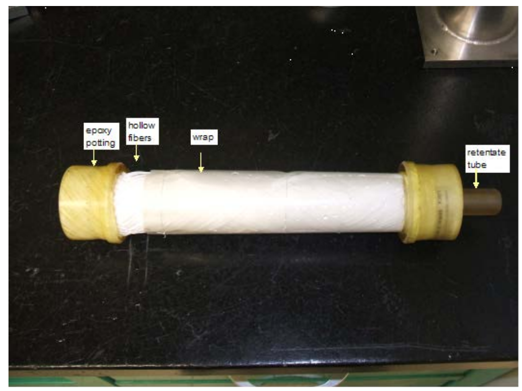


*Figure 21. CMS hollow-fiber membrane module*

**Spiral wound module manufacture:** The membrane was made in CMS facilities by spray coating CMS3 polymer solution on polyacrylonitrile (PAN) flat sheet porous support. The membrane was converted into a spiral-wound module in the facilities of our manufacturing partner Sepro, Inc. The module membrane area is about 1.5 $ft^2$.

**Hollow fiber module manufacture:** The membrane was made in the facilities of our manufacturing partner Porogen Inc. using its proprietary technology. The CMS3 membrane was coated on polyetheretherketone (PEEK) porous hollow fiber support. The module was fabricated in CMS facilities. The module membrane area is about 9.5 $ft^2$.

**Test with EtOH/Water:** The hollow-fiber module and the spiral-wound module were tested sequentially in the ethanol dehydration experimental unit depicted schematically in Figure 13. The feed to the module consisted of a mixture of 50 to 70% Ethanol in the vapor phase at about 110 $^oC$ and 20 Psia. The permeate was maintained under vacuum at a pressure of about 2 Psia. The membrane performance characterized by the water permeability and water-ethanol selectivity, were calculated for each module using the measured process parameters for each test. The results are summarized in Table 15.

**Results and discussion:** As shown in Table 15, the normalized performances, characterized by the permeability and selectivity, of the two module geometries is about the same. However, the hollow-fiber geometry has the distinct advantage that more membrane area it can pack more membrane area per unit volume than the spiral-wound geometry (450 vs. 130 $ft^2/ft^3$). Increasing membrane area density is highly desirable to lower module manufacturing cost.

*Table 15. Ethanol dehydration performance: spiral-wound vs. hollow-fiber modules*

| Module geometry | *Dimension OD x length* | Membrane area ($ft^2$) | Area/volume ($ft^2/ft^3$) | Water permeability (Barrer) | Water/EtOH selectivity |
|---|---|---|---|---|---|
| Hollow fiber | 1.5"x11.5" | 9.5 | 450 | 2600 | 20 |
| Spiral wound | 2"x11.5" | 1.5 | 130 | 2500 | 20 |

**Task 8.0: Demonstrate ability to produce 99.5% FGE.**

Historically CMS membranes have been used for very modest enrichments and low recovery of the permeating species. Examples include converting air to nitrogen enriched air containing 81% nitrogen versus air at 79% nitrogen. This program is converting streams containing 90% ethanol to 99.5% ethanol. This ethanol product will thus require a high degree of water removal over a range of feed and operating conditions and production capacities. Besides attention to cartridge design, significant system design and fabrication enhancements in overall system fluid dynamics will be necessary to assure an ability to produce 99.5% fuel grade ethanol on a consistent basis.

***Planned Activities***: Run experiments to demonstrate that the membrane module can remove the last bit of water for producing ethanol with a maximum of 0.5% water. Run tests with Ethanol containing in the range of 0.5 to 14% water and determine membrane system performance.

***Accomplishments***: We measured the performance of a hollow fiber membrane module system with feed concentrations in the range of 0.5 to 14% water. The data show that the system efficiently removes water from ethanol in the whole range studied. The data also shows that the drying efficiency increases somewhat as the ethanol gets drier. The tests demonstrate that the CMS membrane system can dry ethanol to produce fuel grade ethanol (FGE), i.e., containing no more than 0.5% water by weight.

*Table 16. Test parameters in the ethanol dehydration for producing FGE*

| | |
|---|---|
| Module ID | LGC6-02JA072122 |
| Feed EtOH concentration (weight %) | 86 to 99.6 |
| Membrane type | CMS3 on PEEK hollow fibers |
| Permeate EtOH concentration (weight %) | 2 to 48 |
| Feed temperature ($^oC$) | 100 to 120 |
| Permeate temperature ($^oC$) | 91 to 101 |
| Feed pressure (Psia) | 24 to 31 |
| Retentate pressure (Psia) | 22 to 29 |
| Permeate pressure (Psia) | 4 to 7 |
| Closed end permeate pressure (Psia) | 4.5 to 8 |
| Feed flowrate (Kg/h) | 5 to 13 |
| Permeate flowrate (Kg/h) | 0.4 to 0.54 |
| Stage cut (%) | 3 to 9 |

**Test Conditions and Results:** The same hollow fiber membrane module system used in the long term test was used for this test. The test was run in the same experimental equipment. The test process conditions are summarized in Table 16.

**Effect of Feed %Water on Permeability:** Figure 22 shows that the permeability seems to increase from about 1700 to 2000 barrer as the ethanol gets drier in the range of 14 to 0.4% water in the feed. In the same range, the ethanol permeability is approximately constant and about 100 barrer. Therefore, the water/ethanol selectivity (ratio of water to ethanol permeabilities) increases from about 17 to about 20 as the water content in ethanol decreases from 14 to 0.4% water. This demonstrates that the CMS membrane system dries ethanol efficiently from 14% water to 0.4% water (≤0.5% water is required for fuel grade ethanol). The system drying efficiency increases by about 18% as the ethanol water content decreases from 14 to 0.4%.

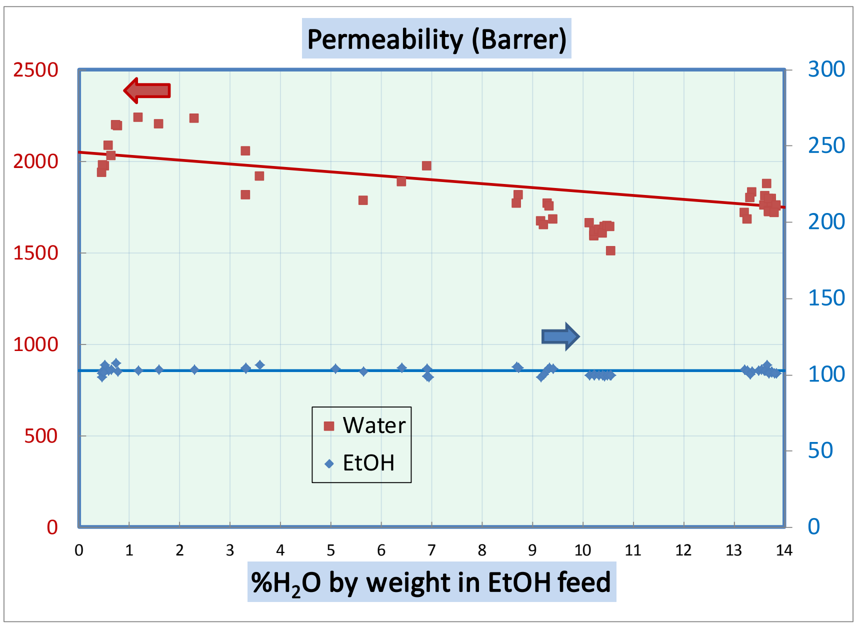


*Figure 22. CMS hollow fiber membrane module*

**Task 9.0: Project Management and Reporting**

Reports were provided in accordance with the Federal Assistance Reporting Checklist following the instructions included therein.

## IDENTIFY PRODUCTS DEVELOPED UNDER THE AWARD AND TECHNOLOGY TRANSFER ACTIVITIES

- ✓ U.S. Patent application (US20120283489), "Removal of Water from Fluids", has been allowed
- ✓ CMS working with two potential users to demonstrate/implement CMS technology in their commercial operations
- ✓ Market development study commissioned by CMS is under way
- ✓ A liquid dehydration platform was established and lubrication oil dehydration systems are being commercialized and field tested
- ✓ We updated the CMS website discussing our work on solvents and EtOH dehydration
- ✓ A partnership was established with Pfloumer Specialty Chemical company and a field test in EtOH dehydration is underway