

## High Surface Area Inorganic Membrane for Process Water Removal

### Improved Energy Efficiency in Ethanol/Water Separation and Natural Gas Dehydration

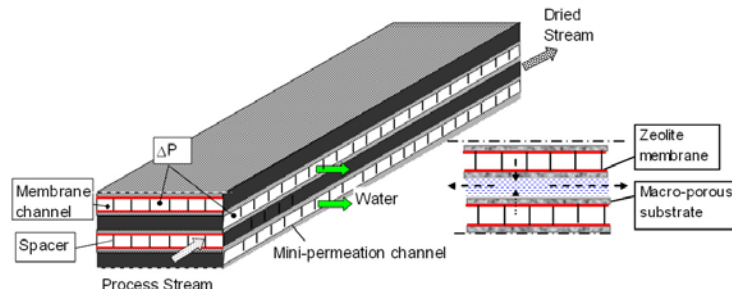
Water removal processes, such as distillation, drying, evaporation, and extraction are all energy-intensive. Mini-channel planar membrane modules made of zeolite and porous metallic substrate materials can remove water or moisture from a range of industrial process streams using less energy consumption than existing adsorption, distillation or solvent extraction technologies. Unlike conventional separation processes, separations with membranes are continuous and operate under constant temperature and pressure so that no adsorption/regeneration cycles need to be performed. Separation membranes also provide the combined performance attributes of chemical and thermal stability, mechanical ruggedness, high permeation flux, and large separation selectivity.

Among all possible applications, this project will target ethanol/water separations in ethanol fuel production and natural gas dehydration. Ethanol production has been a fast-growing industry and corn-to-ethanol conversion accounts for nearly two thirds of the overall energy consumption (including production, transport, conversion, and distribution of ethanol fuel). Approximately 80% of the energy used in ethanol conversion plants is consumed in water removal from the product. Therefore, improvements in water removal from ethanol production would significantly help the U.S. economy by reducing production energy intensity, foreign oil dependence, and green house gas emissions.

### Benefits for Our Industry and Our Nation

In 2009, the U.S. produced of 10 billion gallons of ethanol.<sup>1</sup> Energy consumption is the largest operation cost in ethanol plants.<sup>2</sup> Economic competitiveness of existing corn-fed ethanol plants would be improved by a substantial reduction of the energy consumption. The energy-efficient ethanol/water separation technology would also help development of cellulosic ethanol plants in the future.<sup>3</sup>

The proposed membrane technology, if used in natural gas drying, could result in significant energy saving and green house reductions in the U.S.



Schematics of cross-flow mini-channel membrane device. The Zeolite membrane is prepared on macro-porous metal substrate sheets (50-200Qm thick). Membrane sheets are stacked layer-by-layer to form mini-channel modules (~1mm spacing) of high surface area packing density and of high mass transfer rate.

*Illustration courtesy of Pacific Northwest National Laboratory.*

### Applications in Our Nation's Industry

In principle, any adsorption and absorption process for moisture removal can be replaced with this novel membrane for better energy efficiency. Any distillation and extraction processes for separation of water from hydrocarbons or solvents (such as ethanol) can also be conducted with this membrane technology.

### Project Description

The objective of this project is to demonstrate the fabrication and performance advantages of paper-thin molecular sieve/porous metal sheet membranes of surface area packing density one order of magnitude higher than the conventional membrane tube. The molecular sieve membrane made of zeolite, ceramic oxide-type materials allows permeation of water molecules only while blocking all other molecules. Thus, water molecules can be removed from a process stream without changing its temperature and pressure. The new, transformational, membrane technology will be used for water/ethanol separations and reduce energy consumption by >20% over distillation and adsorption.

### Barriers

- Separation performance of the real-world feedstock has to be experimentally tested. If some species in the feedstock experiences strong adsorption and/or reaction on the zeolite external surface, it may block access of the zeolite pores by water and/or damage the membrane over time.
- If fundamental material issues are not understood and resolved they can cause catastrophic failure when the product and process developments are moved into large scales.

## Pathways

The planar membrane sheet will be prepared from inexpensive raw materials such as metal oxides and the mini-channel membrane module will be assembled layer-by-layer. The suitable material processing methods will be identified and studied to facilitate automation of the manufacturing process in large scales.

The team will first prepare one single membrane sheet and demonstrate separation functions with simulated ethanol/water mixtures. After completion of this phase, they will demonstrate separation performance with real-world feedstock.

## Milestones

This project started in September 2008.

- Sodium aluminosilicate (NaA) zeolite membrane preparation on thin porous metallic support sheets (Completed)
- Demonstrate steady-state performance of prepared membrane with simulated ethanol/water mixtures (Completed)
- Demonstrate fabrication and scale-up feasibility of unique thin porous metal sheets. Such a support sheet is critical to technical and economic viability of the new membrane product technology
- Demonstrate stable separation performance of zeolite/metal sheet membranes with real-world ethanol/water mixtures under practical conditions
- Demonstrate natural gas dehydration of the new membrane
- Define membrane and module manufacturing process windows and establish product cost models
- Complete process design and economics analysis with inputs from experimental data

## Commercialization

All activities will be pursued by closely working with industrial partners. PNNL will closely work with ADMA Products, a producer of porous metallic products for the material development and early-stage assessment of manufacturability. PNNL will work closely with Pacific Ethanol – an end user of the membrane technology to test the membrane under practical conditions and analyze the process economics. This project will identify and develop a zeolite membrane fabrication process that can be readily scaled up to make the membrane product at a cost competitive to the polymeric sheets/plates.

## Project Partners

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(endnotes)

- <sup>1</sup> U.S. Energy Information Administration, Annual Energy Review 2009, DOE/EIA-0384(2009) (Washington, DC: U.S. Department of Energy, August 2010), 290, <http://www.eia.doe.gov/totalenergy/data/annual/pdf/aer.pdf>.
- <sup>2</sup> Hosein Shapouri and Paul Gallagher, USDA's 2002 Ethanol Cost-of-Production Survey, Agriculture Economic Report Number 841 (Washington, DC: U.S. Department of Agriculture, July 2005), [http://www.usda.gov/oce/reports/energy/USDA\\_2002\\_ETHANOL.pdf](http://www.usda.gov/oce/reports/energy/USDA_2002_ETHANOL.pdf).
- <sup>3</sup> Stefan Osborne, Energy in 2020: Assessing the Economic Effects of Commercialization of Cellulosic Ethanol (Washington, DC: U.S. Department of Commerce, November 2007), <http://trade.gov/media/publications/pdf/cellulosic2007.pdf>.