Chemically and Thermally Resistant Novel Perfluoromembrane Reactors for Efficient and Selective Removal of Water from Equilibrium-limited Reactions

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International Conference on Catalysis in Membrane Reactors
Kolkata, India, December 18-21, 2007

Outline

- CMS, Membranes and Features
- Platform Technologies / Background
- Objectives
- Experimental
- Results
- Concluding Remarks

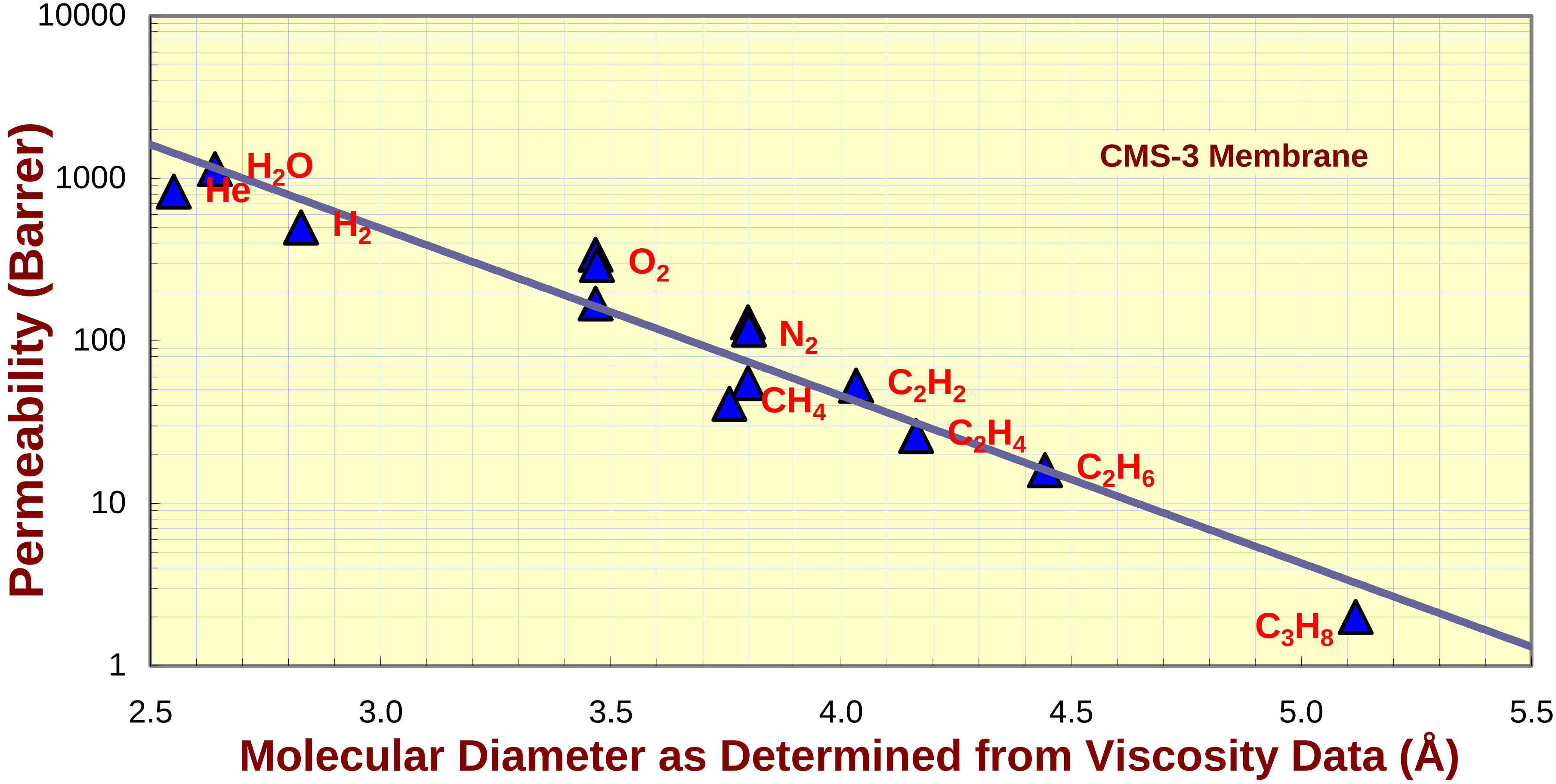
Compact Membrane Systems, Inc.

- A technology development company based in Wilmington, Delaware, USA.
- Membrane products and applications R&D
- Focus on fluorinated polymers
  - Exceptional membrane permeation flux
  - Chemical and thermal resistance
- CMS's three modes of business:
  - Technology Licenses
  - Partner and SBIR Grant funded R&D projects
  - Commercial products

CMS Membranes - Features

- **Glassy Membrane**
  - Transports atmospheric gasses
  - Retains hydrocarbons larger than C_2
- **PTFE-like Polymers**
  - Excellent chemical and thermal resistance
  - Resistant to oxidation reactions
- **Extremely High Gas Permeance**
  - Small membrane devices and associated equipment
- **Repels Hydrocarbons**
  - Non-fouling
  - Retains flux over time

Permeability vs. Molecular Diameter of Gases



CMS Platform Membrane Technologies

- **Gas Separations**
  - Removal of Air from Volatile Organic Compounds (VOC)
  - Oxygen- and Nitrogen-Enriched Air
- **Degassing Liquids and Gas/Liquid Contacting**
  - Power Transformer Oil Degassing
  - Bubble-less Ozonation of Water
- **Dewatering of Organic Chemicals**
  - Dehydration of Fuel Grade Ethanol
  - Removal of Water from Hydraulic Fluids

Gasoline Vapor Emissions from UST

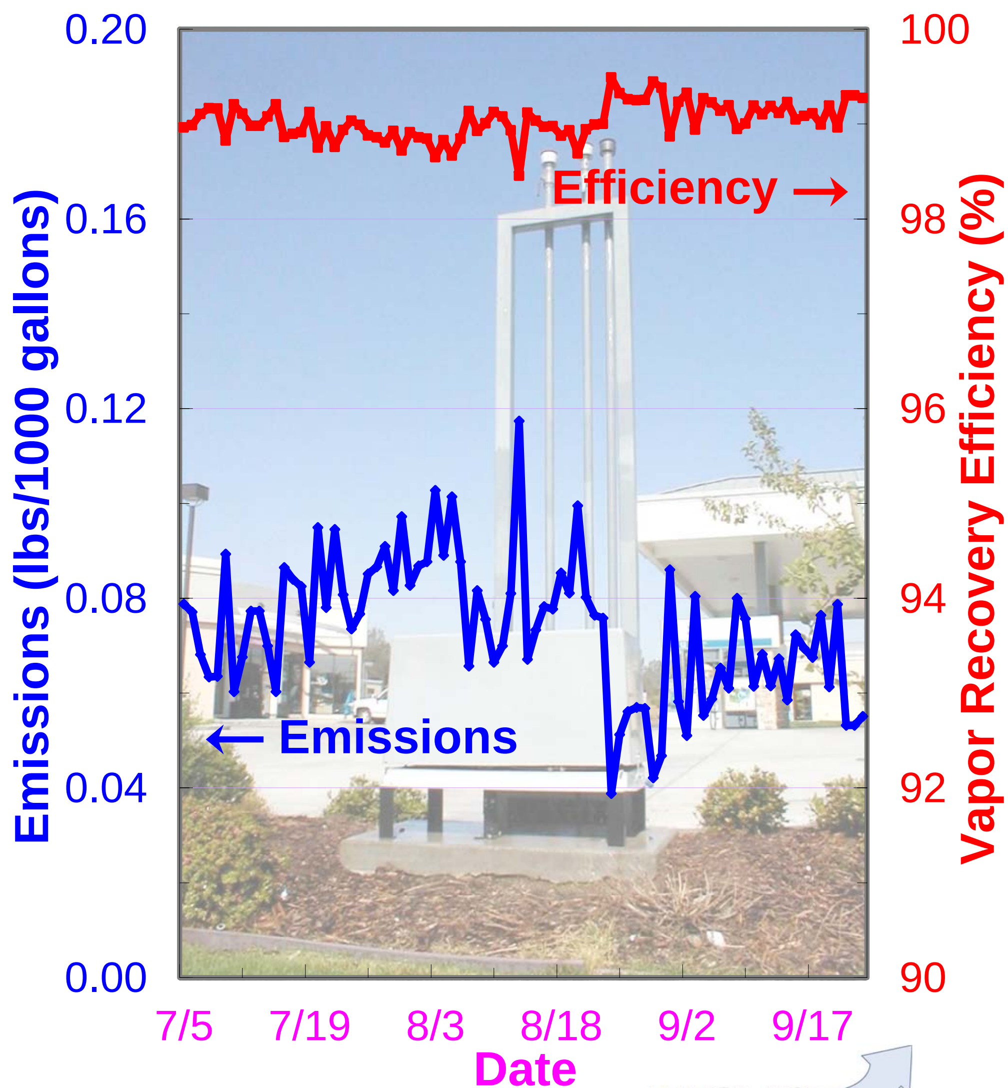
- Gas stations operating without vapor controls emit to the atmosphere 1 to 5 gallons of gasoline for every 1000 gallons pumped.
- These VOCs contribute to the formation of smog, a recognized health hazard.
- Non-renewable energy is lost, and the station has an unnecessary cost.

New Air Quality Regulation

13,000 service stations in California must install Enhanced Vapor Recovery equipment by April, 2009.

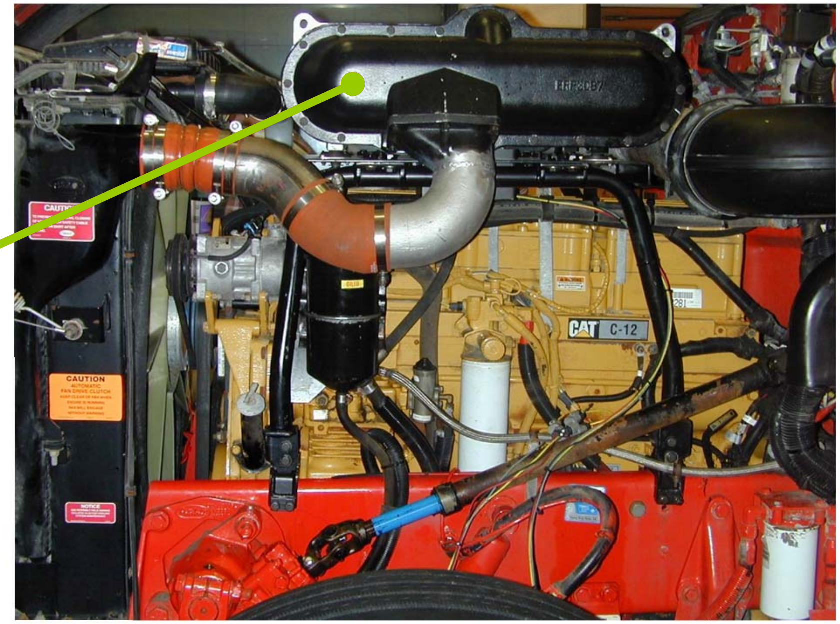
CMS membrane-based vapor processor is the only certified technology that will meet the new California Air Resources Board (CARB) requirement of > 95% vapor recovery.

Vapor Processor for Gasoline Station

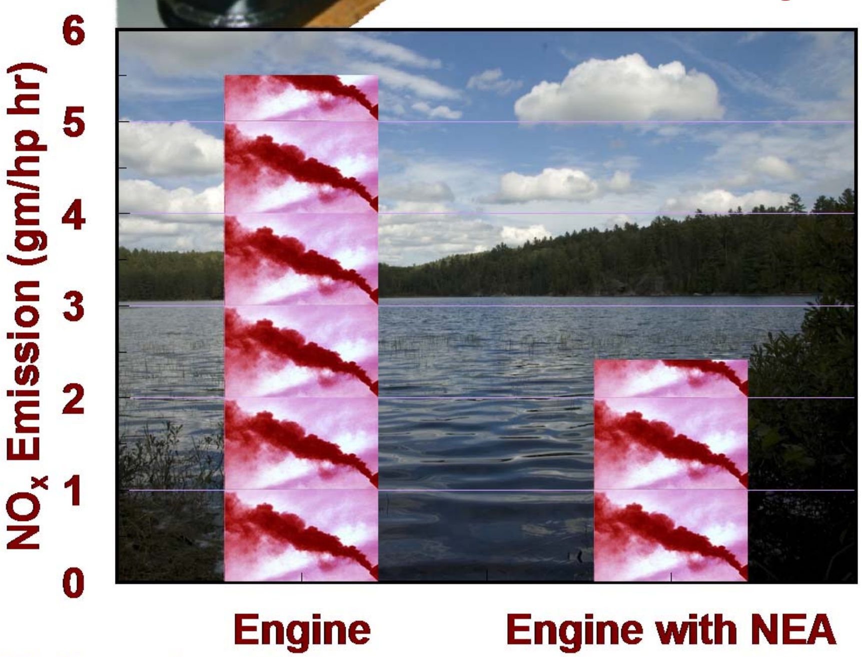


I’m in a hurry buddy, filler’up

NO_x Reduction in Diesel Engines

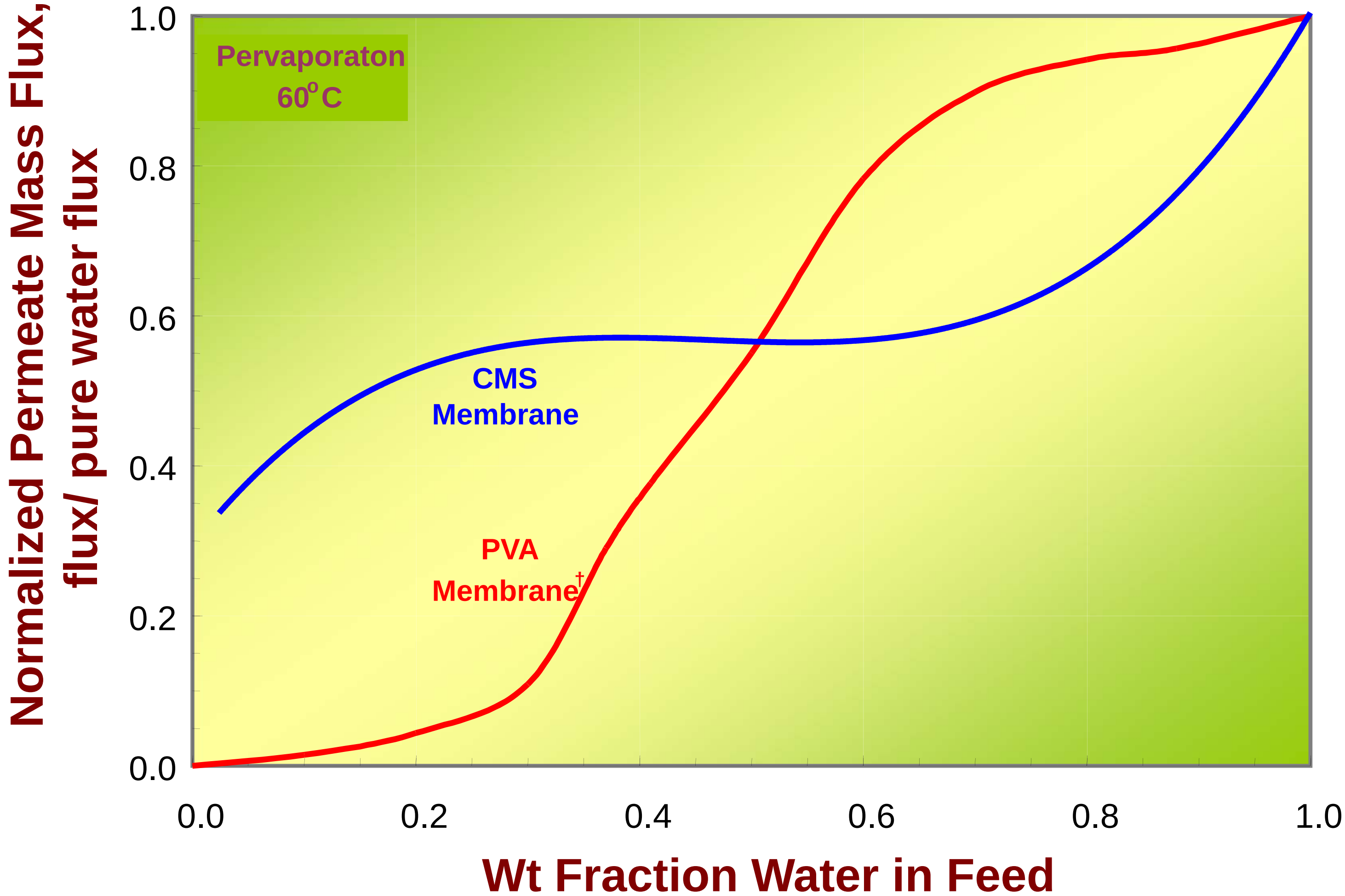


Multi-Cartridge Housing



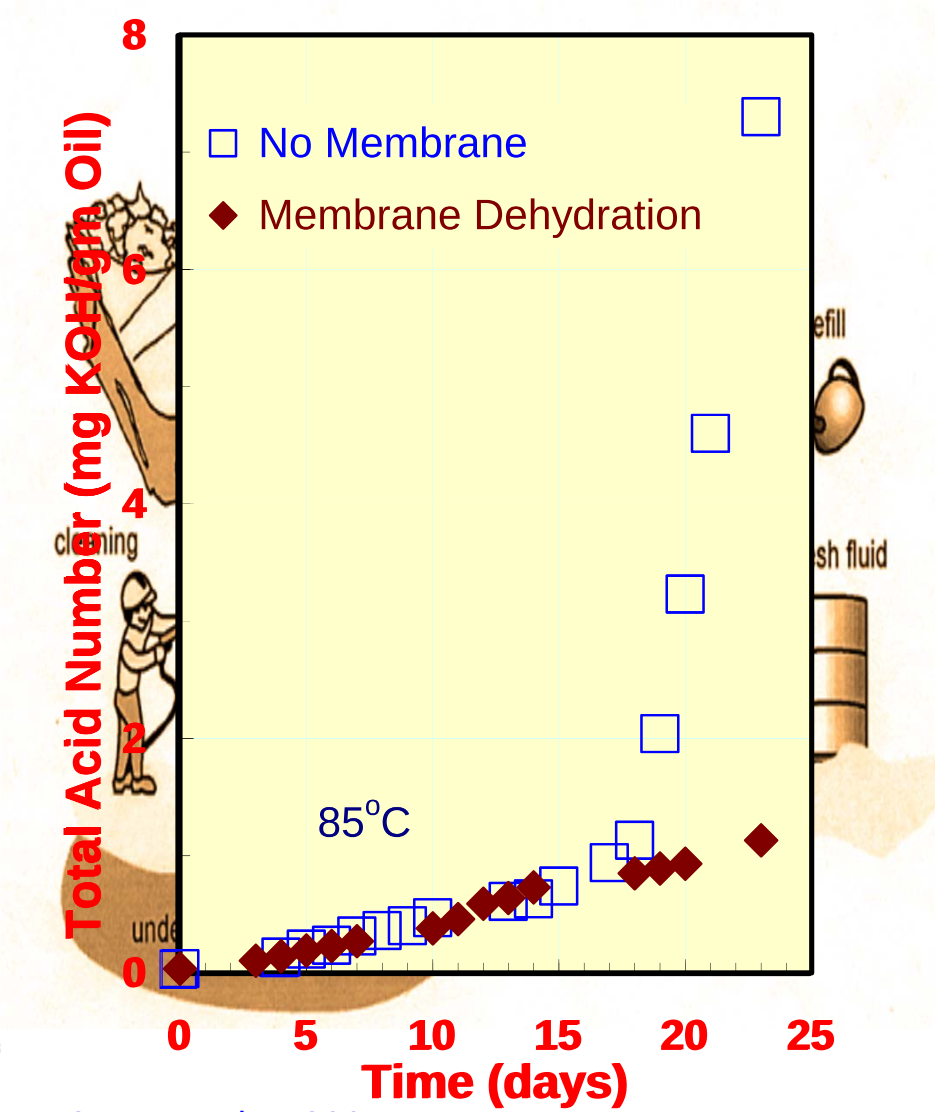
Hollow Fiber Cartridge

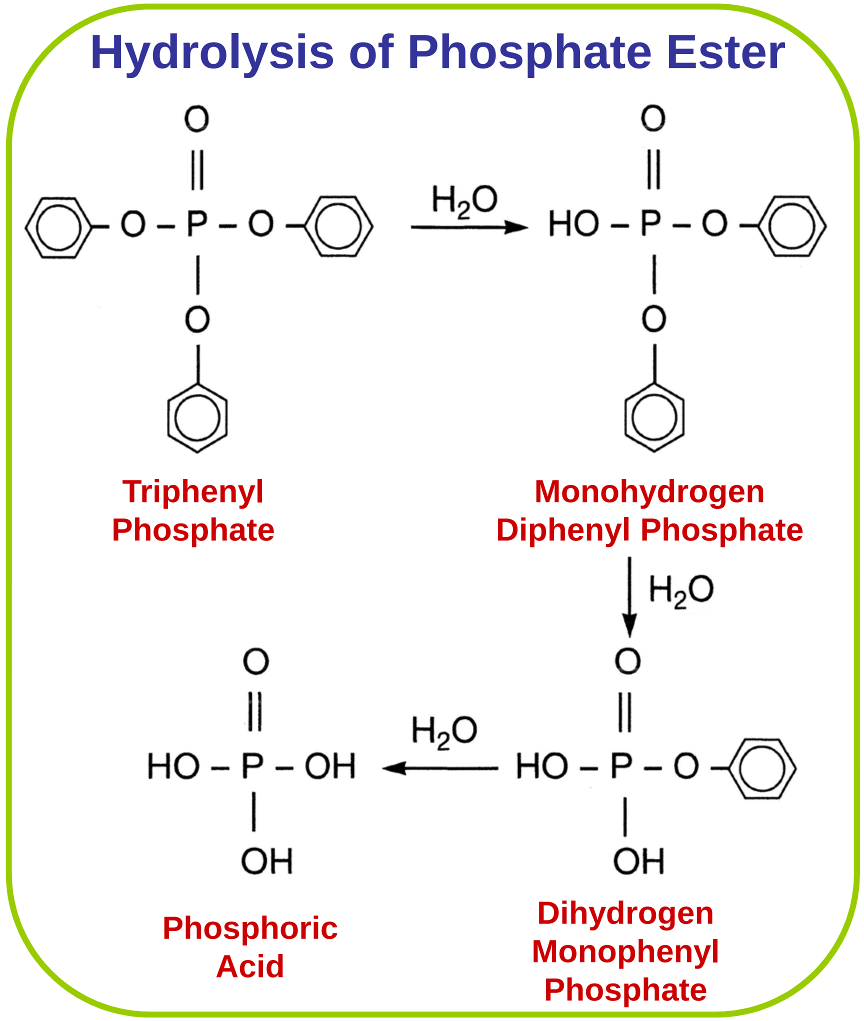
Ethanol-Water Mixture Separation



† R. D. Noble and S. A. Stern, "Membrane Separation Technology Principles and Applications", Elsevier, 1995

Dehydration of Hydraulic Fluids

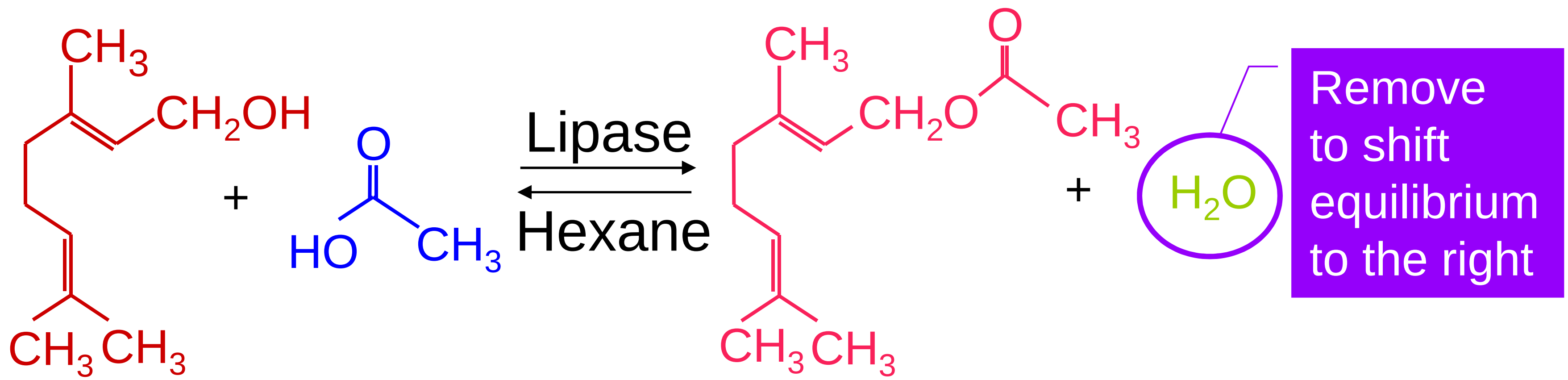




Objective

To demonstrate the feasibility of using a CMS perfluoromembrane reactor system to enhance the yield of an equilibrium-limited esterification reaction by the selective removal of water from the reaction mixture.

Enzyme-Catalyzed Membrane Reactor



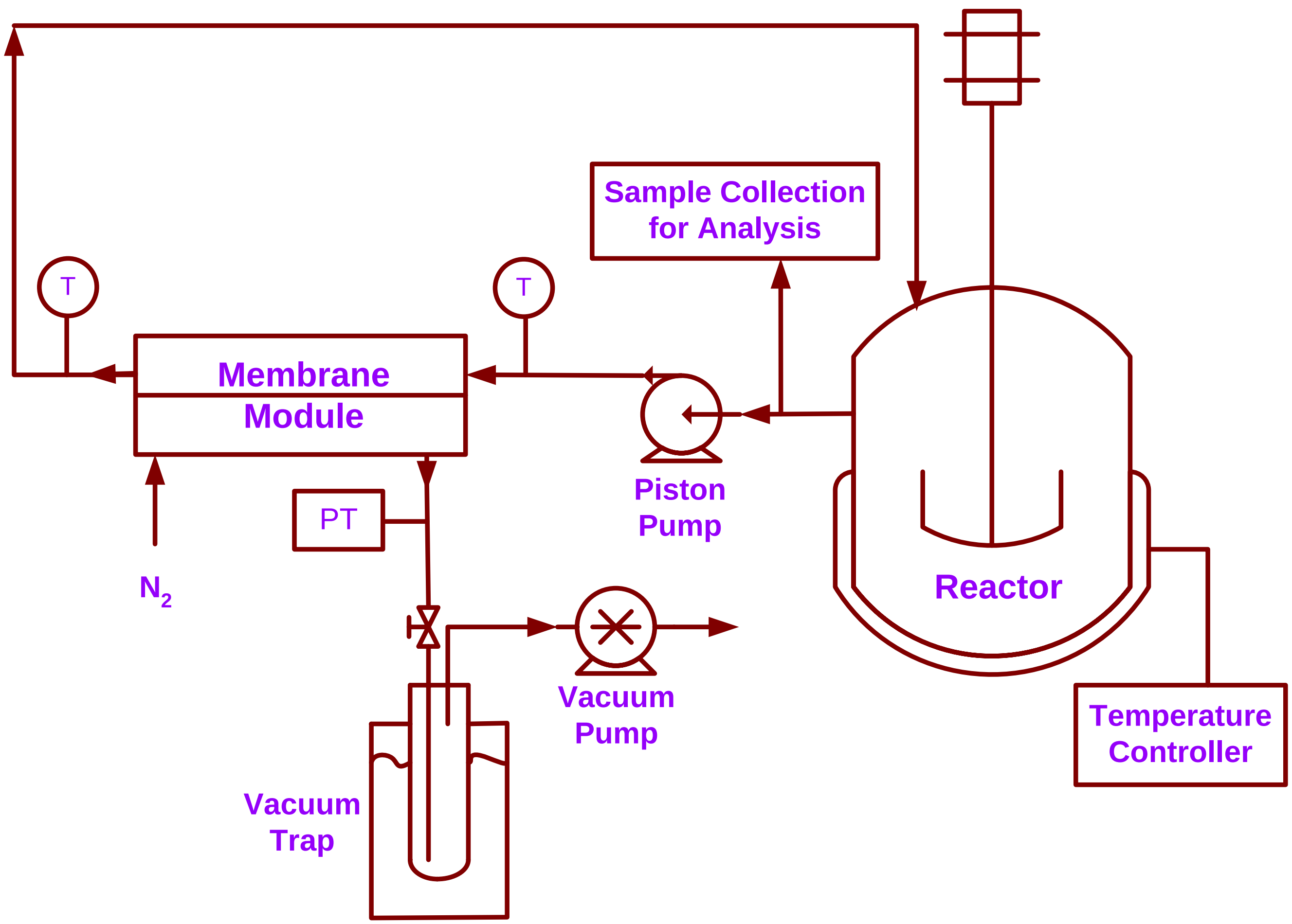
Geraniol **Acetic Acid** **Geranyl Acetate** **Water**

T = 30°C **Alcohol : Acid = 1:1**

Materials - Methods

- **Reactants**
  - **Geraniol + Acetic Acid (for Synthesis)**
  - **Geranyl Acetate + Water (for Hydrolysis)**
- **Solvent**
  - **n-Hexane**
- **Enzyme Catalyst**
  - **Novozym® 435 - Lipase from *Candida Antarctica B***
- **Membrane**
  - **Composite CMS – 3 Flat Sheet and Hollow Fiber**
- **Analytical Techniques**
  - **Gas Chromatograph with FID for Organics**
  - **Karl Fischer Titration for Water**

Experimental Setup Schematic



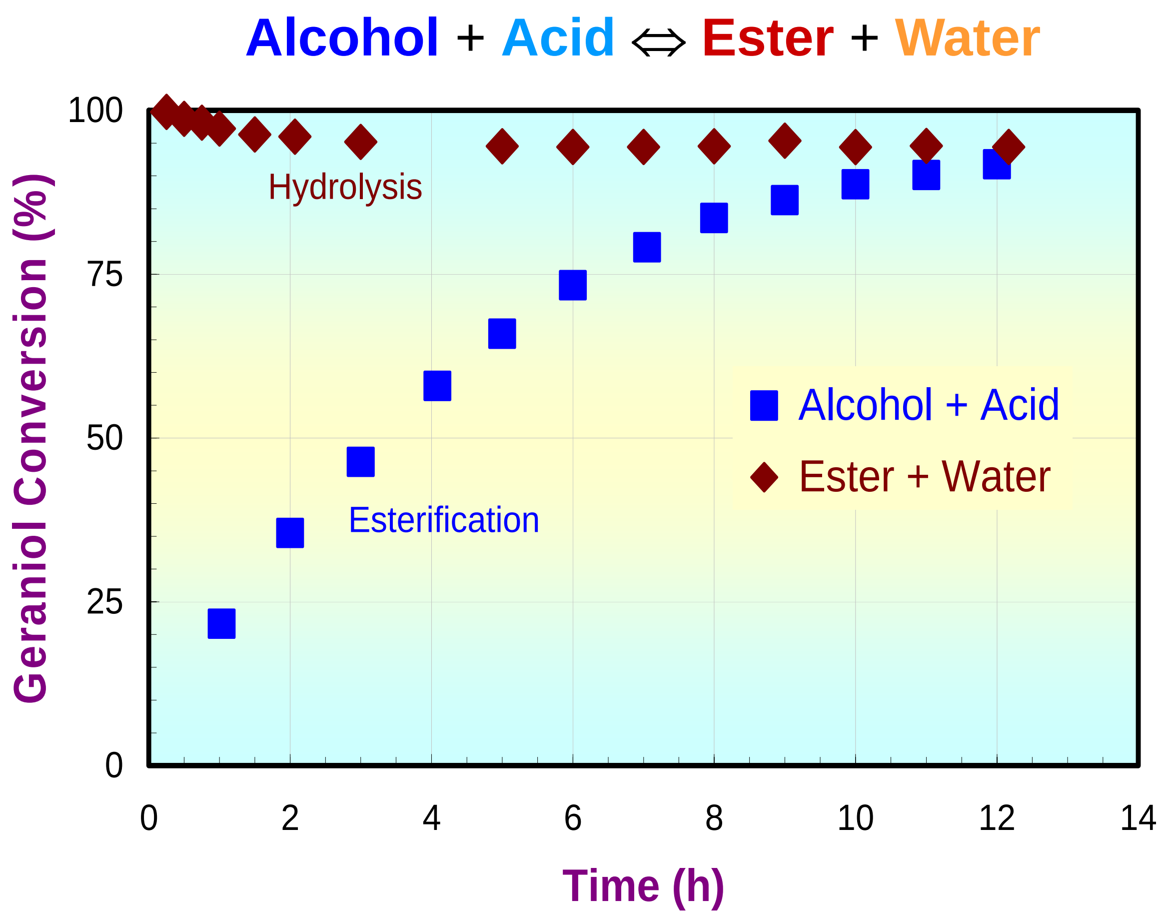
Study Variables

- No Membrane as a Control
- CMS Flat Sheet and Hollow Fiber Membranes
- Vacuum and Combo Modes of Operation
- One Reactant (Acid) in Excess

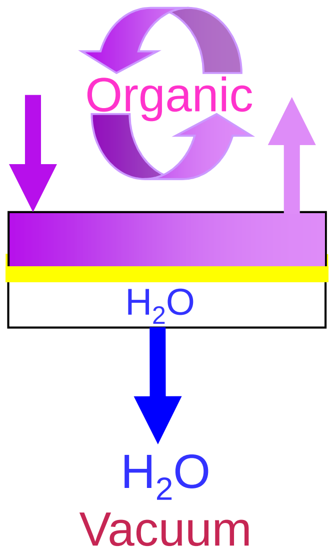
Synthesis and Hydrolysis of Geranyl Acetate (No Membrane)

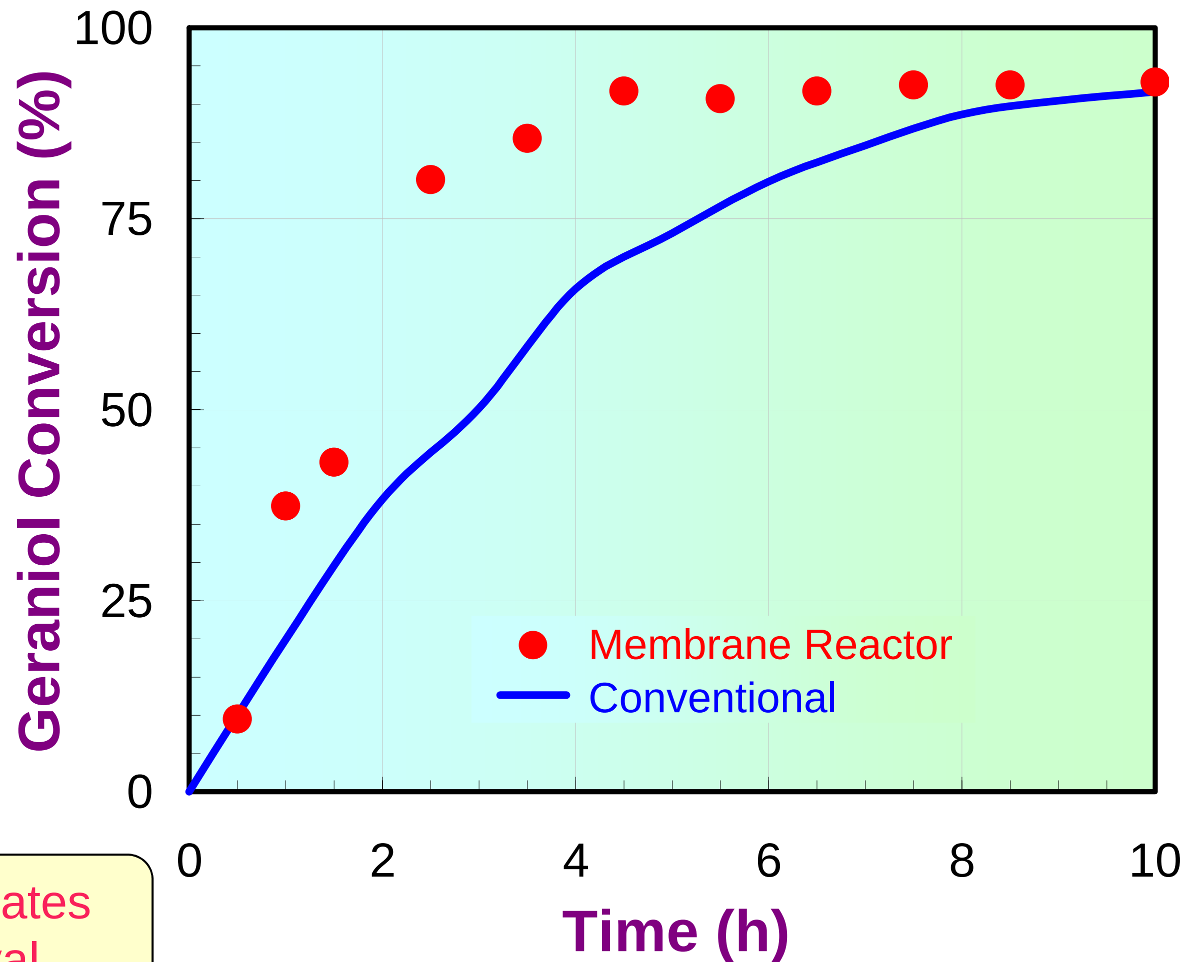
Equimolar Reactants
10 wt% Catalyst, 30°C

Conversion:
94% at Equilibrium



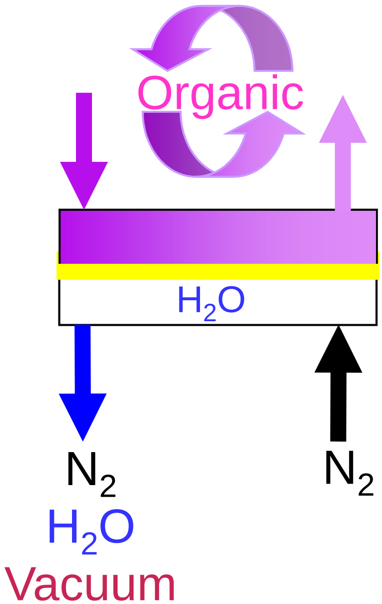
Pervaporation with Flat Sheet Membrane

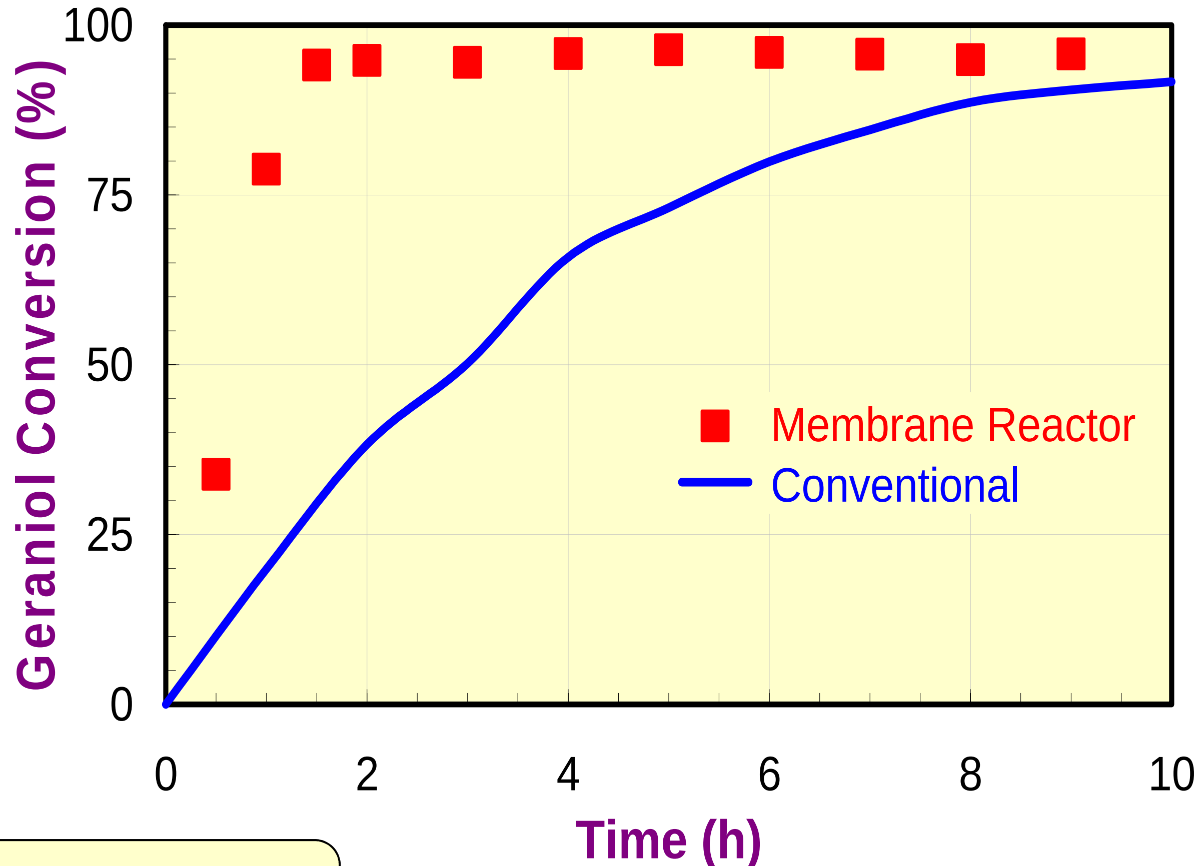




Improved reaction rates
with water removal

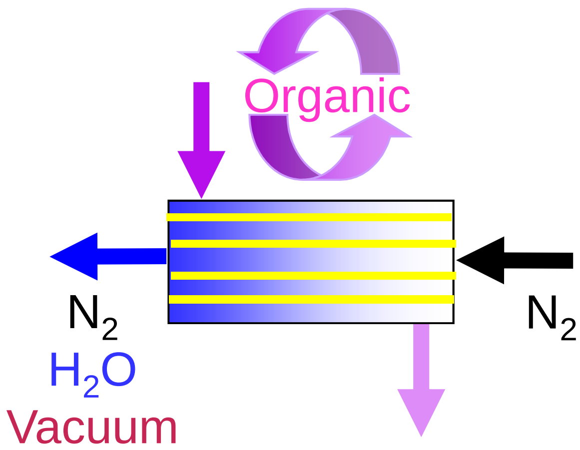
Combo Mode of Operation

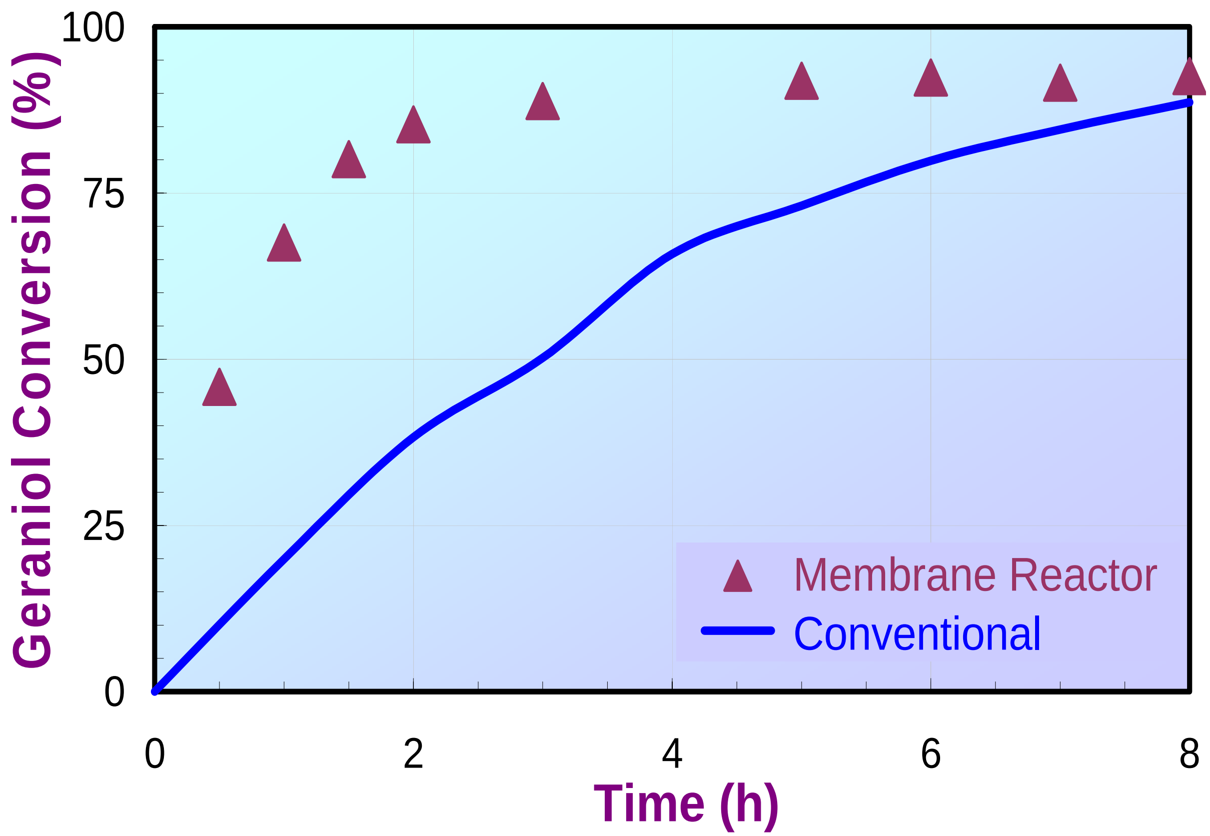




Conversion and Reaction rates are markedly higher with water removal

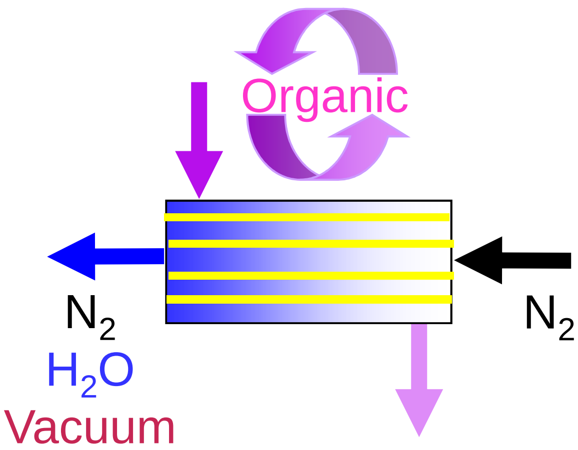
Pervaporation with Hollow Fiber Membrane

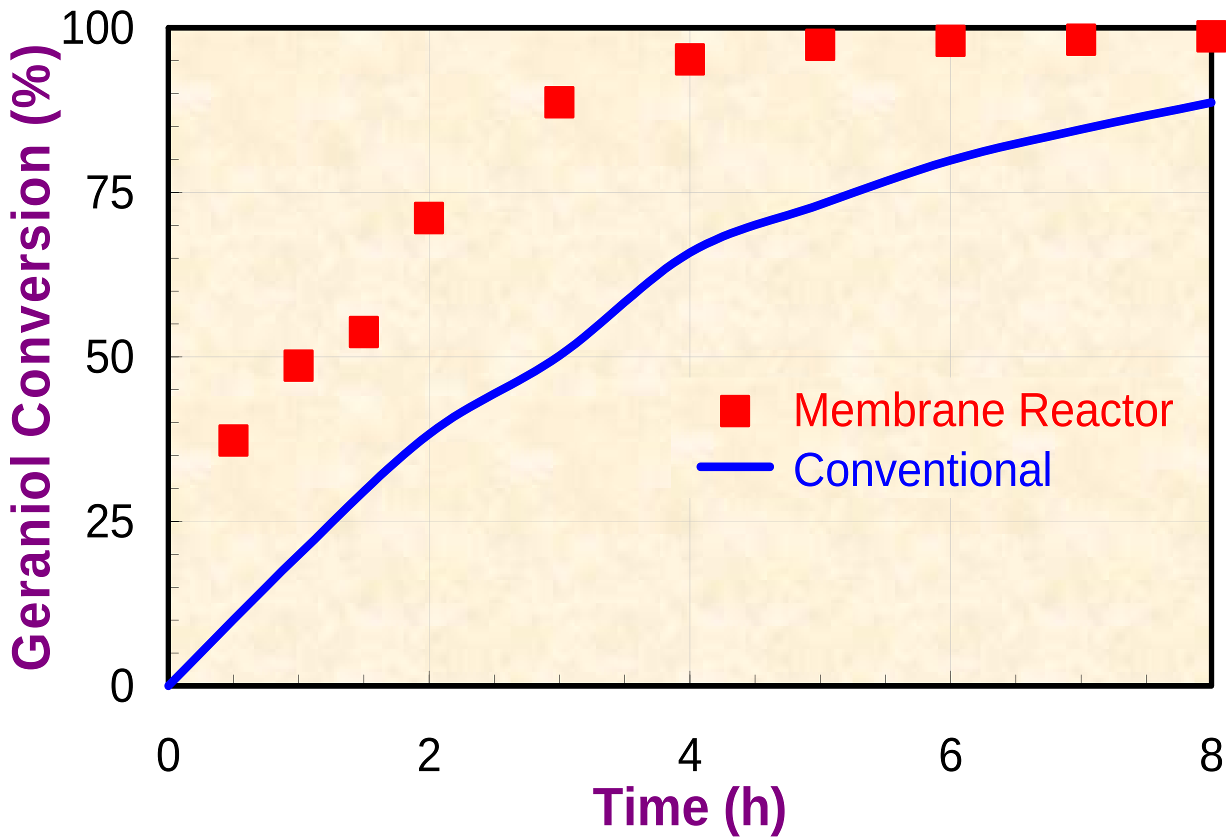




Reaction rates are initially higher, but conversion not above equilibrium.

Effect of Adding an Excess Reactant





Alcohol : Acid = 1:2

Conversion and Rate Enhancement

Process Description	Time for 80% Conversion (hrs)	Maximum Conversion (%)	Rate Enhancement with respect to Control
No Membrane (Control)	7.2	94	1.0
FS Membrane Vacuum	2.5	94	2.9
FS Membrane Vacuum + N_2 Purge	1.1	96	6.5
HF Membrane Vacuum + N_2 Purge	1.5	94	4.8
HF Membrane Vacuum + N_2 Purge + Excess Acid	2.7	99	2.7

FS: Flat Sheet; HF: Hollow Fiber

A Ketalization Reaction

Benzaldehyde + **Octane-1,2-diol** $\rightleftharpoons$ (p-toluenesulfonic acid; toluene) **Dioxolane** + **Water**

T = 80^{o}C **Benzaldehyde : Octane-1,2-diol = 1:1**

Process Description	Time (hrs)	Conversion (%)
No Membrane (Control)	18	67
HF Membrane Vacuum + N_2 Purge	18	88

HF: Hollow Fiber

Concluding Remarks

- Efficient and selective removal of water from equilibrium-limited reactions were realized utilizing CMS membranes in a pervaporation coupled reactor configuration.
- The initial rates of reaction attained in the hybrid membrane-reactor configuration were significantly higher than that reached in a conventional reactor.
- Nitrogen purge in the permeate side enhanced the driving force for water removal as well as the initial rate of reaction.
- Equilibrium conversion and the rate of reaction were increased by doubling the initial molar ratio of acid/alcohol.

Acknowledgement

The authors gratefully acknowledge the support of the **United States Department of Energy** through Small Business Innovation Research (SBIR) Awards.

Thank you for your attention……..