

Dewatering Ethanol with Chemically and Thermally Resistant Perfluoropolymer Membranes

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2008 JMS Review Article on Dehydration of Solvents

- **Polymeric membranes for alcohol dehydration**
 - Poly(vinyl alcohol)
 - Chitosan
 - Alginate
 - Polysulfone
 - Polyimides
 - Polyamides
 - Polyelectrolyte membranes
 - Polyaniline
- **Inorganic membranes for alcohol dehydration**
 - Ceramics
 - Zeolites

**A high free volume hydrophobic and oleophobic
perfluoropolymer membrane**

Journal of Membrane Science, 318, 5-37 (2008).

15 July 2008

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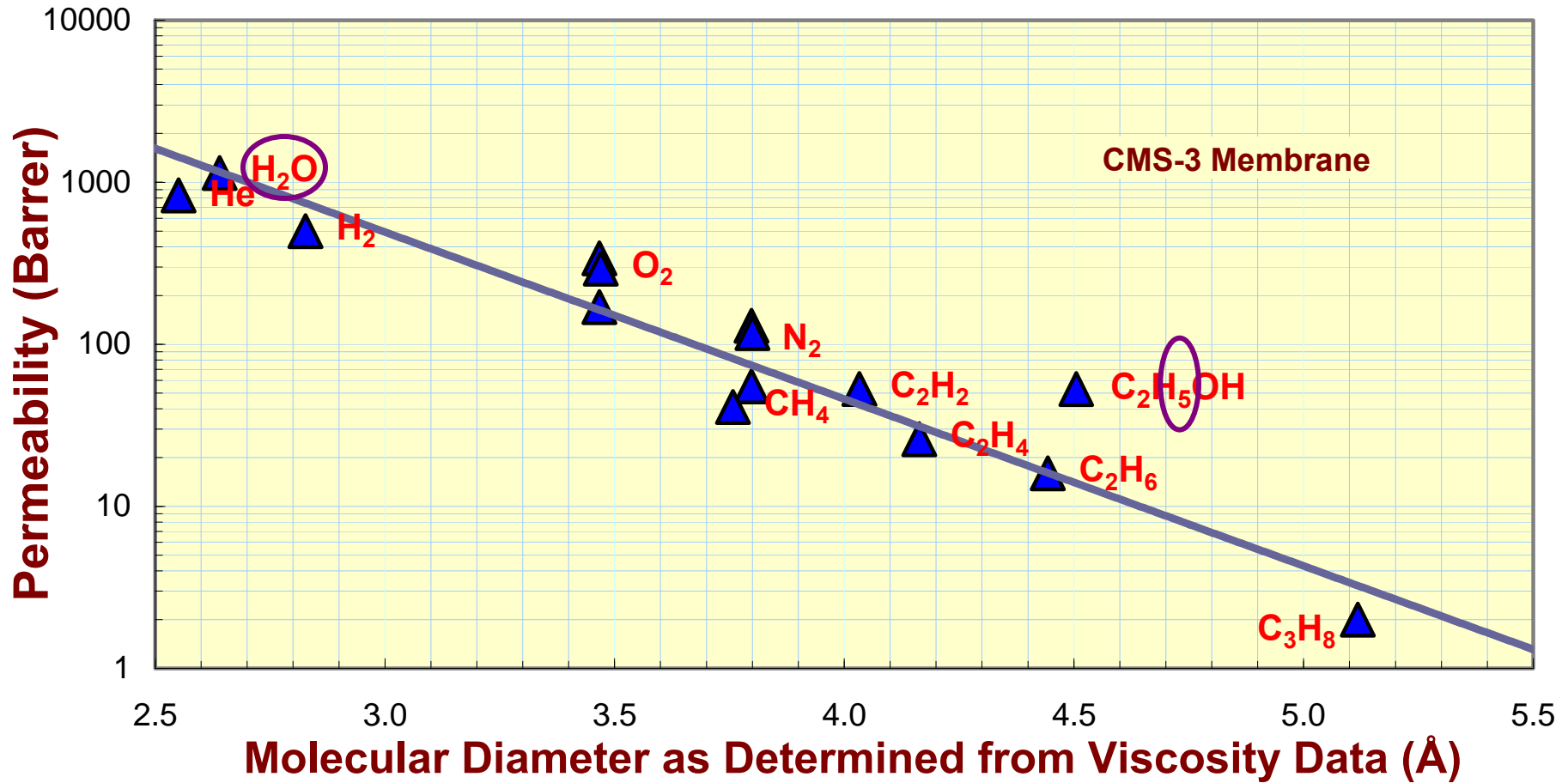
Presentation Outline

- CMS Membranes and Features
- Background
- Pervaporation
- Vapor Permeation
- Energy and Cost Savings
- Concluding Remarks

CMS Membrane Characteristics

- **Glassy Membrane**
 - Transports atmospheric gasses
 - Retains hydrocarbons larger than C₂
- **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

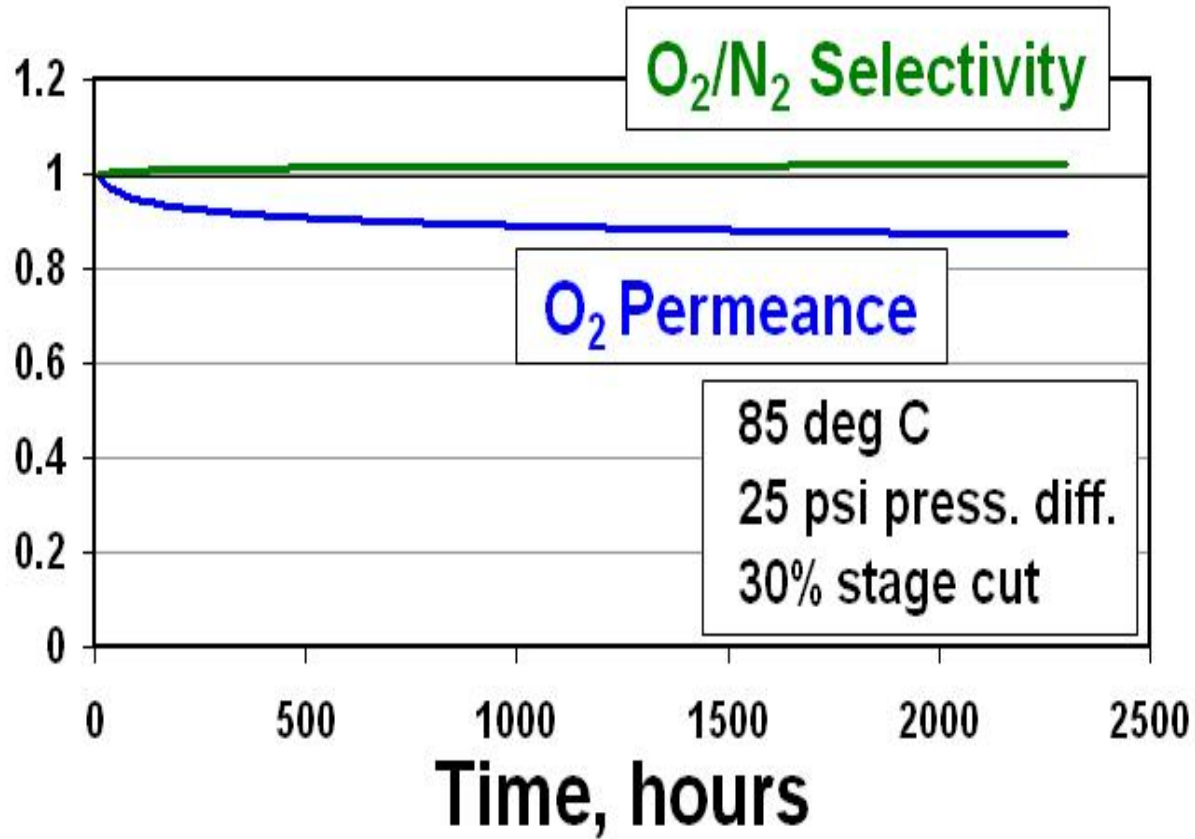


CMS Membrane Chemical Resistance

Reagent	Temperature °C	Δ Wt %	Appearance Change
Carbon Tetrachloride	23	0	None
12 N HCl	60	0	None
Hexanes	23	0	None
MEK	23	0	None
44% NaOH	60	0	None
Perclene®	23	-0.1	None
Ethanol	23	0	None
Mineral Oil	60	0	None

Performance Stability

Normalized Pty



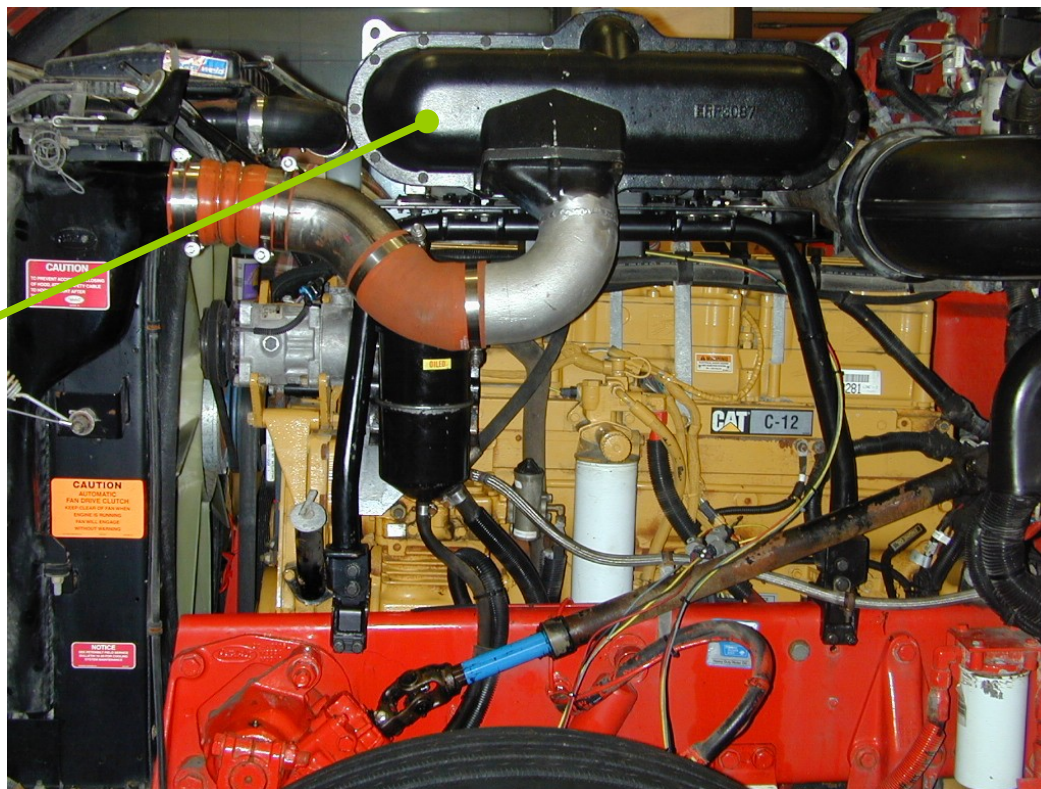
Membranes Under the Hood of a Highway Truck



Multi-Cartridge Housing



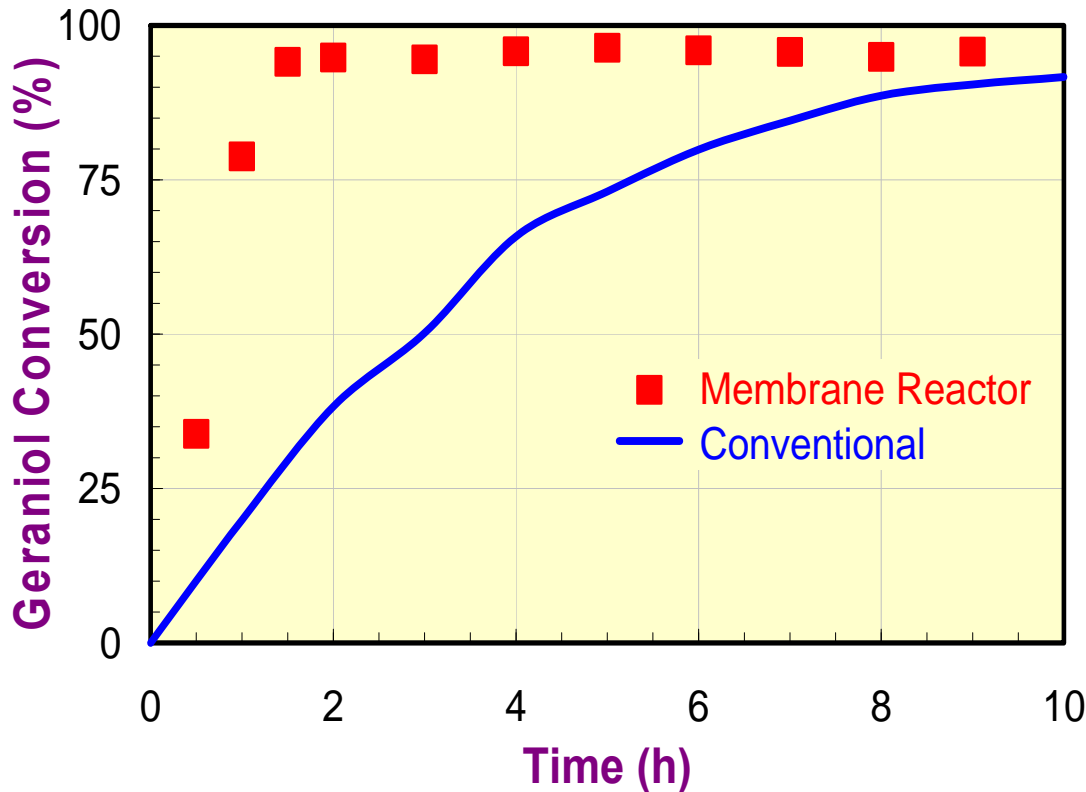
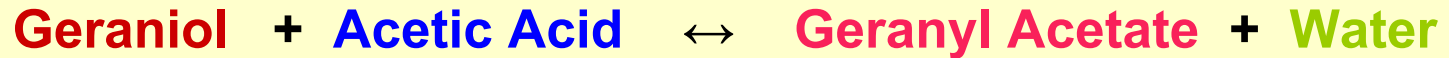
Hollow Fiber Cartridge



Platform Technology – Dewatering Organics

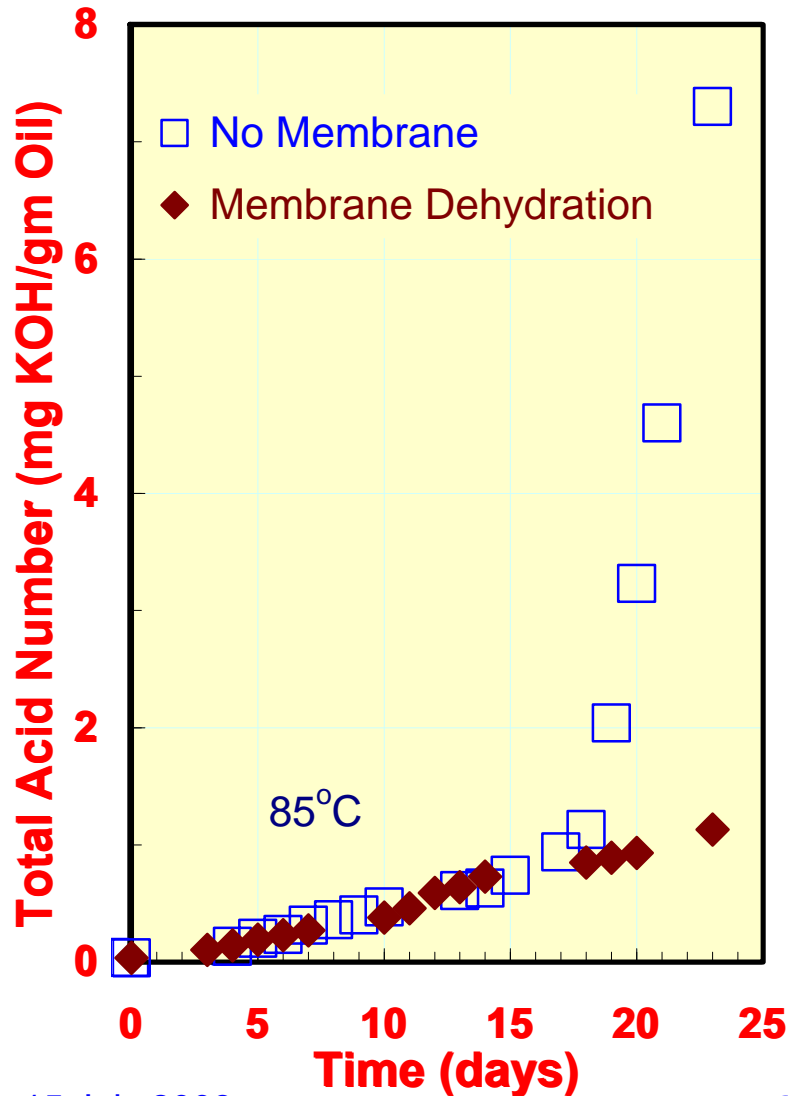
- **Fuel Grade Ethanol**
- **Chemical-Water Azeotropes**
- **Enhancing Reversible Chemical Reactions**
- **Removal of Water from Process Fluids**
 - Hydraulic Esters
 - Lubricating Oils

Geranyl Acetate Synthesis Reaction Coupled with Pervaporation Separation of Water

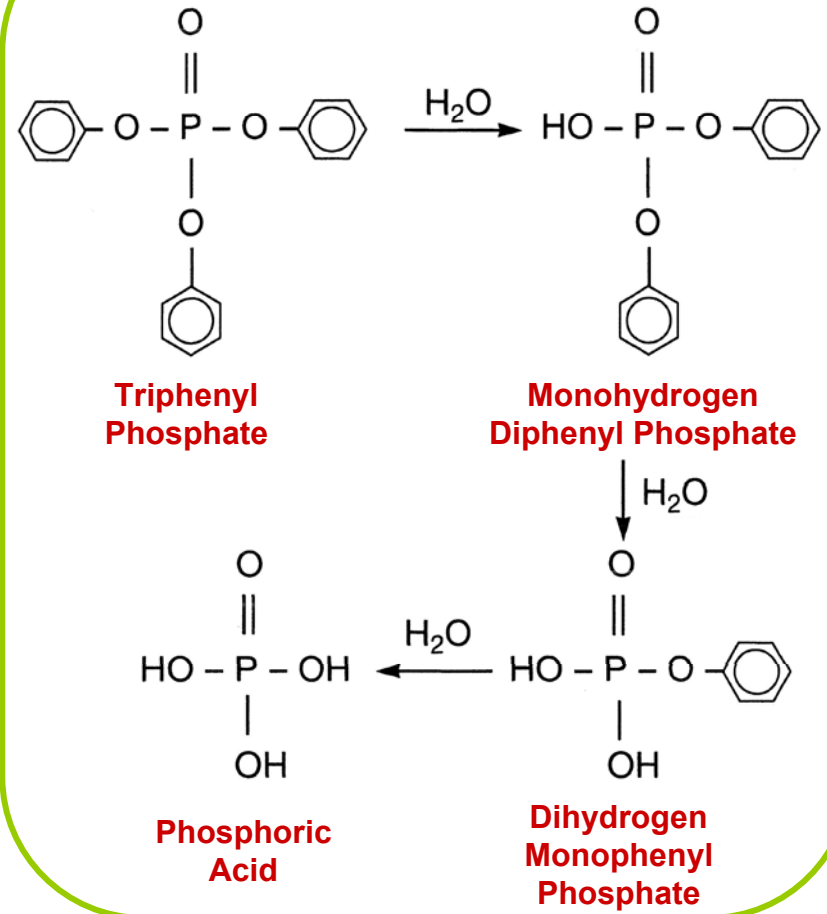


Conversion and Reaction rates are markedly higher with water removal

Dehydration of Phosphate Ester Hydraulic Fluid



Hydrolysis of Phosphate Ester



Water-Ethanol Separation – Test Conditions

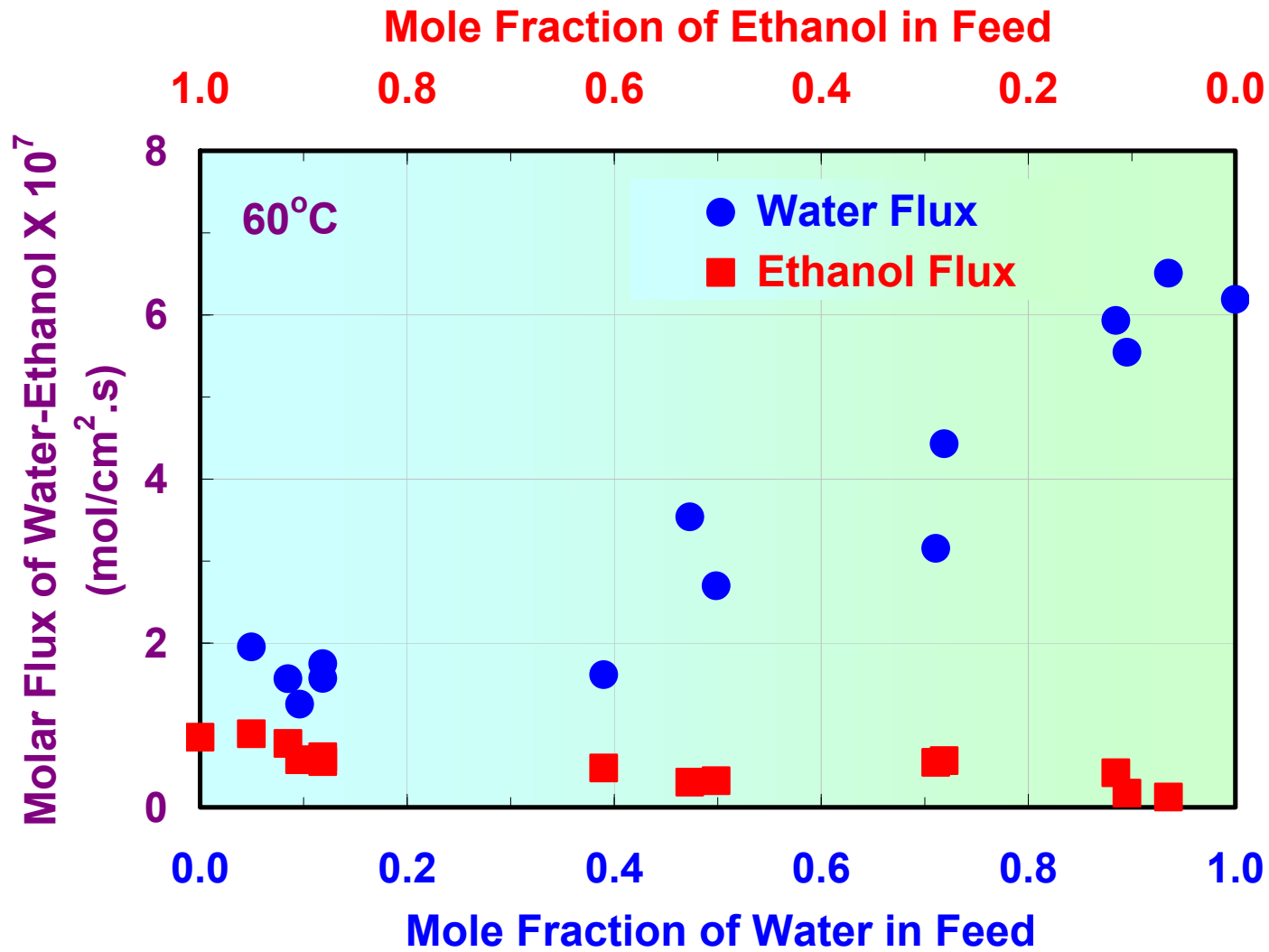
Pervaporation

- Feed ethanol concentration in mixture: 10-95%
- Operating temperature: 50-80°C
- Permeate under vacuum

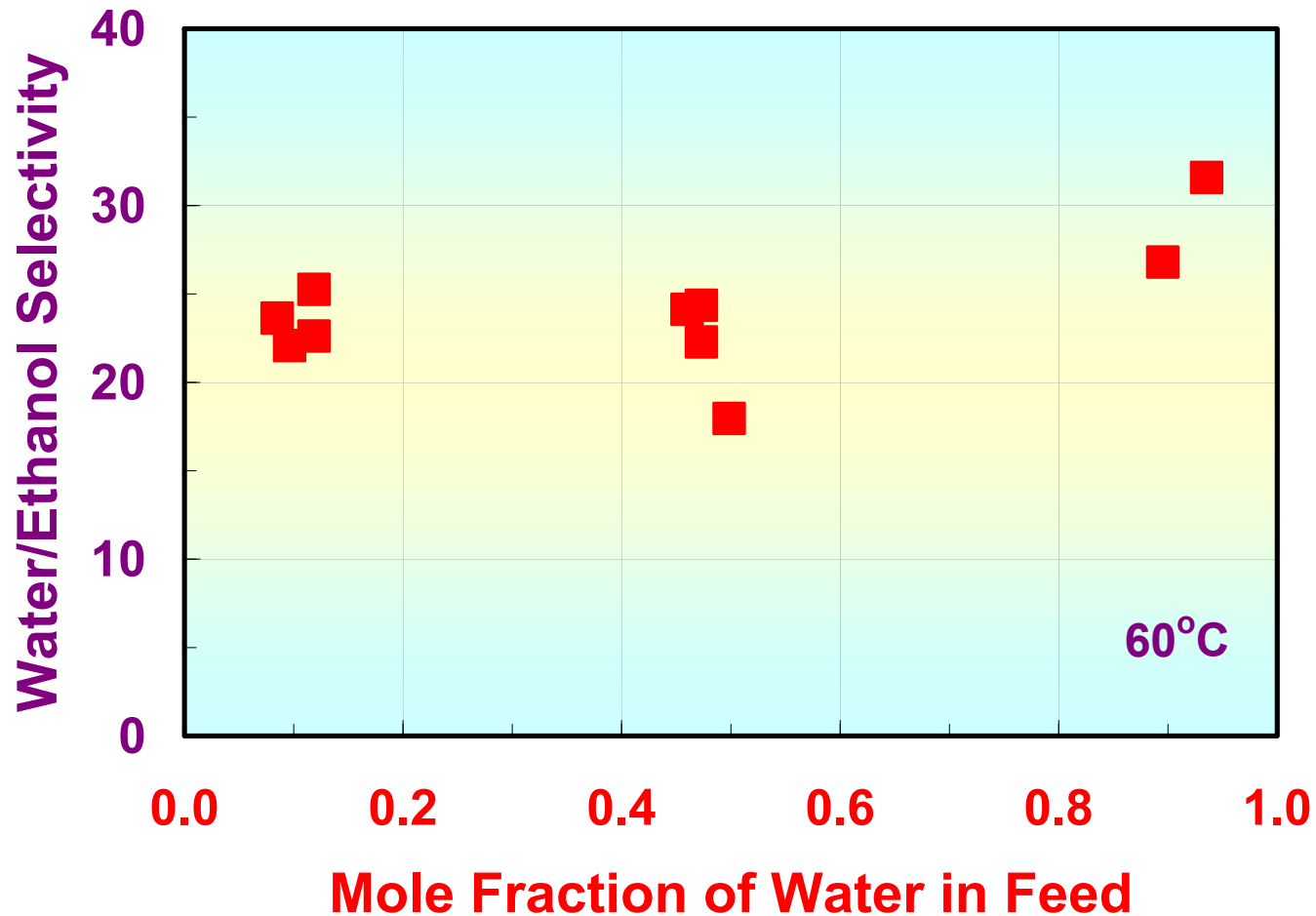
Vapor Permeation

- Feed ethanol concentration in mixture: 75-95%
- Operating temperature: 90-130°C
- Feed pressure: 3-6 psig
- Permeate under vacuum

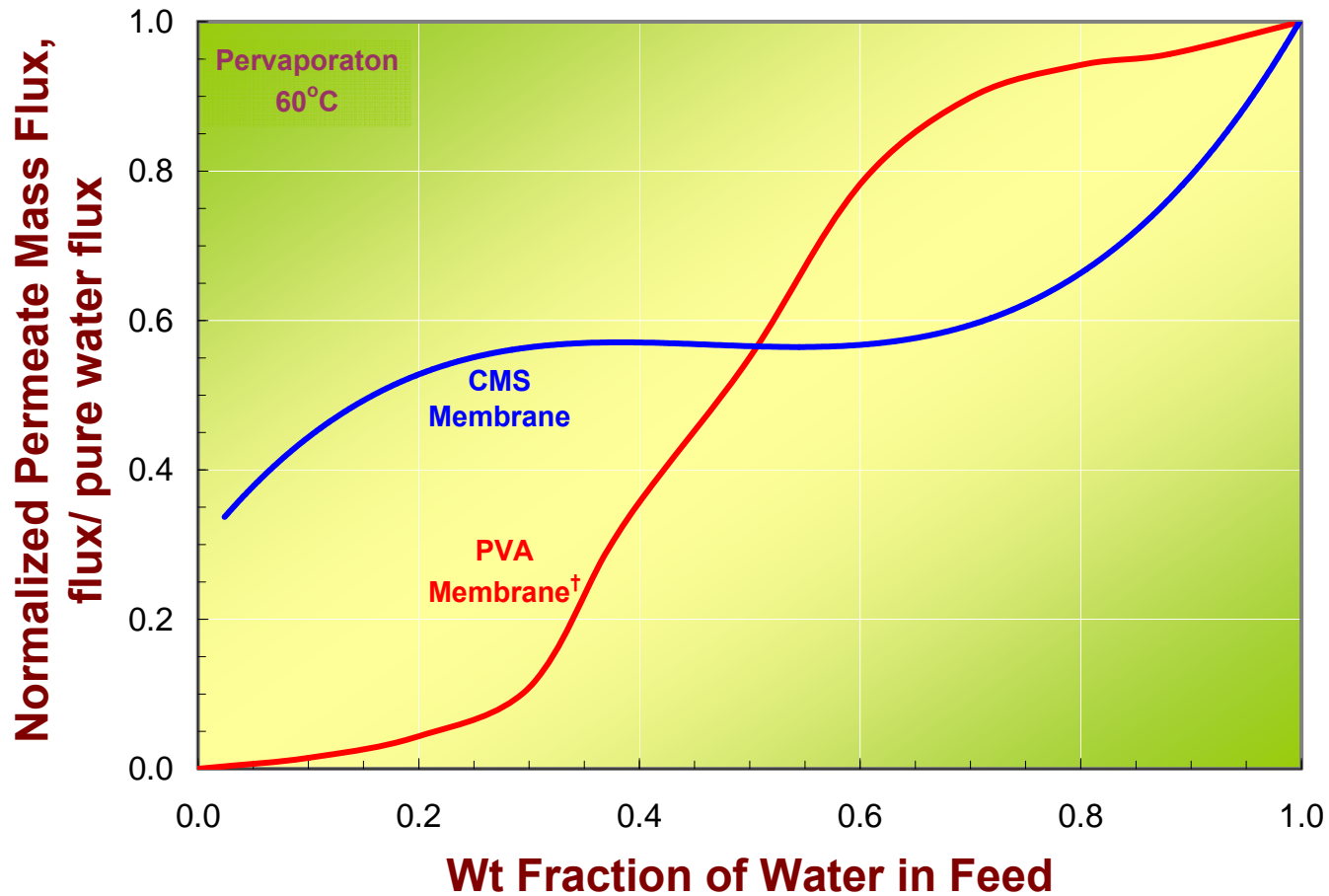
Pervaporation of Water-Ethanol Mixture



Pervaporation of Water-Ethanol Mixture (Contd.)

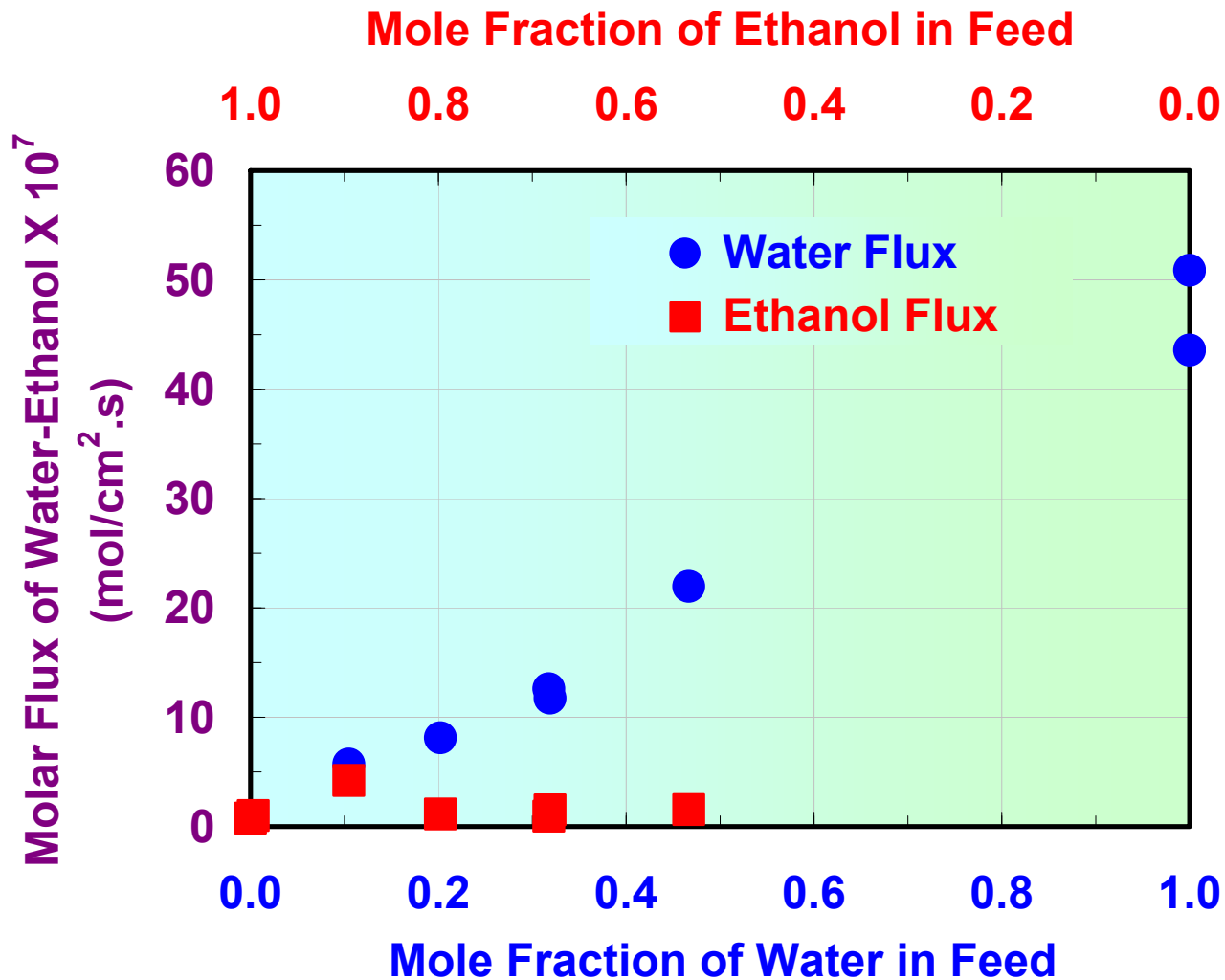


Differences in Water-Ethanol Pervaporation Flux with Membrane Type

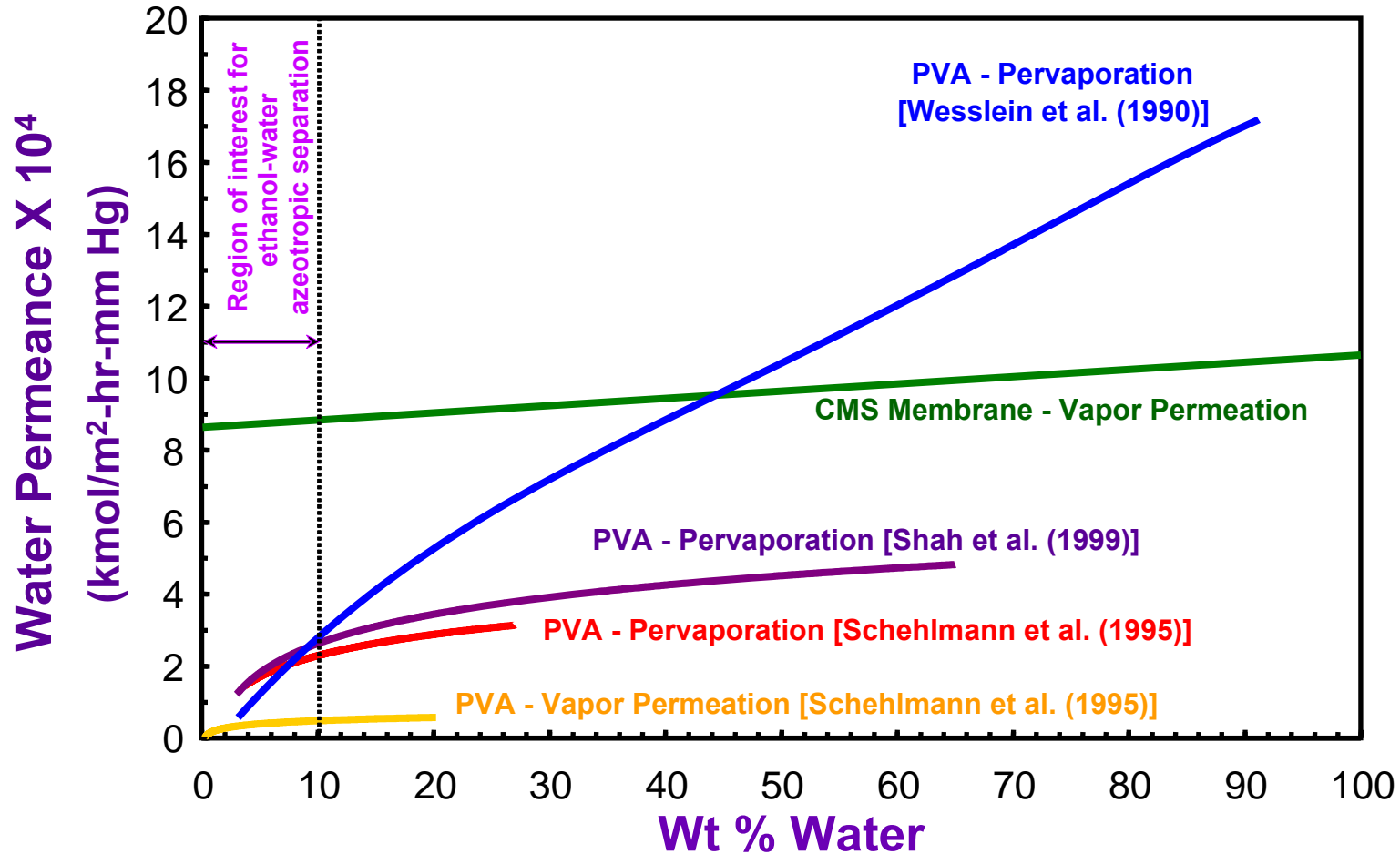


† R. D. Noble and S. A. Stern, "Membrane Separation Technology Principles and Applications", Elsevier, 1995

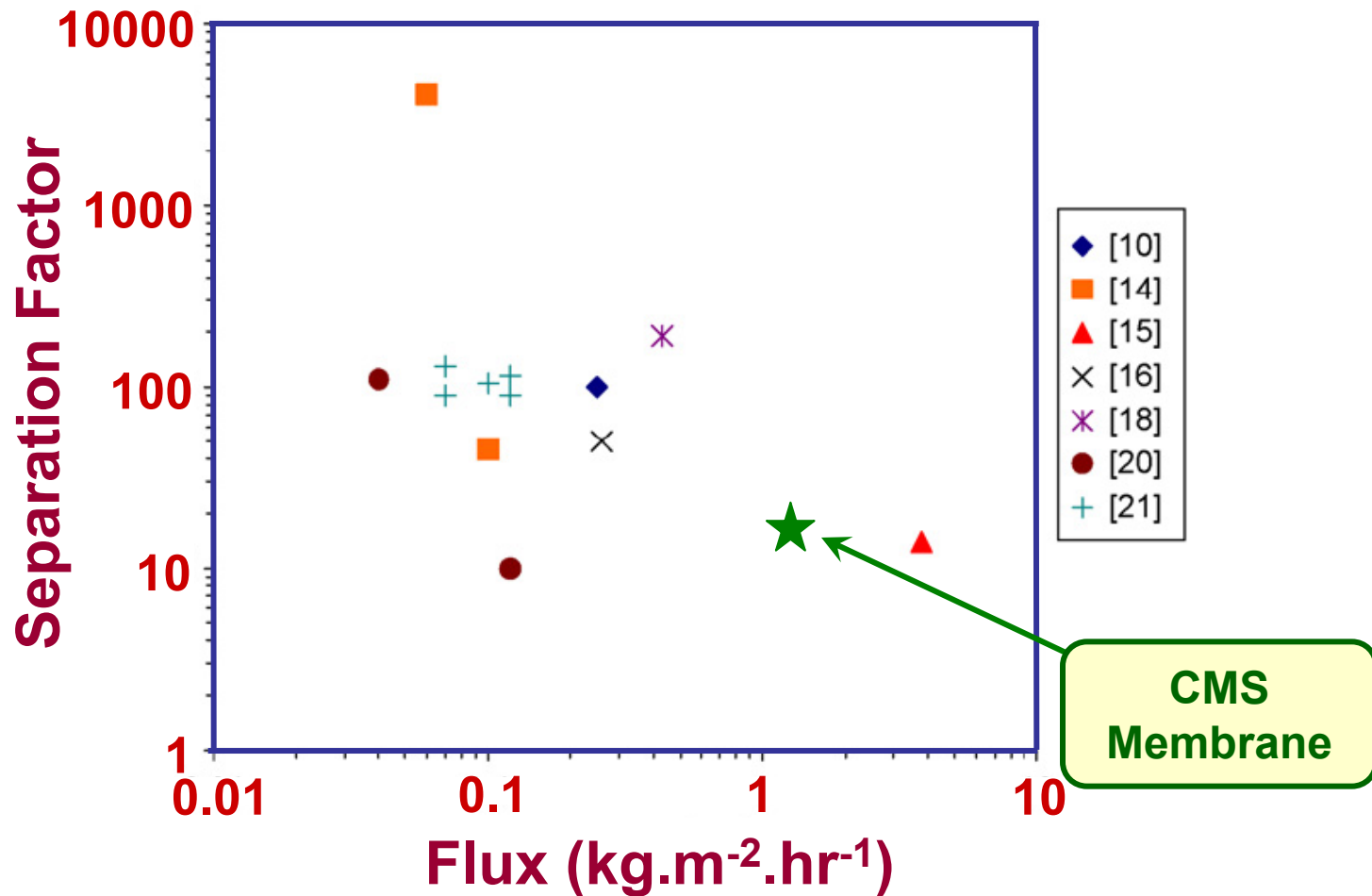
Vapor Permeation of Water-Ethanol Mixture



Comparison of Water Permeances through PVA and CMS Membranes



Membrane Performance Data Comparison



Ref: Chapman et al., JMS, 318, 5-37 (2008).

Vapor Separation Results for Different Water-Solvent Systems

Solvent	Chemical Formula	Molecular Diameter (Å)	Selectivity (Water/Solvent)
Methanol	CH_3OH	3.6	5
Ethanol	$\text{CH}_3\text{CH}_2\text{OH}$	4.5	18
Isopropanol	$(\text{CH}_3)_2\text{CHOH}$	5.2	48

Proposed Schemes Incorporating CMS Membrane

- Alternate to Cycling PSA Mol Sieve Beds for Drying of Organics
- Increased Capacity by Debottlenecking PSA Mol Sieve Beds
- Hybrid Distillation-Membrane System

Energy and Cost Savings Potential

**Basis: FGE Plant 70 Million Gal/year;
Drying 90% Ethanol to 99.5% Ethanol**

System	PSA Mol Sieve	PVA Membrane	CMS Membrane	
			1 - Stage	2 - Stage
Plant Capital Cost, (\$MM)	4.4	8.3	<2.5	<3.5
Recycle (%) Consumes Energy	26	15	26	15
Energy Savings, (Billion BTU/Yr)	-	59	7	34

Aden et al., NREL Report # NREL/TP-510-32438, June 2002.

Future Activities

- Testing at High Pressure
- Membrane Modules for High Temperature FGE Service
- Testing in Pilot Scale Stream
- Refinements in Process Modeling
- Improved Economics

Concluding Remarks

- **A new approach of using a hydrophobic perfluoropolymer membrane for efficient and selective removal of water from ethanol and other solvents has been demonstrated.**
- **Membrane water permeability does not vary appreciably with water concentration.**
- **Permeability of CMS membranes are significantly higher than PVA membranes when operating in water concentration range of interest (8% to 0.5% water).**
- **CMS membrane drier offers a considerable cost advantage over either a PSA drier or a PVA membrane drier.**
- **A two-stage CMS membrane drier offers a reduced recycle to the upstream distillation and a substantial energy savings compared to PSA.**

Acknowledgement

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Mahalo
for your attention.....