

# Hybrid Distillation – Membrane Process to Increase Capacity and Reduce Costs for Production of Propylene and Ethylene

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# Overview

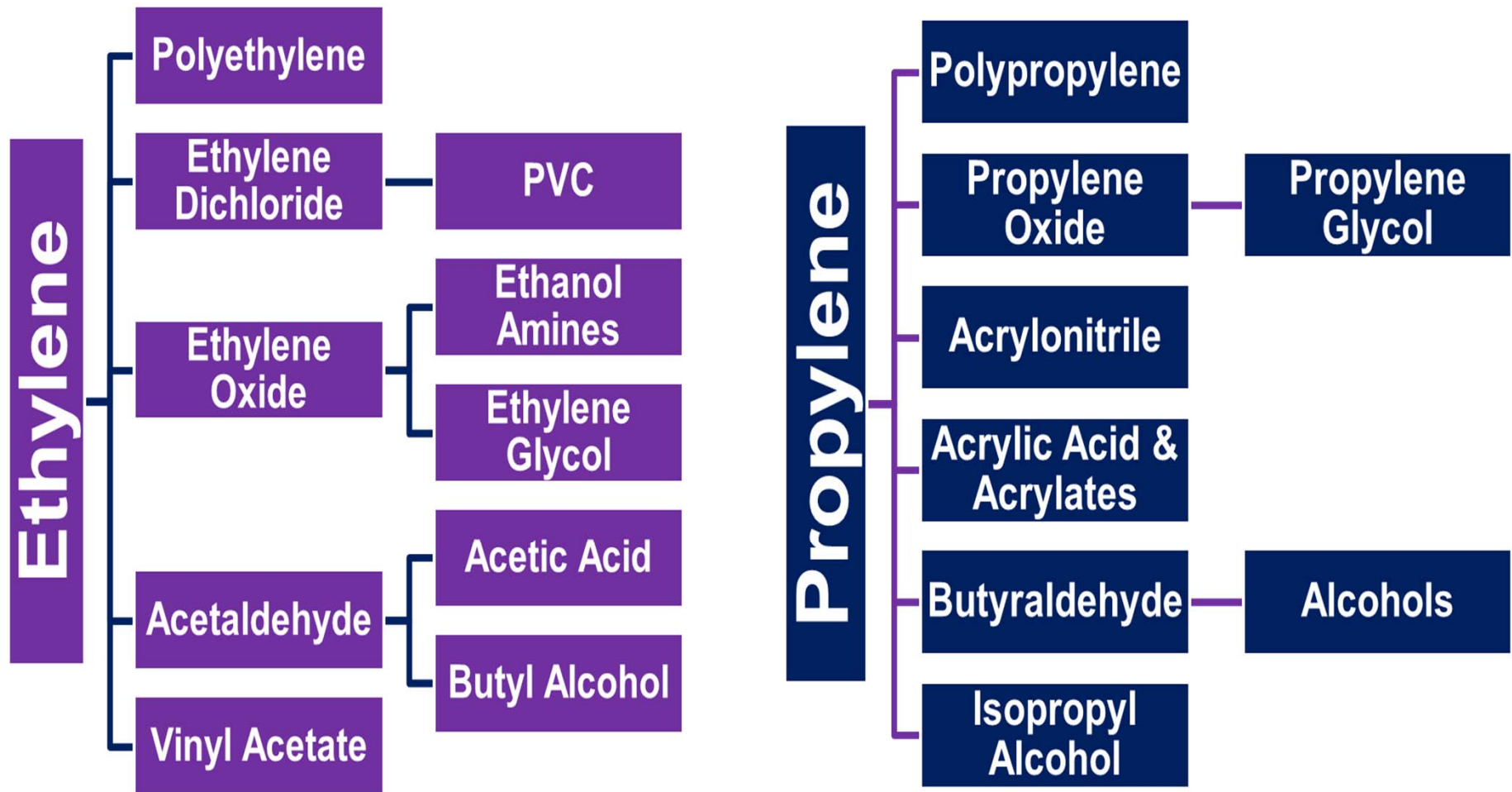
- **Opportunity for Olefin-Paraffin Separation**
- **30 Year Membrane History**
- **CMS Stable Facilitated Transport Membrane**
- **Preliminary Scale-Up**
- **Engineering and Economic Evaluation**
- **Path Forward**

# Olefins are Big

<b>Chemical</b>	<b>Production* (1x10<sup>6</sup> lbs)</b>
Nitrogen / Oxygen	69,600 / 58,300
Ethanol	66,100
<b>Ethylene</b>	<b>52,900</b>
<b>Propylene</b>	<b>31,100</b>
Ammonia	22,700
Chlorine / Sodium Hydroxide	21,500 / 16,600
Ethylene Dichloride	19,400
Benzene	13,300
Ethylene Oxide	5,900
Acetone	3,200

\* 2010 Production of top 10 chemicals

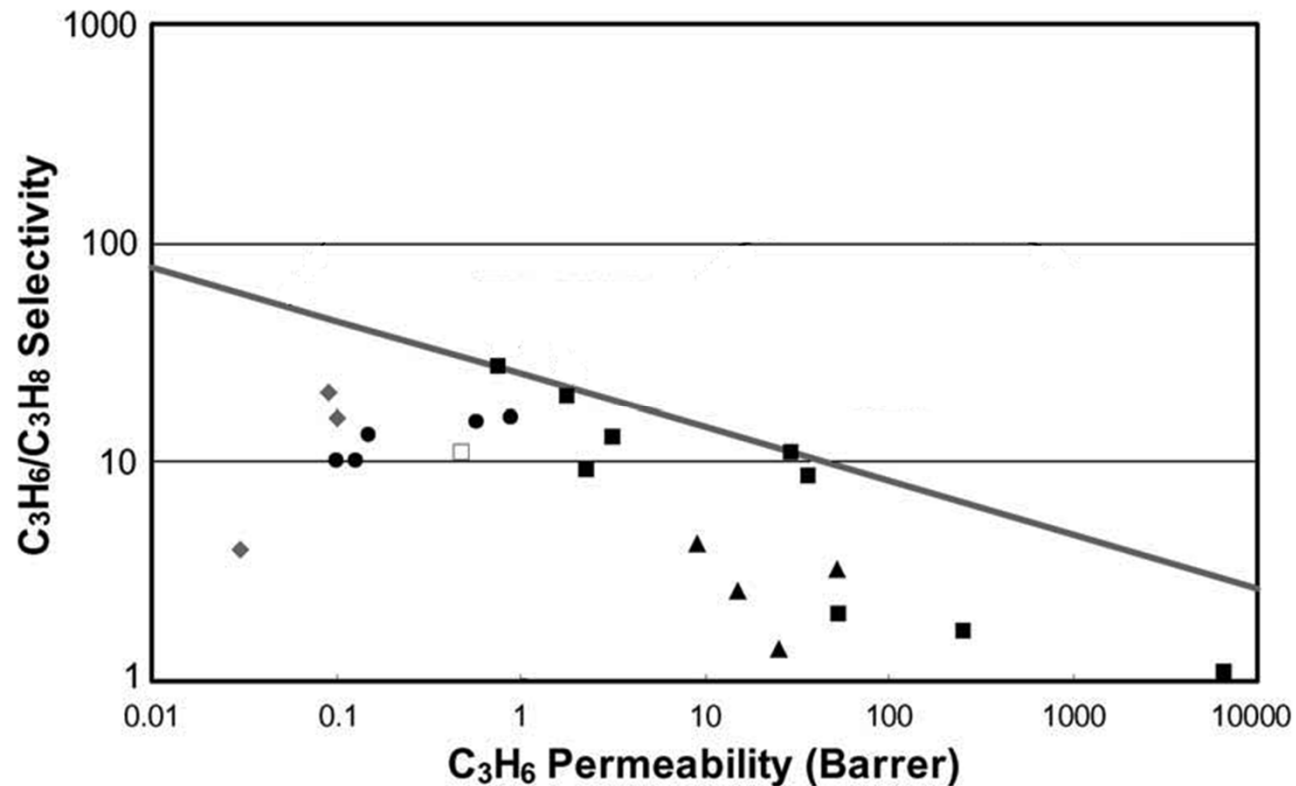
# Ethylene and Propylene Product Chains



# Membrane Can Touch Olefins Multiple Times

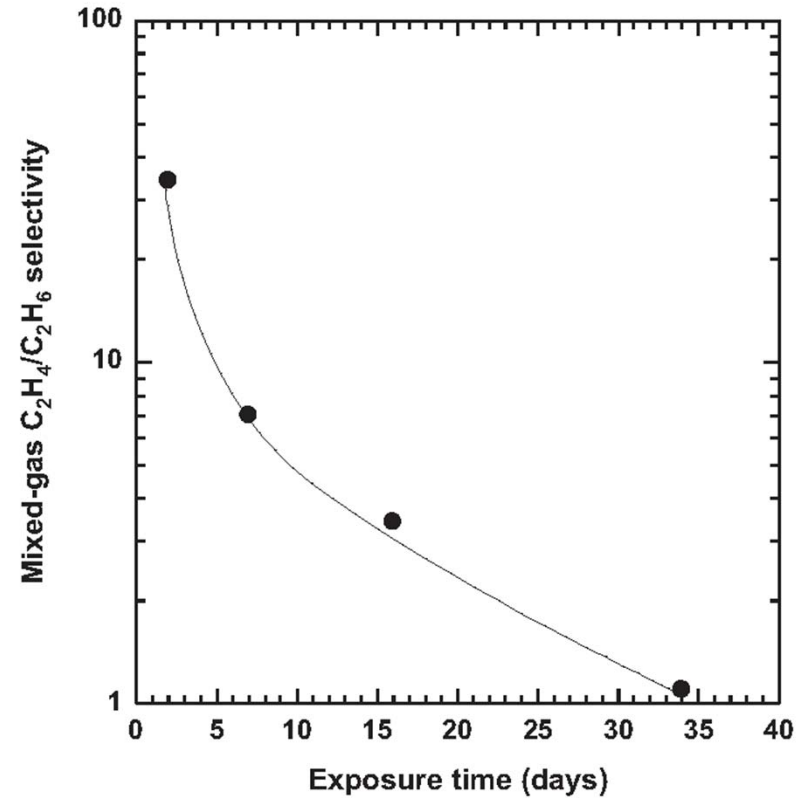
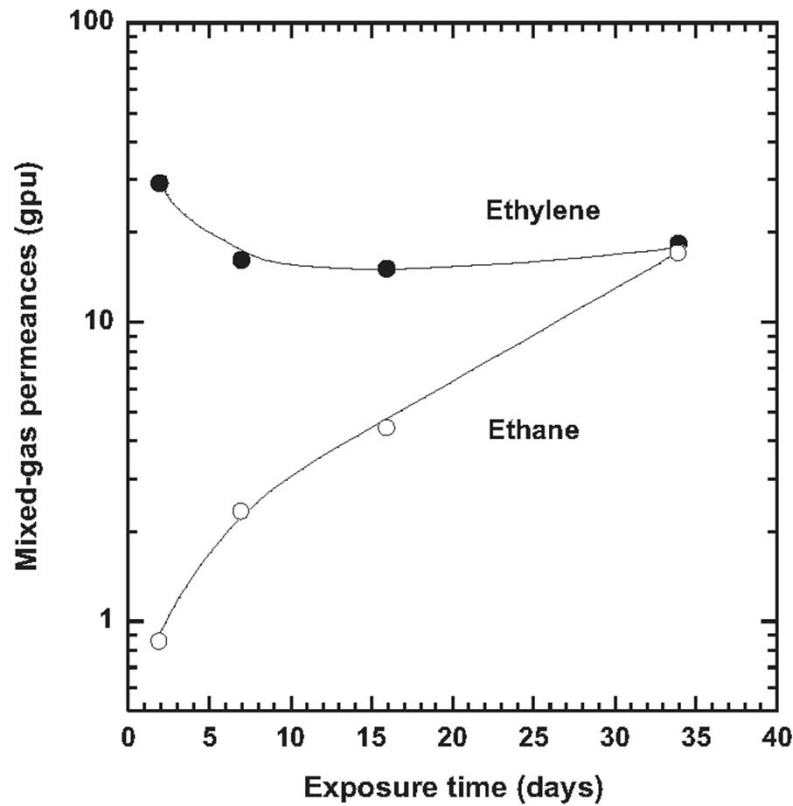
- **Refinery  
(+ New on Purpose Propylene Sites)**
- **Polymer Purge Line**
- **Polymer Silo**

# Experimental Upper Bound Based on Pure Propylene and Propane Permeation Data



Ref: Burns and Koros, *Journal of Membrane Science*, 211, 299 (2003)

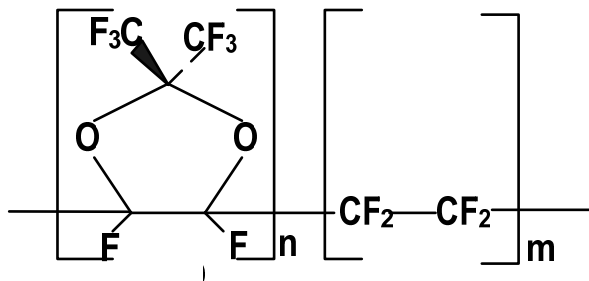
# Historically Membranes for Olefin-Paraffin are Not Stable



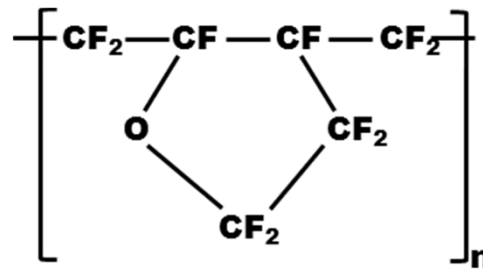
*Ref: Merkel et al., Journal of Membrane Science 447, 177 (2013)*

# Commercial Amorphous Fluoropolymers

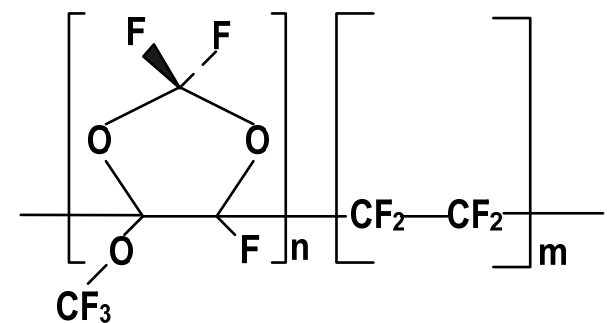
## Teflon AF



## Cytop



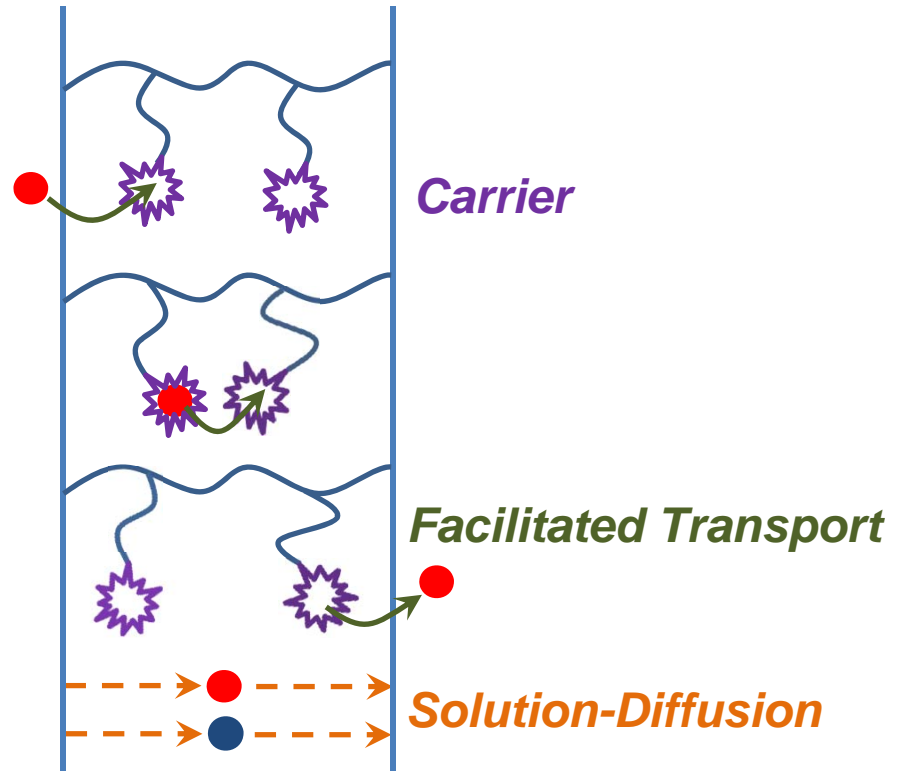
## Hyflon





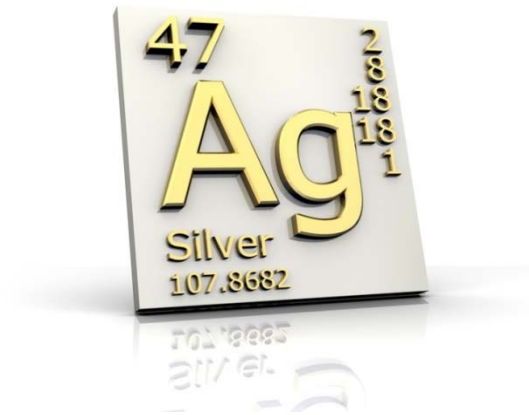
# Facilitated Transport (Fixed Carriers)

Olefin ●  
Paraffin ●



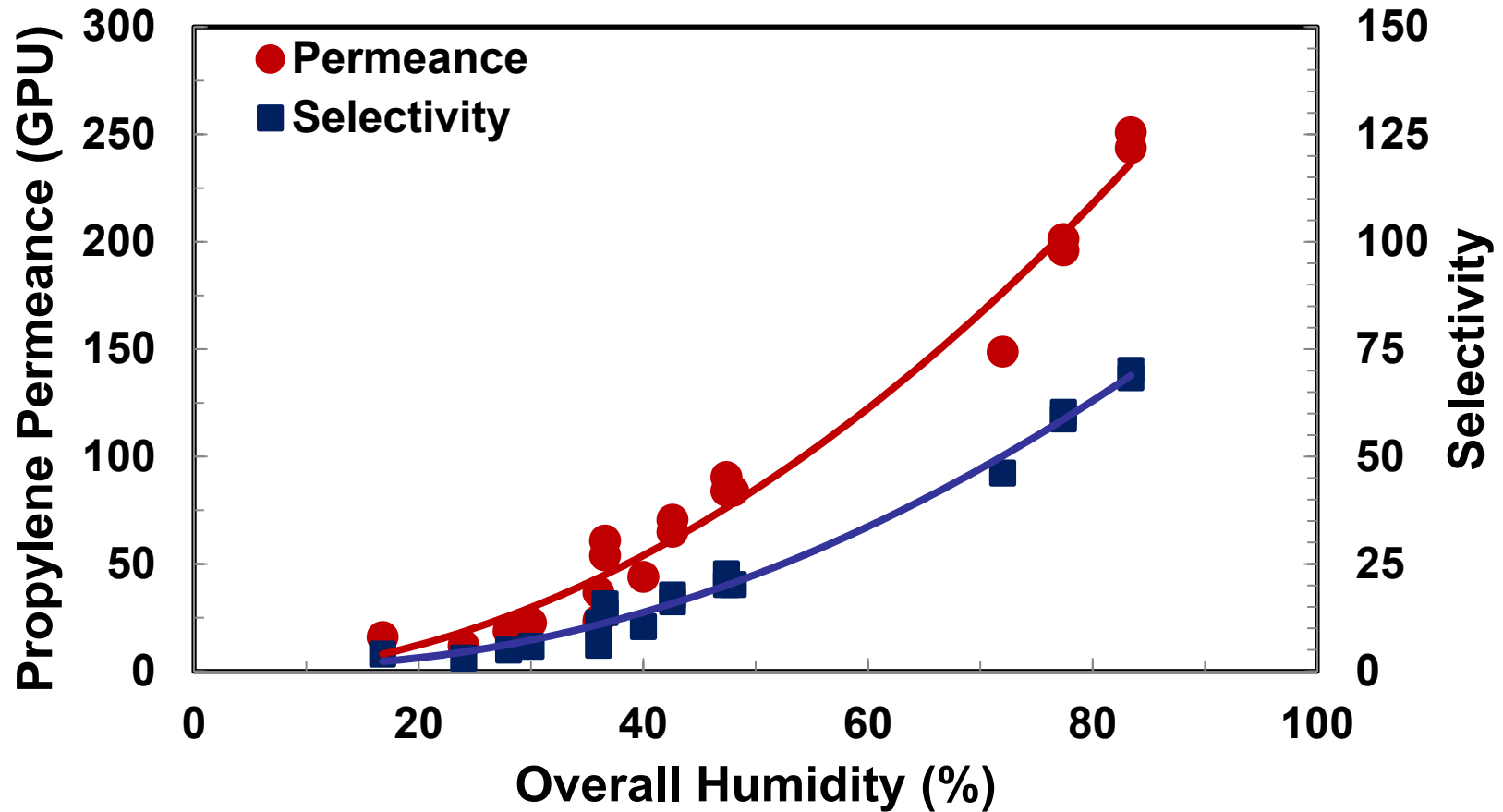
Tarzan swinging from a vine

# Custom Amorphous Fluoropolymer (CAF) and

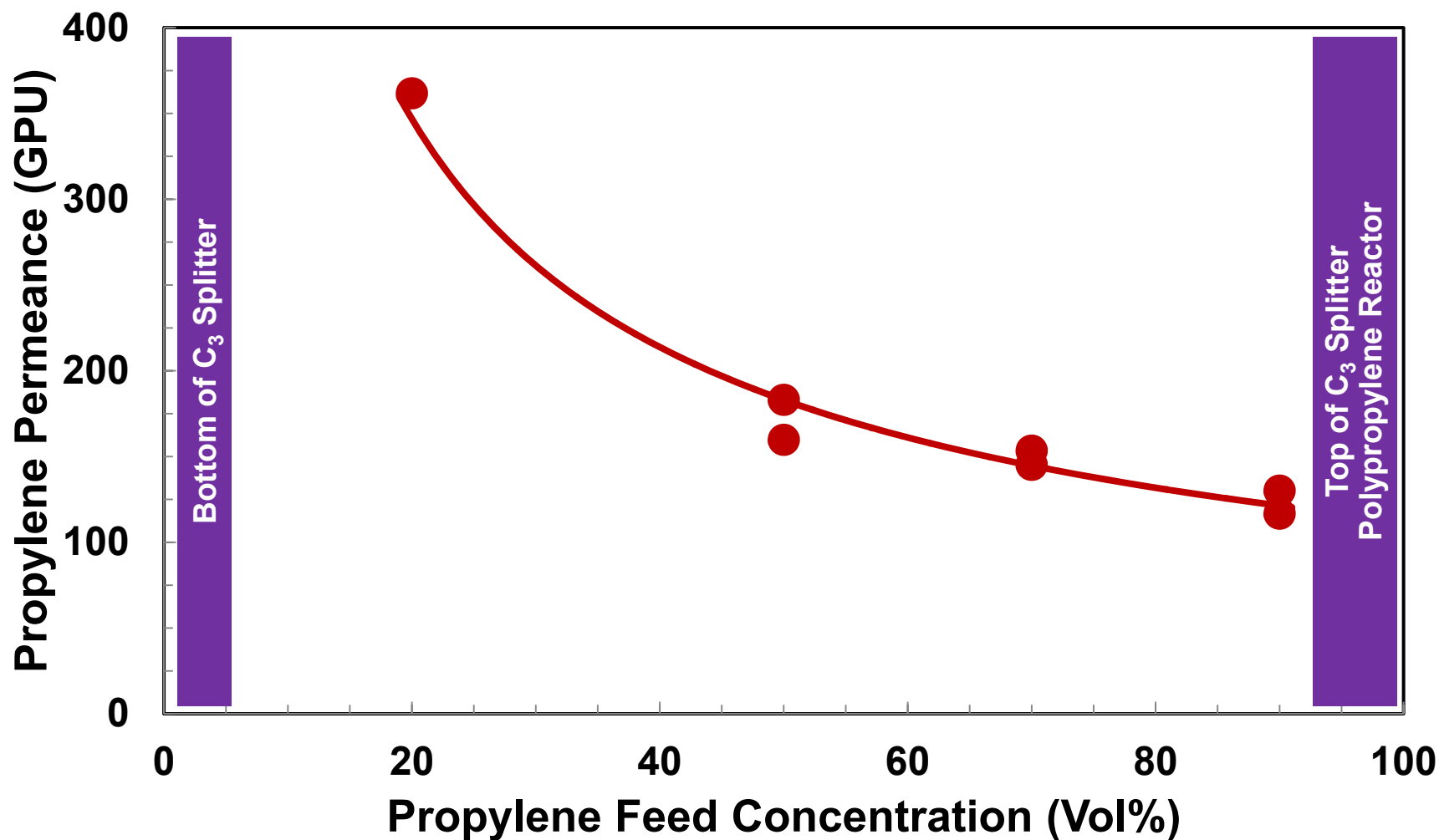


- Silver is part of the polymer chain
- Form stable, high flux, high selectivity facilitated transport membranes
- CAF and new synthesis procedure potentially protects silver

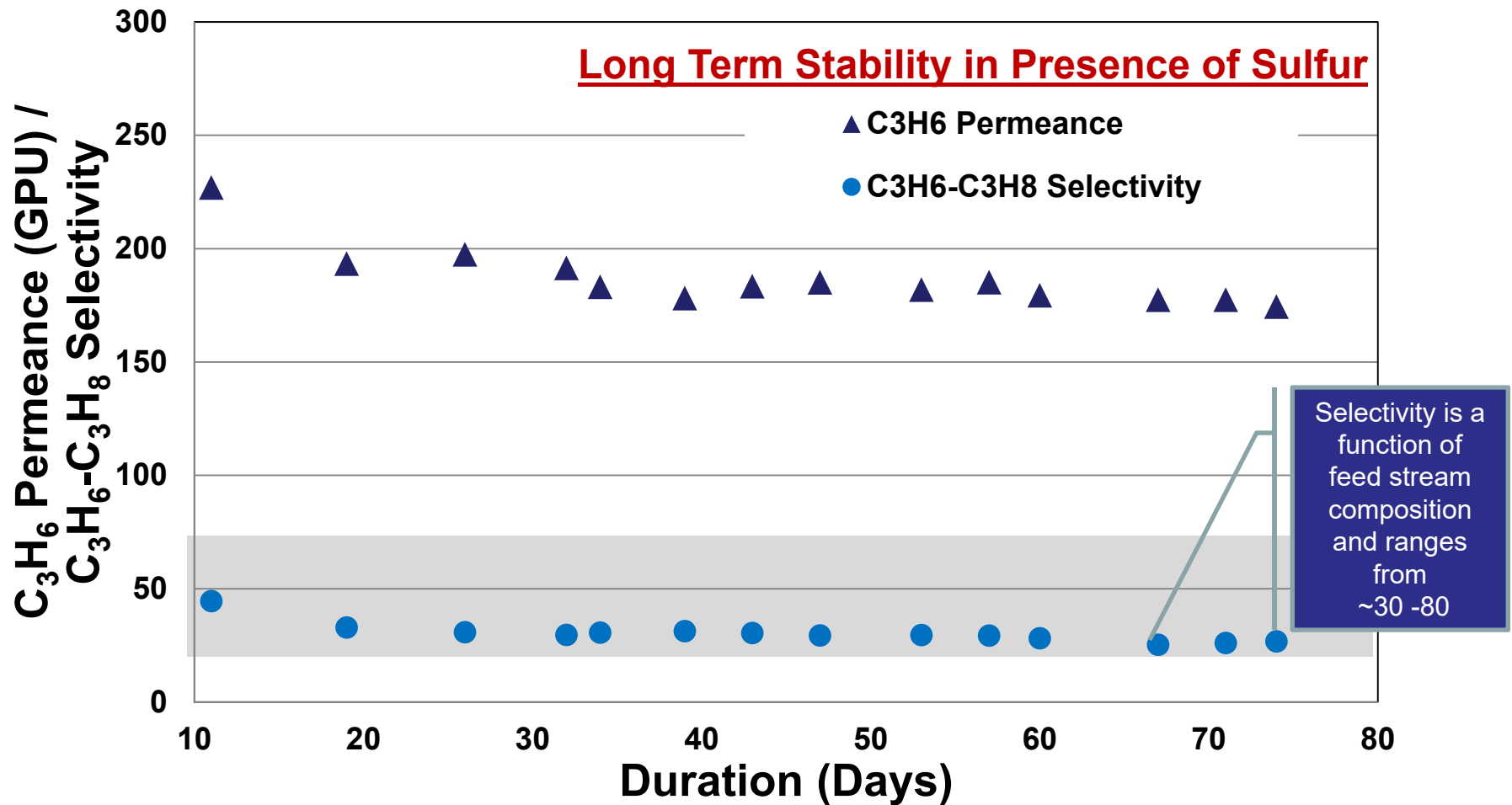
# Variation of Humidity



# Effect of Feed Concentration



# Stable, Strong Performance Over Time



# Ethylene-Ethane Mixture Separation

	<b>Olefin Permeance (GPU)</b>	<b>Paraffin Permeance (GPU)</b>	<b>Selectivity</b>
<b>Ethylene / Ethane</b>	<b>275.5</b>	<b>3.6</b>	<b>76.2</b>
<b>Propylene / Propane</b>	<b>226.5</b>	<b>3.2</b>	<b>70.2</b>

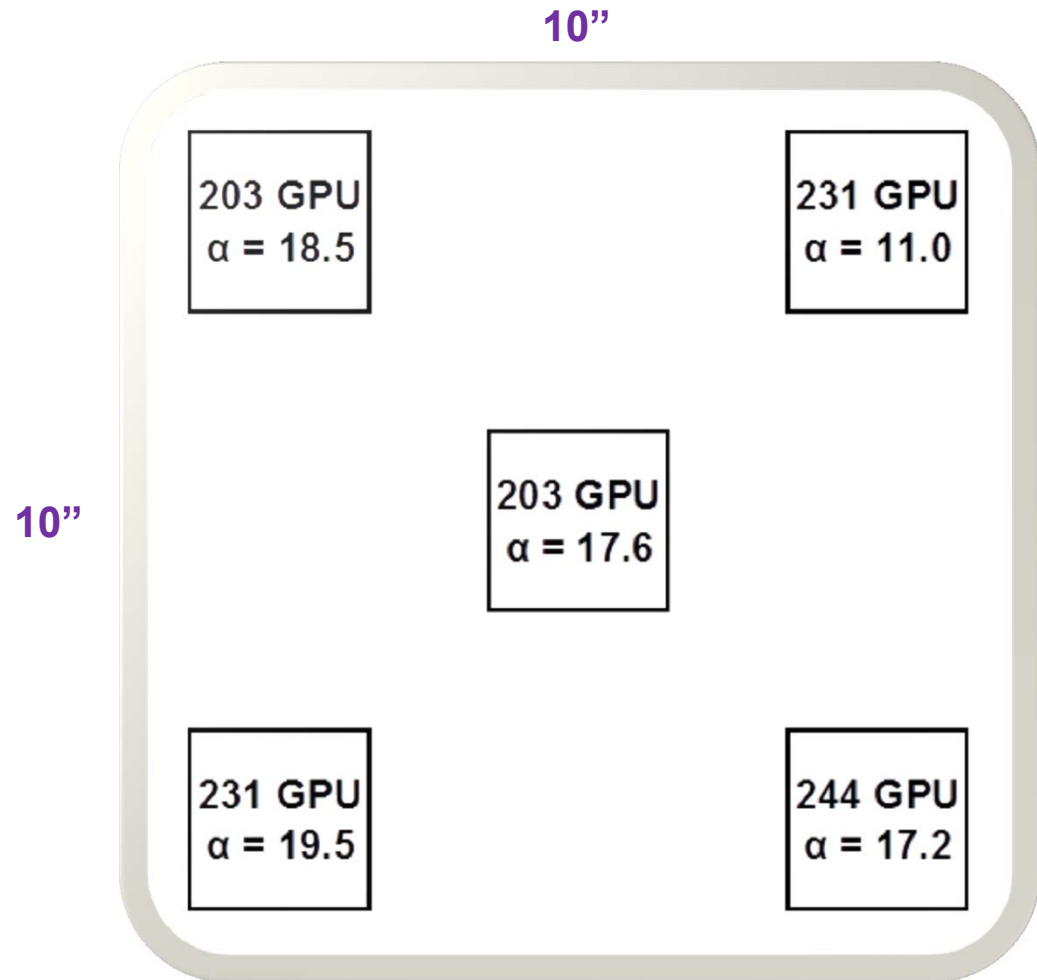
Feed: 20% Olefin - 80% Paraffin; Feed Pressure: 60 psig; Humidified Feed/Sweep; New Membrane

# Preliminary Membrane Scale-up (47 mm Disc vs. 10 inch Square)

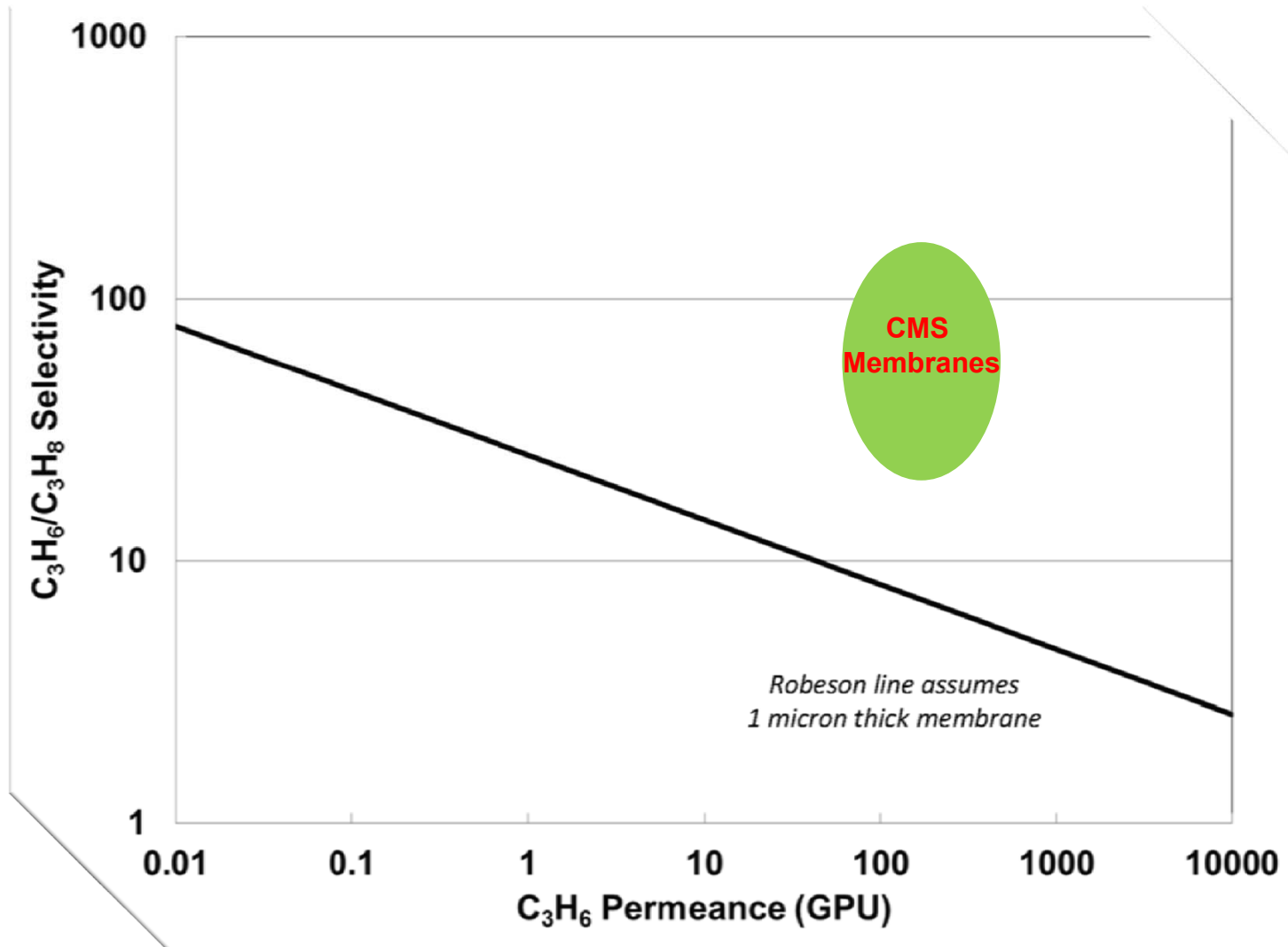
## 47 mm Disc Results

Propylene Permeance (GPU)	Selectivity $C_3H_6/C_3H_8$
256	17.0

Feed: 20%  $C_3H_6$  - 80%  $C_3H_8$   
Feed Pressure: 60 psig



# Permeance and Selectivity Map of CMS Membranes





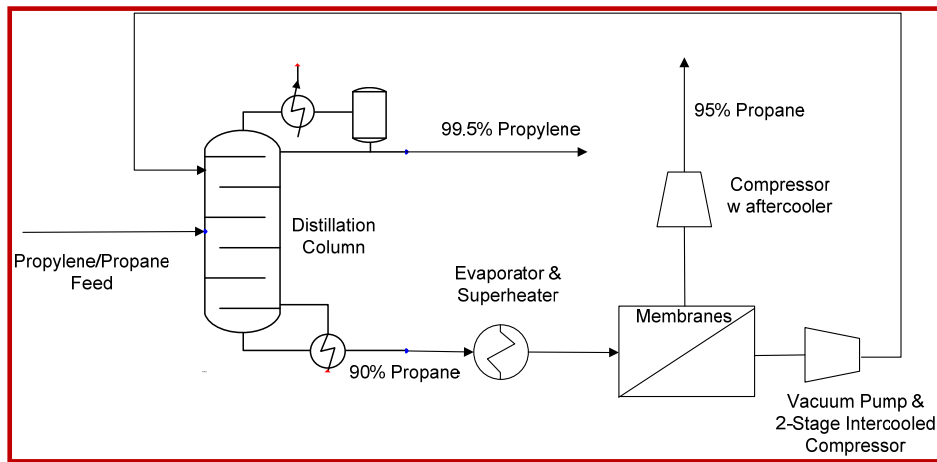
# Engineering and Economic Evaluation

## Key Assumptions: C3 Splitter Analysis

Membrane Permeance (Propylene)	100 GPU
Membrane Selectivity	20
Feed Pressure	110 psia
Permeate Pressure	14.7 psia
Membrane Replacement Rate	33% per year
C3 Splitter Feedstock	50% Propylene
Value of Splitter Feed	21 cents/lb
Price of HD05 Propane	24.5 cents/lb
Price of Propylene	60 cents/lb

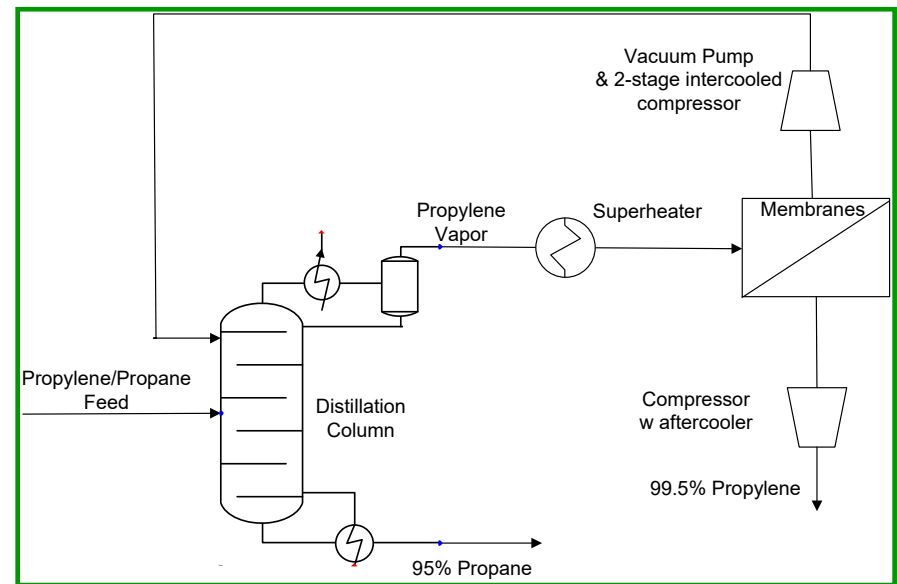
# Distillation-Membrane Hybrid Processes

## Configuration 1



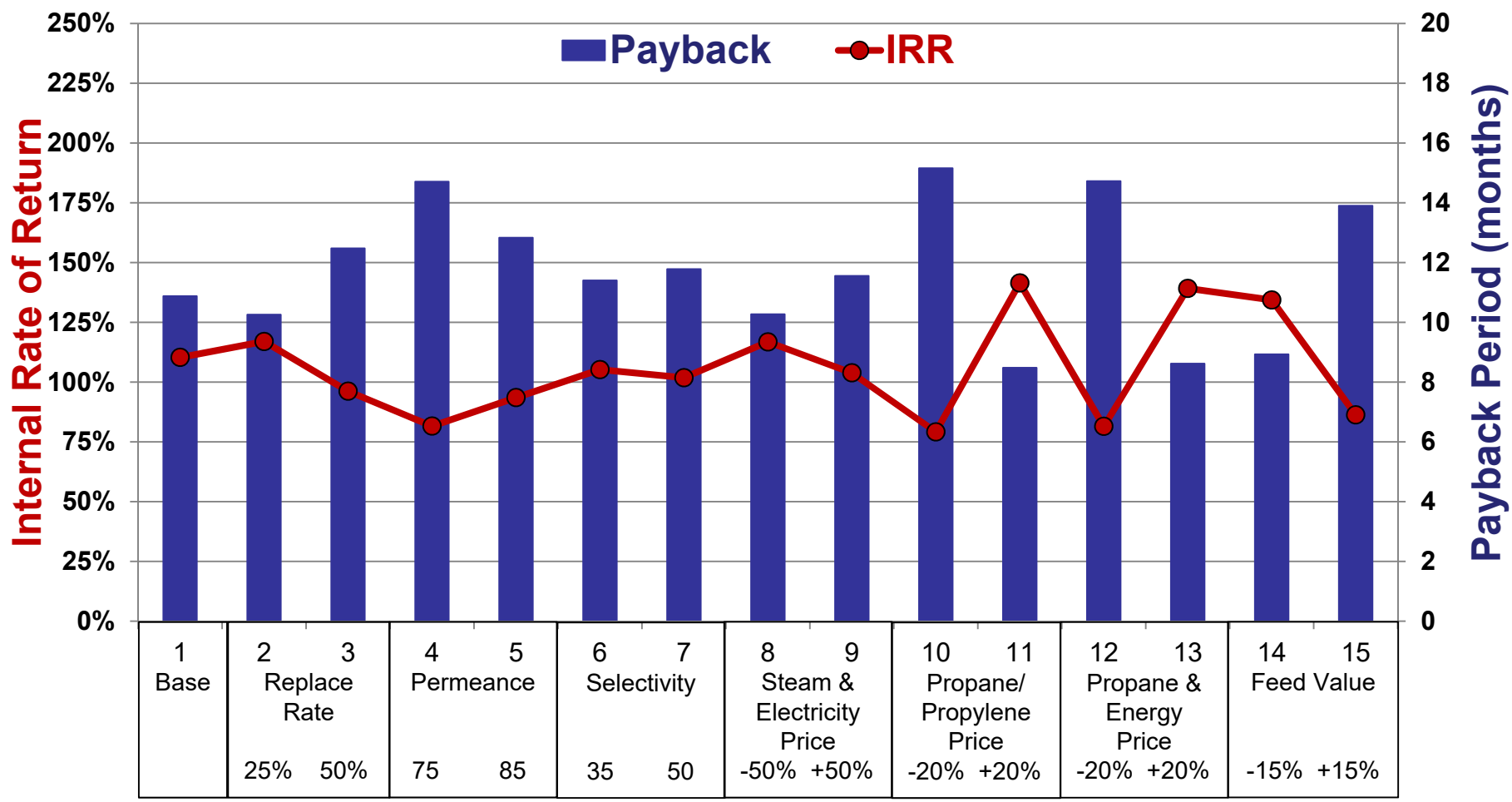
- Membrane separates bottom fraction
- Permeate recycled to column
- Very small increase in flood factor ~1%
- Increases propane purity and propylene yield

## Configuration 2



- Membrane separates distillate
- Retentate recycled to column
- Reduces column top product purity required
- Reduces reflux ratio required & saves energy
- Enables higher feed flow rate to column for greater propane & propylene production

# Membrane Completing Separation of HD10 Propane at Bottom of C3 Splitter with Propylene Capacity of 40,000 Tons per Year

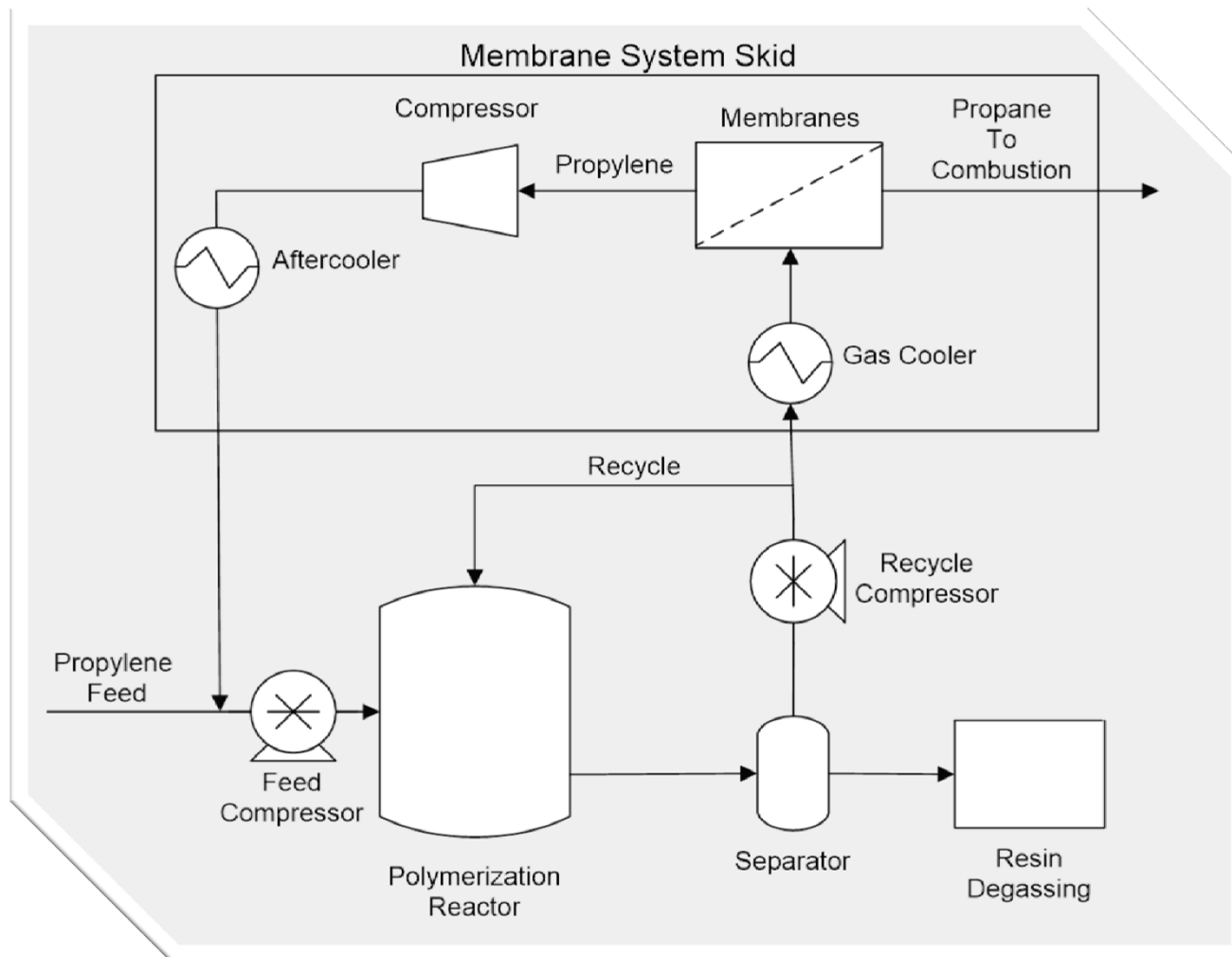


Case

AICHe 2015



# Membrane System for Propylene Recovery from Polypropylene Reactor Purge



# Base Case Economics

Payback	Months
<b>C3 Splitter</b>	<b>~ 11</b>
<b>Polypropylene Reactor Purge</b>	<b>~ 8</b>

# Summary / Path Forward

- **CMS Demonstrated Stable Olefin-Paraffin Facilitated Transport Membrane**
- **Attractive C3 Splitter Economics  
Payback < 15 months**
- **Key Next Steps**
  - ❖ **Optimize Process – 2016**
  - ❖ **Build Larger Membrane Modules – 1H / 2016**
  - ❖ **Demonstrate at Plants – 2H / 2016 - 2017**

# Acknowledgement

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