Membrane vs. Distillation – A Power Demand Study for Hydrocarbon Mixtures

Rakesh Agrawal
Jose Adrian Chavez Velasco
Mohit Tawarmalani*
Davidson School of Chemical Engineering
Purdue University, USA

***Krannert School of Management**
Purdue University

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Distillation processes are widely used in the chemical industry

Just in the U.S., over 90-95% of all separations in Chemical and Petrochemical plants are performed by distillation columns[1]

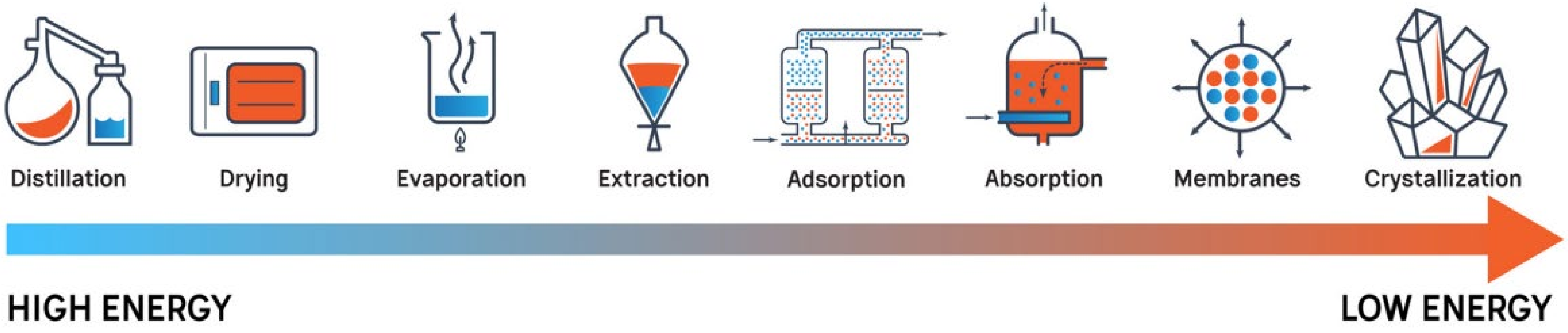
Despite the high relevance, they are not at the forefront of separations research in the USA

https://www.industrialaccess.com

[1] Humprey, Chem. Eng. Prog., 88 (1992), pp. 32-42

Are distillation separations most energy intensive?

According to NASEM Study[2]:



It is stated that[3] replacing thermal methods by membranes could potentially cut energy consumption by a factor of 10

Is it true that distillation processes are generally most energy intensive?

[2]A Research Agenda for Transforming Separation Science, NASEM 2019. The National Academies Press

[3]Sholl, David S., and Ryan P. Lively. *Nature* 532.7600 (2016): 435-438.

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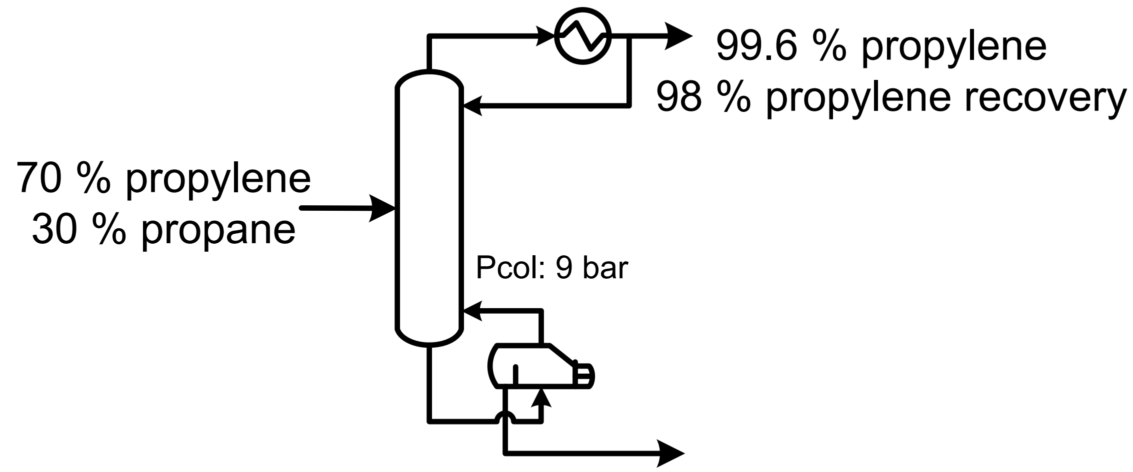
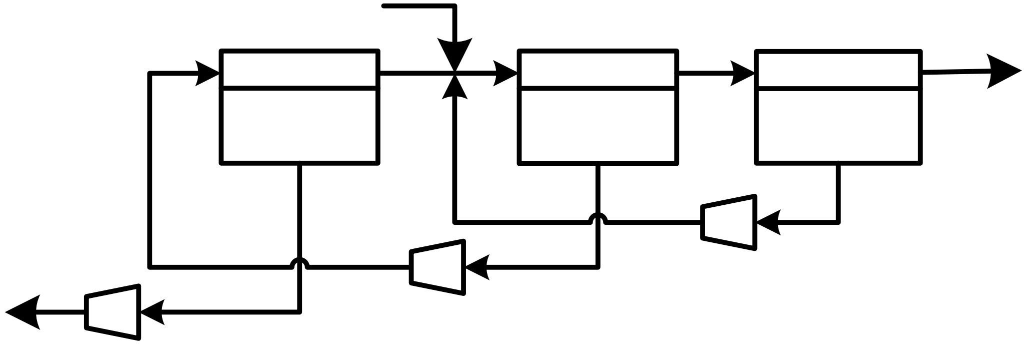
How have two separation methods been compared?
An example: propylene/propane separation





Reboiler heat duty for distillation

$$Q_{dist} = 0.5 \frac{kWh}{lb\ propylene}$$

Compressor work for membranes with permselectivity = 35

$$^4W_{mem} = 0.050 \frac{kWh}{lb\ propylene}$$

It appears that distillation consumes an order of magnitude more energy

[4]Colling et al., (2004). U.S. Patent No. 6,830,691

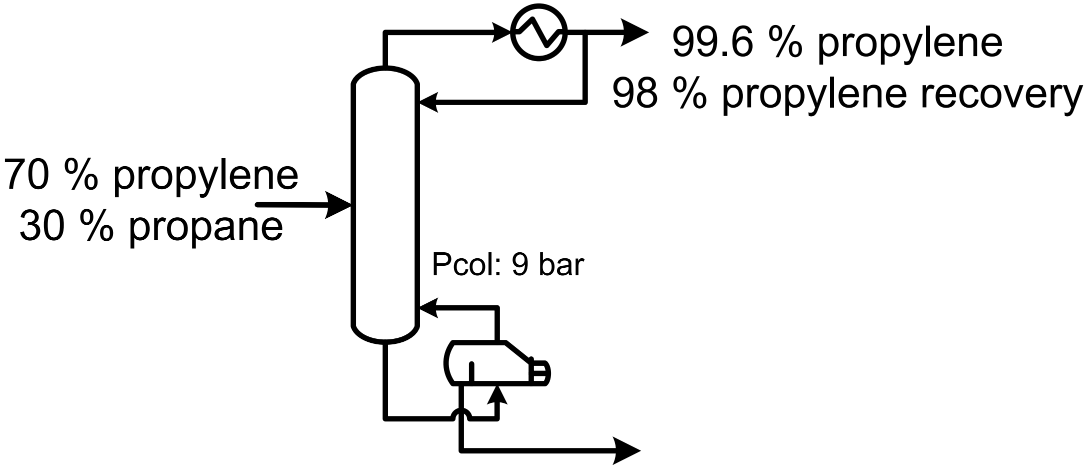
However, Comparing Membranes with Distillation is Not Straightforward

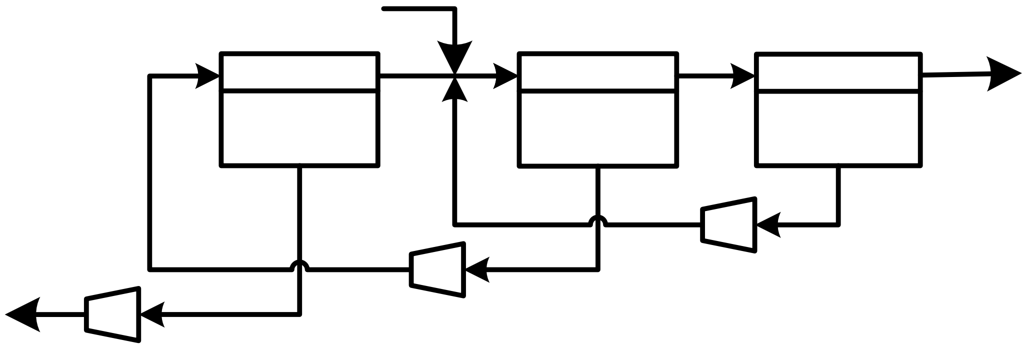
Membranes Use Work (electricity for increasing pressure)

Distillations Use Heat in the Reboiler

Directly Comparing These Two Forms of Energy Generally Results in Wrong Conclusions

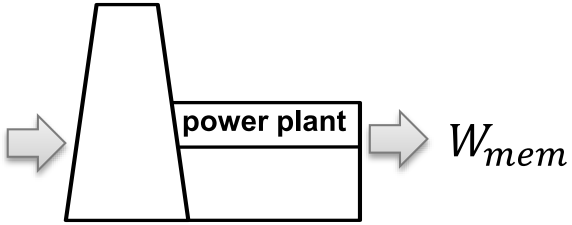
Another common approach employed to compare heat vs work





$\boldsymbol{Q_{dist}}$

$$\boldsymbol{Q_{fuel}} = \frac{W_{mem}}{\eta_{power\ plant}}$$



comparison

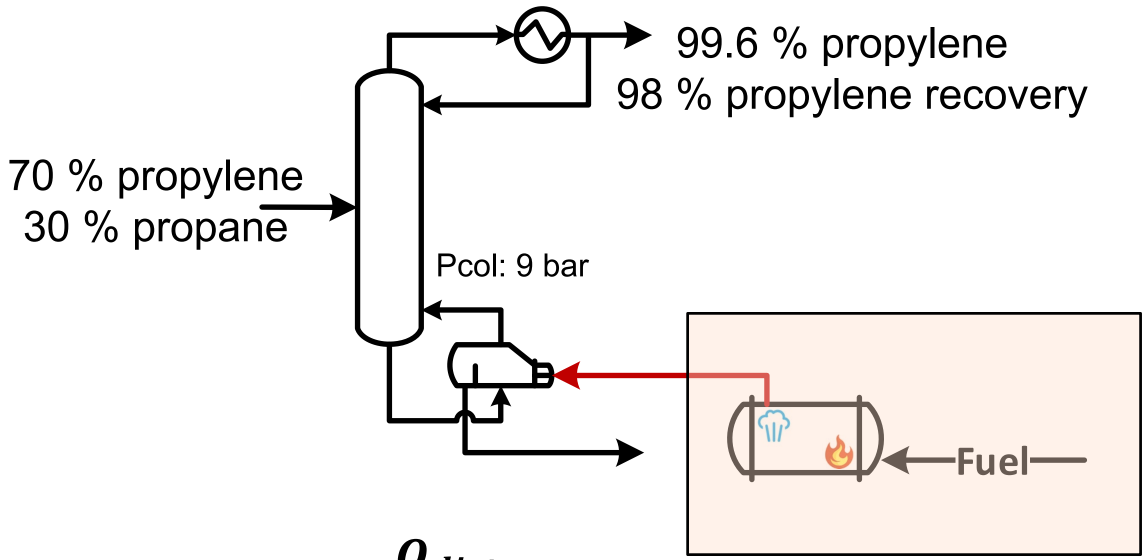
$$Q_{dist} = 0.5\ \frac{kWh}{lb\ propylene}$$

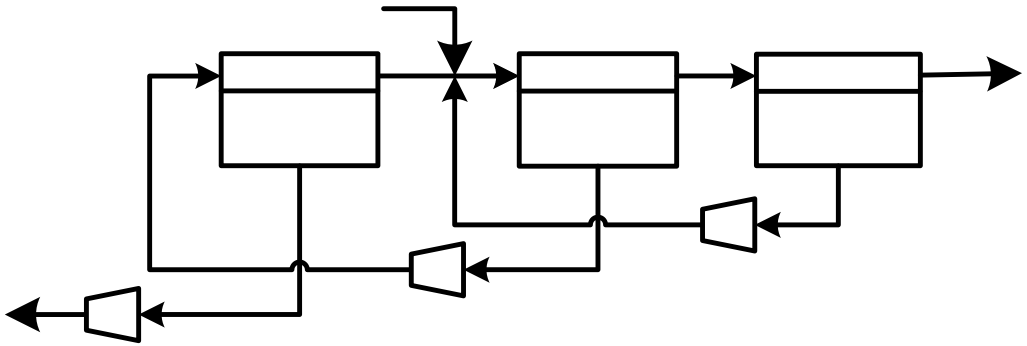
$$Q_{fuel} = 0.1\ \frac{kWh}{lb\ propylene} \qquad (\eta_{power\ plant} = 0.5)$$

However, it is important to account for temperatures when comparing heat

W. J. Koros. AIChE Journal 50, 2326 (2004).

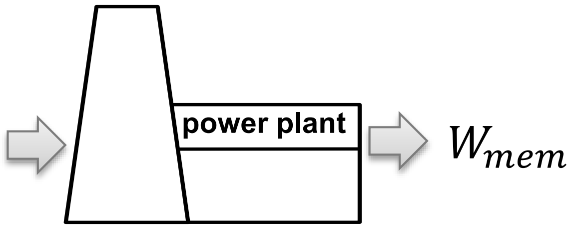
Another common approach employed to compare heat vs work





$\boldsymbol{Q_{dist}}$

$$\boldsymbol{Q_{fuel}} = \frac{W_{mem}}{\eta_{power\ plant}}$$



comparison

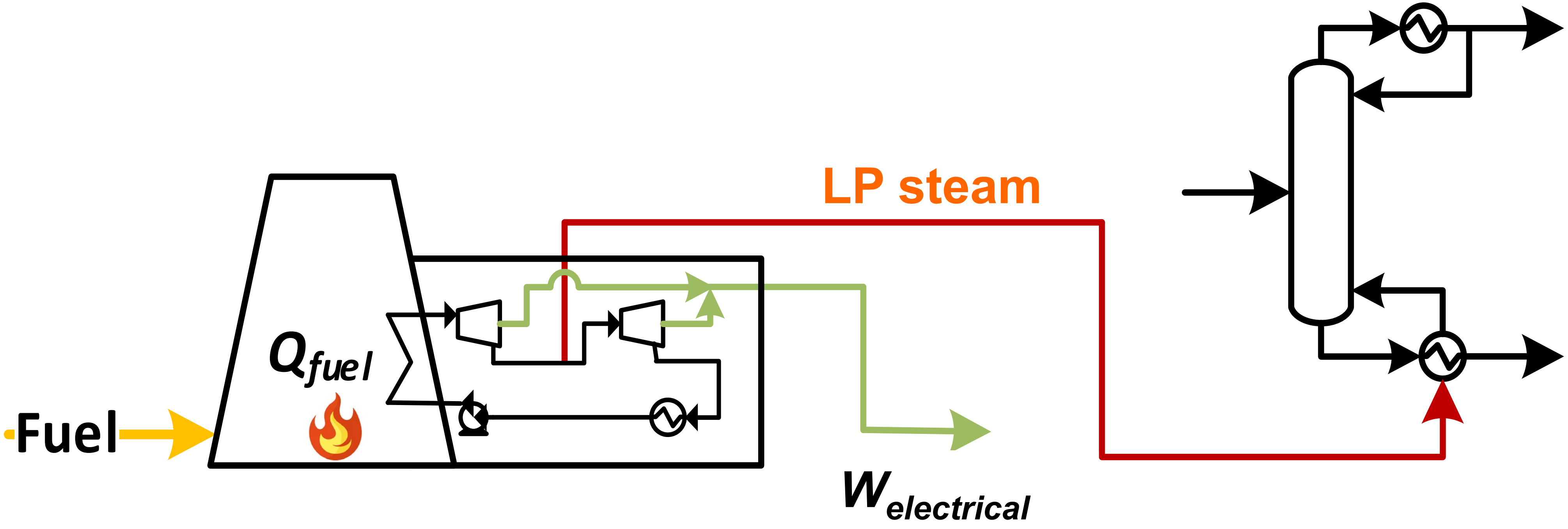
$$Q_{dist} = 0.5\ \frac{kWh}{lb\ propylene}$$

$$Q_{fuel} = 0.1\ \frac{kWh}{lb\ propylene}$$

This approach implicitly assumes that the heat for distillation directly comes from burning fuel

W. J. Koros. AIChE Journal 50, 2326 (2004).

Heat supplied to a distillation can come from a lower temperature source



Effective Q_{fuel} = Amount of additional fuel needed to supply needed LP steam while keeping power generation ($W_{electrical}$) constant

When heat is supplied by LP steam from a power plant, effective Q_{fuel} could be lower than Q_{reb}

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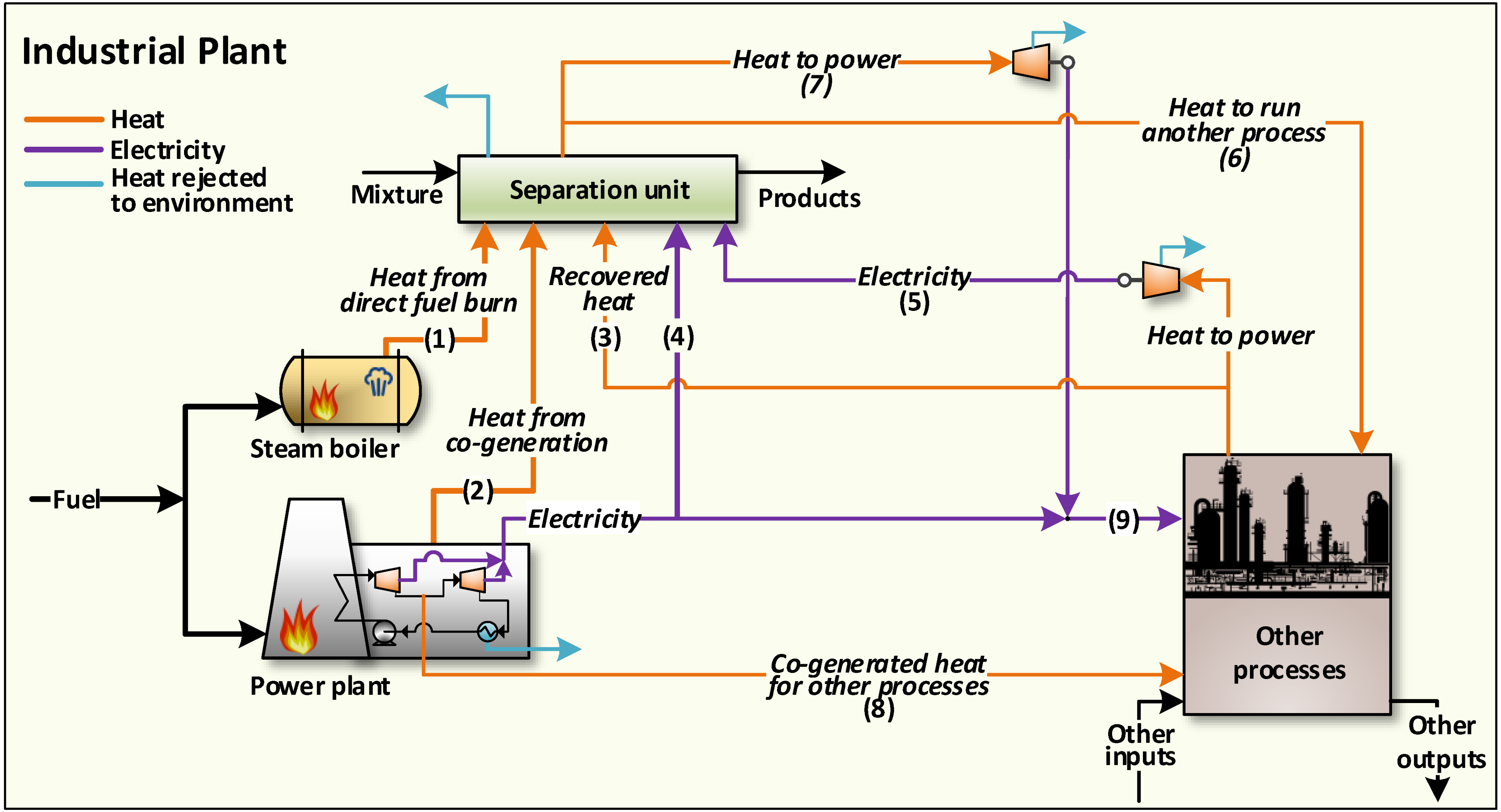
A system level analysis is needed to compare separation processes



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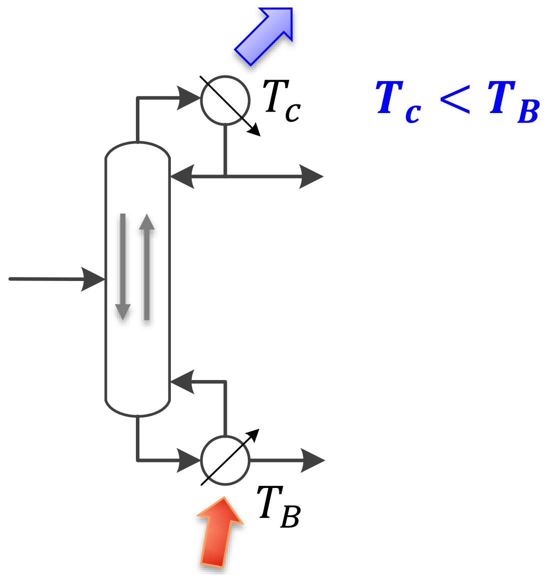
Let Us Compare Both Processes When Each is Powered by Electricity

For Proper comparison, we need to ensure that both processes are at their global minimum in energy.

Distillation can be operated with electrical work input

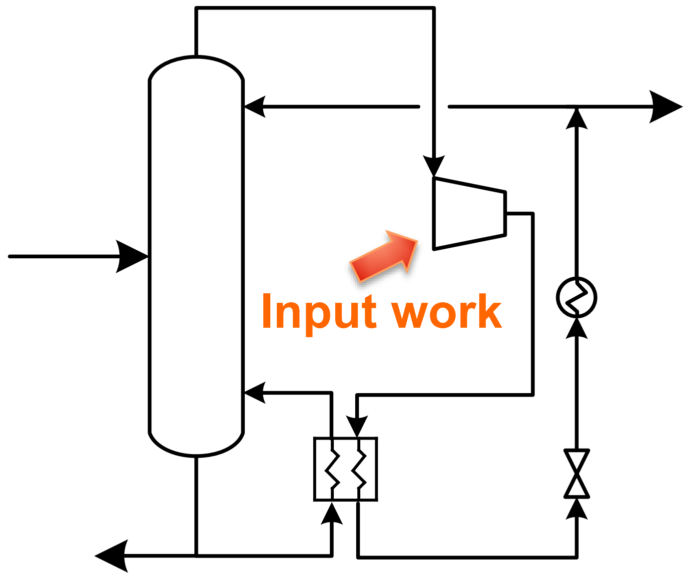
Heat supplied distillation

Heat rejected



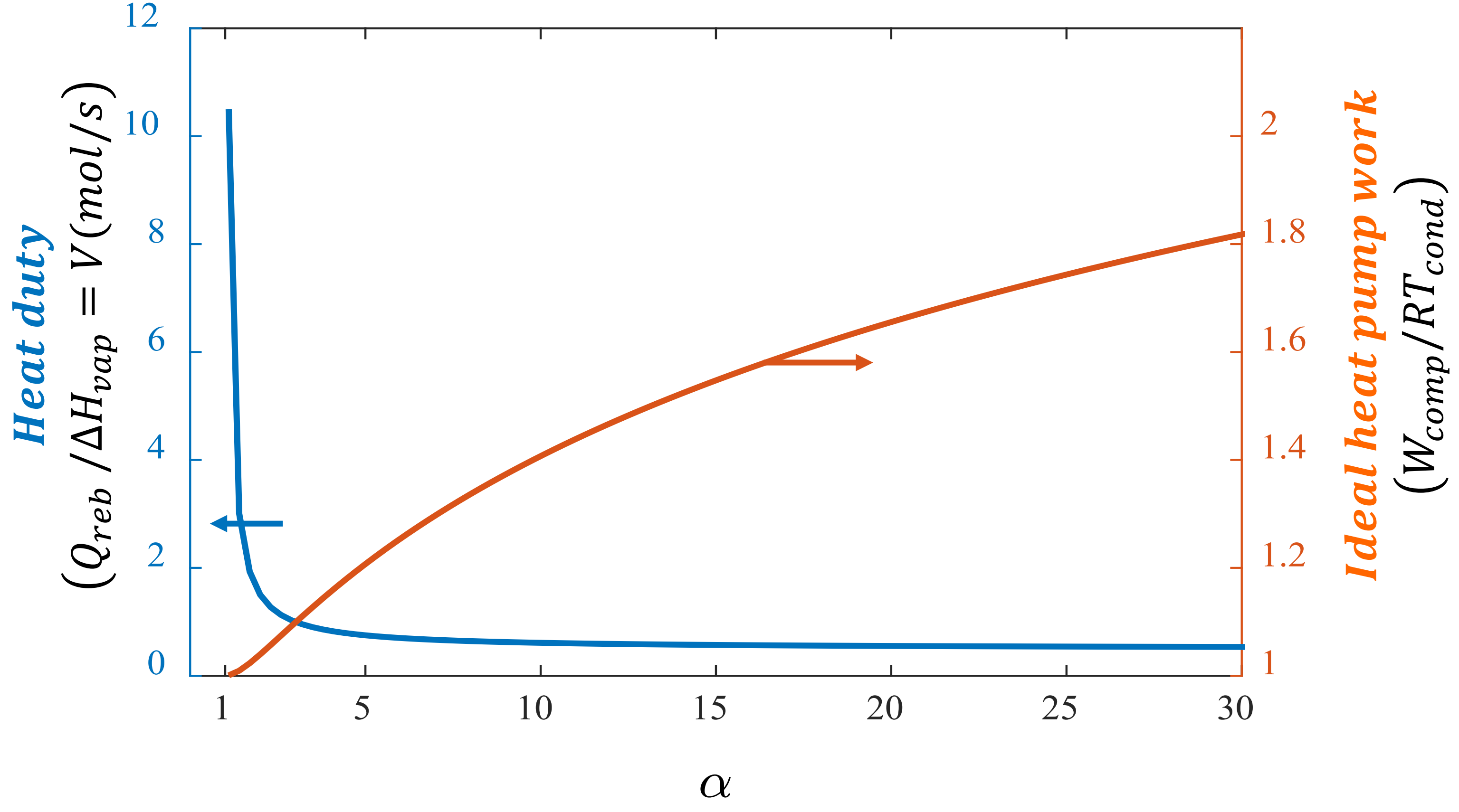
Heat input

Heat Pump (HP) assisted distillation



Sometimes it is more energy efficient to operate distillation with work than with heat

Comparing heat with heat pump work



Simulated conditions

- Saturated liquid feed
- $x_{A,f} = 0.50$
- Complete separation

Heat duty decreases with increasing α

Heat pump work increases with α

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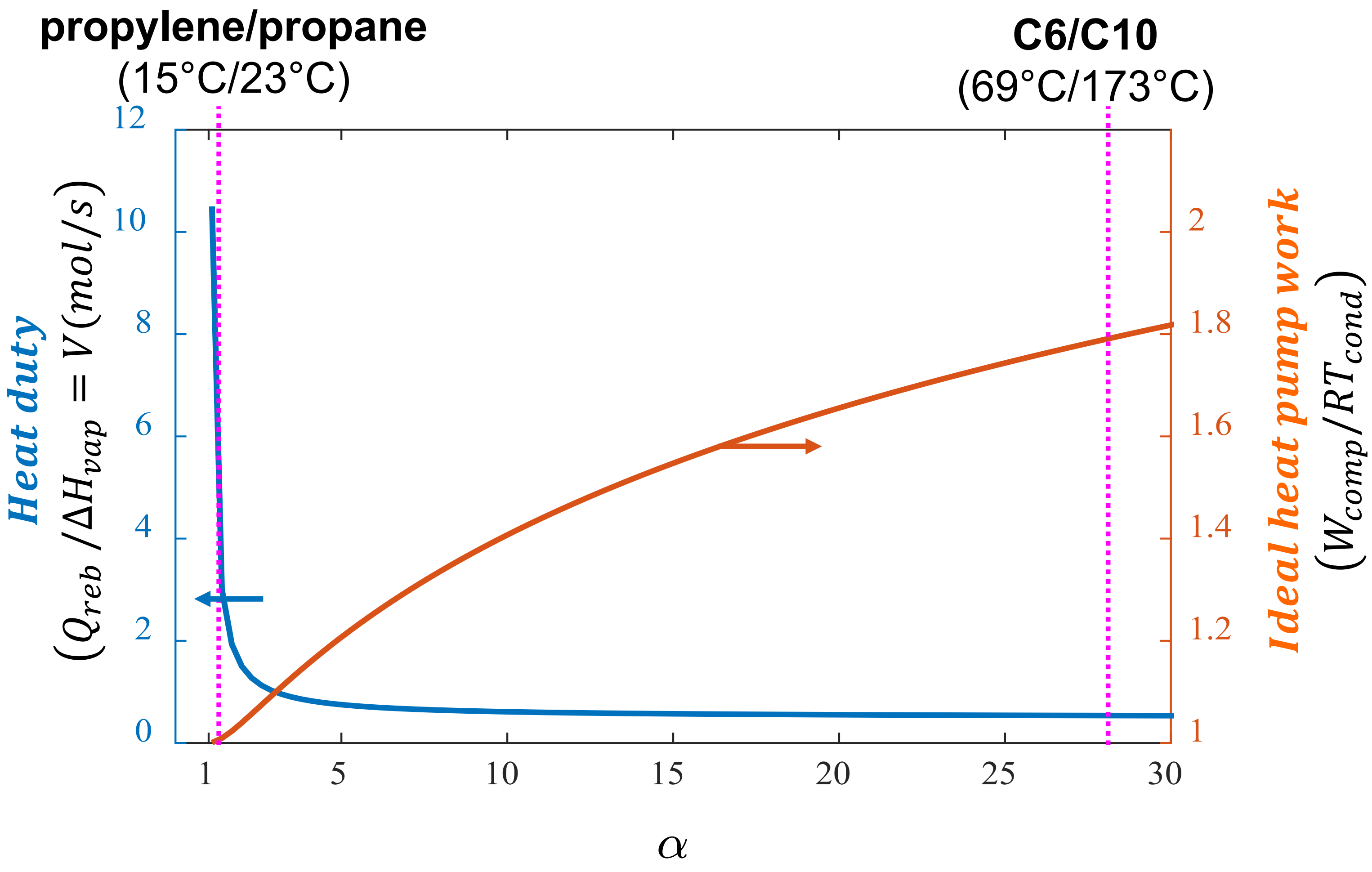
Comparing heat with heat pump work



Simulated conditions

- Saturated liquid feed
- $x_{A,f} = 0.50$
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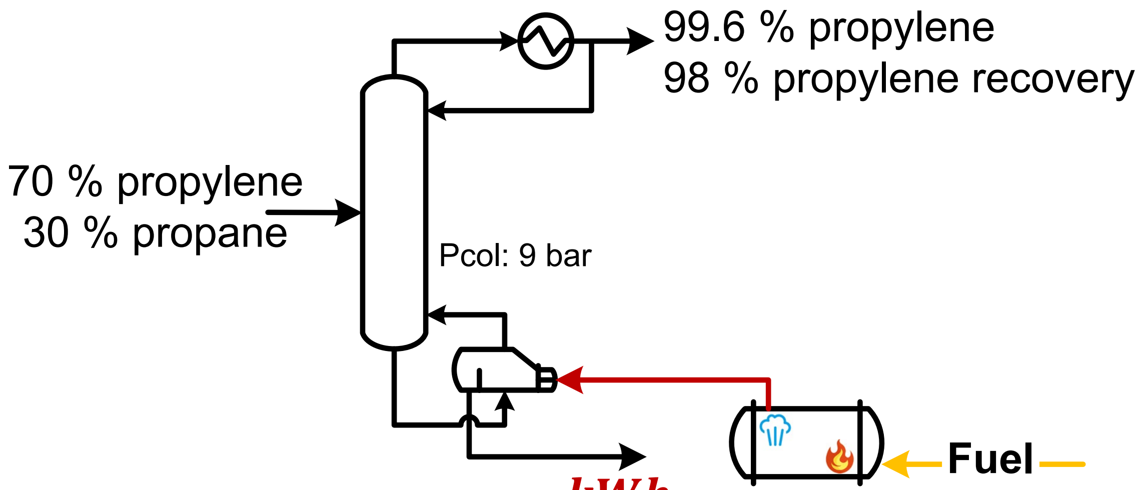
Heat duty decreases with an increase in α

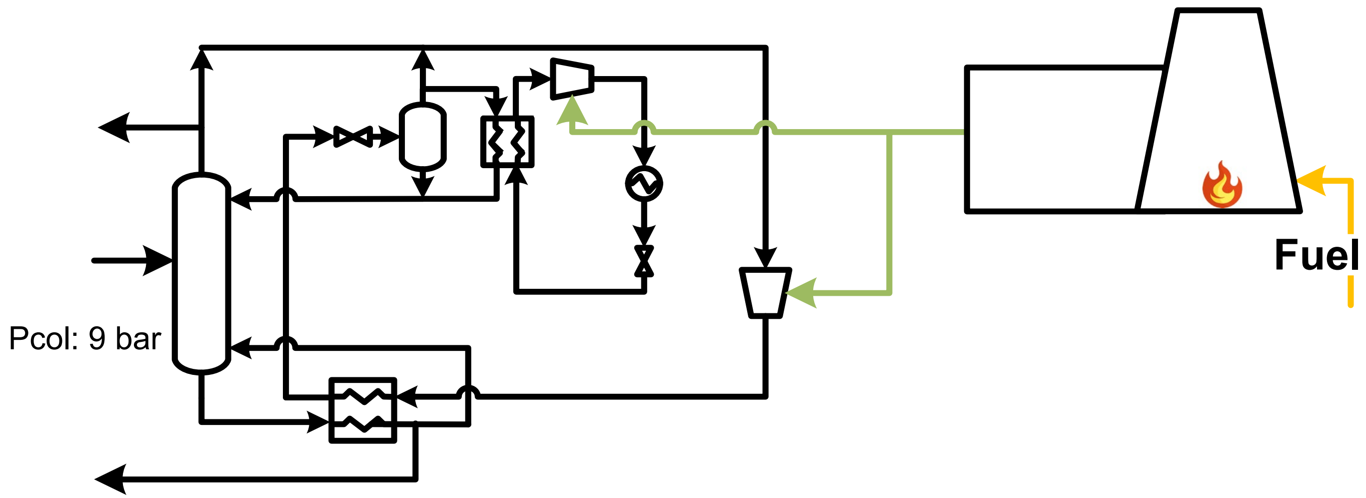
Heat pump work increases with α

Revisiting propane/propylene separation

A more efficient way to operate distillation



$$Q_{reb} = 0.5 \frac{kWh}{lb\ propylene}$$



$$Q_{fuel,Sep} = 0.6 \frac{kWh}{lb\ propylene}$$

$$Q_{fuel,Sep} = 0.04 \frac{kWh}{lb\ propylene}$$

Heat pump distillation consumes 15 times lower fuel than heat supplied distillation for this separation

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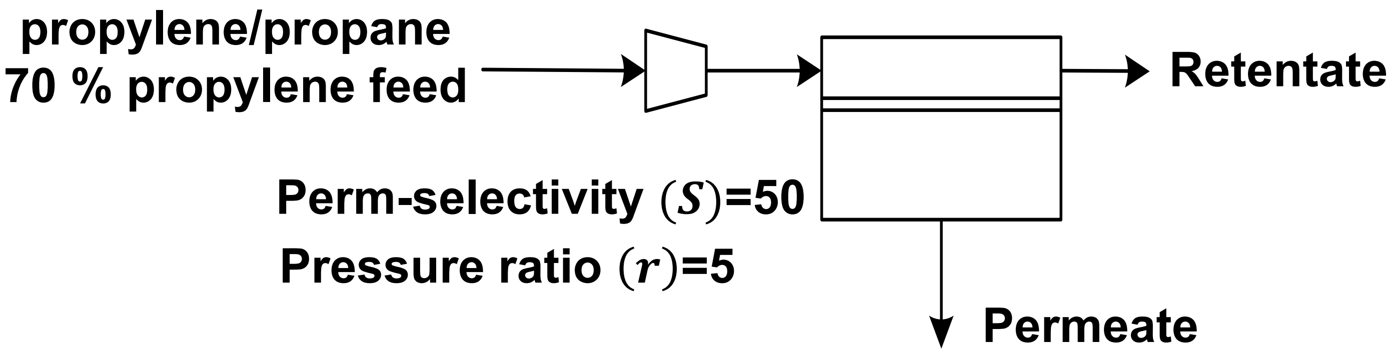
Calculating Power for Membrane Processes

A Single stage membrane Processes is often Limited in Product Recovery and purity

Example: propylene/propane



Propylene recovery (% mol)	Propylene purity in permeate (%mol)
50	98
99	87

Typically, propylene is needed with 99.5% purity and 99 % recovery

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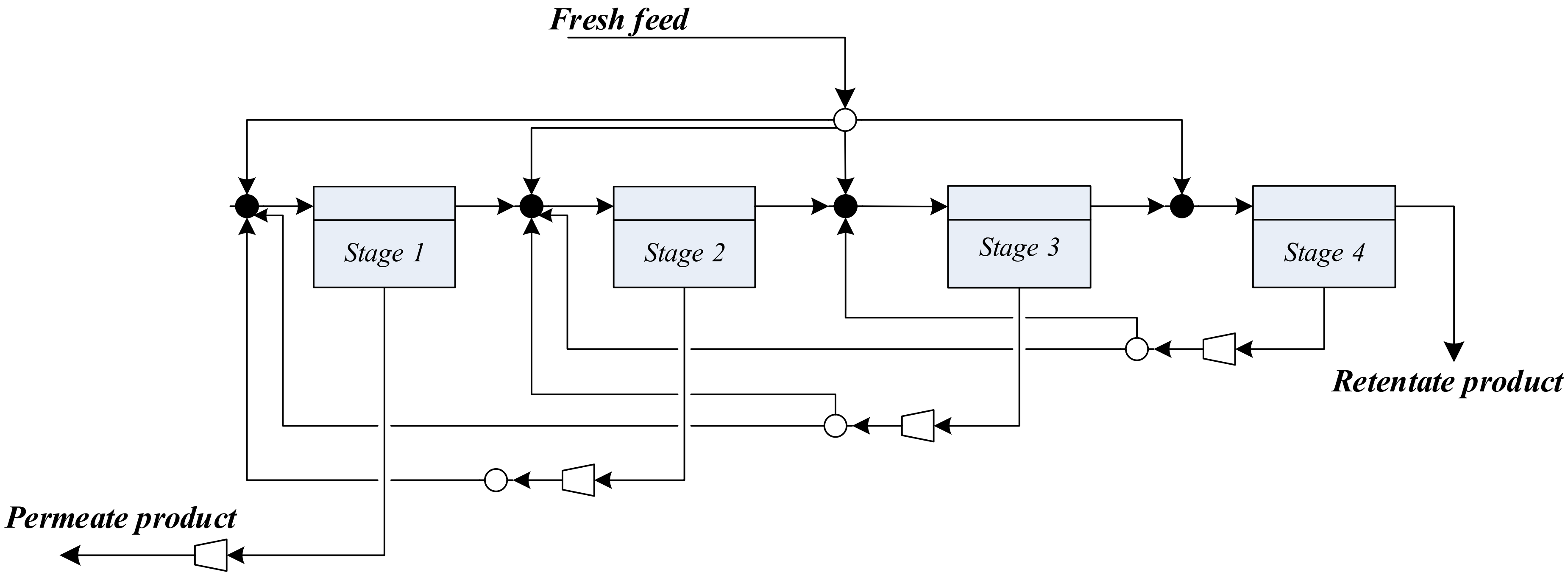
Developed A Membrane Cascade MINLP Optimization Model

A membrane cascade superstructure for gaseous mixtures



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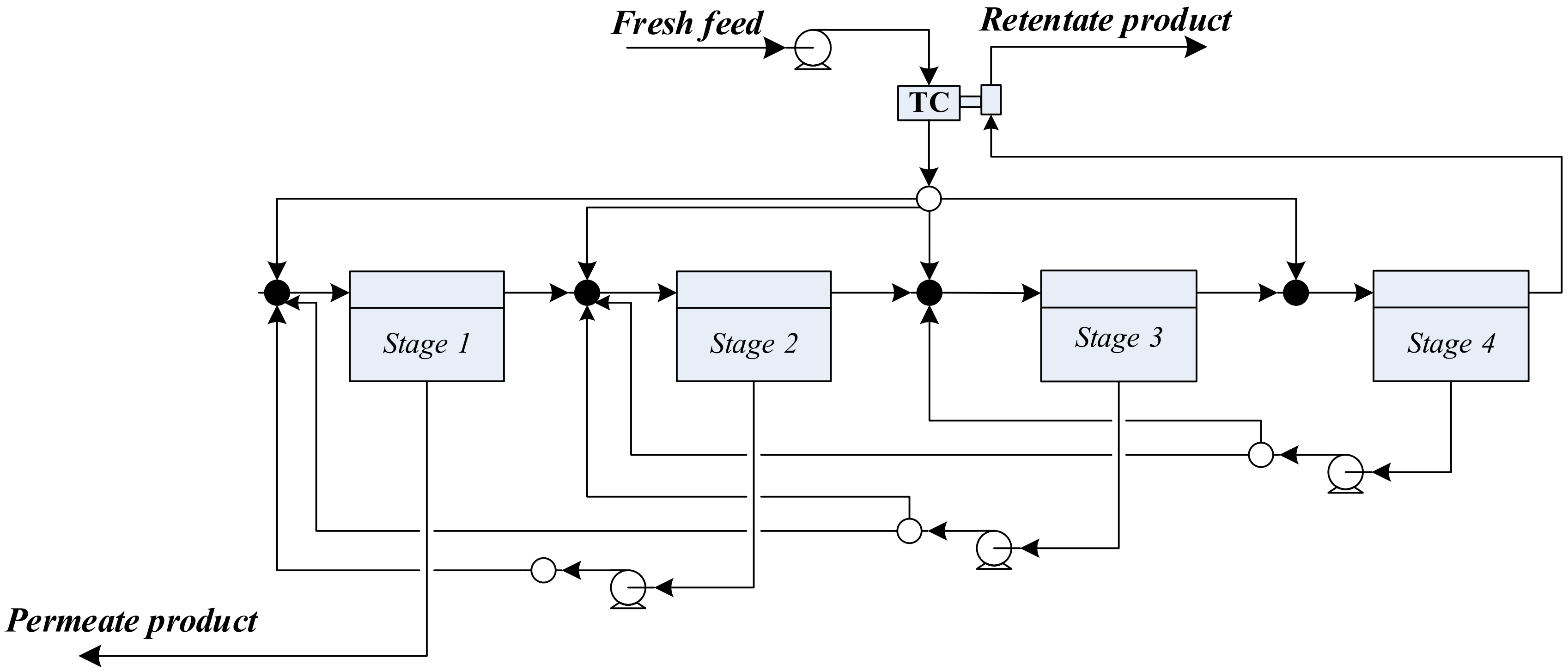
A membrane cascade superstructure for liquid mixtures



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Structure of the membrane cascade optimization model (MINLP)

Objective function: Minimizing total power consumption

Specifications: Feed and product compositions, feed temperature, membrane selectivity, bounds on pressure and flow variables, efficiencies of pressurization equipment, and maximum number of stages

Optimized variables: recycle flows and compositions, trans-membrane pressure ratio or trans-membrane pressure difference

Constraints:

Overall mass balances	Component mass balances	Membrane model for each stage	Objective function
• Linear	• Bi-linear	• Non-convex	• Bilinear

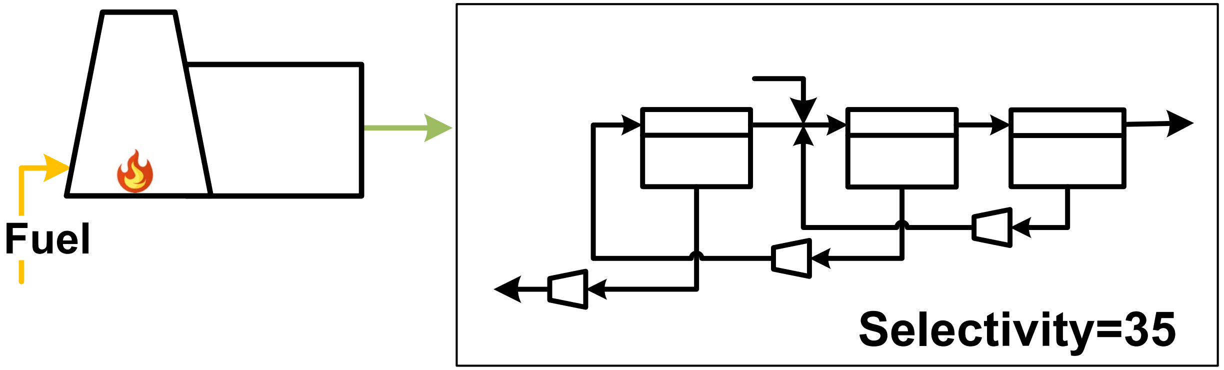
GAMS

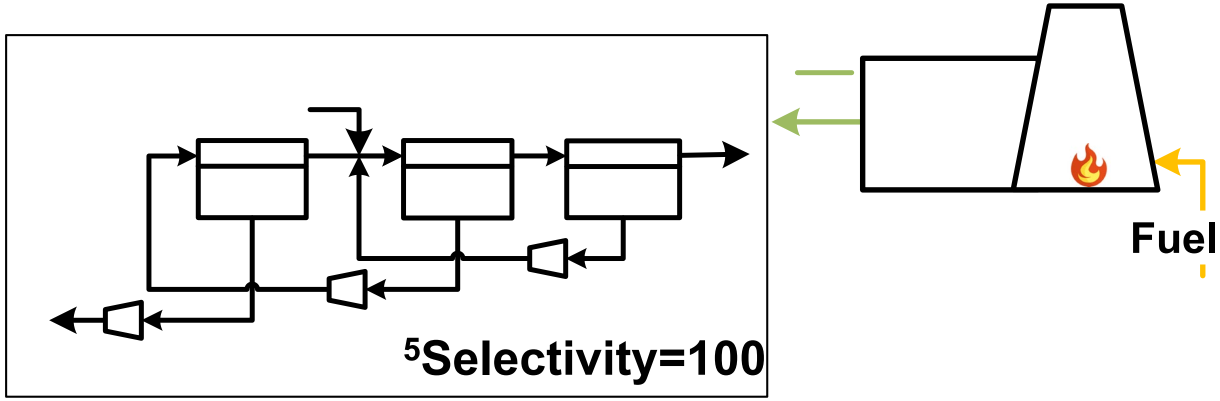
We use the solver BARON[1]

[1]Tawarmalani and Sahinidis. "A polyhedral branch-and-cut approach to global optimization." *Mathematical programming* 103.2 (2005): 225.
J. A. Chavez Velasco, R. Tumbalam Gooty, M. Tawarmalani, and R. Agrawal, Journal of Membrane Science, 119514 (2021)

Revisiting propane/propylene separation

Optimizing membrane cascade with different permselectivities





$$^{4}W_{mem} = 0.050\ \frac{kWh}{lb\ propylene}$$

$$W_{mem} = 0.030\ \frac{kWh}{lb\ propylene}$$

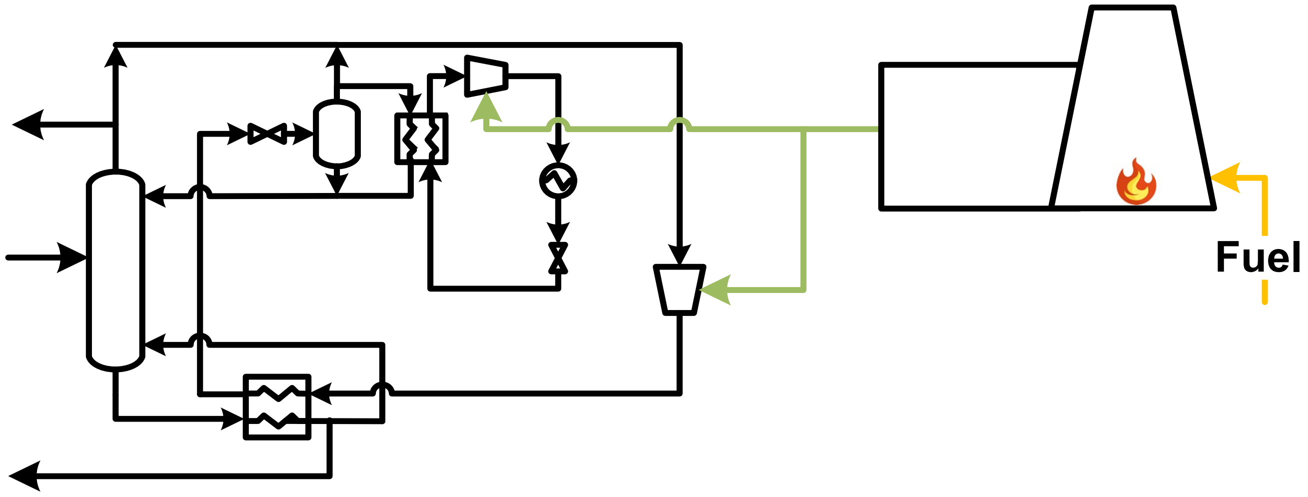
We formulated and solved the MINLP to optimize the membrane cascade power

[4]Colling et al., (2004). U.S. Patent No. 6,830,691
[5]Chae et al. RSC Advances 4.57 (2014): 30156-30161

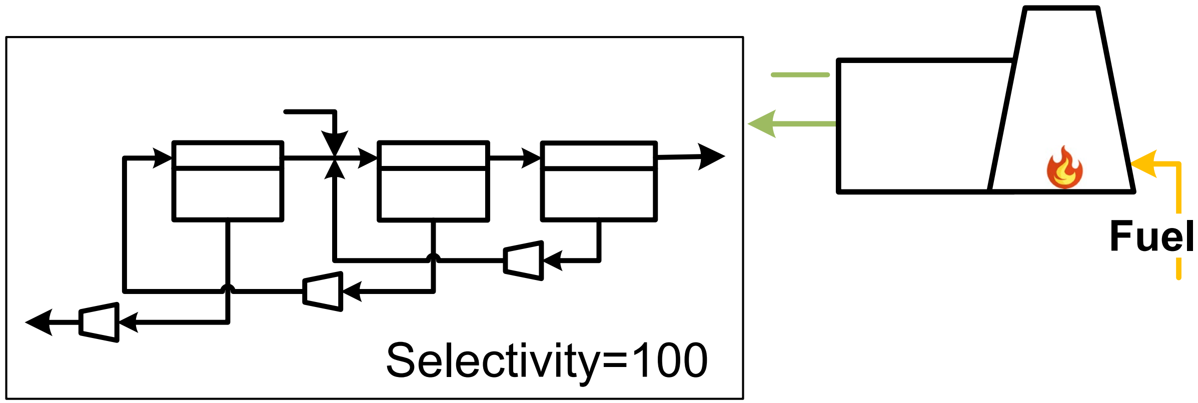
J. A. Chavez Velasco, R. Tumbalam Gooty, M. Tawarmalani, and R. Agrawal, Journal of Membrane Science, 119514 (2021)

Revisiting propane/propylene separation
comparing the two methods with optimized powers

Heat pump distillation



Membranes



$$W_{dist} = 0.02 \frac{kWh}{lb\ propylene}$$

$$Q_{fuel,Sep} = 0.04 \frac{kWh}{lb\ propylene}$$

$$W_{mem} = 0.03 \frac{kWh}{lb\ propylene}$$

$$Q_{fuel,Sep} = 0.06 \frac{kWh}{lb\ propylene}$$

Distillation consumes less energy than the membrane system

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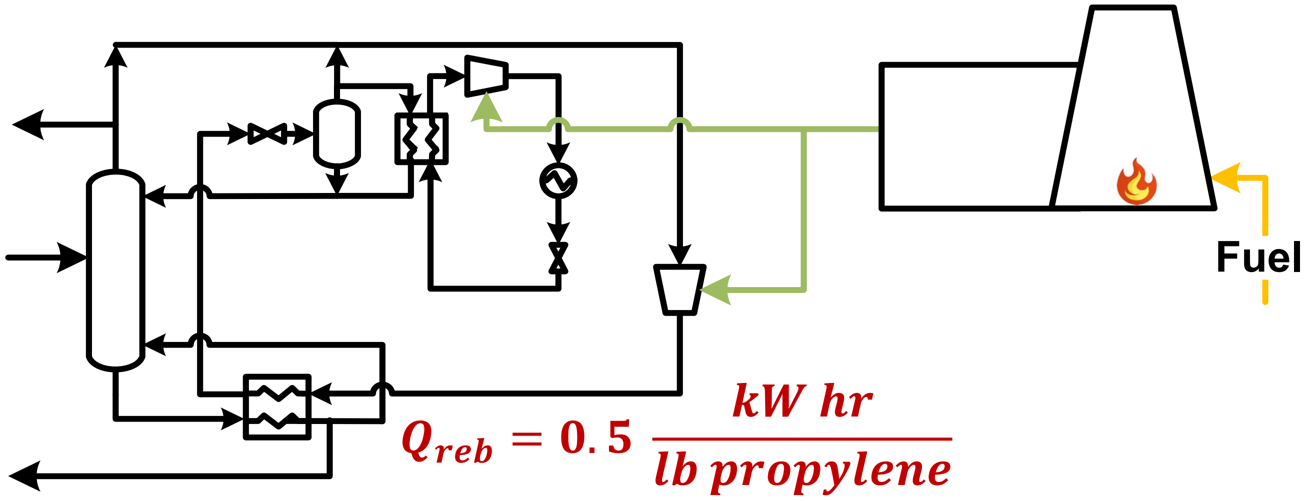
Revisiting propane/propylene separation
comparing the two optimized methods

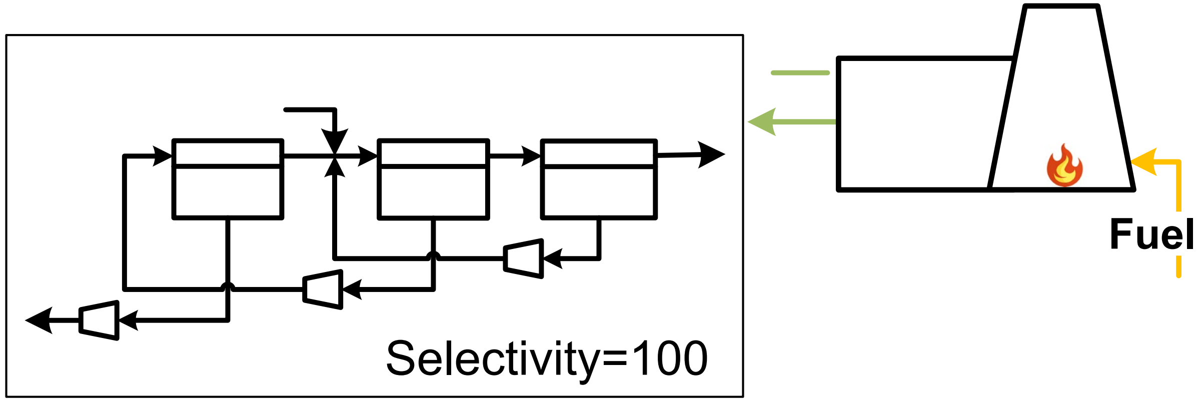
Heat pump distillation



$$Q_{reb} = 0.5 \frac{kW\ hr}{lb\ propylene}$$

$$Q_{fuel,\,Sep} = 0.04 \frac{kWh}{lb\ propylene}$$

Membranes



$$Q_{fuel,\,Sep} = 0.06 \frac{kWh}{lb\ propylene}$$

The actual fuel heat consumed by distillation is over 12 times lower than the reboiler heat

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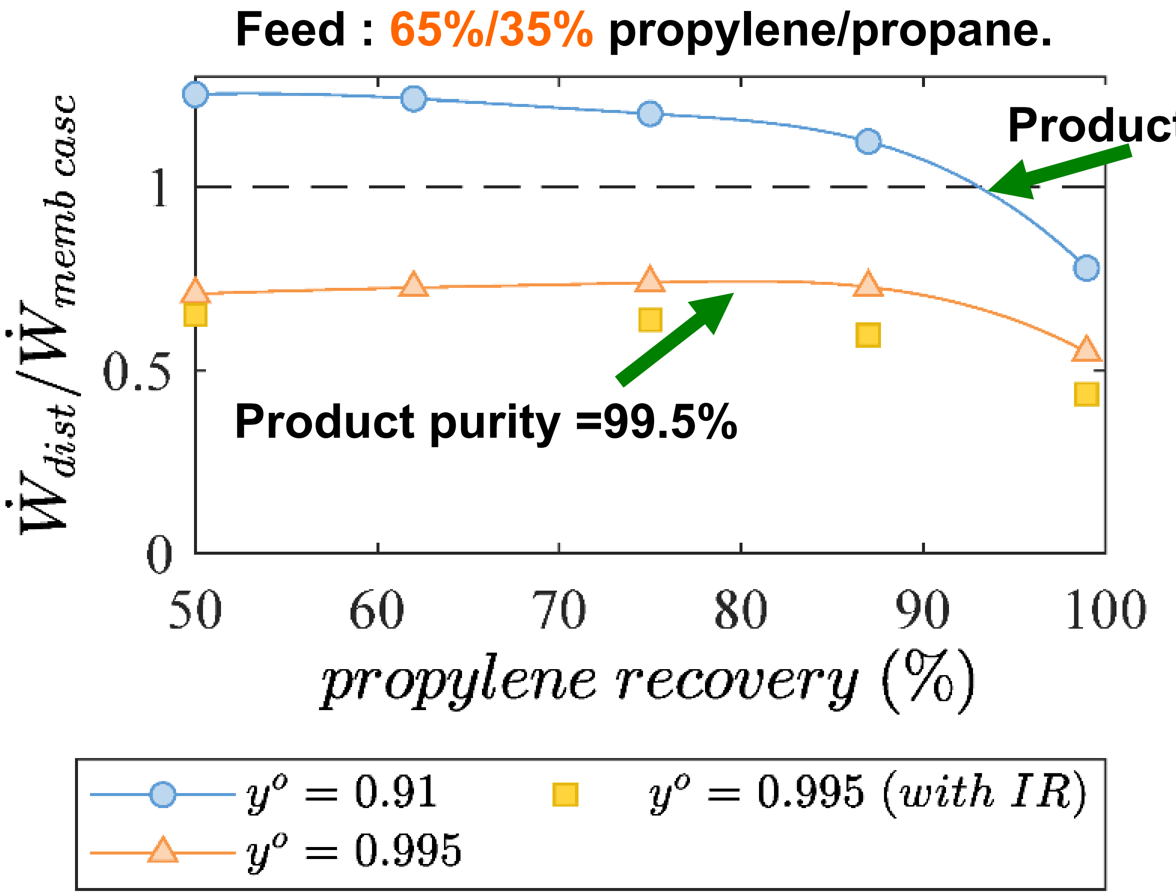
Do non-thermal alternatives have potential to reduce the energy consumption by a factor of 10?

Separation work (kWh/lb propylene)

Thermodynamic minimum:	**0.006**
Heat pump distillation:	**0.02**
Membranes:	**0.03**

The belief that membranes would cut down the energy consumption by a factor of 10 is incorrect for the propane/propylene example

Heat Pump Distillation vs Membrane: propylene/propane



Simulation Parameters

- Membrane selectivity: 50
- 4 stage membrane cascade

For moderate feed concentration, membrane consumes lower power at lower product purity and recoveries

Chavez Velasco, Tawarmalani and Agrawal, Which separation scenarios are advantageous for membranes or distillations? Accepted for publication in AIChE Journal (2022)

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Separation of p-xylene/o-xylene

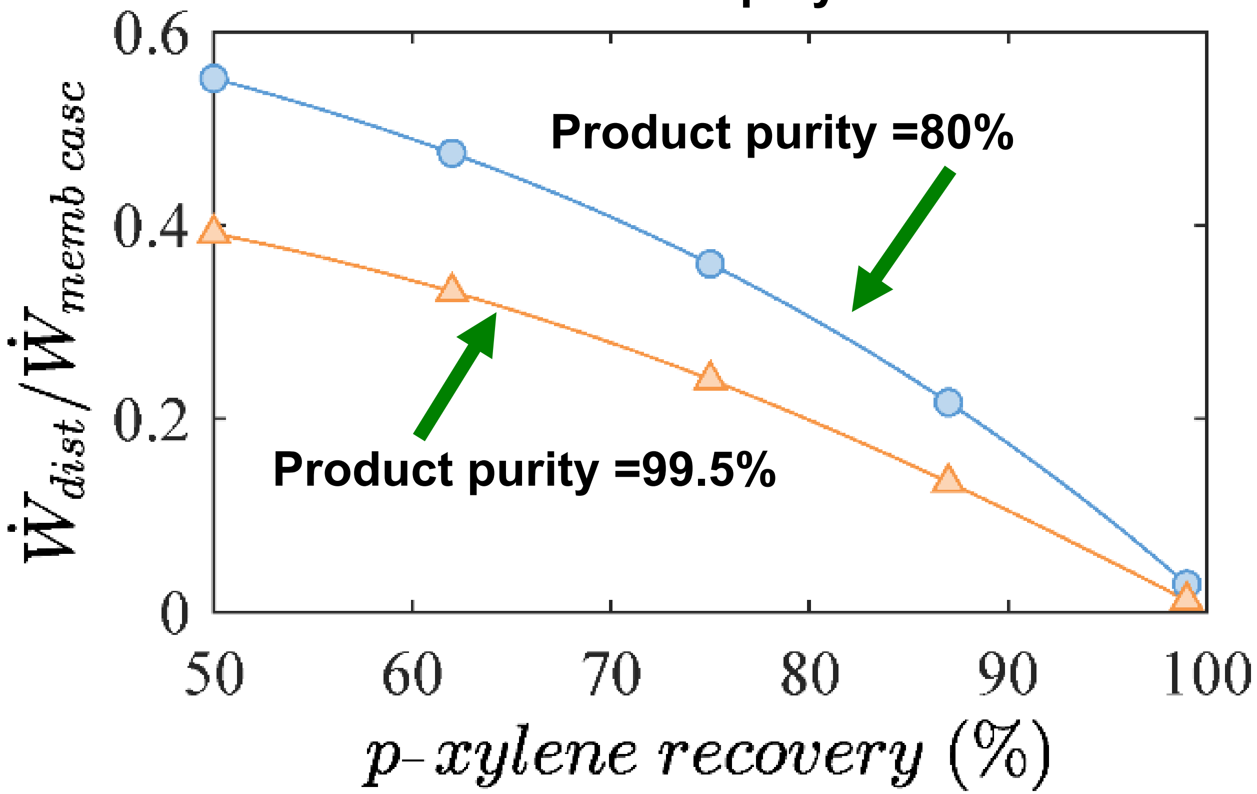
Another case study

Fuel

Heat Pump Distillation vs Membrane: p-xylene/ o-xylene

Membrane Parameters: Selectivity: 50, 4 stage cascade

Feed : 20% p-xylene



Case

- **Low Relative Volatility**
- **Low Feed Concentration**

- **At all product purities and recoveries distillation is much better than membranes.**

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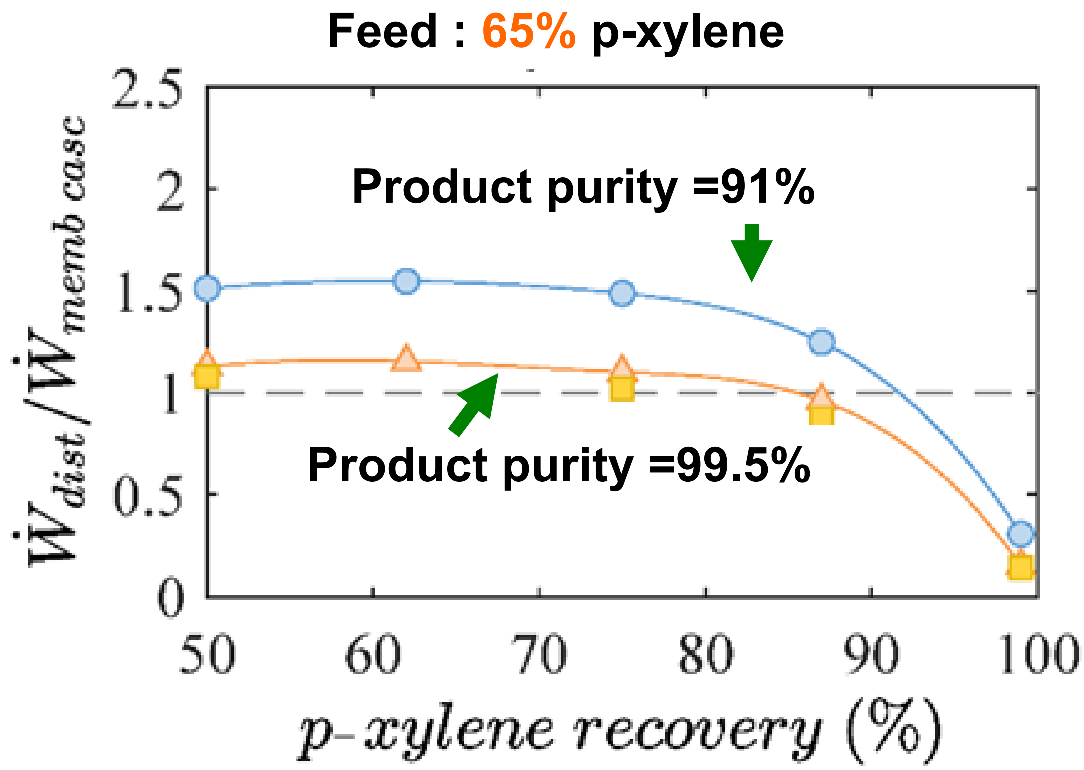
Heat Pump Distillation vs Membrane: p-xylene/ o-xylene

Membrane Parameters: Selectivity: 50, Minimum 4 stage cascade



Case

- **Low Relative Volatility**
- **Moderate Feed Concentration**

- **At high product recovery, distillation is better**
- **At lower recovery and high purity, two are comparable**
- **At lower product purity and recovery, membrane is better**

Chavez Velasco, Tawarmalani and Agrawal, Which separation scenarios are advantageous for membranes or distillations? Accepted for publication in AIChE Journal (2022)

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Heat Pump Distillation vs Membrane: p-xylene/ o-xylene

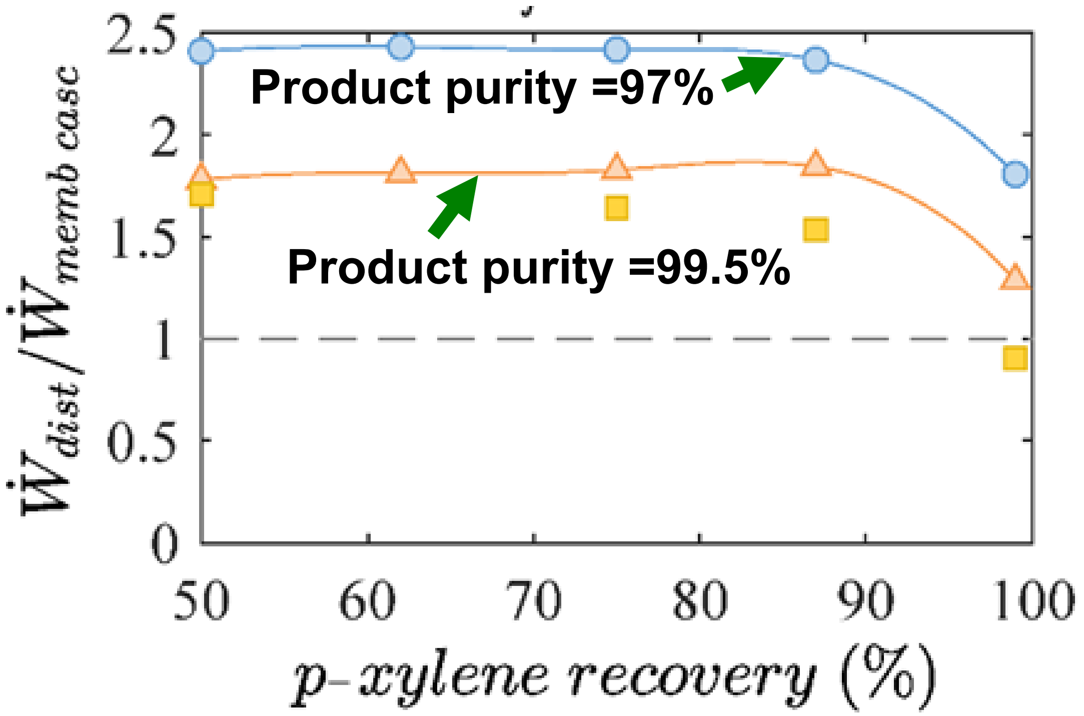
Membrane Parameters: Selectivity: 50, Minimum 4 stage cascade

Case

- **Low Relative Volatility**
- **High Feed Concentration**

- **Membrane is either comparable or better at all product purities and recoveries**

Feed : 90% p-xylene



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However, as relative volatility increases, even for high feed concentrations, distillation begins to demand lower power

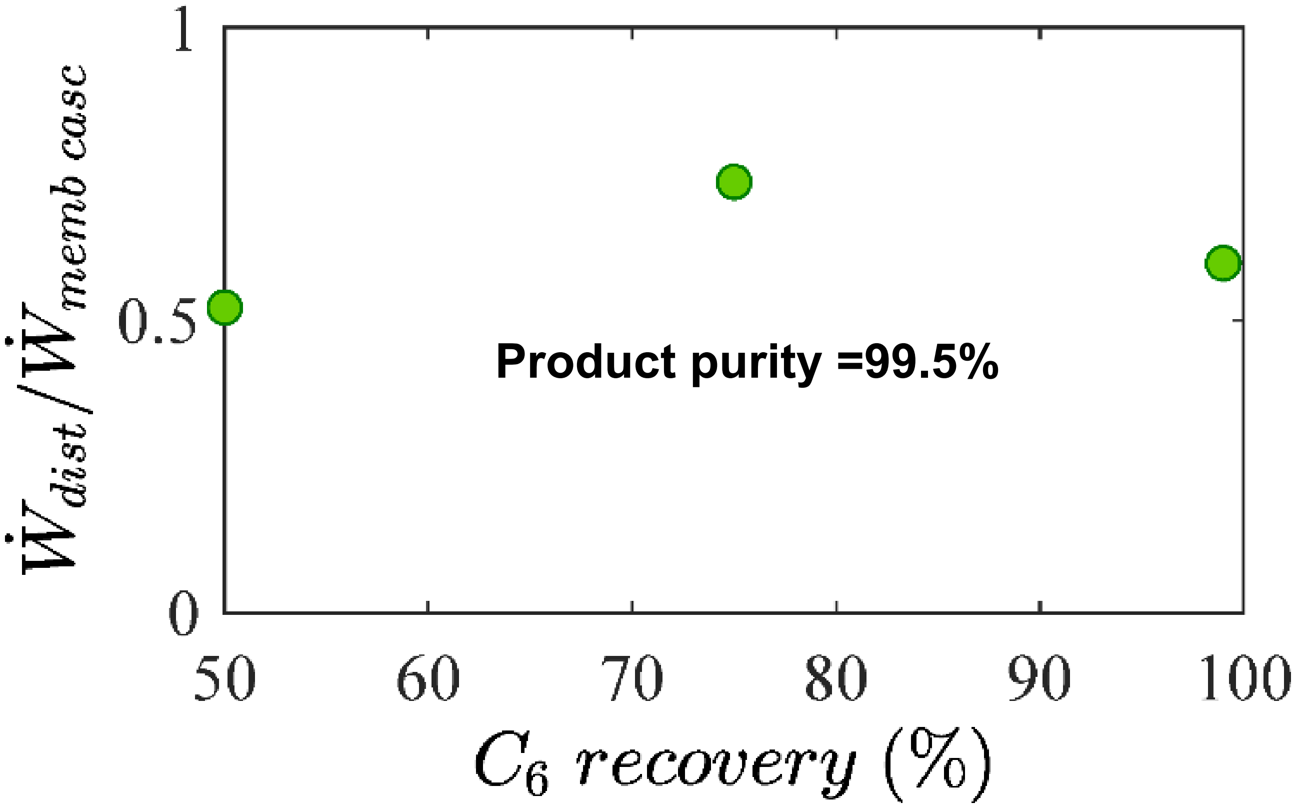
Membrane Parameters: Selectivity: 50, Optimal cascade with maximum 4 stages

Case

- **High Relative Volatility** (Hexane/Decane Mixture)
- **High Feed Concentration**

- Relative volatility for C_6/C_{10} = 14.1

Feed : 90% Hexane/ 10% Decane



Distillation is better at all recoveries

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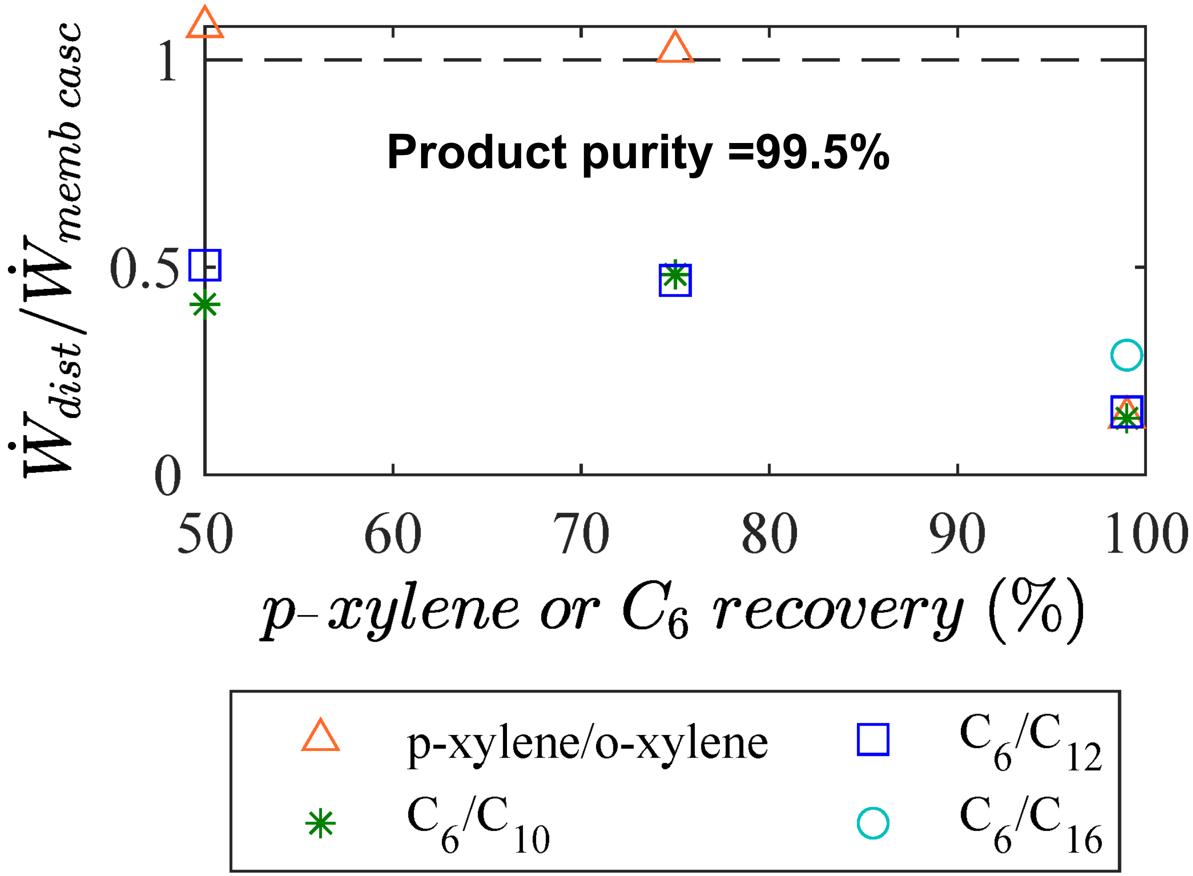
Heat Pump Distillation vs Membrane: Liquid Hydrocarbon Mixtures

Membrane Parameters: Selectivity: 50, Optimal cascade with maximum 4 stages

Feed : 65% volatile/permeable component



Case

- **Moderate Feed Concentration**

- **At high relative volatilities (C_6/C_{10} = 14.1; C_6/C_{12} = 29.2; C_6/C_{16} = 77.3), distillation is better at all recoveries.**

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Cases Considered So Far

More permeable component is also the more volatile component.

The product of interest is enriched in the more permeable/more volatile component

Cases Considered So Far

More permeable component is also the more volatile component.

The product of interest is enriched in the more permeable/more volatile component

For these we may make an attempt to generalize observations…..

First, we Classify All the Studied Feed and Product Cases

Feed		**Product**			
Composition (x_f)		Molar recovery (R)		Purity (y^o)	
$x_f \geq 90\%$	High concentration	$R \geq 99\%$	High	$y^o \geq 99.5\%$	High purity
$x_f \leq 20\%$	Low concentration				
$90\% > x_f > 20\%$	Moderate concentration	$90\% > R \geq 50\%$	Modest	$97\% \geq y^o \geq 80\%$	Modest purity

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Then We Sum Up the Observations

	Feed concentration	Product recovery	Product purity	Lower power option
1.	Low to moderate	High	High	Distillation
2.	Moderate	Modest	High	Toss up[2]
3.	Moderate	Modest	Modest	Likely membrane
4.	Moderate	High	Modest	Distillation
5.	High	High	High	Likely distillation
6.	High	Modest	High	Toss up[2]
7.	Low	Modest	Modest	Distillation

[2] Toss up refers to cases where for close boiling mixtures, membranes have a potential to be the low energy option, however, for higher boiling mixtures, distillation would be preferred.

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Summary: Comparing Energy Efficiency of Membranes & Distillations

For hydrocarbon mixtures, where more permeable component is also the more volatile component and is the desired product:

- **Both membranes and distillations have energy efficient domains.**
- **Distillation is more efficient for high product recoveries (at all tested product purities).**
- **Distillation is more efficient at modest recoveries for high purity products.**
- **For close boiling and highly enriched feeds, membrane provides energy benefits for a high purity product at modest recoveries.**
- **Membranes are more efficient when feed concentration is moderate to high and product recovery and purity are modest.**
- **The factor of energy improvement by membranes is usually limited.**
- **However, distillation can outperform membranes under many situations and often the improvement in energy consumption is substantial.**

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Thank you